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# ADVANCED NANORESEARCH AND APPLICATIONS

Dr. Ram H. Kadam

# ADVANCED NANO RESEARCH AND APPLICATIONS (NCANRA-2024)

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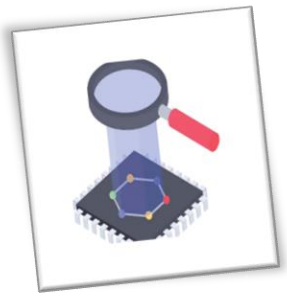

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# ACKNOWLEDGEMENTS

*Dear Esteemed Guests and Participants,*

*I hope this message finds you well. I wis to take a moment to express my sincere gratitude for your invaluable participation and support during the recent* ***NCANRA-2024****. Your enthusiastic presence and contributions played a significant role in making the event a resounding success.*

*Firstly, I am thankful very much to our Patron* ***Hon. Dr. D. B. Patange (Kaka)****, Secretary, SES, Gunjoti, and Principal* ***Dr. D. R. Kulkanri*** *for encouraging us to organize the conference.*

*It was great pleasure to express my science thanks to our esteemed guests* ***Prof. Nikesh Shah, Prof. Sudhir Warkar, Dr. Sagar Shirsat, Prof. Shrikant Choudhari,*** *and* ***Dr. Bhaskar Sathe*** *for their valuable insights as invited talks.*

*I am also thankful to our team members and supporters* ***Dr. S. N. Ibatte, Prof. A. B. Kadam, Prof. Bhausaheb Sontakke, Prof. G. H. Jadahv, Prof. V. B. Kulkarni, Prof. A. R. Shitre, Prof. R. V. Kathare, Prof. U. B. Dindore, Prof. Raghvendra Topare, Prof. V. B. Kawade, Dr. S. T. Alone, Dr. M. L. Mane, Dr. R. M. Tigote, Dr. M. N. Gadsing, Dr. P. B. Undare, Prof. Ramdas Dhokale, Dr. Nitin Padwal, Mr. C. U. Nikam, Mr. C. S. Munnoli, Mr. Arvind Doke, Mr. Shivaraj Manegoale****, for taking endless efforts for the grand success of the conference. I specially thank to my friends* ***Prof. Satish Shelke, Dr. Vinod Barote, Dr. Sagar Shirsath, Dr. Vishnu Shinde,*** *and our BOS members* ***Dr. C. T. Birajdar, Prof. Shafi, Dr. Prashant Sonawane, Dr. Mahesh Mane, Dr. C. M. Kale*** *for extending helping hands in registration purpose.*

*Additionally, I would like to extend my deep sense of appreciation for the assistance provided by my colleagues* ***Prof. K. S. Lohar, Dr. D. P. Chavan, Dr. J. A. Nanaware, Prof. Y. A. Vijapure, Dr. V. S. Hogade, Dr. G. M. Rathod, Prof. B. J. Ugale, Dr. M. G. Ambuse, Dr. R. N. Nigade, Prof. H. S. Bhosale, Prof. R. G. Koli, Prof. S. M. Patange, Prof. I. S. Inamdar,*** *either in helping with logistics, sharing resources, or offering valuable suggestions. Their collaborative spirit and dedication in the success of the conference should not go unnoticed, we are truly grateful for their support. Also, thanks are also due to supporting staff members from teaching and nonteaching for their help and consistent efforts for the success of conference. Thanks also goes to those who are involved directly or indirectly in making the conference as a successful event.*

*Finally, I am thankful to all the valued participants of this conference. I believe that their involvement has not only contributed to the success of this conference but has also fostered meaningful connections within the academic fraternity. Their commitments in advancing the field of nanoscience are commendable, therefore we look forward towards possibility of working together in the future for advancement of nano science.*

*I hereby acknowledge the National Publisher* ***RUSHI Publications,*** *Chhatrapati Sambhajinagar for their efforts in publishing in time the proceedings of the conference with ISBN number and in comprehensive manner.*

*Once again, thanks one and all for your valuable contributions and support. We are genuinely grateful to have you as part of* ***NCANRA-2024,*** *and we look forward to collaborating you again in upcoming events. Thanking you.*

**Prof. R. H. Kadam**
Convenor
(NCANRA-2024)

संस्था स्थापना १९२७
संस्था नोंदणी क्र : एफ-५ उस्मानाबाद
।। न हि ज्ञानेन् सदृशं पवित्रमिह विद्यते ।।
शतकपूर्ती २०२७
Shrikrishna Education Society
श्रीकृष्ण शिक्षण संस्था गुंजोटी, ता.उमरगा, जि. धाराशिव ४१३६०६
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E-mail : skssg1927@gmail.com 9422069904 Secretary - Dr.D.B. Patange

Ref. No. SKESG / / Date : / /20

## Foreword Message from Secretary

It is both an honor and a privilege for me to be associated with the participants of the National Conference on Advanced Nano Research and Applications, organized by the Department of Physics, Chemistry and Mathematics at Shrikrishna Mahavidyalaya, Gunjoti.

The Shrikrishna Education Society, established in 1927 before Independence, has been dedicated to providing education in rural areas, especially for backward classes and girls from this region. In response to the growing need for higher education, the Sanstha opened a degree college with Arts and Science streams in 1991.With a commitment to delivering quality education, the Sanstha actively encourages faculty engagement in research activities. It consistently intends to support to the organization of events that foster intellectual growth. The current conference is specifically designed to instill a scientific attitude among the faculties and students of the area.

I extend my heartfelt congratulations to the organizers of NCANRA-2024 for their painstaking efforts in orchestrating this significant conference. I wish the conference great success, fostering valuable discussions and contributing to the advancement of scientific knowledge in the field of Advanced Nano Research and Applications.

Dr. D.B. Patange
Secretary
Shrikrishna Education Society
Gunjoti, Tq. Omerga

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Shrikrishna Shikshan Sanstha
आज़ादी का अमृत महोत्सव
B++ NAAC
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Principal - Dr.D.R. Kulkarni

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## Principal Message

It is a matter of great pride and honor to the college that Department of Physics, Chemistry and Mathematics are going to publish Full Length Proceeding for the popular abstracts received and presented during National Conference held on "Advanced Nano Research And Applications" on 29-30 January 2024, in association with Dr. B.A.M. University Chhatrapati Sambhajinagar. This national conference proved a platform for scientists, researchers and students from the spheres of Science and Technology to share their ideas, present their latest findings and learn about various developments in the field of science, environment and sustainable development. I am confident that the participants interacted and collected a lot of scientific information from the eminent personalities/speakers. I extend my best wishes to the Organizing team for the purpose of achieving the goal of environmental conservation and sustainable development. I also extend my best wishes for successful compilation of the proceeding of this conference.

Principal
Shrikrishna Mahavidyalaya, Gunjoti
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**Dr. R. H. Kadam**
Professor,
Physics Department

Web: www.skmg.ac.in
E-mail: ram111612@yahoo.co.in
Contact: 09423450152

I am delighted to present the proceedings of the National Conference on Advanced Nano Research and Applications (NCARNA-2024), organized by Shrikrsihna Mahavidyaklaya Gunjoti.

We were honored to have Prof. Nikesh Shah from the Department of Physics at Saurashtra University, Rajkot, Gujarat, as the Chief Guest and Inaugurator, Prof. S.G. Warkar from the Department of Chemistry at Delhi Technological University graced the occasion as the Keynote Speakers. Dr. Baskar Sathe from the Department of Chemistry at Dr. BAMU University, Chatrapati Sambhaji Nagar, Dr. Sagar E. Shirsat from Vivekanand College, Chatrapati Sambhaji Nagar, and Prof. S R Choudhari from the School of Mathematics and Sciences, KBC North University, Jalgaon, were also major part of the esteemed lineup.

We received a total of 46 research papers, with 39 abstract papers accepted. These contributions were categorized into 05 oral sessions, 01 poster sessions, 01 keynote talk and 03 invited talks. NCARNA-2024 explored four major areas—Physics, Chemistry, Mathematics, and their direct applications in socially relevant research areas such as communication systems, stealth technology, remote sensing, and nanoscale devices.

The conference also delved into emerging fields like automated planning, big data analysis, bioinformatics, cloud computing, data mining, distributed computing, and sensor networks—areas crucial for collecting, organizing, and analyzing large datasets to uncover patterns and valuable information.

NCARNA-2024 provided a unique platform for scientists, technologists, engineers, academicians, and researchers from national laboratories, research centers, academic institutions, and industries across India to converge, interact, and share their research activities.

As a convener, I extend my gratitude to Prof. K.S Lohar, Head of the Department of Chemistry, and Prof. Jagadish Nannavare, Head of Mathematics and Dr.M. Kale, V. C. College Sillod. for their unwavering support. Special thanks to the technical program committee, local organizing committee, volunteers, and the staff members of Shrikrishna Mahavidyalay Gunjoti for their dedicated support. A heartfelt acknowledgment is also extended to our co-sponsors, Shrikrishna Mahavidyalaya and Dr. BAMU Chatrapati Sambhaji Nagar.

Finally, my sincere thanks go to all the authors, volunteers, and individuals who directly or indirectly contributed to the success of the conference. Without their cooperation and steadfast support, NCARNA-2024 would not have been possible. A special note of appreciation is reserved for all the students of the Material Science Laboratory for their tireless day-and-night efforts towards the success of the event.

Convener
Dr.R.H.Kadam

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National Conference on
Advanced Nano Research and Applications
(An Edited Book)

# INDEX

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01 National Conference on
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(An Edited Book)

# Effect of Pr substitution on the structural properties of Co-Ni ferrite

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## ABSTRACT

$Pr^{3+}$ substituted Co-Ni nanocrystalline ferrite having a chemical formula $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$ (x = 0, 0.025, 0.050, 0.075, 0.1) was prepared by the sol-gel auto-combustion route. The as-prepared powders were sintered at 500 °C for 4 h in air. The sintering temperature of the samples was confirmed by the thermogravimetric with differential scanning calorimetry. The multiphase spinel ferrite of Pr-substituted Co-Ni ferrite was analyzed by X-ray diffractometry. The lattice constant is increased with doping of $Pr^{3+}$ in Cobalt-Nickel ferrites. The value of crystallite size lies within the range of 25-20 nm which confirms the nanocrystalline nature of the samples. The composition of different elements present in the sample was investigated by energy dispersive spectroscopy, which showed the presence of all elements in good stoichiometry proportion.

***Keywords:*** *sol-gel route; Thermal decomposition; Structural properties; Sol-gel method.*

## INTRODUCTION

In the last decade, ferrite nanomaterial is vastly studied and used in various technologies due to its excellent electric and magnetic properties. The small particle size and uniform size distribution influence the properties of ferrite material. Therefore, the chemically synthesized nanoparticles show outstanding properties compared to their bulk material [1-4]. The spinel ferrite is an important material for the fabrication of microwave and electronic devices. Spinel ferrite has two interstitial sites; tetrahedral (A) and octahedral [B] sites which are occupied by metal ions. The oxygen ions are occupying at close-packed, face-centered-cubic (FCC) structures. In conventional, the divalent oxygen ions ($O^{2-}$) are assumed to affect the magnetic and electrical properties through the super-exchange (SE) and double exchange (DE) interaction models [5]. It is found that spinel ferrite also consists of monovalent oxygen ions ($O^{1-}$) which affects the magnetic and electrical properties [6-8]. Cobalt-nickel (Co-Ni) ferrite possesses semiconducting nature and shows high resistivity, moderate magnetization, and very high magneto-crystalline anisotropy [9, 10]. These properties can be modified by doping the trivalent and divalent ions in place of host ions in the spinel lattice [11-13]. The doping of rare-earth (RE) metal ions can modify the electrical resistivity, dielectric constant, and densification of the ferrite samples [14-16]. Generally, Cobalt-Nickel ferrite shows the inverse spinel structure in which $Fe^{3+}$ and $Co^{2+}$ ions reside at both octahedral and tetrahedral sites while $Ni^{2+}$ ions reside only at octahedral site [17]. The doping of Nickel (40%) in Cobalt ferrite in place Cobalt alters the electrical, magnetic, and structural properties. The ionic radii of all the rare earth metal ions are larger than the all the host ions in the spinel lattice. Therefore, the substitution of rare earth metal ions in Cobalt-Nickel ferrite strongly affects on their physical as well as structural properties. Also, large ionic radii of dopant ions reduce the growth of the crystal which affects the morphology of the ferrite samples [18]. Rare earth praseodymium ($Pr^{3+}$) enters into the lattice and resides at octahedral [B] site by rearranging the host cations among the (A) and [B] sites. Literature on different rare earth (RE) metal ions substituted spinel ferrites are available [19-21] but Pr-substituted Cobalt-Nickel ferrite is still not found to be synthesized and investigated.

In the last few decades, several techniques are developed for the synthesis of ferrite [22]. Among these, we have selected sol-gel auto-combustion route because this route is better for good control of proportion, purity, homogeneity, and morphology. In this research, we have prepared $Pr^{3+}$ substituted Co-Ni ferrite by a sol-gel auto-combustion route. The influences of $Pr^{3+}$ on the thermal and structural properties of Co-Ni have been investigated. The thermo-gravity and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and the energy dispersive analysis of X-ray (EDAX) used to study the different properties.

## EXPERIMENTAL

***Materials:*** The pure (99%) AR grade metal nitrates; ferric Nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}3H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), praseodymium nitrate ($Pr(NO_3)_3{\cdot}5H_2O$), and citric acid ($C_6H_8O_7{\cdot}H_2O$), were used to prepare to the precursor solution of Pr-substituted Co-Ni ferrite.

***Synthesis:*** The required proportion of all above metal nitrates and citric acid with molar ratio 1:3 were dissolved in 100 mL of distilled water. This solution was kept on a hot plate at 90 ºC and mixed continuously using a magnetic stirrer upto the gel formation. During this whole process, the pH of the solution was maintained at 7 by using ammonia solution. Once gel was formed, it is heated at 250 ºC to burn and converted into the fluffy loose powder. This as-prepared powder was grinded and some sample was used to the thermo-gravity and differential thermal analysis (TG-DTA). According to TG/DTA, all the samples were annealed at 500 ºC for 4 h. This reaction was performed in atmospheric air without inert gases.

***Characterizations:*** The as-synthesized and dried powder was characterized via TG/DTA in a nitrogen ($N_2$) atmosphere to decide the crystallization temperature by using Shimadzu SDT Q600 thermal analyzer. The energy dispersive analysis of X-ray (EDAX) was carried out to know the expected amount of the elements and its stoichiometry present in the sample. The XRD spectra were recorded with the help of a Phillips X-ray diffractometer (Model 3710) using Cu Kα radiation (λ=1.5405 Å). The lattice parameters, the oxygen position, and the cation distribution were determined from the XRD patterns.

## RESULTS AND DISCUSSION

***Thermal decomposition***: The variation of decomposition and dehydration of samples produced during the sintering process were investigated thermogravimetric analysis. Thermogravimetric analysis and differential scanning calorimetric studies of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$ (x = 0.05) was carried out in the range of 25- 1000°C, as shown in Figure 1. There are three major total mass loss were observed. In a first step, the mass loss is observed from room temperature to 145 °C in TGA attributed to the loss of hydrated water molecule presented on the surface of ferrite particles. The second step from 145 °C to 417 °C showed mass loss and this is due to the combustion of nitrates and citric acid. Further, in the third step, 417 °C to 494 °C mass loss is due to decomposition of ureacted metal nitrate and residual components, this step clearly shows the formation of metal oxides to metal ferrites with loss of oxygen. The DSC curve shows one exothermic peak around 450 °C, which attributed to oxidation of carbon in citric acid by the oxygen in atmosphere and forming $CO_2$ by evolving heat. This exothermic peak is also due to the combustion of metal nitrate. TGA curve indicate that the total mass loss of the sample from room temperature to 500 °C is 23 %.

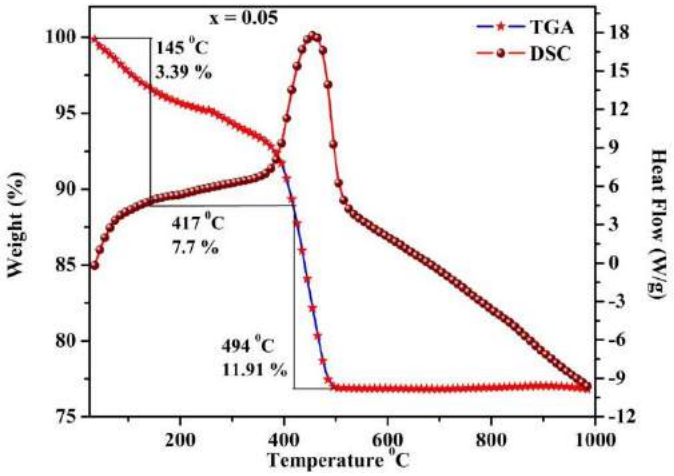


**Fig. 1:** Thermo Gravimetric (TGA) and Differential Scanning Calorimetric (DSC) decomposition pattern of x = 0.05 composition of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$.

There is no mass loss observed after 500 °C which implies only Pr-substituted Co-Ni ferrite sample present above this temperature. It is found that the decomposition has been completed around 500 °C of the Pr-substituted Cobalt-Nickel ferrite. Therefore, we have selected the 500 °C sintering temperature for this series.

**Elemental Analysis:** The elemental composition and their proportion were instigated by Energy dispersive analysis for Pr-substituted Co-Ni ferrite samples. EDAX spectra of all the samples of the Pr-substituted Co-Ni ferrite are shown in Fig. 2. The presence of peaks of the element $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $O^{2-}$ and $Pr^{3+}$ in EDAX spectra are the confirmation of formation Pr-substituted Co-Ni ferrite. There is no impurity observed in EDAX spectra. The theoretical and observed percentages of samples have a close agreement with each other. This exhibits that there was a very low error in the fabrication of the sample by the sol-gel route. From EDAX spectra, it is observed that all the samples of Pr-substituted Co-Ni ferrite are fabricated in good stoichiometric ratio.

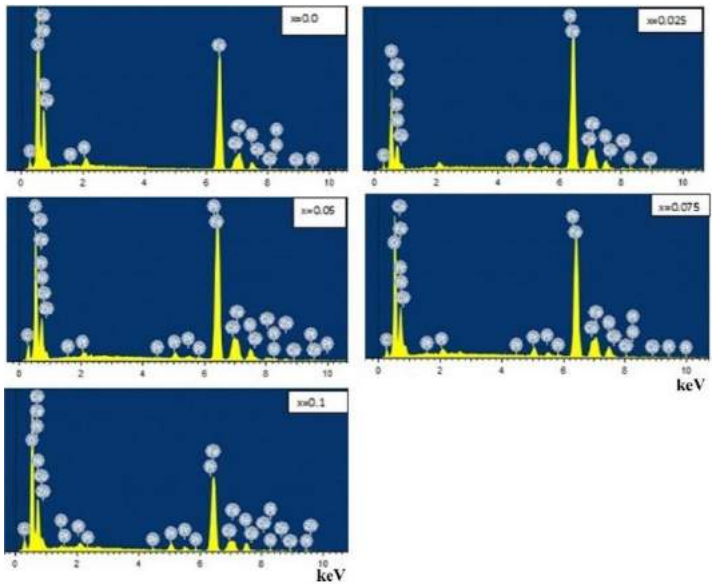


**Fig. 2:** EDAX pattern of all the samples of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$

***Structural properties:*** XRD patterns of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$ (x=0.000, 0.025, 0.050, 0.075, 0.1) are shown in Fig. 3. The observed peaks (220), (311), (222), (400), (422), (333), and (440) are good agreement with standard PDF 01-077-0426. The observed peak shows single-phase cubic spinel crystal at low concentration of $Pr^{3+}$ ions and it is formed with a secondary phase of $PrFeO_3$ at high concentration of $Pr^{3+}$ ions in Co-Ni ferrite. The secondary phase of $PrFeO_3$ was identified by ICCD#00-019-1012. The ionic radius of $Pr^{3+}$ is larger as compared to the $Fe^{3+}$ ion, therefore, it is difficult to dope in place of $Fe^{3+}$ in large fraction. The higher concentration of $Pr^{3+}$ will distort the lattice and form the secondary phases [18]. The lattice constant 'a' was determined by the relation:

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

Where h, k, l are Miller indices and d is interplanar spacing. The calculated values of the lattice constant are summarized in Table 1. It is found that value of 'a' increases from 8.364 - 8.412 Å with Pr composition from x = 0 to x = 0.1 in Co-Ni ferrite. Since ionic radii of $Fe^{3+}$ and $Pr^{3+}$ are 0.67 Å and 1.13 Å respectively [31], therefore, when $Pr^{3+}$ doped in place of $Fe^{3+}$, the lattice will be expanded. Hence, the lattice constant is increased by the substitution of $Pr^{3+}$ ions.

For spinel structure, distances from the O anion to the cations at the tetrahedral (A)-site ($d_{AO}$) is $\sqrt{3}a/8$, distances from the O anion to the cations at the octahedral [B]- site ($d_{BO}$) is $a/4$, the distance from the cations at the (A) sites to those at the [B] sites ($d_{AB}$) is $\sqrt{11}a/8$.]. The calculated values of $d_{AO}$, $d_{BO}$, and $d_{AB}$ are listed in Table 1. It is noticed that all the distances increase with the substitution of $Pr^{3+}$ ions in Co-Ni ferrites. This is due to the difference between the ionic radii of host and dopant ions.
The X-ray density (dx) of the samples was determined by equation;

$$dx = \frac{8M}{Na^3} \quad (2)$$

Where M- molecular mass of corresponding composition, N- Avogadro's number and $a^3$- volume of unit cell.

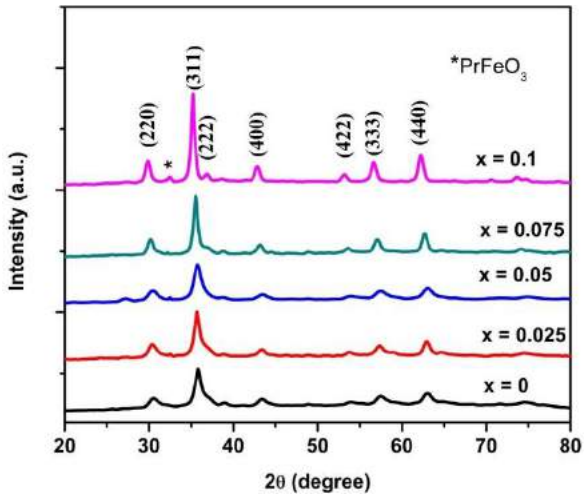


**Fig. 3:** XRD patterns of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$ (x= 0.0, 0.025 ,0.05, 0.075 and 0.1).

The values of 'dx' are presented in Table 1 and it found that its value increases from 5.384to 5.482 g/cm$^3$ with Pr composition. It is well known that X-ray density depends on the molecular weight of the sample. The difference in atomic weight of $Fe^{3+}$ (55.84 amu) and $Pr^{3+}$ (140.90 amu) is responsible for the increase of the X-ray density of the sample with Pr substitution. The Archimedes method was used to determine the bulk density ($d_B$) and its values are shown in Table 1.

**Table 1.** Lattice constant 'a', $d_{AO}$ is distances from the O anion to the cations at the tetrahedral (A)-site, $d_{BO}$ distances from the O anion to the cations at the octahedral-(B) site, $d_{AB}$ is the distance from the cations at the (A) sites to those at the [B] sites, X ray density ($d_x$), bulk density ($d_B$), porosity (ρ), crystallite size from xrd ($t_{xrd}$) and TEM ($t_{TEM}$) and surface area (S) of $Co_{0.6}Ni_{0.4}Fe_{2-x}Pr_xO_4$ (x = 0, 0.025, 0.050. 0.075 and 0.1).

| Comp. x | a (Å) | $d_{AO}$ (Å) | $d_{BO}$ (Å) | $d_{AB}$ (Å) | dx (g/cm$^3$) | $d_B$ (g/cm$^3$) | P (%) | $t_{xrd}$ (nm) | $t_{TEM}$ (nm) | S m$^2$/g |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 8.364 | 1.8109 | 2.091 | 3.4675 | 5.384 | 2.828 | 47.47 | 25.412 | 26.355 | 81.50 |
| 0.025 | 8.376 | 1.8135 | 2.094 | 3.4725 | 5.410 | 2.954 | 45.42 | 25.075 | 27.521 | 83.00 |
| 0.050 | 8.381 | 1.8145 | 2.095 | 3.4746 | 5.448 | 2.974 | 45.41 | 23.754 | 25.231 | 84.93 |
| 0.075 | 8.397 | 1.8180 | 2.099 | 3.4812 | 5.465 | 2.990 | 45.28 | 21.965 | 24.315 | 91.36 |
| 0.100 | 8.412 | 1.8213 | 2.103 | 3.4874 | 5.482 | 3.038 | 44.58 | 20.154 | 23.251 | 97.99 |

It is noticed that the bulk density also increases with Pr-substitution. The crystallite size '$t_{XRD}$' of the sample was measured using the major peak (311) by Scherrer formula:

$$t_{xrd} = \frac{0.9\lambda}{B\cos\theta} \quad (3)$$

Where θ - Bragg angle, B - full width at half maximum, and λ - wavelength of radiation. The values of crystallite size are tabulated in Table 1. The value of crystallite size is decreased with the increase of Pr composition. The value of crystallite size lies within the range of 25-20 nm which confirms the samples are formed in nanocrystalline nature. Using bulk density ($d_B$) and crystallite size ($t_{XRD}$), the specific surface area (S) was measured by the equation:

$$S = \frac{6000}{t_{XRD} d_B} \quad (4)$$

The values of specific surface area are tabulated in Table 1 and it is noticed that the value of 'S' increases with Pr-substitution. The value of 'S' inversely related to crystallite size as well as bulk density. The value of crystallite size is decreased rapidly whereas bulk density is increased slowly with Pr-substitution. The porosity of the samples was measured by the formula;

$$P = \left( \frac{d_X - d_B}{d_X} \right) \times 100 \quad (5)$$

Where $d_B$ and dx are the bulk density and X-ray density respectively. The values of the porosities of the samples are listed in Table 1. It is noticed that porosity decreases with the $Pr^{3+}$ ion concentration in Co-Ni ferrite. This is because of the behavior of both X-ray and bulk density with the composition of $Pr^{3+}$ ions in ferrite samples.

## CONCLUSIONS

Pr-substituted cobalt-nickel ferrite NPs have been fabricated by the sol-gel auto-combustion route. The EDS data shows that the observed and theoretical percentage is in close agreement with each other. The $Pr^{3+}$ doped Co-Ni ferrite samples show the spinel ferrite phase with a small amount of $PrFeO_3$ as a secondary phase at higher concentration of Pr. The lattice constant is increased by increasing the $Pr^{3+}$ ion concentration in Co-Ni ferrite. Samples show excellent properties like high crystallization, moderate soft magnetism which have wide range of applications for memory storage devices.

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# Green Synthesis, Characterization of Iron Oxide Nanoparticles Using Azadirachta Indica Aqueous Leaf Extract

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**ABSTRACT**

Green chemistry has significant role in improving and protecting the global environment and they are even competent over other conventional methods. In the present research work was focused on the synthesis of iron oxide nanoparticles using Azadirachta indica leaf extract as a plant resource. This method has been proven cost effective, simple, economical, eco-friendly and non-hazardous. On treatment of aqueous solutions of ferrous and ferric salts in alkaline medium with Azadirachta indica leaf extract, the rapid formation of stable iron oxide nanoparticles or also known as magnetite nanoparticles is observed to occur. In contrast to previously reported co-precipitation approaches, our synthesis method had utilized a much cheaper and less toxic iron precursor with environmental- ly benign and non-toxic Azadirachta indica leaf extract was used as a reducing and stabilizing agent. It was found that the presence of various biomolecules such as flavonoids and terpenoids of the aqueous leaf extract plays a major role for the formation of $Fe_3O_4$-NPs through infrared spectra analysis. The formation was further confirmed with strong characteristic peak observed at 249 nm for $Fe_3O_4$-NPs through UV-Vis spectroscopy. Besides, the shape was mostly spherical and oval. X-Ray Diffraction (XRD) analysis revealed the purity of synthesized Fe3O4-NPs with crystalline cubic structure phase. Transmission Electron Microscopy (TEM) results illustrated that the size and diameter was in the range from 9-14 nm which agrees with calculated Scherrer equation with average diameter of around 11 nm. Vibrating Sample Magnetometer (VSM) analysis indicated that the samples exhibit superparamagnetic with magnetization value was 82 emu/g. Results confirmed this protocol as a simple, rapid, one-step, eco-friendly, non-toxic and hence can be potentially used in various biomedical applications such as magnetic targeting drug delivery system

***Keywords:*** Azadirachta indica, Eco-friendly, Iron oxide nanoparticles, Magnetite, Non-toxic.

## INTRODUCTION

"Nano" is derived from the Greek word for dwarf. A environment friendly, easily scaled up for large scale nanometer is one billionth of a meter (109) and might be synthesis and in this method there is no need to use high represented by the length of ten hydrogen atoms lined up pressure, energy, temperature and toxic chemicals [9]. in a row [1] Nanotechnology implies the creation and Green synthesis offer better manipulation, control over utilization of materials, devices and systems through the crystal growth and their stabilization. This has motivated control of matter on the nanometer-length scale i.e. at the an upsurge in research on the synthetic routes that allows level of atoms, molecules and supramolecular structures better control of shape and size for various [2-4] Nanotechnology is mainly concerned with synthesis nanotechnological applications of nanoparticles of variable sizes, shapes, chemical. Here in the present work we have reported for the compositions and controlled dispersity and their potential first time the synthesis of green iron nanoparticles using use for human benefits. Although chemical and physical the leaf extract of the plant – (common name - Azadirachta indica (Neem) methods may successfully produce pure, well-defined Leaves). Aqueous Ferric Chloride solution, after reacting nanoparticles, these are quite expensive and potentially with Azadirachta indica (Neem) Leaves extract, led to rapid formation of highly dangerous to the environment. Use of biological stable, crystalline Iron nanoparticles. The rate of organisms such as microorganisms, plant extractor plant nanoparticle synthesis was very high, which justifies use biomass could be an alternative to chemical and physical of plants over microorganisms in the biosynthesis of methods for the production of nanoparticles in an ecometal nanoparticles through greener and safer methods. friendly manner [5-7]. Nanotechnology is a reliable and In the subsequent sections we have described the enabling

environment friendly process for the synthesis synthesis of iron nanoparticles based upon the change in of nanoscale particles. Nanosize results in specific color, change in pH, change in absorbance and the physicochemical characteristics such as high surface area particle size formed after reduction to volume ratio, which potentially results in high reactivity [8]. Biosynthesis of nanoparticles is a kind of bottomup approach where the main reaction occurring is reduction/oxidation. With the antioxidant or reducing properties of plant extracts, they are usually responsible metal compounds into their respective nanoparticles. Green synthesis provides advancement over chemical and physical method as it is cost effective,environment friendly, easily scaled up for environment friendly, easily scaled up for large scale nanometer is one billionth of a meter ($10^{-9}$) and might be synthesis and in this method there is no need to use high represented by the length of ten hydrogen atoms lined up pressure, energy, temperature and toxic chemicals [9]. Green synthesis offer better manipulation, control over utilization of materials, devices and systems through the crystal growth and their stabilization. This has motivated an upsurge in research on the synthetic routes that allows better control of shape and size for various nanotechnological applications.

Here in the present work we have reported for the first time the synthesis of green iron nanoparticles using use for human benefits. Although chemical and physical the leaf extract of the plant Azadirachta indica (Neem). Aqueous Ferric Chloride solution, after reacting with Azadirachta indica (Neem) Fig. 1 Leaves extract, led to rapid formation of highly stable, crystalline Iron nanoparticles.The rate of nanoparticle synthesis was very high, which justifies use of plants over microorganisms in the biosynthesis of metal nanoparticles through greener and safer methods.In the subsequent sections we have described the synthesis of iron nanoparticles based upon the change in color, change in pH, change in absorbance and the particle size formed after reduction.

**Fig. 1**: Azadirachta indica (Neem)

Due to environmental concerns, the green route methods have become increasingly popular to synthesize nanoparticles as they are well known to be environmentally-friendly and help to reduce harmful effects on environment [10]. Nanoparticle is a particle in the nanometre scale which usually in the range of 1 to 100 nm . During the last decade, the exploration of iron oxide nanoparticles ($Fe_3O_4$NPs) has earned numerous attentions as a consequence of their unique characteristics and various potential appli- cations in biomedicine field. Besides, iron oxide nanoparticles also are frequently encountered in most applications be- cause of their biocompatibility, super paramagnetism, high saturation magnetization and low toxicity. They are also the only type of magnetic nanoparticles that are approved by Food and Drug Administration (FDA) for clinical use. The various biomedical applications include magnetic resonance imaging (MRI) contrast agents, hyperthermia, magnetic targeted drug delivery, tissue specific release of therapeutic agents and magnetic field assisted radionuclide therapy [11]. The synthesized nanoparticles will be further studied for application in magnetic targeting drug delivery system. Hence, numerous methods were investigated for synthesis of $Fe_3O_4$-NPs with the aim to produce nanoparticles of different sizes, shapes, controlled dispersity and safer to be use biomedical applications like for magnetic targeting drug delivery system. Among them are sol gel process, co-precipitation, hydrothermal techniques, thermal decomposition, and microemulsion route [12].
However, the drawbacks of these methods include low production rates, high energy consumption and high cost, as well as the re- lease of a large amount of toxic byproducts, the usage of precursors and surfactants in organic solvent that are toxic enough to pollute the environment [13].

Thus, there is a growing need to develop environmentally benign nanoparticle synthesis that does not require harmful chemicals in the synthesis protocol. Synthesis of nanoparticles by plant extracts is an exciting possibility that is under exploration and exploitation. Green synthesis is not only able to reduce environmental impact but attractive enough if they are intended for invasive applications in medicine. It can be efficient alternative to produce large quanti- ties of nanoparticles that are eco-friendly, non-toxic, simpler and less expensive. The ready availability of reducing and capping agent

from the resource plant itself is an additional advantage of this system. In this study, we report the synthesis of $Fe_3O_4$NPs by one-pot reaction by the reduction of aqueous $Fe^{3+}$ and $Fe^{2+}$ ions with the Azadiratcha Indica leaf extract in an alkaline medium. Azadiratcha Indica or also known as neem has medicinal proper- ties such as antibacterial, antifungal and anthelmintic [14]. The alkaline medium in weak base also is more effective compared to using strong base. The water soluble $Fe_3O_4$NPs were character- ized by Fourier Transform Infrared (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Vibrating Scanning Magnetome- ter (VSM).

## EXPERIMENTAL

***Materials:*** In this work, the fresh leaves of Azadirachta indica (neem leaves) were collected from Batu Caves, Selangor, Malaysia. Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) and 25% ammonium hydroxide ($NH_4OH$) were purchased from Sigma Aldrich Chemical Company. All chemicals were of analytical grade and utilized without further purification.

***Methods:***

***Preparation of Azadirachta Indica Aqueous Leaf Extract:*** The leaves were thoroughly washed several times with distilled water to remove dust and then air dried at room temperature to remove the remaining moisture. Then, the dried leaves were cut into small pieces and made into powder. Approximately, 5 g of neem leaf powder was added into 100 mL sterile distilled water and the mixture was heated at constant temperature of 80 °C. Then, the mixture was left to cool at room temperature before vacuum-filtered through Whatman filter paper No. 1 to obtain extract. The extract was stored at 4 °C until further use.

***Synthesis of Iron Oxide Nanoparticles ($Fe_3O_4$-NPs) via Co-Precipitation Method:*** In a typical procedure, 0.40 g iron (II) chloride tetrahydrate (FeCl .$4H_2O$) and 1.10 g of iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) with 1:2 molar ratio were dissolved in 100 mL of sterile deionized water under nitrogen atmosphere. Following this, the resulting mixture was heated up to 80 °C under mild stirring for 10 minutes. Then, 5 mL of aqueous neem leaf extract was added slowly into the resulting mixture and subsequently 20 mL of 25% ammonium hydroxide (NH4OH) was added into the reac- tion mixture drop by drop using burette under vigorous stirring for 30 minutes. The instantaneous black color appearance indicated the formation of $Fe_3O_4$NPs. After 30 minutes, the solution was poured into a beaker and magnetic decantation was carried out in order to remove the supernatant. The intense black precipitate $Fe_3O_4$NPs was then washed with 15 mL deionized water and centrifuged at 5000 rpm for 10 minutes. The supernatant was re- moved. The product was washed again with 10 mL of deionized water followed by centrifugation. The supernatant was removed again. The pellet was transferred to a vial and 10 mL deionized water was added. The obtained black powder was freeze dried overnight and subjected for further characterization.

***Characterization:*** UV-Vis spectral analysis was done by using Perkin Elmer UV-Vis spectrometer Lambda 35 with a resolution of 1 nm between 200 and 600 nm. The size and the morphology of the $Fe_3O_4$NPs was observed by means of a transmission electron microscopy (TEM) using Technai G2 20S Twin TEM, Netherland working at 200 kV.The samples were prepared by drop deposition of a diluted solu- tion onto a carbon-coated copper grid. X-ray powder diffraction (XRD) was used to analyze the structure and identify the phase purity of Fe3O4 compounds. The samples were placed on a flat plate while intensity data were collected as a function of the Bragg angle, θ, in the range 2θ = 10° to 70° with a step size of 0.013° using a PAN analytical X'pert PRO diffractometer in Bragg- Brentono geometry using Cu Kα radiation wavelength $\lambda\alpha_1$ = 1.5405Å, $\lambda\alpha_2$ = 1.5443 Å. The structures were refined with the full-profile Rietveld method using GSAS [15] with the EXPGUI interface [16]. Fourier transform infrared (FTIR) spectra were collected using a Perkin Elmer FTIR spectrophotometer using KBr pellet method with a range of 4000–400 $cm^{-1}$. The magnetic properties of the prepared $Fe_3O_4$ NP were revealed using a vibrating sample magnetometer (VSM, Lake Shore 7404) at room temperature 300K. The magnetization measurements, M as a function of applied field (H) were measured under external magnetic fields up to ±14000 Oe.

## RESULTS AND DISCUSSION

***The Study of Fourier Transform Infrared Spectrum (FTIR) of Azadirachta Indica Leaf Extract and Synthesized $Fe_3O_4$ NPs:*** FTIR analysis of pure Azadirachta indica leaf extract (Fig. 2) and the synthesized $Fe_3O_4$-NPs (Fig. 3) were carried out to identify the potential functional groups of the biomolecules which are fla- vanones and terpernoids in the Azadirachta indica leaf extract which are responsible for the stabilization of iron oxide nanoparti- cles. The strong absorption band around 3324 cm-1 is due to the N-H stretching and bending vibration of amine group NH2 and the overlapping of the stretching vibration of OH attributed to water and Azadirachta indica leaf extract molecules. The de- crease in intensity at 3416 cm-1 implies the involvement of func- tional groups of Azadirachta indica in the reduction process.

The absorption peak at 1633 $cm^{-1}$ (Fig. 3 can be assigned to am- ide C=O stretching indicating the presence of –COOH group in the Azadirachta indica leaf extract. The decreasing intensity at 1633 $cm^{-1}$ (Fig. 3) signifies the involvement of amide C=O stretching in the reduction process. Meanwhile, the absorption peak at 2429 $cm^{-1}$ (Fig. 3) corresponds to alkyne group presents in phytoconstituents of extracts. Hence, the presence of these functional groups validates that flavanones or terpenoids molecules were chemically bonded to the surface of $Fe3O_4$NPs. It is evident from the small shifts in the peak position (Fig. 3 that the fla- vanones or terpenoids adsorbed on the surface of iron oxide nano-particles and capping effect did enhance $Fe_3O_4$-NPs inter-molecular interaction.

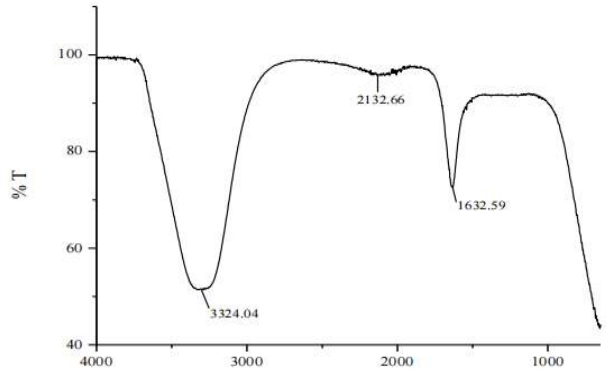


**Fig. 2:** FTIR spectrum of aqueous leaf extract of Azadirachta indica

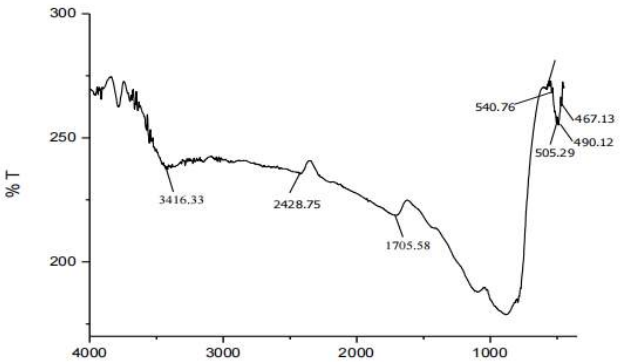


**Fig. 3:** FTIR spectrum of the synthesized $Fe_3O_4$-NPs

It was also observed the occurrence of strong peaks at 541 cm-1, 505 cm-1, 490 cm-1 and 467 cm-1 denote to the Fe-O stretching band of iron oxide nanoparticles. These results are comparable with previous literature that also used neem leaf extract but with a different alkaline medium in which the iron oxide nanoparticles peaks were observed at 513 cm-1, 460 cm-1 and 440 cm-1 [17]. Therefore, these results confirmed that the presence of various biomolecules such as flavonoids and terpenoids in the neem leaf extracts played an important role in the reduction and stability of $Fe_3O_4$NPs [1].

***The Study of Ultraviolet Visible Spectroscopy (UV-Vis):*** The synthesis of $Fe_3O_4$-NPs was confirmed by the UV-visible spectral analysis (Fig. 4). A strong peak at 249 nm region was observed due to the excitation of surface plasmon vibrations in the iron oxide nanoparticles. It is the characteristic absorption peak for iron oxide nanoparticles as reported by literature that obtained strong peak in between 230-250 nm [17], [18]. Hence, it was proven that $Fe_3O_4$NPs also can be synthesized using this one step reaction only.

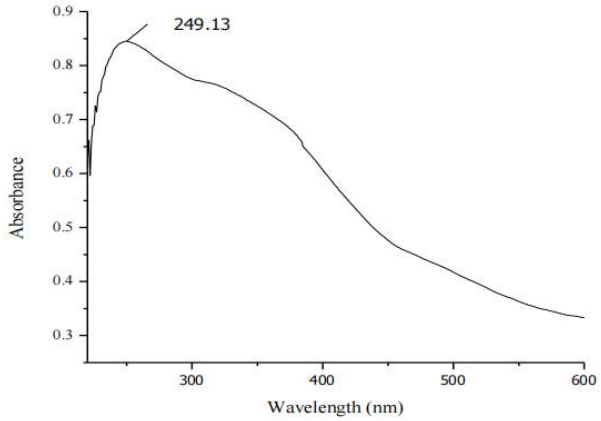


**Fig. 4:** UV-Visible absorption spectra of $Fe_3O_4$-NPs

***The Study of X-Ray Diffraction (XRD):*** Fig. 5 shows the X-Ray powder diffractions of $Fe_3O_4$ at room temperature. The XRD data clearly confirm the crystalline phase of $Fe3O_4$. From the X-ray diffraction patterns, six series of charac- teristic peaks at 2θ = 30°, 36°, 43°,54°, 57° and 63° which correspond to (220), (311), (400), (422), (511) and (440) were observed. All the diffraction peaks were indexed as a cubic structure of $Fe_3O_4$ phase and the calculated lattice parameter of the sample was 8.38 Å is in good agreement with the standard data (JCPDS file PDF:19-0627). The observed lattice parameter is similar with the reported in the literature [19]. No other characteristic peaks are detected in this pattern, indicating that the purity of the synthe- sized sample.

Based on the XRD data, the particle size of iron oxide nanoparticles can be calculated using Scherrer's formula as shown in Equa- tion 1.

$$D = \frac{0.9 \times \lambda}{\Delta \cos\theta} \tag{1}$$

where D is the crystallite size, 0.9 is a constant shape factor, λ is the X-ray wavelength, Δ is the full width at half maximum (FWHM) and θ is the Bragg's angle. The calculated average parti- cle size of $Fe_3O_4$ was found to be 11 nm.

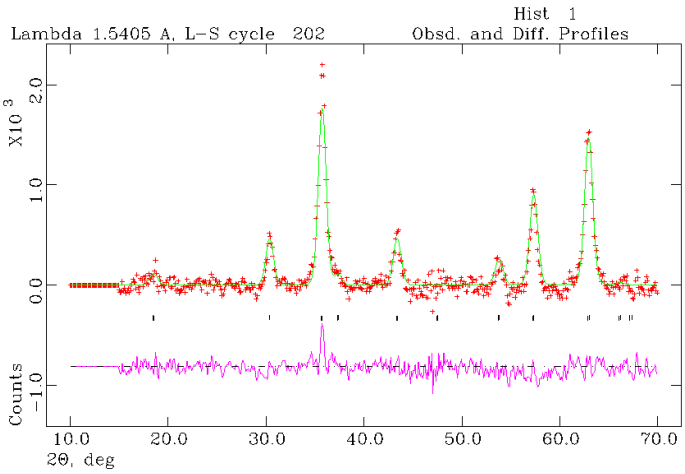


**Fig. 5:** Rietveld refinements of $Fe_3O_4$ against XRD data. Observed, calcu- lated and the difference profiles are represented by red crosses, green lines and pink lines, respectively

***The Study of Transmission Electron Microscope (TEM):*** Shown in Fig. 6 is a representative TEM micrograph of $Fe_3O_4$NPs. As shown in Fig. 6, the particle size distribution of the $Fe_3O_4$NPs is found to be in the range of 9-14 nm. It reveals that the $Fe_3O_4$NPs are well dispersed and predominantly spherical in shape, while some of the NPs were found to be having structures of irregular shape. The particle size agrees with that calculated from Scherrer equation with average diameter of around 11 nm. This result is comparable with previous literature [17] that used the same green route method but differed in the use of alkaline medium in which they used sodium hydroxide. The good correlation between particle sizes obtained from Scherrer equation and TEM supports the crystalline structure of the iron nanoparticles.

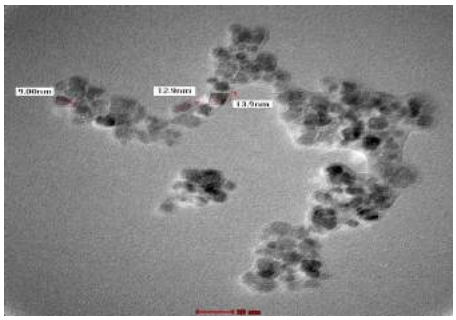

**Fig. 6:** TEM images of $Fe_3O_4$-NPs from Azadirachta indica leaf extract

***The Study of Vibrating Sample Magnetometer (VSM):*** The Fig. 7 shows the variation of magnetization (M) versus the applied magnetic field (H) measured by Vibrating Sample Magnetometer (VSM) at 300 K. No hysteresis loops were observed. The magnet- ization increases with increasing magnetic field and saturates at higher magnetic fields. The plot indicates that the samples exhibit superparamagnetic behavior with approximately zero remenance and coercivity. The saturation magnetization (Ms), determined by using the law approaches to saturation. The magnetization of $Fe_3O_4$ was 82 emu/g which is less than that of the actual magneti- zation of the $Fe_3O_4$ is 92 emu/g [20]. The decrease of the saturation is ascribed to the size effect in which the smaller the size of the nanoparticles, the lower the saturation magnetization value. The saturation magnetization (Ms) of the $Fe_3O_4$ indicates the pres- ence of non-magnetic surface layers resulting from the strong chemical attachment of the stabilizing agent of Azadirachta indica leaf extract to the $Fe_3O_4$'s surface, also observed by FTIR spectroscopy.

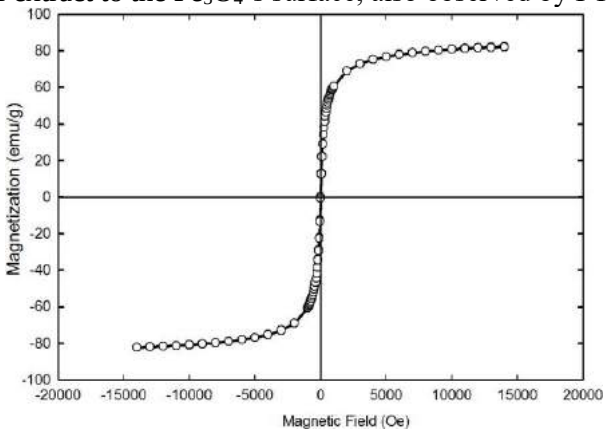


**Fig. 7:** Magnetization versus applied magnetic field for $Fe_3O_4$-NPs

***Macroscopic Observation:*** The $Fe_3O_4$-NPs exhibited a magnetic property in the presence of a magnetic field. It was observed that $Fe_3O_4$NPs were attracted towards external magnetic field when magnetic block was placed next to it as demonstrated in Fig. 8. The powder also was seen to move along when the magnetic block was moved around the vial. This was not observed without external magnetic field.

**Fig. 8:** Magnetic behaviour of iron oxide nanoparticles

## CONCLUSIONS

In this work, we had successfully demonstrated that crystalline $Fe_3O_4$-NPs can be synthesized in a one-step reaction using a green facile approach with the less use of hazardous and toxic chemicals in which contributes to more environmentally and eco-friendly approach. The use of Azadirachta indica

leaf extract as reducing and stabilizing agent also has been proven to be effective and efficient according to FTIR analysis. The results of the $Fe_3O_4$ have been characterized to be crystalline in nature by XRD, and all the diffraction peaks can be indexed to the pure cubic phase. The TEM result confirmed the size of nanoparticles are in the range of 9-14 nm. The magnetic properties are measured by the vibration sample magnetometer (VSM) and the particles have the properties of the saturation magnetization (Ms) of 82 emu/g. The magnetization measurements confirm that the samples are superparamagnetic. In summary, $Fe_3O_4$-NPs synthesized in this work could be useful for biomedical applications as magnetic targeting drug delivery system or contrasting agents due to their small particle size and superparamagnetic property.

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# Cation distribution in nano crystalline $Cd^{2+}$ co-substituted $CuFe_2O_4$ by wet chemical co precipitation method

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## ABSTRACT

Spinel ferrites with general formula $Cu_{1-x}Cd_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) were prepared by wet chemical co-precipitation method.The physical Structural properties of the present spinal system were studied by means X-ray diffraction The X-ray diffraction pattern indicates that sample posses' single phase cubic spinal structure. The lattice constant calculated from X-ray data increases with the substitution of cadmium ions. In the present work the distribution of cations so called cation distribution was investigated by using X-ray intensity ratio calculation. Cation distribution suggests that the $Cu^{2+}$ ions occupy octahedral – B site. $Cd^{3+}$ ions replace $Fe^{2+}$ ions at tetrahedral – A site.

***Keywords:*** *Wet chemical co precipitation, X-ray diffraction, lattice parameter, cation distribution.*

## INTRODUCTION

Spinel ferrites, also known simply as spinels, are a class of ceramic materials with a unique crystal structure that belong to the spinel group. These materials are characterized by their remarkable magnetic, electrical, and structural properties making them widely utilized in various technological applications. The term spinel refers to the crystal structure, which is composed of two different metal cations, typically one trivalent and one divalent arranged in cubic close-packed oxygen lattice.

The general chemical formula for spinel ferrites is $AB_2O_4$, where A and B represent the metal cations occupying specific crystallographic sites within the spinel structure. The most common spinel ferrites are derived from transition metals such as iron. Cobalt, nickel etc. Among them ferrites based on iron (Fe) are particularly significant due to their widespread applications in electronics, telecommunications and magnetic devices.

The electrical properties of ferrites depend upon chemical composition, Methods of preparation and sintering temperature [1, 2]. The wet prepared ferrites have been studied by many workers [3-5]. By. Using co-precipitation, sol-gel, freeze drying, spray drying etc. wet chemical routes, the particle size can be brought down at much lower temperature compared to ceramic technique and which helps to have intimate mixing of reaction of the constituent reactions. These wet chemical methods are reproducible, low cost and requires low temperature. The present work reports cation study of Cd substitution on copper ferrite.

## EXPERIMENTAL

The ferrite system $Cu_{1-x}Cd_xFe_2O_4$ (for x = 0.0, 0.1 and 0.2) were prepared wet chemical co-precipitation method using $CuSO_45H_2O$, $3CdSO_48H_2O$ and $FeSO_47H2O$. The XRD patterns of all were recorded using Cu-$K_\alpha$ radiation on a Pw710 diffractometer. The physical properties of the prepared samples were determined by X-ray powder diffraction technique. The X-ray diffraction (XRD) patterns of all the samples were recorded on a PW710 diffractometer using CuKα radiation in the range of $2\theta = 10^0$ to $90^0$ and scanning rate of one degree per minute.

## RESULTS AND DISCUSSION

***XRD Analysis:*** Fig.1 shows the XRD patterns of the samples of the present system for Cd content X=0.0 0.1and 0.2. These XRD patterns show sharp lines corresponding to single phase cubic spinel

structure. The values of lattice constant 'a' were determined from XRD date and are listed in Table I. It is evident that the lattice constant initially increases with increase in Cd content. The variation of lattice with cadmium concentration can be explained by considering the difference in ionic radii of cadmium and copper. In the present series $Cu_{1-x}$ $Cd_xFe_2O_4$ $Cu^{2+}$ ions of smaller ionic radii (0.70Å) are replaced by larger ionic radii $Cd^{2+}$ (0.99Å) ions. This causes the increase in lattice constant. The x - ray density for each sample was calculated using the relation

$$dx = ZM/NV \quad (1)$$

Where Z is the number of molecules per unit cell (Z=8), M is molecular weight, N is Avogadro's number and V is volume of unit cell. The values of X-ray density listed in Table 1 are found to increase with substitution of cadmium. This shows that the decrease in mass over takes the decrease in volume of unit cell in the present system. The values of particle size t of all the samples estimated by using Scherer's formula [9] are listed in Table 1. It is evident that the particles size is found to vary in the range of 177Å to 80Å.

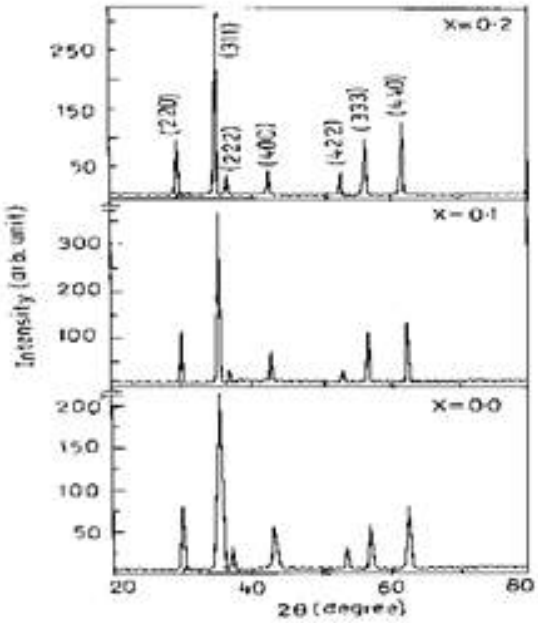


**Fig. 1**: X-ray diffraction patterns of $Cu_{1-x}Cd_xFe_2O_4$

**Table 1:** Lattice constant (a), X-ray density (dx) and particle size for $Cu_{1-x}$ $Cd_xFe_2O_4$

| Composition x | Lattice constant a ($A^0$) | X-ray density dx ($gm/cm^3$) | Particle size t (Å) |
|---|---|---|---|
| 0.0 | a=8.39c=8.43 | 5.381 | 177 |
| 0.1 | 8.42 | 5.432 | 270 |
| 0.2 | 8.45 | 5.482 | 280 |

***Cation distribution:*** In the present work the distribution of cations (so called cation distribution) in $Cu_{1-x}Cd_xFe_2O_4$ was investigated by using X-ray intensity ratio calculation. In this method observed intensity ratios were compared with the calculated intensity ratios for various possible combinations of cations occupying tetrahedral (A) and octahedral [B] sites. In calculating X-ray intensity ratios, the absorption and temperature factors are not taken into consideration since these do not affect the relative intensity calculations for spinels at room temperature. The X-ray intensity ratios were calculated using Burger's formula (equation 1) for the planes (220), (400), (422), and (440), as these planes are sensitive to the cation distribution. It is assumed that $Cd^{2+}$ ions have strong preference for tetrahedral (A) site whereas $Cu^{2+}$ ions preferred to accommodate at tetrahedral (A) site as well as octahedral [B] site. The calculated experimental ratios were then compared with the observed intensity ratios for different combinations of cations and the combinations of cations for which observed and calculated intensity ratios are closely agreed is taken as the correct cation distribution. The cations distribution in $Cu_{1-x}Cd_xFe_2O_4$ obtained by

using X-ray intensity ratio calculations is presented in Table 2.The calculated intensity ratio and observed intensity ratio are given in Table 3.

**Table 2**: Cation distribution of $Cu_{1-x}Cd_xFe_2O_4$

| Comp. 'x' | A-Site | | | B-Site | | |
|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Cd^{2+}$ | $Fe^{3+}$ | $Cu^{2+}$ | $Cd^{2+}$ | $Fe^{3+}$ |
| **0.0** | 0.0 | 0.0 | 1 | 1 | 0.0 | 1 |
| **0.1** | 0.0 | 0.1 | 0.9 | 0.9 | 0.0 | 1.1 |
| **0.2** | 0.0 | 0.2 | 0.8 | 0.8 | 0.0 | 1.2 |

**Table 3**: X-ray intensity ratio calculations of $Cu_{1-x}Cd_xFe_2O_4$

| Comp. 'x' | Intensity ratio | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | I(220/400) | | | I(422/440) | | | I(440/400) | | |
| | $I_{cal}$ | $I_{Obs}$ | R | $I_{cal}$ | $I_{Obs}$ | R | $I_{cal}$ | $I_{Obs}$ | R |
| x=0.0 | **1.17** | **1.12** | **0.05** | **0.194** | **0.19** | **0.004** | **2.063** | **1.9** | **0.163** |
| | 1.2 | 1.12 | 0.08 | 0.2 | 0.19 | 0.01 | 2.09 | 1.9 | 0.19 |
| | 1.23 | 1.12 | 0.11 | 0.2 | 0.19 | 0.01 | 2.117 | 1.9 | 0.217 |
| x=0.1 | **1.55** | **0.884** | **0.666** | **0.229** | **0.17** | **0.059** | **2.379** | **1.412** | **0.967** |
| | 1.385 | 0.884 | 0.501 | 0.216 | 0.17 | 0.046 | 2.247 | 1.412 | 0.835 |
| | 1.635 | 0.884 | 0.751 | 0.235 | 0.17 | 0.065 | 2.446 | 1.412 | 1.034 |
| | 1.291 | 0.884 | 0.407 | 0.207 | 0.17 | 0.037 | 2.147 | 1.412 | 0.735 |
| x=0.2 | **2.037** | **0.62** | **1.417** | **0.29** | **0.074** | **0.216** | **2.777** | **0.608** | **2.169** |
| | 2.145 | 0.62 | 1.525 | 0.297 | 0.074 | 0.223 | 2.859 | 0.608 | 2.251 |
| | 1.493 | 0.62 | 0.873 | 0.248 | 0.074 | 0.174 | 2.348 | 0.608 | 1.74 |

## CONCLUSIONS

A series of cadmium substituted copper ferrites with composition $Cu_{1-x}Cd_xFe_2O_4$ (x = 0.0, 0.1 and 0.2) were prepared by wet chemical co-precipitation method. X-ray diffraction analysis confirms the single-phase cubic spinel structure for all the samples. Decrease in dc resistivity of Cd content is due to electron-hole compensation. Decrease in dc resistivity for Cd is due to hoping mechanism between $Co^{2+}$ and $Co^{3+}$ ions.

## ACKNOWLEDGEMENT

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# The Impact on the student Progress in learning of trigonometry by Mathematical Software GeoGebra

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**ABSTRACT**

The purpose of this study is to determine the effects of dynamic mathematics software GeoGebra on student achievement in teaching of trigonometry. The sample of the study consists of Some of good quality schools from Beed district. The experimental group was subjected to the lessons arranged with the GeoGebra software in computer assisted teaching method, while the control group was subjected to the lessons shaped with constructivist instruction. The data collected after 5 weeks of application show that there is a meaningful difference between experimental and control groups' achievement in trigonometry. This difference is in favour of the experimental group which had lessons with GeoGebra.

***Keywords:*** *Trigonometry, Dynamic mathematics software, GeoGebra, Achievement*

## INTRODUCTION

The computer is a powerful and helpful tool in teaching and learning mathematics, in particular in understanding the mathematical concepts, as it was noted by many authors. There is a struggle to integrate the computer in school. This approach must be read: *"the integration of educational software in education"*. This is a related desire to implement new teaching methods in mathematics. An *"educational software application"* is something that everyone could use on a computer, without having advanced knowledge about computers and programming. Draw, build and investigate properties, change shape and size.

It is often said more about using interactive methods in teaching mathematics and about their implementation in the curriculum. However we appreciate that the first step must be done when the blackboard and chalk are replaced with dynamic image of mathematical phenomena, integrated in dynamic software like GeoGebra. There are no barriers to this and only the wish to use the system can produce the desired success.

Many studies have been working for nearly fifteen years with several mathematical packages including *Logo,Geometer's Sketchpad, Cabri, Derive, Mathematica, Scientific WorkPlace.* In recent years, a number of studies in which dynamic mathematics software GeoGebra is used. The software that provide visual and effective learning environment for students have increased as Technological improvements have increase. One of these softwares, Geogebra, can be defined as Computer Algebra System (CAS) since it includes the symbolical and visualization features such as direct coding of equations and coordinates, defining functions as algebraical. It can also be defined as Dynamic Geometry Software (DGS) since it includes concepts such as points, segments, lines, conic segments and provides dynamic relationships between the concepts .It is the basic feature of GeoGebra that can be approached both CAS and DGS. In education of math, the ability of software making a relationship between geometry and algebra has become an important value in math curriculum.

During the past decades, there has been a great evolution in mathematical software packages. Of a great amount of software, there are two important forms of software contributing to the teaching and learning of mathematics; CAS and DGS. These two tools have had a high influence on mathematics education. However, these are not connected to each other at all. Fortunately there is a software system called GeoGebra that integrates possibilities of both dynamic geometry and computer algebra in one program for mathematics teaching.

***What is GeoGebra**:* Created by Markus Hohenwarter in 2001, GeoGebra represents one such software program that was designed to combine geometry, algebra, and calculus in a single, dynamic environment. GeoGebra is an open-source (freely- available), dynamic mathematics software program created by Markus Hohenwarter for his master's thesis project at the University of Salzburg, Austria. The official GeoGebra website, located at http://www.geogebra.org, features the most recent version of the software download, access to GeoGebraWiki and the User Forum, related publications, and information regarding regional GeoGebra Institutes.

***Why is GeoGebra:*** GeoGebra is a dynamic learning environment that enables its users to create mathematical objects and interact with them. GeoGebra users, mostly teachers or students, can use this environment to explain, to explore, and to model mathematical concepts and the relationships between them, or mathematics in general.

GeoGebra accepts geometric, algebraic, and calculus commands and links multiple representations. It is also an open source mathematics software program. When developing this software, its programmers aimed to enable multiple representations and visualization of mathematical concepts. So, GeoGebra helps the users to create activities incorporating multiple representations of mathematical concepts that are dynamically linked. Using computer in geometry teaching is implemented with the new elementary mathematics curriculum in our country and has become indispensable (MEB, 2005). The most important role of computers in primary mathematics education is stated as "making the learning of abstract concepts easier" in the curriculum. Some previous researches in the area reported that computer use is more effective than the constructivist approach to learning.

***Why is Trigonometry:*** Trigonometry is one of the subjects in mathematics which students experience crucial difficulties in learning. In this study, the efficiency of the computer assisted instruction method, in which the GeoGebra software is used, in the teaching of trigonometric functions and graphs of trigonometric functions subtopics will be determined.

***Purpose of this study:*** The purpose of this study is to determine the effects of dynamic mathematics software GeoGebra on students' achievements in trigonometric functions and graphs of trigonometric functions subtopics which are placed as trigonometry in math class.

## METHODOLOGY

***Research Model:*** The research was conducted in a Pretest-Posttest Control Grouped of Beed District High Schools

***Experiment and Control Group:*** The pretest results show that there was not any statistically significant difference between the groups. Therefore, one of the groups selected as experiment and the other as control group. This experimental study is conducted in the fall semester of 2016-2017 academic years. The experimental group was subjected to the lessons arranged with the GeoGebra software in computer assisted teaching method to observe the effect of dynamic mathematics software GeoGebra, while the control group was subjected to the lessons shaped with constructivist instruction. A computer assisted instructional material was developed by the researchers for that purpose.

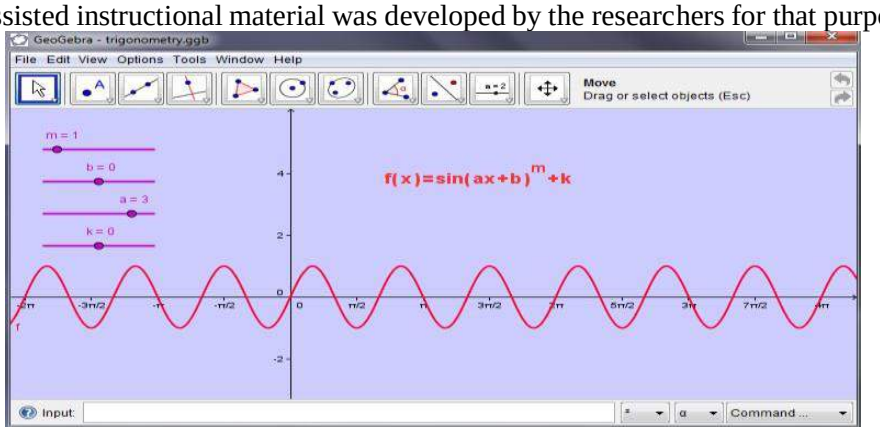


**Fig. 1:** A view of the material for trigonometric functions

***Process:*** A five weeks course which contained twelve main GeoGebra activities and many other practices about the stated achievements has been planned in accordance with the official mathematics curriculum. Then the activities were constructed with GeoGebra for the experiment group. The GeoGebra prepared activities aimed to make the subject more dynamic, concrete and visual. GeoGebra software was introduced in introductory hour of the course. In all of the other sessions, the GeoGebra prepared activities were shared with the students both with visual and dynamic features. Furthermore, examples and drawings on the textbooks were constructed with the GeoGebra during the sessions. In the official curriculum teaching of trigonometric functions and graphs of trigonometric functions subtopics for tenth grade takes total of 20 hours with nine different objectives.

***Achievement Test:*** By examining the target behaviors determined by the Ministry of National Education for the unit trigonometric functions and graphs of trigonometric functions subtopics. The test involved 10 items with open-ended questions. In line with the targets of the given unit, an achievement test consisting of 10 open-ended questions prepared by using different test books and questions previously asked in high school entrance examinations was designed. The achievement test was designed to measure the following objectives that the students in both groups were expected to achieve during the study. The test was prepared by the researchers and checked by five mathematics teachers, three of whom were mathematics educators. The test was piloted with 45 tenth grade students. The main purpose of the pilot was to determine students' difficulties in understanding the tasks used in the test and prepare open-ended explorations in the main study.

***Sample:*** We examine the 55 High School from Beed District 11 block. The sample of the study consists attending to a high school Shri Siddheshwar Vidyalaya in Majalgaon during the 2016-2017 academic year. 50 participants of that sample group were selected into experimental group while the other 51 ones were selected into the control group.


## RESULTS AND DISCUSSION

**Table 1:** Pre- test Post-test Results of Control Group

| Tests | N | Mean | SD | Df | T | Significant |
|---|---|---|---|---|---|---|
| Pre Test | 51 | 38.86 | 8.58 | 21 | -5.36 | 0.000 |
| Post Test | 51 | 54.09 | 9.83 | | | |

As the Table 5.1. is examined, it is seen that there is a statistically meaningful difference between the student's success points of the control group on pre-experimental process and the points on post experimental process (t= -5.36, p<.05). The origin of the difference is seen that students are more successful on post- experimental processes (Mean=54.09), than the pre-experimental processes (Mean =38.86). This finding can be interpreted that the lessons which are studied in constructive approach has a meaningful effect on students' learning of control group.

**Table 2:** Pre-test Post-test Results of Experimental Group

| Tests | N | Mean | SD | Df | T | Significant |
|---|---|---|---|---|---|---|
| Pre Test | 50 | 39.78 | 9.70 | 22 | -16.03 | 0.000 |
| Post Test | 50 | 72.39 | 12.51 | | | |

As the Table 2. is examined, it is seen that there is a statistically meaningful difference between the students' success points of the experimental group on pre-experimental process and the points on post experimental process (t= -16.03, p<.05). The origin of the difference is seen that students are

more successful on post experimental processes (Mean=72.39), than the pre-experimental processes (Mean=38.86). This finding can be interpreted that the lessons in which Geogebra software is used has a meaningful effect on students' learning of the experimental group.

**Table 3:** Independent-T Test Comparing The Result Post-Test Between Groups

| Groups | N | Mean | SD | Df | T | Significant |
|---|---|---|---|---|---|---|
| Control Group | 51 | 54.09 | 9.83 | 43 | 5.43 | 0.000 |
| Experimental Group | 50 | 72.39 | 12.51 | | | |

From the above table, the result of the independent-t test comparing the post-test results of the two groups showed that there was a significant difference between mean performance scores of the control group ( Mean=54.09, SD= 9.83) compared to GeoGebra group ( Mean=72.39, SD= 12,51; t(51) = 5.43, p = .000< .01). The difference between the means is 18.30 points on a 100-point test. This finding indicated that students who had learned trigonometry using GeoGebra was significantly better in their achievement compared to students who underwent the constructivist instruction.

## CONCLUSIONS

In this study, the effects of the computer assisted instruction method in which dynamic mathematics software is used on achievement in the subject of trigonometry are analyzed. With respect to the data belongs to trigonometry achievement pre-test, there is not a meaningful difference between the groups. Throughout the study, both groups' success was increased. According to trigonometry achievement post-test results, the instruction structured according to trigonometry teaching approach is more successful than constructivist instruction. The results of the study indicated that there was a significant difference between the means of the students' scores on the posttest in favor of the GeoGebra group.

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# Everyday Mathematics and Algorithm

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**ABSTRACT**
An **algorithm** is a step-by-step procedure designed to achieve a certain objective in a finite time, often with several steps that repeat or "loop" as many times as necessary. The most familiar algorithms are the elementary school procedures for adding, subtracting, multiplying, and dividing, but there are many other algorithms in mathematics.
***Keywords:*** *Algorithm, arithmetic, procedure etc,*

## ALGORITHAM IN SCHOOL MATHEMATICS

The place of algorithms in school mathematics is changing. One reason is the widespread availability of calculators and computers outside of school. Before such machines were invented, the preparation of workers who could carry out complicated computations by hand was an important goal of school mathematics. Today, being able to mimic a $5 calculator is not enough: Employers want workers who can think mathematically. How the school mathematics curriculum should adapt to this new reality is an open question, but it is clear that proficiency at complicated paper-and-pencil computations is far less important outside of school today than in the past. It is also clear that the time saved by reducing attention to such computations in school can be put to better use on such topics as problem solving, estimation, mental arithmetic, geometry, and data analysis (NCTM, 1989).

Another reason the role of algorithms is changing is that researchers have identified a number of serious problems with the traditional approach to teaching computation. One problem is that the traditional approach fails with a large number of students. Despite heavy emphasis on paper-and-pencil computation, many students never become proficient in carrying out algorithms for the basic operations. In one study, only 60 percent of U.S. ten-year-old achieved mastery of subtraction using the standard "borrowing" algorithm. A Japanese study found that only 56 percent of third graders and 74 percent of fifth graders achieved mastery of this algorithm. A principal cause for such failures is an overemphasis on procedural proficiency with insufficient attention to the conceptual basis for the procedures. This unbalanced approach produces students who are plagued by "bugs," such as always taking the smaller digit from the larger in subtraction, because they are trying to carry out imperfectly understood procedures.

An even more serious problem with the traditional approach to teaching computation is that it engenders beliefs about mathematics that impede further learning. Research indicates that these beliefs begin to be formed during the elementary school years when the focus is on mastery of standard algorithms (Hiebert, 1984; Cobb, 1985; Baroody & Ginsburg, 1986). The traditional, rote approach to teaching algorithms fosters beliefs such as the following:

- mathematics consists mostly of symbols on paper;
- following the rules for manipulating those symbols is of prime importance;
- mathematics is mostly memorization;
- mathematics problems can be solved in no more than 10 minutes — or else they cannot be solved at all;
- speed and accuracy are more important in mathematics than understanding;
- there is one right way to solve any problem;
- different (correct) methods of solution sometimes yield contradictory results; and
- Mathematics symbols and rules have little to do with common sense, intuition, or the real world.

These inaccurate beliefs lead to negative attitudes. The prevalence of math phobia, the social acceptability of mathematical incompetence, and the avoidance of mathematics in high school and beyond indicate that many people feel that mathematics is difficult and unpleasant.

Researchers suggest that these attitudes begin to be formed when students are taught the standard algorithms in the primary grades. Hiebert (1984) writes, "Most children enter school with reasonably good problem-solving strategies. A significant feature of these strategies is that they reflect a careful analysis of the problems to which they are applied. However, after several years many children abandon their analytic approach and solve problems by selecting a memorized algorithm based on a relatively superficial reading of the problem." By third or fourth grade, according to Hiebert, "many students see little connection between the procedures they use and the understandings that support them. This is true even for students who demonstrate in concrete contexts that they do possess important understandings." Baroody and Ginsburg (1986) make a similar claim: "For most children, school mathematics involves the mechanical learning and the mechanical use of facts — adaptations to a system that are unencumbered by the demands of consistency or even common sense."

A third major reason for changes in the treatment of algorithms in school mathematics is that a better approach exists. Instead of suppressing children's natural problem-solving strategies, this new approach builds on them (Hiebert, 1984; Cobb, 1985; Baroody & Ginsburg, 1986; Resnick, Lesgold, & Bill, 1990). For example, young children often use counting strategies to solve problems. By encouraging the use of such strategies and by teaching even more sophisticated counting techniques, the new approach helps children become proficient at computation while also preserving their belief that mathematics makes sense. This new approach to computation is described in more detail below.

Reducing the emphasis on complicated paper-and-pencil computations does not mean that paper- and-pencil arithmetic should be eliminated from the school curriculum. Paper-and-pencil skills are practical in certain situations, are not necessarily hard to acquire, and are widely expected as an outcome of elementary education. If taught properly, with understanding but without demands for "mastery" by all students by some fixed time, paper-and-pencil algorithms can reinforce students' understanding of our number system and of the operations themselves. Exploring algorithms can also build estimation and mental arithmetic skills and help students see mathematics as a meaningful and creative subject.

## ALGORITHAMS IN EVERYDAY MATHEMATICS

*Everyday Mathematics* includes a comprehensive treatment of computation. Students learn to compute mentally, with paper and pencil, and by machine; they learn to find both exact and approximate results; and, most importantly, they learn what computations to make and how to interpret their answers. The following sections describe in general terms how *Everyday Mathematics* approaches exact paper-and-pencil methods for basic operations with whole numbers. For details about particular algorithms and for information about how the program teaches mental arithmetic, estimation, and computation with decimals and fractions, see the *Everyday Mathematics Teacher's Reference Manual*.

In *Everyday Mathematics*, computational proficiency develops gradually. In the beginning, before they have learned formal procedures, students use what they know to solve problems. They use their common sense and their informal knowledge of mathematics to devise their own procedures for adding, subtracting, and so on. As students describe, compare, and refine their approaches, several alternative methods are identified. Some of these alternatives are based on students' own ideas; others are introduced by the teacher or in the materials. For each basic operation, students are expected to become proficient at one or more of these alternative methods.

The materials also identify one of the alternative algorithms for each operation as a *focus algorithm*. The purpose of the focus algorithms is two-fold: (i) to provide back-up methods for those students who do not achieve proficiency using other algorithms, and (ii) to provide a common basis for further work. All students are expected to learn the focus algorithms at some point, though, as always in *Everyday Mathematics*, students are encouraged to use whatever method they prefer when they solve problems.

The following sections describe this process in more detail. Note, however, that although the basic approach is similar across all four operations, the emphasis varies from operation to operation because of differences among the operations and differences in students' background knowledge. For example, it is easier to invent efficient procedures for addition than for division. There is, accordingly,

less expectation that students will devise efficient procedures for solving multidigit long division problems than that they will succeed in finding their own good ways to solve multidigit addition problems.

## INVENTED PROCEDURES

When they are first learning an operation, *Everyday Mathematics* students are asked to solve problems involving the operation before they have developed or learned systematic procedures for solving such problems. In second grade, for example, students are asked to solve multidigit subtraction problems. They might solve such problems by counting up from the smaller to the larger number, or by using tools such as number grids or base-10 blocks, or they may use some other strategy that makes sense to them. This stage of algorithm development may be called the invented procedures phase.

To succeed in devising effective procedures, students must have a good background in the following areas:

- *Our system for writing numbers*. In particular, students need to understand place value.
- *Basic facts*. To be successful at carrying out multistep computational procedures,students need proficiency with the basic arithmetic facts.
- *The meanings of the operations and the relationships among operations*. To solve 37 – 25, for example, a student might reason, "What number must I add to 25 to get 37?"
- Research indicates that students can succeed in inventing their own methods for solving basic computational problems (Madell, 1985; Kamii & Joseph, 1988; Cobb & Merkel, 1989; Resnick, Lesgold, & Bill, 1990; Carpenter, Fennema, & Franke, 1992). Inventing procedures flourishes when:
- the classroom environment is accepting and supportive;
- adequate time for experimentation is allotted;
- computational tasks are embedded in real-life contexts; and
- students discuss their solution strategies with the teacher and with one another.

The discussion of students' methods is especially important. Through classroom discussion, teachers gain valuable insight into students' thinking and progress, while students become more skilled at communicating mathematics and at understanding and critiquing others' ideas and methods. Talking about why a method works, whether a method will work in every case, which method is most efficient, and so on, helps students understand that mathematics is based on common sense and objective reason, not the teacher's whim. Such discussions lay the foundations for later formal work with proof.

The invented-procedures approach to algorithm development has many advantages:

- Students who invent their own methods learn that their intuitive methods are valid and that mathematics makes sense.
- Inventing procedures promotes conceptual understanding of the operations and of base-10 place-value numeration. When students build their own procedures on their prior mathematical knowledge and common sense, new knowledge is integrated into a meaningful network so that it is understood better and retained more easily.
- Inventing procedures promotes proficiency with mental arithmetic. Many techniques that students invent are much more effective for mental arithmetic than standard paper-and-pencil algorithms. Students develop a broad repertoire of computational methods and the flexibility to choose whichever procedure is most appropriate in any particular situation.
- Inventing procedures involves solving problems that the students do not already know how to solve, so they gain valuable experience with non-routine problems. They must learn to manage their resources: *How long will this take? Am I wasting my time with this approach? Is there a better way?* Such resource management is especially important in complex problem solving. As students devise their own methods, they also develop persistence and confidence in dealing with difficult problems.
- Students are more motivated when they don't have to learn standard paper-and-pencil algorithms by rote. People are more interested in what they can understand, and students generally understand their own methods.
- Students become adept at changing the representations of ideas and problems, translating readily among manipulatives, words, pictures, and symbols. The ability to represent a problem in more

than one way is important in problem solving. Students also develop the ability to transform any given problem into an equivalent, easier problem. For example, 32 – 17 can be transformed to 35 – 20 by adding 3 to both numbers.

Another argument in favor of the invented-procedures approach is that learning a single standard algorithm for each operation, especially at an early stage, may actually inhibit the development of students' mathematical understanding. Premature teaching of standard paper-and-pencil algorithms can foster persistent errors and buggy algorithms and can lead students to use the algorithms as substitutes for thinking and common sense.

## ALTERNATIVE ALGORITHMS

Over the centuries, people have invented many algorithms for the basic arithmetic operations. Each of these historical algorithms was developed in some context. For example, one does not need to know the multiplication tables to do "Russian Peasant Multiplication" — all that is required is doubling, halving, and adding. Many historical algorithms were "standard" at some time and place, and some are used to this day. The current "European" method of subtraction, for example, is not the same as the method most Americans learned in school.

The U.S. standard algorithms—those that have been most widely taught in this country in the past 100 years—are highly efficient for paper-and-pencil computation, but that does not necessarily make them the best choice for school mathematics today. The best algorithm for one purpose may not be the best algorithm for another purpose. The most efficient algorithm for paper-and-pencil computation is not likely to be the best algorithm for helping students understand the operation, nor is it likely to be the best algorithm for mental arithmetic and estimation. Moreover, if efficiency is the goal, in most situations it is unlikely that *any* paper- and-pencil algorithm will be superior to mental arithmetic or a calculator.

If paper-and-pencil computation is to continue to be part of the elementary school mathematics curriculum, as the authors of *Everyday Mathematics* believe it should, then alternatives to theU.S. standard algorithms should be considered. Such alternatives may have better cost-benefit ratios than the standard algorithms. Historical algorithms are one source of alternatives. Student-invented procedures are another rich source. A third source is mathematicians and mathematics educators who are devising new methods that are well adapted to our needs today. The *Everyday Mathematics* approach to computation uses alternative algorithms from all these sources.

In *Everyday Mathematics*, as students explain, compare, and contrast their own invented procedures, several common alternative methods are identified. Often these are formalizations of approaches that students have devised. The column-addition method, for example, was shown and explained to the *Everyday Mathematics* authors by a first grader. Other alternative algorithms, including both historical and new algorithms, are introduced by the teacher or the materials. The partial-quotients method, for example, first appeared in print in Isaac Greenwood's *Arithmeticks* in 1729.

Many alternative algorithms, whether based on student methods or introduced by the teacher, are highly efficient and easier to understand and learn than the U.S. traditional algorithms. For example, lattice multiplication requires only a knowledge of basic multiplication facts and the ability to add strings of single-digit numbers, and yet it is more efficient than the traditional long multiplication algorithm for all but the simplest multidigit problems. Students are urged to experiment with various methods for each operation in order to become proficient at using at least one alternative. The alternative-algorithms phase of algorithm development has significant advantages:

- A key belief in *Everyday Mathematics* is that problems can (and should) be solved in more than one way. This belief in multiple solutions is supported by the alternative-algorithms approach to developing computational proficiency.
- Providing several alternative algorithms for each operation affords flexibility. A one-size- fits-all approach may work for many students, but the goal in *Everyday Mathematics* is to reach *all* students. One algorithm may work well for one student, but another algorithm may be better for another student.
- Different algorithms are often based on different concepts, so studying several algorithms for an operation can help students understand the operation.
- Presenting several alternative algorithms gives the message that mathematics is a creative field. In today's rapidly changing world, people who can break away from traditional ways of thinking

are especially valuable.

Teaching multiple algorithms for important operations is common in mathematics outside the elementary school. In computer science, for example, alternative algorithms for fundamental operations are always included in textbooks. An entire volume of Donald Knuth's monumental work, *The Art of Computer Programming* (1998), is devoted exclusively to sorting and searching. Knuth presents many inefficient sorting algorithms because they are instructive.

## FOCUS ALGORITHMS

The authors of *Everyday Mathematics* believe that the invented-procedures/alternative-algorithms approach described above is a radical improvement over the traditional approach to developing computational proficiency. The *Everyday Mathematics* approach is based on decades of research and was refined during extensive fieldtesting. Student achievement studies indicate, moreover, that when the approach is properly implemented, students do achieve high levels of computational proficiency (Carroll, 1996, 1997; Carroll & Porter, 1997, 1998; Fuson, Carroll, & Drueck, 2000; Carroll, Fuson, & Diamond, 2000; Carroll & Isaacs, in press).

In the second edition of *Everyday Mathematics*, the approach described above is extended in one significant way: For each operation, one of the several alternative algorithms is identified as a focus algorithm. All students are expected to learn the focus algorithms eventually, although, as usual in *Everyday Mathematics*, proficiency is expected only after multiple exposures over several years. Students are also not required to use the focus algorithms in solving problems if they have alternatives they prefer. For addition, the focus algorithm is partial-sums; for subtraction, trade-first; for multiplication, partial-products; and for division, partial-quotients. (See the *Everyday Mathematics Teacher's Reference Manual* for details about these and other algorithms.)

The focus algorithms are powerful, relatively efficient, and easy to understand and learn, but they are not meant to short-circuit the invented-procedures/alternative-algorithms approach described above. Students still need to grapple with problems on their own and explore alternative algorithms. The focus algorithms have been introduced for two specific reasons. One is that they provide reliable alternatives for students who do not develop effective procedures on their own. The focus algorithm for subtraction, for example, is introduced in second grade.

Second grade students are not expected to be proficient with the method, though they are expected to be able to solve multidigit subtraction problems in some way, by using counting, number grids, manipulatives, or some other method. A fourth grade student, however, who does not have a reliable method for subtraction despite several years of work with invented procedures and alternative algorithms should focus on the trade-first method so that he or she will have at least one reliable way to subtract with paper and pencil. One aim of the focus-algorithm approach is to promote flexibility while ensuring that all students know at least one reliable method for each operation.

Another reason for introducing focus algorithms is to provide a common ground for the further development of mathematical ideas. Most algorithms for operations with whole numbers, for example, can be extended to decimals. This is easier to show in a class at least one whole-number algorithm for each operation is known by every student. Focus algorithms provide a common language that facilitates classroom discussion.

Focus algorithms were introduced in response to teachers' concerns. However, a teacher who has developed an effective strategy for teaching algorithms, and who feels that the focus-algorithm approach is unnecessary or compromises that strategy, is not obliged to adopt the focus-algorithm approach.

## ALGORITHMIC THINKING

Mathematics advances in part through the development of efficient procedures that reduce difficult tasks to routine exercises that can be carried out without effort of thought. Alfred North Whitehead expressed this idea memorably in his book, *An Introduction to Mathematics* (1911): "It is a profoundly erroneous truism, repeated by all copy books and by eminent people when they are making speeches, that we should cultivate the habit of thinking of what we are doing.

The precise opposite is the case. Civilization advances by extending the number of important operations which we can perform without thinking about them" (p. 61).

An effective algorithm can be used to efficiently solve an entire class of problems, without having to think through each problem from first principles. Knowing algorithms increases students'

mathematical power, which is a principal goal of school mathematics (NCTM, 1989). The approach described in this paper — invented procedures followed by alternative algorithms, with focus algorithms as a backup and a basis for further work — will produce students who understand their methods and can carry them out proficiently so that they can think about more important things, such as why they are doing what they are doing and what their results mean.

The approach improves students' mental arithmetic skills, helps them understand the operations, and develops sound number sense, including a good understanding of place value. The emphasis on multiple solutions, including both inventing new procedures and making sense of others' inventions, encourages the belief that mathematics is creative and sensible. In *Everyday Mathematics*, accordingly, an increase in mathematical power through algorithmic proficiency is achieved at the same time that other important objectives are being met.

## CONCLUSIONS

The authors of *Everyday Mathematics* have also found that the study of paper-and-pencil computational algorithms can be valuable for developing algorithmic thinking in general. For this reason, explicit discussions of algorithms occur in lessons devoted to computation. Algorithmic and procedural thinking includes:

- understanding specific algorithms or procedures provided by other people,
- applying known algorithms to everyday problems,
- adapting known algorithms to fit new situations,
- developing new algorithms and procedures when necessary, and
- recognizing the limitations of algorithms and procedures so they are not used inappropriately.

By studying computational algorithms, students can learn things that will carry over to other areas of their lives. More and more, people need to apply algorithmic and procedural thinking in order to operate technologically advanced devices. Algorithms beyond arithmetic are increasingly important in theoretical mathematics, in applications of mathematics, in computer science, and in many areas outside of mathematics.

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# Principal and Practices in Nano-characterization Techniques

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**ABSTRACT**

Nano-characterization techniques have become increasingly important tools for studying and utilizing nanomaterials across scientific disciplines. As engineered nanomaterials become more complex, advanced characterization methods are necessary to correlate structure with functional properties. This review summarizes the fundamental principles, capabilities, and practical applications of major nano-characterization approaches. We describe imaging tools like electron microscopy, scanning probe microscopy, and super-resolution optical microscopy for visualizing nanoparticles and nanostructures. Spectroscopic methods like X-ray diffraction, small-angle X-ray scattering, dynamic light scattering, infrared and Raman spectroscopy are discussed for gleaning compositional and structural information. Surface analytical techniques are covered for interfacing nanomaterials with biological systems and the environment. Emerging in situ and in operando nano-characterization tools provide dynamic information under working conditions. For each technique, we introduce the physical basis, instrumentation, quantitative analytical capabilities, advantages and limitations, as well as showcase key examples demonstrating their utility for nanoscience research. We conclude with perspectives on future innovations in instrumentation, multi-modal platforms, and artificial intelligence-guided measurements. Thorough understanding of available nano-characterization probes and how to apply them will accelerate discoveries and technology translation.

***Keywords:*** *nanoparticles; nanomaterials; microscopy; spectroscopy; diffraction; scattering; surface analysis*

## INTRODUCTION

The field of nanoscience involves studying and manipulating matter on the nanometer scale, comprising individual atoms and molecules. Engineered nanomaterials, with sizes between 1-100 nm, can exhibit dramatically different physicochemical properties compared to the bulk form due to quantum mechanical effects and increased surface area to volume ratios. Diverse classes of nanomaterials exist today, including metal and metal oxide nanoparticles, quantum dots, nanocrystals, nanowires, nanotubes, graphene, molecularly imprinted polymers and many more. Advanced nanomaterials are enabling breakthrough applications in electronics, energy conversion and storage, catalysis, sensing, biomaterials, and nanomedicine [1].


**Fig. 1:** Different characterization methods for nanoparticles.

As engineered nanomaterials become more complex and multifunctional, sophisticated tools for probing their properties from the atomistic to mesoscale have become absolutely crucial [2]. Characterization techniques validated for bulk materials cannot always directly transfer to analyzing nanoscale structures and phenomena. Special considerations are required for detecting low numbers of

atoms/molecules, interfacing with high energy surfaces, and distinguishing heterogeneities. The characterization technique must also not irreversibly perturb the intrinsic state of the nanomaterial. A thorough understanding of the capabilities and limitations of available techniques is necessary to derive meaningful structure-function correlations.

This review summarizes the fundamental working principles, quantitative capabilities, advantages and caveats of major nano-characterization approaches spanning microscopy, spectroscopy, diffraction, scattering, and surface analysis. For each family of techniques, we provide brief histories of their development, descriptions of modern instrumentation and quantitative models, key case studies demonstrating their application space across nanoscience disciplines, and commentary on future innovations that expand analytical capabilities. Our goal is to provide researchers unfamiliar with specialized characterization tools the foundation to understand how they work and how to productively apply them towards solving nanoscale structure-function questions.

## MICROSCOPY TECHNIQUES

Microscopy remains an invaluable tool within the nano-characterization arsenal due to its capability for direct visualization of nanomaterials and nanostructures [3]. Impressive strides have occurred in spatial resolution, 3D tomographic imaging, in situ capabilities, and correlative techniques complementing other structural and chemical probes. Here we introduce various microscopy modalities applied in nanoscale research along with their working principles and quantitative capabilities.


**Fig. 2:** Microscopy Techniques

1. Electron Microscopy: Electron microscopy (EM) encompasses various techniques utilizing high energy electrons as the imaging probe, which have much lower wavelengths than visible light and can achieve sub-nanometer resolution [4]. In a typical instrument, electrons are thermionically generated and accelerated under high vacuum to energies of 100-300 keV. Electromagnetic lenses focus the electrons into a thin beam (<10 nm) incident onto the specimen. Various signals result from electron-specimen interactions - secondary and backscattered electrons for showing morphology and composition, while transmitted electrons form projective images and diffraction patterns related to crystal structure. Modern advances allow analyzing tiny sample volumes close to the atomic limit, reconstructing 3D morphology, probing internal features via sectioning, and employing various spectroscopic modes for elemental/bonding information. Environmental and in-situ stages permit studying working devices and dynamic processes in gas/liquid ambientes. The major limitation is the need for high vacuum conditions, restrictive for biological samples and operating devices. The requirement of thin electron-transparent samples can also introduce artifacts during delicate specimen preparation steps.

Scanning electron microscopy (SEM) is arguably the most widely available and utilized EM technique [5]. In SEM, a focused electron beam is rastered across the sample and various signals produced by beam-specimen interactions are detected. Secondary electrons emitted from shallow depths reveal morphological information, while scattered backscattered electrons vary with atomic number to indicate contrast between different elemental compositions. SEM instruments are versatile for imaging nanomaterials and devices over a wide range of length scales down to ~5 nm resolution. Dedicated STEM (scanning transmission electron microscopy) modes allow nanodiffraction and spectroscopic mapping of internal features at the atomic scale. Environmental SEM variants permit differential contrast imaging of processes in liquids and gases at reduced pressures.

Transmission electron microscopy (TEM) involves transmitting a broad parallel electron beam through an ultrathin specimen (~50-200 nm thick), with various internal interactions imaged onto a detector [6]. Bright and dark field TEM imaging provides diffraction and mass-thickness contrast

revealing crystal structure, defects, and compositional heterogeneities. In scanning TEM (STEM) mode, focusing the electron beam into a narrow probe facilitates atomic resolution imaging. Analytical TEM techniques like energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) give elemental and bonding information [7]. Powerful abilities include quantification of atom positions and columns via aberration corrected HRTEM and STEM, 3D tomography by serial sectioning/tilting, and in situ heating, biasing, and flow cells to track dynamic processes. Cutting-edge cryo-EM further enables imaging sensitive biological structures like proteins in a near-native fully hydrated state. The main limitations are tedious specimen preparation and only analyzing minerals that can be made electron transparent.

2. Scanning Probe Microscopies: Scanning probe microscopy (SPM) techniques analyze surface properties by scanning an atomically sharp tip in close proximity and measuring various tip-sample interaction forces with ultrahigh precision [8]. Piezoelectric positioners facilitate sub-nanometer scanning, while sensitive electronics quantify probe deflections. Different modalities like atomic force microscopy (AFM), scanning tunnelling microscopy (STM), near-field scanning optical microscopy (NSOM) and electrostatic force microscopy (EFM) allow versatile characterization of topographic, mechanical, electrical and optical properties from the molecular to mesoscale. Unique strengths include real space imaging at up to atomic resolution under diverse environments, along with the ability to manipulate individual atoms and molecules.

AFM utilizes a sharp tip on a flexible cantilever to measure short-range forces between the tip and samples [9]. Attractive van der Waals forces, repulsive contact forces, capillary interactions, chemical bonding, electrostatic forces, friction and other effects can be quantified with pico-newton sensitivity. Plotting the cantilever deflection during scanning reveals detailed topographic images ranging from atomically flat crystals to rough nanoparticles. Additional AFM modalities give nanomechanical mapping of stiffness, adhesion, viscoelasticity and bond rupture forces. Electrical modes measure surface potentials, dopant profiles and charge transport. Advanced instrumentation permits combining AFM with optical and confocal Raman microscopy for correlated structural, mechanical and chemical identification. The minimal sample preparation has encouraged bio-imaging applications. Current goals include improving scan rates and expanding to 3D tomography by probe arrays.

STM utilizes quantum tunneling of electrons between an atomically sharp metallic tip and conductive sample [10], measured as an exponential tunneling current very sensitive to the gap width (~0.5-1 nm). Raster scanning at close proximity thus profiles the sample surface topography, often visualizing individual atoms. Beyond topography, STM also provides electronic density of states mapping useful for metals, semiconductors, and molecular adlayers. Ultrahigh vacuum STM has achieved lateral resolution below 0.1 nm and vertical sensitivity around 0.01 nm, sufficient to resolve chemical bonding configurations. Specialized modes also measure work functions, friction, capacitance, spin polarization and molecular orbitals. In situ STM allows dynamic imaging during surface processes at solid-liquid and solid-gas interfaces. Improving spatial and energy resolution, data acquisition rates, and ability to probe below surface layers represent ongoing efforts.

NSOM utilizes an aperture smaller than the illumination wavelength to overcome the optical diffraction limit [11]. Light is focused through a sub-wavelength aperture at the apex of a tapered optical fiber tip, which is raster scanned in close proximity to the sample. Various optical contrasts arise from interactions in the near-field regime (<10 nm gaps) sensitive to local dielectric properties. NSOM has achieved <20 nm spatial resolution to map optical absorption, resonance spectra, and fields around nanoparticles and nanostructures. Combining NSOM with AFM tips facilitates simultaneous topographic and optical imaging. Tip fabrication and low signal levels currently constrain widespread adoption. Expanding to new contrast mechanisms like single molecule fluorescence, surface enhanced Raman spectroscopy (SERS), infrared absorption and harmonic generation holds promise.

3. Super-resolution Optical Microscopy: In traditional optical microscopes, the spatial resolution limit is around 200-250 nm laterally and 500-700 nm axially, imposed by the diffraction of visible wavelengths [12]. However, several super-resolution techniques have now emerged to routinely breach this limit and image beyond the diffraction barrier. Stochastic super-resolution methods like photo-activated localization microscopy (PALM) and stochastic optical reconstruction microscopy (STORM) temporally separate spatially overlapped fluorophores in time through photoswitching and localization [13]. Localization precisions down to 10-20 nm allow reconstructing fine details like viruses and protein clustering. Stimulated emission depletion (STED) microscopy uses a vortex phase plate to create a null point spread function, enabling ~20 nm resolution [14]. STED has been implemented with various

contrast mechanisms like fluorescence, Raman scattering and lifetime imaging. Structured illumination microscopy (SIM) uses patterned low frequency illumination and computational reconstruction to provide wide-field optical sectioning with 100 nm resolution [15], beneficial for dynamic events in thick cellular volumes. Metalens-based microscopy replaces bulk lens components with flat optical metasurfaces designed using inverse design algorithms to achieve previously unattainable resolution, field-of-view, and aberration-free performance [16]. We anticipate increasingly widespread adoption of super-resolution methods as turnkey commercial systems become commonplace.

## SPECTROSCOPY TECHNIQUES

Spectroscopic tools analyze interactions between electromagnetic radiation and matter to reveal compositional, structural, electronic and dynamic information about nanomaterials [17]. Various implementations cover diverse wavelengths (gamma/X-rays to terahertz), energy/momentum transfers, length scales (atomic to mesoscale) and time resolutions. Spectroscopies are crucial for nanomaterial fingerprinting, probing order/disorder, crystallinity, particle sizes, defect states and interfacial interactions with substrates and ligands. Important techniques like X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, Ultraviolet-visible (UV-vis) absorption spectroscopy and Raman scattering have become indispensable across nano related disciplines. Here we introduce these methods and more advanced synchrotron X-ray and neutron scattering tools revealing nanoscale dimensions, morphology and hierarchical structures.

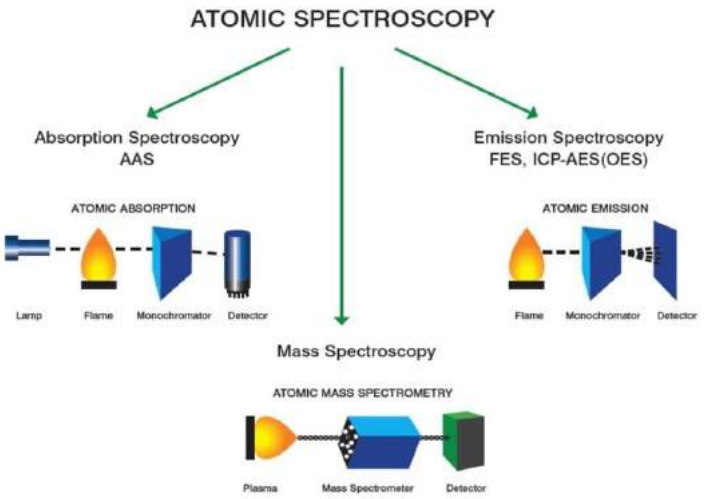


**Fig. 3:** Spectroscopy Techniques

1. X-ray Diffraction and Scattering: Powder XRD utilizes Bragg diffraction of monochromatic X-rays to measure average atomic spacings within crystalline materials [18], providing phase identification and structural parameters like lattice constants, grain/crystallite sizes, preferred orientations and defect densities. Scherrer analysis of peak broadening determines mean coherent diffraction domain sizes down to ~5 nm. Grazing incidence XRD specialized for thin films also provides depth profiling and interface structural information. Limitations include the need for crystalline samples and difficulty distinguishing multiple phases with overlapping peaks. XRD does not directly give spatial imaging.

Small angle X-ray scattering (SAXS) probes nanoscale heterogeneities within materials by monitoring scattering at very low angles where simple particle and pore shapes produce distinct interference signatures [19]. SAXS provides statistical distributions of nanoparticle/pore sizes and shapes between 1-100 nm scale, along with fractal dimensions characterizing hierarchical assemblies. Contrast often arises naturally from electron density differences. In situ measurements are possible for many sample environments (non-destructive). Quantitative structural modeling enables extracting size, shape, spacing and orientation distributions of embedded nanoscale features like precipitates, pores and grains.

Wide angle X-ray scattering (WAXS) at higher angles than SAXS reveals atomic and molecular structures within crystalline and non-crystalline materials [20], complementary to XRD. Interatomic pair correlations produce broad modulation signatures sensitive to bond distances and coordination environments. WAXS is especially useful for disordered systems like polymers, glasses and liquids

which lack long range order. One-dimensional scattering profiles require detailed modeling for unique structure solutions - often aided by molecular dynamics simulations. Two-dimensional scattering patterns also provide spatial anisotropy directions.

X-ray pole figures background-subtract diffuse scattering to specifically isolate diffraction peaks, which are tracked during specimen rotation to map their spatial intensities revealing preferred crystallographic orientations (texture) [21]. Pole figures effectively relate microscopy and diffraction data. The technique aids studying directionally-solidified alloys, epitaxial thin films, crystal twinning and deformation processes.

2. X-ray Photoelectron Spectroscopy: XPS involves irradiating a material with monoenergetic X-rays and measuring the kinetic energy and number of electrons emitted by the photoelectric effect [22]. Elemental composition is identified from the characteristic binding energy of core electrons. Chemical states and bonding are also revealed through subtle binding energy shifts. XPS is surface specific (~5-10 nm probing depth) due to the short inelastic mean free paths of emitted electrons in solids, making it well-suited for analyzing nanoparticle surfaces, interfaces and adsorbate layers. Advantages include high sensitivity (detecting down to 0.1-0.5 atomic % concentrations), simultaneous detection of all elements besides H and He, and bonding chemistry information from characteristic energy shifts up to 10 eV. Limitations are the ultrahigh vacuum environment, limited bulk profiling capability and possibility of beam induced damage. Angle-resolved XPS and combination with ion beam sputtering enables depth profiling layer-by-layer bonding state changes.

3. Infrared and Raman Spectroscopy: Vibrational spectroscopies like FTIR and Raman utilize light-matter interactions (absorption, scattering) to excite molecular bond vibrations and rotations identifying chemical composition and structure [23]. The spectra serve as distinct fingerprints enabling detection and quantification often down to ppm levels. Abundant functional groups (C=O, -NH2, -OH etc.) within organic compounds and ligands attached to nanoparticle surfaces lead to signature peaks in reproducible locations (500-4000 wavenumbers) characteristic of specific atoms and their bonding. FTIR passes broadband IR light through samples, where specific frequencies are absorbed corresponding to vibrational modes. Raman spectroscopy measures inelastically scattered visible photons which lose (Stokes shift) or gain (anti-Stokes) energy after interacting with vibrational modes. Raman requires little sample preparation but is inherently weak - vastly enhanced by SERS for nanomaterials and bio analytes. For dynamic processes, timed spectral series reveal kinetics and transient intermediates. Limitations include spectral congestion forcing peak deconvolution and ambiguities in mixed phase assignation.

4. Dynamic Light Scattering: Dynamic light scattering (DLS) measures time-dependent scattering intensity fluctuations from nanomaterials undergoing Brownian motion to determine particle size distributions and zeta potentials [24]. The diffusion coefficient calculated from intensity autocorrelation relates to a hydrodynamic diameter. Sub-nanometer to micron sizes can be measured for concentrations down to ppm levels. DLS constitutes an essential tool for monitoring stability, agglomeration and fractionation. Limitations include sensitivity to trace larger particles/aggregates, challenges measuring bimodal/broad distributions, and complications from optical transparency or refractive index matching. DLS requires spherical shape assumptions and does not directly measure surface charge. Electrophoretic light scattering methods like phase analysis light scattering (PALS) overcome this by tracking electrophoretic mobility.

5. Nuclear Magnetic Resonance Spectroscopy: Nuclear magnetic resonance (NMR) spectroscopy characterizes local chemical environments within materials by measuring the response of atomic nuclei in magnetic fields [25]. isotopes like 1H, 13C and 15N have an intrinsic quantum mechanical magnetic moment and spin angular momentum. Applying a strong static "polarizing" magnetic field causes nuclear spins to precess around the field axis with characteristic resonance frequencies dependent on the local "chemical shift". Radiofrequency magnetic pulses matched to nuclear precession frequencies induce spin state transitions observable by subsequent relaxation processes. Fourier transformed NMR signals form unique fingerprints identifying chemical composition, bonding connectivity, conformational structure and dynamics. Magic angle spinning solid-state NMR extends applications to non-crystalline solids like polymers, catalysts and biological tissue. NMR sensitivity and resolution drastically improve using advanced cryoprobes and dynamic nuclear polarization with nanomaterials. Challenges remain in further improving detection limits for mass-limited nanosamples.

## SURFACE ANALYSIS TECHNIQUES

Interfaces play crucial roles governing nanomaterial properties during synthesis, processing, storage and working environments [26]. High surface area to volume ratios greatly amplifies interfacial phenomena compared to bulk materials. Surface analysis thus constitutes an indispensable family of techniques providing compositional, chemical bonding and structural information with high surface specificity. These methods aid studying surface ligands, charge transfers, catalytic mechanisms, corrosion processes and nanomaterial-biological interactions [27]. We briefly highlight some widely utilized surface probes.

XPS remains among the most popular methods for surface analysis due to its superb chemical state sensitivity. UHV conditions afford clean surfaces for analysis, but limit studying samples under ambient/solution environments relevant to real applications. Ambient pressure XPS systems with differential pumping now allow spectroscopic characterization of solid-liquid interfaces under Torr pressures [28], although liquid scattering reduces depth resolution compared to UHV-XPS. Other surface techniques like ISS, REELS and AES offer complementary capabilities but have not seen widespread adoption. Secondary ion mass spectrometry (SIMS) utilizes an ion beam to erode surface layers while collecting and analyzing the ionized ejected (sputtered) species [29]. Mass/charge ratio spectra afford sensitivities down to parts per billion with ppm-ppb depth resolution. SIMS provides elemental mapping to study segregation in alloys and dopant distributions in semiconductors. Gas cluster ion beams allow "soft" erosion to minimize subsurface damage for profiling delicate organic overlayers. Still, quantitation challenges remain due to matrix effects

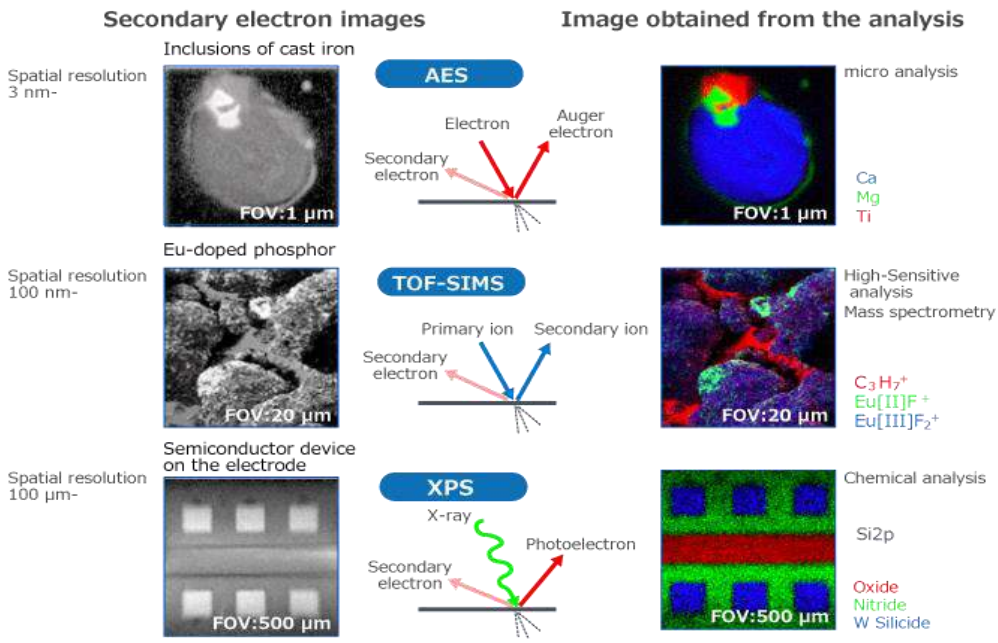


**Fig. 4:** Surface Analysis Techniques

## IN SITU AND IN OPERANDO CHARACTERIZATION

Conventional protocols for nano-characterization often involve analysis under idealized conditions quite different from real working environments. However, the structure, chemistry and properties of nanomaterials depend strongly on ambient conditions like surrounding medium, temperature, illumination etc. [30]. Capturing actual functioning states requires specialized in situ and in operando tools to help bridge this “materials gap”.

In situ refers to studying materials under relevant environments like gases, liquids or temperatures without an applied stimulus. In operando introduces an external stimulus like electrical, optical or mechanical excitation to probe materials under operating conditions [31]. Custom designed cells permit these measurements inside electron microscopes, spectrometers and scattering instruments. One must carefully consider cell geometry, windows, encapsulation materials and signal access ports to optimize data quality while mimicking native environments. Correlating data from multiple operando techniques remains an ongoing challenge.

**Table 1:** In situ and in operando characterization examples for nanomaterials in energy and catalysis.

| System | Techniques | New Insights |
|---|---|---|
| Li-ion battery cathode | In situ TEM, STEM-EELS | Direct visualization of phase evolution, voltage-dependent structure |
| Li-air battery cathode | In situ XRD, XAS | Discharge product localization and depth distribution |
| Water splitting catalyst | In situ/operando XAFS, NAP-XPS | True catalytic active site, structure-function relations |
| Methane reformation catalyst | In situ GISAXS, XRD, XANES | Working surface morphology, carbon fouling process |
| Solar cell absorber | In operando SR-PL, transient absorption | Photogenerated carrier dynamics |
| Gas sensor | In operando E-beam and UV excitation, work function analyzer | Oxygen vacancy migration models |

Table 1 highlights select examples demonstrating in situ and in operando characterization applied to energy conversion/storage electrodes and catalysts - areas which exemplify the power of understanding true working structures and states [32],[33]. Quantitative analytics under functioning conditions provides crucial insights into degradation processes and enables designing next generation nanomaterials resistant against real world stresses [34]-[36]. Operando methods will continue growing in popularity and utility across application-driven projects.

## CORRELATIVE, MULTI-SCALE AND AI-ENHANCED CHARACTERIZATION

Bridging complexity gaps across hierarchical structures and processes demands correlative and multi-scale nano-characterization [37]. No single tool provides complete microscopic to macroscopic information from chemical bonding to bulk properties. Correlative workflows logically link data from complementary techniques probing identical nanoscale locations. For example, correlative cathode ray SEM and atom probe tomography achieves combined nanoscale imaging and 3D chemical mapping unreachable by individual methods [38]. Correlative super-resolution fluorescence localization and SEM improves interpretability of biological structures like cytoskeletal networks. Other productive combinations utilize sequential focused ion beam milling with SEM, TEM or SIMS to expose buried interfaces and undistorted subsurface features.

Statistical multi-scale characterization jointly analyzes nanomaterials data from various instruments to incorporate information across modalities (real space imaging, reciprocal space diffraction, frequency space spectra etc.) and dimensions [39]. Multi-physics models and machine learning integration can interpolate these datasets for complete quantification [40]. Data science approaches like dimensionality reduction, clustering and neural networks extract otherwise inaccessible insights relating structure across scales to ensemble properties like catalytic activity [41], charge transport mobility [42] and mechanical toughness [43].

Automating analytical workflows will increase measurement speed, reproducibility and identifiability of meaningful trends [44], enabled by artificial intelligence and machine learning. Autofocusing STEM instruments via convolutional neural networks now rival human operators. Unsupervised deep learning analysis of cellular cryo EM images achieves near-expert level annotation of macromolecular complexes [45]. Physics-informed neural networks show promise for decoding molecular conformations from low signal spectroscopy. We foresee transformative utility of AI advances applied to accelerating materials discovery.

## CONCLUSION AND FUTURE OUTLOOK

We have summarized working principles and key applications of major nano-characterization techniques spanning microscopy, spectroscopy, diffraction/scattering and surface analysis. Each probe comes with intrinsic strengths like resolution, sensitivity, depth profiling etc. along with practical constraints. Researchers must deliberately match characterization tools with sample properties and analysis goals. Beyond isolated methods, new insight increasingly derives from correlating data across multiple instruments in situ/operando. Improved spatial-temporal coverage through faster measurements will facilitate statistical analysis of dynamics. We envision emerging AI/ML data science

approaches may uncover superior materials knowledge from Nonetheless, expanded sampling statistics carry the danger of overfitting and establishing false structure-property relationships. Researchers thus carry the responsibility of thoughtful physics-based model building with skepticism toward pure datamining. Impactful studies will synergistically link first principles theory, controlled physical experiments and multivariate informatics. Nano-characterization looks toward an exciting future enabling rational design of multifunctional metamaterials and artificial intelligence guided knowledge extraction.

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# Dielectric Relaxation Study of Tropine-Methanol using TDR

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## ABSTRACT

Tropine is a alkaloid it contains a hydroxyl group and behaves as a saturated compound. In the present paper dielectric constant of methanol solution of tropine for the various concentrations is studied. The time domain technique is used for the study in the frequency range from 10MHz to 30GHz. The relaxation time (τ), the static dielectric constant (ε□)□□dielectric constant at higher frequency ($\varepsilon_\infty$) and distribution parameters of mixture of Tropine with methanol are evaluated.

***Keywords:*** *Alkolides, Dielectric constant, TDR, Relaxation time.*

## INTRODUCTION

Tropine is a derivative of tropane containg a hydroxyl group at third carbon.It is also called 3-Tropanol. Benzatropine and Etybenzapropine are derivatives of tropine.It are also a building block of atropine. It is very soluble in water, Diethyl Ether and Ethanol (1). The dielectric constant is one of the important physiochemical properties of the mixed solvent, which enhance most of the biological, pharmaceutical, chemical, physical, analytical laboratory applications (2,3). In literature survey it is found that many research workers have determined the dielectric constant and relaxation time of various mixtures of solutions using TDR method. The study of dielectric relaxation of aqueous in Amides non –Polar solute using Picoseconds time domain technique (4), dielectric relaxation of mixture of 1-Propanol with aniline, 2-cholroaniline and 3-choloroaniline at different temperatures using time domain reflectrometry (5,6). In the present work we have studied the dielectric constant and relaxation time of Tropine -methanol mixtures The dielectric constant and relaxation time for various concentrations of Tropine-methanol in the frequency range 10 MHz to 30 GHz is studied at $25^0$ C.

## EXPERIMENTAL METHODS

***Materials:*** Tropine was obtained commercially from Anand Agency, Pune, made by Acros organics thermo fisher scientific India pvt Ltd. The tropine-methanol solutions were prepared.

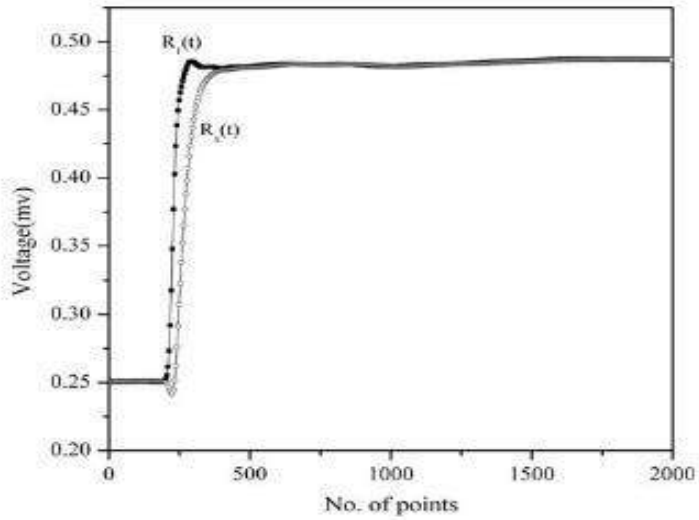


**Fig. 1:** Reflected pulses without sample$R_1(t)$ and with sample $R_X(t)$.

***Measurements:*** The tektronix model No. DSA 8200 digital serial analyzer sampling main frame along with the sampling module 80E08. TDR dielectric measurement system consists of step generator which produces fast rising pulse of the order of picoseconds (7,8). A train of suitable fast rising pulses is applied to a transmission line usually a co-axial line with characteristic impedance 50 □ A co-axial line is connected to sampling device (sample holder). A suitable fast rising pulse **RI(t)** is applied to a transmission line and incident to the sample under study and its reflected part **RX(t)** from the sample solution in the sample holder is shown in Fig. 1.

**Table 1:** Dielectric parameter of Tropine Methanol mixture.

| Conc. | Temp. | $\in_0$ | t(PS) | $\in_\infty$ | β |
|---|---|---|---|---|---|
| 0.01 | 25 °C | 34.36 | 48.95 | 2.00 | 0.943 |
| 0.02 | 25 °C | 33.92 | 47.66 | 2.00 | 0.938 |
| 0.03 | 25 °C | 34.33 | 46.73 | 2.00 | 0.912 |

## RESULT AND DISCUSSION

The recorded pulses are added [q(t)=$R_1$(t)+Rx(t)] and substracted [p (t)=$R_1$(t)- Rx(t)].Further the Fourier transformation of p(t) and q(t) was obtained by Summation and Samulon method for the frequency range 10 MHz to 30 GHz.The complex reflection spectra were determined as follows.(9,10)

$$\rho^*(W) = \left[\frac{c}{jwd}\right]\left[\frac{p(w)}{q(w)}\right] \quad (1)$$

Where p(w)and q(w) are fourier transformation of p(t)and q(t) respectively.c is speed of light.w is the angular frequency.d is effective pin length and j= √. 1

The complex permittivity spectrum of the Tropine-methanol mixtures solution is an asymmetric shape and it is determined by the Harviliak – Negami (HN) equeation (11,12), The complex dielectric permittivity data were fitted to HN model using non – linear least square fit method in order to extract dielectric relaxation time with the following expression (6,11).

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1+(j\omega\tau)^{1-\alpha}\right]^\beta} \quad (2)$$

Where ε□ is the static dielectric constant, ε□□ is the dielectric constant at high frequency. τ is relaxation time, the □ & □ are symmetric and asymmetric distribution of relaxation time respectively.

The value of static dielectric constant ε□ dielectric relaxation time (t), dielectric constant high frequency ε□□ are reported in table – 1 for Tropine- methanol mixture.

The increase in concentration of solution with increasing dielectric constant and systematic change in the dielectric parameters of the solution can be explain on the basis of molecular interaction. The increase in τ values with increase tropine –methanol concentration indicates that number of dipoles increase in solution. The intermediate structure formed rotates slowly there by giving the increase volume of τ in solution.

## CONCLUSION

The dielectric properties of Tropine- methanol mixture have studied using time domain reflectometry technique in the frequency range 10 Mhz to 30Ghz. The deviation in dielectric constant and relaxation times from ideality may be due to interaction in Tropine -methanol mixture dielectric constant and relaxation time goes on decreasing as concentration goes on increases.

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# Effect of thickness on Opto-electrical Properties of $Cd_{0.7}Fe_{0.3}S$ thin films by Chemical Bath Deposition Method

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**ABSTRACT**

The $Cd_{0.7}Fe_{0.3}S$ thin films were prepared by simple and inexpensive chemical bath deposition technique. The thickness of deposited films varied from 560 nm to 828 nm. Optical studies of thin films provide valuable information about their optical properties. The band gap energy for all the sample lie in the range of 1.78 eV to 1.61 eV. The room temperature electrical conductivity of the films varied from $4.21\times10^{-5}$ $(\Omega\text{-cm})^{-1}$ to $10.56\times10^{-5}$ $(\Omega\text{-cm})^{-1}$.

*Keywords: $Cd_{0.7}Fe_{0.3}S$ thin films, optical properties, band gap, electrical conductivity*

## INTRODUCTION

The thickness of thin films has a profound impact on their optical, electrical, mechanical, magnetic, chemical, and thermal properties. These effects are widely exploited in various technological applications and industries, making precise control of thin film thickness a critical consideration. [1-2]

As the thickness of a thin film changes, its optical properties can shift dramatically. Thin film thickness can significantly impact electrical properties, such as conductivity and resistance. In some cases, very thin films can show different electronic behaviors compared to their bulk counterparts. Thin films are also commonly used in microelectronics and integrated circuits, where controlling the film thickness is crucial for achieving desired electrical performance. Thin films often exhibit different mechanical properties compared to bulk materials. These properties are particularly important in applications like flexible electronics, where thin films are subjected to bending and stretching [3-7].

The present paper deals with the optical and electrical properties of $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses.

## EXPERIMENTAL DETAILS

The $Cd_{0.7}Fe_{0.3}S$ thin films of different thicknesses were deposited onto the amorphous glass substrates. The electrode thickness was increased by repeating the number of depositions. Each time the layers were exposed to the fresh quantities of reactants. The layer surface was cleaned after every successive deposition by double distilled water. These deposited films were termed as T1, T2, T3, T4, T5, and T6. The thickness of the deposited samples was measured by gravimetric weight difference method.

## RESULTS AND DISCUSSION

***Thickness studies:*** The thickness of the $Cd_{0.7}Fe_{0.3}S$ thin films is increased by depositing layer after layer on the earlier films. It is seen that, initially, the thickness increased almost linearly with the number of depositions and then saturated. This behavior can be explained as follows. The kinetics of film growth suggests that growth of the film takes place either by ion-by-ion condensation or by adsorption of the colloidal particles from the solution [8-9].

Fig. 1 shows the variation of film thickness with number of layer deposition for $Cd_{0.7}Fe_{0.3}S$ thin film. The terminal layer thickness of the $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses was measured by gravimetric weight difference density method using sensitive microbalance. The thickness of $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses is tabulated in Table 1.

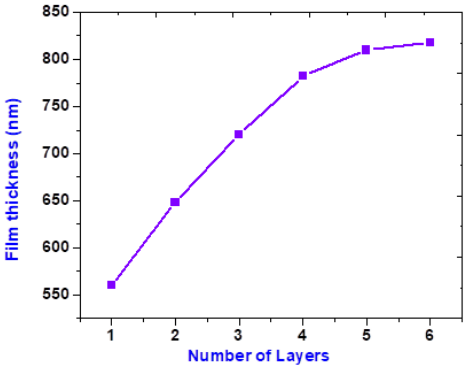


**Fig. 1**: Variation in thickness versus number of layers of $Cd_{0.7}Fe_{0.3}S$ thin films

***Optical absorption studies:*** The optical absorption spectrum of as-deposited $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses on amorphous glass substrate was studied in the wavelength range 300 to 1100 nm. The absorption coefficient (α), optical band gap (Eg) and nature of the transition involved (direct or indirect) were determined by studying the dependence of absorption coefficient (α) on photon energy hν. The variation of (αhν)2 versus (hν) for all the samples is plotted for $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses to determine the nature of transition which are shown in Fig.2.

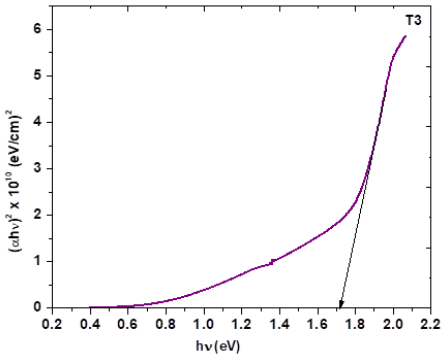


**Fig.2:** Variation of $(\alpha h\nu)^2$ vs. hν for T3= 720 nm

The band gap energy for all the sample lie in the range of 1.78 eV to 1.61 eV. It is observed that the band gap energy ($E_g$) decreases with increase in the film thickness. This is attributed to the crystalline size-dependent properties of the energy band gap [10-11]. The variation of band gap energy with varying thickness is shown in Fig. 3.

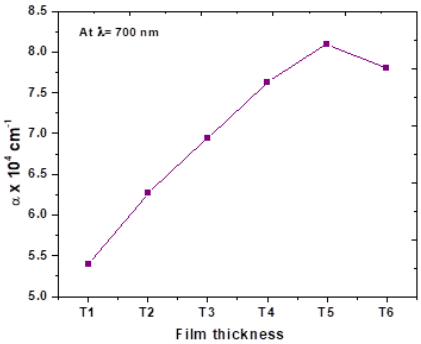


**Fig. 3**: The variation of absorption coefficient (α) with various thicknesses of $Cd_{0.7}Fe_{0.3}S$ thin films.

***Electrical conductivity measurement:*** The electrical conductivity of the $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses were carried out in the temperature range 300K-500 K, using a standard DC two point probe method under dark. A plot of inverse absolute temperature versus log σ for cooling cycle is shown in Fig. 4. It is observed that the electrical conductivity increases with increase in temperature indicating that the film samples are semiconducting. The room temperature electrical conductivity of the films varied from $4.21\times10^{-5}$ $(\Omega\text{-cm})^{-1}$ to $10.56\times10^{-5}$ $(\Omega\text{-cm})^{-1}$. The low values of the room temperature electrical conductivities can be attributed to the dislocations and imperfections of the films. The values of electrical conductivity with varying thicknesses for all the samples are given in Table 1.

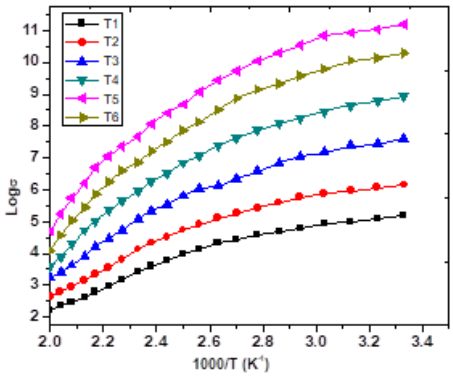


**Fig.4**: Plots of log σ vs. 1000/T for $Cd_{0.7}Fe_{0.3}S$ thin films of different thicknesses.

**Table 1:** Thickness dependent optical and electrical parameters of chemical bath deposited $Cd_{0.7}Fe_{0.3}S$ thin films.

| Thickness nm | Grain Size D (nm) | Engery band gap $E_g$ (eV) | Electrical conductivity $(\Omega\text{-cm})^{-1}$ | Activation energy (eV) | | Barrier height $\Phi_b$ (eV) |
|---|---|---|---|---|---|---|
| | | | 500 K ($\times 10^{-2}$) | L.T. | H.T. | |
| 560 | 28.7 | 1.78 | 4.21 | 0.216 | 0.188 | 0.356 |
| 648 | 29.5 | 1.74 | 5.32 | 0.223 | 0.171 | 0.351 |
| 720 | 30.2 | 1.71 | 6.54 | 0.231 | 0.154 | 0.343 |
| 782 | 30.8 | 1.69 | 8.22 | 0.238 | 0.148 | 0.340 |
| 810 | 31.6 | 1.66 | 10.76 | 0.240 | 0.136 | 0.337 |
| 828 | 31.5 | 1.61 | 9.83 | 0.235 | 0.138 | 0.332 |

## CONCLUSION

The $Cd_{0.7}Fe_{0.3}S$ thin films of various thicknesses were prepared by chemical bath deposition method. As thickness of the film increased, the band gap decreased and it is varied form 1.78 eV to 1.61 eV. The electrical conductivity various thicknesses were carried out in the temperature range 300K-500 K, using a standard DC two point probe method and it is found that electrical conductivity is increased up to 810 nm thickness.

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# A Review on Synthesis and Applications Of Magnetic Spinel Ferrite ($MFe_2O_4$) Nanoparticles

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**ABSTRACT**

Recently there has been a lot of curiosity in magnetic spinel ferrite materials because of their various uses in industrial electronic devices, water treatment, and biological fields. The synthesis, characterization, and potential uses of spinel ferrites in many fields, especially those including doping are the main topics of this article. Because of its excellent electrical and magnetic qualities, spinel ferrite nanoparticles doped with the elements have a wide range of uses, including microwave absorbers, magnetic fields, and biomedicine.

This review goes over the most significant and recent applications of magnetic ferrite nanoparticles. The article covers the synthesis and applications of various kinds of ferrites. The synthesis and usage of spinel ferrites are the main topics of this review. The synthesis and applications of various metal ferrite nanoparticle kinds are covered in this paper, along with opinions on how to select the best magnetic ferrites for a given application.

## INTRODUCTION

Metal oxides possessing spinel structures are known as spinel ferrite materials. Their general chemical formula is $AB_2O_4$, in which A and B stand for different metal cations situated at tetrahedral (A site) and octahedral (B site) locations, respectively. The kinds, amounts, and locations of metal cations inside the crystalline structure greatly influence the physicochemical characteristics of ferrites [1,2]. Nanocrystalline magnetic materials have drawn interest from a variety of disciplines, including physics, chemistry, biology, medicine, materials science, and engineering because of their exceptional and distinctive qualities. When compared to their bulk equivalents, nanomaterials show altered or improved reactivity, thermal, mechanical, optical, electrical, and magnetic properties because of their high surface-to-volume ratio and particle size of up to 100 nm [3-6].

While the bulk materials primary determinant is their chemical composition, the bulk of the properties of nanomaterials are determined by their shape and particle size in addition to their chemical makeup. Furthermore, these characteristics can be adjusted based on the chemical makeup and particle size [3,7-9].

Due to their unique structural, magnetic, optical, electrical, and dielectric properties, as well as their thermal and chemical stability, magnetic $CoFe_2O_4$, $MnFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ nanoparticles have attracted a lot of attention. These nanoparticles have a wide range of technological applications, such as photoluminescence, biosensors, humidity sensors, catalysis, magnetic refrigeration, permanent magnets, magnetic drug delivery and magnetic (hyperthermia) [10,11].

The thermal, structural, morphological, and magnetic properties of doped ferrites ( $Mn^{+2}$ and $Mg^{+2}$) containing various transition metals were described in this work and synthesized by methods, such as co-precipitation, the polyol method and combustion method [12–14].

The review study is divided into three main sections. The first section, "Magnetic spinel ferrites," covers the classification of magnetic spinel ferrites as well as a quick summary of ferrites and their structures. An outline of the principal techniques used in the field of spinel ferrites can be found in the second section, " Methods of synthesis." The third and final section, "Applications of spinel ferrites," provides a summary of the main uses for spinel ferrites.

## MAGNETIC SPINEL FERRITES

The usual formula for spinel ferrites is $MFe_2O_4$, where M is a divalent metal ion and Fe is in the +3 oxidation state[15]. A single unit cell possesses 64 tetrahedral and 32 octahedral sites; however,

only 8 and 24 of these sites, respectively, are occupied by cations[16]. Normal, inverse, and mixed spinels are classified into three categories based on the distribution of cations in the octahedral and tetrahedral positions. Because of this, $ZnFe_2O_4$ is a typical example of a normal spinel, with $Fe^{3+}$ ions found in the octahedral positions and $Zn^{2+}$ ions in the tetrahedral sites.

Furthermore, $NiFe_2O_4$ is the inverse spinel, with half of the $Fe^{3+}$ ions and $Ni^{2+}$ ions located in the tetrahedral sites and the other half in the octahedral sites . This suggests that the magnetic characteristics of spinel ferrites may be affected by the distribution of cations among both interstitial sites. Cobalt ferrite ($CoFe_2O_4$) has been described as a hard-magnetic material among spinel ferrites due to its high Hc, significant cubic magneto crystalline anisotropy, and moderate saturation magnetization (Ms)[17-19].

These qualities make it suitable for magnetic storage as well as several other uses [20]. The key characteristics of $CoFe_2O_4$ NPs, including their low bandgap energy of 2.04 eV, high Ms value, and capacity to absorb visible light, have drawn attention [21,22].

One of the most significant ceramic materials, $ZnFe_2O_4$ NPs, have drawn interest in a variety of applications because of their unique qualities, which include low power loss, high electrical resistivity, high magnetic permeability, and high Curie temperature[23,24].

## METHODS OF SYNTHESIS (CHEMICAL ROUTE)

The most popular method for creating NPs is chemical synthesis, since it can produce a large number of nanoparticles quickly and affordably. In terms of cost, size, and form controllability, all of these synthetic procedures can be divided into two groups based on the kind of solvent used: aqueous solvents and non-aqueous solvents.

***Co-precipitation:*** In this procedure, a base that serves as a precipitating agent is combined with a solution containing stoichiometric amounts of metal salts (chlorides, nitrates, or sulphates) at temperatures high enough to cause precipitation. The size, shape, and characteristics of spinel ferrite NPs are influenced by a number of characteristics, such as PH, temperature, reaction duration, and the kind and ratio of precursors[ 25,26].

***Hydrothermal and Solvothermal synthesis:*** Several wet-chemical techniques are used in hydrothermal and sol-thermal synthesis to produce crystalline $MFe_2O_4$ magnetic nanoparticles. Solvothermal synthesis uses a nonaqueous solution such as methanol, ethanol, or ethylene glycol to dissolve the metal precursors at a moderate temperature and high pressure. The process of creating new compounds by chemical reactions in an aqueous solution above the boiling point of water is referred to as hydrothermal synthesis [27].

***Microemulsion:*** The two most widely used microemulsion techniques for creating magnetic nanoparticles are direct, in which oil disperses in water (o/w), and reverse, in which water disperses in oil (w/o). As a surfactant, one may use a monolayer molecule with an oil-soluble hydrophobic head and a water-soluble hydrophilic tail, or the opposite.

A surfactant, such as dodecyl sulfate, is used to maintain the stability of the solution. In the aqueous phase, the precursor of magnetic nanoparticles is usually distributed as 1-100 nm nanodroplets. Water droplets are encircled by surfactant molecules, creating "micelles" that function as nanoreactors. As a result, magnetic nanoparticles are created inside the micelles, containing the particles and preventing their nucleation, growth, and agglomeration. In order to precipitate the nanoparticles, a second emulsion is added to the solution at the end.

***High-temperature thermal decomposition:*** Magnetic nanoparticles generated at higher temperatures typically have more homogenous size distributions. In addition, high-temperature breakdown can be used to create more crystalline $MFe_2O_4$ MNPs. This method's primary benefit over co-precipitation is that it separates the phases of nanoparticle nucleation and growth, producing monodisperse magnetic particles with a high crystalline structure, homogeneous morphology, and a restricted size distribution [28].

***Sol-gel and sol-gel auto combustion:*** The fundamental drawback of the sol-gel process, despite its simplicity and low cost, is its lack of purity in the end product. Thermal treatment is required to attain high purity and crystalline nanomaterials [29]. The type of precursors present in the initial colloidal solution has a considerable impact on the form and crystallinity of the nanoparticles created using this approach.

***Electrochemical method:*** The transfer of electricity between two or more electrodes (anode and cathode) located in an electrolyte is the basic concept behind an electrochemical synthesis. Through the

application of this technique, the anode may generate metal ion species in the electrolyte, which the cathode can then use stabilizers to help reduce to a metal [30].

***Sonochemical methods:*** High-intensity ultrasound irradiation is utilized for sonochemical processes that depend on the chemical reactions brought on by sonic cavitation and generate distinctive metal ferrite magnetic nanoparticle morphologies [31]. The bubbles oscillate because of the ultrasonic irradiation's continuous compression and expansions. The vibrating bubbles store ultrasonic energy, which grows slowly until the bubbles burst and release the stored energy. A very localized energy explosion that occurs when the bubbles burst quickly and dramatically increases pressure and temperature. The sonochemical method has a narrow size distribution when it is used for creating magnetic nanoparticles, whereas having a promising method to produce magnetic nanoparticles with exceptional magnetic saturation capabilities. This method produces magnetic nanoparticles that are frequently amorphous, porous, and aggregated[32].

***Microwave-assisted synthesis:*** Microwave heating is a powerful technique for producing magnetic nanoparticles with better quality and properties because it speeds up, cleans up, and lowers the cost of chemical reactions compared to conventional methods. It also increases the rate of chemical reactions between different metallic salts. Microwave-assisted synthesis of ferrite nanoparticles with variable size and shape has been considered an environmentally benign method [33].

***Biosynthesis:*** Metal ferritin-based magnetic nanoparticles have historically been produced using magnetotactic and iron-reducing bacteria. Through cobalt doping, this method shows potential for improving the magnetic characteristics of metal ferrite nanoparticles. The type of bacteria and the preparation conditions aerobic or anaerobic determine the phase of the magnetic nanoparticles that are created.

## APPLICATIONS OF MAGNETIC SPINEL FERRITES

***Magnetic applications:*** The magnetization is dependent on grain size because of the difference in exchange contact between tetrahedral and octahedral sites. The magnetic particles used in high-density magnetic recording should be nanoscale in size to limit the exchange contacts between neighboring grains and reduce media noise. The particles also need to have high HC values in order to obtain high storage density. Spinel ferrites' composition, particle size, crystal structure, and cationic distribution between octahedral and tetrahedral sites all influence their magnetic properties (MR, MS, and HC). Moreover, they might behave in ferromagnetic, paramagnetic, and antiferromagnetic ways [34].

***Dielectric applications:*** The dielectric structure is composed of low conductivity grain boundaries separating the good conductor grains. Particle size, density, porosity, cation distribution, structural homogeneity, and other parameters all affect spinel ferrites' dielectric characteristics. In addition, synthesis methods and thermal treatment parameters like temperature, duration, and heating/cooling rates can have a big impact on the dielectric qualities.

***Catalytic applications:*** Because spinel ferrites are easily recovered from reaction mixtures by filtering or by applying an external magnetic field, they are frequently utilized as heterogeneous catalysts. Because of their many recyclings, this approach is both economical and environmentally friendly. Heterogeneous catalytic nanoparticles are important for the selective protection of functional groups and are ecologically and economically benign.

***Sensors:*** Electronic devices called sensors may identify changes in a particular material in a particular environment. High signal-to-noise ratios, low detection limits, and remarkable sensitivity are characteristics of ferrite nanoparticle-based sensors. One of the most popular applications for sensors is the monitoring of changes in humidity.

***Magnetic resonance imaging (MRI):*** Numerous disorders can be treated, diagnosed, and prevented with the use of imaging techniques like positron emission tomography (PET), magnetic resonance imaging (MRI), and ultrasound. Nuclear magnetic resonance and radio frequency pulses serve as the fundamental building blocks of the MRI technology, resulting in finely detailed digital images of structures within the body.

***Photoluminescent applications:*** Among the most significant features of mixed spinel nanostructures, photoluminescence at room temperature is recognized for $CoFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$. A number of properties, including surface oxygen vacancies, flaws, charge carrier entrapment, and transfer efficiency, can be understood from the photoluminescence spectrum.

## CONCLUSION

Due to its special properties, $MFe_2O_4$ materials have drawn a lot of attention recently. These features include high coercivity, elevated anisotropy constant and curie temperature, high electrical resistance, moderate saturation magnetization, low eddy current loss, and stability under mechanical, chemical, and thermal conditions. Out of all the synthesis strategies that have been studied, the synthesis processes have a major impact on how helpful $MFe_2O_4$ is in many applications; effective synthesis processes produce $MFe_2O_4$ that is more durable and can perform better in the conditions that it is generated in. However, further research is necessary to produce large quantities of $MFe_2O_4$ in a cost-effective manner with mono-disperse size and shape for biomedical applications. It's also critical to carefully consider and assess the toxicity of individual $MFe_{2C}O_4$.

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# Co-Mn-Cr magnetic oxide thin film supercapacitors for energy storage at high temperature of synthesized by SILAR method

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## ABSTRACT

Supercapacitors with their fast charge/discharge efficiency, good cycling life offer remarkable properties as energy storage devices compared to conventional energy storage systems. Co-Mn-Cr magnetic oxide thin films of composition $Co_{0.5}Mn_{x/2}Cr_{0.5}Fe_{2-x/2}O_4$ (0.0<x<1) are sintered after being created using the SILAR process. X-ray diffraction, cation distribution, and infrared spectra were examined as structural characteristics. Dielectric characteristics are researched, including the dielectric loss factor and the dielectric constant. The thin films are shown to have spinal structures. As Mn content increases, the lattice constant rises as well. The polarization of space charges is increasing and as a result, the dielectric characteristics are improving.

***Keywords:*** *XRD, Supercapacitors, Thin films, SILAR*

## INTRODUCTION

Because of their quick recharge capabilities, high energy and power densities, extended cycle lives, and safe operation, supercapacitors are the most suited and innovative solution for green energy storage systems. Supercapacitors fill the void left by conventional capacitors and batteries. Global warming, environmental pollution, shortage of fossil fuel and increase in cost of it is economically not good. Because of less availability of nonconventional energy sources, it is necessary to develop safe, green and clean energy sources [1]. Electronic batteries are utilized in electronic gadgets and automobiles to supply the need for energy[2-4] but due to low power density and maintenance it is not convenient to use. Sodium-ion batteries, Lithium-ion batteries, and supercapacitors has been attracted much attention, because they embrace the great potential in an extensive range of applications [8-10]. Different metal oxides like TiO2 [11], RuO2 [12], MnO2 [13], Fe2O3 [14], are extensively studied as electrode materials for pseudocapacitors. Among the transition metal oxides, Ruthenium dioxide (RuO2) is widely recognized as a highly favorable active material for supercapacitor electrodes. This preference arises from its exceptional characteristics, including a higher specific capacitance of 2192 F g-1 at a scan rate of 2 mV s-1, excellent electrical conductivity, low equivalent series resistance (ESR), and a broad potential window spanning from 0.0 to 1.0 V [15,16]. The cited sources provide additional information on the specific capacitance, ESR, electrical conductivity, and potential window of RuO2, thus attributing the information to the respective studies.The usage of thin film technology has transformed the area of electronics, optics, energy storage devices supercapacitors, sensors and magnetism, etc. [17-18]. The SILAR technique was reported for preparation of oxide thin films by Ristov et al. [19]. The capacitance depends on many conditions like method of synthesis, grain size and chemical composition. Ferrite materials are attractive candidates for electrodes in supercapacitors due to their affordability, eco-friendliness, various oxidation states, and abundant availability [20-24]. Ferrites, such MFe2O4 (M = Co, Mn, Ni, Zn, or Mg), are easily synthesized and are ideal for commercial manufacturing on a wide scale. These binary oxides have a large capacitance because redox processes involving two ions take place in them[25]. By sintering the magnetic material under reducing conditions, the valence state undergoes changes, resulting in the formation of individual cations with high conductivity. When such a material is subsequently cooled in an oxygen atmosphere, it is possible to produce a film with high resistivity [26].

## EXPERIMENTAL

Thin films with general formula $Co_{0.5}Mn_{x/2}Cr_{0.5}Fe_{2-x/2}O_4$ (0.0<x<1) were prepared by SILAR method using the AR grade compounds $Cr(NO_3)2{\cdot}6H_2O$, $Fe(NO_3){\cdot}9H_2O$, $Co(NO_3)2{\cdot}6H_2O$, Mn $(NO_3)2{\cdot}4H_2O$, $H_2C_2O_4.2H_2O$ as starting materials. Starting ingredients included Zink nitrate, Manganese nitrate, Copper nitrate, and Ferric nitrate. Without the protection of inert gases, the response technique was usedin an environment of air. Metal nitrates and citric acid were assumed to have a 1:3 molar ratio. To create a transparent solution, A modest amount of water that had been double-distilled was used to dissolve the metal nitrates, then ammonia solution was gradually added to preserve the PH. On a hot plate, the combined solution was continuously stirred. The precursor solution was then spun onto the substrate at a speed of 3000 rpm before being calcined. The film thickness was increased by repeating this technique. To create $Co_{0.5}Mn_{x/2}Cr_{0.5}Fe_{2-x/2}O_4$ films, the precursor films underwent a post-annealing procedure that took place in a vacuum at 600oC for four hours.

## RESULT AND DISCUSSION

The XRD patterns are obtained from Regakuminiflex II set up at the angle 2°/m in between 20° to 80°. Thin film samples were kept in the cavity for analysis at room temperature.Co-Mn-Cr ferrite-related peaks may be seen in the XRD patterns, and there are no additional impurity phases can be seen. The spinel phase's overall crystallinity is increased when Co is replaced by Mn, and all of the peaks are indexed in accordance with information provided on ASTM cards.

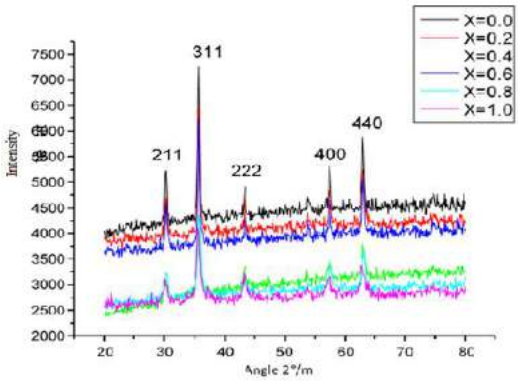


**Fig. 1:** XRD patterns of $Co_{0.5}Mn_{x/2}Cr_{0.5}Fe_{2-x/2}O_4$ (0.0<x<1)

The XRD patterns for present Mn doped thin films having thickness 1µm were analyzed with comparing Co-Cr thin films. Compared samples shows simple cubic structure and also increase in 440 peak shows the increase in lattice constant. It shows that the migration of $Co^{2+}$ ions from octahedral to tetrahedral site. The cation's distribution in the present system was ascertained by looking at X-ray diffraction patterns. The calculated and real intensity ratios were contrasted in this method. The cation distribution in the current investigation is determined using the Bertaut technique [28]. Using the phrase, this algorithm chooses a few pairs of reflections.

$$\frac{I_{hkl}^{Obs.}}{I_{h'k'l'}^{Obs.}} \propto \frac{I_{hkl}^{Calc.}}{I_{h'k'l'}^{Calc.}} \quad (1)$$

**Table 1:** Tetrahedral and octahedral bonds and edges

| X Composition | $d_{AX}$ A° | $d_{BX}$ A° | Tetra Edge (A°) | Octa Edge (A°) |
|---|---|---|---|---|
| 0 | 1.907 | 2,054 | 3.112 | 2.821 |
| 0.2 | 1.904 | 2.050 | 3.104 | 2.823 |
| 0.4 | 1.905 | 2.052 | 3.123 | 2.822 |
| 0.6 | 1.908 | 2.053 | 3.124 | 2.828 |
| 0.8 | 1.102 | 2.055 | 3.126 | 2.912 |
| 1.0 | 1.112 | 2.058 | 3.128 | 2.985 |

Where, $I_{hkl}^{Obs.}$ and $I_{hkl}^{Calc.}$ are respectively, the estimated and measured intensities for reflection (hkl). The literature was used to determine the atomic scattering factor for different ions [29]. The computed cumulative intensity is valid at 0°K, it should be noted. The reported values were obtained

at ambient temperature, therefore in theory, a suitable correction is needed to compare the mean ionic radius (rA, rB) of the Aand B-sites and x accurately.

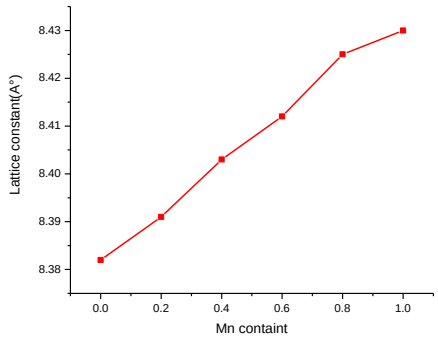


**Fig. 2:** Lattice constant with increasing $Mn^{+3}$ions.

Dielectric properties of prepared thin films depends on several factors like method of synthesis, Chemical composition etc. The sample mount used for measurement of capacitance an loss is shown in figure. The capacitance bridge can be used for measurement of capacitance and dissipation factor. The dielectric constant of given sample is calculated by given formula i.e.

$$C = (C_o+C_s-C_m)/C_o$$

Where, $C_s$- measured capacitance, $C_o$- geometrical capacitance, $C_m$- capacitance of sample holder

$$\varepsilon'' = \frac{\gamma - \gamma_=}{\varepsilon'\omega} \tag{2}$$

Where, $\gamma_=$ and $\gamma$ are DC conductivity and AC conductivity respectively, $\varepsilon'$ is dielectric constant and $\omega$ is frequency. The approximation of experimental dependence was performed in accordance with equation.

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_2}{h}\sum_{i=1}^{n}\frac{P_iD_i}{1+\left(\frac{f}{f_{ki}}\right)^2} + \frac{\varepsilon'_{st}\left[1+\left(\frac{f}{f_t}\right)^m\cos\frac{m\pi}{2}\right]}{\left[1+\left(\frac{f}{f_t}\right)^m\cos\frac{m\pi}{2}\right]^2+\left[\left(\frac{f}{f_t}\right)^m\sin\frac{m\pi}{2}\right]^2} \tag{3}$$

$$\varepsilon' = \frac{\varepsilon'_2}{h}\sum_{i=1}^{n}\frac{P_iD_i}{1+\left(\frac{f}{f_{ki}}\right)^2}\left(\frac{f}{f_{ki}}\right) + \frac{\varepsilon'_{st}\left(\frac{f}{f_t}\right)^m\sin\frac{m\pi}{2}}{\left[1+\left(\frac{f}{f_t}\right)^m\cos\frac{m\pi}{2}\right]^2+\left[\left(\frac{f}{f_t}\right)^m\sin\frac{m\pi}{2}\right]^2} + \frac{\gamma_=}{\varepsilon_0\omega} \tag{4}$$

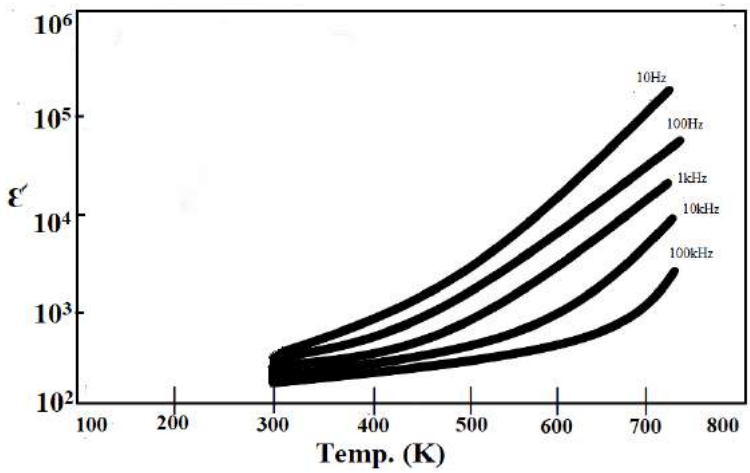


**Fig. 3:** Increase in dielectric constant with temperature

The polarization effect is responsible for the dielectric constant's temperature dependency. The quantity of space-charge carriers controls the polarization of those charges in space. The number of carriers rises as the temperature rises, which enhances the formation of space charge polarization and, as a result, increases the dielectric characteristics.

## CONCLUSIONS

This work suggests that high quality Magnetic oxide thin films can be prepared by SILAR method. In supercapacitors, the surface of these materials is crucial. These materials employ redox technology.The material's spinal structure has been verified by X-ray diffraction.The IR spectrum validates the spinel structure and provides details on the ion distribution between the tetrahedral and octahedral sites. As temperature rises, there are more carriers present, which enhances the build-up of space charge polarization and, as a result, improves the dielectric characteristics.

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# NANOTECHNOLOGY

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**ABSTRACT**

In this paper we present an introduction to the principles and advances made in the fields of nanoscience and nanotechnology including inventions, discoveries and design and study of molecular building blocks (MBBs) studied through nanoscience and applied in nanotechnology. Nanoscience is the study of systems in nanoscale and nanotechnology is the ability to systematicallyorganize and manipulate properties and behaviour of matter in the atomic and molecular levels. Through nanoscience and nanotechnology it has become possible to study and create very useful functional devices, materials and systems on the 1 to 100 nanometres (one billionth of a meter)length scale.

The reasons why nanoscale has become so important are presented. Historical aspects of nanoscience and nanotechnology are introduced starting with the famous 1959 lecture by R.P. Feynman. Considering that recent inventions, discoveries and breakthroughs in atomic and molecular aspects of nanoscale systems have been quite frequent, a selected list of recent advances and future prospects familiar to the author are presented here.

## INTRODUCTION

Nanotechnology deals with the study of extremely small structures ranging from 0.1 to 100 nm. The word ‘nano’ was derived from Greek word meaning ‘dwarf’ or ‘extremely small’ and this technology's the treatment of small atoms, molecules and compounds for the production of materials and devices with special properties such as electrical conductance, chemical reactivity, magnetic effects, optical effects and physical strength. Some important physico-chemical properties of nano particles are given . The development in the field of nanotechnology was started by R. Feyman in 1958 and era of molecular nanotechnology was started recently in 2011. Nanomaterials are classified into nano crystalline and nano structured materials. Some of the examples of nano materials include nanoceramics, carbon nano tubes, metallic nanoparticles, massive nanoparticles, liposome's, dendrimers, quantum dots, nanowires and fullerenes. It is one of the recent development in the field of science and technology and is evolving at a very fast pace in the current years. The two approaches used for the synthesis of nanoparticles are ‘top down’ and ‘bottom up’ approach. Nanotechnology has shown wide applications in various industrial sectors like paper and pulp, cosmetics, textiles, medicine, electronics, transportation, space exploration, energy and environment etc. The demand of nanotechnology is increasing at a fast rate and is expected to impact at least $3 trillion across global economy by 2020. Government of different countries have started to focus on research in the field of nanotechnology for the development of innovative nanosystems and nanostructure materials. Nanotechnology is recognized as new emerging field in third Industrial Master Plan (2005-2020). The current article discusses the physico-chemical properties of nanoparticles, approaches for its synthesis, applications and safety issues.

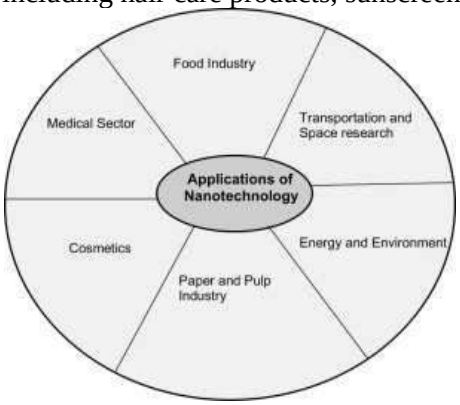
## ORIGIN AND HISTORY OF NANOTECHNOLOGY

The first use of the concepts found in 'nano-technology' (but pre-dating use of that name) was in "There's Plentyof Room at the Bottom", a talk given by physicist Richard Feynman at an American Physical Society meeting atCalifornia Institute of Technology on December 29, 1959. Feynman described a process by which the ability tomanipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so ondown to the needed scale. In the course of this, he noted,scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Vander Waal attraction would become increasingly more significant,etc. This basic idea appeared plausible, and exponential assembly enhances it with parallelism to produce a usefulquantity of end

products. The term "nanotechnology" wasdefined by Professor Norio Taniguchi, Tokyo University of Science in a 1974 paper as follows: Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule. In the 1980s the basic idea of this definition was explored in much more depth by Dr. K. EricDrexler, who promoted the technological significance of nanoscale phenomena and devices through speeches and the books Engines of Creation: The Coming Era of Nanotechnology (1986) and Nano systems: Molecular Machinery, Manufacturing, and Computation, and so the term acquired its current sense. An engine of Creation is considered the first book on the topic of nanotechnology (Drexler, 1992).

## APPLICATIONS OF NANOTECHNOLOGY

Nanotechnology has shown significant applications in different sectors like medicine, electronics, transportation, space exploration, energy and environment ,textiles, cosmetics, food science, paper and pulp. The applications of nanotechnology in various sectors is shown in Nanoparticles are used in medical field to deliver drugs, heat, light and other substances to specific cells in human body with accurate required dose and prevent any side effects. Nanoporous materials, dendrimers, iron nanoparticles and nano robots find application for drug delivery by using this technology. Quantumdotsand magnetic nanoparticles have been used for stem cell research and tissue engineering. Nanotechnology is used for the treatment of various diseases like cancer, neurodegenerative disorders, Parkinson disease, Alzheimer disease and tuberculosis. Catalysis is another application of metal nanopaticles in medical sector to treat various diseases which are caused due to metabolic imbalance. This technology shows marked promising potential in forensic analysed studies. Nanofibres (produced from cellulose and lingo cellulose) are used in papermaking industry due to their abundance, nanofibrillar structure, renewable source, adhesion properties and self assembly into well defined architecture. Nanomodification (nanoscience and nano- engineering) involves the modification of structure at nanometer scale for the development of new generation composites with improved novel properties like superior mechanical performance, self-cleaning, self-healing, self- sensing capability, low electrical sensitivity and self control of cracks. Nanotechnology is also employed for improving the efficiency of energy generation, wind and geothermal power generation and energy storage. Solar cells synthesized using classic nanostructures like quantum dots, fullerenes and carbon nanotubes are cheaper, lighter and more efficient. This advanced technology is not efficient only for renewable energy generation but it is equally useful in the field of non- renewable energy generation for the economic production of fuel from low grade raw material. Nanotechnology plays an important role in food industry with nanofood applications in the form of food additives (nano inside) to improve nutrient composition, texture, flavour and shelf life. Nanomaterials are also used in food packaging ingredients to enhance product shelf life, quality and also to indicate spoil ingredients. Nanocomposites are used for improved packaging with improved barrier properties for the manufacture of edible oils, beer, carbonated drinks and films. Nanosilver, nano magnesium oxide, nanocopper oxide, nano titanium dioxide and carbon tubes are used for active antimicrobial packaging of food products. Engineered nanosensors are being developed to estimate the spoilage of food products using electronic nose, taste, smell, tongue and flavours. Currently, chemical sensors are used by Nestle, MonoPrix Supermarkets and British Airways for the detection of colour change. Development of modified medicated textiles with antimicrobial activity with special functions such as UV- protection, anti-odor, easy clean, stain and water-repellent is another application of nanotechnology. Titanium dioxide, zinc oxide, liposome, nano crystals, nano emulsions, solid lipid nanoparticles, hyper branched polymers and dendrimers are employed in cosmetic products including hair care products, sunscreen, moisturizers and make up.



Market of this advanced technology is increasing at a very fast pace. The use of nanomaterials and nanoproducts is expected to be increased worldwide in the coming years. Many government and private organizations has focused on developing new techniques and products by involving this technology. There is a need of attention and plans of action for research and development activities in nanotechnology. However, previous studies by researchers have shown hazardous effects of some of the nanomaterials on human health and environment. Therefore, there is an urgent need to develop new approaches and standardized test procedures to study the potential hazardous effect of nano particles on human health and environment. The research on developing new engineered nano materials by adapting advanced and more sensitive techniques should also be focused in future.

## NANOTECHNOLOGY APPLIANCES IN ALLIEDSCIENCE SECTOR

***Agriculture:*** Agriculture is the backbone of most developing countries,with more than 60% of the population reliant on it for theirlivelihood (Brock et al., 2011). As well as developingimproved systems for monitoring environmental conditions and delivering nutrients or pesticides as appropriate, nanotechnology can improve ourunderstanding of the biology of different crops and thuspotentially enhance yields or nutritional values. In addition, it can offer routes to added value crops or environmental remediation. Nanotechnology, as a newenabling technology, has the potential to revolutionizeagriculture and food systems. Agricultural and foodsystems security, disease treatment delivery systems,new tools for molecular and cellular biology, newmaterials for pathogen detection and protection of theenvironment are examples of the important links ofnanotechnology to the science and engineering ofagriculture and food systems (Welch and Graham, 1999).Nanotechnology operates at the same scale as a virus or disease infecting particle, and thus holds the potentialfor very early detection and eradication. Nanotechnologyholds out the possibility that "Smart" treatment delivery systems could be activated long before macro symptoms appear. For example, a smart treatment delivery systemcould be a miniature device implanted in an animal thatsamples saliva on a regular basis. Long before a feverdevelops, the integrated sensing, monitoring andcontrolling system could detect the presence of diseaseand notify the farmer and activate bioactive systems such

***Nanofertilizer:*** Fertilizer play pivotal role in the agriculture production up to 35 to 40% of the productivity. To enhance nutrient use efficiency and overcome the chronic problem of eutrophication, nanofertilizer might be a best alternative. Attempts have been made to synthesize nanofertilizer in order to regulate the release of nutrients depending onthe requirements of the crops, and it is also reported that nanofertilizer are more efficient than ordinary fertilizer (Liu et al., 2006).

***Nanofood:*** The definition of nanofood is that nanotechnology techniques or tools are used during cultivation,production, processing or packaging of the food. It does not mean atomically modified food or food produced by nanomachines. Although there are ambitious thoughts of creating molecular food using nanomachines, this is unrealistic in the foreseeable future. Instead nanotechnologists are more optimistic about the potential to change the existing system of food processing and to ensure the safety of food products, creating a healthyfood culture. They are also hopeful of enhancing the nutritional quality of food through selected additives and improvements to the way the body digests and absorbs food. Although some of these goals are further away, the food packaging industry already incorporates nanotechnology in products.

***Food and bioprocess engineering:*** Set of engineering and scientific challenges in the food and bioprocess industry for manufacturing high qualityand safe food through efficient and sustainable means can be solved through nanotechnology. Bacteriaidentification and food quality monitoring using biosensors; intelligent, active, and smart food packaging systems; nano-encapsulation of bioactive food compounds are few examples of emerging applications of nanotechnology for the food industry. Nanotechnology can be applied in the production, processing, safety and packaging of food. A nanocomposite coating process could improve food packaging by placing anti-microbial agents directly on the surface of the coated film. Nanocomposites could increase or decrease gas permeability of different fillers as is needed for different products. They can also improve the mechanical andheat-resistance properties and lower the oxygentransmission rate. Research is being performed to apply nanotechnology to the detection of chemical and biological substances in foods.

***Medicine:*** The biological and medical research communities have exploited the unique properties of nanomaterials for various applications (for example, contrast agents for cell imaging and therapeutics for treating cancer). Terms such as biomedical nanotechnology, nanobiotechnology, and nanomedicine are used to describe this hybrid field. Functionalities can be added to nanomaterials by interfacing them

with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures. Therefore, nanomaterials can be useful for both in vivo and in vitro biomedical research and applications. Thus, the integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug delivery vehicles. Nanotechnology-on-a-chip is one more dimension of lab-on-a-chip technology. Magnetic nanoparticles bound to a suitable antibody, are used to label specific molecules, structures or microorganisms.Gold nanoparticles tagged with short segments of DNA can be used for detection of genetic sequence in a sample. Multi color optical coding for biological assayshas been achieved by embedding different-sized quantum dots into polymeric micro beads. Nanopore technology for analysis of nucleic acids converts stringsof nucleotides directly into electronic signatures (Langer and Tirrell, 2004).

## SOME KEY INVENTIONS AND DISCOVERIES

Scanning Tunneling Microscope (STM): Nanotechnology received its greatest momentum with the invention of scanning tunneling microscope (STM) in 1985 by GK. Binnig and H Rohrer, staff scientists at the IBM's Zürich Research Laboratory (Binnig and Rohrer, 1985). That happened forty-one years after Feynman's predictions. To make headway into a realm of molecule-sized devices, it would be necessary to survey the landscape at that tiny scale. Binning and Rohrer's scanning tunneling microscope offered a new way to do just that. STM allows imaging solid surfaces with atomic scale resolution. It operates based on tunneling current, which starts to flow when a sharp tip is mounted on a piezoelectric scanner approaches a conducting surface at a distance of about one nm (1□). This scanning is recorded and displayed as an image of the surface topography. Actually, the individual atoms of a surfacecan be resolved and displayed using STM.

Atomic Force Microscope (AFM): After the invention of STM it was quickly followed by the development of a family of related techniques which, together with STM, may be classified in the general category of Scanning Probe Microscopy (SPM) techniques. Of the latter technologies, the most important is undoubtedly the atomic force microscope (AFM) developed in 1986 (Binnig, et al., 1986). Figure 2 shows schematic of two typical AFMs that we use in our laboratory at UIC.

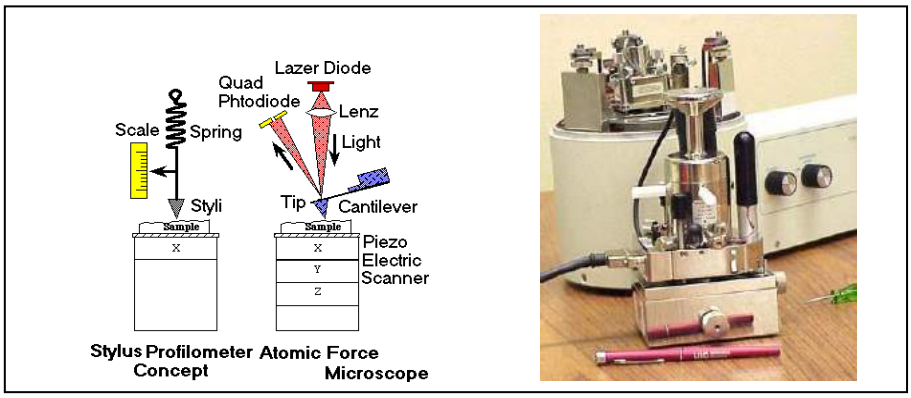



**Fig. 2:** Schematic of a typical AFM and its function as compared with a stylus profilometer.

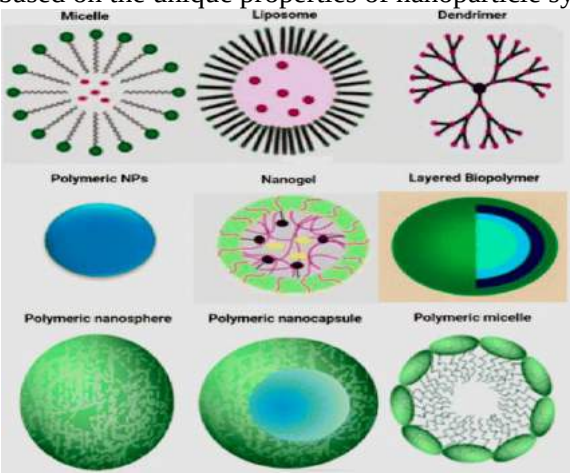
As itis shown an AFM has similarities to a conventional stylus profilometer, but with a much higher resolution in nano scale. In the right-hand side pictures of two AFMs are shown (Mansoori, 2005). AFMs are a combination of the principle of STM and the stylus profilometer. It enables us to study non-conducting surfaces, because it scans van der Waals forces with its "atomic" tips. The main components of AFM are a thin cantilever with extremely sharp (1-10 nm [□] in radius) probing tip,a 3D piezo-electric scanner, and optical system to measure deflection of the cantilever. When thetip is brought into contact with the surface or in its proximity, or is tapping the surface, it being affected by a combination of the surface forces (attractive and repulsive). Those forces cause cantilever bending and torsion, which is continuously, measures via the deflection of the reflected laser beam. 3D scanner moves the sample or, in alternative designs, the cantilever, in 3 dimensions thus scanning predetermined area of the surface. A vertical resolution of this tool is extremely high reaching 0.01 nm [□] is on the order of atomic radius).

## FUTURE CHALLENGE AND POSSIBILITY OF NANOTECHNOLOGY

One of the greatest challenges to the field of nanotechnology is the societal acceptance of new types of technology. It will be important for scientists and engineers in this field to work with other citizens to ensure long-term investments and commercial acceptance of new high technologies, such as nanotechnology. In the last few years, there has been a decreasing investment in research and development on the part of industry.

This is becoming a serious obstacle to introducing nanotechnology into the commercial sector. While government investments in science and technology have not decreased in dollars, they are not growing at a sufficient rate to support American competitiveness in nanotechnology. This is a serious problem that is already having a negative impact on the critical and necessary early stages of science and technology in this field

One of the most important future trends in nanotechnology research will be the integration of these technologies into cutting-edge products. In order to achieve this, it will be increasingly important for teams of industrial, academic and government scientists and engineers to address the complex issues that are raised by nanotechnology. In the specific area of chemically or colloidally prepared nanostructures, some important directions include the development of useful nanoparticles from non-toxic materials, the development of new fabrication strategies that allow for the manufacturing of ultra-pure nanoparticles, the development of scale-up technologies offering the ability to manuscript nanoparticles inexpensively on the many kilogram level, and finally the continuing exploration of new technological applications based on the unique properties of nanoparticle systems



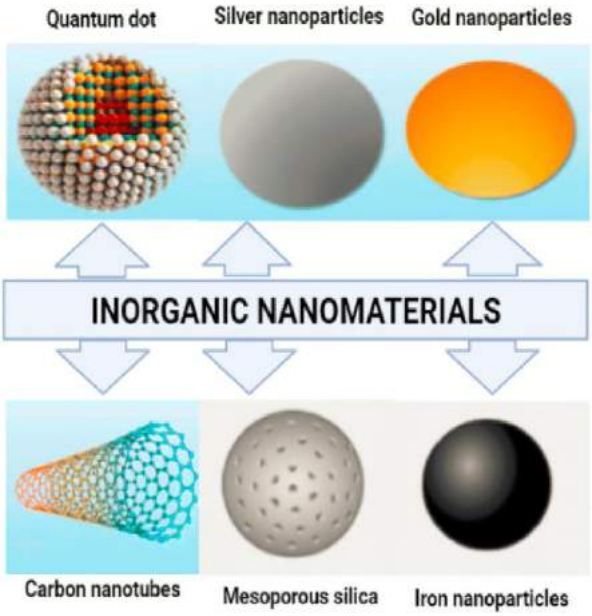

***Classification of Nanomaterials:*** Nanoparticles are categorized into their respective categories based on their morphology, which refers to their structure, as well as their size and shape. The nanoparticles listed below are some of the most significant types currently known.

***Organic nonmaterial's:*** Fig. 1 displays a number of different types of organic nanoparticles, some of which are micelles, dendrimers, liposomes, nanogels, polymeric NPs, and layered biopolymer. Certain organic nanoparticles, such as micelles and liposomes, have a hollow sphere, and they are non-toxic and biodegradable. Organic nanoparticles can also be broken down naturally. This name is also used to refer to nanocapsules, which are extremely sensitive to light and heat.[12] Due to the fact that organic nanoparticles exhibit these properties, they are an excellent option for the transportation of pharmaceuticals. Nanoparticles are also frequently used in the process of transporting target medications to their intended locations. Organic nanoparticles are also sometimes referred to by the label polymeric nanoparticles. The nanosphere or nanocapsule is the most famous form of polymeric or organic nanoparticles.[13] The matrix particles have a solid sphere of mass and adsorb other molecules at the outer boundary of spherical surface. Particles encapsulated the solid mass in the later case.[14] Fig. 1 displaying the organic nanoparticles.

***Inorganic nanomaterials:*** Inorganic nanoparticles do not contain carbon. Inorganic nanoparticles have the advantages of being hydrophilic, non-toxic, and biocompatible with living systems. The stability of inorganic nanoparticles is superior to that of organic nanoparticles.

Magnetic nanoparticles (mNPs) are one of the most significant inorganic nanomaterials.[15] A magnetic core (*e.g.* maghemite (g-$Fe_2O_3$) or magnetite ($Fe_3O_4$)) is generally present.[16] Other metals, such as nickel and cobalt, are also employed, although their applications are limited due to their toxicity

and oxidation vulnerability.[17] Ferritin, a type of protein, is where the vast majority of iron is kept in the human body. Iron oxide mNPs have the ability to digest excess iron and restore the supply in the human body. There is a continuous presence of these cationic mNPs in the endosomes for a considerable amount of time. This continues to be the case over and over again.[18] After that, during the postcellular absorption process that takes place in the endosome and the lysosome, elemental components like iron and oxygen are brought into the body's storage, where hydrolytic enzymes either digest them or cause their destruction. In the human body, homeostasis is the process through which iron levels are maintained and adjusted. Adsorption, excretion, and storage are all processes that contribute to this process. Iron oxide nanoparticles help the body digest any excess iron that may be present.[19] Iron is essential in almost all biological tissues, yet it has a low bioavailability. In certain circumstances, it can damage the cells when they are in the form of free iron or when it is not associated with haemoglobin. Additionally, it can be harmful to cells when it is present alone. Fig. 2 displaying the inorganic nanomaterials.

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# Synthesis, Characterization and Biological Relevance of Pd(II), Cd(II) and Zn(II) Complexes from NOON donor Schiff Base Ligand

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## ABSTRACT

Herein, we report synthesis, characterization and biological properties of three novel Pd(II), Cd(II) and Zn(II) Schiff base complexes. These complexes have been characterized by using UV visible, FT-IR, and powder X-ray diffraction. The IR results confirmed that the tetradentate binding of ligand involving two naphthol oxygen and two azomethine nitrogen. From the powder X-ray diffraction data, we confirmed that Pd(II), Cd(II) and Zn(II) complexes are arranged in a triclinic system. To evaluate the antibacterial activity of newly synthesized Schiff base ligands and their metal complexes were screened by using two Gram-positive and two Gram-negative bacterial strains. It was found that; the newly synthesized metal complexes were more potent compared to the Schiff base ligand. Furthermore, antioxidant activities were determined by the reduction of 1,1-diphenyl-2-picyl hydrazyl (DPPH). These studies exhibited that, the Schiff base ligand possessed better antioxidant activity than their metal complexes.

***Keywords:*** *Tetradentate Schiff base; Pd(II), Cd(II) and Zn(II) complexes; PXRD; antibacterial activity; antioxidant activity.*

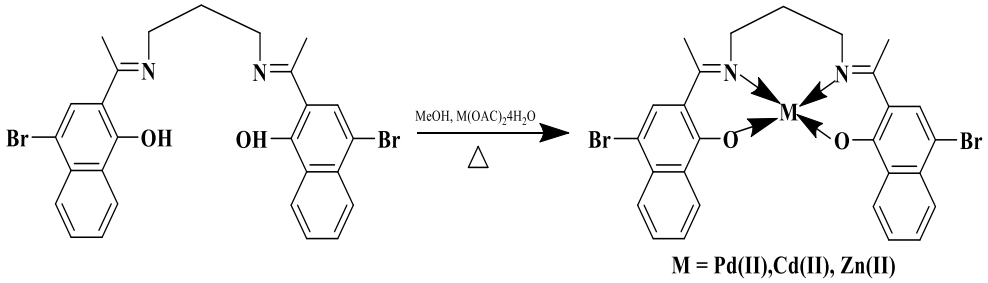
## INTRODUCTION

Transition metal complexes of Schiff bases are the well-known area of research to an inorganic chemist as these complexes possess a wide range of biological activities [1-3]. Schiff bases can be easily prepared by reacting carbonyl compounds with amines in high yields under normal reaction conditions. Schiff bases are known to form a broad range of complexes with various metals [4-5]. The chemical, structural and spectral properties of metal complexes are often strongly dependent on the nature of the ligand structure. More recently, many metal-based drugs have gained significant importance in medicinal chemistry. They are used in the treatment of tumor [6], cancer [7] and anti-inflammatory [8] diseases. In addition to this, Schiff bases and their metal complexes have also exhibited antibacterial [9-10], antioxidant [9-10] and antifungal activities [11-12]. Metal complexes of Schiff bases are also known for various other applications such as catalytic activity [13], alkaline phosphatase inhibition [14], insulin-mimetic properties [14], physicochemical properties [15], magnetic properties [16], phenoxazinone synthase activity [17], photochromic [18] and enzymatic activity [19].
Herein, we report the synthesis of three novel Pd(II), Cd(II) and Zn(II) complexes derived from 2,2'-((pentane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-chloronaphthalen-1-ol) Schiff Base Ligand. These complexes are fully characterized by various physicochemical techniques and their antibacterial and antioxidant activities are studied.

## EXPERIMENTAL

***Synthesis of ligands ($H_2L$):*** The 1:2 molar mixture of pentane -1,3-diamine (10mmol) and 1-(4-bromo-1-1-hydroxynaphthanlen-2-yl)ethanone (20 mmol) in absolute ethanol (25 ml) was refluxed with a catalytic amount of glacial acetic acid (2-3 drops) for about 2-3 h. For better results, the reaction mixture was rest overnight. The needle-shaped pale yellow product ($H_2L$) was filtered off, washed with hot water and recrystallized with absolute ethanol.
***General procedure for synthesis of metal complexes:*** The methanolic solution of Schiff base ligands ($H_2L$) (10mmol) was added with a respective metal acetate (10 mmol) using methanol as a solvent.

The resulting solution had refluxed for 5-7 h. the reaction mixture was cooled to room temperature and immediately separated. After evaporation of the filtrate were obtained as a product.




**Scheme1.** Synthesis of metal complexes.

***Evaluation of antibacterial***

***Antibacterial activity:*** Antibacterial assay of newly synthesized Schiff bases and their metal complexes were screened in vitro against different species of bacteria, Bacillus licheniformis, Bacillus species, Escherichia coli and Staphylococcus aureus by using a well diffusion method. Mueller-Hinton agar (MHA) medium is used for Microbial Suspension (100 ul) containing 108 $CFUml^{-1}$ of bacteria. The extracts were diluted in 100% dimethyl Sulphoxide at the concentrations of 5 mg/ml. The Mueller Hinton agar was melted and cooled to 48-50 ºC and standardized inoculums (1.5 X 108 CFU/ml, 0.5 McFarland) were added aseptically to the molten agar and pours into sterile Petri dishes to yield a solid plate. By using the Well diffusion method the product was prepared in the seeded Agar plate. Incubation of the plates is done in the incubator overnight at 37 ºC. The antibacterial spectrum of the extract had determined for the bacterial species in terms of zone sizes around each well. The diameters of the zone of inhibition were produced by the compound were compared to standard Ampicillin.

***Antioxidant activity:*** The antioxidant activity of synthesized Schiff base ligand ($H_2L$) and their metal complexes were determined by using the DPPH method. The antioxidant activity of these compounds was carried out at different concentrations (12.5, 25, 50 and 100 $\mu$g). Different concentrations of test compounds and standard butylate hydroxyanisole (BHA) were taken in separate test tubes and by adding distilled water each test tube was adjusted to 100 $\mu$L. Hydroxyl radical scavenging activities were determined by the earlier reported method. The percentage scavenging of DPPH free radical for each concentration of test compounds was calculated concerning an absorbance of control using the formula given below.

$$\% \text{ scavenging activity} = \frac{[\text{Control optical density} - \text{Sample optical density}]}{\text{Control optical density}} X\ 100$$

## RESULT AND DISCUSSION

***UV-visible spectra:*** The UV spectra of Schiff bases were studied in the polar solvent while complexes were studied in DMF solvent. The absorption band of Schiff bases is in the range of 350–384 nm due to the n→π* transition of the C=N imine group. Similarly, Pd(II), Cd(II) and Zn(II) complexes of these Schiff bases are absorbed in a similar region but with very low intense bands above 490 nm due to metal-ligand bonding of these metal complexes.

***FT-IR spectra:*** FT-IR analysis of the newly synthesized complexes was also studied and it helped us to understand the coordination between metal ion and ligand. The IR frequencies of ligands and their respective metal complexes are depicted in table 1. In the IR spectrum of the ligand ($H_2L$), absorption bands due to phenolic–OH, azomethine (−C=N) and phenolic ν(C−O) group have appeared at 3399$cm^{-1}$, 1590$cm^{-1}$ and 1322$cm^{-1}$ respectively. In IR spectra of all the complexes, it was observed that the absence of absorption band due to phenolic –OH group at 3399$cm^{-1}$ of ligand indicates the formation of a bond between a metal ion and phenolic oxygen atom. This is further confirmed by the change in absorption frequency of phenolic ν(C-O) which are shown in the region 1275-1277$cm^{-1}$ indicates the coordination to metal ion via oxygen atom of phenolic -OH group. The absorption frequency of the azomethine ν(−C=N) group shifted to a lower frequency and appeared in the region 1520-1531$cm^{-1}$. This confirmed that the involvement of the nitrogen atom of the azomethine group in complexation with a metal ion. The formation of metal-ligand bonding was further confirmed by the appearance of low intense bands in the region 564−575$cm^{-1}$ and 462−491$cm^{-1}$ which were assigned to frequencies of ν(M−O) and ν(M−N) stretching bands appear in the region, respectively.

**Table 1**. IR frequencies of Schiff base ligands and respected metal complexes.

| Compound | ν(HO) | ν(H2O) | ν(C-O) | ν(C=N-) | ν(M-O) | ν(M-N) |
|---|---|---|---|---|---|---|
| $H_2L$ | 3399 | -- | 1322 | 1597 | -- | -- |
| [Pd(L)] | -- | 3425 | 1275 | 1520 | 570 | 491 |
| [Cd(L)] | -- | 3428 | 1277 | 1527 | 568 | 490 |
| [Zn(L)] | -- | 3417 | 1275 | 1531 | 575 | 485 |

***Single crystal X-ray diffraction:*** We were not successful to obtain quality crystals for single crystal X-ray studies. To test the crystallinity of the presented metal complexes, we used the powder XRD pattern of Pd(II), Cd(II) and Zn(II) complexes. Under the powder, the X-ray diffraction pattern of synthesized metal complexes was scanned in the range 0-80(θ) at 1.54 Å wavelength. From XRD data, Pd(II) complex was crystallized with a triclinic system while Cd(II), and Zn(II) complexes are in the monoclinic system having space group P1. The calculated lattice parameters for Pd(II) complexes is ($a \neq b \neq c$) a = 9.1524, b = 13.6320, c = 17.2330 with $\alpha \neq \beta \neq \gamma$ and for Cd(II), and Zn(II) complexes is a = 7.0696, b = 14.8954, c = 05.3504 with $\alpha = \beta \neq \gamma$.

The definite diffraction data of Pd(II), Cd(II) and Zn(II) complexes, like angle (2θ), inter-planar spacing (d- value), FWHM, Crystallite size, dislocation density and microstrain are summarized in table 3. The maximum diffraction pattern of Pd(II), Cd(II) and Zn(II) complexes exhibited at 2θ [d value (Å)] = 23.91(3.71), 30.87(2.89), and 45.84(1.97) respectively. The particle size was calculated by applying Debye-Scherer's formula:

$$D = 0.9\,\lambda / \beta.\cos\theta$$

Where λ is the wavelength of radiation, β is the full width with half maximum (FWHM) of attribute peaks and θ is the diffraction angle.

Also, the various parameters like Crystallite size (L), dislocation density (ρ) and microstrain (ε) were calculated for synthesized Ni(II) and Fe(III) complexes as shown in table 3 using the following equations:

$$L = K\,\lambda / b.\cos\theta$$

$$\rho = 1/L2$$

$$\varepsilon = b.\cos\theta/4$$

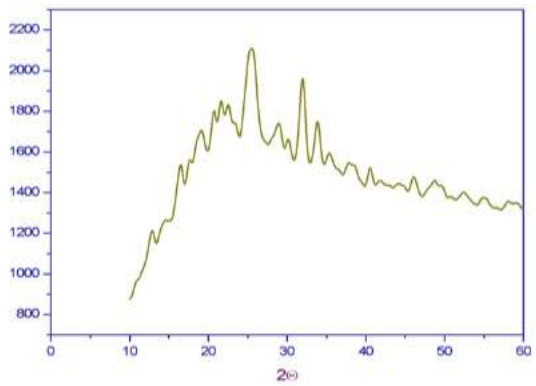



**Fig. 1:** XRD graph of PdL

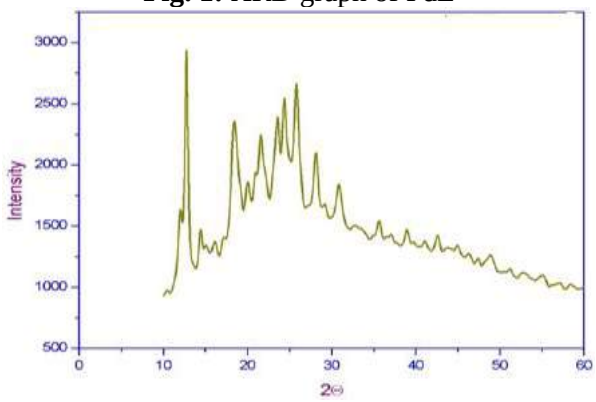



**Fig. 2:** XRD graph of CdL

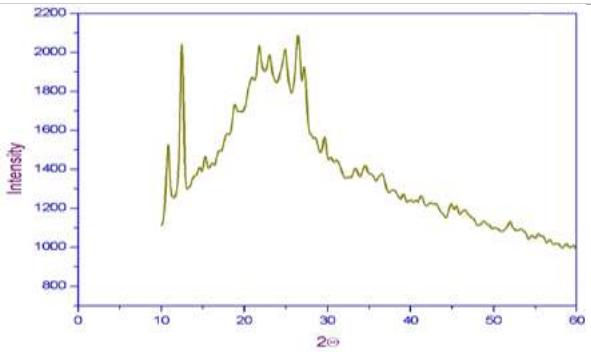



**Fig.3:** XRD graph of ZnL

**Table 2.** PXRD data of metal complexes.

| Complex | [PdL] | [CdL] | [ZnL] |
|---|---|---|---|
| Empirical Formula | $[C_{27}H_{22}Br_2PdN_2O_2]$ | $[C_{27}H_{22}Br_2CdN_2O_2]$ | $[C_{27}H_{22}Br_2ZnN_2O_2]$ |
| Formula weight | 672 | 678 | 627 |
| Temperature | 298 | 298 | 298 |
| Crystal System | Triclinic | Monoclinic | Monoclinic |
| Space Group | P1 | P1 | P1 |
| *a* /Å | 9.1524 | 7.0696 | 7.0696 |
| *b* /Å | 13.6320 | 14.8954 | 14.8954 |
| *c* /Å | 17.2330 | 05.3504 | 05.3504 |
| α / ° | 77 | 90 | 90 |
| β / ° | 76 | 90 | 90 |
| γ / ° | 89 | 78 | 78 |
| Z | 4 | 4 | 4 |
| Volume, $Å^3$ | 2043.36 | 561.36 | 551.10 |

**Table 3.** Multiple peaks fit for metal complexes.

| Compound | No. of peaks | 2θ | d-spacing ( Å) | FWHM B | Crystallite size D(mm) | Dislocation density,$nm^{-}$ ($\delta$ x$10^{-3}$) | Micro strain ($\varepsilon$x$10^{-3}$) |
|---|---|---|---|---|---|---|---|
| PdL | 1 | 12.00 | 7.36 | 1.03 | 7.6940 | 16.8925 | 43.0916 |
| | 2 | 13.58 | 6.51 | 0.68 | 11.6349 | 7.3869 | 25.1862 |
| | 3 | 18.77 | 4.72 | 1.00 | 7.9749 | 15.7231 | 26.6410 |
| | 4 | 20.19 | 4.39 | 0.78 | 10.2505 | 9.5171 | 19.2849 |
| | 5 | 23.91 | 3.71 | 1.05 | 7.5330 | 17.6220 | 21.7298 |
| CdL | 1 | 22.30 | 3.98 | 0.48 | 16.6550 | 3.6050 | 10.7608 |
| | 2 | 25.43 | 3.49 | 1.74 | 4.6541 | 46.1656 | 33.8259 |
| | 3 | 28.62 | 3.11 | 1.58 | 5.0219 | 39.6504 | 27.0584 |
| | 4 | 31.98 | 2.79 | 0.83 | 9.8877 | 10.2283 | 12.7256 |
| | 5 | 33.85 | 2.64 | 0.72 | 11.4833 | 7.5834 | 10.3676 |
| | 6 | 34.80 | 2.57 | 1.54 | 5.3851 | 34.4830 | 21.5215 |
| ZnL | 1 | 10.84 | 8.15 | 0.46 | 17.0785 | 3.4284 | 21.4875 |
| | 2 | 12.48 | 7.08 | 0.48 | 16.3683 | 3.7324 | 19.4730 |
| | 3 | 23.04 | 3.85 | 1.51 | 5.3550 | 34.8715 | 32.4066 |
| | 4 | 26.73 | 3.33 | 1.19 | 6.8069 | 21.5821 | 22.0246 |
| | 5 | 45.84 | 1.97 | 1.09 | 7.9038 | 16.0072 | 11.2610 |

***Antibacterial activity:*** To contribute to the bioinorganic chemistry, In *vitro* evaluation of the

antibacterial activity of the synthesized halo-Schiff base ligands and their metal complexes was carried out by screening them against given microorganisms. The respected microorganisms were standard strains of two gram-positive (*Bacillus cereus* and *Staphylococcus aureus*) and two-gram negative (*Pseudomonas aeruginosa* and *Escherichia coli*) pathogens. Synthesized compounds are active against strains of Gram-Positive as well as Gram-Negative bacteria. According to Overtones concept [20] and Tweedy's chelation theory [20], the antibacterial activity of metal complexes enhanced in comparison with the free ligands. From the reported data, it is also clear that the halogenated Schiff base metal complexes are shown more antibacterial activity than Schiff base ligands [21].

**Table 4.** Antibacterial activity of Schiff bases ligand and metal complexes. (in mm)

| Compound | *B. cereus* | *S. aureus* | *p. aeruginosa* | *E. coli* |
|---|---|---|---|---|
| | | | | |
| ($H_2L$) | 21 | 22 | 10 | 09 |
| [CdL] | 25 | 27 | 13 | 11 |
| [ZnL] | 24 | 26 | 12 | 13 |
| [PdL] | 27 | 29 | 14 | 07 |
| Ampicillin | 26 | 27 | 14 | 11 |

***Antioxidant activity:***The antioxidant activity of the Schiff base ligands and metal complexes was evaluated by free radical scavenging activity by DPPH method comparison with standard butylated hydroxyanisole (BHA). The results of the free radical scavenging activity of compounds at different concentrations are presented in table 5. Among these compounds, Pd(II) complexes showed good scavenging activity than Cd(II) and Zn(II) complexes. The free ligands showed promising antioxidant activity as compared to respective metal complexes, due to the presence of the phenolic –OH group.

## CONCLUSION

A series of Pd(II), Cd(II) and Zn(II) complexes were prepared with tetradentate $N_2O_2$ Schiff base ligand $H_2L$. They are characterized by various spectral techniques such as UV Visible, FT-IR, these metal complexes are studied by PXRD analysis. d-spacing values, FWHM, dislocation density, crystalline size and microstrain of synthesized metal complexes were studied by using PXRD data. The antibacterial activity of all metal complexes showed potent antibacterial activity than the parent ligands. The antioxidant activity of synthesized metal complexes is carried out with BHA as standard. The antioxidant activity of tetradentate Schiff base ligands showed more potency than metal complexes because ligands have a free –OH group to reduce DPPH. Based on all these observations, it was concluded that the tetradentate NOON donor Schiff bases and their metal complexes give versatile and valuable information of coordination compounds and also they may be used as good biological agents.

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# Single-Phase Precursor for the Preparation of Spinel Ferrites via Oxalate Route: The Study of Magnesium Ferrite Synthesis

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**ABSTRACT**

Nano spinel magnesium ferrite ($MgFe_2O_4$) nanoparticles synthesized by oxalate precursor method. Synthesized precursor characterized by Fourier transform infrared (FTIR) spectroscopy and calcinated at 600 °C. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM) were applied for elucidating the structural and magnetic properties of the prepared magnesium spinel ferrite. XRD pattern and IR spectrum confirmed formation of single phase cubic spinel magnesium ferrite. The average crystallite size is 33.9694 nm and lattice constant is 8.370 Å. Very fine spherical $MgFe_2O_4$ particles with some extent of aggregation can be observed in the SEM pictures.

***Key-words:*** *Spinel ferrite, XRD, FTIR, Precursor*

## INTRODUCTION

Ferrites are chemical compounds, ceramic with iron (III) oxide $Fe_2O_3$ as their principal components [1]. Many ferrites are spinels with the formula $AB_2O_4$, where A and B represent various metal cations, usually including iron. Spinel ferrites usually adopt a crystal motif consisting of cubic close-packed (fcc) oxides ($O^{2-}$) with A cations occupying one eighth of the tetrahedral holes and B cations occupying half of the octahedral holes-that is, the inverse spinel structure [2]. Among spinel ferrites, magnesium ferrite ($MgFe_2O_4$) has an inverse spinel structure in which, in the ideal state, all $Mg^{2+}$ ions are in B sites, and $Fe^{3+}$ ions are equally distributed between A and B sites [3]. $MgFe_2O_4$ nanoparticles have various potential applications in magnetic diagnosis and treatment devices, magnetorheological fluids, gas sensors, catalysts, lithium-ion batteries and $SO_2$ adsorbents. As we all know, the magnetic properties of spinel ferrite nanoparticles depend on the microstructure and cation distribution [4].

There are several synthesis approaches which are used to prepare noanoferrites. These include the co-precipitation [1], hydrothermal [5], reverse-micelle [6] and sol–gel auto-combustion [7], precursor [8] etc. methods. Ferrites prepared using precursor method at low annealing temperature possesses the fine particle size, good chemical purity and improved physical properties. In the present study, $MgFe_2O_4$ nanoparticles synthesized by using oxalate precursor method route.

## EXPERIMENTAL

Nano spinel magnesium ferrite was synthesized by the oxalate precursor method [9]. Analytical reagent grade oxalic acid, magnesium sulphate and ferrous sulphate were used for synthesis. Stichometric amount of corresponding magnesium sulphate and ferrous sulphate dissolved in deionized water at 60 $^oC$ to obtain clear solution. Saturated oxalic acid solution added with continuous string till all metal sulphates converted in to metal oxalates, then the precipitate digested for half hour, washed with deionized water till free from sulphates (tested with barium chloride). The oxalate precursor precipitate filtered and dried at room temperature.

## CHARACTERIZATION

The structural parameters investigated by X-ray diffraction Phillips-3710 X-ray diffractometer employed with Cu-$K_\alpha$ radiation ($\lambda$=1.5405Å) were used in the present study. Microstructure investigated by JEOL-JSM-5600-N Scanning Electron Microscope. Magnetic measurements carried at room temperature using PARC EG&G vibrating sample magnetometer. The magnetic measurements were carried out by using a vibrating sample magnetometer (VSM) at room temperature.

## RESULTS AND DISCUSSION

***Structural analysis of $MgFeO_4$ spinel ferrite:*** The IR spectrum (FTIR) of synthesised oxalate precursor [$MgFe_2(C_2O_4)_3.2H_2O$] were recorded in the range of 400–800 $cm^{-1}$ at room temperature and the obtained results are shown in Figure 1. The IR absorption peak at 3335 $cm^{-1}$ assigned to $OH_2$ stretching. The strong single peak at 1630 $cm^{-1}$ can be assigned to the >C=O stretching vibration. The two proximate peaks at 1357 and 1312 cm−1 are attributed to the C−O symmetric and asymmetric vibrations, respectively. The peak at 820 $cm^{-1}$ is due to the O−C−O vibration. Another two IR peaks at 471 and 516 $cm^{-1}$ are from the Fe−O stretching and Mg−O stretching, respectively.

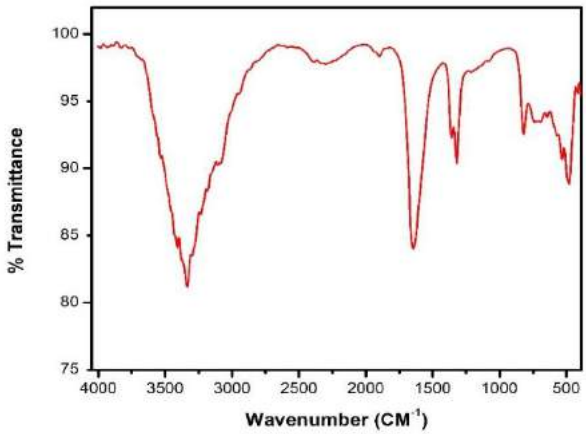


**Fig 1:** IR spectrum of Oxalate Precursor [$MgFe_2(C_2O_4)_3.2H_2O$]

Infrared absorption spectrum (FTIR) of calcinated magnesium ferrite were recorded in the range of 400–800 $cm^{-1}$ at room temperature and the obtained results are shown in Figure 2. Two major IR absorption bands observed, the high wave number band $v_1$ at 553 $cm^{-1}$ is assigned to the tetrahedral complexes, while the lower wave number $v_2$ at 477 $cm^{-1}$ is assigned to the octahedral complexes. In the magnesium ferrite sample, the high wave number $v_1$ represents the vibration of $Fe^{3+}$–$O^{2-}$ in the sub-lattice site A, while the lower wave number band $v_2$ represents the trivalent metal–oxygen vibrations at the octahedral B-sites. The difference in $v_1$ and $v_2$ band positions is expected because of the difference in the $Fe^{3+}$–$O^{2-}$ distances for the octahedral and the tetrahedral sites [10].

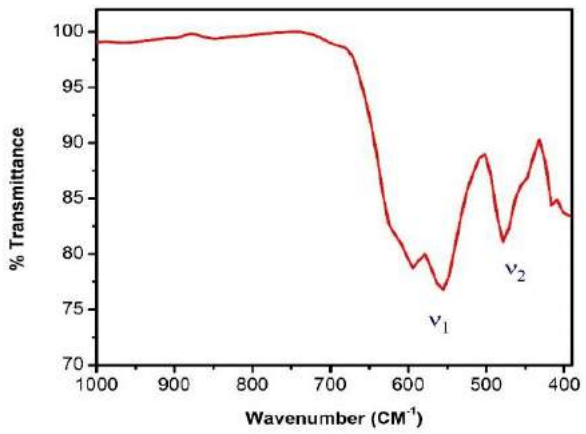


**Fig. 2:** IR spectrum of $MgFe_2O_4$ catalyst

The XRD pattern of the calcinated at 600 ºC magnesium ferrite sample presented in Figure 3. All the peaks in the pattern are characteristic of cubic spinel magnesium ferrite $MgFe_2O_4$ (JCPDS card # 00-001-0114); however, the absence of extra peaks ensures the phase purity [10].

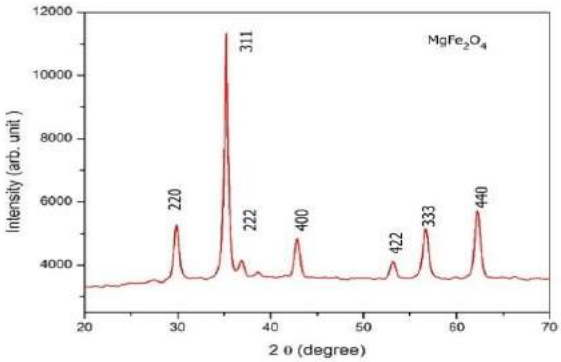


**Fig. 3:** XRD patterns of calcinated $MgFe_2O_4$ catalyst

The diffraction peaks corresponding to (220), (311), (222), (400), (422), (333) and (400) planes of magnesium spinel ferrite were ascribed. The average crystallite sizes of the produced magnesium ferrites for the most intense peak [(3 1 1) plane were calculated from the XRD data using the Debye–Scherrer formula [1] and found 33.9694 nm.

The Lattice parameter 'a' was calculated by using XRD data the equation discussed elsewhere [1],

$$a = d\sqrt{N},$$

where, 'a' is lattice constant, 'd' is inter planer spacing and

$$\sqrt{N} = \sqrt{\left(h^2 + k^2 + l^2\right)}.$$

The calculated value of lattice parameter of magnesium ferrite is A = 8.370 Å, shows that the sample is to be cubic spinel structure.

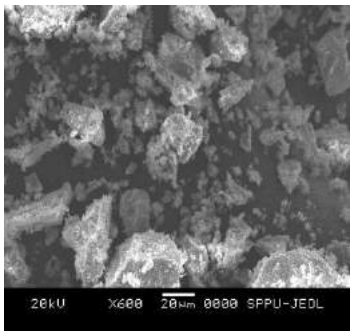


**Fig. 4:** SEM micrograph of calcinated $MgFe_2O_4$ catalyst

As it can be noted in SEM micrograph (Figure 4), calcinated $MgFe_2O_4$ nanoparticles prepared by the oxalate precursor method have a uniform, mono-disperse, and spherical/cubic structure with narrow particle size distribution. Very fine spherical $MgFe_2O_4$ particles with some extent of aggregation can be observed in the SEM pictures.

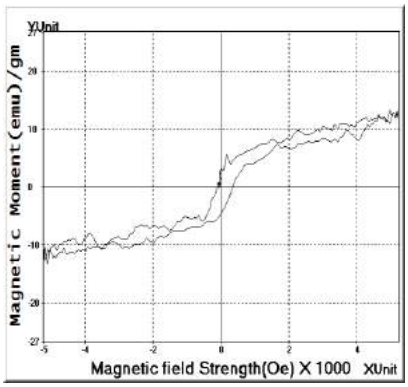


**Fig. 5:** Hysteresis loop of calcinated $MgFe_2O_4$ catalyst

The hysteresis or loop is used to determine the behavior of ferromagnetic materials when placed in the magnetic field. Magnetic hysteresis loop recorded at room temperature is given in Figure 5. Room temperature magnetization results showed a ferromagnetic behavior of the calcinated magnesium ferrite, having saturation magnetization (Ms) is 13.2773 emu/gm, coercivity (Hc) is 195.7034 Oe, and remnant magnetization (Mr) is 3.1654 emu/gm. The sample displayed normal (S-shaped) narrow

hysteresis loop. Narrow loops indicated low coercivity value which indicates that the prepared sample can be easily demagnetized.

## CONCLUSIONS

In conclusion, spinel magnesium ferrite nanoparticles successfully synthesized by oxalate precursor method. XRD pattern and IR spectrum confirmed formation of single phase cubic spinel magnesium ferrite. The average crystallite size is 33.9694 nm and lattice constant is 8.370 Å. Very fine spherical $MgFe_2O_4$ particles with some extent of aggregation can be observed in the SEM pictures.

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# Introduction to Microwave Remote Sensing

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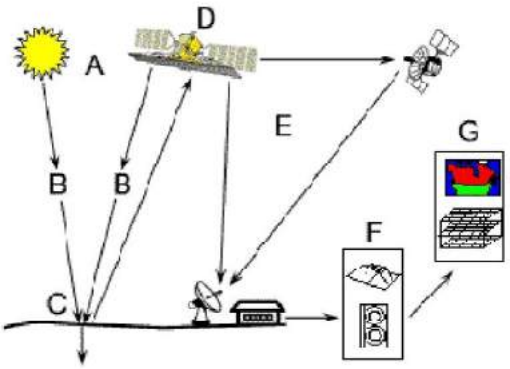
**ABSTRACT**

This article provides a concise overview of the historical development of Microwave Remote Sensing, encompassing various passive and active sensor types. Microwave remote sensing involves the acquisition of valuable data for geophysical studies through the measurement of signals generated by the interaction of microwaves with natural substances. One of the primary advantages of microwave remote sensing lies in its capability to penetrate through cloud cover, dust, haze, vegetation, rain, and even extremely dry soil surfaces. The depth of penetration is directly linked to the wavelength of the microwave signal, which is notably high. Additionally, microwave sensors exhibit the unique ability to operate day and night, unaffected by sunlight or specific illumination conditions. The article also explores related studies, delving into the historical context and the launch details of various satellites dedicated to remote sensing.

***Keywords:*** *Remote Sensing, Microwave Remote Sensing, Active Sensors, Passive Sensors, Microwave Remote Sensing Satellite.*

## INTRODUCTION

"Remote sensing is the scientific discipline focused on gathering information about Earth's surface without direct contact." This field involves the detection and recording of reflected or emitted energy. Data about Earth is collected by capturing the energy reflected from its surface. To initiate remote sensing, an energy source is necessary to illuminate the target. The process encompasses seven key elements: i. Energy source (A), ii. Radiation and the atmosphere (B), iii. Interaction with the target (C), iv. Recording the energy by the sensor (D), v. Transmission, Reception, and Processing (E), vi. Interpretation and analysis (F), vii. Application (G). These elements are illustrated in the figure below [2].




The energy emitted during remote sensing is in the form of electromagnetic radiation. When discussing imaging radar systems, researchers and technicians commonly refer to the frequency and wavelength

of the transmitted and received signals. Maxwell's Wave Theory provides a valuable relationship between wavelength and frequency, and it is expressed as follows:

$$\boldsymbol{c = \lambda * \nu}$$

Where, c= speed of light=3*$10^8$ m/s, $\lambda$ = wavelength, $\nu$ = frequency

if $\nu$ *is expressed in Gigahertz* ($GHz = 10^9 Hz$)*then*

$$\lambda_{cm} = \frac{c}{\nu} = \frac{3 * 10^9\ cm/s}{- * 10^9\ cycles/s}$$

The microwave region, situated within the electromagnetic spectrum, spans wavelengths ranging from approximately 1 mm to about 1 m. This segment is categorized into bands based on the wavelength, as outlined in Table 1.

| **Designation** | **Frequency Range** | **Wavelength Range** |
|---|---|---|
| P-band | 0.3-1 GHz | 30cm-100cm |
| L-band | 1-2 GHz | 15cm-30cm |
| S-band | 2-4 GHz | 7.5cm-15cm |
| C-band | 4-8 GHz | 3.75cm-7.5cm |
| X-band | 8-12.5 GHz | 25mm-37.5mm |
| Ku-band | 12.5-18 GHz | 16.7mm-25mm |
| K-band | 18-26.5 GHz | 11.3mm-16.7mm |
| Ka-band | 26.5-40 GHz | 5.0mm-11.3mm |

Microwave remote sensors find applications on various platforms such as drones, balloons, airplanes, and satellites. The origins of remote sensing trace back to 1858 when balloonist G. Tournachon captured photographs of Paris from his own balloon (Rastogi Sahaj, 2020). Microwave ranges are often delineated into distinct frequency bands, including P, L, S, C, X, Ku, K, and Ka (IEEE radar band). Microwaves, characterized by longer wavelengths compared to visible and infrared radiation, possess unique properties beneficial for remote sensing.

Due to their extended wavelength, microwave radiation can effectively penetrate through cloud cover, dust, haze, vegetation, rain, and even exceptionally dry soil surfaces. This ability allows for image acquisition in diverse weather conditions. Moreover, microwaves can transmit through water and penetrate vegetation canopies, proving advantageous for studying surface water or assessing flood extent.

Microwave remote sensing employs two main types of sensors: (i) passive sensors and (ii) active sensors. Passive sensors, exemplified by Radiometers, detect naturally emitted microwave energy from objects. This energy, reflected or emitted from the surface or transmitted from the subsurface, is captured by passive sensors, benefiting from the long wavelengths that facilitate penetration. Unlike passive optical sensors reliant on reflected sunlight, passive microwave sensors can operate on various platforms without the need for specific orbits. They find applications in hydrology, oceanology, meteorology, agronomy, and more.

Active microwave remote sensors, on the other hand, have their own energy source to illuminate the target. Comprising a transmitter, receiver, antenna, and electronics system, they process and record data. Active sensors come in two types: imaging and non-imaging. Imaging sensors, such as Radar (Radio Detection and Ranging), transmit signals toward the target, detecting backscattering signals. This enables all-weather, day or night imaging, as satellites move along their flight path. Non-imaging sensors, like altimeters and scatterometers, serve alternative purposes within the active microwave remote sensing domain (Fundamentals of Remote Sensing).

## HISTORY OF MICROWAVE REMOTE SENSING SATELLITE

The demand for aerial photography emerged during World War I, primarily for military surveillance purposes. The inaugural Indian active microwave remote sensing satellite, Radar Imaging Satellite (RISAT-1), marked a significant milestone. Successfully launched into a polar sun-synchronous orbit on March 17, 1988, with Soviet assistance from the Baikonur Cosmodrome, it played a crucial role in India's remote sensing capabilities.

Following the triumph of IRS-1A, a pivotal satellite in the Indian Remote Sensing (IRS) program, an identical counterpart, IRS-1B, was launched in 1991. Subsequently, a series of IRS

missions introduced theme-based satellites, including RESOURCESAT and RISAT series, OCEANSAT and INSAT, and CARTOSAT for large-scale mapping.

Until 1995, CORONA, America's first satellite series I program, remained classified, only to be declassified by then-President Bill Clinton. SEASAT, one of the earliest Earth-observing satellites launched by the Jet Propulsion Laboratory (JPL) from Vandenberg Air Force Base, California on June 26, 1978, contributed to advancing remote sensing capabilities. Modified aircraft such as P-51, OV-1, and others were utilized for aerial photography information collection [Rastogi. Sahaj, 2020].

Post-1995, the declassification of CORONA opened up new avenues, and various space agencies, including the Indian Space Research Organization (ISRO), the National Aeronautics and Space Administration (NASA), Roscosmos (Russian Space Agency), the European Space Agency (ESA), and the Japanese Space Agency (NASDA), launched a plethora of active and passive sensors into space.

## CONCLUSION

The historical overview of microwave remote sensing reveals the significant potential of microwave sensors in numerous applications within earth and planetary science. These sensors, leveraging their unique advantages, have prompted the initiation of new mission definitions for studying earth and planetary surfaces, incorporating advanced techniques like interferometry and polarimetry. Microwaves exhibit remarkable penetration capabilities, easily traversing targets such as vegetation canopies and even dry soils.

Looking ahead, the advancement of microwave remote sensing can benefit from the integration of artificial intelligence and machine learning. These technologies hold promise for enhancing achievements in the field, paving the way for more sophisticated and efficient applications of microwave remote sensing in the future.

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# Synthesis, Microstructure and Magnetic Properties of La - Zn Nano Ferrite

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## ABSTRACT

Nano La-Zn ferrite prepared by sol-gel auto-combustion method with glycine as a fuel. Precursor was calcinated at 450 $^{o}$C for four hour. The calcinated sample characterised by XRD, IR, SEM and VSM. The observed lattice constant was 8. 388 Å, the crystalline size 24.694. The I.R. spectra showed two principle absorption bands ($\nu_1$and $\nu_2$) near 600 $cm^{-1}$ and 400 $cm^{-1}$ which is a characteristic feature of spine ferrites and supported the XRD investigations. SEM image revealed well defined nanoparticles with slight agglomeration. Magneton number observed 1.653 $\mu_B$.

***Keywords:*** *La-Zn ferrites; Microstructure; Lattice constant; Saturation Magnetization*

## INTRODUCTION

Ferrites are class magnetic iron oxides which plays an important role due to their extensive technological applications due to their both electrical and magnetic properties [1-2]. $AB_2O_4$ is a general chemical formula of spinel ferrite composed of tetrahedral-A and octahedral-B sites, where divalent-$A^{2+}$, trivalent-$B^{3+}$ and oxygen ions form an fcc close packed structure. The distribution of these ions among A-sites and B-sites determines the characteristics of spinel ferrite [3]. Soft magnetic ferrites are one of the most used non-metallic magnetic materials, because of their high resistivity and low power loss. They include MnZn, NiZn and MgZn ferrites, in which the NiZn ferrites have much higher operating frequency, Curie temperature and resistivity compared with the other two series of ferrites. Public attention has been aroused to the importance of NiZn ferrites because their new applications, such as modern communication, internet, electrical appliance, computer circuits. The development of nano scale magnetic material has been intensively pursued because of the appearance of some unique physical, chemical and structural properties. These properties allow them available widely for electronic devices, e.g. magnetic recording media and magnetic sensors.

Spinel ferrites are extensively used in applications such as sensor, catalysis, biomedicine, MRI, drug delivery, magnetic recording, microwave devices and magnetic ferro-fluids [4-10], etc. The structural, magnetic and electric properties of ferrites governed by many factors including substituents, preparation technique, elemental composition, processing temperature, particle size etc. Numerous techniques been used to synthesis of nano-particles of ferrites are; hydrothermal, ball-milling, sol-gel auto-combustion, co-precipitation, reverse micelle, solid-state [9-14] etc. Amongst these techniques; the sol-gel auto combustion technique is facile, which is easy to control and produce the ferrite nano-particle samples with the large surface area.

Herein we report structural and magnetic properties of the La-Zn ferrite synthesized by sol-gel auto-combustion method.

## EXPERIMENTAL

Nanocrystalline La-Zn ferrites, with composition of $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ were synthesized by the sol-gel auto-combustion method [2] corresponding from analytical grade corresponding metal nitrates having purity 99%, and 97% Glycine [$NH_2$-$CH_2$-COOH], were used in the synthesis without any further treatment. All nitrates were dissolved in distilled water to obtain a mixed solution in desired composition. The reaction procedure was carried out in an air atmosphere without the protection of inert gases. The molar ratio of metal nitrates to glycine was 1:3. The metal nitrates were dissolved together in the minimum amount of double-distilled water required to obtain a clear solution. An aqueous solution of glycine was mixed with the metal-nitrate solution and pH ≅7 of reaction mixture was maintained by gradually addition of the ammonia solution. The mixed solution was kept on a hot plate with constant stirring at 90°C. A viscous brown gel was formed as a result of evaporation of solution. When all of the water molecules were evaporated; the viscous gel obtained and it began to froth, after few a minute, the gel self-ignited and burnt with glowing flints. The auto-combustion completed within a short time, yielding brown coloured ashes referred as the precursor. Finally precursor calcinated at 450 °C for 4 hours to get desired nano ferro- spinels.

The crystallographic structures were identified by X-ray powder diffraction with Cu Kα radiation (λ = 1.5405Å) by Phillips X-ray diffractometer (Model 3710). Morphology and structure of the samples were studied on JEOL-JSM-5600 N Scanning Electron Microscope (SEM). The infrared spectra recorded at room temperature in the range 200 to 800 $cm^{-1}$ using Perkin Elmer infrared spectrophotometer. The magnetic measurements were performed at room temperature using a commercial PARC EG&G VSM 4500 vibrating sample magnetometer.

## RESULT AND DISCUSSION

***Structural Analysis:*** The XRD patterns of calcinated sample shows in the Figure 1. The XRD patterns showed the appropriate peaks to the La-Zn ferrites and with some secondary phases. The secondary phase detected is corresponding to the ortho-ferrite phase of $LaFeO_3$ (JCPDS # 75-0541) [15].

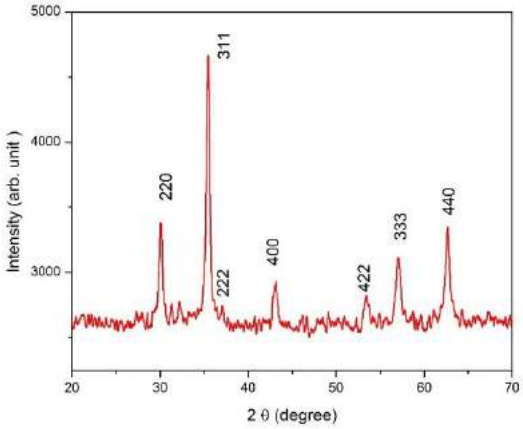


**Fig. 1:** XRD patterns of calcinated $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ ferrite

The lattice constant 'a' was calculated by using equation (1) [9],

$$a = d\sqrt{N} \tag{1}$$

Where, 'a' is lattice constant, 'd' is inter planer spacing and $\sqrt{N} = \sqrt{(h^2 + k^2 + l^2)}$. The lattice constant 'a' calculated was 8.388 Å. The X-ray density '$d_x$' was obtained by using the following relation:

$$d_x = \frac{nM}{N_A V} \tag{2}$$

Where, $d_x$ = X-ray density, n = Number of molecules per unit volume (8 for cubic structure), M = Molecular weight of the composition, $N_A$ = Avogadro's number = 6.02214 x $10^{23}$ and V = Volume = $a^3$. X-ray density observed was 5.6123.

The broad diffraction peaks exhibit the fine particle nature of synthesized ferrite sample. The average crystalline size '$D_{XRD}$' of the prepared sample was determined from the most intense peak (311)

plane of XRD and by using following Scherer relation discussed elsewhere [8]. The calculated crystalline size was 24.694 nm.

The hopping lengths of A and B-sites ($L_A$ and $L_B$ respectively) of synthesised ferrite obtained through the equation discussed elsewhere [10]. The hopping lengths of A and B-sites were $L_A$ = 3.7561 Å and $L_B$ = 2.8951 Å respectively.

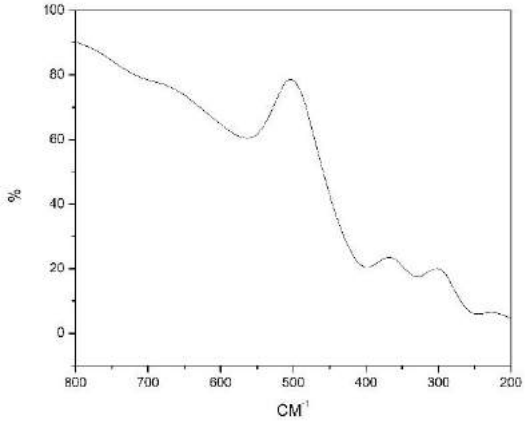


**Fig. 2:** IR spectra of calcinated $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ ferrite

IR spectra for the synthesized ferrite sample showed in Figure 2. The spectrum showed two major absorption bands ($\nu_1$ and $\nu_2$) which is an important characteristic of the ferrites, 572.68 $cm^{-1}$ and 386.27 $cm^{-1}$ respectively. The high frequency band ($\nu_1$) is allocated to the intrinsic lattice vibration of the tetrahedral sites of $Fe^{3+}$–$O^{2-}$. On the other hand, the lower frequency band ($\nu_2$) is ascribed to the stretching vibration of octahedral complexes.

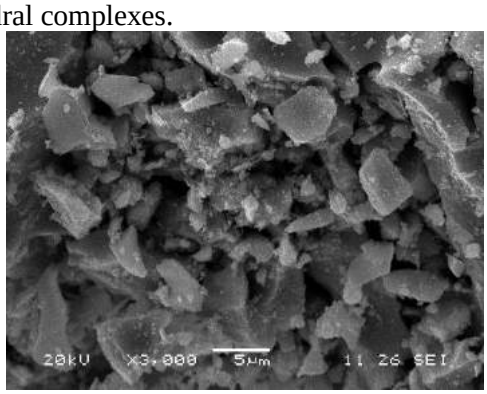


**Fig. 3:** SEM image of calcinated $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ ferrite

SEM micrograph of the prepared ferrite shown in Figure 3. SEM image indicate formation of well defined nanoparticles with slight agglomeration of the sample with inhomogeneous broader grain size distribution. The SEM images showed the amorphous and porous in nature of the prepared sample.

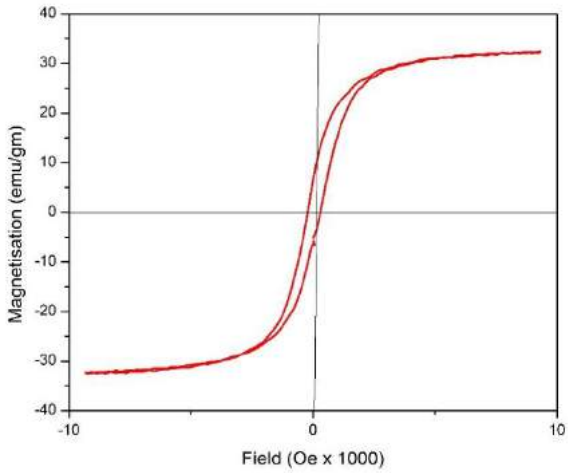


**Fig. 4:** Hysteresis loop of calcinated $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ ferrite

Neel's two sub-lattice models are applied to understand the magnetic behaviour of the samples. According to Neel's two sub-lattice Model of ferrimagnetism Neel's magnetic moment $n_B$ is given by equation [16]. The super-exchange interactions of these samples strongly depend on the distribution of the cations on the tetrahedral, A- and the octahedral, B-site. It is observed from Fig. 4, that saturation magnetization decreases up to certain applied field above which saturation magnetization remains almost constant. Saturation magnetization (Ms) is 33.753 emu/g, remnant magnetization (Mr) is 8.362 emu/g nd coercivity (Hc) is 183.32 Oe, and magneton number ($n_B$) is 1.653 $\mu_B$ derived from hysteresis loops.

## CONCLUSIONS

Nanocrystalline ferrite, with composition $La_{0.1}Zn_{1.0}Fe_{1.9}O_4$ was successfully prepared by the sol-gel auto-combustion method. Precursor was calcinated at 450 $^oC$ for four hour. The observed lattice constant was 8. 388 Å, the crystalline size 24.694. The I.R. spectra showed two principle absorption bands ($\nu_1$and $\nu_2$) near 600 $cm^{-1}$ and 400 $cm^{-1}$ which is a characteristic feature of spine ferrites and supported the XRD investigations. SEM image revealed well defined nanoparticles with slight agglomeration. Magneton number observed 1.653 $\mu_B$.

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# An Efficient Bio-Absorbent For Methylene Blue Dye

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**ABSTRACT**

This study deals with an efficient bio-absorbent for Methylene blue dye. The pomegranate albedo used as low -cost, and environment-friendly adsorbents as a new source for activated carbon. Bioabsorption of methylene blue dye with bio sorbent prepared from albedo of Pomegranate. The dried albedo were ground prior to their activation by carbonization in muffle furnace at 600˚c for 1hours. The Characterization of bio sorbent was made by Fourier transform infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Bio sorption study of Methylene blue (MB) dye studied with help of spectrophotometer.

***Keywords: -****Pomegranate, aldedo, Methylene blue dye,*

## INTRODUCTION

The pomegranate, Punicagranatum L., is one of the oldest edible fruits. This pomegranate is mentioned in the Bible and Koran. It is native to Persia and from there it spread into Asia, North Africa and Mediterranean Europe, including Turkey. [1] The fruits of Punicagranatum (pomegranate) have been used to treat diarrhoea, acidosis, helminthiasis, haemorrhage, dysentery, microbial infections, and respiratory pathologies [2]. In India, pomegranate is considered as a crop of the arid and semiarid regions because it withstands different soil and climate stresses. It succeeds best under hot dry summer and cold winter provided irrigation amenities are available [3].

Owing to its low maintenance cost, tolerant to biotic and abiotic stresses, high yielding potential, better keeping quality and higher nutraceutical fruit value, popularity of pomegranate is increasing among the growers and consumers worldwide [4]. In recent years, with the rapid-growing dye industry, a massive quantity of dye is thrown in waste water, [5] which has been a massive effect to the environmental and human health. Methylene blue (MB) is a usually used cationic dye that can custom a stable solution with aqueous at room temperature. [6]. Above certain concentration it is harmful to human health due to its strong toxicity. In accumulation, almost all dyes are difficult to biodegrade and have some resistance to environmental conditions, and human health. Therefore, it is particularly important to develop effective and low-cost materials to remove MB and other dyes from wastewater and refresh the environment.Adsorption is accepted as the most efficient technique for removing pollutants from wastewater among many other methods thanks to its characteristics such as simplicity of design, high efficiency and economic feasibility [7].Activated carbon is the most widely used adsorbent in adsorption processes; however, it is costly and but has adsorption capacity. Due to this research scientist have concentrated on finding alternative natural adsorbents to activated carbon. Natural adsorbents are preferred for their biodegradable, non-toxic nature, low commercial value.
The goal of this study was to investigate the antimicrobial activity of some of the new popular pomegranatecultivars grown in Turkey. We also aimed to evaluate the correlations between responses bymicroorganisms and pomological

## EXPERIMENTAL

The stock solution was prepared by dissolving 20 mg MB in 1000 ml distilled water. MB solution of different concentrations was prepared by serial dilution from stock solution for preparation of calibration (standard) curve of varying concentrations of dye. A typical process involves 500 gm pomegranate peel were taken this were cut into small peace's washed and dried at 100 $^{O}$c. Then dried

pomegranate albedo dried in muffle furnace at 600°c, for 1h. The final activated powder used for further study for absorption of methylene blue dye.

## RESULT AND DISCUSSION

The concentration of MB solution before and after adsorption were estimated by measuring absorbance at 665 nm with help of spectrophotometer. 0.250 gm of activated carbon derived from waste albedo of Pomegranate was placed in 50 ml flasks containing 6.25, 5.25, 4.25, 3.25, 2.25 mg/L concentration of dye solution of corresponding pH ranging from 5.5 to 6.0.

Then flasks were shaken thoroughly with hand for 5 minutes, after filtration final concentration of dye solution were analyzed by spectrophotometer. The amount of equilibrium uptake of dye is calculated by using equation = (C0 – Ce) V/ W

Qe- is the dye up taken by adsorbent mg/g, $C_0$- is the initial MB concentration, Ce- is the MB concentration (mg/l) after the batch adsorption process, W- is the Mass of adsorbent (gm), V is the Volume of dye solution

| Absorbance of Pure dye | Absorbance of Pure dye + Activated carbon derived from Pomegranate Albedo |
|---|---|
| 1.74 | 1.00 |
| 1.69 | 090 |
| 1.63 | 0.70 |
| 1.54 | 0.28 |

From table shows that on dilution Abs value decreases it show that the activated pomegranate albedo absorbs the MB dye. It was also found that dye uptake capacity changes as dye concentration capacity changes as shown in table 1. The interaction between dye molecule and adsorbent is basically a combined result of charges on dye molecules and adsorbent is basically a combined result of charges on dye molecules and the surface of the adsorbent.

## CONCLUSION

The purpose of this work is to use cost-effective and environmental –friendly adsorbents has been considered as a new source of activated carbon. The study offers the bio absorption of harmful dye with carbonized pomegranate albedo. To consider the potential application of waste pomegranate albedo to absorption of methylene blue dye. This will useful for the farmers to use waste pomegranate albedo to bust economy of farmer and minimize the dye concentration in discharged from industry which contain higher concentration of dyes.

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# A Review on DEPOSITION PROCESS OF CIS THIN FILMS

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**ABSTRACT**
Semiconducting thin films can be grown using a variety of various methods, some of which are expensive and others of which are reasonably priced. Alternative methods for producing CIS thin films involve vacuum evaporation, flash evaporation, sputtering, spray pyrolysis, chemical method, etc. The famous growth techniques for the deposition CIS absorbers have been developed such as thermal vacuum evaporation spray pyrolysis and low-cost non-vacuum process methods, which is deliberated in this review giving importance to absorber. The CIGS thin films are prepared by various vacuum and no vacuum techniques, which are exemplified. The CIS layers are grown onto the metalized glass substrates, hence the seed layer on the substrate determine growth of CIS layer.

***Keywords:*** *Semiconducting thin films, CIS thin films, vacuum and nonvacuum techniques, glass substrates.*

## INTRODUCTION

Process of thin film deposition is the creating thin film coatings onto a substrate glass and other material. The coatings can be made of numerous different materials, from metals to oxides to compounds. Thin film coverings have many different characteristics which are leveraged to improve some portion of the substrate recital. Thin film deposition is an important manufacturing step in the production of many opto-electronic, solid state and medical devices and products, including fibre lesser, optical filters, compound semiconductors electronics, LED displays, precision optics, microscopy & sample slides, and medical implantations. In the review a few diverse technologies and methods that can be used to apply thin film coatings and equipment that can be used to enhance the thin film deposition process.
There may be no one perfect thin film deposition method or system. The technique and configuration of prime depends on the recital and production requirements that are exclusive to many applications.

## METHODS OF THIN FILMS DEPOSITION

***VACUUM EVAPORATION:*** The greatest degree of compositional control over the stoichiometry can be achieved whenever $CuInSe_2$ thin film solar cells are deposited directly from three elemental sources, as described by Michelsen and Chen in their first study. Three elements effusion cells, each with two separate heaters, are used to deposit vast areas of deposits. Tantalum filament heating causes the $CuInSe_2$ to co-evaporate from their separate carbon crucibles. For $CuInSe_2$ the temperature ranges of 1100–1250 $^0$C can be used. The thickness of the samples is monitored by the quartz crystal. A pump with a liquid nitrogen trap is utilized to provide a chamber base pressure of 104–105 Pa. A standard spacing of 20 cm can established between the source and substrate. Substrates undergo heating to temperatures between 175 - 400 $^0$C using tungsten lights with parabolic reflectors or resistive heaters. Two resistive heated crucibles are used in a dual source evaporation method to make up for the loss of chalcogenide (Se or S) during the evaporation process. The chalcogenide partial pressure can be controlled to produce p- or n-type films. Films of device quality are successfully produced using this technique [1–7]. $CuInSe_2$ thin films can produced by annealing Se-evaporated onto Cu–In alloy from graphite effusion source under argon flow at 45 $^0$C for 15 minutes, in contrast to Cu and In layers, which are successively vaporized onto either glass or Si substrates from tungsten boats by the process of thermal evaporation at RT and annealed at 150 $^0$C [8]. CIS powder is used as a source to deposit the

chosen orientation of single phase CIS thin films onto glass substrates at substrate temperatures between 150 and 300 $^0$C. Similar methods are used to create the $CuInSe_2$ ingots, which require heating Cu–In–Se to 1100 $^0$C for ten hours [9].

***FLASH EVAPORATION:*** For large area coatings, the effusion cell evaporation technique can be replaced with the flash evaporation approach. However, using properly constructed evaporation boats is necessary to prevent spitting [10]. To deposit CIS thin films onto glass substrates, the $CuInSe_2$ sintered powder has been continually dropped via a glass tube that vibrating mechanically or electromagnetically at a typical frequency of 50 Hz onto a molybdenum boat that can be heated to between 1173 and 1500 $^0$C. An extra Se source with a graphite boat is added to the system to make up for the loss of Se in the films. Because the chalcopyrite CGS, CIS, and CIGS powder or sinter compound is utilized at a low source temperature [11–13].

***SPUTTERING:*** Sputtering has the benefits of having a relatively low chamber temperature as compared to other methods and easy controllability of the deposition process through the use of plasma current. The film's minimal loss indicates that its composition is essentially the same as its goal. Four-inch-diameter pure Cu, In, and Se targets are employed with 60 mA DC current and 100 W of RF power, respectively. $CuInSe_2$ thin films are produced by depositing 0.27 mm Cu, 0.6 mm In, and 1.46 mm thick Se layers onto glass substrates or Mo-coated glass at room temperature. The Cu/In/Se stack is then selenium-selenized at 250–400 $^0$C in an encased carbon block. It has been discovered that crystalline $CuInSe_2$ thin films perform well at 320 $^0$C, the annealing temperature [14]. CuxSe and $In_2Se_3$ are discovered to be contaminants on the Se target during sputtering; these can be avoided by adjusting the target's configuration, location, and/or power levels. The growth rate of 4-5 A$^{\circ}$ /s is achieved by maintaining a Se flux that is more than three times that of the combined metal fluxes. Five centimeters is the usual distance maintained between the substrate and the target. Because amorphous Se has a lower heat conductivity than polycrystalline Se, the latter is employed to prevent abnormal power discharge [15]. The deposition period of each sputtering is varied to alter the composition of CIS layers. After that, the Cu, In, and Se are deposited and heated to 400 $^0$C for one hour while under vacuum. For sputtering, the highly ionized plasma beam produced by a traditional glow discharge is directed at the target. For Cu, In, and Se depositions, respectively, the anode voltage (V)/current (A) of 80/025, 80/0.25, and 75/0.2 as well as the cathode V/A of 10/12, 10/12, and 9/12 are applied. Cu, In, and Se are deposited at deposition periods of 330 s, 360 s, and 30-180 min, respectively [16]. In the hybrid technique, there are various ways to grow CIS thin films. Using a sputtering process, Cu and In are progressively deposited onto Mo-coated glass substrates to create 1 mm thick layers. Thermal evaporation is then used to remove 1 mm thick Se from these layers. After being annealed in a graphite box at a temperature range of 100–600 $^0$C in a vacuum of 1.333 Pa, the Cu/In/Se stack sample transforms into $CuInSe_2$. The quartz tube contains the box [17]. Piekoszewski et al. first produced thin films by sputtering tiny, ungrounded $CuInSe_2$ pieces for the coarse and fine CIS targets, which had dimensions of 5 cm and 0.2 cm, respectively[18, 19].

***PULSED LASER DEPOSITION:*** With a typical wavelength of 193 nm and pulse width of 25 ns, the PLD ArF excimer laser deposits CIS films onto glass substrates at a substrate temperature of 550 $^0$C by striking the CIS pellet via the quartz window. During film deposition, a chamber pressure of 1-3X10-3 torr is maintained. CIS sintered powder is pressed at 8.6X107 Pa to create the CIS pellet. To prevent heating on it and ensure uniform film growth, the goal rotation speed of 15 rpm is kept constant. The temperature of the substrate is 500 $^0$C, and the target and substrate are separated by 3 cm [20, 21].

***SPRAY PYROLYSIS:*** One of the less expensive methods, spray pyrolysis, has been used by a number of organizations to prepare $CuInSe_2$ films. Using chemical solutions of cuprous, indium, and N N-dimethyl thiourea (NDTU), Pamplin and Feigelson [22, 23] successfully deposited the sphalerite form of $CuInSe_2$ semiconductors and their solid solutions onto glass substrates at a substrate temperature of 350 $^0$C by spraying. For $CuInSe_2$ thin film spray deposition, an aqueous solution containing AR grade $CuCl_2$, $InCl_3$, and selenourea (NDSU) is utilized. A small amount of HCl is added to the solution to change its pH. The preparation of the solution happens right before the spray starts. Compressed air is used as the carrier gas for applying the films to heated glass slides; the spray rate needs to be regulated. Degenerate and chalcopyrite $CuInSe_2$ films can be sprayed-deposited, according to thermodynamic simulations of the deposits performed under equilibrium conditions [25].

***ELECTRODEPOSITION:*** One needs either conductive or metal substrates in order to place the CIS layer. Bhattacharya [26] made the initial attempt to electrodeposit $CuInSe_2$ films. $CuInSe_2$ films are then attempted to be deposited many times from aqueous solutions containing copper, indium, and selenium precursors. The second method involves selenium electrodeposited Cu-In alloy film, which

can be achieved using solution techniques or by annealing the film under $H_2Se$ [27, 28]. It is discovered that the films made using this technique peel off, which causes the gadget to malfunction [27, 29]. Furthermore, the extreme toxicity of $H_2Se$ raises grave issues for safety. The main priorities are to obtain films with appropriate stoichiometry and morphology. Researchers look into how annealing affects the structural characteristics of $CuInSe_2$ films that are electrodeposited [30]. $CuCl_2$, $InCl_3$, $SeO_2$, and pH 1.5 aqueous solutions are used for electrodeposition to form the films onto FTO, with potentials ranging from -0.5 to -0.9 V [31].

***SOLVTHERMAL TECHNIQUE:*** CuCl and $InCl_3$ are added after the powdered Se has been dissolved in anhydrous ethylenediamine and swirled for two hours. After 2 hours of stirring, the mixture is heated for 24 hours at 200°C in a stainless steel autoclave lined with teflon. After being extracted from the solution, the chalcopyrite CIS nanoparticles are cleaned using ethylene and distilled water [31].

## CONCLUSIONS

The different technique has the many advantages and is a simple and inexpensive technique. The process can be protracted to large area coatings. Specially a SPT process that contributes certain thin films with quality comparable to other conventional techniques. The starting materials are AR grade inorganic salts and organic compounds. The properties of films can be suitably modified by varying the atomic/ionic concentrations of the constituent species in the starting solution.

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# STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES OF Ni-Cu-Cd SPINEL FERRITES

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## ABSTRACT

Cadmium ($Cd^{2+}$) substituted nickel- copper mixed ferrites having the general formula $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ (x = 0.0, 0.2, 0.3, 0.4) were synthesized using double sintering ceramic technique. The effect of $Cd^{2+}$ substitution on structural and magnetic properties of nickel-copper ferrites were investigated using X-ray diffraction, cation distribution, IR, magnetization and A.C. susceptibility technique. XRD data were used to calculate structural parameters and to find the cation distribution. The IR spectra of all the samples were taken in the range of 200-800cm$^{-1}$. IR spectra shows high frequency band ($\nu_1$) lie at around 600 cm$^{-1}$and low frequency band ($\nu_2$) around 400 cm$^{-1}$. Using IR data force constant $K_t$ and $K_o$ have been obtained. The hysteresis data indicate that saturation magnetization, magneton number increases upto x = 0.3 and then decreases with increase in cadmium content. Magnetization study reveals that the structure remains collinear up to x = 0.1 only, beyond which it shows non collinear behaviour by showing the canting effect. The Curie temperature obtained from A.C. susceptibility decreases with increase in cadmium content x.

***Keyword:** Ferrite, XRD, IR study, magnetization and A. C. Susceptibility.*

## INTRODUCTION

Spinel ferrites with the general chemical formula $MFe_2O_4$ (M = Co, Ni, Mn, Cu, Zn, Cd etc.) have acquired tremendous technological importance because of their interesting magnetic, electrical, chemical properties and good thermal stability. Ferrites material are insulating magnetic oxides, they possess high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high Curie temperature, high permeability and moderate permittivity. They are also used as magnetic data storage, gas sensors and catalyst due to their interesting electrical and magnetic properties. These properties of spinel ferrites depend on various factors such as method of preparation, chemical composition, type and amount of dopant [1].

Many scientists have studied Ni and Cu ferrite for their structural, electrical and magnetic properties [2, 3]. The substitution of divalent non magnetic $Cd^{2+}$ ions in mixed Ni-Cu spinel ferrites may lead to interesting magnetic as well as electrical and dielectric properties. It has been reported that the addition of $Zn^{2+}$ or $Cd^{2+}$ in spinel ferrites can give rise to a variety of magnetic structures [4].It has been reported that substituted nickel ferrite have been the subject of extensive investigation because of their utility in micro-wave devices, computer memory chips, magnetic recording media. In order to investigate the influence of non magnetic $Cd^{2+}$ ions in mixed Ni-Cu spinel ferrite, a systematic study of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ (x = 0.0, 0.2, 0.3, 0.4) ferrite system has been carried out. In the present work, we have investigated the structural and magnetic properties of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ of spinel ferrite system and the results are presented in this paper.

## EXPERIMENTAL TECHNIQUE

The polycrystalline samples of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ (with x = 0.0 to 0.4) spinel ferrite system have been prepared by the standard ceramic technique. The starting materials NiO, $Fe_2O_3$, CuO, CdO all AR grade were used. The oxides were mixed thoroughly in stoichiometric proportion and then

reground to very fine powder by using agate mortar for about three to four hour. The mixed powder was then pre-sintered at 1253K for 16 hour. The pre-sintered powders were again ground and granulated using 2% polyvinyl alcohol as a binder. Granulated mixture was then pelletized in disc shaped form by applying pressure of six ton/inch$^2$ and finally sintered at 1393K in a Indfur programmable furnace for 16 hour in air atmosphere and then slowly cooled to room temperature at the rate of 2K per minute.

The powder X-ray diffraction patterns of all the samples were recorded by Phillips X-ray diffractometer (Model 3710) using Cu-Kα radiation (λ = 1.5406Å) in the 2θ range $20^0$-$80^0$ at room temperature. The X-ray intensity calculations were carried out in order to determine the cation distribution for all the compositions of the system. The XRD data have been used to determine the values of lattice parameter, X-ray density, particle size and other structural parameters.The infrared spectra of a prepared sample were recorded at room temperature within the range 200 to 800 cm$^{-1}$ on the infrared spectrometer (Model 783, Perkin-Elmer) The position of threshold frequencies corresponding to different vibration modes is observed in the spectra and which is used to calculate the force constant $K_0$ and $K_t$ corresponding to octahedral and tetrahedral complexes respectively. The analysis of infrared data is done using Waldron's analysis [5].

The saturation magnetization (Ms), remanence magnetization (Mr) and coercivity (Hc) were measured at room temperature using high field hysteresis loop technique. Using saturation magnetization magneton number $n_B$ for all the samples was calculated [6].The A.C. susceptibility measurements of all the samples under investigations were made in the temperature range 300–925K using a double coil setup [8], Curie temperature of all the samples was determined.

## RESULTS AND DISCUSSION

***Structural analysis:*** The room temperature X-ray diffraction patterns of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ are shown in Fig. 1(a, b). All the Braggs peaks that appeared in the XRD patterns belong to cubic spinel phase. The analysis of X-ray diffraction patterns of the samples revealed the formation of single phase cubic spinel structure. No extra peak was observed in the XRD patterns. The Bragg peaks are found to be sharp, intense and shifts towards lower 2θ angle on substituting $Cd^{2+}$ ions in place of $Cu^{2+}$ ions. Using the inter planner spacing'd' values and corresponding Miller indices, the average lattice constant of all the samples was calculated using the relation

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (1)$$

The values of lattice parameter 'a' are given in Table 1. It is observed from Table-1 that the lattice constant increases with increasing cadmium content x. The observed increase in lattice constant is due to the replacement of smaller $Cu^{2+}$ ions of ionic radii (0.72Å) by larger $Cd^{2+}$ ions of ionic radii (0.97 Å). Similar variation of lattice constant was observed in Ni-Cu-Zn spinel ferrite [8]. The variation of lattice constant 'a' (Å) and diffraction angle 2θ of (311) plane as a function of cadmium content x is shown in Fig.2 It can be observed that the lattice parameter increases linearly with increase in cadmium content where as Bragg's angle 2θ decreases with $Cd^{2+}$ content x.

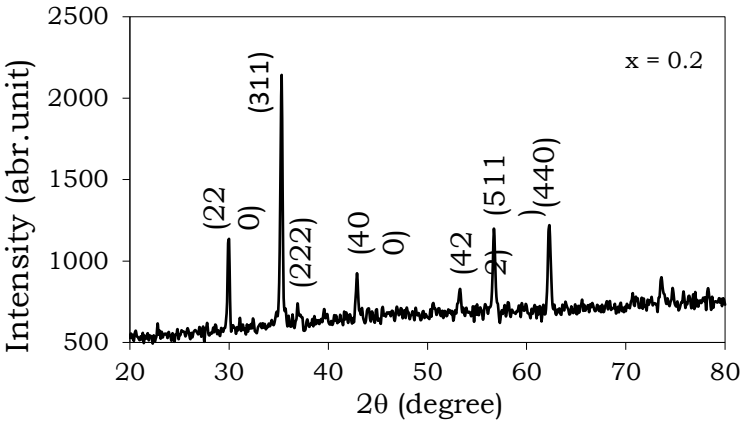


**Fig. 1:** Typical XRD patterns of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ (for x = 0.2).

The X-ray density, calculated according to the relation

$$d_x = \frac{ZM}{N_a a^3} \quad (2)$$

where, 'Z' is number of molecules per unit cell (Z = 8 for spinel cubic ferrite), 'M' is the molecular weight, '$N_a$' is Avogadro's number and 'a' is lattice constant, and are listed in Table-1. It can be observed from Table-1 that X-ray density increases with increase in cadmium content x. The observed increase in X-ray density is attributed to the fact that the unit cell volume increases due to increase in lattice constant. The bulk density of each sample was calculated by using the mass and volume of the samples. The values of bulk density are given Table-1.

The percentage porosity of each sample was calculated using the relation

$$P\ (\%) = (1 - \frac{d_B}{d_x}) \times 100 \quad (3)$$

where, $d_B$ is the bulk density, $d_x$ is the X-ray density

The high values of porosity may be due to substitution $Cd^{2+}$ ions and also due to the high sintering temperature. Our results on X-ray density, bulk density and porosity are in good agreement with those reported in the literature [9, 10].Particle size of all the samples was determined using Scherrer formula [11]. The highest intensity peak (311) of the XRD patterns was considered for the determination of full width at half maximum (FWHM). The particle size varies in between 3- 4 µm.

**Table: 1:** Lattice constant (a), X-ray density ($d_x$), bulk density ($d_B$) particle size (t) and porosity (P) of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ .

| Comp. x | a (Å) | dx (gm/cm$^3$) | $d_B$ (gm/cm$^3$) | P (%) | t (µm) |
|---|---|---|---|---|---|
| 0.0 | 8.367 | 5.370 | 4.003 | 25.466 | 3.652 |
| 0.2 | 8.423 | 5.479 | 3.939 | 28.176 | 3.442 |
| 0.3 | 8.453 | 5.529 | 4.231 | 23.480 | 3.750 |
| 0.4 | 8.488 | 5.5682 | 3.931 | 29.394 | 3.035 |

***Cation distribution:*** The magnetic properties of spinel ferrite depend on the distribution of cations among the available sites. In the present series ($Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$) cation distribution of all the samples were obtained using X-ray diffraction method. The X-ray intensity for the (hkl) plane is obtained by the well known Burger's formula [12]. The values of multiplicity factor 'P' and Lorentz polarization factor '$L_P$' are taken from the literature [13]. The planes (220), (400) and (422) are considered to be sensitive to cation distribution [14] and hence they are used in X-ray intensity ratio calculations. In calculating the cation distribution of the present series site preference energies of the constituent ions are taken into account. According to site preference energies, $Cd^{2+}$ ions occupy tetrahedral (A) site by replacing $Fe^{3+}$ ions, $Ni^{2+}$ ions occupy octahedral [B] sites and $Fe^{3+}$ and $Cu^{2+}$ ions occupy both tetrahedral (A) and octahedral [B] sites.The X-ray intensity ratios using the planes (220), (400) and (422) were calculated for various possible combinations of cations. The combination of cations for which observed and calculated intensity ratio agrees close to each other is taken to be the correct cation distribution. The cation distribution obtained using the X-ray intensity ratio calculation method used in the present work is summarized in Table 2. It is observed from Table 2 that $Cd^{2+}$ ions occupy A site as expected, $Ni^{2+}$ ions occupy B site whereas $Fe^{3+}$ and $Cu^{2+}$ ions occupy both A and B sites.

**Table: 2:** Cation distribution of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$.

| x | A-Site | | | B-Site | | |
|---|---|---|---|---|---|---|
| | $Cd^{2+}$ | $Cu^{2+}$ | $Fe^{3+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Fe^{3+}$ |
| 0.0 | 0.0 | 0.0030 | 0.9970 | 0.5 | 0.497 | 1.0030 |
| 0.2 | 0.2 | 0.0020 | 0.7980 | 0.5 | 0.298 | 1.2020 |
| 0.3 | 0.3 | 0.0015 | 0.6985 | 0.5 | 0.1985 | 1.3015 |
| 0.4 | 0.4 | 0.0010 | 0.5990 | 0.5 | 0.099 | 1.4010 |

***Infrared spectroscopy:*** The IR spectra of all the compositions were obtained in the wave number range 200-800 cm$^{-1}$. The absorption band $\nu_1$ is assigned to tetrahedral group complexes, while the band $\nu_2$ is

attributed to octahedral group complexes. The IR absorption spectra for the series $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ is presented in Fig 2. As usual IR spectra show two bands, the higher frequency band $\nu_1$ is seen to near 600 $cm^{-1}$ and the lower frequency band $\nu_2$ is seen near 400 $cm^{-1}$[15]. The values of $\nu_1$ and $\nu_2$ are given in Table 3. The difference in the band position is observed from Table 3 is expected because of the difference in the $Fe^{3+}$- $O^{2-}$- $Fe^{2+}$ distance for the octahedral and the tetrahedral complexes.

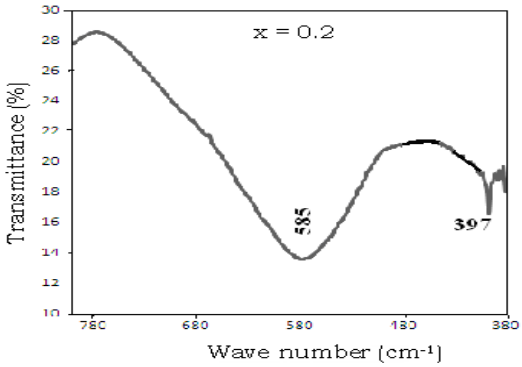


**Fig.2:** IR Spectra of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$ (for x = 0.2) .

The IR absorption data have been used to compute force constant $K_t$ and $K_o$ using the analysis of Waldron [5]. The values of $K_t$ and $K_o$ are given in Table 3. The bond length $R_A$ and $R_B$ [16] have been also calculated and the values were presented in Table 3. It is observed from Table 3 that $K_t$ increases whereas $K_o$ decreases. The bond length $R_A$ and $R_B$ both increases as cadmium content x increase.

**Table 3:** Vibration bands frequency ($\nu_1$,$\nu_2$), Force constant ($K_t$, $K_o$) and Bond length ($R_A$, $R_B$) of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$

| x | $\nu_1$ ($cm^{-1}$) | $\nu_2$ ($cm^{-1}$) | $K_t$x $10^5$ (dyne/cm) | $K_o$x $10^5$ (dyne/cm) | $R_A$ (Å) | $R_B$ (Å) |
|---|---|---|---|---|---|---|
| 0.0 | 590 | 399 | 1.482 | 0.988 | 1.898 | 1.990 |
| 0.2 | 585 | 397 | 1.751 | 0.965 | 1.911 | 2.004 |
| 0.3 | 583 | 396 | 1.886 | 0.954 | 1.917 | 2.011 |
| 0.4 | 581 | 395 | 2.018 | 0.943 | 1.925 | 2.019 |

***Magnetic properties:*** The magnetic hysteresis parameters like saturation magnetization ($M_s$), remanence magnetization ($M_r$), coercivity ($H_C$), remanence ratio and magneton number ($n_B$) obtained from hysteresis loops are given in Table 4. Saturation magnetization increases up to x = 0.3 and then decreases with the increase in Cd concentration. Similar results about saturation magnetization have been reported by other researchers [17, 18]. Increasing trend of saturation magnetization can be explained on the basis of Néel's two sub-lattice model [16] whereas the decreasing trend suggests that there are triangular type spin arrangements on B site which cannot be explained by Néel's two sublattice model. When non-magnetic divalent $Cd^{2+}$ ions are substituted in ferrite lattice, they tend to specifically occupy tetrahedral sites by transferring $Fe^{3+}$ ions to octahedral sites. This behaviour of cadmium can be attributed to 1) their favoritism by polarization effect and 2) site preference of cations also depends upon their electronic configurations. $Cd^{2+}$ ions show marked preference for tetrahedral sites where their free electrons respectively can form a covalent bond with the free electrons of the oxygen ion. This forms four bonds oriented towards the corners of a tetrahedron. $Ni^{2+}$ ions have marked preference for an octahedral environment due to the favorable fit of the charge distribution of these ions in the crystal field at an octahedral site [19]. As non-magnetic cadmium ions prefer to go into tetrahedral lattice and transfer some iron ions of large magnetic moment (5 $\mu_B$) to octahedral site resulting in an increase in saturation magnetization.This ordering gives rise to a canting angle among magnetic spins i.e. Yafet–Kittel (Y–K) angles, which have been calculated using the formula

$$n_B = M_B \cos\theta_{yk} - M_A \quad \text{.....(4)}$$

where, $\theta_{xy}$ represents Y–K angle, $M_A$ is magnetic moment of tetrahedral (A) site and $M_B$ is magnetic moment of octahedral [B] site.

**Table: 4:** Saturation magnetization (Ms), Remanence magnetization (Mr), Coercivity (Hc), Magneton number ($n_B$), Yafet-Kittel angle ($\theta_{yk}$) and Curie temperature (Tc) measured from A.C. susceptibility of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$.

| x | Ms (emu/gm) | Mr (emu/gm) | Hc (Oe) | $n_B(\mu_B)$ | | $\theta_{yk}$ (degree) | Tc (K) |
|---|---|---|---|---|---|---|---|
| | | | | Obs. | Cal. | | |
| 0.0 | 57.450 | 11.36 | 32.252 | 2.436 | 1.52 | 0 | 723 |
| 0.2 | 69.345 | 1.155 | 57.255 | 3.061 | 3.32 | 15.21 | 640 |
| 0.3 | 70.342 | 3.955 | 36.113 | 3.167 | 4.21 | 30.19 | 593 |
| 0.4 | 65.795 | 36.252 | 52.743 | 3.020 | 5.11 | 42.07 | 560 |

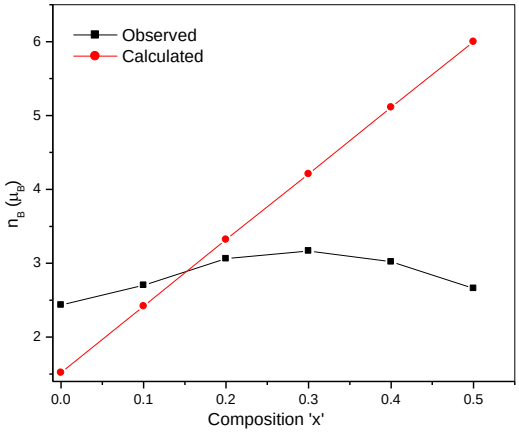


**Fig.3:** Variation of Magneton number ($n_B$) with composition (x) of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$

The values of Y–K angles for samples with x = 0.0 and 0.1 is zero which indicates that magnetization of this composition can be explained with Neel's two sub lattice theory. It is clear from Table 4 that magneton number increases up to a certain value i.e. x = 0.3 and then decreases with increase in Cd content x. Fig. 3 show the variation of observed and calculated magneton number with composition x. It can be seen that there is a discrepancy between observed and calculated magnetic moment. The values of Y–K angles increases with the increase in Cd concentration from x = 0.2 (Fig. 3). The non-zero Y–K angles suggest that the magnetization behavior cannot be explained on Neel's two sub-lattice model due to the presence of spin canting on B sites. The rise in Y–K angles with the increase in Cd shows that triangular spin is favored in B site that decreases the A–B interaction.

Magnetic ordering present in the compound which varies as a function of method of preparation, chemical composition, microstructure and grain size affect the magnetic susceptibility. The variation of A.C. susceptibility as a function of temperature and composition x is studied in the present work. Thermal variation of A.C. susceptibility of all the samples is shown in Fig. 4. All the samples exhibit ferrimagnetic behaviour. The plots of $\chi_T/\chi_{RT}$ are used to determine the Curie temperature and the values are given in Table 4. It is clear from Table 4 that Curie temperature goes on decreasing with the addition of Cd content. This is attributed to the decrease in A-B interaction resulting from the replacement of magnetic $Fe^{3+}$ ions by non-magnetic $Cd^{2+}$ ions. The decrease in $T_C$ is uniform and linear. According to Neel's model A-B interaction is most dominant in ferrites; therefore, Curie temperature of the ferrites is determined from the overall strength of A-B interaction. The strength of A-B interaction is a function of the number of $Fe_A^{2+}$-$O^{2-}$-$Fe_B^{3+}$ linkages, which in turn, depends upon the number of $Fe^{3+}$ ions in the formula unit and their distribution amongst tetrahedral (A) and octahedral [B] site. In the present system $Cu^{2+}$ ($1\mu_B$) ions are replaced by non magnetic $Cd^{2+}$ ions. Also the cadmium ions have strong preference to tetrahedral (A) site due to that iron ions ($5\ \mu_B$) of high magnetic moment move to

octahedral [B] site. This results in decreasing the A-B interaction, which leads to decrease in Curie temperature ($T_C$).

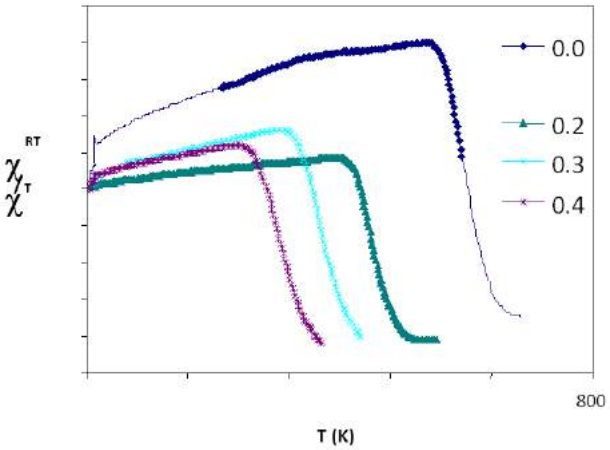


**Fig. 4:** Variation of A.C. Susceptibility ($\chi_T/\chi_{RT}$) with temperature T(K) of $Ni_{0.5}Cu_{0.5-x}Cd_xFe_2O_4$.

## CONCLUSIONS

The single phase cubic spinel structure of prepared ferrite is confirmed from the sharp and well defined intensity peaks seen in the XRD patterns. It is found that lattice constant increases with increase in cadmium substitution x. Cation distribution was studied on the basis of intensity ratio calculations. This leads to the conclusion that $Cd^{2+}$ resides at A site, $Ni^{2+}$ occupies B site whereas $Cu^{2+}$ and $Fe^{3+}$ diverts towards both the sites. IR spectra illustrate the presence of two absorption bands located at 400 $cm^{-1}$ and 600 $cm^{-1}$ which is a characteristic of a spinel ferrite. The force constant $K_t$ increases whereas $K_o$ decreases. The bond length $R_A$ and $R_B$ both increases as cadmium content x increase. Magnetization study reveals that the structure remains collinear up to x = 0.1 only, beyond which it shows non collinear behaviour by showing the canting effect. The substitution of cadmium in nickel-copper mixed ferrite results in decrease in Curie temperature. Thus, substitution of $Cd^{2+}$ ions in mixed Ni-Cu spinel ferrite influences the structural and magnetic properties of Ni-Cu ferrite.

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# DC electrical resistivity analysis of $Li^+$ doped Cobalt ferrite Nanoparticles

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## ABSTRACT

Now a day spinel ferrite nonmaterial's are studied more due to their widespread applications in the electronics industry and energy storage devices. The $Li^+$ doped Cobalt ferrites with the general formula $Co_{1+x}Li_xFe_{2-x}O_4$ (x =0.0, 0.1, 0.2, 0.3, 0.4) were prepared using wet chemical method i.e. sol-gel auto combustion method. Structural characterization of the samples was carried out using X-ray powder diffraction technique. The XRD confirmed the cubic phase of $Co_{1+x}Li_xFe_{2-x}O_4$ ferrite with the crystallite size. The crystallite size and other structural parameters such as lattice constant, volume of a cubic unit cell, X-ray density, and porosity of the samples are calculated. The lattice parameter of the sample was found to be increases with increasing $Li^+$ content (x). The porosity is increased with increasing $Li^+$ content as evident from XRD. Crystallite size is calculated by using Debye Scherrer method. The sol–gel auto-combustion method was used for synthesize substituted Cobalt spinel ferrite. This is a novel method as it is combination of the chemical sol–gel process and the combustion process. The present work was to synthesize $Li^+$ doped Cobalt ferrite using citrate assisted sol-gel auto combustion and to understand the effect of $Li^+$ ion doping on the structural properties cobalt ferrite.

**Keywords:** X-ray diffraction, spinel ferrite, Nanoparticles, Sol-gel auto combustion, Bulk density, Porosity.

## INTRODUCTION

The cubic spinel structured cobalt ferrite nanoparticles have been the subject of current interest because of their applications in electric devices and telecommunication which often differs from their bulk counterpart [1]. The properties such as high saturation magnetization, high coercivity, strong anisotropy as well as chemical stability are not observed in the bulk sample. Spinel ferrite has general formula $(A^{2+})[B_2^{3+}]O_4^{2-}$ where $A^{2+}$ and $B^{3+}$ are the divalent and trivalent cations occupying tetrahedral (A) and octahedral [B] sites[2]. Ferrite has Face-centered cubic structure and cations and oxygen anions formulation. When divalent cation occupies both tetrahedral as well as octahedral sites, inverse spinal is formed [3]. Similarly, a mixed structure can also be formed when divalent cations is distributed in both sites. The $CoFe_2O_4$ is a partially inverse spinel with $Co^{2+}$ ions, occupy the octahedral [B] site and $Fe^{3+}$ ions occupy both tetrahedral (A) site and octahedral [B] site [4]. Substituted cobalt ferrites are widely used as magnetic materials due to their low dielectric losses. Large number of researchers have been carried out work on the structural, morphological, magnetic, electrical, dielectric, optical etc. properties of spinel cobalt ferrites with a view to improve these properties for the desired applications [5].It is excepted that doping of mono-valent metal ions $Li^+$ in Cobalt ferrite may show the fascinating properties which can be employed for different applications.

## EXPERIMENTAL DETAILS

***Materials:*** Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$], Nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$], ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$], lithium nitrate [$LiNO_3$.6H2O] and citric acid [$C_6H_8O_7{\cdot}H_2O$], ammonia solution [$NH_3.H_2O$] acetone, distilled water were used. All chemicals used were of analytical grade and the solutions were prepared with distilled water.

***Synthesis of $Li^+$ doped Cobalt ferrite nano particles:*** Ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], lithium nitrate [$Li(NO_3).6H_2O$], Cobalt nitrate [$Co(NO_3)_2{\cdot}9H_2O$] were dissolved together in a minimum amount of distilled water to get clear solution. The citric acid was used as a fuel. The citric acid to nitrate ratio was considered to be 1:3. An aqueous solution of citric acid was mixed with metal nitrate solution. The mixed solution was kept on magnetic stirrer and constantly stirred at 300rpm by maintaining the

temperature at 60°C.to form a homogeneous solution. The solution was transformed into a sol and then a gel is formed by evaporation of the water. The ammonia solution was slowly added to maintain the pH at 8 of the mixed homogeneous solution. The temperature after the gel formation is increased to 120°C. At this temperature the gel get burnt converting into fine loose powder of $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) nanoparticles. This sample was then manually grinded and kept for calcinations at 500°C in furnace for 4 hours to remove the moisture and impurity if any present in the sample. Pellets were prepared with KBr hydraulic press in 2–3 mm thickness and 10 mm diameter size. The samples in powder form were used to characterize the material

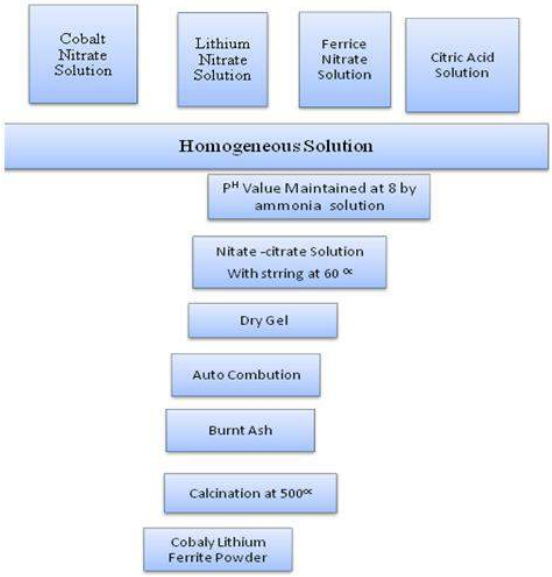


**Fig.** Flow chart for the synthesis of cobalt-Lithium ferrite using citrate-gel auto combustion technique

***Characterizations:*** X-ray diffractometer (XRD) with Cu-Kα radiation(□λ=1.5405 *A*° ) and 2Θ□scanning ranges from 20° to 80°, at a scanning speed of ~ 2° /min, were characterized to verify the phase purity and structure of prepared material.

## RESULTS AND DISCUSSION

***X-ray diffraction analysis:*** The X-ray diffraction (XRD) pattern of all $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3,0.4) nanoparticles were recorded using X-ray diffractometer at room temperature in the 2θ range of 20° to 80°.

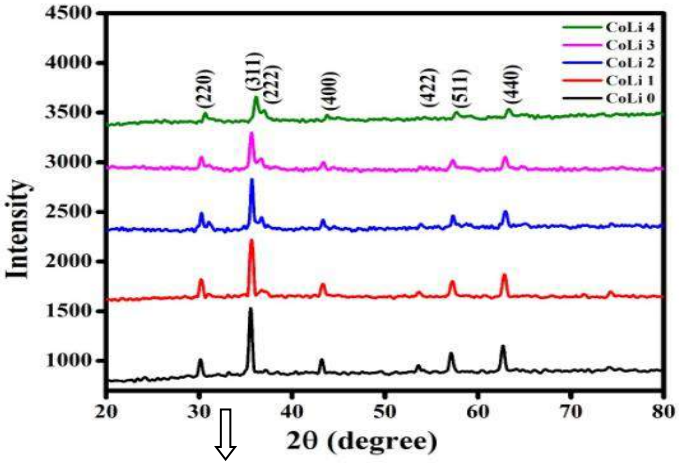


**Fig. 1:** X-ray diffraction patterns of $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3,0.4)

**Fig. 1** displays the XRD patterns of all the samples. Using Bragg's law, all the peaks in the XRD pattern were indexed. All the peaks belonging to the cubic spinel structure are verified by the XRD patterns, indicating that the prepared specimens have a single-phase existence. XRD pattern is compared with JCPDS card number 00-0022-1086 in order to identify the crystalline phases present

[7]. In the XRD patterns, all the peaks observed are extreme and slightly wider, indicating the nano crystalline nature.

***DC electrical resistivity analysis:*** The plot of DCelectrical resistivity (ρ) for $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3 and 0.4) nanoparticles is shown in **Fig. 2**. It is evident from **Fig. 2** that, resistivity has been increased with the substitution of Li content (x). The plot exhibits the semiconducting behavior as DC resistivity of present spinel ferrites nanoparticles decreases with increasing in temperature[8]. The potential explanation for the increase in resistivity is that $Fe^{3+}$ ions are decreased, which in turn reduces the likelihood of hopping between $Fe^{3+}$ and $Fe^{2+}$ ions. The conduction mechanism in spinel ferrites is related to the hopping of the electrons between the ions of the same element. Mobility of charge carriers (drift) reduces resistivity with temperature. Using the Arrhenius reference, the activation energy values for all the samples were determined[9].

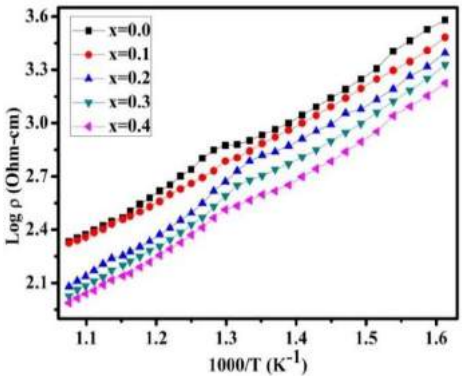


**Fig 2:** DC electrical resistivity (ρ) for $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3,0.4)

## CONCLUSIONS

Monovalent $Li^+$ doped cobalt ferrite nanoparticles with composition $Co_{1+x}Li_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) nanoparticles were successfully synthesized via citric acid assisted sol-gel auto combustion route. X-ray diffraction study revealed the single phase formation and nano crystalline nature of all the prepared nano particles.The lattice parameter, crystallite size, and Unit cell volume of crystalline phase reduced systematically with the increase in $Li^+$ mole, concentration. DC electrical resistivity of

the samples decreases with increasing in the temperature which indicate the semiconducting behavior of nano ferrites with the significant influence of the Lithium doping on electrical properties. Small polaron hopping and thermally activated mobility of charge carriers was operative in $Co_{1+x}Li_xFe_{2-x}O_4$ and confirmed by DC electrical measurements.

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# PHYSICAL AND DIELECTRICAL PROPERTICS OF $In^{3+}$ SUBSTITUTED YTTRIUM IRON GARNET

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**ABSTRACT**

The garnet having the general formula $Y_3In_xFe_{5-x}O_{12}$ (x= 0.0, 0.1and 0.3) were synthesized using double sintering ceramic technique. The samples were characterized by X-ray diffraction technique. The X-ray diffraction studies of compositions revealed the formation of single phase cubic structure with lattice constant ranging from 12.37 to 12.42 Å up to x= 0.3. The dielectric properties were investigated using LCR meter (hp HEWLETT) in the frequency range 100 Hz to 1 MHz. The dielectric constant (ε′), dielectric loss (ε″) dielectric loss tangent (tanδ), was measured as a function of frequency by using LCR meter. The frequency dependence of dielectric measurements was carried out for all the samples.

***Keyword:*** *YIG, Structure, dielectric study.*

## INTRODUCTION

Ferrites represent an important category of materials, which are in great demands due to their numerous applications in many fields. The electrical and magnetic properties of ferrites are strongly dependent on their chemical composition and their method of preparation [1, 2]. It is important to optimize the electrical and magnetic properties of ferrites, for desired applications. Due to their interesting properties scientists, researchers and engineers are still interested in designing the various types of ferries material substituted with different cations with different valencies and prepared by different techniques.

Among the various types of ferrites rare earth garnet especially yttrium iron garnet (YIG) is of great importance for scientist and technologist because of their applications in microwave communication devices such as circulators, gyrators and phase shifters because of its small ferromagnetic resonance line-width, high electrical resistivity and low dielectric loss in microwave regions in many fields [3]. Yttrium iron garnet (YIG) is microwave ferrite, which in polycrystalline form has specific characteristics. The magnetic and crystallographic properties of the magnetic iron garnet have been studied by many workers [4-7]. Substituted iron garnets have found extensive use in wide band non reciprocal microwave devices [8].

## EXPERIMENTAL

The samples of $In^{3+}$ substituted $Y_3In_xFe_{5-x}O_{12}$ garnets with x = 0.0 .0.1 and 0.3 were prepared by well known double sintering ceramic method in which a molar ratio of analytical $Y_2O_3$, $Fe_2O_3$ and $In_2O_3$ (all 99.99% pure AR grade chemicals, Mumbai) were mixed thoroughly in stoichiometric proportions and then ground to very fine powder by using agate mortar for about 3 hr. These mixtures in powder form were pre-sintered in a Indfur Programmable muffle furnace at 1200 $^0$C for 24 hrs and cooled to room temperature slowly at the rate of 2 $^0$C/min. The samples were reground and re-fired at 1350 $^0$C for 30 hr and slowly cooled to room temperature at the rate of 2$^0$ C/min., and then reground for 1 hr. The fine powdered sample was pelletized under the pressure 5 ton/inch$^2$.

## RESULT AND DISCUSSION

Mixed garnet ferrites system under investigation has been structurally investigated by X-ray diffraction technique. The XRD pattern shows the reflections namely (321), (400), (420), (422), (431), (521), (611), (444), (640), (642), (800), (842). No extra peaks other than cubic structure have been observed in the XRD pattern. The Bragg peaks are sharp and intense. The lattice parameters are calculated using XRD data and are given in table-1. It is observed from table-1 that lattice constant increases with increase in indium content 'x'. The ionic radii of yttrium (0.89Å) $Fe^{3+}$ is (0.67Å) and indium (0.81Å) hence we observe variation in the lattice parameter with indium substitution. The bulk density of all samples was measured using Archimedes principle and values are tabulated in table-1. Bulk density increases with increase in indium content 'x'. Using the values of molecular weight and volume of the sample X-ray density was calculated. The values of X-ray density are also listed in table-1.

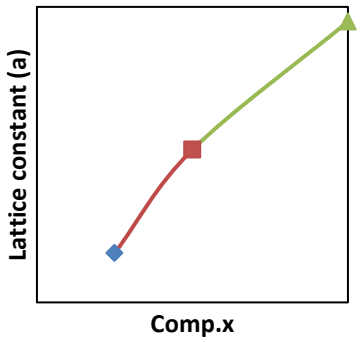


**Fig:1** Variation of lattice constant with the Indium concentration x .

X-ray density increase with composition 'x'. The observed variation in X-ray density is attributed to increase in volume of the samples. The crystallographic parameters (lattice constant, X-ray density) are in good agreement with reported values [9] .The most intense peak (420) of XRD pattern was used to evaluate particle size of the samples. The particle size was calculated by using Scherer's formula, the values of particle size for all the composition is listed in table-1.

**Table: 1** Lattice constant (a), X-ray density (dx), bulk density ($d_B$) porosity (P) and particle size (t) of $Y_3In_xFe_{5-x}O_{12}$.

| x | a (Å) | dx ($gm/cm^3$) | $d_B$ ($gm/cm^3$) | P (%) | t (µm) |
|---|---|---|---|---|---|
| 0.0 | 12.370 | 5.179 | 4.13 | 20.25 | 3.42 |
| 0.1 | 12.391 | 5.194 | 4.15 | 20.10 | 3.03 |
| 0.3 | 12.417 | 5.244 | 4.23 | 19.34 | 3.18 |

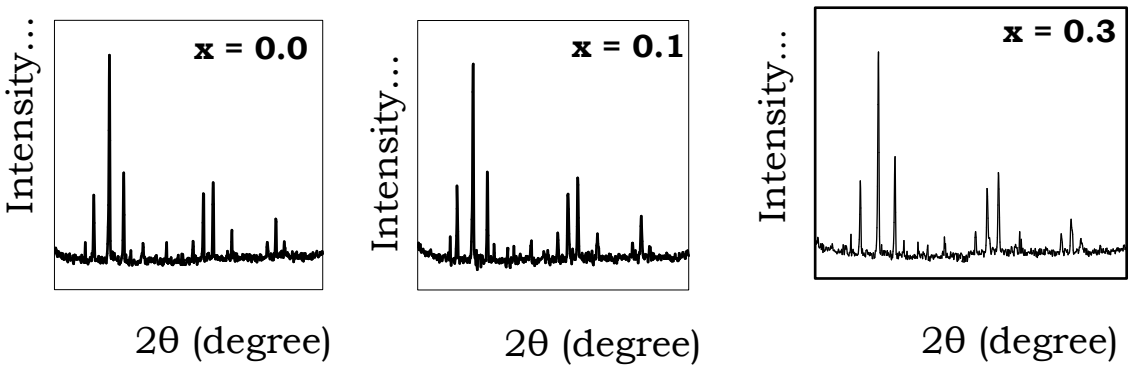


**Fig. 2:** XRD patterns of $Y_3In_xFe_{5-x}O_{12}$ (x = 0.0, 0.1 and 0.3).

***Frequency dependence of dielectric properties:*** The dielectric constant measurements were carried out on disc shaped pellets as a function of frequency by using two probe method. The real ε′ and imaginary ε″ parts of the dielectric constant and loss tangent tanδ of $Y_3In_xFe_{5-x}O_{12}$ were computed according to

Smith and Wijn [10, 11]. The variation of the dielectric constant ε′ and dielectric loss ε″ with respect to frequency at room temperature is shown in Fig 5(a) . It can be observed from figures 5(a) that, dielectric constant (ε′) and dielectric loss (ε″) both decreases with increase in frequency. It can also be observed that dielectric loss (ε″) decreases with increasing frequency much more rapidly than (ε′). This behaviour of dielectric constant is attributed by assuming that mechanism of polarization in ferrite is similar to that of conduction mechanism. Iwauchi [12] reported strong co-relation between the conduction mechanism and dielectric behaviour of the ferrites. Fig. 5(b) shows the variation of dielectric loss tangent with frequency at 300K for all the values of 'x'. It is observed from Fig. 5(b) that, the parameter tanδ decreases exponentially with the increase of frequency.

**Table: 2:** Room temperature dielectric constant (ε′), dielectric loss (ε″) and dielectric loss tangent (tanδ) at 100 Hz, 10 KHz and 1 MHz of $Y_3In_xFe_{5-x}O_{12}$.

| x | Frequency | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 100 ( Hz ) | | | 10 ( KHz ) | | | 1( MHz ) | | |
| | ε ' | ε " | tanδ | ε ' | ε " | tanδ | ε ' | ε " | tanδ |
| 0.0 | 864 | 268 | 0.31 | 714 | 120 | 0.28 | 487 | 112 | 0.23 |
| 0.1 | 870 | 296 | 0.34 | 800 | 256 | 0.32 | 490 | 127 | 0.26 |
| 0.3 | 892 | 374 | 0.42 | 854 | 341 | 0.40 | 505 | 172 | 0.34 |

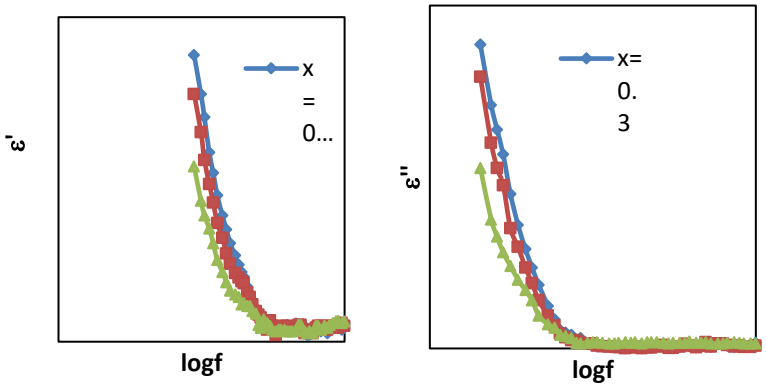


**Fig.5(a):** Variation of dielectric constant (ε’) and dielectric loss (ε’’) with logarithm of frequency (Log F) of $Y_3In_xFe_{5-x}O_{12}$.

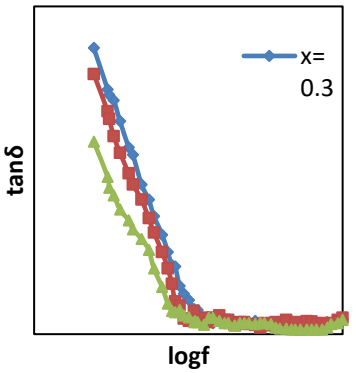


**Fig.5(b):** Variation of dielectric loss tangent (tanδ) with logarithm (log f) of $Y_3In_xFe_{5-x}O_{12}$.

## CONCLUSION

The garnet system In-YIG has been success fully prepared by ceramic technique. The structural parameter (lattice parameter) increases slightly with $In^{3+}$ substitution. The dielectric constant (ε′) and dielectric loss (ε″) both decreases with increase in frequency. It can also be observed that dielectric loss (ε″) decreases with increasing frequency much more rapidly than (ε′). This behaviour of

dielectric constant is attributed by assuming that mechanism of polarization in ferrite is similar to that of conduction mechanism. The parameter tanδ decreases exponentially with the increase of frequency.

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# Investigation of Dielectric Properties of Browntop Millet (*Urochloa ramosa*) and Correlation with LLB Formulae.

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## ABSTRACT

Celebrating 2023 as International Year of Millet the nature of the variation of dielectric properties with frequency, temperature, and product density are discussed. Reflectometric Techniques for measurement of dielectric properties are briefly reviewed, and graphical data on the dielectric properties of Browntop Millet as functions of moisture content, frequency, temperature, and bulk of density are presented. Applications in the electrical measurement of the moisture content and in the dielectric heating of these materials are discussed. The effect of packing density and temperature on dielectric parameters, relaxation time ($\tau_p$), conductivity ($\sigma_p$), moisture content of Browntop Millet was assessed. The results show that there was a systematic increase in dielectric constant (ε') and loss factor (ε") with increasing values of relative packing fraction ($\delta_r$) and decrease in dielectric constant and loss factor with increasing temperature. Moisture content is measured using Thermo-gravimetric method. Experimental results of different relative packing fractions were further used to obtain transformation to 100% solid bulk using correlation equations of Landau-Lifshitz- Looyenga and Bottcher. There is a fair agreement between experimental values and theoretical values of different dielectric parameters. It shows cohesion in the particles of Browntop Millet powder under investigation.

***Key Words:*** *Dielectric constant, Dielectric Loss, Loss Tangent, Relaxation Time, Packing fractions,*

## INTRODUCTION

*Browntop Millet* is native to India, particularly in the dry regions of Karnataka and Andhra Pradesh. *Browntop Millet* has good levels of dietary fiber (12%) which helps in maintaining a healthy digestive system. It also has a low glycemic index that helps in managing diabetes. Serotonin in Browntop Millet helps in relaxing the nervous system. It is very helpful in bronchitis and Asthma. Browntop Millet also boosts kidney and liver function. Browntop millet is adaptable to almost all upland soil, and normally occurs in non-wetlands. People suffering from intestinal disorders can increase their difficulty due to the over consumption of Brown Top Millet. Though millets are a good source of amino acids, high content of amino acids can cause trouble with digestion. The effect of packing density, moisture content and temperature on dielectric parameters such as dielectric constant (ε'), dielectric loss (ε"), loss tangent (tanδ), relaxation time ($\tau_p$), conductivity ($\sigma_p$) for Brown Millet was assessed. The results show that there was a systematic increase in dielectric constant (ε') and loss factor (ε") with increasing values of relative packing fraction ($\delta_r$) and decrease in dielectric constant and loss factor with increasing temperature. Experimental results of different relative packing fractions were further used to obtain transformation to 100% solid bulk using correlation equations of Landau-Lifshitz- Looyenga and Bottcher.

## EXPERIMENTAL DETAILS

The complex permittivity relative to free space is represented here as ε = j , where ε ′ is the dielectric constant and ε ″ is the dielectric loss factor. The real part of the permittivity represents the energy storage capability in the electric field in the dielectric material, and the imaginary part represents the energy dissipation capability of the dielectric by which energy from the electric field is converted into heat energy in the dielectric. Often, the loss angle of dielectrics is of interest, and the tangent of the loss angle δ is used, where tan / δε = ″ The conductivity of the dielectric, σ ωε0 = S/m, is also of interest, where 0 ε is the permittivity of free space, $8.854 \times 10^{-12}$ F/m, and ω π = 2 f , where f is frequency in Hz. Dielectric constant (ε') and dielectric loss (ε") were measured by using reflectometric technique [4, 5, 10].

Measuring the reflection co-efficient from air dielectric boundary of sample in the microwave X – band at 9.85 GHz frequency at 20º, 35º and 50ºC temperature. The following equations were used to determine the dielectric parameters.

$$\in' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \text{..... (1)}$$

$$\in'' = \frac{1}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \alpha_d \beta_d \quad \text{..... (2)}$$

Where, $\lambda_0$ = the wavelength in free space. $\lambda_c = 2a$ is cut-off wavelength of the wave guide. a – is broader dimension of the rectangular wave guide. αd = is the attenuation introduced by the unit length of the dielectric materials. βd = 2□$\lambda_d$ is phase shift introduced by the unit length of the dielectric materials. $\lambda_d$ = wavelength in the dielectric powder.

Detail regarding the procedure is given in [12]. In the present investigation, small quantity of powder was introduced in the cell and the plunger was brought over the powder column. A pressure was allowed to exert by plunger on powder in the dielectric cell. The height of the powder column and the corresponding reflection co-efficient was measured by means of a crystal pick-up in the directional coupler. This process was repeated at every addition of powder in the cell. The relationship between reflected power and height of the powder column was approximately given by a damped sinusoidal wave. The distance between two adjacent minima's of the curve gave half the dielectric wavelength ($\lambda_d$=2L).

For the determination of dielectric parameters of Browntop Millet three samples of various particle sizes were prepared by using sieves of different size. For the comparison of correlation formulae between powder and bulk, the packing fraction ($\delta_r$) were taken as the ratio of density of powder and the density of the finest crushed closely packed particle assembly of the sample. The conductivity ($\sigma_p$) and relaxation time ($\tau_p$) were obtained by using following relations.

$$\sigma_p = \omega \in_0 \in'' \quad \text{..... (3)}$$

$$\tau_p = \frac{\in''}{\omega \in'} \quad \text{..... (4)}$$

Where, ω - is angular frequency of measurement (9.85 GHz). $\varepsilon_o$ - is permittivity of free space.

For low loss materials, dielectric constant (ε') and loss factor (ε") for bulk materials can be correlated with their powder form by the relations derived independently by Landau-Lifshitz and Looyenga,8□.

$$\in'_S = \frac{\left[\left(3\delta + 2\in'_p - 2\right)\in'_p\right]}{\left(3\delta - 1\right)\in'_p + 1} \quad \text{..... (5)}$$

$$\in''_S = \left(\frac{\in''_P}{\delta_r}\right)\left(\frac{\in'_S}{\in'_P}\right)^{2/3} \; for \frac{\in''}{\in'} << 1 \quad \text{.... (6)}$$

Where, $\varepsilon'_s$ – is the dielectric constant for the material in bulk, $\varepsilon'_p$ – is the dielectric constant of powder sample at relative packing fraction (δr). $\varepsilon''_s$ and $\varepsilon''_p$ – are the dielectric losses for solid and powder respectively.

The results obtained have been verified with values obtained from Bottcher's equation

$$\in'_S = \frac{\left(2\in'_P + 3\delta - 2\right)\left\{\left(3\delta - 1\right)\left(\in'^2_P + \in''^2_P\right) + \in'_P - 2\in''^2_P\right\}}{\left(3\delta - 1\right)^2\left(\in'^2_P + \in''^2_P\right) + 2\in'_P\left(3\delta - 1\right) + 1} \quad \text{.....(7)}$$

$$\in''_S = \frac{2\left(3\delta - 1\right)\left(\in''^3_P + \in'^2_P \in''_P\right) + \in''_P\left(3\delta - 2\right) + 4\in'_P \in''_P}{\left(3\delta - 1\right)^2\left(\in'^2_P + \in''^2_P\right) + 2\in'_P\left(3\delta - 1\right) + 1} \quad \text{.....(8)}$$

## RESULTS AND DISCUSSIONS

Dielectric constant (ε') and dielectric loss (ε") along with the values of relative packing fraction (δr) of Browntop Millet powder are given in table -1. The values of ($\varepsilon'_p$) and ($\varepsilon''_p$) obtained experimentally for different grain sizes and temperature showed that, there is simultaneous increase in dielectric constant (ε') and loss factor (ε") with increasing temperature. This was expected, because with higher values of relative packing fraction (δr) the inter particle hindrance offered to the dipolar

motion for a compact medium will be much higher than for less bounded particles. Such observations have been already made by other workers [2, 9, 11] for higher values of packing fraction.

Values of relaxation time ($\tau_p$) loss tangent (tanδ) conductivity ($\sigma_p$) and values of moisture content with relative packing fraction and different temperature revealed that there was increase in ($\sigma_p$), ($\tau_p$) and (tanδ) with the increasing values of packing fraction (δr). There was systematic decrease in ($\sigma_p$), ($\tau_p$) and (tanδ), moisture percentage with increasing values of temperature. Such behavior is expected because when polar molecules are very large, the rotator motion of the molecules is not sufficiently rapid for the attainment of equilibrium with the field. The increase in conductivity therefore suggests that at higher compactions, no micro cracks are developed in the sample due to high mechanical pressure. The decrease in relaxation time ($\tau_p$) with increasing temperature may be due to increase in the effective length of dipole. In addition, due to increasing temperature, number of collisions increase causes increase in energy loss and thereby decreasing relaxation time.

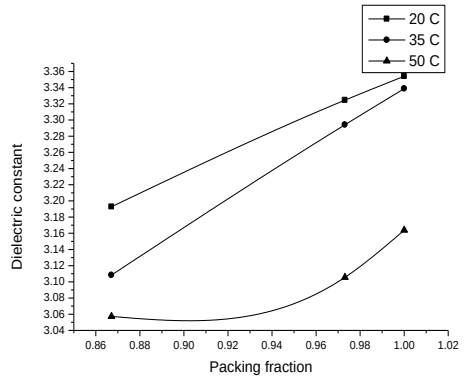


Fig.1: Packing fraction Vs Dielectric constant

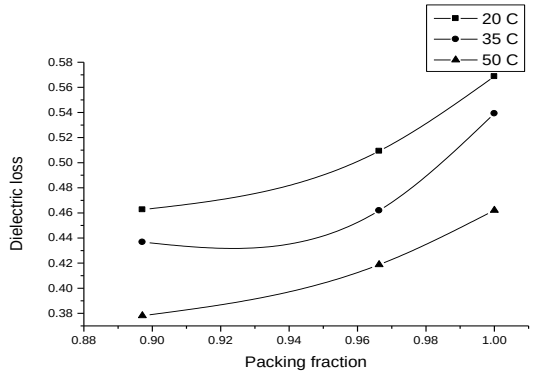


Fig.2: Packing fraction Vs Dielectric loss

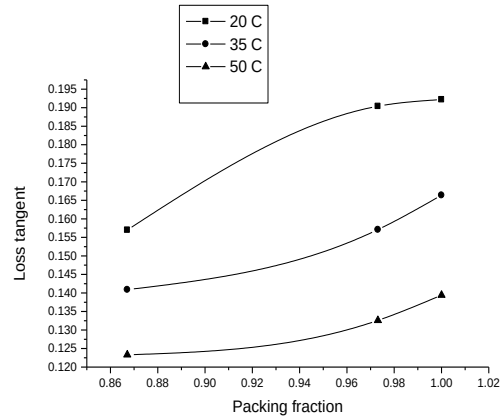


Fig.3: Packing fraction Vs Loss tangent

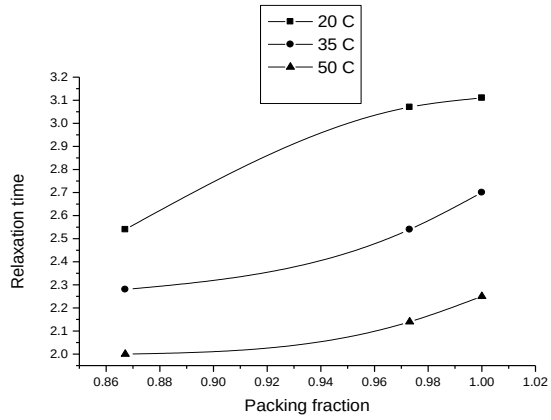


Fig.4: Packing fraction Vs Relaxation time

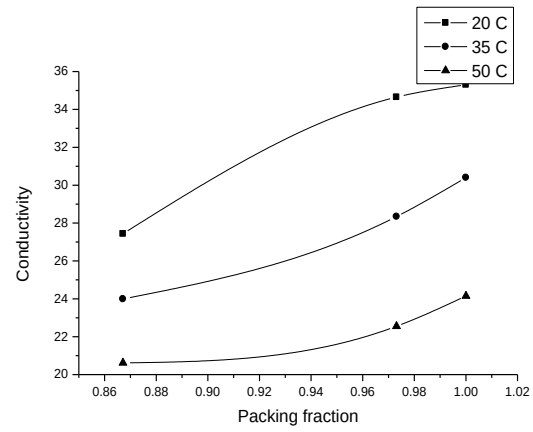


Fig.5: Packing fraction Vs Conductivity

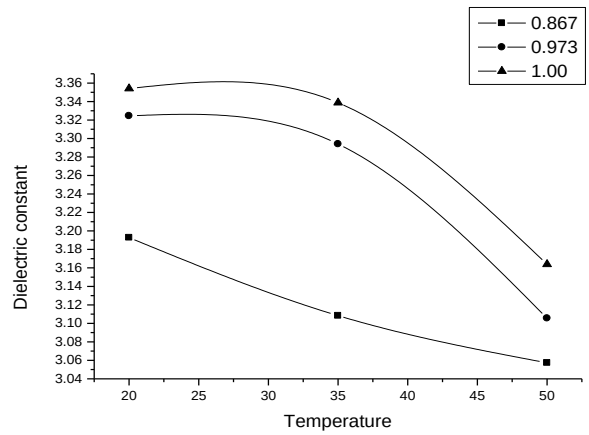


Fig .6 : Temperature Vs Dielectric constant

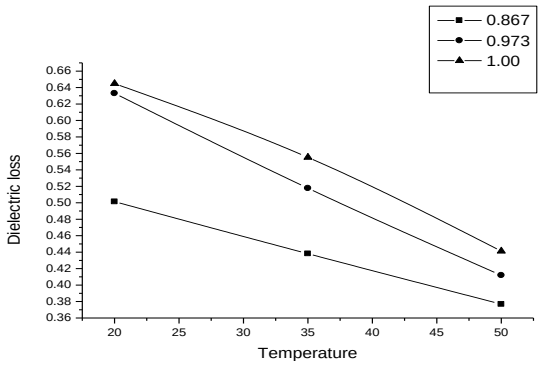


Fig.7 : Temperature Vs Dielectric loss

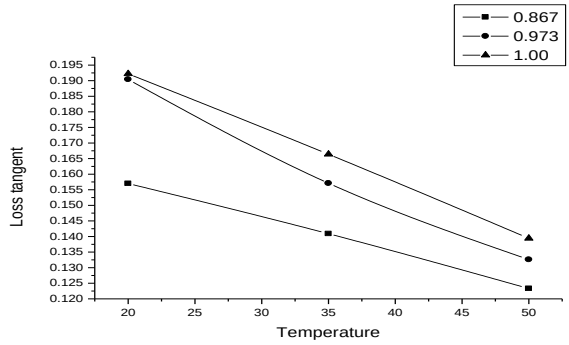


Fig.8 : Temperature Vs Loss tangent

Table -2 shows measured and computed values of dielectric parameters for bulk from powder measurements. The results reported at δr = 1 are those measured on the finest crushed powder sample packed very closely in a wave-guide cell pressing it under a fixed pressure, so as to obtain minimum voids between the particles. Out of the three powder samples of different packing fractions, the samples having minimum particle size is defined as finest which is about 0.70μm. In this case, we assumed it as solid bulk for getting correlation between powder and solid bulk. The correlation formulae were used to find other value for (δr >1). The bulk values obtained for (ε') and (ε") are same to the measured values and those calculated from [8], are closer to the values calculated from [3] formulae. The values of packing density increase linearly with the values of dielectric constant, dielectric loss and conductivity increases (Fig.1-5). There was a simultaneous decrease of dielectric constant, dielectric loss and conductivity with increase in the temperature.

## CONCLUSIONS

Thus, it was found that experimentally measured values of (ε') and (ε") at (δr = 1) are similar to those calculated from Landau-Lifshitz-Looyenga formulae. There was agreement between the values obtained experimentally and calculated theoretically by using Bottcher's formulae. The correlation formulae of Landau-Lifshitz-Looyenga and Bottcher can be used to provide accurate estimate of (ε') and (ε") of powder materials at known bulk densities. It may be thus, predicted that Browntop Millet having cohesion in its particles and serve as a continuous medium.

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# Sol-gel Auto-combustion Preparation and Structural Properties of Ni-Zn Ferrites

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**ABSTRACT**

The nano spinel nickel zinc ferrite prepared by using sol-gel auto-combustion method. The prepared precursor was calcinated at 600 °C for 4 hours. The calcinated spinel ferrite powder characterized by XRD, IR and SEM. The XRD patterns illustrates the single-phase cubic structure without any secondary phase. The lattice constant, particle size and the X-ray density determined from XRD pattern analysis. The Infrared spectra showed two major bands, the higher frequency band '$\upsilon_1$' 571.53 $cm^{-1}$assigned to tetrahedral site and the lower frequency band '$\upsilon_2$' 432.34 $cm^{-1}$ assigned to octahedral site. The SEM image confirm spherical particles with slight agglomeration.

***Keyword:** Ni-Zn ferrite, XRD, Infrared spectra, Microstructure*

## INTRODUCTION

Ferrites exist in numerous crystalline forms among which, spinel structure is the most studied. Magnetic nanoparticles remain to be a interesting subject of attention from both fundamental and application point of view. [1] The performance of these materials in their bulk form where the grain dimensions are in micrometer scales is limited to a few megahertz frequency due to their higher electrical conductivity and domain wall resonance. Ni Zn ferrite is a soft magnetic material that has spinel structure. [2] Ni-Zn ferrites are well known and have been used for many years in the electrical and electronic industries. Nowadays, these materials are largely studied in the search for enhanced properties and new applications, especially in the nanometric scale as ultrafine powders and thin films. [3]

Preparation methodology is essential for controlling the physical properties of the materials, such as magnetic, electrical and optical properties [4]. In other words, the synthesis procedure determines the structural and microstructural characteristics of the materials, such as cation distribution, particle size, microstrain and kinds of defects [5-7]. Different methods for the synthesis of nanocrystalline ferrites have been developed in order to optimize low-cost synthesis/material with the desired characteristics ratio. Numerous techniques been used to synthesis of nano-particles of ferrites are; hydrothermal, ball-milling, sol-gel auto-combustion, co-precipitation, reverse micelle, solid-state [8-14] etc. Amongst these techniques; the sol-gel auto combustion technique is facile, which is easy to control and produce the ferrite nano-particle samples with the large surface area.

In the view the above discussion the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles prepared by using sol-gel auto-combustion method and characterised by XRD, IR and SEM and results are presented in the paper.

## EXPERIMENTAL

Nano crystalline Ni-Zn ferrite, with composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was synthesized by the sol-gel auto-combustion method. [8] Analytical reagent grade all nitrate were dissolved in distilled water to obtain a mixed solution. The reaction procedure was carried out in an air atmosphere without the protection of inert gases. The molar ratio of metal nitrates to citric acid was 1:3. The metal nitrates were dissolved together in the minimum amount of double distilled water. An aqueous solution of citric acid was mixed with the metal-nitrate solution, and ammonia solution was slowly added to adjust the pH ≅7. The mixed solution was placed on a hot plate with continuous stirring at 90 °C. During evaporation, the solution formed a very viscous brown gel. When all of the water molecules were removed from the

mixture, the viscous gel began to froth. After few a minutes, the gel ignited and burnt with glowing flints. The decomposition reaction continued until the entire citrate complex was consumed. The auto combustion was completed within a minute, yielding brown-colour ashes referred to as the precursor. The prepared precursor was calcinated at 600 $^{o}$C for 4 hours. The calcinated sample characterized by X-ray investigations using Phillips X-ray diffract meter (Model 3710) using Cu-$K_{\alpha}$ radiation ($\lambda$=1.5405Å). The infrared spectra of all the samples were recorded at room temperature in the range 200 $cm^{-1}$to 800 $cm^{-1}$. The microstructure was determined Scanning electron microscopy. The Infra-red spectroscopies for all compositions at room temperature were recorded in the range of 200-800 $cm^{-1}$ using the Perkin Elmer infrared spectrophotometer.

## RESULT AND DISCUSSION

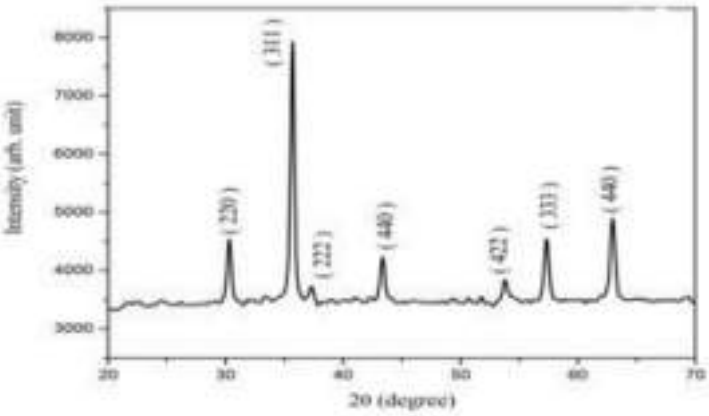


**Fig. 1:** XRD patterns of calcinated Ni-Zn ferrite

The XRD pattern of calcinated Ni-Zn ferrite shown in fig 1. The XRD patterns exhibit peaks corresponding to the Ni–Zn ferrites without any other impurity phases and crystal structure is cubic spinel with the corresponding planes such as (220), (311), (222), (400), (422), (333) and (440) formed. The lattice constant 'a' calculated by using equation **[9]**. The lattice constant observed is 8.345Å.
The X-ray density '$d_x$' was calculated by using the following relation,

$$d_X = \frac{8M}{Na^3} \quad (1)$$

Where, $d_x$ = X-ray density, n = Number of molecules per unit volume (8 for cubic structure), M = Molecular weight of the composition, $N_A$ = Avogadro's number = 6.02214

The observed of X-ray density was 5.43 g/$cm^3$. $\times_{10}{}^{23}$, V = Volume = a3. The average crystallite size of the sample was estimated using the high intensity 311 peak and the Scherer equation [12]. The calculated average crystallite size is 29.36 nm.

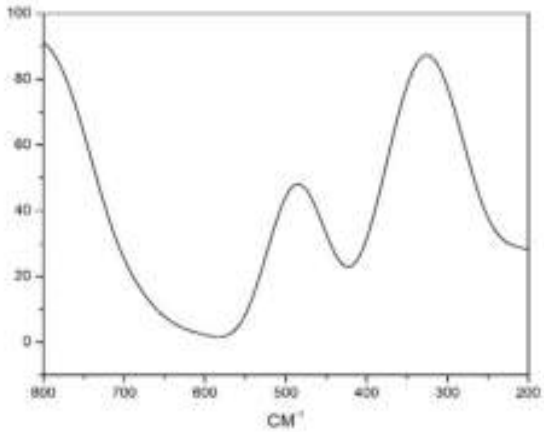


**Fig. 2:** IR spectra of calcinated Ni-Zn ferrite

IR spectra of the Ni–Zn ferrite, recorded at room temperature in the frequency range 700–200 $cm^{-1}$, are shown in Fig. 2. The Infrared spectra showed two major bands, the higher frequency band '$\upsilon_1$' 571.53 $cm^{-1}$assigned to tetrahedral site and the lower frequency band '$\upsilon_2$' 432.34 $cm^{-1}$ assigned to

octahedral site. The high frequency band ($\nu_1$) is allocated to the intrinsic lattice vibration of the tetrahedral sites of $Fe^{3+}$–$O^{2-}$. On the other hand, the lower frequency band ($\nu_2$) is ascribed to the stretching vibration of octahedral complexes. The higher vibration of the tetrahedral sites compared with that of octahedral sites can be due to the shorter bond length of the tetrahedral cluster and the long bond length of the octahedral cluster.

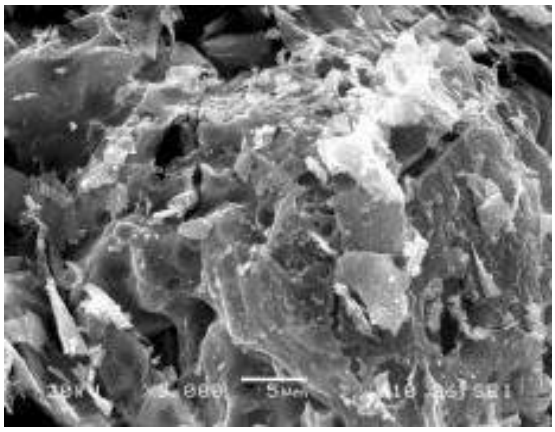

**Fig. 3:** SEM image of calcinated Ni-Zn ferrite

The morphology of the sample was studied by scanning electron microscopy. (SEM) The typical SEM image sample is shown in the fig.3. It can be seen from fig.3. The fine crystals with slight agglomeration observed in SEM image. This agglomeration indicates that the prepared samples are high reactivity.

## CONCLUSIONS

Nano crystalline Ni-Zn ferrite, with composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was successfully synthesized by the sol-gel auto-combustion method. The prepared precursor was calcinated at 600 $^oC$. The XRD patterns exhibit peaks corresponding to single phase cubic spinel structure. The observed lattice constant, X-ray density and average crystallite size 8.345Å, 5.43 g/cm$^3$and 29.36 nm respectively. The Infrared spectra showed two major bands, the higher frequency band '$\upsilon_1$' 571.53 cm$^{-1}$assigned to tetrahedral site and the lower frequency band '$\upsilon_2$' 432.34 cm$^{-1}$assigned to octahedral site. The fine crystals with slight agglomeration observed in SEM image.

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# SYNTHESIS,CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BIOACTIVE LIGAND

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**ABSTRACT**

This study presents the synthesis of a heterocyclic ligand derived from a 1,3,4-thiadiazole moiety in an alcoholic medium. The synthesized ligand undergoes comprehensive characterization through elemental analysis, UV-Vis, FT-IR spectroscopy, mass spectroscopy, 1H NMR &13C-NMR, and molar conductance measurement. In vitro antibacterial and antifungal assays indicate moderate activity against S. aureus, B. subtilis, F. Oxysporum, and A. Niger using the Kirby-Bauer disc diffusion method.

***Keywords:*** *Heterocyclic ligand 1,3,4 Thiadiazole, Metal Complexes, Antibacterial activity.*

## INTRODUCTION

Schiff bases synthesized from an amino and carbonyl compound are significant class of ligands that coordinate to metal ions by azomethine group and had been studied broadly.(1) In azomethine derivatives, the -C=N- linkage is important for biological activity, a lot of azomethine had been reported to possess remarkable antibacterial, antimalarial, antifungal, and anticancer activitiesii.1,3,4-Thiadiazole is heterocyclic compound was first described in 1882 by Fischer farther it has been developed by Bush and his groups[2] .Girdler in 1956 has demonstrated the true nature, of the ring system iniii.1,3,4-Thiadiazole derivatives have interesting biological activity probably due to strong aromaticity of this ring system, which leads to great in vivo stability and generally, a deficient in toxicity for higher vertebrates, including humans[3]. When diversified functional groups that interact with biological receptors that attached to this ring, compounds possessing outstanding properties are access. Except for some antibacterial sulfonamides (albucid and globucid), is no longer used clinically, but which having historical importance, the most interesting and important examples is constituted by 5amino-l,3,4-thiadiazole-derivativesiv.[4-6]Farther addition, the chemistry and the applications of these novel Schiff bases thiadiazoles group containing moieties derivatives could be extensively studied by coordinating to various metal ions. As a result, the structural activity relationship study of 1,3,4-thiadiazoles could be enlarge in the future developmentv-xi. Present study the synthesis and characterization of new heterocyclic ligand 4-bromo-2(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-6-methoxyphenol.Moreover ,the preliminary in vitro antibacterial and antifungal screening activities of the ligand are carried out and the results are reported herein.[7-9]

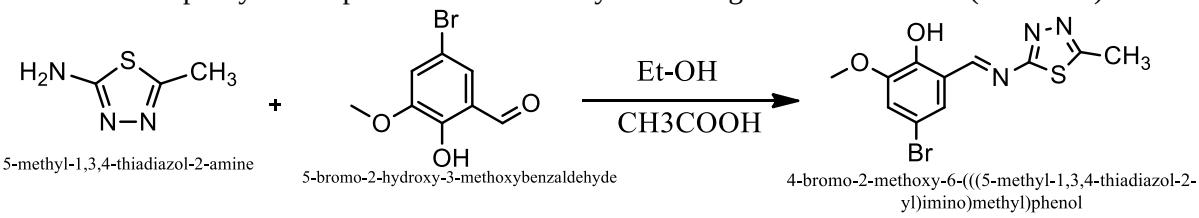
## MATERIALS AND METHODS

***Experimental:*** All chemical of analytical grade.5-bromo-2-hydroxy-3-methoxy benzaldehyde and 5-methyl-1,3,4-thiadiazole-2-amine from Sigma- Aldrich and Alfa Aesar used without further purification. Dist. Ethanol used for synthesis of ligand, diethyl ether (Sigma-Aldrich). IR Spectra recorded on Perkin Elmer Spectrometer in range 4000-400 cm-1 KBr pellets. 1H and 13C-NMR Spectra were recorded on BRUKER AVANCE III HD NMR 500 MHz spectrophotometer. The C, H and N analyses were carried out using a Euro-E 3000. Magnetic susceptibility measurements for the synthesized complexes were obtained at room temperature using Room Temperature magnetic moments by Guoy's method in B.M.Electronic Spectra using DMSO on Varian Carry 5000 Spectrometer.Mass Spectra were recorded on Bruker IMPACT HD. Biological Activity: Schiff Base

ligand evaluated in vitro their antibacterial activity against two bacteria,viz, B. Subtilis; S. aureus,Two fungi strains A. niger and F. oxysporumby Kirby-Bauer disc methodxii.The fungal and bacterial strains subcultured on PDA media and Nutrient Agar media. The stock solution was prepared in DMSO (1 mg mL-1) solution for test. The stock solution again diluted using sterilized water to dilute to 500 ppm. The bacteria were subculture in agar medium and disc were kept incubated for 37oC at 30 hrs. The standard for antibacterial activity is Ciprofloxacin and antifungal activity is Miconazole was also screen under same condition for comparison of bioactivity. Activity was measure and calculated by zone of inhibition in mm surrounding the discs. The experimental value compare with standard drug value of ligand

***Biological Activity:*** Schiff Base ligand evaluated in vitro their antibacterial activity against two bacteria,viz, *B. Subtilis*; *S. aureus*,Two fungi strains *A. niger and F. oxysporum*by Kirby-Bauer disc method[12]. The fungal and bacterial strains subcultured on PDA media and Nutrient Agar media. The stock solution was prepared in DMSO (1 mg mL-1) solution for test. The stock solution again diluted using sterilized water to dilute to 500 ppm. The bacteria were subculture in agar medium and disc were kept incubated for 37oC at 30 hrs. The standard for antibacterial activity is Ciprofloxacin and antifungal activity is Miconazole was also screen under same condition for comparison of bioactivity. Activity was measure and calculated by zone of inhibition in mm surrounding the discs. The experimental value compare with standard drug value of ligand.

***Synthesis of Schiff base Ligand:*** The mixture of 1:1 5-bromo-2-hydroxy-3- methoxybenzaldehyde (2.31g,0.01mol) with 5-methyl-1,3,4-thiadiazole-2-amine (1.33 g, 0.01 mol) dissolved in ethanol. Then add Few drops of glacial acetic acid was added .The resultant mixture stirred for 4-5 hrs the yellowish colored precipitate of Ligands was obtained. Wash with Ethanol recrystallized with Ethanol and Ether then dried. The purity of compound was checked by TLC using Silica Gel method (Scheme.1).




**Scheme.1 Synthesis of ligands**

***Results and Discussion:*** The ligand (Fig.1) 4-bromo-2-methoxy-6-(((5-methyl-1,3,4-thiadiazol-2-yl)imino)methyl)phenol is stable at room temperature in solid state. The ligand is soluble in organic solvent like DMSO, DMF. The physical and analytical data shown in Table 1.

Spectral evaluation shows formation of ligand.

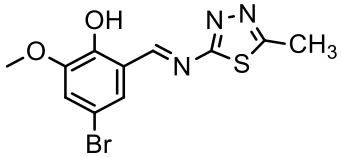
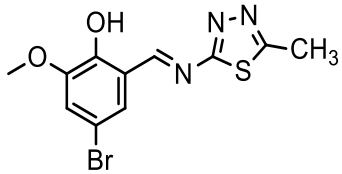


**Figure1: Structure of Schiff base Ligands (L).**

**Table 1.Structure of Heterocyclic Ligands**

| Entry | Products | Time (h) | Yield (%) | M.P (ºC) |
|---|---|---|---|---|
| **L** |  | 5-6 | 78 | 248 |

**Characterization data of Heterocyclic Ligands 4-bromo-2-methoxy-6-(((5-methyl-1,3,4-thiadiazol-2-yl)imino)methyl)phenol (Table.1,L):**

Dark Yellow;M.F. C11H10BrN3O2S;Yield : 78% ; M.P.248oC;Molar Cond.(DMSO 1×10-3conc., ohm-1 cm2 mol-
1):6.62; UV(DMSO, cm-1): 282 (π→π* tran. of benzene ring), 368 (n→π* azomethine moieties and phenolic -OH.); IR(KBr Cm-1) : ν =3323 (O-H str. in aromatic ring),ν= 1633 (C=N azomethine),

ν=1493 (-C=N-N=C str.in Thiadiazole ring), ν=1268 (C-O Phenolic), ν=1026 (N- N Thiadiazole ring), ν=756 (C-S-C str.in thiadiazole ring) ; 1H NMR (400 MHZ.DMSO d6) δ ppm: δ = 11.23(s,1H,Ar-OH), δ =8.80 (s,1H,CH=N), δ = 7.10-7.56( s,2H,Ar-CH), ; 13C NMR (DMSO-d6, 400 MHZ,) δ ppm : δ =150.6-121.6 (C1-C6 Aromatic), δ =161.7 (C7,-C=N- Azomethine), δ =155.6 (C8Thiadiazole ring), δ = 181.3 (C9 Thiadiazole ring), δ = 52.2 (C10 - OCH3-).; MS (70 eV) m/z :347 [M+H,100%],Anal.Calcd.ForC10H8BrN3O2S2 :C, 34.69; H,
2.33;N, 12.14;S, 18.52.Found : C, 34.60; H, 2.31;N, 12.02;S, 18.46.

***Results and Discussion:*** The IR spectra of 4-bromo-2-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-6methoxyphenol Schiff base Heterocyclic ligand and its complexes are listed in Table 2. The Infrared Spectra of the free ligands are compared with the metal complexes in order to determine the coordination sites that may be involved in a chelation. There are important peaks in the spectra of the ligand, which is different in complexes helps to Confirm the formation of metal complexes IR spectra of 4-bromo-2-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)6-methoxyphenol ligand HL Schiff base Heterocyclic ligand most characteristic bands at 33183335 cm-1 ν(O-H), 1628-1645 cm-1 ν(C=N, azomethine) and 1262-1269 cm-1 ν(C-O). The Heterocyclic ligand spectra showed bands at 3314-3340 cm-1 and 1333-1350 cm-1 due to the deformation and stretching of the phenolic –OH [13]. The band 1628-1645 cm-1 due to the azomethine (-C=N-)group of the Schiff bases Heterocyclic ligand[14-15].The phenolic λ(C–O) stretching vibration that appeared band at 1262-1269 cm-1 in ligands. The band of ν(C–S–C) at 751–756 cm-1 of the Thiadiazole ring of ligand[16].The 1H-NMR spectra of Heterocyclic ligand were recorded in Dimethyl Sulphoxide solution using TMS as a standard. The spectra of Heterocyclic ligand shows singlet at δ7.10-7.56 ppm due to aromatic proton. while azomethine (-C=N-) proton resonate at singlet δ8.80 ppm the phenolic-OH has signal singlet at δ11.23 ppm and Thiadiazole containing (–SH) group shows singlet at δ13.40 ppm [17].13C-NMR of Heterocyclic Ligand, peak appeared at δ152-160 ppm imine group (-C=N-),peak 180-182 ppm Due to carbon sulphur C-SH bonding in Thiadiazole.120-136 ppm because of aromatic carbon,155-172 ppm peak because of (Table. 4) Ar-OH group [18].Mass Spectra of Heterocyclic ligand shows the peak at m/z 347 which is M+H peak at 100% intensity this peak support to the structure formation of ligand.Molar conductance of Heterocyclic ligand were observed at room temperature at 1×10-3M DMSO Solution. The studies show imperceptible molar conductance value is 6.62 ohm-1cm2mol-1results shows in table 5.it is observed that all ligand was non-electrolytic in nature [19-20].The electronic absorption spectral data of the Heterocyclic ligands is taken in DMSO as a solvent.The band appearing at 225-321 is due to transition of benzene ring of the ligand. The other band due to free ligands 321-373 nm due to transition for azomethine groups and phenolic –OH[21].

***Antimicrobial activity :*** The antimicrobial activity on two gram positive bacteria i.e S. aureus and B.Subtlistwo fungi i.e A. nigerand F.Oxysporumwas taken.The synthesized Heterocyclic ligand show good biological activity against microorganism. The bactericidal and fungicidal analysis of the compounds are given in Tables 2.

| **Compounds** | **Antibactrial Activity** | | **Antifungal Activity** | |
|---|---|---|---|---|
| | ***S.aureus*** | ***B.subtilis*** | ***A.niger*** | ***F.oxysporum*** |
| | **Diameter of inhibition Zone in mm** | **Diameter of inhibition Zone in mm** | **Diameter of inhibition Zone in mm** | **Diameter of inhibition Zone in mm** |
| | **500ppm** | **500ppm** | **500ppm** | **500ppm** |
| **Ligands(HL)** | 20 | 20 | 15 | 22 |
| **Ciprofloxacin(Standard)** | 36 | 34 | 29 | --- |
| **Miconazole(Standard)** | --- | --- | 30 | 25 |

## CONCLUSION

The Novel Synthesis, characterization, and antimicrobial activity of ligand(L) by conventional method. The antimicrobial activity data show heterocyclic ligand (L) is biologically potent to all pathogenic microorganisms. These type of study helps to decrease emerging problems in drug resistance microorganism in health sciences.

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# Impact of Solvent on Cobalt Ferrite: Structural, Morphological, Optical and Electrical Properties

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## ABSTRACT

Synthesis and characterization of Cobalt ferrite powders by a sol- gel combustion process is focused in the present work. The prepared precursors were calcined at 560 °C for 5 hours inorder to get cobalt ferrite powder. The effect of solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract) on $CoFe_2O_4$ and its structural, morphological, optical and electrical, properties was investigated. EDX measurements for $CoFe_2O_4$ NPs which indicate, the grown NPs are homogeneous and uniform. The morphology of prepared $CoFe_2O_4$ ferrite samples with various solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract) was studied using a scanning electron microscopy. The band gap energy is varies from 1.4 to 1.5 eV. The band gap energy was studied using UV-Visible Spectroscopy. The optical characterization on $CoFe_2O_4$ ferrite samples were carried out using the Fourier Transform Infrared Spectroscopy (FT-IR) techniques. The formation of the ferrite is confirmed by FT-IR results. Dielectric Properties were studied for various samples, the dielectrics and AC conductivity of samples is decreases with increasing frequency of LCR-Q meter of samples with various solvents.

***Keywords:*** *Cobalt ferrite, EDX, SEM, FT-IR, UV-VISIBLE, Dielectric Properties.*

## INTRODUCTION

Ferrites are electrically insulating material and have good electrical, magnetic and mechanical properties. Among the different types of ferrites, the $CoFe_2O_4$ spinel ferrite is one of the most versatile from the view point of their large number of potential applications. $CoFe_2O_4$ ferrite possesses large crystalline anisotropy and reasonable magnetization, as potential predominant magnetic and electrical resistive material, which has been applied in high density magnetic recording media, high performance electromagnetic and spintronic devices [1, 2]. Spinel $CoFe_2O_4$ has Face Centered Cubic (FCC) structure with a large unit cell. There are two kinds of lattice for cation occupancy.
Mainly two sites A (tetrahedral) and B (octahedral). In a normal spinel structure $Co^{2+}$ occupying tetrahedral A sites, while $Fe^{3+}$ is sitting on the octahedral B sites. In inverse spinel structure A site being $Fe^{3+}$ ions while B sites populated by $Co^{2+}$ and $Fe^{3+}$ ions.

Ferrite can be prepared by using various experimental techniques like ceramic, hot spraying, evaporation condensation, matrix isolation, laser-induced vapour phase reactions and aerosols but most types of Nano-particles prepared by these methods gives broad particle size distribution and coarse particles so additional milling is required.Other chemical methods are co-precipitation, sol-gel, ball milling, citrate precursor, hydrothermal, micro emulsion [3-11]. Among above mentioned methods, a sol-gel process is less complicated and inexpensive method than the others.

In present work we focused on the synthesis and properties of cobalt ferrite powders prepared by a sol-gel autocombustion technique. This is unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of desired metals and some organic fuel giving rise to porous fluffy product with large

surface area. The effect of different solvents on structural, electrical, optical, morphological properties of prepared cobalt ferrite particles has been investigated.

## MATERIALS AND METHODS

***Experimental Procedure:*** A sol-gel autocombustion method is used to prepare $CoFe_2O_4$ particles with different solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract).Starting materials are Cobalt (II) nitrate ($Co(No_3)_2$. $6H_2O$, Mw = 291.04 g/mol.), Iron nitrate ($Fe(No_3)_3$. $9H_2O$, Mw = 404.00 g/mol.) and Citric acid ($C_6H_8O_7 \cdot H_2O$, Mw = 210.14 g/mol.). An aqueous solution of citric acid was mixed with metal nitrates and different solvents under vigorous stirring. To adjust pH of 7.0, the ammonia solution was slowly added in mixture. The solution was heated on hot plate at 80 °C to evaporate the water. During evaporation, the solution become viscous and finally formed a gel and by continuous heating the gel is ignited, the combustion rapidly propagated forward until all the gel burnt out completely to form ash and porous product was obtained. The ash-burnt obtained powder was calcined at 560 °C for 5 hours to get final product of cobalt ferrite powder

***Characterization:*** The structural characterization on $CoFe_2O_4$ ferrite samples with different solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract) were carried out using the Fourier Transform Infrared Spectroscopy (FT-IR). Morphology of prepared $CoFe_2O_4$ powder samples were studied using a scanning electron microscopy. Band gap energy was studied using UV-Visible spectroscopy; Electrical properties were studied using Dielectric characterization.

## RESULTS AND DISCUSSION

***Structural Properties:*** (i) EDX properties and elemental mapping images:

The EDX measurements for $CoFe_2O_4$ NPs which indicate, the grown NPs are stoichiometric and homogeneous with a uniform distribution. For CFO NPs, the EDX micrographs confirmed the existence of Fe, Co and O without the presence of any signature of substituted metals. The EDX analysis for $CoFe_2O_4$ NPs confirmed that impurity elements were found in the some solution of synthesized samples [12].

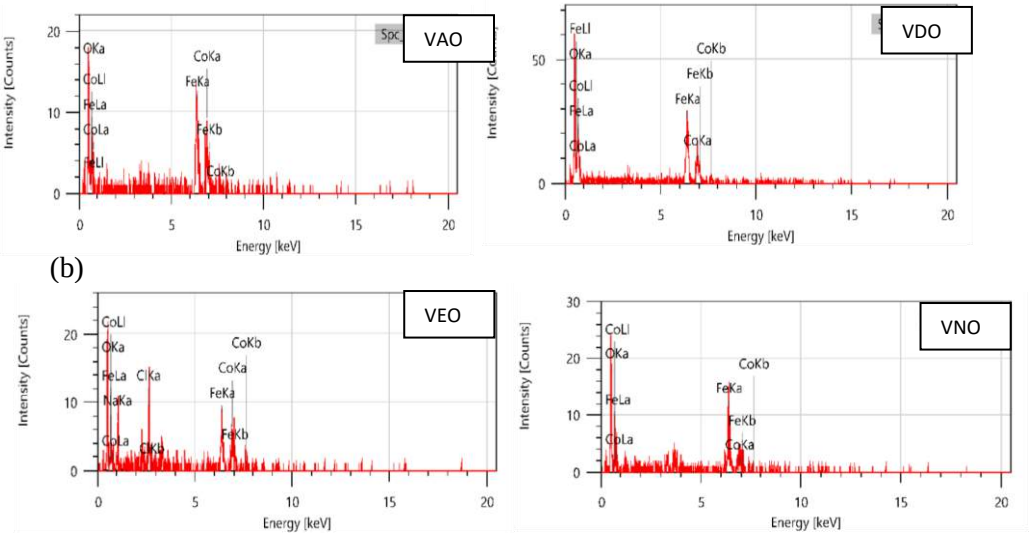


**Fig.3.**1.i. EDX measurement graphs of $CoFe_2O_4$ powders for different solvents (a) Aloevera extract, (b) Distilled water, (c) Egg white solution and (d) Neem extract.

***Morphological Properties:*** Micrographs were recorded on a LEO SEM model no. S - 440i. The SEM images of all $CoFe_2O_4$ ferrite samples are shown in figure 3.1.ii. (a-d). It is clear from Fig. 3.1.ii.(a-d) that grown $CoFe_2O_4$ particles are well developed; having non-uniform morphology with the individual particles are typically in nanometer size but there is agglomeration of particles. It is well known that the magnetic inter-particle interaction is dominant betweenlarger magnetic particles due to the magnetic attractive force. There is the magnetic attractive force among non-uniform coarse crystals lead to the formation of agglomeration. We conclude from SEM analysis that non-uniform morphology and grown $CoFe_2O_4$ particles have agglomeration due to magnetic force.

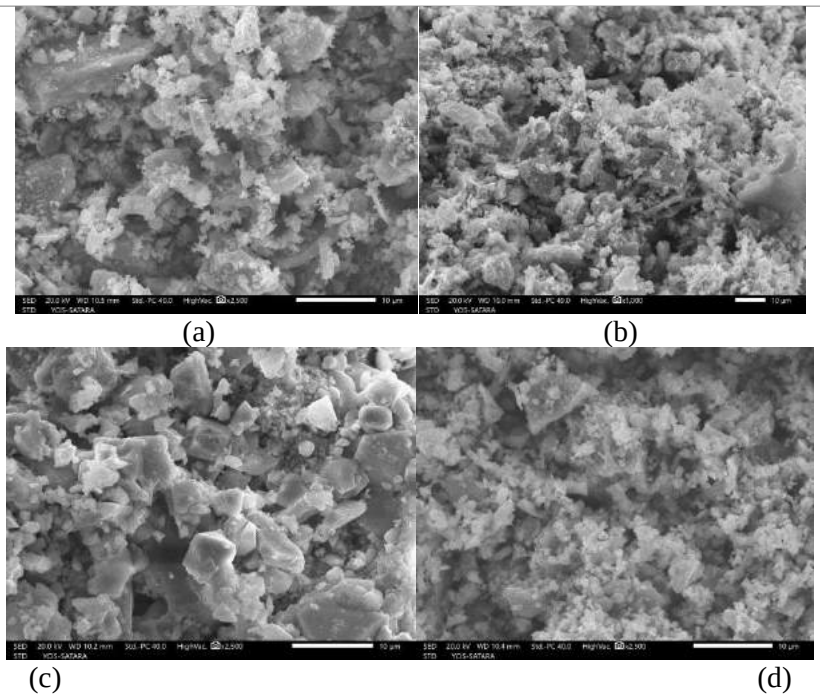


**Fig.3**.1.ii. SEM micrographs of $CoFe_2O_4$ powders sintered at 560 □C for 5 hrs for different solvents (a) Aloevera extract, (b) Distilled water, (c) Egg white solution and (d) Neem extract.

***Optical Properties:*** (i) FT-IR Characteristics:

Infrared absorption spectra (FT-IR) of calcined $CoFe_2O_4$ powders with different solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract) were recorded on a Bruker Tensor 27 spectrometer in wave number range of 400-4500 $cm^{-1}$. FT-IR spectra of all samples are shown in figure 3.2.i.

The existence of strong absorption bands around 528 $cm^{-1}$ and 560 $cm^{-1}$ are due to stretching of metal oxygen (M-O), which attributed to the formation of the ferrite phase [13].

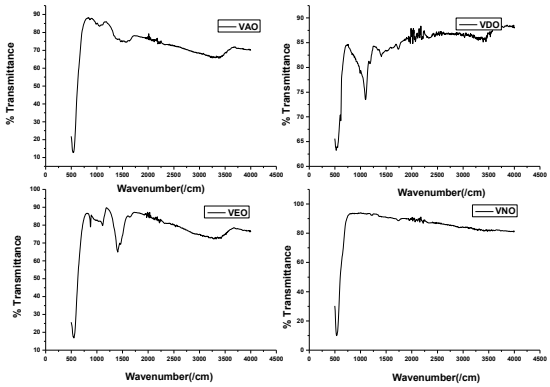


**Fig. 3.2:** i- FT-IR spectra of $CoFe_2O_4$ powders calcined at 560 ºC for 5 hours in air atmosphere.

***UV-Visible Spectroscopy:*** The optical property of the $CoFe_2O_4$ with different solvents was observed by taking UV-Vis absorption spectroscopy shown in figure 3.2.a and figure 3.2.b. The values of $\lambda_{max}$ vary from 746.55 to 850.50 nm with variation in solvents. On the basis of absorption peaks, the band gap of samples were calculated from formula [14],

$$E = \frac{hc}{\lambda} \text{ ---------- } (1)$$

Where, $\lambda$ = maximum value of wavelength or Absorption peak value, h = $6.6261\times10^{-34}$ $m^2$ kg / s or $6.626\times 10^{-34}$ Joule sec. c = velocity of light = $3\times10^8$ m/s, E = absorbed energy in an electronic transition

The impurity bands created due to the formation of level of impurity inside an energy gap.

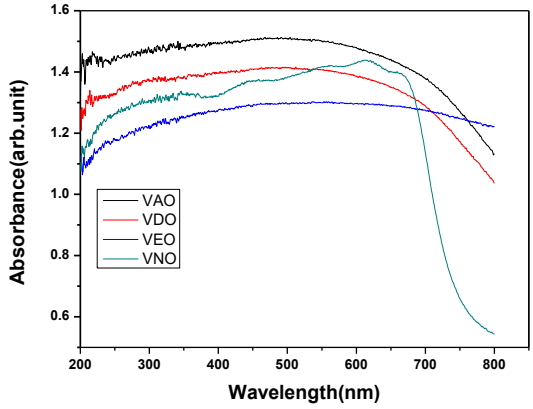


**Fig. 3.2:** ii.a-UV-Visible Spectra of $CoFe_2O_4$ for different solvents

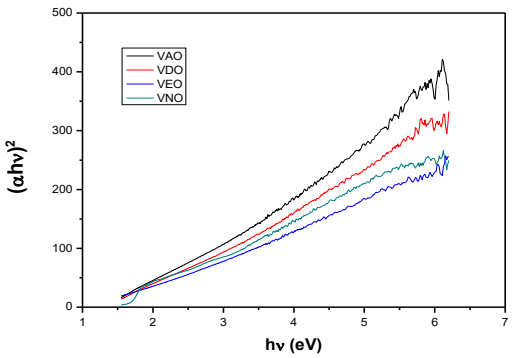


**Fig. 3.2:** ii.b- Tauc plot of $CoFe_2O_4$ for different solvents

***Electrical Properties:*** The study of the dielectric constant was studied using Maxwell-Wagner type of interfacial of polarization and Koop's theory [15].The electron displacement in direction of applied field causes interaction in between ions i.e. $Fe^{2+}$ and $Fe^{3+}$. Variation in thickness of pellet is done due to exchange in electron $Fe^{2+} \leftrightarrow Fe^{3+}$ with alternating variation in electric field with variation in polarization, oxygen vacancies, defects in grain boundary, interfacial dislocation. The dispersion relation observed using dielectric constant with frequency variation shown in figure 2, exhibits inverse relation between in dielectric constant and frequency. The decreasing of dielectric constant and dielectric loss with increasing frequency is shown from figure.3.3.a and figure 3.3.b figure 3.3.c gives the information of AC conductivity of $CoFe_2O_4$ that increasing with frequency linearly due to conduction by electron exchange between ions of same element with different valencies.

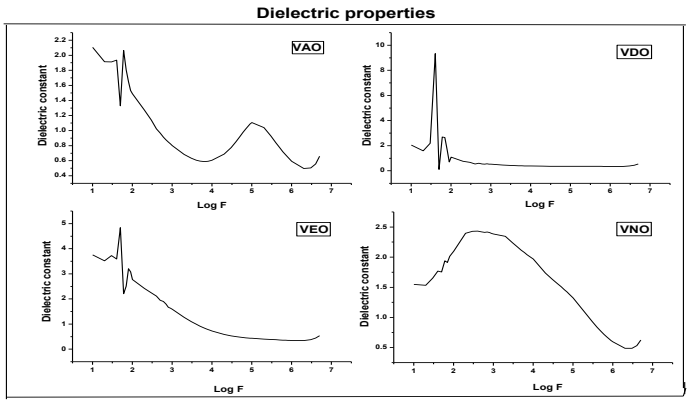


**Fig. 3.3:** a-Dielectric constant variance with frequency for $CoFe_2O_4$ with different solvents

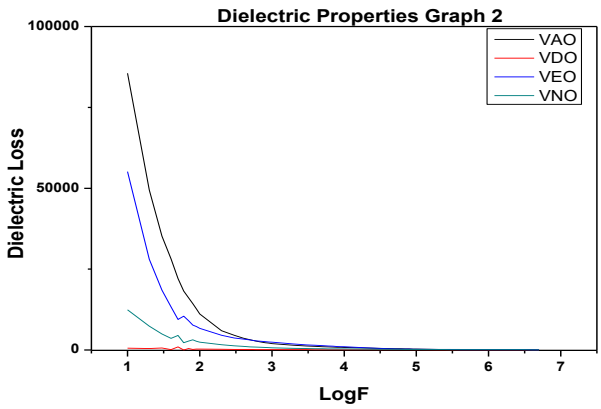


**Fig. 3.3:** b- Dielectric loss variance with frequency for $CoFe_2O_4$ with different solvents

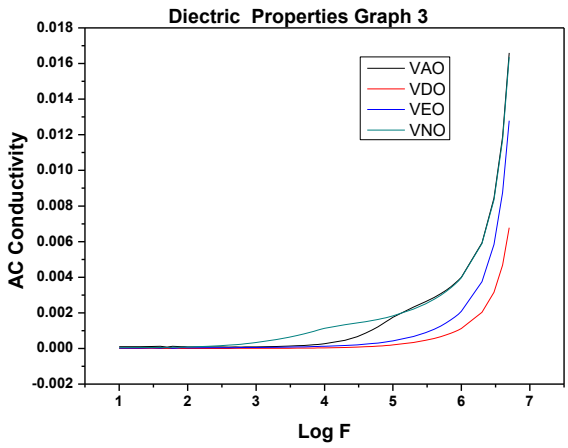


**Fig. 3.3:** c- AC conductivity variance with frequency for $CoFe_2O_4$ with different solvents.

## CONCLUSIONS

Spinel ferrite $CoFe_2O_4$ powders with different solvents (Aloevera extract, Distilled water, Egg white solution, Neem extract) were successfully synthesized using a sol-gel auto combustion method. Experiments results of FTIR, UV-Visible Spectroscopy, Dielectric Properties and SEM summarized as follows:

(i) EDX measurements for $CoFe_2O_4$ NPs which indicate, the grown NPs are stoichiometric and homogeneous with a uniform distribution.

(ii) SEM micrographs show non-uniform morphology and grown $CoFe_2O_4$ particles have agglomeration due to magnetic force.

(iii) FT-IR results confirm the formation of the ferrite.

(iv) The band gap energy of the cobalt ferrite for different samples obtained from UV-Vis spectra varies for different solvents.

(v) The dielectric constant and loss tangent decreases with frequency value and increasing conductivity, measured as a function of frequency by using L.C.R.-Q meter in frequency range 100 Hz to 5 MHz with accuracy 0.001 Hz.

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3. The Dielectric characterization was done in Swami Ramanand Teerth Marathwada University,Nanded.
4. The Synthesis of cobalt ferrite was done from Anantrao Thopte college Bhor, Pune.

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(An Edited Book)

# Cr-Al co-doped Sr-hexaferrites: Sol-gel synthesis and structural characterization

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## ABSTRACT

Cr-Al co-doped strontium hexaferrites with the chemical composition $SrFe_{12-2x}Cr_xAl_xO_{19}$ (x = 0.0, 0.1, 0.2, 0.3 and 0.4) were successfully synthesized through the sol-gel auto-combustion method. The structural characteristics of the prepared samples were thoroughly examined using X-ray diffraction technique. The X-ray diffraction pattern affirmed the presence of a single-phase hexagonal structure in Cr-Al substituted strontium ferrite. Notably, the lattice parameters a and c exhibited a decline with the incorporation of Cr-Al ions. The crystallite size demonstrated variation with the x content, ranging between 17 and 15 nm. In summary, this study comprehensively explores the synthesis and structural characteristics of Cr-Al substituted strontium hexaferrites, shedding light on the nuanced effects of Cr-Al incorporation on the material's properties.

***Keywords:*** *Rare earth free, sol-gel method, hexaferrites, lattice constant.*

## INTRODUCTION

Over the past few decades, considerable focus has been directed towards both pure and doped forms of strontium hexaferrite, owing to their noteworthy electrical and magnetic properties. These materials find applications in various technological domains, including microwave devices, recording media, signal processing devices, and as components in permanent magnets [1]. Strontium hexaferrite is employed as a permanent magnet due to its substantial saturation magnetization (Ms), elevated coercivity (Hc), exceptional resistivity, and superior chemical stability [2].

Various synthesis techniques are employed to produce strontium hexaferrite, and the substitution of different ions significantly influences its structural, morphological, magnetic, and electrical properties. The distribution of various ion substitutions occurs in octahedral, tetrahedral, and trigonal bipyramidal sites [3]. For microwave applications, it is essential for the material to exhibit high resistivity [4]. Researchers have conducted studies by doping various ions to substitute suitable cations, thereby modifying the magnetic and electrical properties of strontium hexaferrite. This effort aims to enhance its applicability in various fields. In the citrate precursor method synthesis of $SrFe_{12-x}Al_xO_{19}$ hexaferrite, the replacement of Fe by $Al^{3+}$ ions result in a reduction of saturation magnetization and an increase in coercivity. This phenomenon is attributed to the diminished crystallite size and lattice parameter defects induced by the substitution of $Al^{3+}$ ions in the ferrite structure. [5, 6].

Utilizing the sol-gel auto combustion technique, the successful synthesis of strontium ferrite with Cr-Al ion substitutions, denoted by the chemical composition $SrFe_{12-2x}Al_xCr_xO_{19}$ (where x = 0.0, 0.1, 0.2, 0.3 and 0.4), has been achieved. This research aims to explore the impact of $Al^{3+}$-$Cr^{3+}$ substitution on the structural, morphological, magnetic, dielectric, and electrical properties of strontium hexaferrite, as well as its potential applications in diverse fields

## METHODOLOGY

***Materials:*** The $Al^{3+}$-$Cr^{3+}$ ion-substituted strontium hexaferrite, with the formula $SrFe_{12-2x}Al_xCr_xO_{19}$ (where x = 0.0, 0.1, 0.2, 0.3 and 0.4), was synthesized using the sol-gel auto-combustion method. The nanoparticles of $Al^{3+}$-$Cr^{3+}$ substituted strontium hexaferrite were composed of starting materials,

including AR grade strontium nitrate $Sr(NO_3)_2$ (Sigma-Aldrich, 99.9%), ferric nitrate $Fe(NO_3)_3.9H_2O$ (Acros, 99.9%), aluminium nitrate $Al(NO_3)_3.9H_2O$ (Sigma-Aldrich, 99.9%), chromium nitrate $Cr(NO_3)_3.9H_2O$ (Sigma-Aldrich, 99.9%), and citric acid monohydrate (Acros, 99.9%). The mentioned nitrates were blended in accordance with their proportional quantities.

***Synthesis:*** The synthesis process involved dissolving all nitrates in 100 mL distilled water to achieve uniform mixing, followed by placement on a magnetic stirrer with a hot plate at 90 °C. The solution underwent continuous stirring, and citric acid was introduced into the nitrate solution with a molar ratio of 1:3. To maintain a pH value of approximately 7, ammonia was added dropwise. Gel formation occurred after 3-4 hours, resulting in a viscous brown gel. This gel was subjected to a hot plate at 100 °C, initiating combustion, and yielding fine powder of yttrium-substituted strontium hexaferrite. The obtained sample underwent pre-sintering at 700 °C for 4 hours in a muffle furnace, followed by cooling to room temperature. The sintered powders were ground for 2 hours to achieve a uniform ferrite mixture. Subsequently, the samples underwent final sintering at 1100 °C for 6 hours, producing crystalline nanoparticles. Pellets of the prepared samples, with a diameter of 10 mm and a thickness of 1 mm, were formed using a uniaxial hydraulic pressing machine, employing PVA as a binder. The prepared pellets underwent a final sintering at 1100 °C in a muffle furnace for 6 hours.

***Characterization:*** The structure of the prepared samples was examined using the X-ray diffraction technique (Ultima-IV, Rigaku). X-ray diffraction patterns were captured at room temperature within the 2θ range of 20° to 80°, employing CuKα radiation (λ=1.5404 Å).

## RESULTS AND DISCUSSION

Fig. 1 depicts the X-ray diffraction (XRD) patterns of $SrFe_{12-2x}Al_xCr_xO_{19}$ samples sintered at 1100°C for x= 0, 0.1, 0.2, 0.3, and 0.4. All XRD patterns exhibited diffraction peaks that closely matched the standard peaks, indicating the absence of impurities. The recorded diffraction peaks spanned the 2θ range of 20°-80°. The positions of these peaks, corresponding to planes (110), (107), (114), (201), (203), (205), (206), (209), (217), (2011), (1015), (1016) and (317), were indexed based on the standard diffraction pattern of hexagonal ferrite (COD Card No. 96-100-8857). Notably, the yttrium concentration had a discernible impact on the diffraction peak intensity for (107) and (114) planes. X-ray diffraction analysis confirmed the hexagonal structure of the samples. The calculated values of lattice constants a and c, following the standard relation [7], revealed a decrease in the composition's lattice parameters a (5.8727 Å) and c (23.0380 Å) with rising Al-Cr concentration in strontium hexaferrite. This phenomenon can be ascribed to the disparity in the ionic radii of $Al^{3+}$ (0.51 Å), $Cr^{3+}$ (0.63) and $Fe^{3+}$ (0.67 Å) [8]. Additionally, the ratio of lattice parameters c/a decreased with increasing Al-Cr content

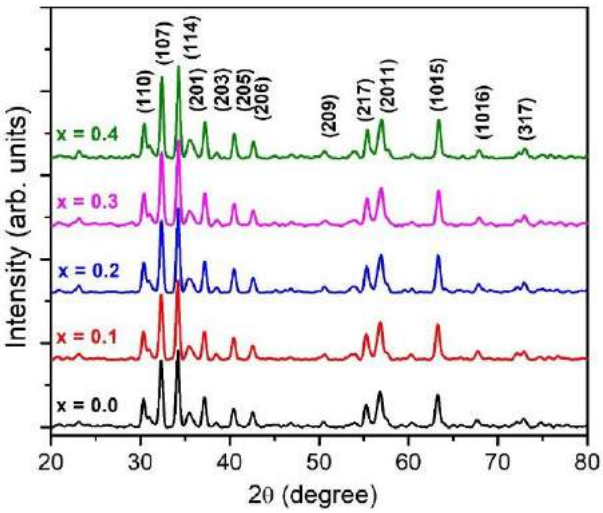


**Fig. 1:** X-ray diffraction patterns of $SrFe_{12-2x}Al_xCr_xO_{19}$.

The crystallite size was determined using the Debye-Scherer equation, considering the most intense peak (114) [9]. For yttrium-substituted strontium hexaferrites, the crystallite size decreased within the range of 17 to 15 nm, which was notably smaller compared to other hexaferrites [10, 11]. Concurrently, the X-ray density of the samples exhibited an increase with x concentration, ranging from 5.091 to 5.223 g/cc. The bulk density of the prepared samples also saw an increase, ranging from 3.48 to 3.86 g/cc. It was observed that the porosity of the samples decreased with the augmentation of Al-Cr

ion substitution in hexaferrite. The calculated values for X-ray density, bulk density, porosity, and specific surface area of all samples are presented in Table 1 [12].

**Table 1:** Lattice parameter (a, and c), c/a ratio, X-ray density ($d_x$), bulk density ($d_B$) and percentage porosity (P) for $SrFe_{12-2x}Al_xCr_xO_{19}$

| 'x' | 'a' (Å) | 'c' (Å) | c/a | '$d_X$' (gm/cc) | '$d_B$' (gm/cc) | 'P' (%) |
|---|---|---|---|---|---|---|
| 0.0 | 5.8727 | 23.0380 | 3.9229 | 5.091 | 3.48 | 31.64 |
| 0.1 | 5.8700 | 23.0238 | 3.9223 | 5.106 | 3.57 | 30.08 |
| 0.2 | 5.8661 | 22.9994 | 3.9207 | 5.132 | 3.61 | 29.66 |
| 0.3 | 5.8636 | 22.9888 | 3.9206 | 5.179 | 3.79 | 26.82 |
| 0.4 | 5.8620 | 22.9861 | 3.9212 | 5.223 | 3.86 | 26.10 |

## CONCLUSIONS

Utilizing the sol-gel auto-combustion method, strontium hexaferrites substituted with Al-Cr ions were successfully synthesized. The X-ray diffraction (XRD) patterns verified the formation of a singular phase comprising both pure and yttrium-substituted strontium hexaferrite. The lattice parameters a and c exhibited a decrease with the yttrium substitution content, attributed to the disparity in ionic radii between $Fe^{3+}$, $Cr^{3+}$ and $Al^{3+}$ ions.

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# Optimizing Computational Efficiency with Scilab: A Comprehensive Exploration

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**ABSTRACT**

The relentless advancement of computational tasks in scientific, engineering, and industrial domains necessitates a deep exploration of strategies to optimize performance. This research paper delves into the intricacies of computational efficiency using Scilab, an open-source numerical computing environment. The primary objective is to investigate, analyze, and optimize the performance of numerical methods within the Scilab framework.Commencing with an elucidation of fundamental numerical methods, including accuracy, stability, and efficiency considerations, this study establishes a foundational understanding. This forms the basis for evaluating and improving computational performance. The research subsequently navigates the terrain of Scilab's capabilities, spotlighting tools and features conducive to the optimization of numerical computations. A comparative analysis pits LU factorization against other numerical methods, such as Gaussian elimination and Cholesky decomposition. This section provides insights into the strengths and limitations of LU factorization, helping discern its optimal application contexts. Real-world case studies in engineering and science highlight the applicability of LU factorization in solving complex problems. Illustrative examples from structural engineering, fluid dynamics, and optimization demonstrate how LU factorization contributes to overcoming computational challenges in these domains.

## INTRODUCTION

In the era of escalating computational demands, the pursuit of optimizing computational performance stands as a pivotal challenge across scientific, engineering, and industrial landscapes. This paper embarks on a comprehensive exploration of strategies to enhance computational efficiency, focusing on the utilization of Scilab, a robust open-source numerical computing environment. The overarching goal is to conduct a thorough study, analysis, and optimization of numerical methods within the Scilab framework.

The introduction sets the stage by acknowledging the burgeoning complexity of computational tasks and the imperative need for efficiency. It provides context to the significance of numerical methods in addressing intricate mathematical problems and emphasizes the pivotal role Scilab plays in this domain. The narrative then seamlessly transitions to the foundational principles of numerical methods, laying the groundwork for subsequent discussions.

Fundamental aspects such as accuracy, stability, and efficiency are introduced, underscoring their critical role in assessing the performance of numerical algorithms. This segment of the introduction aims to provide a comprehensive understanding of the challenges and considerations inherent in numerical computations. The focus then shifts towards Scilab, positioning it as a versatile platform equipped to tackle these challenges through its user-friendly interface and powerful computational capabilities.

***Direct Methods for Solving Systems of Linear Equations:*** Solving systems of linear equations is a fundamental problem in numerical computing with wide applications in various fields. Direct methods, also known as factorization or elimination methods, offer a robust approach to efficiently solve such systems. This section delves into the direct methods employed within Scilab for optimizing computational performance when dealing with linear systems.

1. ***Introduction to Linear Systems:*** Linear systems play a crucial role in representing relationships among variables in numerous scientific and engineering problems. A system of linear equations is typically expressed as Ax=b, where $^{A}$ is the coefficient matrix, X is the vector of unknowns, and *b* is the right-hand side vector.

2. ***Gaussian Elimination:*** One of the classic direct methods is Gaussian elimination, where a series of elementary row operations are performed to transform the augmented matrix $[A|b]$ into an upper triangular form. This process simplifies the system, making it amenable to straightforward back-substitution for solution.
3. ***LU Factorization*:** LU factorization, or decomposition, is a pivotal direct method employed for enhancing computational efficiency. In this method, the coefficient matrix $A$ is decomposed into the product of a lower triangular matrix $L$ and an upper triangular matrix $U$. This factorization allows for efficient solving of systems with different right-hand sides.
4. ***Cholesky Decomposition:*** Cholesky decomposition is specifically applicable to symmetric positive definite matrices. It decomposes the matrix into the product of a lower triangular matrix and its transpose. Leveraging the symmetry of such matrices, Cholesky decomposition offers a computationally advantageous approach.
5. ***Scilab Implementation:*** Scilab provides built-in functions for performing these direct methods, such as '**linsolve'** for Gaussian elimination, '**lu'** for LU factorization, and '**chol'** for Cholesky decomposition. These functions encapsulate optimized algorithms and facilitate the seamless integration of direct methods into broader computational workflows.
6. ***Performance Considerations:*** The choice of a direct method depends on the characteristics of the linear system. Gaussian elimination is versatile but may be computationally expensive for large systems. LU factorization is advantageous for systems with multiple right-hand sides, while Cholesky decomposition excels in symmetric positive definite cases.
7. ***Case Studies and Performance Evaluation:*** This section will explore practical case studies to exemplify the application of direct methods within Scilab. Performance benchmarks will be employed to evaluate the efficiency gains achieved through these methods in real-world scenarios.

## GAUSSIAN ELIMINATION

Gaussian elimination stands as one of the cornerstone direct methods for solving systems of linear equations, a pivotal component of numerical computing. This section focuses on the detailed exploration of Gaussian elimination within the broader context of optimizing computational performance using Scilab.

1. ***Fundamentals of Gaussian Elimination:*** Gaussian elimination is a systematic process that transforms a system of linear equations into an upper triangular form through a sequence of elementary row operations. This method simplifies the system, paving the way for straightforward back-substitution and solution extraction.
2. ***Scilab Implementation:*** Scilab provides a powerful and user-friendly environment for implementing Gaussian elimination. The built-in function '**linsolve'** encapsulates the Gaussian elimination algorithm, allowing users to efficiently solve systems of linear equations without the need for manual matrix manipulation.

```
A = [2 3 -4; 1 -1 1; 3 1 -2];
b = [9; 8; 3];
x = linsolve(A, b);
```

3. ***Partial Pivoting for Numerical Stability:*** While Gaussian elimination is a robust method, issues of numerical stability can arise, especially in the presence of large condition numbers or near singular matrices. Addressing this, Scilab incorporates partial pivoting, a technique that enhances stability by permuting rows during the elimination process.
4. ***Computational Complexity and Optimization:*** Gaussian elimination, while effective, can be computationally demanding for large systems. This section delves into strategies for optimizing its performance. Techniques such as vectorization and parallelization, inherent to Scilab's capabilities, can be leveraged to enhance computational efficiency.
5. ***Case Studies:*** Practical case studies will be employed to demonstrate the application of Gaussian elimination within Scilab. The focus will be on showcasing its effectiveness in solving systems of various sizes and complexities.
6. ***Performance Evaluation:*** A critical aspect of this exploration involves benchmarking the performance of Gaussian elimination. Comparative analysis with other direct methods and consideration of computational resources will shed light on the efficacy and limitations of this approach.
7. ***Real-World Applications:*** Gaussian elimination finds applications in diverse fields, from structural engineering to electronic circuit analysis. This section will highlight real-world scenarios where

Gaussian elimination, implemented through Scilab, plays a pivotal role in solving complex systems of linear equations.

8. ***LU Factorization:*** LU factorization, also known as LU decomposition, stands as a pivotal direct method for solving systems of linear equations. In the pursuit of optimizing computational performance, this section meticulously explores the principles, implementation, and performance considerations of LU factorization within the Scilab environment.
9. ***Introduction to LU Factorization:*** LU factorization involves decomposing a square matrix *A* into the product of a lower triangular matrix *L* and an upper triangular matrix *U*. This factorization facilitates efficient solving of linear systems, particularly those with multiple right-hand sides, as it decouples the process of elimination and back-substitution.
10. ***Mathematical Foundation:*** A deeper understanding of the mathematical underpinnings of LU factorization lays the groundwork for its application. This section briefly delves into the theory behind the decomposition process, emphasizing its significance in numerical computing.
11. ***Scilab Implementation:*** Scilab simplifies the implementation of LU factorization with its built-in functions. The **lu** function allows users to perform LU factorization effortlessly, providing both the lower and upper triangular matrices along with the necessary permutations.

```
A = [2 3 -4; 1 -1 1; 3 1 -2];
[L, U, P] = lu(A);
```

12. ***Pivoting Strategies for Stability:*** To address numerical stability concerns, especially when dealing with ill-conditioned matrices, LU factorization incorporates partial pivoting. This section elucidates the importance of pivoting strategies and their impact on the stability of the factorization process.
13. ***Computational Efficiency:*** LU factorization is known for its computational efficiency, particularly when solving multiple systems with the same coefficient matrix. Leveraging Scilab's capabilities, this section explores optimization techniques, including vectorization and parallelization, to enhance the computational performance of LU factorization.
14. ***Case Studies:*** Practical case studies showcase the versatility of LU factorization within Scilab. Examples of varying system sizes and complexities illustrate its applicability in real-world scenarios.
15. ***Performance Evaluation and Comparison:*** Performance benchmarks, including comparisons with other direct methods, shed light on the computational advantages of LU factorization. Considerations of memory usage, execution time, and accuracy contribute to a holistic evaluation
16. ***Applications in Engineering and Science:*** LU factorization finds extensive applications in diverse fields such as structural engineering, fluid dynamics, and quantum mechanics. This section explores how Scilab's implementation of LU factorization contributes to solving complex problems in these domains.

***Scilab Implementation:*** Scilab, as a powerful numerical computing environment, plays a central role in the efficient implementation of various numerical methods. This section focuses on the practical aspects of utilizing Scilab for numerical computations within the context of optimizing computational performance.

1. ***Introduction to Scilab:*** Scilab, an open-source software, provides a versatile platform for numerical analysis, data visualization, and algorithm development. This section briefly introduces Scilab's features, emphasizing its user-friendly interface, extensive library of functions, and compatibility with diverse operating systems.
2. ***Basic Syntax and Data Structures:*** Understanding the basic syntax and data structures in Scilab is fundamental for effective implementation. This section provides a concise overview of Scilab's syntax, emphasizing the usage of matrices and vectors for representing numerical data.
3. ***Numerical Methods in Scilab:*** Scilab offers a rich set of built-in functions for a wide range of numerical methods, from solving linear systems to optimization and differential equations. This subsection provides a glimpse into the diversity of numerical methods supported by Scilab, showcasing its capabilities in addressing complex mathematical problems.
4. ***Scilab Implementation of Gaussian Elimination:*** Building upon the theoretical foundation of Gaussian elimination, this subsection demonstrates the practical implementation of this method within Scilab. The use of the **linsolve** function and its parameters will be highlighted, offering insights into the seamless integration of Gaussian elimination into Scilab workflows.

```
A = [2 3 -4; 1 -1 1; 3 1 -2];
b = [9; 8; 3];
```

```
x = linsolve(A, b);
```

5. ***Scilab Implementation of LU Factorization:*** Similarly, the section explores the implementation of LU factorization using Scilab's lu function. Emphasis will be placed on the ease of obtaining the lower and upper triangular matrices, as well as the permutation matrix when required.

```
A = [2 3 -4; 1 -1 1; 3 1 -2];
[L, U, P] = lu(A);
```

6. ***Optimizing Numerical Computations in Scilab:*** Scilab provides tools for optimizing numerical computations, such as vectorization and parallelization. This subsection explores how these techniques can be employed to enhance the computational performance of numerical methods implemented in Scilab.
7. ***Case Studies:*** Real-world case studies exemplify the practical application of numerical methods within Scilab. These examples showcase the versatility and efficiency of Scilab in solving complex mathematical problems across various domains.
8. ***Performance Evaluation:*** The section concludes with a discussion on evaluating the performance of numerical methods implemented in Scilab. Considerations include execution time, memory usage, and comparisons with alternative methods to provide a comprehensive performance analysis.

***Performance Considerations*:** Optimizing the computational performance of numerical methods within the Scilab environment involves a nuanced understanding of various factors. This section delves into critical considerations that impact the efficiency of numerical computations, emphasizing strategies to enhance performance and expedite the solution of complex mathematical problems.

1. ***Algorithmic Complexity:*** The choice of numerical method significantly influences computational performance. Some methods exhibit higher algorithmic complexity than others, impacting execution time and resource utilization. This section explores the trade-offs between different numerical algorithms within the Scilab framework.
2. ***Vectorization:*** Leveraging vectorized operations is a key strategy for enhancing computational performance in Scilab. Vectorization allows for parallel processing of array elements, reducing the need for explicit loops and boosting the efficiency of numerical calculations. Practical examples within Scilab demonstrate the impact of vectorization on execution speed.

```
% Non-vectorized version
for i = 1:n
result(i) = A(i) * B(i);
end

% Vectorized version
result = A .* B;
```

3. ***Parallelization:*** Scilab supports parallel computing through the use of parallel constructs. This section explores how parallelization can be harnessed to distribute computational tasks across multiple cores, further expediting the solution of large-scale problems.

```
// Parallelized loop
parfor i = 1:n
result(i) = some_function(A(i));
ends
```

4. ***Memory Management:*** Efficient memory usage is crucial for optimizing performance. Scilab's memory management capabilities, including garbage collection and smart memory allocation, contribute to minimizing memory overhead. Best practices for managing memory resources effectively are discussed in this section.
5. ***Data Types and Precision:*** The choice of data types and precision in Scilab impacts both computational accuracy and performance. Balancing precision requirements with the computational cost of higher precision types is explored, offering insights into optimizing numerical calculations.
6. ***Scilab Profiling Tools:*** Scilab provides built-in profiling tools that aid in identifying bottlenecks and optimizing code. Profiling reveals the time spent in different functions and can guide users in refining their implementation for improved performance.
7. ***External Libraries Integration:*** Integration with external libraries, particularly optimized linear algebra libraries, can significantly enhance computational performance. This section discusses how Scilab can interface with external libraries to leverage specialized functions for certain numerical operations.

8. ***Real-World Performance Benchmarks:*** Practical benchmarks and case studies within Scilab illustrate the application of these performance considerations in real-world scenarios. These examples provide a tangible understanding of how the discussed strategies contribute to optimizing computational efficiency.

## CONCLUSION

In the dynamic landscape of numerical computing, the optimization of computational performance within the Scilab environment emerges as a multifaceted endeavor. This study has meticulously explored critical considerations that wield substantial influence over the efficiency of numerical computations, unveiling strategies to expedite the solution of intricate mathematical problems.Algorithmic complexity stands as a pivotal factor, influencing the choice of numerical methods and, consequently, impacting execution time and resource utilization. The exploration of trade-offs between different algorithms within the Scilab framework provides a foundational understanding for practitioners seeking to balance accuracy and efficiency. Vectorization emerges as a powerful strategy for enhancing computational performance, allowing for parallel processing of array elements. The showcased examples in Scilab vividly demonstrate the transformative impact of vectorization on execution speed, underlining its significance in optimizing numerical calculations. Parallelization, as supported by Scilab's parallel constructs, offers an avenue to distribute computational tasks across multiple cores. This section has delved into the practical implementation of parallelized loops, showcasing how parallelization can be harnessed to address the computational demands of large-scale problems. sEfficient memory management, an often underestimated consideration, plays a crucial role in optimizing performance. Scilab's memory management capabilities, including garbage collection and smart allocation, contribute to minimizing memory overhead. Best practices for effective memory management have been elucidated to guide practitioners in resource optimization. The choice of data types and precision within Scilab holds implications for both computational accuracy and performance. Striking a balance between precision requirements and computational costs is essential, and this section provides insights into making informed decisions. Scilab's built-in profiling tools stand out as invaluable aids in identifying bottlenecks and refining code for improved performance. Profiling tools unveil the time spent in different functions, guiding users in optimizing their implementations effectively. Integration with external libraries, especially optimized linear algebra libraries, offers a notable avenue for enhancing computational performance. This section has discussed how Scilab can interface with external libraries, harnessing specialized functions to streamline certain numerical operations. Real-world performance benchmarks and case studies within Scilab serve as tangible illustrations of the discussed strategies in action. These examples offer a practical understanding of how considerations such as algorithmic complexity, vectorization, parallelization, memory management, data types, and external library integration collectively contribute to optimizing computational efficiency.

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# Greening the Catalysts: Nanostructured Catalysts in Pursuit of Sustainable Chemistry

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**ABSTRACT**

This research paper explores the pivotal role of nanostructured catalysts in driving sustainable chemistry practices. With a focus on their unique properties and applications, the paper aims to contribute to the advancement of environmentally friendly catalytic processes. The study delves into the enhanced reactivity, selectivity, and efficiency of nanostructured catalysts, showcasing their potential to revolutionize traditional catalysis and foster greener chemical transformations. By examining the applications of nanostructured catalysts in various domains, from green synthesis methodologies to sustainable energy production, the paper provides insights into their significant contributions to the overarching goal of achieving a more sustainable and eco-friendly chemistry landscape.

***Keywords:*** *Nanostructured catalysts, sustainable chemistry, green catalysis, catalytic applications, enhanced reactivity, selectivity, case studies, challenges, opportunities.*

## INTRODUCTION

The landscape of contemporary chemistry is undergoing a profound shift driven by an escalating global awareness of the environmental impact of conventional chemical processes. The urgent call for sustainability resonates across scientific disciplines, compelling researchers to explore innovative strategies that align with the principles of green chemistry. At the forefront of this transformative endeavor are nanostructured catalysts, poised as formidable instruments capable of reshaping traditional catalysis. This introduction delineates the critical need for sustainable practices, unveiling the promising role of nanostructured catalysts in ushering in a new era of green chemistry.

***Types of Nanostructured Catalysts:*** Nanostructured catalysts encompass a diverse array of materials that exhibit unique characteristics at the nanoscale, providing distinct advantages in catalytic processes. The types of nanostructured catalysts are broadly classified based on their composition, structure, and properties. Here are some common types:

1. **Metal Nanoparticles:**
- **Composition:** Comprising metals such as gold, silver, platinum, and palladium.
- **Properties:** Metal nanoparticles possess high catalytic activity due to their large surface area and unique electronic properties. They find applications in various catalytic reactions, including hydrogenation and oxidation.
2. **Metal Oxide Nanoparticles:**
- **Composition:** Consisting of metal oxides like titanium dioxide (TiO2), zinc oxide (ZnO), and cerium oxide (CeO2).
- **Properties:** Metal oxide nanoparticles exhibit excellent catalytic properties, often used in environmental remediation, photocatalysis, and redox reactions due to their specific surface reactivity and electronic structure.
3. **Carbon-based Nanostructures:**
- **Composition:** Includes carbon nanotubes (CNTs), graphene, and carbon dots.
- **Properties:** Carbon-based nanostructures offer high conductivity and surface area, making them effective catalyst supports. They find applications in electrocatalysis, fuel cell technologies, and as support materials for other catalytic nanoparticles.
4. **Metal-Organic Frameworks (MOFs):**

- **Composition:** Organic ligands coordinated with metal ions to form porous structures.
- **Properties:** MOFs provide high surface areas, tunable pore sizes, and unique chemical functionalities. They are employed in gas storage, separation, and catalysis due to their well-defined structures.

5. **Bimetallic and Alloy Nanoparticles:**

- **Composition:** Consists of two or more different metal species in the nanoparticle structure.
- **Properties:** Bimetallic nanoparticles combine the catalytic properties of multiple metals, leading to enhanced performance. They are utilized in reactions such as selective hydrogenation and dehydrogenation.

6. **Core-Shell Nanoparticles:**

- **Composition:** Core made of one material, surrounded by a shell of another material.
- **Properties:** Core-shell nanoparticles offer improved stability, selectivity, and catalytic activity. They find applications in various catalytic processes, including gas-phase reactions and biomass conversion.

7. **Ceria-based Nanocatalysts:**

- **Composition:** Cerium oxide (ceria) nanoparticles, often doped with other metals.
- **Properties:** Ceria nanoparticles exhibit redox properties, making them suitable for catalytic applications, especially in automotive catalysis and fuel cells.

8. **Semiconductor Nanoparticles:**

- **Composition:** Includes semiconductor materials such as quantum dots.
- **Properties:** Semiconductor nanoparticles have unique optical and electronic properties. They find applications in photocatalysis and solar-driven catalytic processes.

9. **Polymeric Nanoparticles:**

- **Composition:** Organic polymers engineered at the nanoscale.
- **Properties:** Polymeric nanoparticles are used as catalyst supports, providing stability and easy functionalization. They find applications in various organic transformations.

10. **Heterogeneous Nanocatalysts:**

- **Composition:** Combinations of different nanostructured materials, such as metal nanoparticles supported on metal oxides or carbon materials.
- **Properties:** Heterogeneous nanocatalysts leverage the synergistic effects of different materials, enhancing catalytic efficiency and selectivity.

***Catalytic Applications in Green Chemistry:*** Catalysis plays a pivotal role in the realm of green chemistry by enabling more efficient, selective, and environmentally benign chemical transformations. Nanostructured catalysts, with their unique properties, further enhance the catalytic applications in green chemistry. Here are some key catalytic applications within the context of green chemistry:

1. **Sustainable Synthesis:**

- *Objective:* To develop methodologies for synthesizing chemicals and pharmaceuticals with minimal environmental impact.
- *Nanostructured Catalysts:* Metal and metal oxide nanoparticles are employed to facilitate efficient and selective transformations, reducing the need for harsh reagents and minimizing waste generation.

2. **Selective Oxidation and Reduction:**

- *Objective:* To selectively oxidize or reduce compounds in a controlled manner, avoiding over-oxidation or excessive use of reducing agents.
- *Nanostructured Catalysts:* Metal nanoparticles and metal oxides serve as effective catalysts for selective oxidation and reduction reactions, contributing to the synthesis of fine chemicals and pharmaceutical intermediates.

3. **Photocatalysis:**

- *Objective:* To utilize light energy for initiating chemical transformations, reducing reliance on traditional energy-intensive processes.
- *Nanostructured Catalysts:* Semiconductor nanoparticles, such as titanium dioxide (TiO2) and zinc oxide (ZnO), enable photocatalytic reactions for environmental remediation and sustainable synthesis.

4. **Biomass Conversion:**

- *Objective:* To convert renewable biomass feedstocks into valuable chemicals and fuels, reducing dependence on fossil resources.

- *Nanostructured Catalysts:* Bimetallic and alloy nanoparticles play a crucial role in catalyzing biomass conversion reactions, such as hydrodeoxygenation and hydrogenation, with enhanced activity and selectivity.

5. **Water Treatment:**

- *Objective:* To develop efficient processes for water purification and pollutant degradation, addressing environmental challenges.
- *Nanostructured Catalysts:* Metal and metal oxide nanoparticles exhibit photocatalytic and catalytic activities for degrading pollutants and promoting water treatment processes.

6. **Carbon Capture and Utilization (CCU):**

- *Objective:* To capture and utilize carbon dioxide (CO2) for the synthesis of valuable chemicals and fuels.
- *Nanostructured Catalysts:* Catalytic conversion of CO2 into chemicals like formic acid or methane is facilitated by metal nanoparticles, contributing to carbon-neutral processes.

7. **Hydrogenation and Dehydrogenation:**

- *Objective:* To perform hydrogenation and dehydrogenation reactions efficiently, contributing to the synthesis of fine chemicals and renewable energy carriers.
- *Nanostructured Catalysts:* Bimetallic and core-shell nanoparticles are utilized for enhancing the selectivity and efficiency of hydrogenation and dehydrogenation reactions.

8. **Enantioselective Catalysis:**

- *Objective:* To perform chiral catalysis for the synthesis of enantiomerically pure compounds, reducing the need for separation steps.
- *Nanostructured Catalysts:* Chiral ligands supported on nanoparticles enable enantioselective catalysis, providing a sustainable approach for the synthesis of pharmaceuticals and agrochemicals.

9. **Catalytic Upgrading of Waste:**

- *Objective:* To convert waste streams, such as plastic or biomass waste, into valuable products.
- *Nanostructured Catalysts:* Catalytic processes utilizing metal and metal oxide nanoparticles contribute to the sustainable conversion of waste materials into fuels and chemicals.

10. **Green Energy Production:**

- *Objective:* To harness renewable energy sources for the production of fuels and chemicals.
- *Nanostructured Catalysts:* Photocatalytic and electrocatalytic processes involving nanostructured materials contribute to green energy production, such as solar-driven water splitting for hydrogen generation.

***Enhanced Reactivity and Selectivity:*** Enhanced reactivity and selectivity are key attributes that make nanostructured catalysts particularly advantageous in various catalytic applications. The unique properties derived from the nanoscale dimensions of these catalysts contribute to their ability to accelerate reactions and dictate specific pathways. Below are insights into how nanostructured catalysts achieve enhanced reactivity and selectivity:

**1. High Surface Area:**

- **Enhanced Reactivity:** Nanostructured catalysts possess significantly higher surface areas compared to their bulk counterparts. This increased surface area provides more active sites for catalytic reactions, allowing for a greater number of interactions between the catalyst and reactants.
- **Improved Selectivity:** The abundance of active sites allows for more controlled interactions between the catalyst and reactants, often leading to increased selectivity by promoting specific reaction pathways over undesired side reactions.

**2. Size-Dependent Properties:**

- **Enhanced Reactivity:** As catalyst particle size decreases, quantum effects and size-dependent properties become more prominent. This can result in altered electronic structures and energy levels, leading to enhanced catalytic reactivity.
- **Improved Selectivity:** Size-dependent properties can influence the binding energies of reactants on the catalyst surface, influencing the reaction pathways and favoring specific products, thus improving selectivity.

**3. Tunable Catalytic Activity:**

- **Enhanced Reactivity:** The chemical composition and structure of nanostructured catalysts can be precisely tailored, allowing for the adjustment of catalytic activity. This tunability enables the optimization of catalysts for specific reactions, enhancing reactivity.

- **Improved Selectivity:** Tailoring the catalyst's composition and structure enables the fine-tuning of its interactions with reactants, promoting specific reaction pathways and, consequently, improving selectivity.

**4. Improved Mass Transport:**

- **Enhanced Reactivity:** Nanostructured catalysts often exhibit improved mass transport properties due to their smaller dimensions. This facilitates the efficient transport of reactants to the active sites on the catalyst surface, enhancing overall reactivity.
- **Improved Selectivity:** Efficient mass transport can reduce the chances of unwanted side reactions by ensuring that reactants reach the active sites without encountering hindrances or competing pathways.

**5. Quantum Confinement Effects:**

- **Enhanced Reactivity:** Quantum confinement effects become pronounced at the nanoscale, influencing the electronic properties of nanoparticles. This can result in increased electron mobility and enhanced catalytic reactivity.
- **Improved Selectivity:** Quantum confinement effects can impact the electronic structure of the catalyst, influencing the adsorption and activation of specific reactants, thereby contributing to improved selectivity.

**6. Synergistic Effects in Bimetallic Catalysts:**

- **Enhanced Reactivity:** Bimetallic nanostructured catalysts leverage synergistic effects between the different metals, leading to enhanced catalytic activity. Cooperative interactions between metals can facilitate more efficient catalysis.
- **Improved Selectivity:** The synergy between metals in bimetallic catalysts can influence the binding energies of reactants, favoring specific reaction pathways and improving overall selectivity.

***Catalytic Processes for Sustainable Energy:*** Catalytic processes play a crucial role in advancing sustainable energy solutions by facilitating efficient and environmentally friendly energy conversion and storage. Nanostructured catalysts, with their unique properties, contribute significantly to various catalytic processes aimed at sustainable energy production. Here are key catalytic processes within the realm of sustainable energy:

**1. Hydrogen Production via Water Splitting:**

- **Objective:** To generate hydrogen as a clean and renewable fuel source through the electrolysis of water.
- **Catalytic Role:** Nanostructured catalysts, often composed of metal oxides or metal sulfides, enhance the efficiency of water electrolysis by promoting the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

**2. Photocatalysis for Solar Fuel Generation:**

- **Objective:** Utilizing solar energy to drive catalytic reactions for the production of solar fuels, such as hydrogen or hydrocarbons.
- **Catalytic Role:** Semiconductor nanoparticles, like titanium dioxide (TiO2) or other metal oxides, act as photocatalysts, absorbing solar energy and initiating chemical transformations, contributing to solar-driven fuel production.

**3. Carbon Dioxide (CO2) Reduction:**

- **Objective:** To convert CO2 into valuable fuels and chemicals, mitigating greenhouse gas emissions.
- **Catalytic Role:** Nanostructured catalysts, including metal nanoparticles and metal-organic frameworks (MOFs), promote the reduction of CO2 to chemicals like methane or formic acid through electrocatalytic or photocatalytic processes.

**4. Methanol Synthesis from Renewable Resources:**

- **Objective:** Sustainable production of methanol, a versatile chemical and potential energy carrier, from renewable resources.
- **Catalytic Role:** Nanostructured catalysts, often based on copper-zinc oxide or other bimetallic systems, enhance the synthesis of methanol from carbon dioxide and hydrogen derived from renewable sources.

**5. Fuel Cell Catalysis:**

- **Objective:** Efficient conversion of chemical energy into electricity through fuel cells, with hydrogen as a common fuel.

- **Catalytic Role:** Nanostructured catalysts, such as platinum-based nanoparticles supported on carbon, play a critical role in catalyzing the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) within fuel cells.

**6. Ammonia Synthesis:**

- **Objective:** Sustainable synthesis of ammonia, a key component in fertilizers and a potential energy carrier.
- **Catalytic Role:** Nanostructured catalysts, often based on iron-based materials, enhance the synthesis of ammonia through catalytic nitrogen reduction reactions.

**7. Biomass Conversion to Biofuels:**

- **Objective:** To convert biomass feedstocks into biofuels, contributing to sustainable alternatives to fossil fuels.
- **Catalytic Role:** Nanostructured catalysts, including metal nanoparticles or bifunctional catalysts, facilitate biomass conversion processes, such as hydrodeoxygenation and hydrogenolysis.

**8. Electrolysis for Energy Storage:**

- **Objective:** To store excess renewable energy by converting it into chemical energy through electrolysis.
- **Catalytic Role:** Nanostructured catalysts, often based on transition metals or their oxides, enhance electrocatalytic reactions during both water electrolysis and electrolysis for the production of chemicals like hydrogen peroxide.

**9. Catalytic Processes in Solar Cells:**

- **Objective:** To convert sunlight into electricity using photovoltaic devices.
- **Catalytic Role:** Nanostructured materials, such as perovskite nanoparticles or quantum dots, contribute to the development of efficient catalytic layers in solar cells.

**10. Thermal Catalysis for Sustainable Chemicals: - Objective:** To produce sustainable chemicals and fuels through catalytic processes driven by thermal energy. - **Catalytic Role:** Nanostructured catalysts with high thermal stability and surface reactivity are employed in thermal catalysis for the production of valuable chemicals from renewable feedstocks.

***Green Synthesis of Nanocatalysts:*** The green synthesis of nanocatalysts involves employing environmentally friendly and sustainable methodologies for the preparation of nanoscale catalytic materials. This approach aims to minimize the use of hazardous reagents, reduce energy consumption, and promote the use of renewable resources. Here are key aspects and strategies involved in the green synthesis of nanocatalysts:

**1. Sustainable Precursors:**

- *Selection of Eco-friendly Starting Materials:* Green synthesis begins with the choice of precursors that are benign, renewable, and environmentally friendly. Natural extracts, plant-derived compounds, and bio-based precursors are often favored.

**2. Biogenic Synthesis:**

- *Utilization of Biological Systems:* Green synthesis often involves the use of biological systems such as plants, fungi, bacteria, or algae. These organisms act as templates or reducing agents, facilitating the formation of nanocatalysts in a sustainable manner.

**3. Plant Extracts and Phytochemicals:**

- *Plant-Mediated Synthesis:* Plant extracts rich in phytochemicals serve as reducing and capping agents for the synthesis of nanocatalysts. This method is advantageous due to the abundance of plant resources and the eco-friendly nature of the extracts.

**4. Green Solvents:**

- *Replacement of Conventional Solvents:* The choice of solvents is critical in green synthesis. Green solvents, such as water, ethanol, or other biodegradable solvents, are preferred over traditional organic solvents to minimize environmental impact.

**5. Microwave and Ultrasound-Assisted Synthesis:**

- *Energy-Efficient Techniques:* Green synthesis methods often incorporate microwave or ultrasound-assisted techniques to reduce reaction times and energy consumption. These techniques promote rapid and efficient nanocatalyst formation.

**6. Biomass-Derived Materials:**

- *Utilization of Biomass:* Biomass-derived materials, such as agricultural residues or waste products, can serve as precursors or templates for the synthesis of nanocatalysts. This approach reduces dependence on conventional raw materials.

**7. Green Reducing Agents:**

- *Substitutes for Hazardous Reducing Agents:* Traditional reducing agents like borohydrides or hydrazine, which can be hazardous, are replaced with greener alternatives. Ascorbic acid, polyphenols, and sugars are examples of environmentally benign reducing agents.

**8. Bio-based Ligands:**

- *Incorporation of Natural Ligands:* Green synthesis involves the use of natural ligands, such as proteins or amino acids, which can act as stabilizing agents for nanocatalysts. This approach enhances the biocompatibility of the resulting nanomaterial.

**9. Template-Free Synthesis:**

- *Simplicity and Sustainability:* Template-free methods, where the nanocatalyst forms without the need for external templates or structures, contribute to the simplicity and sustainability of the synthesis process.

**10. Green Analytical Techniques:** - *Eco-friendly Characterization:* Utilizing analytical techniques with minimal environmental impact for the characterization of nanocatalysts is aligned with the principles of green synthesis. Techniques such as green chromatography and low-impact spectroscopy methods are preferred.

**11. Green Scale-Up Strategies:** - *Considerations for Large-Scale Production:* Green synthesis methods should be scalable and amenable to large-scale production to ensure practical applicability and reduce the environmental footprint associated with nanocatalyst manufacturing.

***Challenges and Opportunities:*** The green synthesis of nanocatalysts presents both challenges and opportunities, reflecting the evolving landscape of sustainable nanotechnology. Addressing these challenges while leveraging opportunities is crucial for advancing environmentally friendly catalytic materials.

**Challenges:**

**1. Standardization and Reproducibility:**

- *Challenge:* Achieving reproducibility and standardization in the green synthesis of nanocatalysts can be challenging due to the inherent variability of bio-based or natural precursors.
- *Mitigation:* Developing standardized protocols and analytical methods, as well as optimizing reaction conditions, can enhance reproducibility.

**2. Scalability:**

- *Challenge:* Transitioning from laboratory-scale to industrial-scale green synthesis poses challenges in terms of maintaining efficiency and minimizing costs.
- *Mitigation:* Implementing scalable processes, considering the availability of sustainable resources, and optimizing reaction parameters for large-scale production.

**3. Understanding Mechanisms:**

- *Challenge:* The complex mechanisms involved in the green synthesis of nanocatalysts may not be fully understood, limiting precise control over the resulting materials.
- *Mitigation:* Ongoing research to elucidate reaction pathways and mechanisms, combined with advanced characterization techniques, can enhance understanding and control.

**4. Stability and Longevity:**

- *Challenge:* Some green-synthesized nanocatalysts may exhibit lower stability or longevity compared to conventionally synthesized counterparts.
- *Mitigation:* Incorporating stabilizing agents, optimizing synthesis parameters, and exploring new materials that balance green principles with enhanced stability.

**5. Toxicity and Biocompatibility:**

- *Challenge:* Assessing the toxicity and biocompatibility of green-synthesized nanocatalysts is a critical concern for applications in biological and environmental systems.
- *Mitigation:* Rigorous toxicity studies, biocompatibility assessments, and adherence to regulatory guidelines are essential for ensuring safe applications.

**Opportunities:**

**1. Multifunctional Nanocatalysts:**

- *Opportunity:* Green synthesis offers the potential to engineer multifunctional nanocatalysts with tailored properties, combining catalytic activity with functionalities like sensing or imaging.
- *Leveraging:* Harnessing multifunctionality opens doors to diverse applications, including biomedical diagnostics and environmental monitoring.

**2. Integration with Renewable Resources:**

- *Opportunity:* The use of renewable resources as precursors aligns with the principles of sustainability and contributes to the development of a circular economy.
- *Leveraging:* Exploring diverse biomass sources and waste materials for green synthesis can enhance resource efficiency.

**3. Biocompatible Nanocatalysts:**

- *Opportunity:* Green synthesis allows for the incorporation of biocompatible materials, enabling applications in medicine, drug delivery, and other biological contexts.
- *Leveraging:* Tailoring nanocatalysts for compatibility with biological systems opens avenues for therapeutic and diagnostic applications.

**4. Eco-friendly Characterization Techniques:**

- *Opportunity:* Utilizing green analytical techniques for nanocatalyst characterization complements the sustainable synthesis approach.
- *Leveraging:* Employing techniques like green chromatography, low-impact spectroscopy, and eco-friendly imaging methods aligns with the overall green synthesis philosophy.

**5. Environmental Remediation:**

- *Opportunity:* Green-synthesized nanocatalysts can be tailored for efficient environmental remediation, addressing pollution and waste management challenges.
- *Leveraging:* Designing nanocatalysts with specific functionalities for pollutant degradation contributes to sustainable solutions for environmental protection.

**6. Collaboration and Interdisciplinary Research:**

- *Opportunity:* Green synthesis encourages collaboration between disciplines, fostering interdisciplinary research involving chemistry, biology, and materials science.
- *Leveraging:* Collaborative efforts enable a holistic approach to challenges, integrating diverse expertise for comprehensive solutions.

## CONCLUSION

The green synthesis of nanocatalysts stands at the intersection of innovation, sustainability, and interdisciplinary collaboration. While challenges exist, ranging from standardization issues to the need for a deeper understanding of complex synthesis mechanisms, the identified opportunities provide a roadmap for transformative advancements in catalytic materials.Addressing challenges related to reproducibility and scalability necessitates the development of standardized protocols, analytical methods, and scalable processes. Ongoing research efforts focused on elucidating the intricate mechanisms of green synthesis, combined with advanced characterization techniques, will enhance our ability to precisely control the properties of nanocatalysts. Stability concerns can be mitigated through the incorporation of stabilizing agents, optimization of synthesis parameters, and exploration of new materials that strike a balance between green principles and enhanced stability. Rigorous assessments of toxicity and biocompatibility are paramount to ensuring the safe deployment of green-synthesized nanocatalysts in biological and environmental applications, aligning with regulatory guidelines. On the flip side, a spectrum of opportunities emerges from the inherent capabilities of green synthesis. The potential to engineer multifunctional nanocatalysts opens doors to applications in diverse fields, ranging from biomedical diagnostics to environmental monitoring. Integrating renewable resources as precursors aligns with sustainability principles and contributes to the development of a circular economy, enhancing resource efficiency.

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# Exploring the Microstructural Analysis through sol-gel synthesis of rare earth doped Co-Cr ferrites

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## ABSTRACT

Ce doped Co-Cr spinel ferrites were successfully synthesized using the sol-gel technique, allowing precise control over composition and demonstrating the versatility of this method in achieving desired properties. The X-ray diffraction technique was employed the structure and phase purity of the samples. Elevating the cerium concentration results in an expansion of the lattice lengths of cubic spinels. XRD analysis confirms the crystalline nature with cubic FCC lattice. W-H analysis and SSP analysis confirms the nanocrystalline nature of the samples and the strain induced in the crystal lattice is found to be tensile. Values of lattice parameters which vary from 8.3839 Å to 8.3965 Å with Ce substitution. X-ray density increases from 5.294 g/cc to 5.460 g/cc with Ce addition where as specific surface area decreases from 66 $m^2$/gm to 53 $m^2$/gm.

***Keywords****: Spinel ferrite, sol-gel method, lattice constant, lattice strain, crystallite size.*

## INTRODUCTION

The significance of spinel ferrite has increased due to their extensive use in various technological and scientific applications. This is attributed to their high chemical stability and the ability to adjust optical, electrical and magnetic properties based on the introduction of impurity elements [1]. Over the last two-three decades, there has been thorough exploration of ferrite nanoparticles, driven by their potential applications in ferrofluids technology, magnetic storage devices, magnetic imaging, sensors, catalysts, hyperthermia, drug delivery, and wastewater treatment [2-4]. In the contemporary era, researchers are drawn to mixed ferrites featuring a cubic spinel structure, thanks to their easily adjustable properties that hold considerable relevance in various modern applications [5].

Within the category of ferromagnetic ceramics, cobalt ferrite, characterized by its spinel structure, exhibit distinctive qualities. These include a high coercive force (>5000 Oe), elevated magnetocrystalline anisotropy, a high Curie temperature, excellent chemical stability, and mechanical hardness, rendering it well -suited for applications in magneto -optical recording media [6-7]. The electro-magnetic properties of spinel ferrites are significantly influenced by both the nature and quantity of impurities introduced into the spinel lattice. Additionally, the properties of spinel ferrites are affected by factors such as the method of preparation, sintering temperature, and sintering conditions [8].

Enhancing our comprehension of the structural, magnetic and electrical characteristics of rare earth (RE) doped spinel ferrites proves highly beneficial for customizing properties to meet specific application requirements. In the current study, we employed the sol-gel auto-combustion technique to prepare $Ce^{3+}$ doped Co-Cr ferrite system. Our objective is to examine alteration in the structural and microstructural properties of Co-Cr ferrite resulting from the incorporation of rare earth (RE) ions, especially $Ce^{3+}$ ions. We conducted as analysis of the structural and microstructural properties using X-ray diffraction technique.

## METHODOLOGY

Polycrystalline nanoparticles of $CoCr_{0.2}Ce_xFe_{1.8}O_4$ (x = 0.0, 0.025, 0.050, 0.075, and 0.1) were synthesized through the sol-gel auto-ignition process. High-purity (>98.5%) metal nitrates, including $Co(NO_3)_2{\cdot}H_{12}O_6$, $Cr(NO_3)_3{\cdot}H_{18}O_9$, $Ce(NO_3)_3{\cdot}H_{18}O_9$, and $Fe(NO_3)_3{\cdot}H_{18}O_9$ were utilized as starting materials. The nitrates were dissolved in double-distilled deionized water with their stoichiometric proportions. Citric acid, a chelating agent, was added in a 1:3 ratio to the metal nitrate-citrate solution. The pH was maintained at 7 by adding liquid ammonia slowly, and the solution was continuously stirred on a hot plate at 90 $^0$C for 2-3 hours, resulting in the formation of a viscous gel. Afterward, the dark brown gel underwent self-ignition, turning into brown ash. The ash powders were then sintered at 800 $^0$C for 6 hours to obtain the final product. Structural investigations were conducted using X-ray diffraction (XRD) at room temperature within the 2θ range of 20 to 70 degrees, employing Cu-Kα radiation with an incident wavelength of λ = 1.5406 Å.

## RESULTS AND DISCUSSION

The powder X-ray diffraction patterns for all the samples of $CoCr_{0.2}Ce_xFe_{1.8}O_4$ reveal reflection lines indexed by the planes (220), (311), (222), (400), (422), (333), (440), (620), and (533) as illustrated in the left panel of Fig. 1. These reflection planes correspond to the cubic spinel structure with space group Fd3-m, in agreement with the international crystallographic database (COD No. 96-153-3573) [9]. No impurities are detected in the XRD patterns, indicating the successful incorporation of $Ce^{3+}$ ions into the Co-Cr crystal lattice in small amounts.

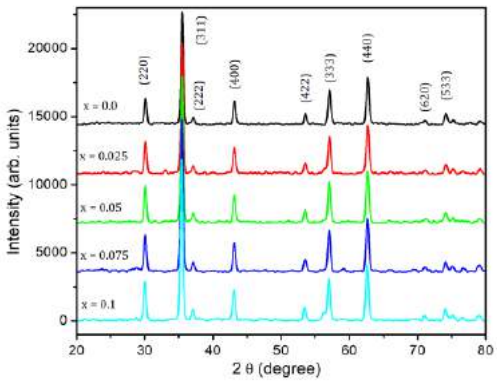


**Fig. 1:** X-ray diffraction patterns of $CoCr_{0.2}Ce_xFe_{1.8}O_4$

It is evident that the inclusion of $Ce^{3+}$ ions in the Co-Cr ferrite results in a dilution of peak intensity and a slight shift of peak positions towards lower diffraction angles. The experimental values of the lattice parameter 'a' were calculated using the following relation [10]:

$$a = d\left(h^2 + k^2 + l^2\right)^{1/2} \quad (1)$$

In the provided equation, 'd' represents interplanar spacings, and (h k l) denotes Miller indices. Table 1 represents the values of lattice parameter 'a' with the addition of $Ce^{3+}$ ions in the Co-Cr spinel ferrite crystal lattice. The successful integration of $Ce^{3+}$ ions into the spinel lattice is evident from the slight shift of diffraction angles towards lower values, resulting in an expansion of the lattice length 'a' from 8.3839 Å to 8.3965 Å.

**Table 1:** Lattice parameter (a), X-ray density ($d_X$), bulk density ($d_B$), porosity (P), and specific surface area (S) for the series $CoCr_{0.2}Fe_{1.8-x}Ce_xO_4$.

| 'x' | 'a' (Å) | '$d_X$' (gm/cc) | '$d_B$' (gm/cc) | 'P' (%) | 'S' ($m^2$/gm) |
|---|---|---|---|---|---|
| 0.0 | 8.3839 | 5.294 | 4.865 | 8.11 | 66 |
| 0.025 | 8.3857 | 5.338 | 4.848 | 9.18 | 64 |
| 0.050 | 8.3892 | 5.379 | 4.826 | 10.29 | 61 |
| 0.075 | 8.3929 | 5.419 | 4.798 | 11.47 | 56 |
| 0.1 | 8.3965 | 5.460 | 4.801 | 12.07 | 53 |

Average crystallite size was estimated by using well-known Debye-Scherrer equation given below [11]:

$$t_{D-S} = \frac{0.9\lambda}{B\cos\theta} \quad (2)$$

In the provided equation, λ represents the wavelength of the incident X-ray, B is the full width at half maximum (FWHM), and θ is the position of the Bragg's line. From Equation (2), it is evident that the average crystallite size varies from 18.46 to 20.13 nm with $Ce^{3+}$ substitution. This suggests a close dependence of the crystallite size on the concentration of $Ce^{3+}$, with an increase observed as the concentration of $Ce^{3+}$ rises. The specific surface area 'S' is estimated using a relation discussed elsewhere [19]. Table 1 shows the values of specific surface area 'S' with $Ce^{3+}$ substitution in Co-Cr ferrites. It is noteworthy that 'S' decreases with the addition of $Ce^{3+}$ ions. This trend in specific surface area further underscores the influence of $Ce^{3+}$ concentration on the structural characteristics of the Co-Cr ferrites.

The Williamson-Hall (W-H) method is an alternative approach that provides a more comprehensive understanding of both average crystallite size and the micro-strain induced in a material. This method is particularly useful for gaining insights into the structural characteristics and deformations present in the crystal lattice. By applying the Williamson-Hall analysis, researchers can extract valuable information about the crystallite size and micro-strain, contributing to a more nuanced understanding of the material's properties [12-13].

$$\beta \mathrm{Cos}\theta = \frac{C\lambda}{t_{W-H}} + 4\varepsilon \mathrm{Sin}\theta \qquad (3)$$

where C is a constant (approximately 0.94 for uniform crystallites), and ε represents the strain induced. By plotting W-H graphs between 4Sin(θ) and βCos(θ), the Y-intercepts provide the values of the average crystallite size (tW-H), while the slopes are utilized to estimate the micro-strain values. The obtained average crystallite size and micro-strain values from Figure 2 are presented in Table 2. The average crystallite size '$t_{W-H}$' ranges from 18.6 nm to 23.7 nm, showing good agreement with results obtained from the Scherrer method. Positive strain values indicate the presence of tensile strain induced in the crystal lattice. The introduction of $Ce^{3+}$ ions in Co-Cr ferrites leads to an increase in the induced strain, ranging from $0.309 \times 10^{-4}$ to $6.12 \times 10^{-4}$. This suggests that the substitution of $Ce^{3+}$ ions have a noticeable impact on the strain characteristics of the crystal lattice.

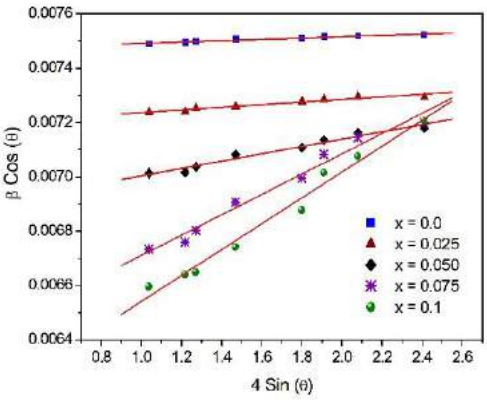


**Fig. 2:** W-H plots of $CoCr_{0.2}Ce_xFe_{1.8}O_4$

**Table 2:** Average crystallite size (t) and lattice strain (ε)for $CoCr_{0.2}Fe_{1.8-x}Ce_xO_4$.

| 'x' | Scherer | W-H | | SSP | |
|---|---|---|---|---|---|
| | 't' (nm) | '$t_{W-H}$' (nm) | $\varepsilon \times 10^{-4}$ | '$t_{SSP}$' (nm) | $\varepsilon \times 10^{-3}$ |
| 0.0 | 18.46 | 18.6 | 0.309 | 18.6 | 1.83 |
| 0.025 | 19.06 | 19.4 | 0.643 | 19.3 | 2.49 |
| 0.050 | 19.50 | 20.5 | 1.84 | 20.1 | 4.27 |
| 0.075 | 19.84 | 22.3 | 4.67 | 21.4 | 6.60 |
| 0.1 | 20.13 | 23.7 | 6.12 | 22.1 | 7.46 |

The Williamson-Hall method is considered reliable for estimating strain and size when the peak broadening is isotropic. However, for a more comprehensive understanding of strain and size parameters, the Size-Strain Plot (SSP) method offers an alternative that is not dependent on the isotropic nature of peak broadening. This method operates on the assumption that the size profile can be estimated

using a Lorentzian function, while the strain profile can be estimated using a Gaussian function. The SSP method provides a more versatile approach for characterizing the size and strain parameters, allowing for a broader application beyond the constraints of isotropic peak broadening. The relationship between strain and size in the SSP method is governed by the following relation [14]:

$$\left(d_{hkl}\beta_{hkl}\mathrm{Cos}\theta\right)^2 = \frac{K\lambda}{t}\left(d_{hkl}^2\beta_{hkl}\mathrm{Cos}\theta\right) + \left(\frac{\varepsilon}{2}\right)^2 \quad (4)$$

Plots are created between $d_{hkl}^2\beta_{hkl}\mathrm{Cos}\theta$ and $\left(d_{hkl}\beta_{hkl}\mathrm{Cos}\theta\right)^2$. The reciprocal of the slopes in these plots provides the values for the crystallite size 't', while the root mean square values of the Y-intercept yield the strain values (Table 2). The obtained values for both average crystallite size and lattice strain are found to be in good agreement with the results obtained from Debye-Scherrer and Williamson-Hall analyses. This consistency across multiple analytical methods enhances the reliability of the reported crystallite size and lattice strain parameters.

## CONCLUSIONS

The synthesis of polycrystalline nanoparticles of $CoCr_{0.2}Fe_{1.8-x}Ce_xO_4$.through the sol-gel auto-combustion route was successful. X-ray diffraction (XRD) analysis indicates the phase purity and cubic spinel structure of the samples. The average crystallite size, as determined by the Scherrer equation, falls within the nanometre range of 18 – 20 nm, and this size range is consistent with the results obtained from Williamson-Hall (W-H) analysis and Size-Strain Plot (SSP) method.

Both the W-H and SSP methods affirm that the lattice strain induced in the crystal lattice is of the tensile type, with positive strain values increasing with the addition of $Ce^{3+}$ ions. This comprehensive agreement across multiple analyses strengthens the credibility of the reported results regarding crystallite size and lattice strain parameters.

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# XRD investigation and structural development in Dy substituted cobalt ferrite.

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## ABSTRACT

Polycrystalline ferrite nanoparticles of Fe-rich cobalt ferrites doped with rare earth $Dy^{3+}$ ions were synthesized by using sol-gel auto-combustion method. Powder X-ray diffraction (XRD) technique was employed to study the structural, microstructural and cation distribution. XRD peak profile analysis confirms the cubic spinel structure of the samples with space group Fd-3m. Lattice constant shows increasing trend from 8.3882 to 8.4016 Å with $Dy^{3+}$ substitution. Average crystallite size obtained from Scherrer equation is pound in nano-meter range. The specific surface area goes on decreasing with increase in $Dy^{3+}$ substitution. The decrease in specific surface area is associated with increase in crystallite size. The allied parameters such as tetrahedral bond length ($d_{AX}$), octahedral bond length ($d_{BX}$), tetrahedral edge ($d_{AXE}$), shared and unshared octahedral edge ($d_{BAX}$, $d_{BXEU}$) were computed by using XRD data.

***Keywords:*** *Sol-gel Method, lattice constant, cation distribution, crystallite size, allied parameters.*

## INTRODUCTION

Presently, there is a widespread integration of research and production focused on nano-particles spanning from a few nanometers to micrometers. These particles find diverse applications, notably serving as information carriers in biotechnology and medicine. Among the various nano-materials, magnetic nanomaterials stand out as particularly promising in the field of current nanotechnology. The magnetic nanoparticles derived from ferrites hold significant appeal for fundamental scientific exploration, offering valuable insights into the intricate connections between magnetic properties and the crystal chemistry and structure, as highlighted in prior studies [1].

Cobalt ferrite nanoparticles emerge as promising contenders for the miniaturization of antennas, owing to their remarkable fusion of magnetic and dielectric properties. This unique amalgamation positions them as key players in meeting the burgeoning requirements of high-frequency applications anticipated in the future. The evolving landscape of technology underscores the need for downsizing electronic devices and elevating operational frequencies. In response to this demand, current efforts are concentrated on harnessing the potential of nanotechnology to enhance the performance of these materials and achieve size miniaturization. Notably, the cobalt ferrite compound has demonstrated a noteworthy correlation between its structure and magnetic interactions, as elucidated in previous studies [2, 3].

Several reports have documented the synthesis of nanocrystalline spinel ferrites with rare earth ($RE^{3+}$) substitution, achieving a single-phase structure through diverse chemical routes, despite the significant disparity in ionic radius between $RE^{3+}$ and $Fe^{3+}$ ions [4-8]. To our knowledge, there is a dearth of existing reports addressing the amalgamation of cobalt ferrite. This study marks our endeavour to explore the combination of Co-Dy ferrite for the first time.

## METHODOLOGY

The $Co_{0.9}Fe_{2.1-x}Dy_xO_4$ (x = 0.0-0.1) samples were synthesized through the sol-gel auto-combustion method, utilizing AR grade citric acid ($C_6H_8O_7{\cdot}H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$),

dysprosium nitrate ($Dy(NO_3)_3 \cdot 9H_2O$), and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$). The metal nitrates were accurately weighed and fully dissolved in distilled water, followed by stirring the solution for thirty minutes. This solution was then combined with citric acid in a manner that the molar ratio of these nitrates to citric acid reached 1:3 in the final sample. The mixed solution was kept on to a hot plate with continuous stirring at 90 ºC. During evaporation, the solution became viscous and finally formed a very viscous brown gel. When finally, all water molecules were removed from the mixture, the viscous gel began frothing. After few minutes, the gel automatically ignited and burnt with glowing flints. The auto-combustion was completed within a minute, yielding the brown-coloured ashes termed as a precursor. The as prepared powder then annealed at 600 ºC for 4 h. X-ray diffraction analysis, conducted at room temperature using Cu-Kα radiations with a wavelength of 1.5406 Å, was employed to confirm the formation of the crystallographic phase in the nanocrystalline ferrite material.

## RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of representative samples from $Co_{0.9}Fe_{2.1-x}Dy_xO_4$ (x = 0.0 and 0.1) are illustrated in Figure 1.

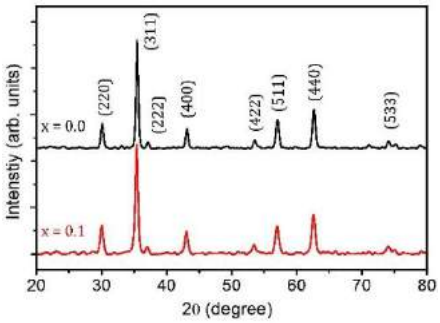


**Fig. 1:** XRD patterns of $Co_{0.9}Fe_{2.1-x}Dy_xO_4$ (x = 0.0 and 0.1)

The XRD patterns display peaks characteristic of $Dy^{3+}$ substituted Co- ferrites, with no discernible presence of impurity phases. The data signifies a single-phase spinel structure with cubic symmetry. Absence of additional lines confirms the absence of secondary phases, and the data were cross-referenced and indexed against COD card No. 96-900-5838. The lattice parameter 'a' was determined using the following equation [9],

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

Here, 'd' represents the interplanar spacing, and (hkl) denotes the index of the XRD reflection peak. The observed trend reveals a rise in the lattice constant 'a' from 8.3882 to 8.4016 Å with an increase in $Dy^{3+}$ substitution in cobalt ferrite. The variation of lattice constant with $Dy^{3+}$ substitution is shown in Figure 2. This increase in the lattice constant is attributed to the ionic radii of the involved ions. In the current ferrite system, the larger $Dy^{3+}$ ions with a 1.77 Å ionic radius substitute the smaller $Fe^{3+}$ ions, which have a 0.67 Å ionic radius.

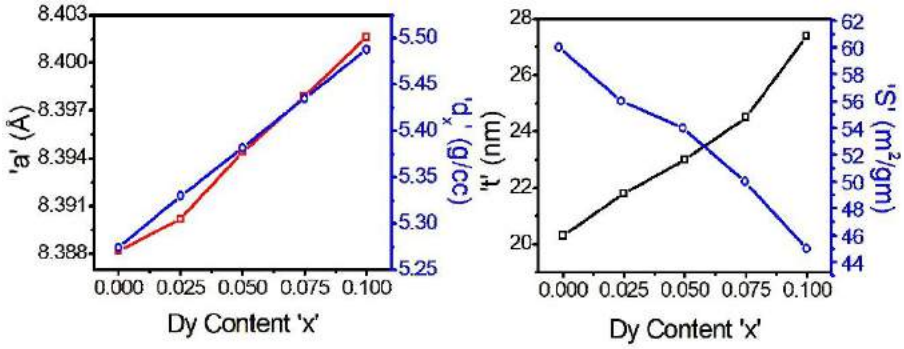


**Fig. 2:** (Left Pannel) variation of lattice parameter 'a' and X-ray density '$d_X$' (right panel) variation of crystallite size 't' and specific surface area 'S' for $Co_{0.9}Fe_{2.1-x}Dy_xO_4$

The X-ray density (dx) for all samples in the series was determined using the relation discussed elsewhere [9]. Left panel of Figure 2 illustrates the trend of X-ray density variation with $Dy^{3+}$ substitution. As depicted in Figure 2, there is a noticeable increase in X-ray density with an increase in $Dy^{3+}$ substitution. This growth occurs gradually with the rise in $Dy^{3+}$ concentration because the increases in mass outweighs the increasing in the volume of the unit cell.

The average crystallite diameter '$D_{XRD}$' of powder estimated from the most intense (311) peak of XRD and using the Scherrer formula,

$$t_{XRD} = \frac{0.9\lambda}{B\cos\theta} \quad (2)$$

where λ is the wavelength used in XRD, B is the full width of half maximum in (2θ), θ is the corresponding Bragg angle. Right panel of Figure 2 shows that the crystallite diameter increases from 20 to 27 nm with increase in $Dy^{3+}$ substitution.

The specific surface area (S) was calculated from the diameter of the particle in nanometer and the measured density in g/cm$^3$ using the relation,

$$S = \frac{6000}{Dd_B} \quad (3)$$

where D is the average crystallite size and $d_B$ is the bulk density. The variation of surface area (S) with Dy content x is shown in Figure 2 (right panel). The specific surface area goes on decreasing with increase in $Dy^{3+}$ substitution. The decrease in S is associated with increase in crystallite size.

The bond length of tetrahedral A-site and octahedral B-site i.e. shortest distance between site cations and oxygen ions along with tetrahedral edge, shared and unshared octahedral edge, are calculated using the formulae given below by inserting the values of lattice constant and oxygen position parameter in to these formulas.

$$d_{AX} = a\sqrt{3}\left(u - \frac{1}{4}\right) \quad (4)$$

$$d_{BX} = a\left[3u^2 - \left(\frac{11}{4}\right)u + \frac{43}{64}\right]^{\frac{1}{2}} \quad (5)$$

$$d_{AE} = a\sqrt{2}\left(2u - \frac{1}{2}\right) \quad (6)$$

The variations of these structurally important parameters are listed in Table 1.

**Table 1:** Allied parameters of $Co_{0.9}Fe_{2.1-x}Dy_xO_4$

| **'x'** | $d_{AX}$ | $d_{BX}$ | $d_{AXE}$ | $d_{BAX}$ | $d_{BXEU}$ |
|---|---|---|---|---|---|
| 0.0 | 1.7929 | 2.1105 | 2.9278 | 3.0036 | 2.9658 |
| 0.025 | 1.7830 | 2.1171 | 2.9117 | 3.0211 | 2.9666 |
| 0.050 | 1.7730 | 2.1246 | 2.8953 | 3.0405 | 2.9683 |
| 0.075 | 1.7630 | 2.1318 | 2.8790 | 3.0593 | 2.9698 |
| 0.1 | 1.7530 | 2.1392 | 2.8626 | 3.0782 | 2.9714 |

It can be observed from table 1, that the tetrahedral bond ($d_{AX}$) and tetra edge ($d_{AXE}$) decreases with $Dy^{3+}$ substitution and octahedral bond ($d_{BX}$), shared and unshared octahedral edge ($d_{BXE}$, $d_{BXEU}$) are increased with increase in $Dy^{3+}$ substitution. This trend could be related to the higher radius of $Dy^{3+}$ ions compared to $Fe^{3+}$ ions.

## CONCLUSIONS

$Dy^{3+}$ doped cobalt ferrite nanoparticles were successfully synthesized by sol-gel auto – ignition technique. Incorporation of $Dy^{3+}$ ions increase the lattice constant from 8.3882 to 8.4016 Å. Crystallite size increases from 20 nm to 27 nm with $Dy^{3+}$ substitution in cobalt ferrite. Tetrahedral bond ($d_{AX}$) and tetra edge ($d_{AXE}$) decreases with $Dy^{3+}$ substitution and octahedral bond ($d_{BX}$), shared and unshared octahedral edge ($d_{BXE}$, $d_{BXEU}$) are increased with increase in $Dy^{3+}$ substitution.

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# Citrate-Nitrate Auto-Combustion Synthesis of $La_{1-x}Pr_xFeO_3$ Nano Perovskites: Effect of $Pr^{3+}$ Dopant on Structural Properties

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## ABSTRACT

$La_{1-x}Pr_xFeO_3$ perovskites with composition x = 0.00 to x=0.10 in the step of 0.025 were synthesized by using the citrate-nitrate auto-combustion method and their thermal, structural and magnetic properties were investigated. The synthesized precursors analyses by differential scanning calorimetry and thermal gravimetric analysis (DSC/TGA) show phase transition takes place in $Pr^{3+}$ ion doped $LaFeO_3$ perovskites in the range around 700ºC. The synthesized perovskites were characterized by X-ray diffraction (XRD). The XRD patterns confirmed the orthorhombic structure, $Pr^{3+}$ doped $LaFeO_3$ perovskite with space group *Pbnm* without any impurity phase. The Debye-Scherer formula is used to calculate the crystallite size of the synthesized samples. The I.R. spectra of samples were analyzed to know the presence of possible functional groups and vibrating band position respectively. The energy dispersive analysis (EDS) confirmed the excepted stoichiometric elemental composition of samples. Scanning electron microscopy (SEM) analysis indicates the formation of a crystalline Nano nature and the high-resolution transmission electron microscopy (HRTEM) of the sample shows a polycrystalline nature.

***Keywords:*** *Nanomaterial; Pr3+ doped perovskites; Orthorhombic; Spectral studies.*

## INTRODUCTION

Inorganic perovskite-type oxide having formula $ABO_3$ where A is a rare earth element and B Is the 3d- transition metal remain prominent are have wide applications in different technologies such as solid-oxide fuel cells [1], chemical sensors [2], catalyst [3], thermoelectric [4] and magnetic material [5]. The examples of perovskite-type compounds are $LaFeO_3$, $SmFeO_3$, $GdFeO_3$, $NdFeO_3$ and $BiFeO_3$ [6-7]. Among these compounds, $LaFeO_3$ (Lanthanum Orthoferrites) is well known and widely studied because of its ferromagnetic behavior.

Undoped and doped Lanthanum orthoferrites commonly prepared by solid-state reaction method require high annealing temperature for a long time. After grinding the obtained products are less homogeneous with high porosity. During solid state reaction no control on particle size, due to this disadvantage several chemical methods have been proposed including Co-precipitation [8], Electro spinning [9], Hydrothermal [10], Sol-gel auto combustion [11], Sonochemical synthesis [12], Microemulsion method [13]. Among these methods, Sol-gel auto combustion is widely adopted because the advantages of this method are controlled size, low-temperature thermal decomposition, cost-effectiveness and less complicated.

In the sol-gel method, the final calcination temperature was in the range of 500-950$^0$C [14]. Lanthanum orthoferrite is known to be an antiferromagnetic material, therefore many researchers attempt to improve its magnetic property by replacing La/Fe sites with various metal ions such as La, Al, Ga, Mg, Ca, Ce, Cu etc. [15, 16, 17, 18] resulting in distortion of structure and reduction of particle size resulting in uncompensated surface spins [19,20].

In the present work, we report rare earth element $Pr^{3+}$ dopant doped due to its smaller ionic radius [1.13Å] which replaces La [1.27Å], resulting in structure distortion and improving the magnetic properties of $LaFeO_3$. In this work, $La_{1-x}Pr_xFeO_3$ (x= 0.00, 0.025, 0.050, 0.075, 0.10) nanoparticles were prepared by sol-gel auto combustion method. The structural, Optical, and Morphological properties were studied by XRD, FT-IR, Fe- SEM, and HR- TEM.

## METHODOLOGY

Lanthanum doped Perovskite $LaFeO_3$, $La_{1-x}Pr_xFeO_3$ in step of 0.025(x= 0.00, 0.025, 0.050, 0.075, 0.10), nanoparticles were synthesized by citrate nitrate auto combustion method. The metal nitrates, Lanthanum nitrate hexahydrate La $(NO_3)_3 6H_2O$ Praseodymium nitrate hexahydrate Pr $(NO_3)_3.6H_2O$, Ferric nitrate nonahydrate Fe $(NO_3)_3.9H_2O$ and Monohydrate citric acid ($C_6H_8O_7$.H2O) were used as starting materials. The nitrates were weighed according to the compositions of the desired samples. The stoichiometric amounts of metal nitrates and citric acid with a molar ratio of 1:1 were mixed with 100 ml deionized water. The ammonia is used to adjust the pH ≅ 7 . The precursor mixture was heated at 700°C to obtain a dried product. The powders were grinded in to fine powder and analyzed by TGA/DSC to know the annealing temperature. Then samples were calcinated at 600°C for four hours.

## CHARACTERIZATION

The samples were analyzed by X-ray diffraction to determine phases, crystalline structure, and crystalline size and lattice parameters. The analysis was performed employing Rigaku Ultima IV with radiation, scan rate $1^0$/ min and scanning range is 20-$80^0$. Scanning electron microscopy was used for morphological characterization and determination of average size. The instrument used to perform SEM is Zeiss Gemini SEM 450.

## RESULTS AND DISCUSSION

The thermal decomposition and crystallization temperature of synthesized precursors of $La_{1-x}Pr_xFeO_3$ were done by TGA/DSC method. Fig 1. Shows TGA/DSC curve.

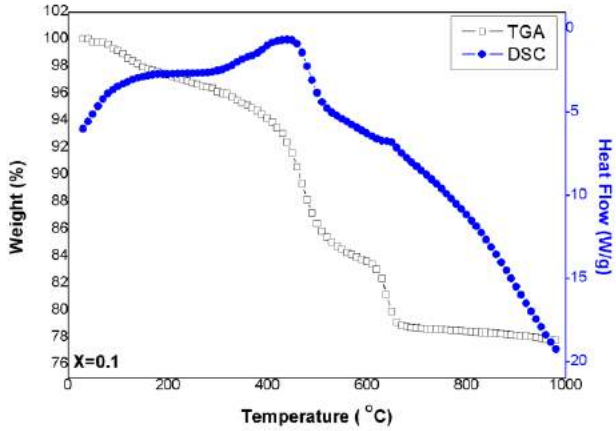


**Fig.1:** TGA/DSC curve. $La_{1-x}Pr_xFeO_3$

Fig.1.indicates weight loss between temperature 100 to 750°C in three major steps and weight loss remain constant above 750 to 1000°C. The TGA curve shows the three remarkable peaks. At temperature around 100°C, there is a slightly exothermic reaction takes place with the loss of coordinated water, near $125^0$C maximum energy is released i.e. exothermic reaction with loss of coordinated water and samples are converted into metal hydroxides. With continuous heating near about $600^0$C, the metal hydroxides are converted into metal oxides. This is an endothermic reaction. Above $700^0$C there is another weight loss indicates metal hydroxides are converted into metal oxides. This is also an endothermic reaction and there is the formation of perovskite. Above 800°c there is a slight increase in weight loss and slight exothermic peaks are observed. It is due to the oxidation of $Fe^{++}$ to $Fe^{+++}$ [21].

Fig 2 Shows the XRD pattern of calcinated precursors. The precursor shows an orthorhombic phase with phase group *Pbnm*. The orthorhombic structure of sample X=0.00 of $LaFeO_3$ in the standard form JCPDS, No. 88- 0641 indicate there is no extra peak without impurity. The crystalline size of all samples was calculated by using Full Width at Half Maxima of the most intensive peak 121 by Scherrer's equation. The crystalline size is obtained in the range of 22-28 nm. [22,23] The average crystalline size decreased with an increase in $Pr^{+3}$ ion concentration. The values of lattice parameters (a, b and c) were in good agreement with that of orthorhombic x= 0.00 $LaFeO_3$ (with a= 5.52658Å, b=5.55740Å and c=7.86623Å)

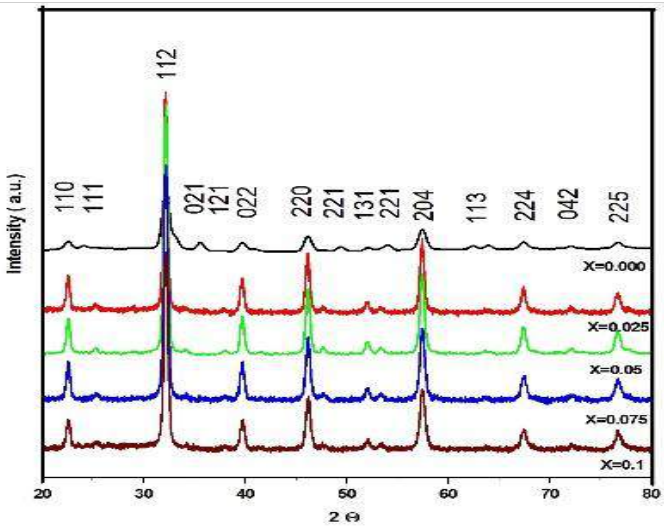


**Fig.2:** XRD pattern of $LaFeO_3$, $La_{1-x}Pr_xFeO_3$ (x= 0.00, 0.025, 0.050, 0.075, 0.10)

With the increase in concentration of dopant $Pr^{3+}$ ions, with composition 'x' the valves of lattice parameter and unit call volumes increase. The dependence of the lattice parameter depends upon the type of dopant cation in orthoferrites. It is observed that an increase in the value of radii substituting $Pr^{+3}$ ion (140.91 Å) to $La^{+3}$ cation (138.91 Å) is due to a systematic increase in values of 'a' and 'b' parameter about a slight decrease in value of (b-a) The obtained data indicates that distortion increases with decrease in the values of substituted $Pr^{+3}$ ion. The calculated parameter are listed in Table No.1.The unit cell volume values are tabulated in Table No.1. indicate an increase in the value of crystal lattice, the unit cell values are increased up to X=0.050 then decreases due to structural distortion and ratio (c/a). Similar types of results were reported by M. W. Lufaso and P.M. Woodward. [24]

**Table 1:** Lattic parameter and unit cell volume of, $La_{1-x}Pr_xFeO_3$ (x= 0.00, 0.025, 0.050, 0.075, 0.10)

| Composition 'x' | 'a'Å | 'b'Å | 'c'Å | Unit cell Volume Å | Crystalline size 't' nm |
|---|---|---|---|---|---|
| x=0.00 | 5.5180 | 5.5180 | 7.8163 | 237.9936 | 22 |
| x=0.0.25 | 5.5265 | 5.5265 | 7.8547 | 240.5011 | 24 |
| x=0.050 | 5.5407 | 5.5407 | 7.8662 | 241.9385 | 25 |
| x=0.075 | 5.5570 | 5.5570 | 7.8691 | 242.7626 | 27 |
| x=0.10 | 5.6122 | 5.6122 | 7.8966 | 247.1231 | 28 |

Fig 3. Shows FT-IR spectra of $La_{1-x}Pr_xFeO_3$, x=0.00 it gives information about chemical bonding by the perovskite-type material. Fig. 3. Shows an absorption peak at 528 $cm^{-1}$ which refers to the Fe-O stretching vibration mode [25] The stretching mode is also observed at a range of 848 $cm^{-1}$.

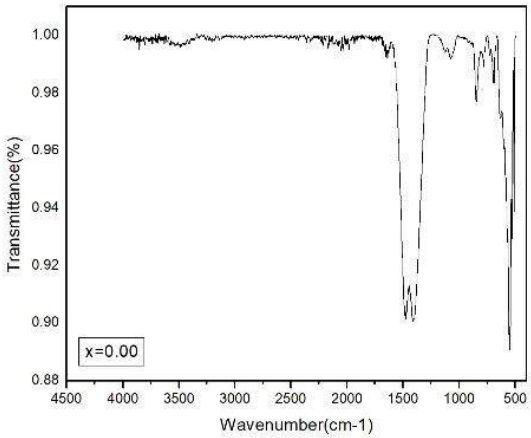


**Fig 3:** FT-IR spectra of $La_{1-x}Pr_xFeO_3$ ,x=0.00

Fig. 4 shows Fe-SEM Images of the La1-x $Pr_xFeO_3$ x=0.00 sample including elemental distribution and composition of Sample. In Fig. 3 the EDAX mapping revealed that the sample consists of elements La, Pr, Fe and 0 which are relatively uniformly distributed on the sample surface. The quantitative EDAX analysis confirmed that chemical composition was in good agreement with stoichiometric chemical composition. Similar types of results are obtained for other samples.

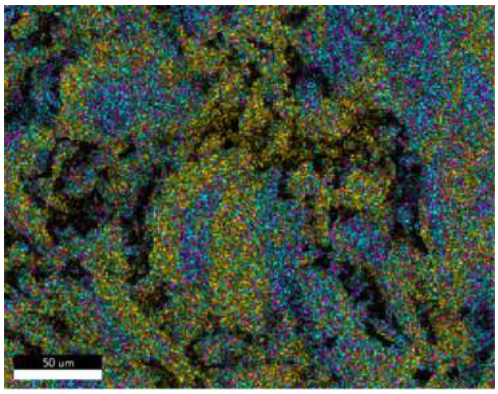



**Fig. 4.a**. Fe-SEM Images of the La1-x $Pr_xFeO_3$ x=0.00

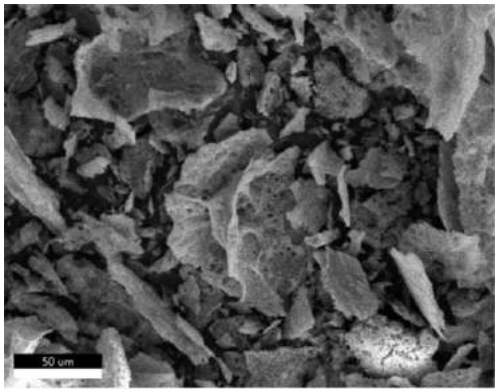


**Fig. 4.b** .SEM Images of the La1-x $Pr_xFeO_3$ x=0.00

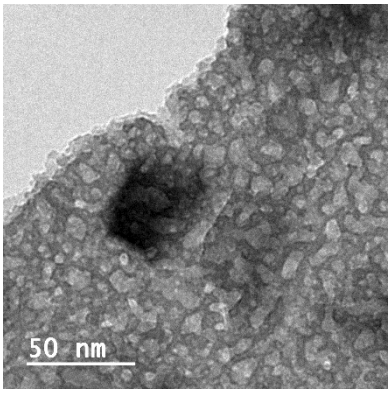


**Fig.5.**T.EM Images of the La1-x $Pr_xFeO_3$ x=0.00

The TEM images give information about the size and structure of synthesized samples. Fig. 5. Represents a typical TEM image of $La_{1-x}$ $Pr_xFeO_3$ x=0.00. It shows a monodispersed particle with an average size 18nm. which is consistent with the average size obtained from the peak of Full Width at Half Maxima of peak 121 of X-ray diffracting studies and indicate $LaFe0_3$ nanoparticles are having crystalline nature.

## CONCLUSIONS

In the present study undoped and $Pr^{+3}$ doped $LaFeO_3$ perovskite with composition (X=0.00, 0.025, 0.050, 0.075 and 0.10) successfully synthesized by sol-gel auto combustion method and analyzed by XRD, IR, Fe-SEM & TEM. The results show that the prepared samples were single-phase with phase group *Pbnm*. without any impurities and uniform size distribution. With the increase in concentration of dopant $Pr^{+3}$ion geometry of $LaFeO_3$ perovskite changed. The FT-IR analysis gives information about chemical bonding in perovskite-type material. The Fe-O stretching mode was observed at 848 $cm^{-1}$. The Fe-SEM EDAX mapping analysis showed that all samples consisted of and detected La, Pr, Fe and O elements with relatively uniform distribution on the sample surface.

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# Synthesis and study the structural and optical properties of polypyrrole

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**ABSTRACT**

Pyrrole as monomer and ammonium persulphate as an oxidant used as the starring materials with ratio of 1:1 for the synthesis of polypyrrole. The ecofriendly and cost effective chemical oxidative polymerization technique was employed for the synthesis of polypyrrole at room temperature. As prepared polypyrrole sample were characterized by X-ray diffraction (XRD) and UV visible spectroscopy. The XRD study explored the structural properties and it confirmed the prepared polypyrrole sample is amorphous in nature. UV-Vis. spectroscopy technique confirmed the conducting states corresponding to the absorption bands of conducting polymers. In prepared polypyrrole the UV-vis. absorption peaks originated at ~459 nm which corresponds to bandgap of ~3.5 eV. Thus, the used characterization techniques confirmed that the prepared polypyrrole sample is in proper form and it may be used for various technological applications.

***Keywords:*** *PPY, XRD, UV-Vis., Bandgap*

## INTRODUCTION

Conducting polymers (CPs), a unique class of organic materials that were originally shown in the 1970s, have drawn increasing attention from the scientific community because of their distinctive features and wide range of uses [1]. Due to the superior optoelectronics and physicochemical characteristics of CPs, they are being investigated more and more for biomedical uses such drug delivery, tissue engineering, and bioimaging. In addition, CPs are used in gas sensors, biosensing applications, supercapacitors, and microwave absorption layers. The most researched CPs are polyaniline (PANI) and polypyrrole (PPY), in particular, which have grown in technological significance because of their unique mechanical, chemical, optical, and electrical characteristics. In tandem with material science, a new technology known as nanotechnology has experienced exponential growth [2,3]. When compared to bulk materials, nanotechnology may create materials with remarkable properties since it can customise many types of materials to nanometer sizes. Due to their synergistic influence over individual materials, composites of CPs with other nanomaterials have recently piqued interest.

Polypyrrole (PPY) is a cheap, easily synthesised compound with excellent optical characteristics, high electrical conductivity, and strong thermal and environmental stability among the numerous varieties of CPs. Generally, the conductivity in PPY created by polarons and bi-polarons (charge) which may be stabilised by the right choice of doping ions. Owing to its remarkable properties, the PPY finds application in a wide range of fields, including biomedical, sensing, energy storage, optoelectronics, and more.

In this study, we reported the simple techniques for the preparation of polypyrrole. Then the structural and optical properties have been explored [4,5].

## EXPERIMENTAL

***Materials:*** Pyrrole was purified and all other chemicals (AR grade) used in present investigation used without any further purification. Pyrrole($C_4H_5N$), ammonium peroxydisulfate ($(NH_4)_2S_2O_4$) and sulphuric acid ($H_2SO_4$) were purchased from Molychem India.

***Characterization:*** X-ray diffractometer (XRD) (Mini Flex II, Rigaku, Japan) with CuKα radiations of wavelength 1.5406 Å was used to study the structural properties. Ultra-violet-visible (UV-vis) portable spectrophotometer BLACK-Comet-SR (Stellar Net, USA) was used to explore the optical properties.

***Synthesis of PPY :*** Pure PPY was synthesized by chemical oxidative method using acidic media. In short, pyrrole (0.1 mol/L) was oxidized with 0.1mol/L of ammonium peroxydisulfate at 0-5 $^{O}$C in 1.0 mol/L $H_2SO_4$ for 2 hr.

## RESULT AND DISCUSSION

***Structural study (XRD):*** The structural properties of the PPY sample was studied from the X-ray diffraction (XRD) pattern analysis. Fig. 1 picturised the typical XRD of pattern of PPY. Pure PPY samples shows a weak and broad characteristic peak cantered at about 2θ = 20-30$^{O}$ in the XRD pattern. The XRD pattern strongly confirms the PPY sample is in the proper form [6].

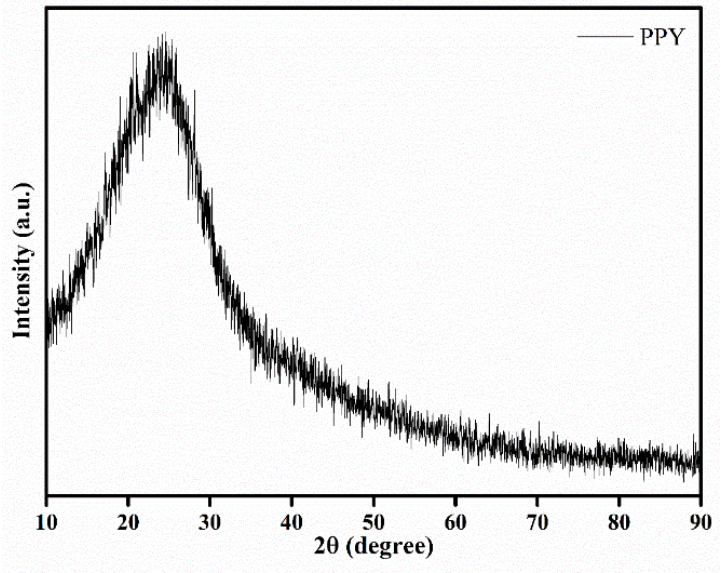


**Fig.1:** XRD spectrum of PPY

***Optical Study (UV-Vis.):*** Optical properties of the PPY sample were evaluated by Ultraviolet–visible (UV-Vis.) spectroscopy. Fig. 2 (a) shows the UV–Vis. absorption spectrum of PPY and 2(b) shows the Tauc's plot which gives the bandgap energy.

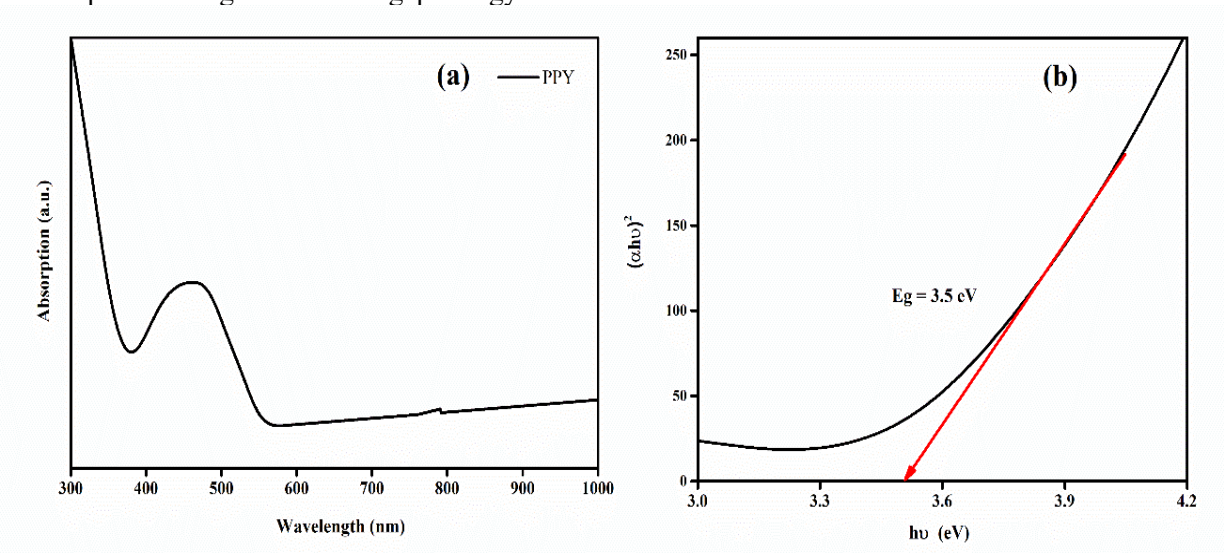


**Fig. 2:** (a) UV-Vis. absorption spectra of PPY and 2 (b) Bandgap Using Tauc's Plot

The optical absorptions spectrum shows peak at ~ 459 nm is assigned to polaron band. The bandgap energy was calculated using the Tauc's plot and it shows 3.5 eV. The optical bandgap energy confirms that the prepared PPY sample is in semiconductor form [7].

## CONCLUSION

In this work, the synthesis of PPY using chemical oxidation technique was reported. The structural and optical properties of the synthesised PPY was studied by XRD and UV-Vis. spectroscopy. The XRD study shows the prepared PPY sample is semicrystalline and in pure form. The UV-Vis. absorption spectrum shows the absorption peak at wavelength 459 nm. The bandgap of the prepared PPY sample calculated using Tauc's plot and it is exhibited as 3.5 eV. According to the structural and optical properties of the prepared PPY sample it may be used for the optoelectronic devices.

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# SYNTHESIS OF PYRAZOLE DERIVATIVES BY USING MAGNETICALLY RECOVERABLE IRON DOPED NANOCATALYSTS

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**ABSTRACT**

6-amino-3-methyl-4-phenyl-1,4-dihydropyran [2,3-c] pyrazolo-5-carbonitrile were synthesized using aromatic aldehydes, hydrazine hydrate, malononitrile, and ethyl acetoacetate in the presence of a magnetically recoverable iron-doped catalyst. The synthesis was conducted using a green technique. Catalysts are easily recovered and can be reused up to four times without significantly losing their catalytic activity. A few advantages of this procedure are its short reaction time, simple setup, use of a mild solvent and reusable catalyst.

***Keywords:*** *Heterogeneous nano catalyst, green synthesis, pyrazole derivatives.*

## INTRODUCTION

The synthesis of dihydropyrano [2, 3-c] pyrazole derivatives has become more interesting in recent years due to their bioactivity profiles. A rich source of compounds with biological significance is the Pyranopyrozole nucleus. This moiety gives compounds a variety of pharmacological characteristics and is crucial to numerous biological reactions, which include analgesics, anti-inflammatory, antibacterial, and anticancer properties. They are adaptable synthetic building blocks and the fundamental components of numerous medicinal medicines. [1,2]. Dihydropyrano [2, 3-c] pyrazoles can be synthesized using a variety of techniques. It consists of the use of meglumine, cocamidopropyl betaine (CAPB), urea, Amberlyst A21, piperidine, isonicotinic acid, ethylenediammonium diformate (EDDF), triethylamine, ionic liquid (1-butyl-3-methylimidazolium tetrafloroborate), $Ba(OH)_2$, L-proline, γ-allumina, per-6-amino-β-cyclodextrin (per-6-ABCD), molecular sieves, NaBr, etc. Several cases have demonstrated successful outcomes using these reported approaches. Nevertheless, there are drawbacks to some synthetic strategies as well, such as the use of homogenous catalyst that is difficult to separate from the reaction mixture and reuse, the use of metal catalyst, high reaction times, harsh reaction conditions, environmental hazards, and laborious work-up procedures [3-7].

For this reason, researchers should pay close attention to catalyst recovery and recycling. Researchers studying recycling need to concentrate on finding a catalyst that is easily recovered and efficiently used for multiple cycles, as the homogeneous catalyst experienced problems with recovery. Heterogeneous catalysts are significant in each of these areas. The nanocatalysts are very important in all these aspects since they are magnetically recoverable. Furthermore, it was shown that using nanocatalysts resulted in higher yields and faster reaction times.[8-13]. In order to account for all of these details, we synthesized the magnetically recoverable iron-doped $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ (x = 0.0, 0.05, 0.10, 0.15), using the sol gel method as described in the literature [14]. Dihydropyrano [2, 3-c] pyrazole derivatives are prepared using this synthetic catalyst.

## EXPERIMENTAL

Using silica gel-percolated plates, the purity of the produced product was assessed (TLC). An electro thermal micro melting point apparatus was used to determine the uncorrected melting point. Using a spectrometer, IR and $^{13}C$ NMR spectra were analyzed. $^{1}H$ NMR spectra in $CDCl_3$ were obtained on a Bucker spectrometer.

***General procedure for synthesis:*** The reaction was carried out using 1 mmol of benzaldehyde, 1 mmol of ethyl acetoacetate, 1 mmol of hydrazine hydrate, 1 mmol of malononitrile, and 0.1 mmol of $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ (Lewis Acid) catalyst in the presence of ethanol medium at room temperature. Another crucial aspect that was examined for model reaction **5a** was the recovery of the catalyst. After the reaction was completed, which was monitored using TLC, the catalyst was recovered. A strong magnet is employed to push the catalyst to the bottom of the flask for recovery. Separation of the reaction mixture from the catalyst took place after it had collected at the bottom of the flask. Acetone was used to repeatedly wash the resultant catalyst. The reaction for the next cycle was completed by adding fresh substrate to the flask. **Table 1** show that the $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ ferrite catalyst had a significant decrease in catalytic activity after being reused three to four times. A heterogeneous catalyst can benefit greatly from the use of a powerful magnet to quickly separate these magnetic $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ ferrites. This method can lead to a very clean reaction. Extracting the catalyst was done by filtering the reaction mixture. Throughout the night, the reaction mixture was kept in storage. The solid product was suction filtered to produce a pure product, which was then recrystallized from ethanol. The analysis of the final product is inspected by characterized by IR, $^1$H NMR, and $^{13}$C NMR.

**Table 1:** Reusability of $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ nanocatalysts

| No. of cycles | Yield % |
|---|---|
| First | 70 |
| Second | 66 |
| Third | 61 |
| Fourth | 58 |

***Spectral analysis***

**6-Amino-3-methyl-4-phenyl-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5a) White solid**

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 1.63 (3H, s), 4.46 (1H, s), 6.77 (2H, s, -$NH_2$), 7.08-7.54 (5H, m), 11.89 (1H, s, -NH);

$^{13}$C NMR (100 MHz, DMSO-d6): δ 9.9, 35.99, 57.9, 97.43, 120.9, 125.79, 127.49, 128.22, 135.56, 144.21, 154.67, 160.9;

IR (KBr, $cm^{-1}$): 2191 (CN), 3276 ($NH_2$)

**6-Amino-4-(4-methoxy-phenyl)-3-methyl-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5b) White solid**

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 1.74 (3H, s), 3.69 (3H, s), 4.43 (1H, s), 6.36 (2H, s, -$NH_2$), 6.76 (2H, d, J = 8.6 Hz), 7.02 (2H, d, J = 8.6 Hz ), 11.83 (1H, s, -NH);

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 10.19, 35.91, 55.16, 55.35, 61.26, 113.84, 114.19, 120.48, 126.84, 128.70, 130.04, 135.40, 136.57, 160.97, 162.11;

IR (KBr, $cm^{-1}$): 2190.99 (CN), 3251 ($NH_2$)

**6-Amino-4-(4-bromo-phenyl)-3-methyl-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5c) White solid**

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 1.75 (3H, s), 4.57 (1H, s), 6.88 (2H, s, -$NH_2$), 7.05 (2H, d, J = 8.4 Hz), 7.36 (2H, d, J = 8.3 Hz), 12.08 (1H, s, -NH)

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 10.02, 35.2, 56.9, 96.89, 119.9, 120.9, 130.01, 131.7, 136.9, 143.4, 154.9, 161.01

IR (KBr, $cm^{-1}$): 2188 (CN), 3377 ($NH_2$)

**6-Amino-4-(4-fluoro-phenyl)-3-methyl-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5d) White solid**

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 1.73 (3H, s), 4.48 (1H, s), 6.25 (2H, s, -$NH_2$), 6.94 (2H, d, J = 8.4 Hz), 7.11 (2H, d, J = 8.3 Hz), 11.82 (1H, s, -NH)

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 10.15, 36.18, 58.48, 97.49, 115.34, 120.97, 129.44, 136.09, 140.15, 155.18, 160.27, 161.03, 162.70

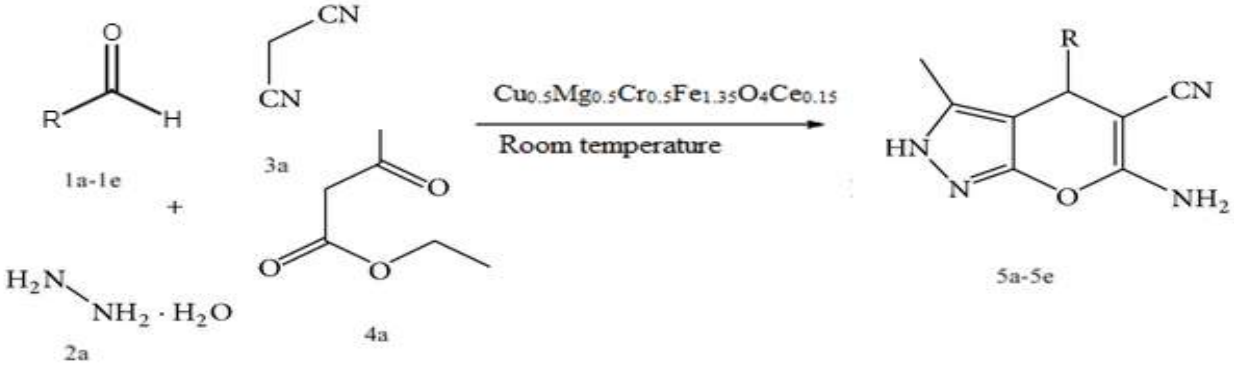
IR (KBr, $cm^{-1}$): 2188 (CN), 3377 ($NH_2$)

**6-Amino-4-(4-hydroxy-phenyl)-3-methyl-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile (5e) White solid**

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 1.69 (3H, s), 4.47 (1H, s), 6.66 (2H, d, J = 8.4 Hz), 6.86 (2H, s, -$NH_2$), 7.01 (2H, d, J = 8.4 Hz), 9.27 (1H, s, -OH), 12.09 (1H, s, -NH);
$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 9.8, 35.8, 57.35, 98.8, 116.0, 120.5, 127.9, 134.9, 135.8, 154.9, 156, 160.8;
IR (KBr, $cm^{-1}$): 2170 (CN), 3378 ($NH_2$)

## RESULT AND DISCUSSION

The effectiveness of the catalyst was checked under various optimized conditions. After checking the optimization conditions, $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.35}O_4Ce_{0.15}$ was the best composition used to synthesize 6-amino-3-methyl-4-phenyl-1,4-dihydropyran [2,3-c] pyrazolo-5-carbonitrile (5a) from 1 mmol of benzaldehyde, 1 mmol of hydrazine hydrate, 1 mmol of malononitrile, and 1 mmol ethyl acetoacetate. The different compositions of catalysts utilized for the synthesis of **5a** products (**Table 2**) and among these best results were obtained by using catalyst $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.35}O_4Ce_{0.15}$ in ethanol medium. Thus, by using the catalyst $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.35}O_4Ce_{0.15}$ other derivatives are synthesized in an ethanol medium, and their results are tabulated in **Table 3**.




**Scheme 1:** Reaction between aromatic aldehyde, hydrazine hydrate, malononitrile and ethyl aceto acetate

**Table 2:** Reaction between Benzaldehyde, ethyl aceto acetate and urea by using catalyst $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5-x}O_4Ce_x$ at different concentration (x = 0.0, 0.05, 0.10, 0.15)

| Sr.No. | Catalyst | Solvent | Yield in % | Time (Hour) |
|---|---|---|---|---|
| 1 | $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.5}O_4$ | Water<br>Ethanol | -<br>25 | 15<br>09 |
| 2 | $Cu_{0.5}Mg_{0.5}Cr_{0.5}\ Ce_{0.05}Fe_{1.45}O_4$ | Water<br>Ethanol | -<br>31 | 15<br>09 |
| 3 | $Cu_{0.5}Mg_{0.5}Cr_{0.5}\ Ce_{0.10}Fe_{1.40}O_4$ | Water<br>Ethanol | 10<br>52 | 15<br>08 |
| 4 | $Cu_{0.5}Mg_{0.5}Cr_{0.5}\ Ce_{0.15}Fe_{1.35}O_4$ | Water<br>Ethanol | 15<br>78 | 15<br>07 |

**Table 3:** Reaction between aromatic aldehyde, Hydrazine hydrate, Malononitrile and Ethyl aceto acetate in ethanol medium using catalyst $Cu_{0.5}Mg_{0.5}Cr_{0.5}Fe_{1.35}O_4Ce_{0.15}$

| Sr No. | R | Product | Yield in % | Time (hr) |
|---|---|---|---|---|
| **1** | $-C_6H_5$ | **5a** | **78** | **7.0** |
| **2** | $4\text{-}OCH_3\text{-}C_6H_5$ | **5b** | **80** | **6.5** |
| **3** | $4\text{-}Br\text{-}C_6H_5$ | **5c** | **76** | **7.5** |
| **4** | $4\text{-}F\text{-}C_6H_5$ | **5d** | **81** | **7.0** |
| **5** | $4\text{-}OH\text{-}C_6H_5$ | **5e** | **76** | **7.8** |

## CONCLUSION

**In the synthesis of** dihydropyrano [2, 3-c] pyrazole derivatives, we successfully utilized the magnetically recoverable iron-doped catalyst. This catalyst gives us a good yield, and the required reaction time is low. Also, the efficiency of the catalyst for reuse is good, and it is up to four cycles. To carry out the reaction, we used a mild solvent.

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# Synthesis of $Tio_2$ Nanoparticles via Chemical Coprecipitation Method and Exploration of the Structural and Optical Properties

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## ABSTRACT

Owing to the fascinating properties of titanium dioxide ($TiO_2$) nanoparticles, it employed in various technological applications. In fact, in this paper we have been presented the synthesis of $TiO_2$ nanoparticles via simple and cost effective chemical coprecipitation method. For synthesis of $TiO_2$ nanoparticles titanium tetrachloride ($TiCl_4$) and NaOH precursors were employed. The structural and optical properties of as synthesized nanoparticles were explored using XRD analysis and UV-vis spectroscopy respectively. XRD study confirmed that as prepared nanoparticles are pure $TiO_2$ in anatase phase with tetragonal crystal system and average particle size shows as 12 nm determined by Scherrer equation. The optical band gap was calculated using tauc's plot and it was found 3.09 nm.

***Keywords:*** *$TiO_2$ nanoparticles, XRD, UV-Visible properties, Bandgap.*

## INTRODUCTION

Recently nanotechnology gained tremendous attention in the research community. From the last decade remarkable research activities found to be extensively carried out in nanoscience and nanotechnology. The novel nanometre scale materials with excellent and unique physical and chemical properties have been developed [1]. Nanomaterials have exceptional optical, electronic, magnetic and catalytic properties when compared to their bulk counterpart. Unique properties in the nanomaterials are developed due to high surface to volume ratio, surface defects, and quantum confinement effect etc. Synthesis tools of the nanotechnology provides the desire or targeted shapes and size nanoparticles which enhanced its various properties. Due to the extraordinary physicochemical and electrooptical properties force the nanomaterials in various technological applications [2]. Nanomaterials synthesis can be used top-down and the bottom-up approach. In top-down approach includes the techniques such as mechanical milling, laser ablation, etching, sputtering, and electro-explosion etc. Whereas, in bottom-up techniques PVD, CVD, sol-gel and co-precipitation method etc. can be employed [3]. Among the various types of nanomaterials mostly, the metal oxide nanoparticles have emerged as potential candidates for the distinctive applications such as electronics, antibacterial activity, biosensor, defence, optics, energy storage industry and catalysis etc [4].

The most studied metal oxide nanoparticles are the Au, Ag, $TiO_2$, CuO, ZnO, NiO, $Fe_3O_4$ etc. Among the various types of metal oxide nanoparticles $TiO_2$ acquired its own dignitary position in nanomaterials due to their unique properties and applications. $TiO_2$ is a white colour nanomaterial and exists naturally in three crystalline forms; anatase, rutile and brookite. Due to the extraordinary properties $TiO_2$ nanoparticles can be used for the application such as paints, printing ink, plastics, paper, synthetic fibers, rubber, condensers, ceramics, electronic components and cosmetic etc. as well as it used in photovoltaics and photocatalysis [5].

In this work, we prepared the nano-dimensional $TiO_2$ material via chemical co-precipitation method. As synthesised nanoparticles were characterised by XRD and UV-vis. spectroscopy and explored the structural and optical properties.

## EXPERIMENTAL

Chemical co-precipitation method was employed for the synthesis of $TiO_2$ nanoparticles. In short, AR grade titanium tetrachloride ($TiCl_4$) and sodium hydroxide (NaOH) were used as starting materials.

Both chemicals $TiCl_4$ (1M) and NaOH (1M) prepared separately in 50 ml distilled water and mixed NaOH in $TiCl_4$ at room temperature with constant stirring for 2h. As a result of reaction white precipitate obtained which was further filtered and washed several times with distilled water. Then the acquired product was dried at room temperature and sintered at 200 $^{O}$C for 12 h. X-ray diffraction (XRD) and UV-Vis. spectrum were recorded using a Rigaku Mini flex-II diffractometer with CuKα radiation (λ=1.541 Å) and Perkin Elmer UV spectrophotometer respectively.

## RESULT AND DISCUSSION

***STRUCTURAL STUDY (XRD):*** Fig.1. shows the diffused XRD pattern of $TiO_2$ nanoparticles which identify the phase purity crystal structure. The XRD pattern of the synthesised $TiO_2$ nanoparticles exactly match with the JCPDS reference code (96-901-5930). The obtained XRD pattern of as synthesised $TiO_2$ nanoparticles indexed to tetragonal crystal system with anatase phase. The average crystallite size of as synthesised $TiO_2$ nanoparticles exhibited as 12 nm which was calculated by Scherer's equation based on XRD data.

***Optical Study (UV-Vis.):*** The optical properties of as-synthesized $TiO_2$ explored via UV-Vis. spectroscopic analysis. Fig. 2(a) shows the optical absorption of $TiO_2$ in wavelength range 300-900 nm. The spectrum exhibited the absorption peak at ~ 335 nm which appears in UV region. Fig. 2(b) shows the Tauc's plot which provide indirect band gap of $TiO_2$ nanoparticles and it is found as 3.09 nm [6].

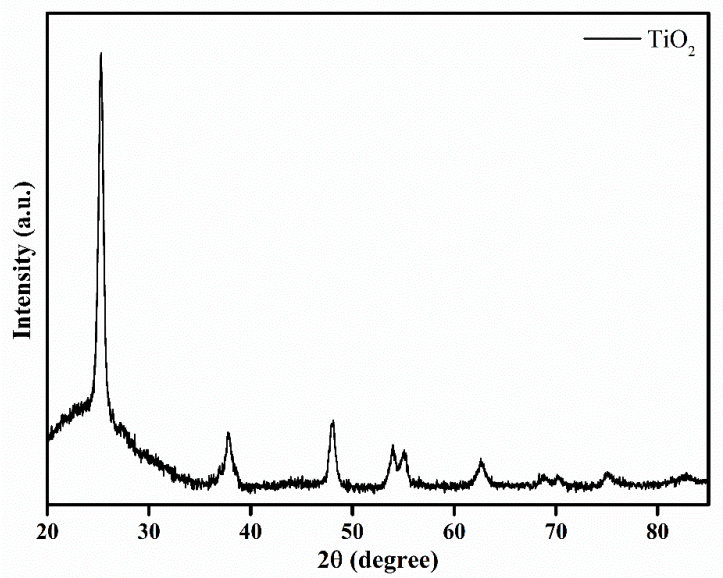


**Fig. 1:** XRD pattern of $TiO_2$ nanoparticles

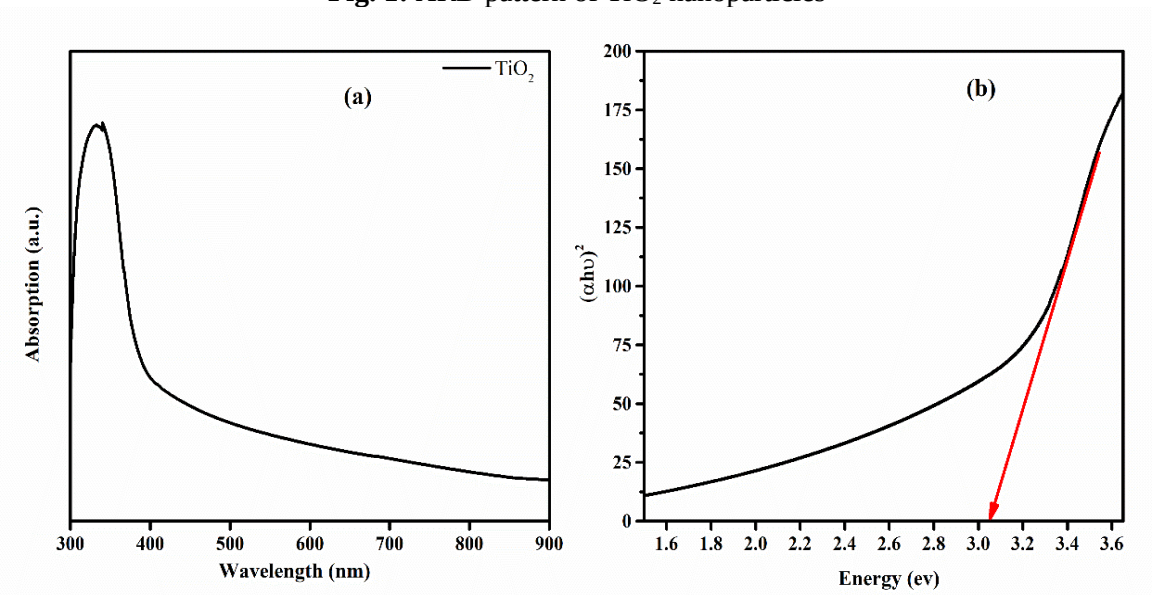


**Fig. 2 (a):** UV-vis. absorption spectrum and 2 (b) Tauc's plot to calculate bandgap of $TiO_2$

## CONCLUSIONS

In brief, we have successfully synthesized $TiO_2$ nanoparticles by most prominent and effective coprecipitation method. As prepared $TiO_2$ nanoparticles were characterised by XRD and UV-Vis. spectroscopy which explored the structural and optical properties. XRD study shows that the prepared material is $TiO_2$ nanoparticles with anatase phase with average particle size of the 12 nm. UV-Vis. analysis provide the indirect band gap of $TiO_2$ nanoparticles which was found to be 3.09 eV. Thus, the prepared $TiO_2$ can be employed for the photocatalytic and photovoltaic applications due to the excellent structural and optical properties.

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# Photon absorption coefficient of elemental solids Ag, Cu and Fe in the energy range 0.360MeV-1.33MeV

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## ABSTRACT

The photon absorption coefficient of thin uniform multiple foil attenuators (Ag, Cu, Fe) were determined in the energy range 0.360MeV-1.33MeV with a view to study the effect of atomic numbers and photon energy on absorption coefficient under collimated narrow beam geometry set-up. The measurements were taken for the linear absorption coefficient (μ), mass absorption coefficient (μ/ρ) and total photon interaction cross-section of different elemental solids of uniform thickness 0.15 cm, on NaI(Tl) detector using scintillation counter. The result shows that; as atomic number increases linear attenuation coefficient (μ), mass attenuation coefficient (μ/ρ) and total photon interaction cross-section decreases, also the linear attenuation coefficient increases.

***Keywords:*** *Linear attenuation, Mass attenuation, Total Photon interaction.*

## INTRODUCTION

The interaction of photon through material is of wide interest in industrial, medical and agriculture studies. With the advent of nuclear era, large number of isotopes and radiations generating equipments have came into existence. As a result, the protection from harmful radiation has become eminent. One of the important factors needed in radiation protection and shielding is the gamma ray attenuation coefficient. The present studies are aimed to protect individuals from harmful gamma radiation which has led us to present studies. Apart from this, the need of shield to protect against gamma radiation has further lead to extensive measurements on attenuation coefficient in different multi-elemental materials. There is an important parameter for characterizing the penetration and diffusion of gamma rays in the medium which is called mass attenuation coefficient. This parameter mainly depends on the photon energy, the nature of the material and the medium through which radiation passes. Till date, several investigators have carried out the systematic studies of attenuation coefficients by using narrow beam geometry [1-3] from time to time. The accurate values of photoelectric cross-section for photon radiation in several materials are needed in solving various problems in radiation physics and radiation dosimetry. The photon cross-section data which are most often used are the compilation of reports from National Bureau of Standard, USA [4]. It is evident to note that most of the data are based on theoretical compilation and only a few are based on experimental measurements. Such a comparison is necessary to ensure that theoretically predicted values do indeed agree with experimental results [5]. This is particularly true in the case of low energy photons. Although a number of experimental measurements are reported in the literature [6], the work actually carried out is limited to a few energy points and materials. Further the experimental techniques used by different workers are not identical; hence it is difficult to inter compare the experimental results [7]. When photons are transmitted through a well collimated geometry properly aligned using LASER beam, the multiple scattered photons are not only minimized but also, prevented from reaching the detector and so are not measured. However, as the collimator size and sample thickness increases, the probability of multiple scattered photons reaching the detector increases. Thus, along with the unattenuated photons the multiple scattered photons are also measured.

The attenuation of gamma radiation through elements is interesting from its application point of view in industrial, medical and agricultural fields. Large numbers of researchers have studied linear

attenuation coefficient and mass attenuation coefficient of several elements with a view to understand the attenuation of gamma rays and provide the experimental data for various applications [8]. The attenuation of gamma rays in elements has been studied for variable energy and using narrow beam geometry. The study of attenuation coefficient of several elements can throw light on shielding properties and to find the density of materials. Taking into considerations the importance of gamma ray attenuation we have carried out systematic investigations of linear attenuation and mass attenuation coefficient of several elements such as Silver, Copper and Iron, for variable energy 0.360 MeV–1.33 MeV using narrow beam geometry technique. The elemental solids (moderate to high atomic numbers) under investigations are pure and have a thickness of 0.15 cm. The results obtained on linear attenuation, mass attenuation coefficient and total photon interaction cross-section of Silver, Copper and Iron are presented in the paper.

## EXPERIMENTAL DETAILS

The linear attenuation coefficient, mass attenuation coefficient and total photon interaction cross-section of Silver, Copper and Iron for varying energy have been measured using narrow beam geometry technique. The experimental set-up of narrow beam geometry used in the present measurement is shown in Fig.1.

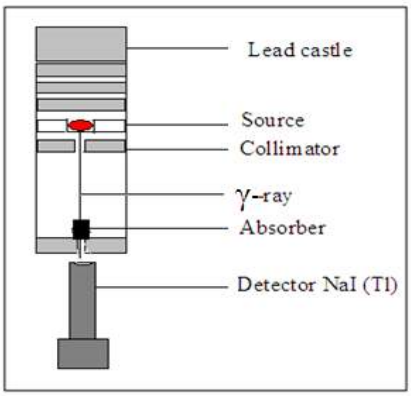


**Fig.1**: Schematic Apparatus used for the measurement of γ-ray absorption coefficient

The mono-energetic gamma radiations are derived from several radioactive sealed sources having photon energies ranging from 0.360 MeV to 1.33 MeV. The counting setup consists of source holder, incident and transmitted photon beam passing through collimators of Lead, well aligned. To minimize radiation exposure and background radiation contribution, the radioactive source was kept in a Lead source holder and placed subsequently in the Lead castle which is well shielded from all sides [9].

The transmitted photon beam is detected by a NaI(Tl) scintillation gamma photo spectrometer. The optimum voltage of 800 Volt was chosen to provide good resolution characteristic for the isotopes used. The detector was calibrated for various photon energies using radioactive isotopes $Ba^{133}$, $Cs^{137}$, $Na^{22}$ and $Co^{60}$. The photon transmission measurements were done under a narrow beam counting geometry employing high resolution scintillation detector. The NaI(Tl) detector was used in the present work. The NaI(Tl) scintillation detector used in the present work is 4.5 cm in diameter and 5.0 cm thick and is supplied by Nucleonix Enterprises, India. The experimental set-up consists mainly of two collimators of diameter 0.2 cm which is well aligned by LASER beam so as to provide a scatter free collimated photon beam. To establish the optimum collimation condition, the gamma ray spectra of $Cs^{137}$ source were taken with the incident and transmitted collimated beam and were found to be identical and had unchanged energy resolution characteristic. The photon spectra thus taken establish that the energy of transmission photon did not change appreciably due to scattered or fluorescent radiation emanating from the collimators. A provision was made midway between the collimators to introduce absorbers which were in the form of thin uniform foils. The entire system was arranged vertically over the NaI (Tl) detector, ensuring that the central axis of incident and transmitted collimator are coaxial.

The source holder was kept over the collimator so as to allow, a narrow well collimated photon beam from the collimator incident normally on the thin absorber. The gamma spectrums from each source of photon energy 0.360 MeV to 1.33 MeV were recorded on the single channel analyzer pre set to record counts under the full energy absorption peak as shown in Fig 2.

The transmitted photons from the absorbers were accumulated for a set time so as to provide statistical variation within one percent. For absorption study of gamma ray, thin and uniform foils of high purity 99.9% of Silver, Copper and Iron were used in the present study. The areal densities of absorbers were obtained by comparing their weight measured on a micro balance, with their area. The counts under the full energy absorption peak of the recorded spectrum were taken without and with absorbers placed in sequence. The photon spectrum was recorded several times for each additional foil of thickness ranging from 0.15 cm to 1.50 cm. For each added foil thickness, average counts under the full energy absorption peak were obtained. The entire counting system was arranged in a dust free room to minimize contribution from scattered photon and also from contamination arising from the atmosphere and sealed radioactive sources stored in the laboratory. Care was taken to maintain, temperature variation due to environmental change as minimum so as to avoid any shift in the photo peak position of recorded gamma spectra. The average number of transmitted photon through different absorber foils were corrected for background and plotted against thickness to represent a linear curve on a semi-log graph paper. The slope of the graph provides the accurate value of linear attenuation coefficient μ ($cm^{-1}$) for specific gamma energy and absorber. Thus, experimental values of linear attenuation coefficient obtained using 0.2 cm diameter collimator were checked for contribution from scattered photons arising from different collimators of varying sizes.

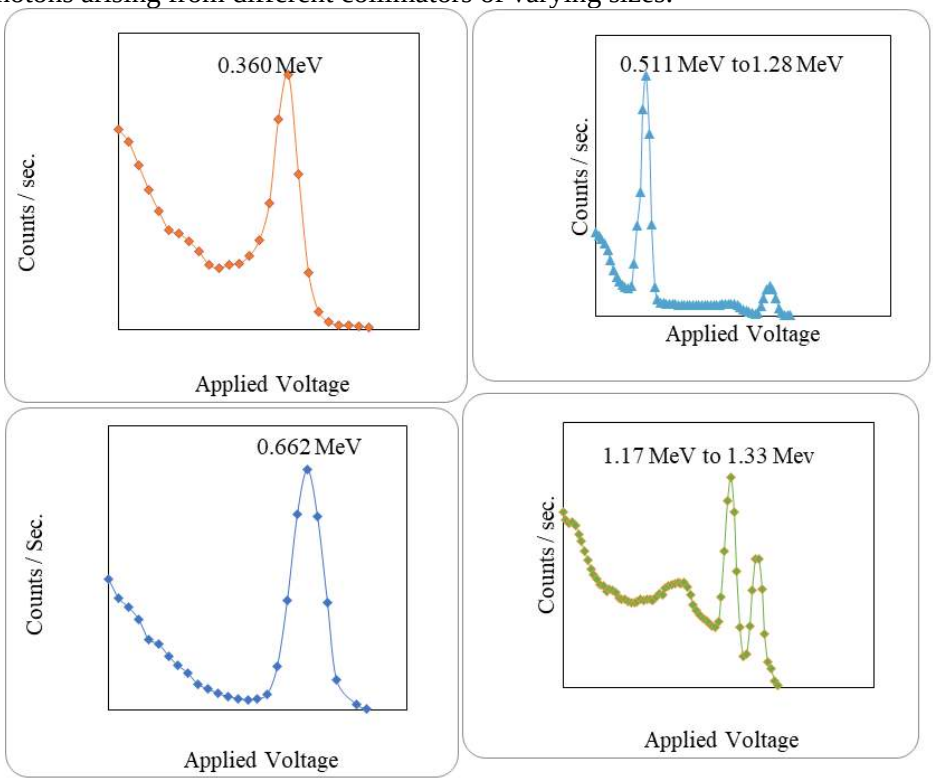


**Fig.2:** Gamma spectra of $Ba^{133}$, $Cs^{137}$, $Na^{22}$, and $Co^{60}$

## RESULT AND DISCUSSION

***Linear attenuation coefficient:*** The probability of multiple scattered photon leads to the variation in the attenuation coefficient due to changes in thickness of multiple foil staging and variation in gamma ray energies. There is definitely some kind of correlation between absorber thicknesses due to attenuation coefficient gets affected. The linear attenuation coefficient μ ($cm^{-1}$) for collimator diameter 0.2 cm is calculated using following relation and experimental results are given in Table 1.

$$I = I_o \exp[-\mu t] \quad (1)$$

where, I and $I_o$ are the photon intensities with and without absorber respectively, and 't' is thickness of the foil expressed in centimeter.

Table 1 illustrates the variation of linear attenuation coefficient as a function of gamma ray energy for collimator diameter (0.2 cm). From these results, it is seen that the linear attenuation coefficient decreases exponentially with increasing gamma energy and increases with atomic number of the absorber (for pure elements Ag, Cu, and Fe). The linear attenuation coefficient increases for all energies under study indicating identical trends in the results reported in the literature [10]. Fig 3

represents the variation of linear attenuation coefficient as a function of photon energy for collimator diameter 0.2 cm for Silver, Copper and Iron. From these plots it is observed that linear attenuation coefficient of all the elements under investigation decreases exponentially as photon energy increases.

**Table 1** Experimentally measured values of linear attenuation coefficient (μ) for collimated photon beam of 0.2 cm diameter in the energy range (0.360 MeV-1.33 MeV) for Ag, Cu and Fe.

| Energy | Linear attenuation coefficient μ($cm^{-1}$) | | |
|---|---|---|---|
| (MeV) | Ag | Cu | Fe |
| 0.360 | 0.7045 | 0.5362 | 0.4777 |
| 0.511 | 0.5421 | 0.4365 | 0.3674 |
| 0.662 | 0.4844 | 0.3823 | 0.3225 |
| 1.170 | 0.3745 | 0.3052 | 0.2621 |
| 1.280 | 0.3362 | 0.2825 | 0.2445 |
| 1.330 | 0.3147 | 0.2557 | 0.2245 |

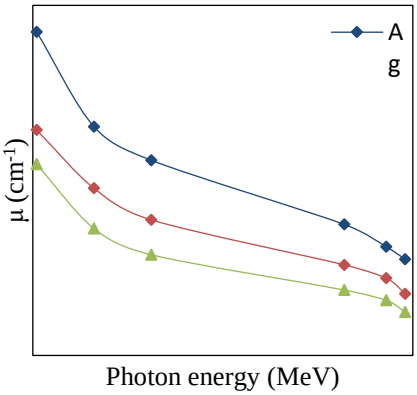


**Fig 3:** Plots of photon attenuation coefficient (μ) v/s photon energy (MeV) for Ag, Cu and Fe (0.2 cm collimation).

***Mass attenuation coefficient:*** The ratio of the linear attenuation coefficient μ ($cm^{-1}$) to the density ρ (gm $cm^{-3}$) is called the mass attenuation coefficient (μ/ρ) and has the dimension of area per unit mass ($cm^2$/gm). In the present study, the mass attenuation coefficient has been calculated using the following relation,

$$\mu_m = \mu/\rho \quad (cm^2/gm) \qquad (2)$$

where, ρ- is the density of the thin absorber and

μ-is the linear attenuation coefficient.

The mass attenuation coefficients for moderate to high atomic number of (Ag, Cu and Fe) under study are given in table 2 for varying photon energy.

From table 2 it is observed that, as the photon energy increases, the mass attenuation coefficient of all elements under study decreases. Our results are in accordance with the literature reports [11].

**Table 2** Experimentally measured values of mass attenuation coefficient (μ/ρ) for collimated photon beam of 0.2 cm diameter in the energy range (0.360 MeV-1.33 MeV) for Ag, Cu and Fe.

| Energy | Mass attenuation coefficient μ/ρ($cm^2.gm^{-1}$) | | |
|---|---|---|---|
| (MeV) | Ag | Cu | Fe |
| 0.360 | 0.0672 | 0.0601 | 0.0580 |
| 0.511 | 0.0517 | 0.0489 | 0.0468 |
| 0.662 | 0.0462 | 0.0428 | 0.0411 |
| 1.170 | 0.0357 | 0.0342 | 0.0334 |
| 1.280 | 0.0320 | 0.0316 | 0.0312 |
| 1.330 | 0.0300 | 0.0298 | 0.0286 |

The variations of mass attenuation coefficient with photon energy for all the elements under study are shown in Fig 4.

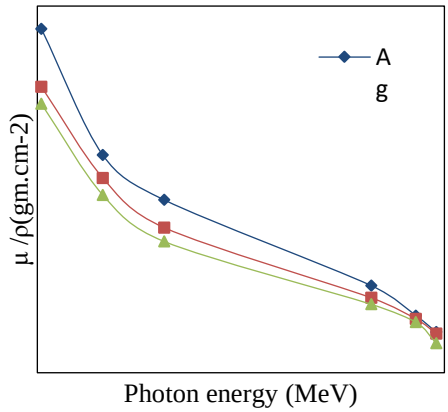


**Fig 4:** Plots of photon attenuation coefficient (μ/ρ) v/s photon energy (MeV) for Ag, Cu and Fe (0.2 cm collimation).

The common feature of all these plots is that they exhibit similar trend. The mass attenuation coefficient decreases exponentially with increasing photon energy from 0.360 MeV to 1.33 MeV. As the photon energy increases, intensity of gamma ray increases, this causes decrease in mass attenuation coefficients. It is observed from these plots that maximum value of mass attenuation coefficient is associated with Silver element that has high atomic number and high density. The minimum value of mass attenuation coefficient is observed in case of Iron with low atomic number and density.

***Total photon interaction cross-section:*** The mass attenuation coefficients ($cm^2/gm$) have been converted into the total photon interaction cross-sections, expressed in units of barns/atom by using the relation (3) given below. The values obtained from varying photon energy for collimator diameter (0.2 cm) are given in Table 3.

**Table 3:** Experimentally measured values of total photon interaction cross-section ($\sigma_{total}$) for collimated photon beam of 0.2 cm diameter in the energy range (0.360 MeV-1.33 MeV) for Ag, Cu and Fe.

| **Energy** | **Total photon attenuation coefficient $\sigma_{Total}$(barn / atom)** | | |
|---|---|---|---|
| **(MeV)** | **Ag** | **Cu** | **Fe** |
| 0.360 | 11.94 | 6.287 | 5.297 |
| 0.511 | 9.186 | 5.115 | 4.274 |
| 0.662 | 8.208 | 4.477 | 3.753 |
| 1.170 | 6.343 | 3.577 | 3.050 |
| 1.280 | 5.685 | 3.305 | 2.849 |
| 1.330 | 5.330 | 3.117 | 2.612 |

$$\sigma_{tot} = \mu_m \left( \frac{A}{N_A} \right) \times 10^{24} \quad (3)$$

It is observed that the total photon interaction cross- section of all the elements under study decreases, as the photon energy increases. The variation of total photon interactions cross-section with photon energy is shown in Fig 4. From figure it is seen that, as atomic number increases from iron to Silver, the total photon cross-section also increases. Our experimental results on total photon interaction cross-section as a function of photon energy are in analogues with the literature reports [12].

## CONCLUSIONS

In the present measurements results reported is predominantly experimental and therefore no comparison is needed. The experimental measurements described were preferred in collimation geometry and provide a set of data on attenuation coefficients, mass attenuation coefficients and total photon interaction cross section. From the above measurements, it can be concluded that the effect of multiple scattered photons in the measurements of attenuation coefficient of elemental solids is significant in Silver, Copper and Iron and can further be minimized by using well collimated narrow beam counting geometry. As most accurate values of attenuation are needed in radiation dosimetry, diagnostic and therapeutically applications attempt should be made to minimize multiple scattered contributions while evaluating the attenuation coefficient values correctly. Finally, it is concluded that the attenuation coefficient can be measured more accurately for health care, and radiation dosimetric applications.

From our studies on linear attenuation coefficient, mass attenuation coefficient and total photon interaction cross-section as a function of photon energy on various elements (Ag, Cu and Fe) it can be concluded that the collimator size largely affects the attenuation of gamma ray in elements under investigation. The best results of attenuation coefficients are observed for 0.2 cm diameter of collimator. Based on our results, it can be concluded that

1) The linear attenuation coefficient increases exponentially with increasing photon energy.
2) The linear attenuation coefficient increases from moderate (Fe) to high atomic number (Ag).
3) The mass attenuation coefficient increases exponentially with increasing photon energy.
4) The mass attenuation coefficient increases from moderate to high atomic number.
5) The total photon interaction cross-section increases with increasing photon energy. The increase is exponential in nature.
6) The total photon interaction cross-section increases from moderate to high atomic number.
7) For effective attenuation coefficient, the collimator diameter of 0.2 cm size is most suitable.

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# Characterization Techniques used in nanomaterials-A Review

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**ABSTRACT**

Nanostructure have attached huge interest as rapidly growing class of materials for many applications several techniques have been used to characterize the size, crystal structure, elemental composition and variety of other physical properties of nanoparticles. Nanomaterial is important for understanding their properties and application which is about 1 to 100 mm nano science can be used across other field like chemistry, electronic engineering, physic and material science. This review describes the instruments and experimental step up for various measurements towards the characterization of the synthesized Nano crystals. The techniques adopted to characterize the nanoparticles are X-ray diffraction (XRD), SEM, EDX, TEM, DC-Conductivity, Particle size analyzer, UV-visible spectroscopy, thermogravimetric analysis. This paper will be brief idea of various techniques which are used to characterize the nano materials.

***Keywords:*** *Nanomaterials, XRD, SEM, EDX, TEM, DC…Etc.*

## INTRODUCTION

The principal objective of this review is to summarize the present knowledge on the use, advance advantages and weakness of large number of experimental techniques that are available for the characterization of nanoparticles. This field is defined primarily by unit of length, the nanometer at which lies the ultimate control over the form and function of matter. The fundamental nanotechnology lies in the fact that properties of Material change Dramatically. When their size is reduced to the nanometer range. But measuring this nano dimension is not a very easy task. These characterizing mono-sized material is also and emerging field posing lot of challenges to scientist and Technologists. Nano characterization techniques to allow a better control of Morphology, size and dimensions of material in nano range[2].The important characterization techniques used for nanotechnology research in a various application have been discussed in this paper.

## CHARACTERIZATION OF NANOPARTICLES

Two of the main parameters studied in the characterization of nanoparticle are size and shape. We can also major size distribution, degree of aggregation, surface charge and surface area and to some extent evaluate the surface chemistry. Size distribution and organic Ligand and present on the surface of the particles may affect other properties and possible application of the nanoparticles. In The crystal structure of the nanoparticles and their chemical compositions are thoroughly investigated as first step after Nano-particle synthesis. There are important challenges in the analysis of nanoparticle because of the interdisciplinary nature of the field, the absence of suitable reference material for the calibration of analytical tools, the sample preparation for analysis and the inter-precipitation of the data. in addition, these are unmated challenges in the characterization of nanoparticles. such as measurement of their concentration especially in Scaled-up production. as well as their analysis in complex materials. The nanomaterial prepared in several ways to the maximum extent. On the surface Ligand that influence the physical properties in addition do not present only techniques that are might classify as common but we also show of modern techniques that are used to monitor the Kinetics of nanoparticles formation and studying. through some recent advances in the controlled defect that affect nanoparticle properties in a crucial manner.[3]

## CHARACTERIZATION TECHNIQUES

***X-Ray Diffraction [XRD]:*** X-ray Diffraction is one of the most extensively used techniques for the characterization of nanoparticle typically XRD provides information regarding the crystalline structure, nature of the phase the lattice structure of crystalline substance like unit size dimensions, bond angles, chemical composition and crystallographic structure of nature and manufactured material.[4] XRD is a based on the constructive interference of X-Ray and the sample concern which should be crystalline. The X-ray which are generated by CRT are filtered. collimated and then directed towards to words the sample. An advantage of the XRD techniques commonly performed in sample of powder form usually after drying their corresponding Colloidal Solutions, is that it results in statistically representive, volume averaged values.

X-ray powder diffraction (XRD) is Rapid analytical technique primarily used for Phase identification on the crystalline material and can provide information on unit cell dimension and atomic spacing. The X-ray generated by cathode ray tube, filtrate to produce nano-chromatic radiation, Collineated concentrated and directed towards the sample. The interaction incidence monochromatic rays with the sample interference when condition satisfy bragg's law $n\lambda = 2d\sin\theta$.This equation wavelength ($\lambda$) electromagnetic radiation to the diffraction angle($\theta$) and lattice Spacing(d) in a crystalline sample through arrangement of $2\theta$ angles. All possible diffraction directions on of the lattice are attend to the random orientation of the powered materials.

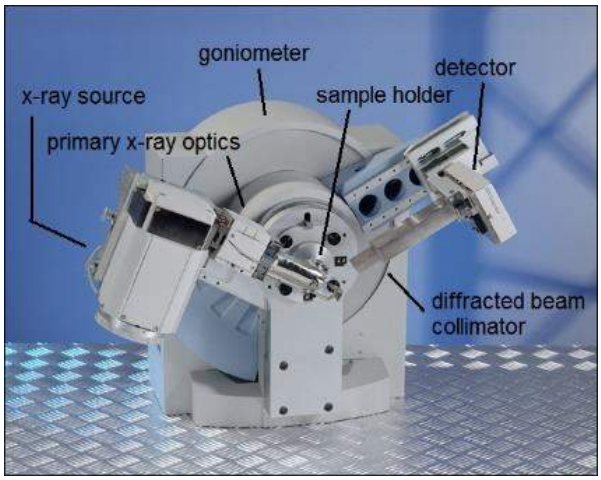


**Fig.1:**XRD-Diffraction Equipment

***Scanning Electron Microscopy (SEM):*** Scanning electron microscopy (SEM) is a widely used method for the high-resolution imaging of surface that can be employed to also characterize nanoscale materials. SEM is a type of electron microscope that images a sample by scanning it with high energy beam of electron in a raster scan pattern[4,5] .The electron interact with the atoms that make up the sample producing signals that contain information about the sample surface topography, composition and properties such as electrical conductivity. SEM analysis illustrated its Superiority compared to Nano-SEM analysis of inorganic NPS in complex biological system. Nano-SEM has Lower Spatial resolution of around 50 nm while SEM is able to achieve resolution down to 1 nm in size.

**Fig.2:** Scanning electron microscopy (SEM)-Set up

SEM micrographs have a large depth of field yielding a characteristic Three-dimensional appearance useful for understanding the surface structure of sample. The Beam passes through electromagnetic lenses focusing on to the Specimen. The different types of electrons are emitted from the specimen a detector catches the secondary electron and an image of the sample surface is constructed by comparing the intensity of the second electron to the scanning primary beam. The data collected is over a pre-selected area of the sample surface,2-D image is generated that shows the various special variations with magnification range of 20X-30000X with a special resolution of 50-100 nm on scan areas, with 1 cm to 5 µm in width. These analyses particular points as be seen EDX operations which helps in determining the chemical compositions of the sample concerned.

***Energy Dispersive X-ray [EDX]:*** Energy dispersive x-ray Spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of sample. The variations of X-Ray fluorescence Spectroscopy which relies the investigation of sample interaction between electromagnetic radiation and matter, analyzing X-ray [4,5].The fundamental principle that each element has a unique atomic structure allowing X-ray that are characteristic of an elements atomic structure to be identified from one another. To stimulate the emission of X-rays for from specimen high-energy beam of charged particles. such as electron of X-rays is focused on to the sample.an atom within the sample contain ground state electron in discrete electron shells bound the nucleus. The incident beam excite on electron in an inner shell ejecting it from shell creating on electron hole the electron from an outer, higher-energy Shell the fills the hole and the difference in energy between higher energy shell and the lower energy shell may be release x-rays. The X-rays emitted from specimen can measured by an energy dispersive spectrometer. The difference in energy between the two Shells of the atomic structure of the element from which they were emitted.

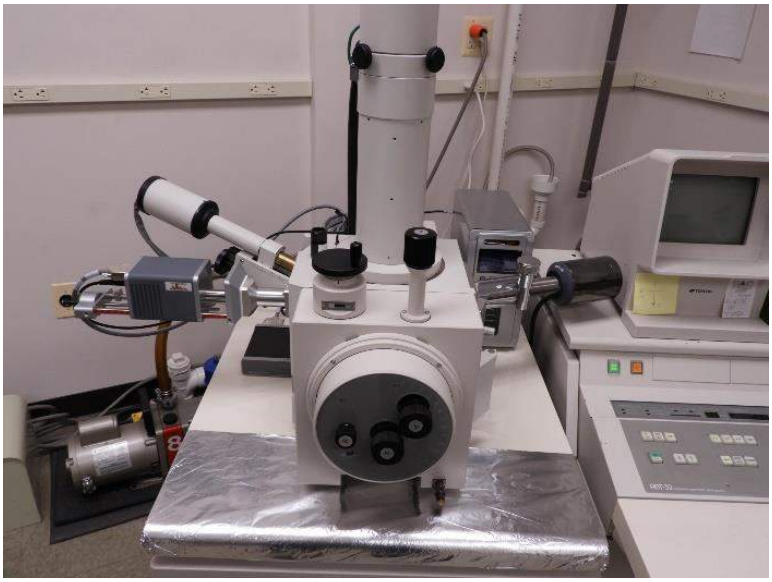

**Fig.3:** Energy Dispersive X-ray [EDX] Analyzer

***Transmission Electron Microscope [TEM]:*** Transmission electron microscope is a microscopy technique that exploits the interaction between a uniform current density electron beam and a thin sample, When the electron beam reaches the sample, part of the electron are transmitted, while the rest are elastically scattered. TEM is constituted of-

1.two or three condenser lenses to focus the electron beam on the sample.

2.An objective lens to form the difference in the back focal plane the image of the sample.

3. some intermediate lens to magnify the image on screen.

if the sample is thin < 200 nm and the light chemical elements the image very low contrast on its focused. The crystalline parts in Bragg orientation appear dark & the amorphous or not Bragg oriented parts appear bright. This imaging mode is called bright filed mode, This mode is called dark filed mode. The Dark filed mode and bright filed mode are used for imaging materials to nanometer scale. The micro diffraction patterns of the crystal permit to obtain the summary of its lattice and collect its interplanar distance.

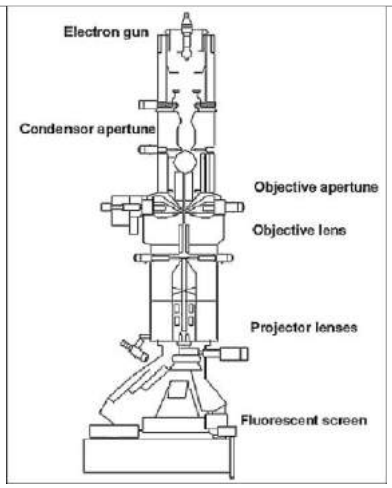


**Fig.4:** Components of transmission electron microscopy (TEM) instrument

***Thermo Gravimetric Analysis [TGA]:*** This technique a nanomaterial sample is heated and component with the different degradation temperature decompose and vaporize and a change of mass is recorded. It is thermal analysis technique which measures the weight change in the material as a function of temperature and time in a controlled environment. This is very useful to investigate the thermal stability of material it's behavior in different atmospheric thermogravimetric analysis is a type of testing performed on samples that determine change in weight in relation to change in temperature and temperature change. TGA is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas which dissociate into the air. The original mixture the total mass of impurities Liberating upon heating, The Stoichiometric ratio can be used to calculate the percentage mass of the substance in a sample. Inorganic and Organic components in materials decomposition points of explosive and solvent residues. Thermal analysis and weight loss of the sample are observed by S-11EXSTAR 600, TGA-6300. Thermal analyzer as a simultaneous measurement of these two material properties not only improve productivity but also simplifies interpretation of the result.

**Fig.5:** Thermo Gravimetric analyser (TGA)

***Particle Size Analyzer (PSA):*** The technique of particle size analyzer is ideally suited for the determination on of the size of particles in the nanometer size range. Nano-series uses optics that provides exceptional level of sensitivity and allows the determine of the size of sample that contain very small particles that are present very low concentration. In addition, the back scattered optics allows for the measurement of sample at Higher concentration then possible conventional DLS instruments using $90^0$ detection angles. Particle size is important parameter for the characterization of nanoparticles. The technique of dynamic lights scattering is well suited to the measurement of the size of nanoparticles dispersion

**Fig.6:** Particle Size Analyser (PSA)

***Ultraviolet Visible Spectroscopy:*** Ultraviolet visible spectrophotometer involving the Spectroscopy of photons in the UV visible region. it uses light in the visible adjacent near UV and infrared range .and UV- visible spectrophotometer are mainly used to measure transmission or Absorption in liquid and transparent solid, light through the sample and then monitoring the remaining light in a detector. UV-visible spectrophotometer the light is in the wavelength 800-200 nm. It is hard to reach a lower wavelength 200 nm as oxygen start to absorb light below wavelength. When the light passes through the sample some of the molecule in the sample will absorb lights various wavelength of spectrum depending their chemical bands and structure. Spectrophotometer records the wavelength at which absorption occur together with the degree of absorption at each wavelength at which absorption occur together with the absorption at each wavelength resulting spectrum is presented as a graph of absorbance versus wavelength.

**Fig.7:** UV-Visible Double Beam Spectrophotometer

## CONCLUSION

The role of several different techniques for the characterization of nanomaterial though this compressive summary of nanoparticle characterization methods we demonstrated the use of each one of them emphasizing on their advantages and limitations as well as on explaining how they can complement each other. The basic principles of characterization techniques X-rays diffraction, SEM, TEM particle size analyzer uv-visible Spectroscopy are discussed. Nano particle characterization parameter includes surface area and porosity solubility particle size distribution. Surface analysis, shape and size of interactive surface. In this way researchers will be helped for the choice of the most suitable techniques for their characterization together the ability to assess their use in more precise manner. Therefore, we finally hope that a careful reading of this will help to identify which valuable techniques merit efforts for further technical improvements.

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# Bio Nanoparticles: Building Blocks of Nanotechnology

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## INTRODUCTION

It has been observed that in the development of science and technology different disciplines have been emerged as important branches which have helped in the development of technology. One such branch which is playing very important role in modern medicinal system is Nanoscience and nanotechnology. The term Nanoscience refers to the study of structures and molecules on the scale of nanometer ranging from 1 to 100 nm. The prefix 'Nano' is referred to a Greek prefix meaning 'dwarf' or something very small and depicts one thousand millionth of a meter ($10^{-9}$ m). Nanotechnology is the branch of applied science which utilizes Nanoscience in practical applications. Nanotechnology is one of the most promising technologies of the present century.

The National Nanotechnology Initiative (NNI) of the United States define Nanotechnology as "a science, engineering, and technology conducted at the nanoscale (1 to 100 nm), where unique phenomena enable novel applications in a wide range of fields, from chemistry, physics and biology, to medicine, engineering and electronics". Nanoscience is a convergence of physics, materials science and biology, which deal with manipulation of materials at atomic and molecular scales; while nanotechnology is the ability to observe measure, manipulate, assemble, control, and manufacture matter at the nanometer scale [1].

After fifteen years of the pioneer lecture of Richard Feynman introducing the concept of nanotechnology in 1959, Norio Taniguchi, a Japanese scientist was the first to use and define the term "nanotechnology" in 1974 as: "nanotechnology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule" [2].

## HISTORY OF NANOTECHNOLOGY

In the ancient world nanoparticles and their structures have been used by Romans in fourth century AD. The Lycurgus cup represents one of the most outstanding achievements in ancient glass industry which is preserved in British museum. It is the oldest famous example of dichroic glass. This glass seems to be of two different types of glass, which change color in certain lighting conditions. This means that the Cup have two different colors: the glass appears green in direct light and red-purple when light shines through the glass.

During the 9th–17th centuries, glowing, glittering "luster" ceramic glazes used in the Islamic world, and later in Europe contained Ag or copper (Cu) or other nanoparticles. The Italians also employed nanoparticles in creating Renaissance pottery during 16th century [3]. In 1857, Michael Faraday studied the preparation and properties of colloidal suspensions of "Ruby" gold. Their unique optical and electronic properties make them some of the most interesting nanoparticles. Faraday demonstrated how gold nanoparticles produce different-colored solutions under certain lighting conditions.

## NANO PARTICLES

Nanoparticles are spherical, polymeric particles composed of natural or artificial polymers. They range in size between 10 and 500 nm. As a consequence of their spherical shape and high surface area to volume ratio, these particles have a wide range of potential applications. Nanoparticles are distinguished from micro particles size between 1-1000 µm, "fine particles" sized between 100 and 2500 nm, and "coarse particles" size from 2500 to 10,000 nm, because their smaller size drives very

different physical or chemical properties, like colloidal properties and ultrafast optical effects or electric properties.

Nanoparticles occur widely in nature and are studied in many disciples of science such as chemistry, physics, geology, and biology. They are an important component of atmospheric pollution, and key ingredients in many industrialized products such as paints, plastics, metals, ceramics, and magnetic products. The production of nanoparticles with specific properties is a branch of nanotechnology.

Many properties of nanoparticles, for example stability, solubility, and chemical or biological activity, can be altered by coating them with various substances referred as functionalization. Functionalized Nano material based catalysts can be used for catalysis of many known organic reactions. Nanoparticles can be linked to biological molecules that can act as address tags, directing them to specific sites within the body specific organelles within the cell, or causing them to follow specifically the movement of individual protein or RNA molecules in living cells.

## BIO NANOPARTICLES

Bio-based nanoparticles are getting importance due to their eco friendly and economic nature. They are mainly synthesized by following bottom-up approach. Because of highly catalytic activity of nanoparticles providing surface area, ion exchange capacity, fluorescence activity, and presence in different dimension such as metals, ceramics, and magnetic they are used in the field of agriculture such as soil nutrients, crop protectants, environment cleanup, contaminant detection, and reduction of post-harvest losses [4].

There are many types of nanoparticles differing with size, shape, compositions, and function. Nanoparticles are very small in size and dimension. Nanoparticles can be coated with the biological molecules which provide the ability to interact with specific target site. Bio-nanoparticles are the building blocks for nanotechnology; they are better built, long lasting, cleaner, safer, and smarter products for use across industries, including communications, medicine, transportation, agriculture and other industries. Some of the bio nanoparticles which are mentioned are as below.

1. ***Liposomes as Nanoparticles:*** Size of liposomes is found to be in the range of 10-100 nm. Liposomes are spherical vesicles that contain a single or multiple bi-layered structures of lipids that self-assemble in aqueous systems. Liposomes have marked their importance in biophysical research applied for research in drug delivery process. Liposomes have diverse range of compositions, abilities to carry and protect many types of bio-molecules.
2. ***Albumin-bound Nanoparticles:*** Albumin is a versatile biomaterial for synthesis of nanoparticles [6]. Furthermore, albumin can bind to special receptors over expressed on cancer cells and enhance nanoparticles binding and internalization. Albumin-bound nanoparticles use the endogenous albumin pathways to carry hydrophobic molecules in the bloodstream. Albumin naturally binds to the hydrophobic molecules with non-covalent reversible binding, avoiding solvent-based toxicities for therapeutics [7-8].
3. ***Polymeric Nanoparticles:*** The use of polymers as biomaterials has grown tremendously in last decades. Different types of polymeric materials have been used in variety of biomedical research.
4. ***Quantum dot:*** Quantum dots are semiconductor particles that are having less than 10 nm in diameter which are used as nanoparticles. Quantum dots display unique size-dependent electronic and optical properties. They have several significant advantages over many organic fluorophore dyes for optical applications. They are widely used in biological research as fluorescence imaging tools for applications such as cell labeling and bimolecular tracking. The small size of quantum dots also enables them to be suitable for biomedical applications such as medical imaging and diagnostics [9-12].

## APPLICATIONS

Some of the applications of nanomaterials to biology or medicine is given below can be put forth as below without their detailing. Biological nanoparticles now a day find important applications in Fluorescent biological labels, Drug and gene delivery, Bio detection of pathogens ,Detection of proteins, Probing of DNA structure, Tissue engineering, Separation and purification of biological molecules and cells etc.

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# X-ray investigations and microstructural analysis of Nd doped Co-Ni ferrites

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## ABSTRACT

Polycrystalline nanopowders of Nd doped Co-Ni spinel ferrites were synthesized by suing sol-gel auto combustion technique. The powders were sintered at 600 $^0$C for 6 hours in air atmosphere. The final powders were characterized by using powder X-ray diffraction (XRD) technique. The analysis of XRD data reveals the cubic spinel structure of the samples with secondary phase of $\alpha$-$Fe_2O_3$. Williamson – Hall, Size – strain plot and Halder – Wagener methods have been adopted for the estimation of average crystallite size and lattice strain induced in the crystal lattice. Average crystallite size obtained from W-H analysis is found in the range 16.5 to 21.1 nm which is analogus with the results obtained from SSP and H-W analysis. Lattice strain induced in the crystal lattice is of tensile type and shows increasing trend with $Nd^{3+}$ substitution in Co-Ni lattice.

***Keywords:*** *Spinel Ferrite, W-H analysis, SSP method, H-W Method, lattice strain.*

## INTRODUCTION

Semiconductor nanoparticles, falling within the 1 to 100 nm range, manifest distinctive size-related physical traits that set them apart from their larger counterparts [1,2]. Elastic characteristics assume a pivotal role among these traits, exerting influence on optical and surface properties. Notably, Cobalt Nickel (Co-Ni) nanoparticles are widely employed in optoelectronics, with applications spanning light-emitting diodes [3] and solar cells [4]. exhibit cubic (zinc blende) and hexagonal (wurtzite) lattice structures [5], attainable through diverse synthesis methods [6–8]. The intrinsic strain within nanocrystals, arising from confinement in size, can be fine-tuned by adjusting synthesis parameters like pH and concentration, thereby influencing optical and related properties [9]. X-ray Diffraction (XRD) analysis serves as a crucial tool in unveiling crystallinity, showcasing discernible peaks corresponding to reflection planes [10]. Nanocrystals undergo peak broadening due to both size-dependent and strain-induced factors [11], with sources of lattice strain encompassing dislocation density, point defects, grain boundaries, and stacking faults [12–15]. Analysis of XRD peak broadening, utilizing methodologies such as Williamson-Hall, Warren-Averbach, and Balzar, indirectly determines the size and intrinsic strain of nanocrystals. Williamson-Hall analysis, particularly via the Uniform Deformation Model (UDM), Uniform Stress Deformation Model (USDM), and Uniform Deformation Energy Density Model (UDEDM), calculates elastic parameters like strain, stress, and energy density. The Size Strain Plot (SSP) focuses on low-angle XRD peaks for precise size estimation, surpassing Williamson-Hall in accuracy [16–18]. The Halder-Wagner Method, assuming peak broadening as a Voigt function, estimates average size and strain [19].

This investigation juxtaposes the elastic parameters of chemically synthesized Co-Ni nanocrystals using diverse models of the Williamson-Hall plot, in conjunction with SSP and the Halder-Wagner Method.

## EXPERIMENTAL DETAILS:

Nanoparticles with the chemical composition $Co_{0.7}Ni_{0.3}Nd_xFe_{2-x}O_4$, where x takes values of 0.0, 0.05, 0.1, 0.15, and 0.20, was synthesized employing a sol-gel auto-combustion methodology. Analytical grade $Co(NO_3)$ •$6H_2O$, $Ni(NO_3)_2$•$6H_2O$, $Fe(NO_3)_3$•$9H_2O$, $Nd(NO_3)_3$•$6H_2O$ (99.99% pure), and citric acid was utilized as meticulously measured raw precursors. Citric acid served as a complexing agent to achieve a transparent solution with a uniformly distributed metal ion composition. The amalgamated mixture underwent a 2-hour stirring process to attain a homogeneous and clear solution, subsequently being heated to 100°C using a hot plate magnetic stirrer. The solution's pH was further adjusted to 7 by the incremental addition of ammonia solution. Evaporation of the resulting solution on a hot plate, coupled with continuous stirring, induced the formation of a continuous gel network. Continuous heating of the gel precipitated a rapid, flameless auto-combustion reaction, releasing a substantial volume of gases and yielding a burned powder of the final product. The resultant burned gel was meticulously ground to obtain a finely divided ferrite powder, utilizing an Agate Mortar and pestle. Subsequently, the ground powders were subjected to sintering in an air environment at 600°C for a duration of 6 hours, followed by a controlled cooling process to achieve room temperature.

## RESULTS AND DISCUSSION

***X-ray Diffraction (XRD):*** Figure 1 Shows X-ray diffraction (XRD) patterns of $Nd^{3+}$-doped Ni-Co spinel ferrite nanoparticles, represented by the formula $Co_{0.7}Ni_{0.3}Nd_xFe_{2-x}O_4$, where x varies (0.0, 0.05, 0.1, 0.15, and 0.20). Synthesized via the sol-gel auto-combustion method, these nanoparticles incorporate $Nd^{3+}$ ions in concentrations ranging from x=0.05 to 0.20. With a larger ionic radius (0.983 Å) than $Fe^{3+}$ ions (0.64 Å), $Nd^{3+}$ ions were introduced in minimal concentrations to avoid significant alterations in cation distribution and consequent effects on structural and magnetic properties. XRD analysis confirms all compositions exhibit a cubic spinel ferrite structure, featuring matched diffraction peaks (220), (311), (222), (400), (422), (333), (440) and (533) in the Fd3m space group. secondary peaks Appears like $*= \alpha -Fe_2O_3$, common in rare earth-doped ferrites was observed [20]. Additionally, the larger ionic radius of $Nd^{3+}$ ions may induce lattice distortion and lower lattice fringe alignment [21].

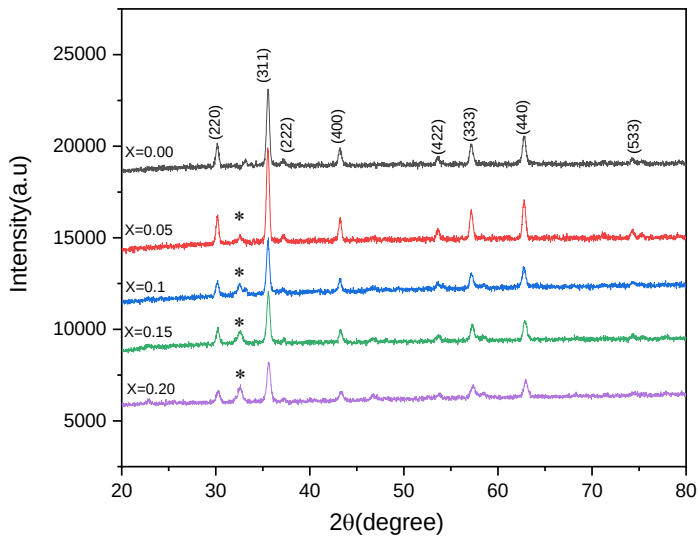


**Fig 1:** XRD plot of $Co_{0.7}Ni_{0.3}Nd_xFe_{2-x}O_4$ for (x=0.00,0.05,0.1,0.15.0.20)

## WILLIAMSON- HALL METHOD

Internal strain in nanocrystals primarily results from imperfections in crystal structure and lattice distortions, leading to the broadening of X-ray diffraction peaks. The Scherrer formula, commonly used for peak broadening, neglects the effect of microstrain. The Williamson-Hall (W-H) method, a simplified approach, addresses both size-induced broadening ($b_{size}$) and strain-induced broadening ($b_{strain}$) [22].

In this method, the total physical broadening ($b_{total}$) is the sum of $b_{size}$ and $b_{stra}$

$$\beta = \beta_{Size} + \beta_{Strain} \quad (1)$$

Stokes' law establishes a relationship between strain (Ɛ) and broadening, expressed as:

$$\varepsilon = \frac{\beta_{Strain}}{4\tan\theta} \quad (2)$$

The total broadening ($b_{hkl}$) measured in radians for specific (hkl) planes is given by:

$$\beta_{hkl} = \beta_d + \beta_{Strain} \quad (3)$$

In the Scherrer formula, size-induced broadening ($b_{d)}$is expressed as $k_\lambda$/Dcosθ where k is a constant, λ is the X-ray wavelength, D is the average particle size, and θ is the diffraction angle. Consequently, the total broadening is:

$$\beta_{hkl} = \frac{k\lambda}{D\,Cos\,\theta} + \frac{4\varepsilon}{\tan\theta} \quad (4)$$

Rearranging equation (4) yields:

$$\beta_{hkl}\,Cos\,\theta = \frac{k\lambda}{D} + 4\varepsilon\,Sin\,\theta \quad (5)$$

Equation (5) represents a linear relationship. A graph can be plotted with Sinθ as the abscissa and ($b_{hkl}Cos\theta$)as the ordinate for XRD peaks of (220), (311), (222), (400), (422), (333), (440) and (533) [23].

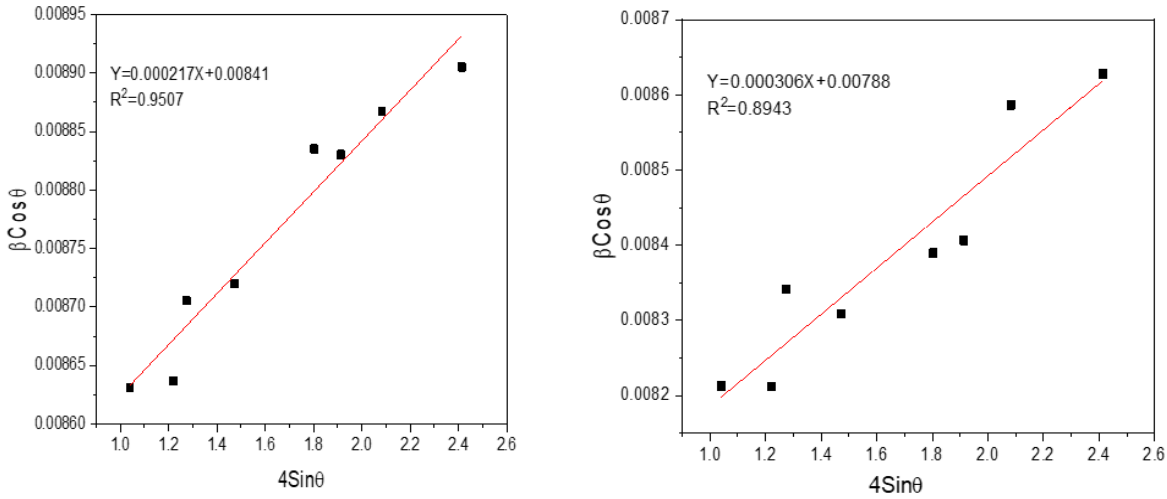


**Fig 2:** Williamson-Hall plot for (X=0.00,0.05)

## SIZE-STRAIN PLOT

The Williamson-Hall (W-H) method characterizes isotropic peak broadening resulting from the combination of size and strain effects as a function of the diffraction angle (2θ). For a more precise assessment of size and strain values, the 'size-strain plot' (SSP) method is employed. In SSP, the peak profile is modeled as a convolution of two functions, Lorentzian ($b_L$) for size broadening and Gaussian ($b_G$) for strain broadening [24,25 -27]. The SSP method prioritizes reflections at lower 2θ angles, enhancing accuracy and precision.

According to the SSP model, the total XRD broadening is given by

$$\beta_{hkl} = \beta_L + \beta_G \quad (6)$$

The SSP model incorporates the relationship between crystallite size and lattice strain through the following relation:

$$\left(\frac{\left(d_{hkl}^2\beta_{hkl}\,Cos\,\theta\right)^2}{\left(d_{hkl}\beta_{hkl}\,Cos\,\theta\right)^2}\right) = kD\frac{\left(d_{hkl}\beta_{hkl}\,Cos\,\theta\right)^2}{4} + \frac{\varepsilon^2}{4} \quad (7)$$

where $d_{hkl}$ represents the lattice spacing for different hkl planes.

$$d_{hkl}^2 = a^2\left(h^2 + k^2 + l^2\right) \quad (8)$$

The SSP model is graphically represented by plotting ($d^2_{hkl}.b_{hkl}$. Cosθ ) against ($d_{hkl}.b_{hkl}$.Cosθ )$^2$ (Fig. 3). The slopes of these straight-line graphs yield the respective average sizes for $Co_{0.7}Ni_{0.3}Nd_xFe_{2-x}O_4$

as 11.41nm and 11.96 nm. Simultaneously, the strain values are determined from the intercepts as 7.72 x $10^{-4}$ and 7.38 x $10^{-4}$

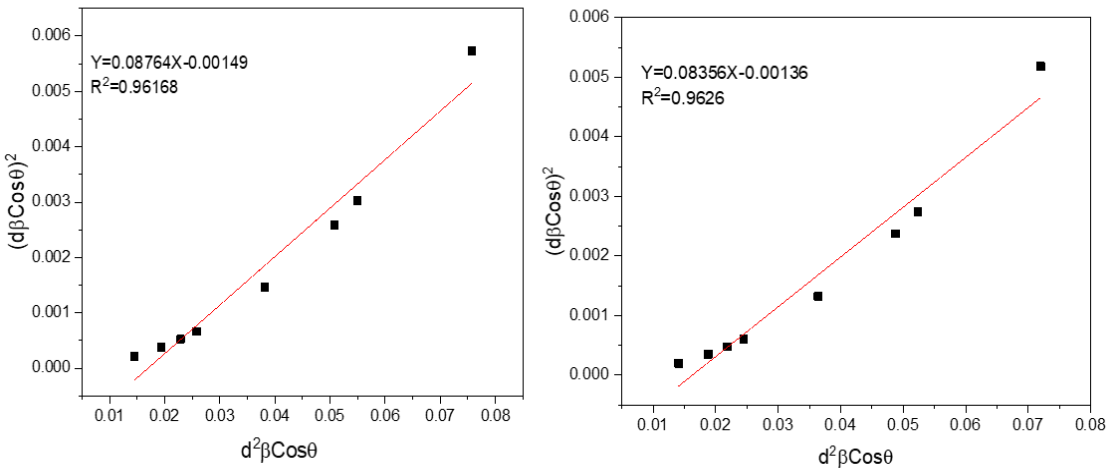


**Fig 3:** Size- Strain plot for (X=0.00,0.05)

## HALDER- WAGNER METHOD

XRD peak broadening, as observed in the SSP method, deviates from precise description by Lorentzian and Gaussian functions. The Gaussian function fits well in the peak region, but its tails fall off rapidly, while the Lorentzian function matches well with the tails but not the peak region. To address this, the Halder-Wagner (H-W) method proposes the use of a symmetric Voigt function, a convolution of the Lorentzian and Gaussian functions, accurately capturing the entire XRD peak profile [25,28]. The H-W method, emphasizing the lower and mid-angle region with minimal overlapping, is particularly suitable for assessing size and strain [29,30].

According to the Halder-Wagner Method, the Full Width at Half Maximum (FWHM) is expressed

$$\beta_{hkl}^2 = \beta_L \beta_{hkl} + \beta_G^2 \quad (9)$$

$$\left(\frac{\beta_{hkl}}{d_{hkl}}\right)^2 = \frac{1}{D}\left(\frac{\beta_{hkl}}{d_{hkl}}\right)^2 + \varepsilon^2 \quad (10)$$

Where $\beta_{hkl} = \beta hkl \frac{\cos\theta}{l}$ and $d_{hkl} = \frac{2\sin\theta}{l}$

Halder-Wagner plots are obtained by plotting the term $\left(\frac{\beta_{hkl}}{d_{hkl}}\right)$ along the abscissa and $\left(\frac{\beta_{hkl}}{d_{hkl}}\right)^2$ along the ordinate (Fig.4). The intercept of the plot provides the intrinsic strain, while the slope offers the average size. The average sizes calculated from the slope are 87.26 nm and 89.28 nm for $Co_{0.7}Ni_{0.3}Nd_xFe_{2-x}O_4$. The respective strain values, calculated from the intercept, are 3.99 x $10^{-3}$ and 4 x $10^{-3}$ for indicating a lower strain compared to the SSP method.

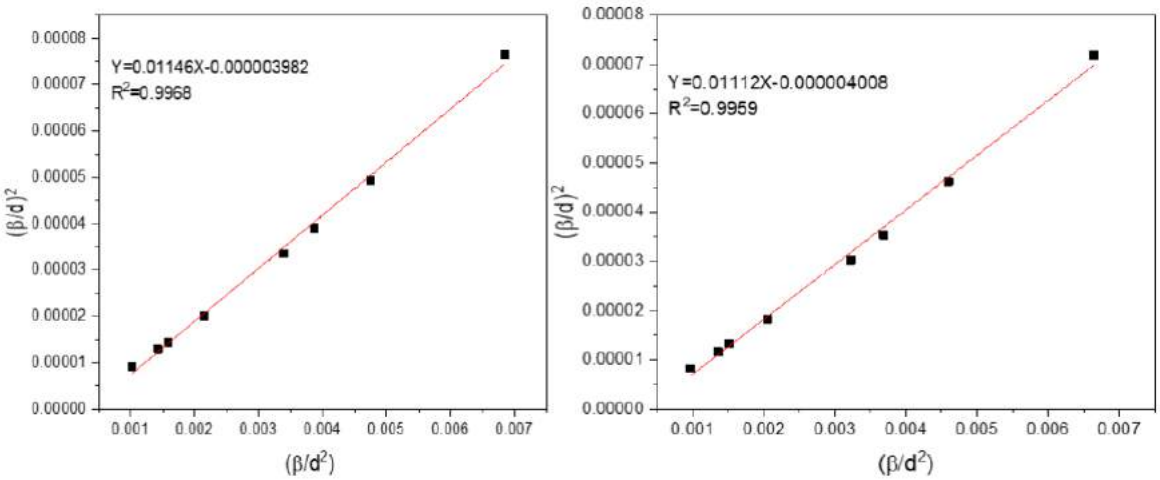


**Fig 4:** Halder-Wagner Method for (X=0.00,0.05)

**Table 1:** The results of crystallite size and lattice strain of the Williamson-hall method, Size-strain plot method, and Halder-Wagner method

| Composition | Williamson-hall method | | Size-Strain plot | | Halder-Wagner method | |
|---|---|---|---|---|---|---|
| | D(nm) | Ɛ x $10^{-4}$ | D(nm) | Ɛ x $10^{-4}$ | D(nm) | Ɛ x $10^{-3}$ |
| X=0.00 | 16.5 | 2.18 | 11.41 | 7.72 | 87.26 | 3.99 |
| X=0.05 | 17.6 | 3.06 | 11.96 | 7.38 | 89.28 | 4 |
| X=0.1 | 18.8 | 3.92 | 12.62 | 7.01 | 93.1 | 3.93 |
| X=0.015 | 19.9 | 4.66 | 13.07 | 6.78 | 95.05 | 3.97 |
| X=0.2 | 21.1 | 5.25 | 13.64 | 6.48 | 97.75 | 3.94 |

## CONCLUSIONS

The Halder-Wagner method, appears to be a technique that emphasizes high accuracy in its results. The method utilizes equations designed to position points as closely as possible to a straight line in a diagram. This approach likely contributes to the precision of the measurements obtained using the Halder-Wagner method.One notable aspect is the convergence in results between the Halder-Wagner method and two other methods mentioned: the Williamson-Hall method and the Size-strain plot method. All three methods seem to share a commonality in relying on graphical representations to calculate crystal size and micro strain. This convergence in results suggests a consistency and reliability across these different techniques, reinforcing their validity for determining crystallographic parameters.

In summary, the Halder-Wagner method is highlighted for its accuracy, with a notable agreement in results when compared to the Williamson-Hall method and the Size-strain plot method. The reliance on graphical representations in these methods underscores the importance of visualizing diffraction patterns for extracting information about crystal size and micro strain**.**

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# ANTAGONISTIC ACTIVITY OF *TRICHODERMA* ISOLATES AND *RUMEX ACETOSA* LEAF SPOT AND WILT CAUSATIVE AGENTS

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## ABSTRACT

Biological control of plant pathogens using antagonistic fungi can be successfully utilized especially within the frame work of integrated disease management system. Efficacy of different isolates of *Trichoderma* species against two pathogenic fungi causing leaf spot (*Alternaria tenuissima*) and wilt (*Fusarium proliferatum*) on Chuka, *Rumex acetosa* L. by dual culture technique under *in vitro* conditions. Generally *Trichoderma* used as a biological control for the inhibition of growth of the pathogens. Different isolates of *Trichoderma viride* (12), *T. harzianum* (12), *T. koningii* (07), *T. pseudokoningii* (05) and *T. virens* (10) strains were isolated and used for antagonistic study. Results indicated that, among *T. viride* isolates, $Tv_1$ & $Tv_5$ showed maximum antagonism, whereas $Tv_7$ and $Tv_{10}$ showed minimum antagonism against *A. tenuissima F. proliferatum* showed significant inhibition by $Tv_4$ and reduced the percent inhibition by $Tv_8$ and $Tv_6$. In case of *T. harzianum* isolates, $Th_3$ and $Th_{10}$ showed maximum inhibition on *A. tenuissima* while in *F. proliferatum*, $Th_5$ increased the inhibition and decreased in $Th_3$ and $Th_7$. *Trichoderma koningii* showed better results in $Tk_7$ isolate whereas decreased $Tk_4$ over *A. tenuissima*, but in *F. proliferatum* reduced rate was more in $Tk_4$ and $Tk_2$. Isolates of *T. pseudokonongii* found maximum inhibition in $Tp_5$ over *A. tenuissima* and significant inhibition in $Tp_3$ over *F. proliferatum*. *Trichoderma virens* isolates were found significant inhibition in $Tvr_4$ and $Tvr_9$ and 50% reduction over *A. tenuissima* and $Tvr_4$ increased the percent inhibition and decreased the $Tvr_7$ in case of *F. proliferatum.* Among all isolates $Tk_4$ (42.77%) found least and $Tvr_4$ (86.66%) found most effective against *A. tenuissima*, whereas $Tv_8$ (23.21%) showed minimum and $Tv_4$ (90%) found better antagonism against *F. proliferatum* .It is concluded that the *T.viride* and *T.virens* is suitable for antagonistic activity against tested pathogens.

**Key words:** *Alternaria tenuissima* , *Fusarium proliferatum*, isolates of *Trichoderma* species, dual culture,

## INTRODUCTION

Chuka , *Rumex acetosa* L.(Polygonaceae) is an important vegetable crop in many diseases have been reported (Correl and Monelok, 1994; Sumner, 1991; Walker, 1952; Bhale, 2002;) to be causes discolouration, spoilage of seeds, germination effects, rotting and wilting of seedlings and leaf spot,. Among them leaf spot (*Alternaria tenuissima*) and wilt (*Fusarium proliferatum*) diseases to be found severe in the field (Bhale, 2011). Only practical solution seems to be use of resistant variety. However, resistant varieties for these diseases are not available in the literature. Moreover, the crop loss due to these diseases is substantial as it leads to capital losses up to 20 to 60% (Bhale *et al.*, 2010). Biocontrol agents for protection of seeds and control of seed borne diseases offer farmers an alternative source of chemical fungicides which is highly effective (Callan *et al*., 1997). Fungicides such as metalaxyl, are however expensive and growers tend to use lower than optimum dosages (Csoinos and Bertrand, 1994). Furthermore, the use of fungicides, besides being expensive and involving risks to the environment associated with the application of chemicals, is not totally effective and may lead to the appearance of new, resistant strains of pathogens (Bruin and Edgington, 1980). *Trichoderma* has been the focal point of a number of studies concerning their ability to control plant pathogens. Strains of the species *T. harzianum* has shown effectiveness when used in disease control caused by several fungi, including *Sclerotium rolfsii*, a widely distributed and highly destructive plant pathogen (Benhamou and Chet, 1996), and *Sclerotinia sclerotiorum* affecting runner beans (Inbar *et al.* 1996). In a similar fashion, strains of *T. harzianum*, *T. koningii*, and *T. longibrachiatum* have been effective in *Armillaria* control in tea (Osando and Waudo, 1994), while *T. koningii* has been used for *Fusarium solani* corn rot control

(McAllister *et al*. 1994). *Trichoderma harzianum* (Th1), *T. viride* (Tv1) and*T. spirale* (Ts3) isolates showed different inhibitory effect against R*hizoctonia solani* (RS) and *Fusarium oxysporum* f.sp. *phaseoli* (Nashwa *et al*.,2008). *Trichoderma* strains could reduce significant diseases caused by fungal pathogens including: *Phytophthora palmivora*, *Rhizoctonia solani*, *Fusarium* spp., *Sclerotium rolfsii* and *Pythium* spp**. (**Tran, 2010). The *Trichoderma viride* isolate Tr 8 could be further exploited for commercial scale up under localized climatic conditions (Mishra *et al.*, 2011**).**

It is therefore necessary to develop alternative ways of control. One such alternative is biological control, in which microorganisms are selected for their ability to antagonize pathogens. Therefore an investigation was undertaken to evaluate the efficacy of different isolates of *Trichoderma* species against the pathogenic fungi such as *A. tenuissima* and *F. proliferatum* of chuka.

## MATERIAL AND METHODS

### Isolation of *Trichoderma* spp

Rhizosphere soils of irrigated and non irrigated plants were collected from different locality of Marathwada region of Maharashtra state. From the rhizosphere soil samples, desired strain of *Trichoderma* species were isolated by using potato dextrose agar (PDA) and *Trichoderma* selective medium (TSM) by dilution plate technique (Johnson, 1957). The isolated strains were identified by reculturing on another petriplates containing sterilized TSM. The isolated strains were identified up to species level based on colony characters, growth of fungus, structure of mycelium, conidiophores and conidia. All *Trichoderma* spp. fungi were purified by hyphal tip technique and identified on the basis of cultural, microscopic and morphological characters (Kubicek and Harman, 2002). The isolated strains of *Trichoderma* species were maintained on PDA and TSM slants. This was maintained throughout the study by periodical transfers on (PDA) medium under aseptic conditions, to keep the culture fresh and viable.

### Isolation of test pathogens

Test fungi *A. tenuissima and F. proliferatum* were isolated from the diseased part viz leaf spot and wilt of Chuka (*Rumex acetosa* L.) respectively Earlier, the pathogencity of test fungi were confirmed in inoculating chuka seedlings properly. The isolated test fungi were purified on aseptic conditions and maintained on PDA slants.

### Dual culture experiment

Antagonistic efficacy of different isolates of *Trichoderma* species such as *T. viride, T. harzianum, T. koningii, T. pseudokoningii* and *T. virens* were tested against the isolated pathogenic test fungi using Morton and Stroube (1955) method. *Trichoderma* species and test fungi were inoculated at 6 cm apart. Three replications were maintained for each treatment and incubated at 27± 2° C for 7 days. Monoculture plates of both are served as control. After 7 days, radial growth of test fungi and *Trichoderma* isolates were measured. Colony diameter of test fungi in dual culture plate was observed and compared with control. Antagonistic effect of *Trichoderma* spp., as decrease of the mycelial growth of pathogenic fungi was determined using the Vincent (1947) method.

## STATISTICAL ANALYSES

Statistical analyses of the experiment was performed using the handbook of biological statistics by Mungikar (1997).

## RESULTS AND DISCUSSION

### Isolation of *Trichoderma* species and test pathogens

Five species of *Trichoderma*, T. *viride* (12), *T. harzianum* (12*), T. koningii* (07), *T.pseudo koningii* (05) and *T. virens* (10) were isolated from irrigated and non-irrigated rhizosphere soil of Marathwada region. Results indicated that *A. tenuissima and F. proliferatum* were significantly influenced by various isolates of *Trichoderma* species under study at 7 days after inoculation (DAI).

### Dual culture experiment

Table 1 indicated that *T. viride* isolates on growth of *A. tenuissima* $Tv_1$ and $Tv_5$ showed maximum antagonism as compared to other isolates. However, $Tv_7$ and $Tv_{10}$ decreased the antagonism. While in case of *F. proliferatum* showed greater inhibition by $Tv_4$ followed by $Tv_3$, but $Tv_8$ and $Tv_6$ reduced the percent inhibition. *Trichoderma harzianum* isolates on growth of *A. tenuissima* were found more percent inhibition in $Th_3$ and $Th_{10}$. In case of *F. proliferatum* increased the percent inhibition in $Th_5$ whereas decreased in $Th_3$ and $Th_7$ (Table 2).

**Table 1.** Influence of *T. viride* isolates on the radial growth (RG) (mm) of *A. tenussima* (AT) and *F. proliferatum* (FP) Seven days after inoculation.

| Isolates | Locations | RG of AT | Inhibition (%) | RG of FP | Inhibition % |
|---|---|---|---|---|---|
| $Tv_1$ | Naldurg | 14.20 | 84.44 | 40.20 | 55.50 |
| $Tv_2$ | Osmanabad | 17.20 | 81.58* | 27.30 | 69.66 |
| $Tv_3$ | Latur | 22.30 | 75.22 | 12.50 | 86.11 |
| $Tv_4$ | Nanded | 35.34 | 61.00 | 10.00 | 91.00 * |
| $Tv_5$ | Jalna | 15.95 | 82.16* | 44.23 | 50.85 |
| $Tv_6$ | Aurangabad | 27.00 | 70.00 | 54.15 | 38.72$^+$ |
| $Tv_7$ | Beed | 54.15 | 37.72 $^+$ | 27.00 | 70.00 |
| $Tv_8$ | Paranda | 25.10 | 72.11 | 61.00 | 32.22 $^+$ |
| $Tv_9$ | Ashti | 18.95 | 78.94 | 47.60 | 47.12 |
| $Tv_{10}$ | Omerga | 49.20 | 44.12 $^+$ | 29.00 | 67.77 |
| $Tv_{11}$ | Ahmedpur | 36.35 | 56.61 | 69.11 | 23.21 $^+$ |
| $Tv_{12}$ | Hingoli | 27.50 | 69.44 | 47.60 | 47.11 |
| CD(P=0.05) | | | 13.14 | | 9.53 |

DAI- Days after inoculation, * - Increased percent inhibition, +- Decreased percent inhibition

*Trichoderma koningii* isolates on growth of *A. tenuissima* showed more antagonism in $Tk_7$ but decreased in $Tk_4$. But in case of *F. proliferatum* found more percent inhibition in $Tk_3$ as compared to other but reduced the percent inhibition $Tk_4$ and $Tk_2$ (Table 4). At 7 days after incubation (DAI), *T. pseudokoningii* isolates on growth of *A. tenuissima* was observed maximum in $Tp_5$ and in case of *F. proliferatum* was found maximum in $Tp_3$ (Table 4). Table 5 illustrated that *T. virens* isolates on growth of *A. tenuissima,* maximum percent inhibition showed $Tvr_4$ and $Tvr_9$ but 50% inhibition was found in case of $Tvr_7$. Maximum percent inhibition was observed in $Tvr_4$ and minimum in $Tvr_7$ in case of *F. proliferatum*

Among all isolates of *T.viride*, isolate no $Tv_1$ for *A. tenuissima* and isolate no $Tv_4$ for *F. proliferatum* was found suitable for antagonism. In *T. harzianum*, isolate no $Th_4$ for *A. tenuissima* and isolate no $Th_5$ for *F. proliferatum* was found maximum percent antagonism. In case of *T. koningii*, isolate no $Tk_7$ for *A. tenuissima* and isolate no $Tk_3$ for *F. proliferatum* was found significant antagonism. In *T. pseudokoningii* isolate no $Tp_5$ for *A. tenuissima* and isolate no $Tp_3$ for *F. proliferatum* was observed bioefficacy. In *T.virens* isolates no $Tvr_4$ and $Tvr_9$ were suitable for antagonism but maximum percent inhibition was failed in *F. proliferatum.*

Several workers have been reported that the use of *Trichoderma* species against number of plant pathogenic fungi (Brisa *et al.*, 2007; El-Mougy *et al.*, 2007; Dubey *et al.*, 2007; Harman, 2006).*Trichoderma viride* and *T. koningii* were found to be effective against *Rhizoctonia solani* (Mukhopadhyay, 1987), *T. hamatum* against *R. solani* (Lewis *et al*., 1990). In *in vitro,* control of *R. solani, F. oxysporum* and *Macrophomina phaseolina* were achieved with *T. koningii, T. hamatum* and *T. harzianum* (Arora, 1990). *Trichoderma harzianum* and *T. viride* were antagonistic to *F. oxysporum* f. sp. *lycopersici* (Gaikwad *et a*l., 1999) and to *R. solani* (Yadav and Tripathi, 1999). Recently, Waghmare and Kurundkar (2011) reported efficacy of *Trichoderma* species against *F. oxysporum* f. sp. *carthami* causing wilt of safflower and found that isolates no 29 and 33 were found minimum growth of the pathogen as compared to others. The species of *Trichoderma* significantly inhibited the mycelial growth of plant pathogens (Rajkonda *et al*., 2011).

According to Papavizas & Lumsden (1980) the mechanisms involved in the control of pathogens by *Trichoderma* spp. are probably: antibiosis, lysis, competition and mycoparasitism. Biological control may be more prudent to search for biological antagonists against specific pathogen and evaluate blends of antagonists for wider applications (Baker and Cook, 1974). In addition as suggested by Papavizas (1985) research should be directed towards the improvement of strains of biological agents that are more capable of becoming established and surviving under adverse field conditions. *Trichoderma viride* and *T. virens* is useful for formulation and proliferate the colony in the soil. Thus, it is obvious that biological control offers, durable environmentally safe and cost effective alternative to chemical for the efficient management of plant disease. Isolates of *Trichoderma* species were influenced by very significantly (P = 0.05) as a part of its antagonism against tested pathogens.

## CONCLUSION

*Trichoderma* species play an important role in controlling fungal plant pathogens, especially soil borne fungal pathogens. The use of *Trichoderma*-based products is not only safe for the farmers and consumers but it is also good for the environment. However, much more work needs to be done to develop stable, cost effective, easy to produce and easy to apply formulations.

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**Table 2.** Influence of *T. harzianum* isolates on the radial growth (RG) (mm) of *A. tenuissima* (AT) and *F. proliferatum* (FP) seven days after inoculation.

| Isolates | Locations | RG of AT | Inhibition (%) | RG of FP | Inhibition% |
|---|---|---|---|---|---|
| $Th_1$ | Tuljapur | 20.12 | 77.70 | 30.12 | 66.10 |
| $Th_2$ | Kallam | 34.12 | 62.08 | 37.10 | 58.77 |
| $Th_3$ | Ausa | 45.00 | 50.00 | 56.00 | 35.67 |
| $Th_4$ | Nanded | 13.00 | 87.66 * | 61.37 | 31.81 + |
| $Th_5$ | Badnapur | 41.17 | 54.25 | 17.42 | 80.64 * |
| $Th_6$ | Beed | 22.39 | 75.12 | 35.00 | 61.11 |
| $Th_7$ | Paithan | 24.11 | 73.21 | 50.23 | 45.18 |
| $Th_8$ | Paranda | 27.67 | 69.25 | 29.14 | 67.62 |
| $Th_9$ | Patoda | 35.00 | 61.11 | 47.17 | 47.58 |
| $Th_{10}$ | Nilanga | 15.20 | 83.22* | 24.27 | 73.03 |
| $Th_{11}$ | Udgir | 34.00 | 62.22 | 29.00 | 67.77 |
| $Th_{12}$ | Parbhani | 40.22 | 55.31 | 55.52 | 38.3 + |
| CD(P=0.05) | | | 7.11 | | 11.11 |

DAI- Days after inoculation, * - Increased percent inhibition, +- Decreased percent inhibition

**Table 3.** Influence of *Trichoderma koningii* isolates on the radial growth (RG) (mm) of *A. tenuissima* (AT) and *F. proliferatum* (FP) seven days after inoculation.

| Isolates | Locations | RG of AT | Inhibition (%) | RG of FP | Inhibition% |
|---|---|---|---|---|---|
| $Tk_1$ | Naldurg | 26.00 | 71.10 | 35.00 | 61.10 |
| $Tk_2$ | Osmanabad | 27.12 | 69.86 | 50.11 | 44.32 + |
| $Tk_3$ | Latur | 37.00 | 58.88 | 30.25 | 68.50* |
| $Tk_4$ | Aurangabad | 51.50 | 42.77 + | 57.44 | 36.17 + |
| $Tk_5$ | Jalna | 28.11 | 68.76 | 39.39 | 56.23 |
| $Tk_6$ | Parbhani | 32.35 | 64.05 | 38.57 | 57.14 |
| $Tk_7$ | Nanded | 13.35 | 87.30 * | 31.11 | 65.43* |
| CD(P=0.05) | | | 11.87 | | 11.20 |

DAI- Days after inoculation, * - Increased percent inhibition, +- Decreased percent inhibition

**Table 4.** Influence of *Trichoderma pseudokoningii* isolates on the radial growth (RG) (mm) of *A. tenuissima* (AT) and *F. proliferatum* (FP) seven days after inoculation.

| Locations | Locations | RG of AT | Inhibition (%) | RG of FP | Inhibition% |
|---|---|---|---|---|---|
| $Tp_1$ | Ausa | 25.00 | 75.40 | 36.00 | 62.11* |
| $Tp_2$ | Tuljapur | 29.25 | 67.50 | 37.25 | 58.61 |
| $Tp_3$ | Jalna | 22.11 | 75.43 | 24.00 | 73.33 |
| $Tp_4$ | Sillod | 39.15 | 56.50+ | 47.00 | 47.77 + |
| $Tp_5$ | Ardhapur | 15.00 | 85.11* | 33.00 | 65.11* |
| CD(P=0.05) | | | 4.65 | | 4.75 |

DAI- Days after inoculation, * - Increased percent inhibition, +- Decreased percent inhibition

**Table 5.**Influence of *Trichoderma virens* isolates on the radial growth (RG) (mm) of *A. tenuissima* (AT) and *F. proliferatum* (FP) seven days after inoculation.

| Locations | Locations | RG of AT | Inhibition (%) | RG of FP | Inhibition % |
|---|---|---|---|---|---|
| $Tvr_1$ | Naldurg | 24.00 | 74.00 | 27.00 | 70.00 |
| $Tvr_2$ | Murum | 24.15 | 73.16 | 30.11 | 66.54 |
| $Tvr_3$ | Beed | 29.11 | 67.65 | 34.39 | 61.78 |
| $Tvr_4$ | Badnapur | 10.00 | 90.16* | 20.22 | 80.62* |
| $Tvr_5$ | Kannad | 32.00 | 64.44 | 41.11 | 54.32 |
| $Tvr_6$ | Parbhani | 21.37 | 76.25 | 33.13 | 63.18 |
| $Tvr_7$ | Nilanga | 47.11 | 47.65 + | 52.11 | 45.32+ |
| $Tvr_8$ | Udgir | 27.35 | 69.61 | 34.11 | 62.10 |
| $Tvr_9$ | Nanded | 11.20 | 88.66 * | 33.12 | 63.20 |
| $Tvr_{10}$ | Hingoli | 31.34 | 65.17 | 28.05 | 68.83 |
| CD(P=0.05) | | | 8.13 | | 8.59 |

DAI- Days after inoculation, * - Increased percent inhibition, +- Decreased percent inhibition

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# Implications of pH and Sintering temperature on Structural Properties of Lithium Ferrite Nanoparticles

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## ABSTRACT

Lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$) nanoparticles with two pH values were synthesized by sol-gel auto combustion method and sintered at two different temperatures for the investigation of effect of pH and sintering temperature on structural parameters. Prepared samples were characterized by XRD and Raman. Formation of spinal structure is confirmed by XRD pattern with presence of secondary peak at $600^0$c which vanishes at $800^0$c temperature. Lattice parameter and crystallite size found to be increased with increasing sintering temperature and with decreasing stains and dislocation density in crystal lattice. Effect of pH value on lattice parameter was also observed. Formation of spinal structure was confirmed by the Raman spectra and effect of sintering temperature on it was also observed.

***Keywords:*** *$Li_{0.5}Fe_{2.5}O_4$, sol-gel, pH, sintering temperature, XRD, Raman*

## INTRODUCTION

"Ferrites" indeed refer to a class of magnetic materials that are typically non-metallic and ceramic in nature composed of iron oxide ($Fe_2O_3$) along with other metal oxides having increasingly importance in various technological fields due to their unique magnetic and electrical properties [1]. Spinal ferrite is magnetic material having interesting physicochemical properties such as high Curie temperature, saturation magnetization, resistivity, good hysteresis properties etc. [2-3] that make them valuable in development of more efficient and compact storage devices, helping to reduce unwanted electromagnetic interference in electronic circuits, manufacturing of microwave devices and in the recording & retrieval of information [4-5]. Lithium and substituted lithium ferrite is one of the interesting material in group of spinal ferrite having unique properties and applications due to arrangement of ions in the crystal lattice. It is a potential material for use as a cathode material in rechargeable lithium-ion batteries [6]. spinel type lithium ferrite has two its two crystalline forms namely as ordered α-$LiFe_5O_8$ and disordered β-$LiFe_5O_8$. In the ordered form of lithium ferrite $Fe^{3+}$ ions are positioned at both octahedral and tetrahedral sites within the crystal lattice and Lithium ions (Li+) are exclusively found in the octahedral positions within the cubic primitive unit cell. However, in disordered form of lithium ferrite rapid cooling of the samples from 800 °C to room temperature results in Inverse spinal structure belongs to space group Fd3m with random distribution of $Fe^{3+}$ and $Li^+$ ions [7-8]. Various chemical methods have been used, such as co-precipitation, hydrothermal sol-gel method and Auto-combustion method etc. Among these Auto-combustion synthesis is commonly employed method due to its simplicity, cost-effectiveness, and the ability to yield materials with improved properties [9-10]. Several factors affect on properties of ferrite material such as sintering temperature and time, particle size, value of pH, type and amount of dopant etc. The sintering temperature and time is crucial in the fabrication of ferrite materials to achieve the desired combination of density, microstructure, and magnetic properties for specific applications. Adjusting these parameters allows

manufacturers to tailor ferrite materials to meet the requirements of various electronic and magnetic devices [11]. Another important factor is value of pH which influence on particle size, shape, and overall structure. Considering influence of pH on structural and magnetic properties it is possible to use these materials to investigate its possible use in specific applications such as drug delivery, catalysis, or magnetic resonance imaging (MRI) etc.

In the present work lithium ferrite nanoparticles were synthesized using sol-gel auto combustion route for different values of pH and sintered at different temperature. The prepared samples were characterized by XRD and Raman to investigate effect of pH and sintering temperature on structural properties of lithium ferrite.

## EXPERIMENTAL PROCEDURE

To synthesize Lithium Ferrite nanoparticles ($Li_{0.5}Fe_{2.5}O_4$) by Sol- gel Auto combustion method precursors Lithium nitrate ($LiNO_3$), Ferric nitrate ($FeN_3O_9.H_2O$) and Citric acid ($C_6H_8O_7$) were dissolved in 200ml distilled water. The homogeneous solution was continuously stirred with 800 RPM and heated at about $77^0$C using magnetic stirrer and needle. 31 ml and 60 ml Ammonia was added to maintain pH value 7 and 8 respectively. Without considering presence of inert gases in laboratory reaction procedure was carried out in air atmosphere. After a several hours of heating very viscous brown gel were formed. When all water molecules get removed then viscous gel starts frothing. After few minutes it ignites automatically and burnt with glowing flints. Finally, resultant product was obtained in powder form after completion of combustion process. This powder was sintered at $600^0$c and $800^0$c in muffle furnace for 6 hours.

The obtained samples were characterized by XRD and Raman to analyze structural properties of prepared samples.

## RESULT AND DISCUSSION

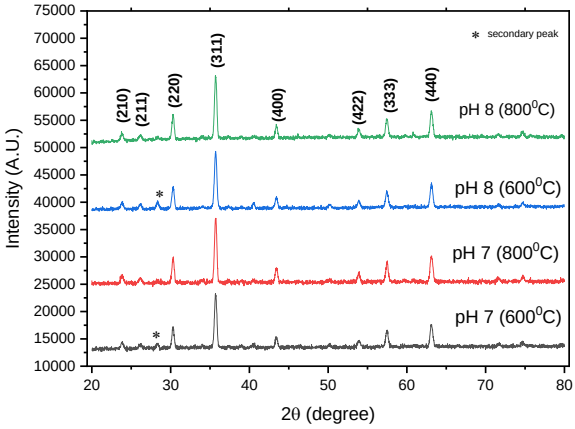


**Fig. 1. XRD patterns of the samples of $Li_{0.5}Fe_{2.5}O_4$**

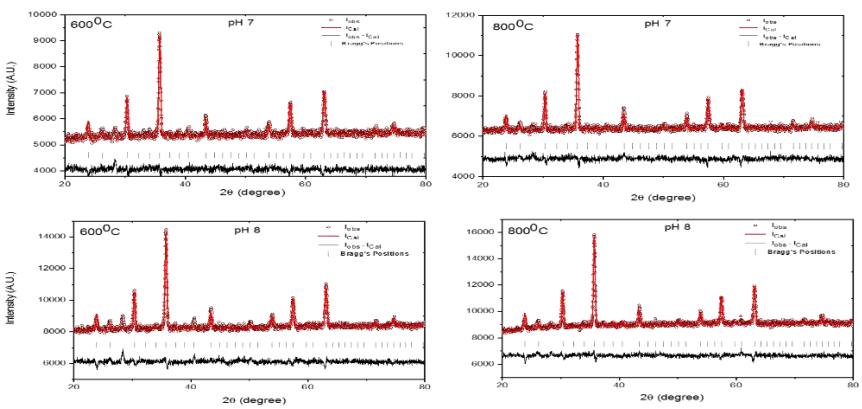


**Fig.2.** Rietveld refined XRD patterns of all the samples of $Li_{0.5}Fe_{2.5}O_4$

Fig.1 shows XRD patterns of lithium ferrite nanoparticles ($Li_{0.5}Fe_{2.5}O_4$) (pH=7 and pH=8) sintered at $600^0$c and $800^0$c. The peaks with hkl values (210), (211), (220), (311), (400), (422), (333), (440) observed in all samples which exactly matches with standard cod database file (COD database code: 1541958). One additional peak in small amount is observed in both samples of pH=7 and pH=8 sintered at $600^0$c confirmed using X'pert high score software but not observed for sample sintered at $800^0$c indicates sintering temperature ≤ $700^0$c required for formation of pure spinel structure without existence of impurity phases [12].

The structural parameters such as lattice constant (a), crystallite size, volume and X-ray density illustrated in table.1.

**Table 1.** Structural parameters of all prepared samples.

| **Sintering temperature ($^0$C)** | **Lattice Parameter ($A^0$)** | **Volume $(A^0)^3$** | **Crystallite size (nm)** | **X-ray density ($gm/cm^{-1}$)** |
|---|---|---|---|---|
| **pH 7** | | | | |
| 600 | 8.331 | 578.2 | 22.88 | 4.76 |
| 800 | 8.333 | 578.6 | 23.17 | 4.75 |
| **pH 8** | | | | |
| 600 | 8.332 | 578.3 | 21.45 | 4.76 |
| 800 | 8.334 | 578.9 | 23.21 | 4.75 |

**Table 2 .** Rietveld refined cell parameters along with R factor for all prepared samples.

| **Sintering temperature ($^0$C)** | **$R_p$** | **$R_{wp}$** | **$R_{exp}$** | **$\chi 2$** |
|---|---|---|---|---|
| **pH 7** | | | | |
| 600 | 60.2 | 32.6 | 25.1 | 1.69 |
| 800 | 57 | 29.8 | 22.86 | 1.73 |
| **pH 8** | | | | |
| 600 | 55 | 28.5 | 20.4 | 2.03 |
| 800 | 52.2 | 26 | 19.28 | 1.81 |

The lattice parameter (a) is related to the interplanar spacing ($d_{hkl}$) given by the formula [13]

$$a = d_{hkl} (h^2 + k^2 + l^2)^{1/2} \quad (1)$$

The Scherer equation used for estimation of the average crystallite size based on the broadening of XRD peaks due to the finite size of the crystallites given as below [13]

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where: *D* is the average crystallite size, *K* is the Scherrer constant (typically around 0.9, but its exact value depends on the shape of the crystallites), $\lambda$ is the wavelength of the X-ray radiation used, $\beta$ is the full width at half maximum (FWHM) of the XRD peak, $\theta$ is the Bragg angle.

The following formula is used to calculate the volume of the cubic unit cell where "a" is the length of one side of the cube. Since lithium ferrite is cubic, all three sides (a, b, c) are equal.

$$V = (a)^3 \quad (3)$$

The X-ray density is determined using the following relation

$$\boxed{d_x = \frac{nM}{N_A V}} \quad (4)$$

Where, n = number of molecules in a unit cell of spinel, NA= Avogadro's number, M = molecular weight.

It is observed that Lattice parameter (a) and crystallite size is found to be increased with increasing value of sintering temperature because during sintering process, the heat promotes atomic diffusion and rearrangement, helping to reduce lattice defects and internal strains within the material on

the other hand it also causes the particles to merge or agglomerate and results in formation of larger crystallites lead to an increase in the average size of nanoparticles [13-14] for the confirmation of above results some other structural parameters such as Lattice strain, Micro strain, stacking fault and dislocation density were calculated and summarized in table.3

**Table 3.** Structural parameters of all prepared samples.

| Sintering temperature ($^0$C) | Lattice Strain x $10^{-3}$ | Micro strain x $10^{-3}$ | Stacking Fault | Dislocation Density x $10^{-15}$ |
|---|---|---|---|---|
| **pH 7** | | | | |
| 600 | 4.944 | 1.515 | 0.446 | 1.911 |
| 800 | 4.881 | 1.496 | 0.446 | 1.862 |
| **pH 8** | | | | |
| 600 | 5.270 | 1.616 | 0.446 | 2.173 |
| 800 | 4.872 | 1.494 | 0.446 | 1.857 |

Lattice strain refers to the deformation or distortion of the crystal lattice structure in a material micro strain also indicates deformation in crystal lattice in small scale. When it comes to nanoparticles due to surface defects, crystal defects and stress during synthesis plays a significant role in influencing of their mechanical, electronic, and optical properties. For the present work it is observed that Lattice strain, Micro strain and dislocation density found to be decreased with increasing value of sintering temperature. The stacking fault indicates deviation in regular stacking sequence of atomic planes which was found to be almost constant for all the samples.

In consideration with effect of pH it is observed that value of lattice parameter (a) is greater for pH 8 as compared to pH 7 the same result was observed for cobalt doped lithium ferrite synthesized by sol- gel Auto combustion method [12]. Because variation in pH results in transformation of one phase to another phase in crystal lead to significant changes in lattice parameters.

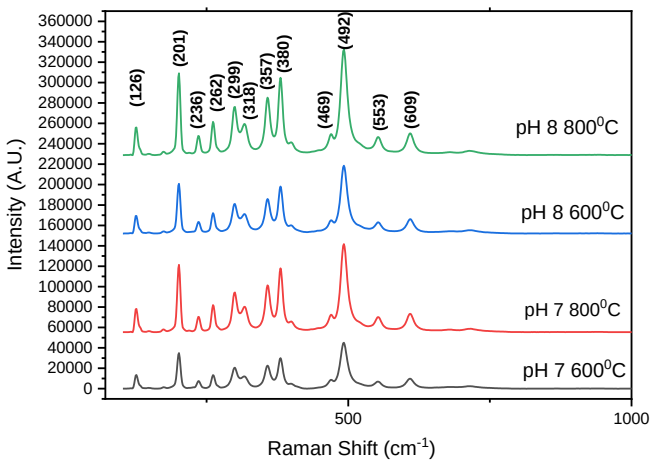


**Fig. 3:** Raman Spectra of all the samples of $Li_{0.5}Fe_{2.5}O_4$

***Raman Measurement***

Raman spectroscopy is a technique can provide insights into the molecular and crystal structure of the material. Raman modes are associated with specific symmetries of the crystal structure and labeled according to their symmetry representations. The relation of Raman modes for ordered structure of Lithium ferrite is given as

$$\nu = 6A1(R) + 14E(R) + 22F2(R) + 20F1(IR) \quad (5)$$

Where, $\nu$ represents the Raman shift, which is the change in frequency of the scattered light., $A1(R)$, $E(R)$, $F2(R)$, $F1(IR)$ are different vibrational modes associated with crystal symmetry., The coefficients (6, 14, 22, 20) indicate the number of modes for each symmetry type.

Raman spectra of lithium ferrite nanoparticles (pH=7 and pH=8) sintered at 600$^0$c and 800$^0$c is shown in fig.3 the vibration modes obtained are (126), (201), (236), (262), (299), (318), (357), (380),

(469), (492), (492), (553), (609) etc.in which vibration mode ≈ 492 $cm^{-1}$ have higher intensity in all samples. Literature survey suggest that spectral vibrations less than 700 $cm^{-1}$ indicates formation of spinal structure [16].

As discussed earlier ordered α-$LiFe_5O_8$ and disordered β-$LiFe_5O_8$ are the two crystalline forms of spinal ferrite. According to literature the vibration modes at 202 and 236 $cm^{-1}$ are not expected in disordered β-$LiFe_5O_8$ phase. The presence of these modes in sample indicates formation of ordered α-$LiFe_5O_8$ phase [17].

If we consider the effect of sintering temperature on Raman spectra it was seen that peak intensity of samples sintered at $800^0$c is greater than sample sintered at $600^0$c for both vales of pH indicates increase in crystalline size which is one more confirmation XRD result. Because as crystallite size increases, the number of scattering centers within the illuminated volume increases, resulting in an increment in the number of Raman-active molecules contributing to the signal. This increment in the number of scattering centers can lead to an increase in Raman peak intensity.

## CONCLUSION

In the conclusion, $Li_{0.5}Fe_{2.5}O_4$ nanoparticles with pH value 7 and 8 was successfully synthesized vis sol gel auto combustion technique and sintered at two temperatures $600^0$c and $800^0$c. increment in lattice parameter, crystallite size and reduction in strains are investigated as effects on sintering temperatures on structural parameters of Lithium ferrite nanoparticles. Significant changes in lattice parameters was observed due to variation in pH value. Formation of spinal structure was confirmed by Raman spectra and implications of sintering temperature on Raman peaks intensity and its indirect relation with crystallite size was also confirmed.

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# Microwave Synthesis for an efficient one pot synthesis of polyhydroquinolines using Choline hydroxide as a catalyst under solvent free conditions.

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**ABSTRACT**
The synthesis of polyhydroquinoline derivatives via Hantzsch condensation is excellent route by using four component coupling reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate in the presence of heterogeneous catalyst Choline hydroxide under solvent free condition.

***Keywords:****Aldehyde; Dimedone; Choline hydroxide catalyst; Hantzsch reaction.*

## INTRODUCTION

4 Substituted 1,4 dihydropyridine (1,4-DHP) nucleus is a fertile source of biologically important molecules possessing various important pharmacological properties such as vasodilator, antihypertensive, bronchodilator antitherosclerotic, hepto-protective, antitumor, antimutagenic,geroprotective and antidiabetic agents[1-4]. From recent studies 1-4 DHP shows several medicinal applications which include neuroprotectantand platelet anti-aggregatory activity, in addition cerebral antiischemic activity in the treatment in the of Alzheimer's disease [5-7]. An efficient Hantzsch condensation polyhydroquinoline derivatives via a four component coupling reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate in the presence of $HClO_4$-$SiO_2$ under solvent free conditions at 90°C temperature[8]. $Yb(OTf)_3$ promoted one pot synthesis of polyhydroquinoline derivatives via Hantzsch reaction of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate at ambient temperature in excellent yield[9]. Photocatalytic oxidation of 1,4 dihydropyridine to pyridine has been extensively investigated[10]. Here in the present work, developed new efficient method for synthesis of polyhydroquinoline using Choline hydroxide catalyst under solvent free conditions.

## MATERIAL AND METHODS

A mixture of aldehyde (1mmol), dimedone (1mmol), ethyl acetoacetate (1mmol), ammonium acetate (1.5mmol),Choline hydroxide (50mg) wastaken in open vial and placed under microwave radiation at 110 to 120 $^0$C. The reaction was confirmed by thin layer chromatography, the resulting solid product was treated with EtOAc followed by water and a brine solution and dried with anhydrous $Na_2SO_4$. The solution was concentrated in vaccum to afford the crude product. The pure product was obtained by further recrystallization using absolute alcohol.

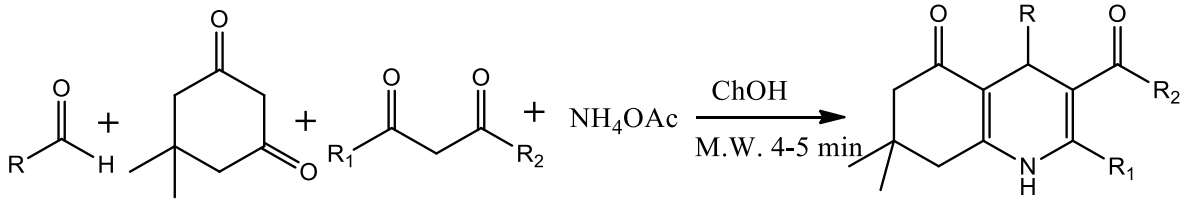

**Table:** Microwave assisted Hantzsch condensation for synthesis of polyhydroquinolines derivatives using Choline hydroxide as a catalyst under solvent free conditions.

| Entry | R | R1 | R2 | Time (min.) | Product | Yield | Melting point (°C) Observed | Melting point (°C) Reported |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | OEt | 5 | 2a | 85 | 203-204 | 202-204[9] |
| 2 | 4-F-$C_6H_4$ | $CH_3$ | OEt | 4 | 2b | 82 | 185-186 | 184-186[9] |
| 3 | 4-$OCH_3$-$C_6H_4$ | $CH_3$ | OEt | 4 | 2c | 84 | 256-257 | 257-259[9] |
| 4 | 4-$CH_3$-$C_6H_4$ | $CH_3$ | OEt | 5 | 2d | 80 | 261-262 | 260-261[9] |
| 5 | 3-$NO_2$-$C_6H_4$ | $CH_3$ | OEt | 5 | 2e | 82 | 178-179 | 177-178[10] |

The structure of the product was determined from their spectroscopic (UV, IR, NMR, Mass) data.

***Spectroscopic data:***

**Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-fluorophenyl)-5(6*H*)-oxoquinolin-3-carboxylate (2b).** Yellow solid, mp 185-186 $^{O}$C. IR (KBr): 3292, 2959, 1696, 1649, 1608, 1487, 1380, 1219, 1025, 764 cm-1. $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 0.92 (s, 3H, $CH_3$), 1.07 (s, 3H, $CH_3$), 1.18 (t, *J* = 7.3 Hz, 3H, $CH_3$), 2.13-2.25 (m, 4H, 2 ×$CH_2$), 2.38 (s, 3H, $CH_3$), 4.05 (q, *J* = 7.33 Hz, 2H, $CH_2$), 5.02 (s, 1H, CH), 5.8 (s, 1H, NH), 6.85-6.89 (m, 2H, ArH), 7.23-7.27 (m, 2H, ArH). 13C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.2, 26.4, 29.0, 32.1, 35.2, 50.1, 50.3, 59.0, 103.4, 110.0, 114.2, 114.3, 114.4, 129.0, 129.1, 144.1, 145.1, 149.4, 169.8, 194.2. LCMS: *m*/*z* = 356 (M-H)-. Anal. Calcd for $C_{21}H_{24}NO_3F$: C, 70.58; H, 6.72; N, 3.92; F, 5.32. Found: C, 70.52; H, 6.79; N, 3.87; F, 5.28.

**Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-methoxylphenyl)-5(6*H*)-oxoquinolin-3-carboxylate (2c).** Yellow solid, mp 256-257 $^{O}$C. IR (KBr): 3276, 2956, 1703, 1648, 1606, 1496, 1381, 1215, 1031, 765 cm-1. 1H NMR (200 MHz, $CDCl_3$ + DMSO-$d_6$ ): δ = 0.95 (s, 3H, $CH_3$), 1.09 (s, 3H, $CH_3$), 1.21 (t, *J* = 7.2 Hz, 3H, $CH_3$), 2.01-2.10 (m, 4H, 2 ×$CH_2$), 2.30 (s, 3H, $CH_3$), 3.70 (s, 3H $OCH_3$), 4.00 (q, *J* = 7.2 Hz, 2H, $CH_2$), 4.80 (s, 1H, CH), 6.65 (d, *J* = 7.3 Hz, 2H, ArH), 7.10 (d, *J* = 7.3 Hz, 2H, ArH ), 8.65 (s, 1H, NH). 13C NMR (75 MHz, DMSO-d6) δ 14.1, 18.2, 26.4, 29.1, 32.1, 34.7, 50.2, 50.5, 54.8, 58.9, 103.2, 110.1, 113.0, 113.1, 128.2, 128.3, 139.8, 144.6, 149.1, 157.2, 166.9, 194.2. LCMS: *m*/*z* = 368 (M-H)-. Anal. Calcd for $C_{22}H_{27}NO_4$:C, 71.54; H, 7.31; N, 3.79; Found: C, 71.59; H, 7.35; N, 3.84.

## RESULT AND DISCUSSION

The classical method for the preparation of polyhydroquinoline derivatives involves the reaction of aldehyde with ethyl acetoacetate and ammonia, in acetic acid or in refluxing in alcohol. However, this method suffers from several drawbacks such as long reaction time, excess of organic solvent and lower product yield[11]. All the starting materials in the ratio of 1:1:1:1 mixture of aldehyde, dimedone, ethyl acetoacetate and ammonium acetate catalyzed by Choline hydroxide catalyst is a microwave assisted green reaction in solvent free condition.

## CONCLUSION

In conclusion, we reported Choline hydroxide recyclable and reused green catalyst for Hantzsch reaction. Some of the efficient feature for this method such as simplicity of the experiment, mild reaction condition, high yield, short reaction time and easy work up. Hence such simple and lucidness makes this method attractive for the synthesis of polyhydroquinoline derivatives.

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# Study of catalytic effect of Cr Mn Fe metal ion chelates of Hydrazones on alcohol fermentation

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**ABSTRACT**

Fermentation has been widely used for the production of a wide variety of substances that are highly beneficial to individuals and industries. Ethanol is one of the most useful products which obtained in formation reaction. A microorganism Saccharomyces Cerevisiare is used. Healthy micro-organism can increase the production of alcohol. There are metal and metal salts which affect the physiology of Saccharomyces Cerevisiareand act as the catalyst. In present work different metal ion chelates are used to study the catalytic effect of metal ion chelates.

***Key words**. – Saccharomyces Cerevisiareand, Ligand, metal ion chelates biomass.*

## INTRODUCTION

Metal complexes of hydrazones have garnered attention as versatile compounds with potential applications in various chemical processes, including their utilization in fermentation reactions. Hydrazones, formed through the condensation of hydrazine derivatives with carbonyl compounds, exhibit unique structural features that make them promising ligands for metal coordination. The coordination chemistry of hydrazones with metal ions opens up avenues for the development of efficient catalysts and co-factors in fermentation reactions, impacting reaction kinetics and overall process efficiency.

The incorporation of metal-hydrazone complexes in fermentation processes is motivated by their ability to modulate the reaction environment and influence key biochemical transformations. These complexes serve not only as catalysts but also as stabilizing agents for enzymes, influencing the overall yield and selectivity of the fermentation reactions.

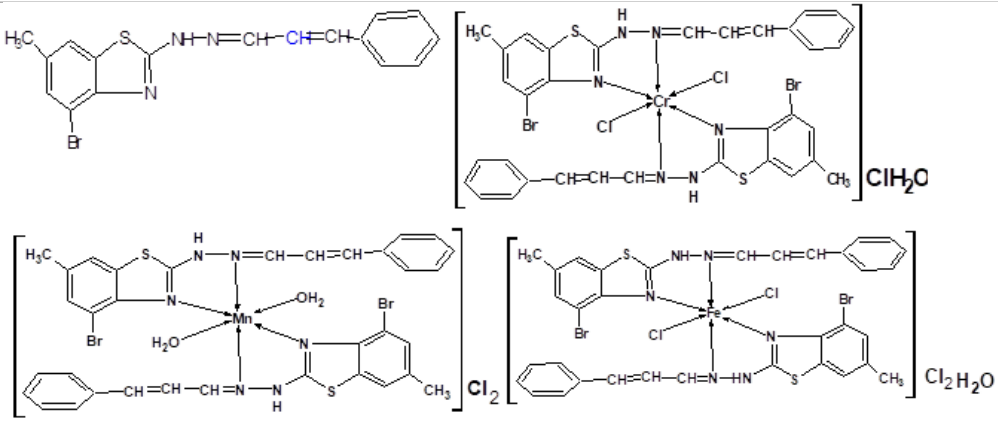
Several studies have explored the catalytic properties of metal-hydrazone complexes and their impact on fermentation processes. The electronic and steric properties of the metal center, as well as the characteristics of the ligands, contribute to the catalytic activity and selectivity of these complexes (1). Researchers have investigated the tenability of metal-hydrazone complexes, allowing for the optimization of reaction conditions and the enhancement of specific enzymatic activities crucial in fermentation (2).

The dual functionality of metal-hydrazone complexes, acting as catalysts and exhibiting antimicrobial properties, is particularly advantageous in fermentation reactions. The ability to control microbial contamination while simultaneously accelerating biochemical transformations makes these complexes valuable tools in biotechnological applications (3).

As the field of metal-hydrazone complex research continues to evolve, the potential for further innovations in the design and application of these complexes in fermentation reactions is apparent. The exploration of novel metal-hydrazone systems and their integration into bioprocessing strategies holds promise for advancing the efficiency and sustainability of fermentation-based production processes.

## METERIAL AND METHODS

Ligand- 2-(Cinnamyl)-4-bromo-6-methyl benzothiazolyl hydrazones is consider as CBMBTH) and its metal ion chelates which is previously reported. The structure of ligand and its metal ion chelates are as follows.



***Microorganism**:* yeast used in the study was Saccharomyces Cerevisieae collected from local market. The culture was mainted on solid yeast medium.

*Molasses*. - The molasses were obtained from Bhaurao Co. op. sugar industries, Laxmi Nagar, Nanded. Batch process is adopted in fermentation.

The % of reducing sugar is about 40% the molasses were diluted to prepare different concentration of sugars. The production medium is supplemented with nitrogen and Phosphate . The pH of medium was adjusted to 5.

***Media composition*:**

| | |
|---|---|
| KH2PO4- | 0.1% |
| (NH4)2SO4 | 0.5% |
| MgSO4 7H2O | 0.05% |
| Yeast extract | 0.1% |
| pH | 5 |

The pH of medium was adjusted by putting drop by drop dil sulphuric acid .2-(Cinnamyl)-4-bromo-6-methyl benzothiazolyl hydrazones (It consider CBMBTH) and metal salts were added in different experimental fermentation containers.

The fermentation flask were arranged and they were labeled along with yeast catalyst. Metal salt and metal chelates were added. pH were adjusted.

## EXPERIMENTAL

To study the effect of the metal ions and metal chelates different experiment were carried out. All the fermentation flask were sterilized. All solution which are used for the experiment were also sterilized. 5 fermentation flask (sterilized) were arranged and they were labeled from 1 to 5

Fermentation flask no.1 is used as control, Fermentation flask no. 2 is used to study the effect of 2-(Cinnamyl)-4-bromo-6-methyl benzothiazolyl hydrazones and flask no.3 were used to study the effect $CrCl_3$ salt 0.05 gm. were added. In flask no. 4 $[Cr (CBMBTH)_2 Cl_2]Cl.H_2O$

In flask no.5 and 6, 0.05 gm $[Mn (CBMBTH)_2 (H_2O)_2] Cl_2$ , and $Fe(CBMBTH)_2 Cl_2.]Cl.H_2O$.

Solution like 0.05 % $KHSO_4$, 0.5% $(NH_4)_2SO_4$, 0.05 % $MgSO_4 7H_2O$ and as mentioned above different metal ion were added . The pH of the experiment is adjusted by putting drop by drop dil. $H_2SO_4$. The fermentation reaction were carried out for 24 hours. In each fermentation flask 10 ml 1% molasses solution and media

Estimation of biomass.-

The quantity of biomass depends upon yeast growth takes place.

The dry biomass were measured by transferring the content of conical flask through the filter paper. The residue of biomass which is collected on the filter paper is dried by keeping it in oven at 100°C. The mass of biomass were recorded and it is given in the table.

Estimation of ethyl alcohol:-

Spectroscopic method is used to determine the alcohol generated in the fermentation process. Fermented wash were taken in distillation flask. 15 ml distillate were collected in the conical flask. 5 ml $K_2Cr_2O_7$ (0.1N) in 0.1N $H_2SO_4$ solution were added it is warmed at 60°C. The color obtained. The optical density of solution were measured from standard graph. The ethanol generated during fermentation were determined.

| Sr. No | Flask No. | Compounds | %wt. of biomass | % Alcohol |
|---|---|---|---|---|
| 1 | 1 | Control | 1.09 | 2.05 |
| 2 | 2 | (CBMBTH) | 1.15 | 2.16 |
| 3 | 3 | $CrCl_3$ | 1.21 | 2.60 |
| 4 | 4 | $[Cr\ (CBMBTH)_2\ Cl_2]Cl.H_2O$ | 1.92 | 2.98 |
| 5 | 5 | $[Mn\ (CBMBTH)_2\ (H_2O)_2]\ Cl_2$ | 1.83 | 2.75 |
| 6 | 6 | $[Fe(CBMBTH)_2\ Cl_{2.}]Cl.H_2O$ | 1.58 | 2.63 |

## RESULT AND DISCUSSION

References indicates that some microelement affects growth of yeast. The effect of $Cr^{+2}$, $Mn^{+2}$, $Fe^{+3}$ and their complexes were used fermentation process. The table no.1 gives information regarding effect of metal ion and their chelates on fermentation process.

***Effect of* Cr$^{+3}$ *metal ion and their metal chelates on fermentation***

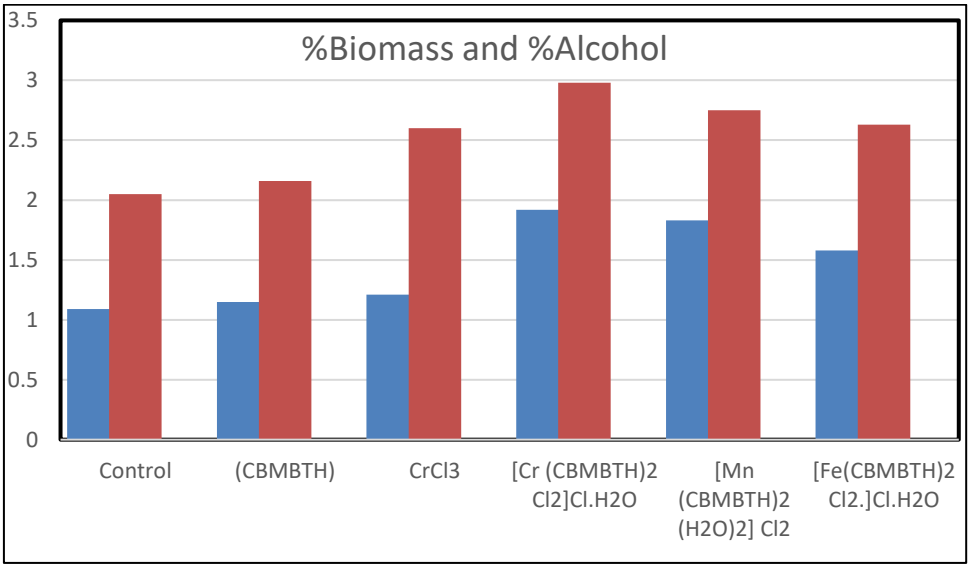
Table no. 1 deals with effect of $Cr^{+3}$ and their chelates on the fermentation process, graph no.1. Indicates that $Cr\ (CBMBTH)_2\ Cl_2]Cl.H_2O$ yield 1.92 % biomass and it generate 2.98 % alcohol indicating this complexes enhance the fermentation.

***Effect of Mn$^{+2}$ and their metal ion chelate on fermentation***

The result indicate that $[Mn\ (CBMBTH)_2\ (H_2O)_2]\ Cl_2$ increase the rate of fermentation % of biomass is obtained is 1.83 and % alcohol is 2.75 formation is more as compared to control.

***Effect of Fe$^{+3}$ metal ion and their metal chelates on fermentation.***

The table also indicate that $Fe\ (CBMBTH)_2\ Cl_{2.}]Cl.H_2O$ metal chelate enhances the rate of reaction and gives 1.58% biomass and generaten2.63 % alcohol.




Graphical representation of %Biomass and %generated alcohol.

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# DIELECTRIC RELAXATION STUDY OF HYDROXY AND AMINE FUNCTIONAL GROUP MOLECULES TIME DOMAIN REFLECTOMETRY TECHNIQUE

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**ABSTRACT**

The complex permittivity spectra of ethanolamine with triethanolamine were determined in the frequency range of 0.1 GHz to 20 GHz using time domain reflectometry (TDR) in the temperature range 10°C to 40°C for 11 different concentrations of the system. The static dielectric constant ($\varepsilon_0$), dielectric constant at high frequency ($\varepsilon_\infty$) and relaxation time ($\tau$) have been obtained by the least square fit method. For the temperature range considered here, the permittivity decreases and relaxation time increases with increase the percentage of triethanolamine in the system. The dielectric constants for the mixtures have been fitted with the modified Bruggeman model.

## INTRODUCTION

Dielectric relaxation of liquid mixture gives information about molecular interactions. In this work, we report the dielectric study of ethanolamine-triethanolamine mixture. The ethanolamine (ETA) and triethanolamine (TEA) are the highly polar liquids and multifunctional compounds. Ethanolamine (the one hydroxy group and primary amine function) mixed with triethanolamine (the three hydroxy groups and tertiary amine function). The objective of the present paper is to report the dielectric relaxation study for ethanolamine and triethanolamine mixtures.

## EXPERIMENTAL SECTION

ETA and TEA (AR grade, Qualigens fine chemicals Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared at 11 different volume percentage of TEA from 0 % to 100 % in steps of 10 %. Using these volume percents the mole fraction is calculated as

$$x_1 = (v_1\rho_1/m_1) / [ (v_1\rho_1/m_1) + (v_2\rho_2/m_2) ]$$

where $m_i$, $v_i$, and $\rho_i$ represent the molecular weight, volume percent, and density of the $i^{th}$ (i=1, 2) liquids, respectively. The density and molecular weight of the liquids are as follows:

Ethanolamine - Density - 1.0180 gm.cm$^{-3}$ Mol. Wt.- 61.08

Triethanolamine - Density - 1.1242 gm.cm.$^{-3}$ Mol. Wt.- 149.18

The complex permittivity spectra were studied using the time domain reflectometry [1-4] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used. A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In the experiment, time window of 5 ns was used. The reflected pulse without sample $R_l(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ±1°C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system is circulated. The temperature at the cell is checked using the electronic thermometer.

## DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range 0.1 to 20 GHz using Fourier transformation [5-6] of

$$\rho^*(\omega)=(\chi/\varphi\omega\delta)[\pi(\omega)/\theta(\omega)] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t)+R_x(t)]$ respectively, c is the velocity of light, $\omega$ is angular frequency, d is the effective pin length and $j=\sqrt{-1}$ .

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [1].

The experimental values of □* were fitted □with the Debye equation [7]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

with $\varepsilon_0$, $\varepsilon_\infty$ and $\tau$ as fitting parameters. A nonlinear Least-Squares fit method [8] was used to determine the values of dielectric parameters.

## 4. RESULTS AND DISCUSSION

The static dielectric constant ($\varepsilon_0$), dielectric constant at high frequency ($\varepsilon$ ) and relaxation time ($\tau$) are listed in Table 1. The information related to liquids 1 and 2 interaction may be obtained by excess properties [9] related to the permittivity and relaxation times in the mixture. The excess permittivity $\varepsilon^E$ is defined as

$$\varepsilon^E=(\varepsilon_0 - \varepsilon_\infty)_\mu-[(\varepsilon_0 - \varepsilon_\infty)_1 \ \xi_1+(\varepsilon_0 - \varepsilon_\infty)_2 \ \xi_2 ] \quad (3)$$

**Table 1.** Temperature dependent dielectric relaxation parameters for ETA-TEA mixtures

| $x_2$ | T = 10°C | T = 20°C | T = 30°C | T = 40°C |
|---|---|---|---|---|
| $\varepsilon_0$ | | | | |
| 0.0000 | 33.57(0) | 31.84(0) | 29.68(0) | 28.57(0) |
| 0.0478 | 33.38(3) | 30.85(4) | 29.71(1) | 27.84(1) |
| 0.1016 | 32.16(2) | 30.63(3) | 29.80(1) | 27.71(3) |
| 0.1623 | 31.99(7) | 30.58(4) | 29.87(2) | 27.54(6) |
| 0.2316 | 30.55(2) | 30.47(5) | 30.06(4) | 27.09(5) |
| 0.3114 | 30.76(5) | 30.42(6) | 29.78(7) | 27.01(3) |
| 0.4041 | 29.52(6) | 30.38(5) | 29.74(5) | 26.97(8) |
| 0.5134 | 27.48(4) | 29.84(4) | 29.54(6) | 26.82(5) |
| 0.6440 | 26.84(3) | 28.12(3) | 29.22(4) | 26.80(5) |
| 0.8027 | 24.52(2) | 27.84(3) | 29.13(2) | 26.75(2) |
| 1.0000 | 19.80(0) | 29.83(0) | 28.09(0) | 26.71(0) |
| $\varepsilon_\infty$ | | | | |
| 0.0000 | 3.40(0) | 2.87(0) | 2.18(0) | 1.53(0) |
| 0.0478 | 3.70(1) | 2.90(1) | 2.30(2) | 0.48(1) |
| 0.1016 | 4.00(1) | 2.92(3) | 2.68(3) | 0.39(2) |
| 0.1623 | 4.11(2) | 3.07(2) | 2.56(1) | 0.21(3) |
| 0.2316 | 4.24(2) | 3.34(3) | 2.41(1) | 0.12(2) |
| 0.3114 | 4.46(1) | 3.56(1) | 2.40(2) | 0.62(2) |
| 0.4041 | 4.25(1) | 3.31(1) | 2.36(1) | 1.13(3) |
| 0.5134 | 4.10(2) | 2.98(2) | 2.35(2) | 1.28(1) |
| 0.6440 | 3.93(3) | 2.97(1) | 2.28(1) | 1.32(2) |
| 0.8027 | 3.73(2) | 2.96(2) | 2.26(1) | 1.48(2) |
| 1.0000 | 3.43(0) | 2.94(0) | 2.24(0) | 1.63(0) |
| $\tau(\pi\sigma)$ | | | | |

| | | | | |
|---|---|---|---|---|
| 0.0000 | 203.75(0) | 147.84(0) | 119.64(0) | 98.72(0) |
| 0.0478 | 273.47(3) | 178.68(1) | 153.63(2) | 114.79(1) |
| 0.1016 | 328.12(5) | 235.50(3) | 188.89(5) | 135.21(4) |
| 0.1623 | 352.11(7) | 278.79(3) | 197.22(4) | 180.28(5) |
| 0.2316 | 412.05(4) | 289.99(4) | 220.58(4) | 199.23(9) |
| 0.3114 | 420.05(4) | 324.52(7) | 248.36(6) | 214.13(7) |
| 0.4041 | 448.61(2) | 389.56(5) | 266.30(4) | 243.77(4) |
| 0.5134 | 469.33(7) | 412.13(4) | 293.69(5) | 258.82(4) |
| 0.6440 | 490.49(3) | 439.03(5) | 313.62(7) | 273.01(2) |
| 0.8027 | 523.72(1) | 486.73(2) | 338.72(2) | 289.33(1) |
| 1.0000 | 560.14(0) | 502.20(0) | 383.81(0) | 320.83(0) |

*$x_2$ is the mole fraction of TEA in ETA. Number in bracket represent error in the corresponding value, e.g. means 153.63(2) means 153.63 ± 0.2.

where x- mole fraction and suffices m, 1, 2 represents mixture, liquid 1 (ETA) and liquid 2 (TEA) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

(i) $\varepsilon^E = 0$ indicates the liquid 1 and 2 do not interact at all.

(ii) $\varepsilon^E < 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles get reduced. The liquid 1 and 2 may form multimers leading to the less effective dipoles.

(iii) $\varepsilon^E > 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_\mu - [(1/\tau)_1 \xi_1 + (1/\tau)_2 \xi_2] \quad (4)$$

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is inverse of the relaxation time) in the resonant spectroscopy [10]. The information regarding the dynamic of liquid 1 and 2 interactions from this excess property is as follows:

(i) $(1/\tau)^E = 0$ : There is no change in the dynamics of liquid 1 and 2 interaction.

(ii) $(1/\tau)^E < 0$ : The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.

The Kirkwood correlation factor g [11] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids. The g for pure liquid may be obtained by the expression

$$\frac{4\Pi N\mu^2\rho}{9kTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \quad (5)$$

where μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, N is Avogadros number.

For the mixture of two polar liquids 1, 2 eq. 4 is modified by [12] with the following assumptions:

Assume that for the mixture, $g^{eff}$ is effective correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}\phi_1 + \frac{\mu_2^2\rho_2}{M_2}\phi_2\right) g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad (6)$$

with $\phi_1$ and $\phi_2$ as volume fractions of liquids 1 and 2 respectively. The Kirkwood correlation factors, $g^{eff}$ which gives angular correlation between the molecules of the system.

## CONCLUSION

Dielectric relaxation parameters are reported in the paper for binary mixture of ethanolamine and triethanolamine molecule for various temperature and concentrations. The dielectric constant decreases and relaxation time increases with an increase in the percent of triethanolamine. This data provide information regarding solute-solvent interaction in liquids.

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# Effect of $Zn^{2+}$ substituted Magnesium Ferrite and Some Physical properties

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## ABSTRACT

Some magical structural and magnetic properties of Zn substituted Magnesium ferrites having general formula $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.0 to 1.0) were synthesized by the typical wet chemical co-precipitation method. The samples were annealed at 700- 900$^0$C for 11 h and were studied by means of XRD, magnetization measurements. Tetrahedral edge, shared and unshared octahedral edge for the typical samples were also studied. The XRD analysis showed that all the samples had single-phase cubic spinel structure. The variation of lattice constant with Zn concentration deviates from Vegard's law. The standard Parameter $\sigma_s$ and $n_B$ measured at 350 K using high field hysteresis loop technique decreases with increasing *x*, suggesting decrease in ferrimagnetic behaviour. Curie temperature $T_C$ deduced from AC susceptibility data decreases with *x*, suggesting a decrease in ferrimagnetic behaviour.

***Keywords:*** Structural-Magnetic Properties, Ferrite, Wet-Chemical method

## INTRODUCTION

Recent interest in the study of several spinel type ferrites which are characterized by high electrical resistivity, high dielectric constants, and low losses [1]. Due to wide range technological applications especially at high frequency ranges; the ferrites have been attracting the researchers in large number [2,3,4]. $ZnFe_2O_4$ is a normal spinel ferrite. The synthesis of nano particles at low temperature by various methods in view of the potential applications of these nano size magnetic materials in different technological areas [5, 6]. Synthesis and application of magnetic nano particles is subject of interest of several researchers because of their unique properties that makes them attractive and interesting from scientific view and technological significance of enhancing the performance of the existing materials [7, 8]. The nano-size materials exhibit unusual physical and chemical properties significantly different from those of their bulk counter part because of their extremely small size and large specific area [9, 10]. Nano-size ferrites with uniform particles size and narrow size distribution are desirable for a variety of applications viz. magnetic data storage ferro-fluids, medical imaging, drug delivery etc. [11, 12], so their synthesis and characterization have attracted increasing attention in the last five years. The ability to produce nano size magnetic materials has opened new applications for magnetic materials.

Ferrites, ferromagnetic cubic spinel possesses the combined properties of magnetic materials and electrical insulators. They have been extensively investigated and being the subject of great interest because of their importance in many technological applications. The important, structural, electrical and magnetic properties of nano size ferrites are responsible for their application in various fields. The spinel ferrites belong to an important class of magnetic materials, because of their remarkable magnetic properties particularly in radio frequency region, physical flexibility high electrical resistivity, mechanical hardness, and chemical stability.

Magnesium ferrite, $MgFe_2O_4$ is a soft magnetic n-type semi-conducting material [13], which finds applications in absorption, sensor and in magnetic technologies. According to crystal structure $MgFe_2O_4$ is inverse spinel ferrites whose degree of inversion depends on the heat treatment. In the present study, zinc substituted magnesium ferrite ($Mg_{1-x}Zn_xFe_2O_4$) system is prepared by wet chemical co-precipitation technique. The results obtained on electrical and magnetic properties are presented in this work.

In this paper we propose the synthesis of the $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.0 and 1.0) ferrite system using the wet chemical co-precipitation technique and attempt to characterize the electrical and magnetic properties of the ferrite samples using XRD, SEM and hysteresis loop tracer technique. The purpose of the present work was to study the lattice parameter, x-ray density particle size, porosity, and surface area of the samples. The X-ray diffraction patterns show the existence of spinel structure with reflection planes (220), (311), (222), (400), (422), (333) and (440).

## EXPERIMENTAL DETAILS

The samples of $Mg_{1-x}Zn_xFe_2O_4$ spinel ferrite systems with varying x [x = 0.0- 1.0] were synthesized via wet chemical co-precipitation technique. AR grade sulphates of magnesium, zinc and ferrous were used for the preparation of Mg-Zn ferrites. The aqueous solutions of sulphate were prepared using stoichiometric molar proportion. The solutions were mixed and allowed to settle for 24 hours. The initial pH of the solution was measured. A two molar NaOH solution was prepared and slowly added to the mixed solution. $H_2O_2$ was also added simultaneously in the mixed solution to increase the oxidation reaction. The solution was constantly stirred and heated at low temperature i.e. $60^0$C during the addition of NaOH and $H_2O_2$. The NaOH was added in the solution until the precipitate becomes dark brownish in colour and pH of the precipitation become 11. The precipitation is washed several times by acetone and then by double distilled water and then filtered to get-fine particles of Mg-Zn ferrites. The fine powders were then heated at $150^0$C to remove water molecules. The powders were then sintered at $900^0$C for 11 hours.

All the synthesis powders were characterized using XRD technique at room temperature. The XRD patterns were recorded in the 2θ range of $20^0$-$80^0$ using Cu-$K_\alpha$ radiation. Microstructure and particle size of all the samples were studied using scanning SEM.

Each of the sintered disc shaped pellets were polished before electrical measurement for ensuring a good electrical contact.

The magnetic measurements viz. magnetizations were carried out using pulse field hysteresis loop tracer (Magneta Company), applying 50Hz frequency. The a.c. susceptibility double coil set up operating at a frequency of 263Hz and in r.m.s. field of 100 Oe was used to record temperature variation susceptibility. The susceptibility and magnetization apparatus was calibrated with nickel prior to the measurements.

## RESULTS AND DISCUSSION:

***Structural properties:*** The single-phase cubic spinel structure formation was confirmed from X-ray diffraction patterns. All the peaks were sharp and do not contain any impurity phase. All the peaks of the XRD pattern were indexed using Bragg's law. The XRD patterns of some samples Fig.1.

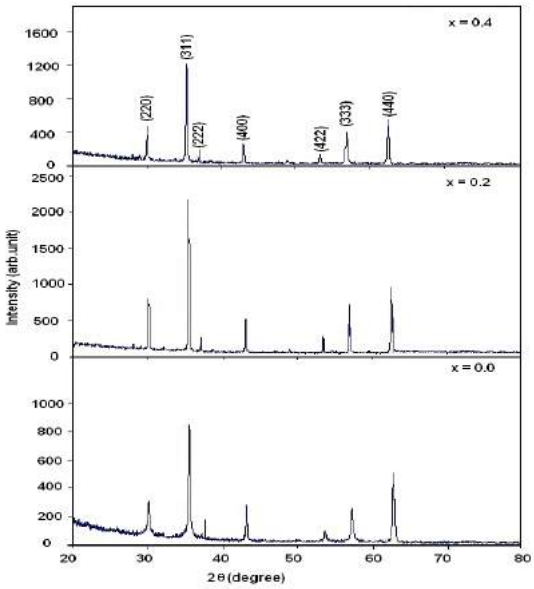



**Fig. 1:** XRD patterns

The values of lattice parameter 'a' determined from the XRD data with an accuracy of $\pm 0.002A^0$ for all the samples are listed in Table as a function of $Zn^{2+}$ content x. Table indicates that the lattice constant increases with the substitution of $Zn^{2+}$ ions. It is clear from Table that lattice parameter

increases 'a' with the addition of ion $Zn^{2+}$. This behavior can be explained on the basis of difference in ionic radii. The increases lattice constant is due to replacement of larger ions $Zn^{2+}$ ($0.83A^0$) by smaller ions (0.63 Å). Usually, in a solid solution of soft ferrite within the miscibility range, a linear change in the lattice constant with concentration of the composition is observed [15].

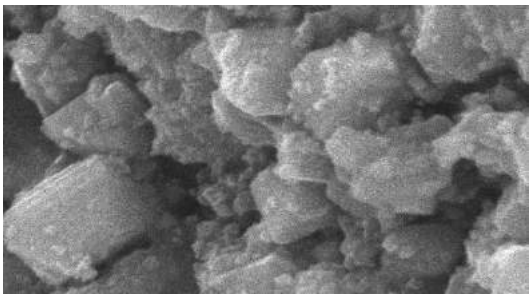
The X-ray density increases with increasing $Zn^{2+}$ content 'x'. This is related to the fact that, the increase in molecular weight overtakes the increase in volume of the unit cell. The porosity is an important parameter in deciding magnetic susceptibility of the samples. The variation of porosity with $Zn^{2+}$ concentration is tabulated in Table. It is observed that porosity increases as the concentration of is increases. It is due to ionic radius. The specific surface area values are given in Table 1.

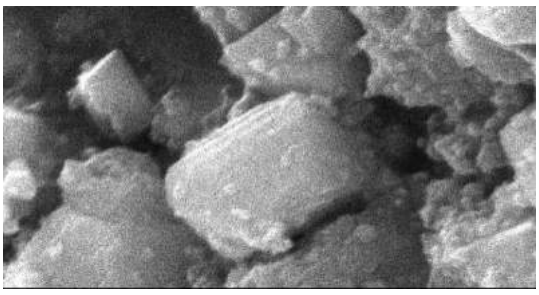
**Table 1:** Structural parameters.

| Composition (x) | Lattice constant (a) | Particle size (t)(nm) | x-ray density dx | Porosity P | Area $m^2/gm$ |
|---|---|---|---|---|---|
| 0.0 | 8.3730 | 22.162 | 4.5264 | 18.795 | 38.525 |
| 0.2 | 8.3804 | 23.791 | 4.6996 | 25.463 | 41.326 |
| 0.4 | 8.3946 | 29.163 | 4.8603 | 25.982 | 42.657 |
| 0.6 | 8.4135 | 31.197 | 5.0109 | 29.795 | 45.218 |
| 0.8 | 8.4254 | 32.625 | 5.1722 | 32.376 | 51.412 |
| 1.0 | 8.4341 | 32.673 | 5.3381 | 33.261 | 52.893 |

It shows that specific surface area values range from 35 $m^2/gm$ to 55 $m^2/gm$. It indicates that Wet chemical co-precipitation method successfully yields nano-size ferrite particles. The average particle size was calculated from X-ray line broadening, using the Scherrer formula. The particle size was also calculated from SEM images. The micrographs reveal that grains were composed of very fine particle. The particle size estimated shows increasing nature with increase in Zn content. This may be explained on the basis of hypothesis that the reaction condition, which favored the formation of new nuclei may vary regularly with Zn content. The distance between magnetic ions i.e. hopping length in octahedral site is $(1/4)a^2$, whereas for the tetrahedral site it is given by $(1/4)a^3$ [16].

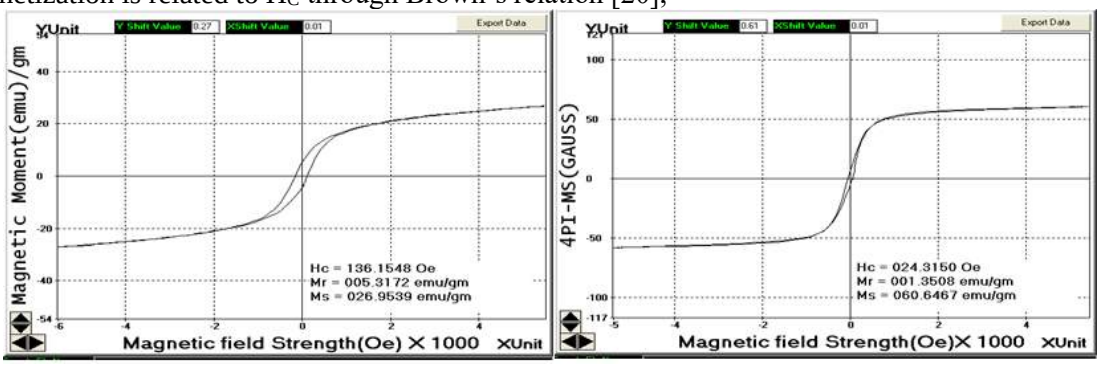
The values of lattice parameter 'a' and oxygen positional parameter 'u' are used to calculate tetrahedral and octahedral bond length ($d_{Ax}$ and $d_{Bx}$), tetrahedral edge, shared and unshared octahedral edge ($d_{AXE}$, $d_{BXE}$ and $d_{BXEU}$) using the formula given elsewhere [14] and the values presented graphically in Fig. 2 which shows that the tetrahedral edge $d_{AXE}$ decreases, unshared octahedral edge $d_{BXEU}$ does not vary much with composition while shared octahedral edge $d_{BXE}$ decreases. This could be related to the larger radius of $Zn^{2+}$ ions as compared to Mg ions and the fact that $Zn^{2+}$ occupies strongly tetrahedral A- site.





***Magnetic properties:*** The magnetic properties like saturation magnetization (*Ms*) and Coercivity (*Hc)* were studied using the high field hysteresis loop technique [17]. Fig. shows the hysteresis curves of the sample at room temperature for the typical sample x = 0.2 and 1.0. The reduction of saturation magnetization in the synthesized nanoparticles is attributed to the existence of a ''dead'' surface layer for each particle in which magnetic moments do not contribute to the magnetization in the applied field [18]. These particles exhibit superparamagnetic behavior at room temperature. The lower *M*s Values associated to the particles with smaller size and also could be attributed to the fact that surface distortion due to interaction of the transition metal ions with the oxygen atoms in the spinel lattice can reduce the net magnetic moment in the particle. This effect is especially prominent for the ultrafine particles due to their large surface to volume ratio [19]. It is clearly observed from Fig. that the coercivity ($H_C$) increases as $Zn^{2+}$ content x increases, this behaviour is similar to that of porosity. Porosity affects

magnetization process because pores work as a generator of demagnetizing field. As the porosity increases high field is needed to push the domain wall and thus $H_C$ increases. The saturation magnetization is related to $H_C$ through Brown's relation [20],




Magnetic hysteresis loops (M-H) were recorded at room temperature using pulse field magnetization technique M-H loops of all the samples are shown in Fig.5. Using these loops, the saturation magnetization ($M_S$) are obtained and the values are presented in Table 2.

**Table 2:** Magnetic Properties.

| Comp. | Mr | $M_S$ | Hc Oe | Mr/Ms |
|---|---|---|---|---|
| 0.0 | 5.31 | 66.95 | 136.15 | 0.079 |
| 0.1 | 4.47 | 62.26 | 27.65 | 0.071 |
| 0.2 | 1.35 | 60.64 | 24.3 | 0.022 |
| 0.3 | 0.34 | 17.18 | 10.04 | 0.020 |

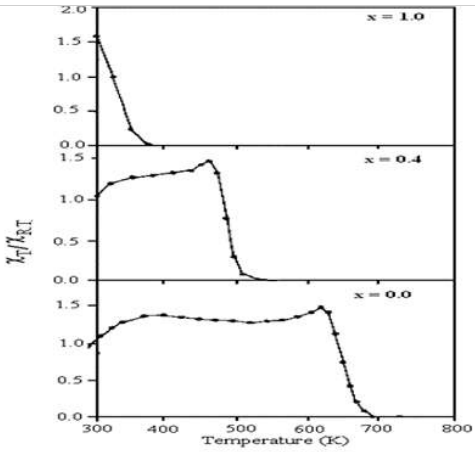
It is seen from table that the saturation magnetization $M_S$ decreases with the increase of non-magnetic zinc composition. This may be attributed to the weakening of exchange interactions due to non-magnetic $Zn^{++}$ ions. The magneton number $n_B$ for all the samples were calculated using the values of $M_S$. Like saturation magnetization magneton number also decreases with substitution of $Zn^{++}$ ions. The values of magneton number are also given in Table . The values of saturation magnetization and magneton number are less compared to the bulk Mg-Zn ferrite. The lower values of $M_S$ and $n_B$ are attributed to nano size nature of the presently investigated sample.

The magnetic moment ($n_B$) per formula unit in Bohr magneton ($\mu_B$) was calculated experimentally using the relation [2]

$$n_B = \frac{Molecular\,weight \times \sigma_S}{5585 \times \rho_{th}} \quad (1)$$

where, $\rho_{th}$ is the bulk density of the sintered sample. The $\sigma_S$ was calculated from M-H loops from the relation [22], $\sigma_S = (1-P) \times M_S \times d$, where, P is the porosity, and $M_S$ is the saturation magnetization. It is found that the specific saturation magnetization increases with the increasing substitution of $Zn^{2+}$ ions. This can be attributed to the fall in density and increase in porosity. Since $Zn^{2+}$ ions have a strong preference for tetrahedral-A sites [23]. The magnetic moment per formula unit ($n_B$) calculated from Neel's sub two lattice models using the relation $n_B^N = M_{B(x)} - M_{A(x)}$ where $M_B$ and $M_A$ are the B and A sub-lattice magnetic moments in $\mu_B$. It is evident that $n_B$ decreases with increasing x suggesting a decrease in ferrimagnetic behaviour with increasing x. The calculated $n_B^N$ values are in close agreement with experimental values confirming a collinear magnetic structure for A-sub lattice dilution indicating strong A-B coupling ($J_{AB}$).

The thermal variation of a. c. susceptibility of all polycrystalline samples was obtained using a double coil set up [24]. From the plots of thermal variation inverse a. c. magnetic susceptibility for x=0.0,0.4and1.0 are given in Fig.. Figure also shows an inset for variation of Curie temperature ($T_C$) with composition. Curie temperature ($T_C$) determined from $\chi_T/\chi_{RT}$ versus temperature plot decreases with addition of $Zn^{2+}$ ions. It is well known that when $Fe^{3+}$ ions are replaced by paramagnetic or diamagnetic ions, Curie temperature falls. When $Fe^{3+}$ (5μB) ions of A-site replaced by paramagnetic $Zn^{2+}$(3μB) ions A-B interaction gets weakened. The observed fall in Curie temperature in the present system is attributed to this weakening of A-B exchange interaction.




## CONCLUSIONS

Wet chemical co-precipitation method plays an important role in governing the properties of the ferrite system. The nano particles of $Mg_{1-x}Zn_xFe_2O_4$ have been obtained successfully by wet chemical co-precipitation method. It is found that the lattice constants increase with increasing Zn content x. The addition of zinc inhibited the grain growth and decreased the sample's density. It is clearly observed that the values of saturation magnetization decrease with the addition of Zn. The magnetic moment calculated and observed are in good agreement with each other, which suggest that the structure is collinear. The data on Curie temperature obtained from susceptibility plots shows decreasing trend with zinc substitution. The decrease in Curie temperature is attributed to weakening in A-B interaction.

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# Structural and Elastic properties of Cobalt ferrite nanoparticle synthesized by using green synthesis route

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## ABSTRACT

Cobalt ferrite nanoparticle was synthesized using green synthesis method from an aqueous solution containing metal nitrates and extract of lemon juice. The structural characteristics of the synthesized cobalt ferrite nanoparticle were determined by using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) techniques. X-ray diffraction patterns confirm the complete formation of spinel cubic structure with nanophase. The lattice constant of $CoFe_2O_4$ nanoparticle is fall in order of 8.3954 Å. The FTIR spectra exhibit two main fundamental absorption bands, one for the tetrahedral site at 569 $cm^{-1}$ and the other for the octahedral site around 379 $cm^{-1}$.Using the experimental value of lattice parameter, different structural parameters such as bond length, site radii, tetrahedral edge, shared and unshared octahedral edges, hopping length, cation-cation and cation-anion bond distances and bond angles were determined. The force constants corresponding to tetrahedral and octahedral site and Elastic parameters such as Young's modulus, Bulk modulus, Modulus of rigidity, Debye temperature, and Wave velocity were estimated

## INTRODUCTION

Ferrites with cubic spinel structure represent very important class of magnetic materials. The combination of electric and magnetic properties makes them very useful in many technological applications. On the basis of crystal structure, ferrites are classified into three groups namely spinel ferrite, hexagonal ferrite and garnet. The spinel ferrite can be represented with a chemical formula $MFe_2O_4$ (where M denotes divalent metal cations like cobalt, zinc, copper, nickel, manganese, magnesium etc) possess two sub-lattice that is tetrahedral A and octahedral B sites. Among the different spinel ferrites, cobalt ferrite ($CoFe_2O_4$) has inverse spinel structure in which all the $Co^{2+}$ ions are located in B sites, and $Fe^{3+}$ ions are equally distributed between A and B sites[1]. Cobalt ferrite is known to be the best promising magnetic materials due to its high saturation magnetization, high coercivity, high electrical properties, high magneto-crystalline anisotropy, high Curie temperature, good mechanical properties and chemical stability which make it a best material for the electronic components used in computers, recording devices, and magnetic cards [2–7]. Now a day's these ferrite nanoparticles are extensively used for drug delivery, cell labeling and sorting, magnetic resonance imaging and sensing, cell thawing agents, as well as catalytic applications [8-11]. The structural and magnetic properties are basically depends on the synthesis methods. The synthesis methods such as co-precipitation method, solid state method, sol-gel method, auto combustion method, precursor technique, hydrothermal technique etc. have been developed and used for the preparation ferrite nanoparticles. These methods are neither eco-friendly nor economical also have multiple disadvantages and are difficult for large-scale synthesis [12]. The Green synthesis method is found to be more advantageous than the present chemical synthesis techniques since it most economical, reduces pollution, and enhances environmental and human health safety [13]. The aim of the present work is to synthesize cobalt ferrite nanoparticles by green synthesis method and to investigate its structural and elastic properties.

## EXPERIMENTAL

$CoFe_2O_4$ ferrite nanoparticle was synthesized using green synthesis method using AR grade of cobalt nitrate ($Co(NO_3)_2.6H_2O$), and ferricnitrate ($Fe(NO_3)_2.9H_2O$) and extract of lemon juice. Extract of lemon juice mixed in a saturated solution of cobalt nitrate and iron nitrate was utilized for the synthesis of the cobalt ferrite nanoparticles. Aqueous solutions of cobalt nitrate and iron nitrate were

prepared separately and heated on a magnetic stirrer for 5 min at 40°C, and then both were mixed drop wise with the extract of lemon juice. This mixture was heated at 85°C on a magnetic stirrer until dry cobalt ferrite nanomaterial was obtained. The as-synthesized powder was heated at 200°C in oven for 4 h to remove any moisture content and then further sintered for 4 h at 1000°C. The structural characterization was made using X ray diffraction in 2θ range of $20^0$ to $80^0$ at room temperature using CuKα, λ = 1.5406 Å radiation. An FTIR spectrum was recorded using in the range 350 to 800 $cm^{-1}$.

## RESULTS AND DISCUSSION

***X-ray diffraction:*** Fig. 1 represents X-Ray diffraction (XRD) pattern of $CoFe_2O_4$ synthesized by using green synthesis techniques. XRD pattern shows the Braggs reflections (220), (311), (222), (400), (422), (511), (440) and (533).

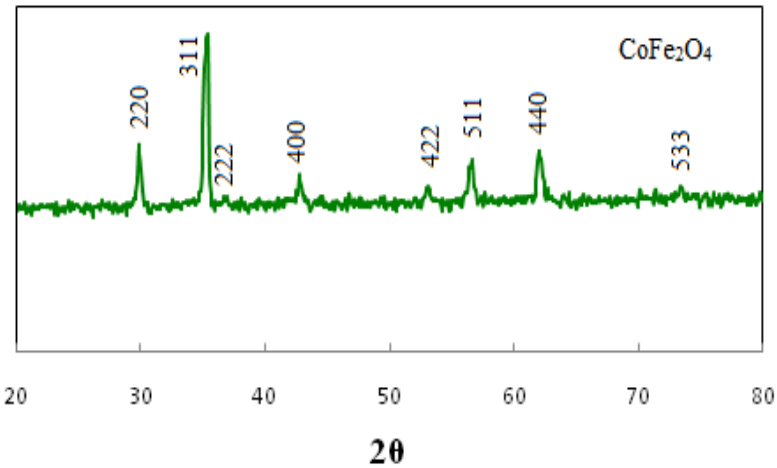


**Fig. 1:** X-ray diffraction pattern of $CoFe_2O_4$ nanoparticle.

All the reflections belong to cubic spinel structure confirming formation of single phase cubic structure with nanophase. The structural parameters were determined from XRD data and tabulated in Table 1. The lattice constant of $CoFe_2O_4$ nanoparticles synthesized using the present synthesis route is fall in order of 8.3954 Å and is closely agree with reported value in the literature [14]. To confirm nano-crystalline nature of synthesized $CoFe_2O_4$, the crystallite size was calculated using Scherrer's formula. From the most intense (311) peak the average crystallite size of the particle was found to be 26 nm. X-ray density of the cobalt ferrite sample is found to be 5.2675 $g/cm^3$ whereas the bulk density is 4.3854 $g/cm^3$. Using the experimental value of lattice parameter, different structural parameters such as bond length [$d_{AX}$, $d_{BX}$], site radii [$r_A$, $r_B$], tetrahedral edge [$d_{XX}$], shared and unshared octahedral edges [$d'_{XX}$, $d''_{XX}$], hopping length [$L_A$, $L_B$], cation-cation (Me-Me) and cation-anion (Me-O) bond distances and bond angles **($\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$, $\theta_5$)** for cobalt ferrite synthesized by using present green synthesis techniques were determined using the relations [15] and are summarized in Table 1.

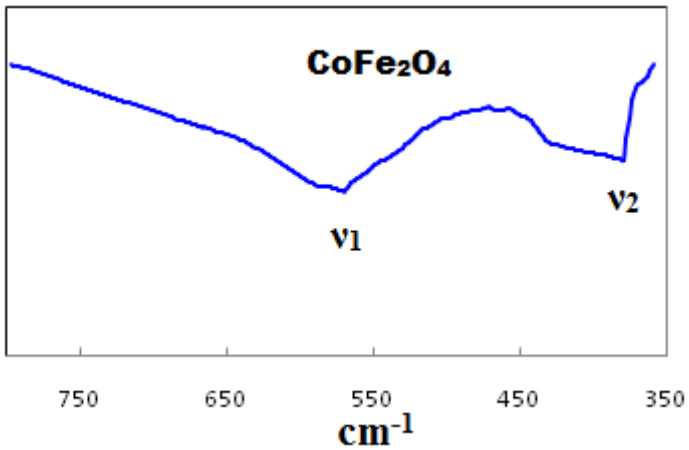


**Fig. 2:** FTIR spectra for $CoFe_2O_4$ nanoparticle

***Fourier Transform Infrared Spectroscopy:*** Fig. 2 represents FTIR spectra of $CoFe_2O_4$ synthesized by using green synthesis technique recorded at room temperature in the range of 350 – 800 cm-1. The appearance of two absorption bands corresponds to stretching vibration of tetrahedral and octahedral complexes ($\nu_1$ and $\nu_2$) confirms the formation of spinel type structure. This confirms the XRD analysis, where the materials show all the characteristic reflections of cubic spinel ferrites.

The positions of $\nu_1$ and $\nu_2$ are tabulated in Table 2. It is observed that the absorption bands for present ferrite system are found to be in the expected range of high frequency band $\nu_1$ is at 569 $cm^{-1}$ and low frequency band $\nu_2$ is at 379 $cm^{-1}$. The absorption band $\nu_1$ was caused by stretching of tetrahedral metal ion and oxygen bonding, whereas $\nu_2$ was caused by the vibration of oxygen in the direction perpendicular to the axis joining tetrahedral ion and oxygen ion. The elastic modili such as Young's Modulus, Bulk Modulus, Shear Modulus, and Longitudinal Modulus, Poisson's ratio, longitudinal velocity, Transverse velocity, mean velocity and Debye temperature were determined using the relations [15] and tabulated in Table 2. The ratio of Bulk modulus to Rigidity modulus represents the Ductibility/brittleness nature of synthesized material. If this ratio is larger than the critical value 1.75, the material is said to be ductile in nature and if lower than 1.75 then the brittle nature. Hence for the present synthesized cobalt ferrite, the ratio has the value 1.79 so it is ductile in nature.

**Table 1:** Values of structural parameters of $CoFe_2O_4$ ferrite nanoparticles

| Parameter | Value |
|---|---|
| Experimental lattice parameter a (Å) | 8.3954 |
| Theoretical lattice parameter $a_{th}$ (Å) | 8.4432 |
| Crystallite size nm | 26 |
| X – ray density g/$cm^3$ | 5.2675 |
| Bulk density g/$cm^3$ | 4.3854 |
| Ionic radius $r_A$ | 0.5327 |
| Ionic radius $r_B$ | 0.6857 |
| Oxygen parameter u | 0.3971 |
| Tetrahedral bond length $d_{AX}$ | 2.1394 |
| Octahedral bond length $d_{BX}$ | 1.9310 |
| Shared tetrahedral edge $d_{XX}$ | 3.4936 |
| Shared octahedral edge $d'_{XX}$ | 2.4428 |
| Unshared octahedral edge $d''_{XX}$ | 2.9913 |
| Hopping length $L_A$ | 3.6353 |
| Hopping length $L_B$ | 2.9682 |
| Effective bond length R | 2.0175 |
| Cation-Cation (M-M) bond distances b | 2.9682 |
| c | 3.4805 |
| d | 3.6353 |
| e | 5.4529 |
| f | 5.1411 |
| Cation-Anion (M-O) bond distances p | 1.9130 |
| q | 2.1394 |
| r | 4.0966 |
| s | 3.7425 |
| Bond Angles in degrees (A-O-B) $\theta_1$ | 118.25 |
| (A-O-B) $\theta_2$ | 126.34 |
| (B-O-B) $\theta_3$ | 89.97 |
| (B-O-B) $\theta_4$ | 127.72 |
| (A-O-A) $\theta_5$ | 62.30 |

**Table 2:** Values of vibrational bands and elastic constants of $CoFe_2O_4$ ferrite nanoparticles

| Parameter | Value |
|---|---|
| Vibrational band on tetrahedral (A) site $\nu_1$ $cm^{-1}$ | 569.12 |
| Vibrational band on octahedral (B) site $\nu_2$ $cm^{-1}$ | 379.33 |
| Force constant of tetrahedral (A) site $K_t$ (N/m) | 139.25 |
| Force constant of octahedral (B) site $K_o$ (N/m) | 87.26 |
| longitudinal wave velocity $V_L$ (m/s) | 5546.29 |
| transverse wave velocity $V_T$ (m/s) | 3202.15 |
| Mean wave velocity ($V_m$) (m/s) | 3554.99 |
| Longitudinal modulus (L) (GPa) | 134.90 |
| Shear modulus (G) (GPa) | 44.96 |
| Bulk modulus (B) (GPa) | 74.94 |
| Young modulus (E) (GPa) | 112.41 |
| Poissons ratio ($\sigma$) | 0.25 |
| elastic moduli corrected to zero porosity $E_0$ (GPa) | 169.25 |
| $G_0$ (GPa) | 66.87 |
| $B_0$ (GPa) | 120.25 |
| $L_o$ (GPa) | 209.42 |
| $\sigma_0$ (GPa) | 0.2654 |
| Debye temperatures $\theta_D$ (K) | 453.88 |
| Debye temperatures $\theta_1$ (K) | 681.85 |
| Bulk modulus to Rigidity modulus $B_0/G_0$ | 1.79 |

## CONCLUSIONS

[1] Cobalt ferrite nanoparticle was successfully synthesized using green synthesis method from an aqueous solution containing metal nitrates and extract of lemon juice.

[2] X-ray diffraction patterns confirm the complete formation of spinel cubic structure with nanophase.

[3] The appearance of two absorption bands in FTIR corresponds to stretching vibration of tetrahedral and octahedral complexes confirms the formation of spinel type structure.

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# Synthesis of $Y^{3+}$ doped Cu-Zn ferrites Nanoparticles by sol-gel auto combustion method and analysis of structural parameters.

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## ABSTRACT

Nano Ferro Spinel Compounds with composition $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$, with composition x=0.0, x= 0.025, 0.050, 0.075, 0.1were synthesized by conventional sol-gel auto combustion method. The synthesized samples' calcination temperature is confirmed by TGA/DTA analysis and finally annealed at a temperature of 450ºC for 6 Hrs. The synthesized samples phase analyzed by X-ray diffractometry confirmed the single-phase cubic structure of samples with space group *Fd3m* without any impurity phase. Structural parameters such as lattice parameter, crystallite size cell volume were calculated, from structural analysis, it is clear that the Yttrium doped and undoped copper zinc ferrite lattice, parameter and cell volume gradually increases with the increase in the concentration of Yttrium deponent with composition x, the crystallite size of all the sample was calculated by Debye-Scherers formula and it is in the range of 30-38 n.m. FT-IR measurement confirmed the presence of all the functional groups. The presence of all the functional groups which are related to the $AB_2O_4$ form the vibrational stretching and asymmetric stretching modes represent the formation of spinel structure.

***Keyword**: Sol-gel auto combustion, TGA / DTA XRD, FT-IR*

## INTRODUCTION

Ferrite nanoparticles are a member of a large group of magnetic nanoparticles and nowadays have a considerable amount of attention due to their electrical magnetic and catalytical applications as compared to bulk particles. These particles have improved catalytic, dielectric and magnetic properties and they possess high resistivity and negligible eddy current losses. [1] . Ferrite nanoparticles show distinguishable physicochemical parameters, such as high chemical stability, electrical resistance, Curie temperature, mechanical hardness and surface area [2]. These materials are used in microwaves, digital tapes and recording media [3], also they are used in drug delivery, de-toxification, magnetic anti-cancer drugs magnetic resonance imaging, magnetic cell separation etc. [4,5].

The structural morphological properties and applications of nano-ferrite spinel compounds depend on the method of synthesis, composition, depends etc. The rare earth elements having remarkable triple plus valance and large ionic radius and concentration play an outstanding role in changing the properties of compounds due to the occurrence of 4f-($RE^3$ ) – 3d ($Fe^{3+}$) couplings. The difference in ionic radii between $RE^{3+}$ and $Fe^{3+}$ atoms leads to lattice strain resulting in deformation or defect in microstructure or form of secondary phase [6] Previous study reported that, the dopant rare earth element ($RE^{3+}$) in Cu-Zn ferrite with solubility equal to 0.15 increases lattice constant of concentration of dopant increases above 0.15 composition, the secondary phases are identified in cobalt, ferrites, Nickel, Zinc Spinel ferrite. [7, 8].

Nano ferrite spinel compounds are synthesized by different methods, such as co-precipitation, hydrothermal, sol-gel auto combustion, electro-chemical, thermal decomposition of precursor, and microemulsion methods. [9] The sol-gel auto-combustion method is generally preferable method due to its simplicity, and good control of the crystalline size, they are more uniform and homogenous less distributed in size, and samples are synthesized in large amounts in a relatively short time as compared to other methods.

In this search work, Yttrium doped Cu-Zn ferrite nanoparticle composition x =0.0, x = 0.025,x = 0.050, x =0.075, x =0.1, were synthesized by using the sol-gel auto-combustion method. In this study, we investigate the structural parameters of synthesized samples.

## METHODOLOGY

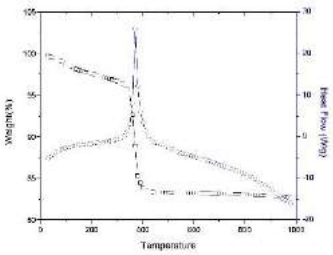
The Yttrium doped Cu-Zn ferrites were synthesized by sol-gel auto-combustion method, by using stoichiometric among of copper nitrate hexahydrate (Cu $(NO_3)_3.6H_2O$ Zinc nitrate hexahydrate, (Zn $(NO_3)_2.6H_2O$) Ferrite nitrate nona-hydrate $Fe(NO_3)_2.9H_2O$, Yttrium nitrate hexahydrate $Y(NO_3)_3.6$ and Citric acid anhydrous ($C_6H_80_7$) All the chemicals are of analytical grade and are used without purification and are brought from Sigma- Aldrich.

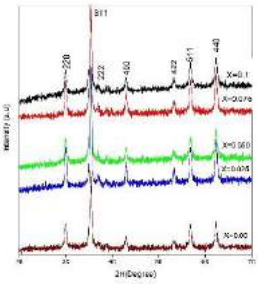
Yttrium doped $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$, with composition composition x =0.0, x = 0.025 x = 0.050, x =0.075, x =0.1 synthesized by sol gel auto-combustion method. The metal nitrate was dissolved together in the minimum quantity of deionized water to gel clear solution, an aqueous solution of citric acid with a metal nitrate ratio of 1:1 mixed with metal nitrate solution, then ammonia solution was slowly added to adjust $_PH \equiv 7$, the mixed solution kept on a hot plate with continuous stirring at temperature 70° C. The viscous brown gel obtained, itself ignites and is burnt with glowing flint. The auto combustion was completed with yielding brown color ash. These samples were analyzed by TGA/DTA, annealed at a temperature 450ºC for 6 Hrs, and analyzed by, X-ray diffractometry (XRD) in the range of 20-70 and FTIR spectroscopy, for analysis of structural parameters.

## RESULT AND DISCUSSIONS

***TGA and DTA analysis:*** The TGA and DTA curves of the as-prepared sample are shown in Fig. 1. TGA curve shown at the temperature range of $125^0$C to $150^0$C shows a slight exothermic reaction resulting in loss of crystallization water, in the range of temperature 325 to $375^0$C observed exothermic reaction related to precursor loss coordinated water and converted into metal oxides, from temperature 500 to $600^0$ C metal crystallization takes place indicated by a sharp exothermic peak which corresponds to the conversion of metal oxide into ferrite, there is no any peaks wear observed the TGA/DTA similar types of thermal decomposition patterns results were in agreement with available literature [10,11].

***XRD analysis:*** XRD spectra of the samples annealed at temperatures 450ºC for 6 Hrs is illustrated in Fig. 2.



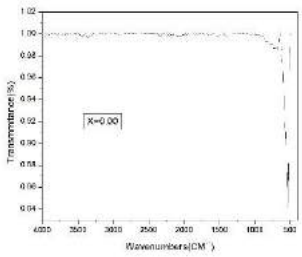




**Fig.1.** TGA/DTA Analysis of x=0.0 **Fig.2.** XRD Patterns of x= 0.00 to 0.1 **Fig.3** FT-IR Spectra of x=0.0

These patterns correspond to peaks of (110),(220),(311),(222),(511) and (440)The diffraction peaks correspond to composition x=0.00 of $Cu_{0.5}$ $Zn_{0.5}$ $Fe_2O_4$ spinal ferrite matched with JCPDS card No. 77-0012 of ICOD data card is 8.388Å but our experimental value was higher, possibly due to the presence of secondary phase hematite or to the Jahn-Teller effect,[12], and observed 8.3890Å No impurity phase was observed, with an increase in concentration of dopant Yttrium ions, the peaks were slightly shifted from lower to higher angle and intensity of peaks slightly increased to crystal growth. The lattice parameter 'a' of $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$,x=0.0, 0.025, 0.05, 0.075 and 0.100 were increases with increase in concentrations of $Y^{3+}$ doped from 8.3890 to 8.4813 Å due to substitution of $Fe^{3+}$ ions with atomic radii. by $Y^{3+}$ ions, similar types of results were also observed in the literature [12,14] and tabulated in Table No.1.

The average crystalline size was calculated by the Scherer equation, which is given below. (311) peak

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

In equation (1), the λ is 0.15406 nm, β is the full-width half maximum of the main diffraction peak (311) [16,17]. The calculated size of crystallites was in the range of 30-38 nm confirming the nanocrystalline nature of samples, and values are tabulated in table No.1.

The X-ray density was theoretically calculated by using the following equation

$$dx = 8M/Na^3 \quad (2)$$

In this equation, the M is molecular mass of the samples, N is Avogadro's number and a is the lattice parameter. It is observed that the X-ray density increased with an increase in $Y^{3+}$ ion concentration [17].

**Table 1.** Lattice constant (Å ), particle size (nm), and X-ray density (g $m^3$ ) of $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$ samples

| Composition 'x' | Lattice constant, 'a' (Å ) | Particle size, 'D' (nm) | X-ray density, '$d_x$' (g $m^3$ ) |
|---|---|---|---|
| x = 0.00 | 8.3897 | 30 | 5.0912 |
| x = 0.025 | 8.4126 | 32 | 5.0996 |
| x = 0.050 | 8.4326 | 34 | 5.1823 |
| x = 0.075 | 8.4492 | 37 | 5.2012 |
| x = 0.100 | 8.4813 | 38 | 5.2146 |

***FTIR ANALYSIS:*** Fourier Transform Infra-Red Spectroscopy (FTIR) is the technique frequently employed in materials science to probe the stretching and bending vibrations that are characteristic features of metal-oxygen bonds. FTIR spectra of x =0.0 composition of $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$, nanoparticles recorded at room temperature shown in Fig.3.

Demonstrates the presence of two fundamental absorption bands which are attributed to the normal and inverse cubic spinel ferrites. Generally the higher frequency absorption band '$\nu_1$' appears in the range of 500 to 600 $cm^{-1}$ and represents the intrinsic vibration of the tetrahedral group, while the octahedral groups are represented by the lower frequency absorption band '$\nu_2$' in the range of 350–490 $cm^{-}$1.[19,20] Since the tetrahedral site dimensions are less as compared to the octahedral, the band frequency of '$\nu_1$' is higher than the '$\nu_2$' absorption band [20]. The characteristic bands that appear at wavenumber 572.42 $cm^{-1}$ are attributed to the metal-oxygen stretching vibration of $Fe^{3+}$-$O_2$ [21]. The spectrum shows absorption bands at 1638.32 $cm^{-1}$ corresponding to $NO_3$, and also due to the presence of carboxyl group (COO-) The broadband that appears at 3440.23 $cm^{-1}$affiliated with hydrogen-bonded O-H stretching vibration. The difference in intensity of 'and '$\nu_2$' absorption bands is due to the changes in the bond length of $Fe^{3+}$-$O_2$ at tetrahedral A sites and octahedral B-sites.[22]

It can be observed from the FT- IR spectrum that the absorption band '$\nu_1$' intensity increases with an increase in $Y^{3+}$ ion substitution concentration, while band '$\nu_2$' does not show any changes. The variation in the intensity of '$\nu_1$' is caused by the nature of the lanthanum ion which prefers to occupy the octahedral B-site and forces the iron ion into the A-site with an increase in the $Y^{3+}$ concentration

## CONCLUSIONS

The $Cu_{0.5}$ $Zn_{0.5}$ $Fe_{2-x}$ $Y_x$ $O_4$ nanoparticles were successfully synthesized by sol–gel auto-combustion method. From TGA/ DTA studies annulling temperatures confirmed. The data of XRD showed that all samples belonging cubic spinel structure. With increase in concretion of dopant $Y^{3+}$ ions does not change the spinel structure of the ferrite. And with increase in concentrations of $Y^{3+}$ doped from 8.3890 to 8.4813 Å due to substitution of $Fe^{3+}$ ions with atomic radii. by $Y^{3+}$ ions, The average crystalline size was calculated by the Scherer equation , observed in the range of 30 to 38 nm.The formation of the spinel structure of the sample was also confirmed from the FT-IR measurement. With the content of $Y^{3+}$ ion increasing, the absorption peak of Fe–O bond moves to the high frequency direction.

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# Existence and Uniqueness Result For Fractional Reaction-Diffusion Equations Via Monotone Method

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**Abstract**

In this paper, an attempt has been made to consider the review on the study of existence and uniqueness of solutions of fractional reaction-diffusion equations with initial and boundary conditions involving Riemann-Liouville, Caputo and Hilfer type fractional derivative via well known constructive and computational method widely known as monotone method. Study of existence and uniqueness of solutions of system of problem is also considered and monotone method is developed for such problem.

**Keyword:** Riemann-Liouville fractional derivative; monotone method; coupled upper and lower solutions; existence and uniqueness

**Mathematics Subject Classification(2020)**:26A33,26A48, 34A08.

## 1 Introduction

The derivative of noninteger order was introduced around 17th century with a qurey posed by L'Hospital to Liebnitz and necessary calculus was developed by 19th century [10, 26] known as fractional calculus. A wide class of applications of fractional calculus in science and technology are discussed in [10, 27]. A list of mathematicians who have provided important contributions up to the middle of last century, includes Laplace, Fourier, Abel, Liouville, Riemann, Grunwald, Letnikov, Levy, Marchaud, Erdelyi, and Riesz. However, for three centuries, the theory of fractional calculus was developed mainly as a purely theoretical field of mathematics. Fractional calculus play a vital role in the analysis of scientific problems in a broad array of fields such as physics,

engineering, biology and economics [1, 26]. There is no doubt that fractional calculus has become an existing new mathematical method of solution of diverse problem in mathematics, science and engineering.

There are some good methods for studying fractional differential equations such as power series method[27], compositional method [27], variational Lypanov method [4], generalized monotone method [2, 3], quasilinearization method [5], iteration method [17, 9] and Adomian decomposition method [6, 7]The investigation of the theory of fractional differential equations has been started independently recently [13] parallel to the well-known theory of ordinary differential equations. One of the important and widely known method is the monotone method.The method of lower and upper solution is employed successfully in the study of existence-comparison and uniqueness of solutions of initial value problems of a nonlinear differential equations [11]. An excellent account of these results are given in the elegant book by Ladde et.al [11].

The basic results on the solution of fractional reaction-diffusion equations involving Riemann-Liouville,Caputo derivatives of arbitrary order is developed in [14, 15, 16, 17, 18, 19, 25]. Many researchers recently attracted towards the monotone method and developed it for initial value and boundary conditions [14, 15, 17, 20] and studied existence and uniqueness of solutions of these problems. Existence and uniqueness of solutions of system of Riemann-Liouvile fractional reaction-diffusion equations was studied by Nanware and Kundgar in [21, 24] when the function is mixed quasimonotone.In this paper we developed monotone method for fractional reaction-diffusion equations and obtained existence and uniqueness of the solutions for the considered problem.

The paper is organized as follows: Second section deals with preliminary definitions, properties of Euler Gamma function, Mittag-Leffler function and definitions of fractional derivative and fractional integrals. In third section preliminary results and monotone method for fractional reaction-diffusion equations and improved results by Nanware and Kundgar are considered. Fourth section is devoted to monotone method for system of fractional reaction-diffusion equations and study of existence and uniqueness of solutions for the considered problems. Last section comprises of the monotone method for finite system of fractional reaction-diffusion equations and study on the existence and uniqueness of solutions of the considered problem.

## 2 Preliminaries

In this section, we recall known results, some definitions and which are needed to next sections

**Definition 2.1**[27] The Gamma function, $\Gamma(q)$, is defined by

$$\Gamma(q) = \int_0^\infty s^{q-1}e^{-s}ds \quad q \in \mathbb{C}$$

**Definition 2.2**[15] The Caputo (left-sided) fractional derivative of $u(t)$ of order $q$, $n-1 \leq q \leq n$, is given by

$$^{c}D^{q}u(t) = \frac{1}{\Gamma(n-q)} \int_0^t (t-s)^{n-q-1} u^n(s) ds, \quad t \in [0, \infty), t > t_0,$$

where $\Gamma(.)$ is Euler-Gamma function.
**Definition 2.3**[17] The Riemann-Liouville fractional integral of a function $u(t)$ is defined as

$$D^{-q}u(t) = \frac{1}{\Gamma(q)} \int_0^t (t-s)^{q-1} u(s) ds.$$

**Definition 2.4**[17] The Riemann-Liouville (left-sided) fractional derivative of a function $u(t)$ is defined as

$$D^{q}u(t) = \frac{1}{\Gamma(1-q)} \frac{d}{dt} \int_0^t (t-s)^{q-1} u(s) ds, t > 0.$$

**Definition 2.5**(Hilfer fractional derivative) The generalized Riemann-Liouville fractional derivative of order $0 \leq p \leq 1$ and $0 < q < 1$ with lower limit $a$ is defined as

$$D_{a+}^{p,q}u(t) = I_{a+}^{p(1-q)} \frac{d}{dt} I_{a+}^{(1-p)(1-q)} u(t).$$

for functions such that the expression on the right-hand side exists.
**Definition 2.6**[27] The two parameter Mittag-Liffler function is defined as

$$E_{p,q}(t^p) = \sum_{k=0}^{\infty} \frac{(t^p)^k}{\Gamma(pk+q)}, \tag{2.1}$$

where $p, q > 0$. Furthermore, for $p = q$, (2.1) reduces to

$$E_{p,p}(t^p) = \sum_{k=0}^{\infty} \frac{(t^p)^k}{\Gamma(pk+p)},$$

If $q = 1$ in (2.1), then we have:

$$E_{p,1}(t^p) = \sum_{k=0}^{\infty} \frac{(t^p)^k}{\Gamma(pk+1)},$$

If $q = 1 = p$ in (2.1), then we have:

$$E_{1,1}(t) = e^t,$$

Where $e^t$ is the usual exponential function.
Consider the initial value problem for the linear Riemann-Liouville fractional differential equation of order $q$ as

$$D^q u = \lambda u + f(t), \qquad \Gamma(q) u(t) t^{1-q} \mid_{t=0} = u^0 \tag{2.2}$$

where $\lambda \in \mathbb{R}$ and $h \in C[J_0, \mathbb{R}]$, has integral representation of the solution of equation (2.2) is

$$u(t) = u^0 t^{q-1} E_{q,q}(\lambda t^q) + \int_0^t (t-s)^{q-1} E_{q,q}[\lambda(t-s)^q] f(s) ds.$$

Now we begin with following problems for which existence and uniqueness of the solutions is considered by many researchers. Consider the Riemann-Liouville fractional reaction-diffusion equation

$$\partial_t^q u - k u_{xx} = f(x,t,u) \quad on \quad Q_T, \tag{2.3}$$

$$u(0,t) = A(t), u(L,t) = B(t) \quad in \quad \Gamma_T.$$

$$\Gamma(q) t^{1-q} u(x,t) \mid_{t=0} = f^0(x) \quad x \in \Omega$$

where $f \in C[\Omega \times [0,T] \times \mathbb{R}, \mathbb{R}]$, $\Omega = [0,l]$, $J = (0,T]$, $Q_T = J \times \Omega$, $k > 0$ and $\Gamma_T = (0,T) \times \partial\Omega$. Here ${}^c\partial_t^q$ is the partial Riemann-Liuoville fractional derivative with respect to time $'t'$ of order $q$, $0 < q < 1$. This is called fractional reaction-diffusion equation with initial and boundary conditions. Results for the existence and uniqueness of solution for this fractional reaction-diffusion equation with initial and boundary conditions was obtained in 2018 by Chhetri and Vatsala [17] by applying monotone method. The results due to Nanware and Kundgar are extended for system of nonlinear fractional reaction-diffusion equations when the function $f(x,t,u_1,u_2)$ is quasimonotone nondecreasing function are discussed in section 4. The results due to Nanware and Kundgar are more generalized for finite system of nonlinear fractional reaction-diffusion equations when the functions $f(x,t,u_1,u_2....u_N)$ is mixed quasimonotone function are discussed in section 5.

Recently Nanware et.al [23] considered the Hilfer fractional reaction-diffusion equation with initial and boundary conditions

$$\partial_t^{p,q} u - k u_{xx} = f(x,t,u) \quad on \quad Q_T. \tag{2.4}$$

$$u(0,t) = A(t), u(L,t) = B(t) \quad in \quad \Gamma_T.$$

$$u(x,t) \mid_{t=0} = f^0(x) \quad x \in \Omega$$

where $f \in C[[0,L] \times [0,T] \times \mathbb{R}, \mathbb{R}]$, $\Omega = [0,L]$, $J = (0,T]$, $Q_T = J \times \Omega$, $k > 0$ and $\Gamma_T = (0,T) \times \partial\Omega$. Here $\partial_t^{p,q}$ is partial Hilfer fractional derivative. This is called Hilfer fractional reaction-diffusion equation with initial and boundary conditions. The existence and uniqueness solution for this Hilfer fractional reaction-diffusion equation with initial and boundary conditions is obtained by Nanware et.al. By applying monotone method. The results due to Nanware and Kundgar are extended for system of nonlinear fractional reaction-diffusion equations when the function $f(x,t,u_1,u_2)$ is quasimonotone nondecreasing function are discussed in section 4. The results due to Nanware and Kundgar are more generalized for finite system of nonlinear fractional reaction-diffusion equations when the functions $f(x,t,u_1,u_2....u_N)$ is mixed quasimonotone function are discussed in section 5.

# 3 Monotone Method for Fractional Reaction-Diffusion Equations

In this section, firstly we consider basic results and the Riemann-Liouville, Caputo and Hifer fractional reaction- diffusion equation with initial and boundary conditions for which monotone method is developed by [17, 25] etc. They have successfully applied the monotone method to obtain existence and uniqueness of solution of these problems.

**Lemma 3.1** [17, 18] [Comprision Results] Let $m(t) \in C_p[[0,T],\mathbb{R}]$ be such that for some $t_1 \in (0,T]$, $m(t_1) = 0$, and $t^{1-q}m(t) \leq 0$ on $[0,t_1]$, then $D^q m(t_1) \geq 0$.

**Note:** In the above theorem, if $m$ is a function of $(x,t)$, then the conclusion is true with the partial derivative of $m$ with respect to $t$ of order $q$.

The following Lemmas are useful to obtaining the convergence of the solutions

**Lemma 3.2**[17] Let $E_{q,1}(-\lambda t^q)$ be the Mittage-Leffler function of order q, where $0 < q \leq 1$. Then, $\frac{E_{q,1}(-\lambda_1 t^q)}{E_{q,1}(-\lambda_2 t^q)} < 1$, where $\lambda_1, \lambda_2 > 0$ such that $\lambda_1 = \lambda_2 + c$ for $c > 0$.

**Lemma 3.3**[17] Let $E_{q,q}(-\lambda t^q)$ be the Mittage-Leffler function of order q, where $0 < q \leq 1$. Then, $\frac{E_{q,q}(-\lambda_1 t^q)}{E_{q,q}(-\lambda_2 t^q)} < 1$, where $\lambda_1, \lambda_2 > 0$ such that $\lambda_1 = \lambda_2 + c$ for $c > 0$.

Now, we show the convergence of the above solutions using Lemma 3.2 and Lemma 3.3 above. We can split the solution of (2.3) as $u_1(x,t)$, $u_2(x,t)$ and $u_3(x,t)$ respectively as follows:

(a) $u_1(x,t)$ is the solution of (2.3), when $f(x,t,u) = 0$, $A(t) = 0 = B(t)$,

(b) $u_2(x,t)$ is the solution of (2.3), when $A(t) = 0 = B(t)$, $f^0 = 0$,

(c) $u_3(x,t)$ is the solution of (2.3), when $f(x,t,u) = 0$, $f^0 = 0$.

**Theorem 3.1**[17] $u_1(x,t)$, $u_2(x,t)$ and $u_3(x,t)$ converge when $|f^0(x)| < N_1$, $N_1 > 0$, $|f(x,t,u)| < N_2$, $N_2 > 0$; $|A(t)| < M_1$, $M_1 > 0$ and $|B(t)| < M_2$, $M_1, M_2 > 0$, respectively.

**Theorem 3.2**[17] [Comparison result ] Assume that

(i) $v(x,t), w(x,t) \in C^{2,q}[Q_T,\mathbb{R}]$ are natural lower and upper solutions of (2.3), respectively and $\Gamma(q)t^{1-q}v(x,t) \mid_{t=0} \leq \Gamma(q)t^{1-q}w(x,t) \mid_{t=0}$, $v(0,t) \leq w(0,t)$, $v(L,t) \leq w(L,t)$.

(ii)$f(x,t,u)$ satisfies the one sided Lipschitz condition

$$f(x,t,u_1,) - f(x,t,u_2) \leq M(u_1 - u_2),$$

whenever $u_1 \leq u_2^*$ and $M > 0$. Then $v(x,t) \leq w(x,t)$ on $J \times \Omega$.

**Theorem 3.3**[17] Assume that

(i) $v(x,t), w(x,t) \in C^{2,q}[Q_T,\mathbb{R}]$ are coupled lower and upper solutions of type I of (2.3)respectively.

(ii)Assume $F(x,t,u) = f(x,t,u) + g(x,t,u)$, where $f$ is a nondecreasing function and $g$ is a nonincreasing function respectively for $(x,t) \in Q_T$ in $u$

(iii)Let $f(x,t,u)$ and $g(x,t,u)$ satisfy the one sided Lipschitz condition

$$f(x,t,u_1) - f(x,t,u_2) \leq L(u_1 - u_2),$$
$$g(x,t,u_1) - g(x,t,u_2) \geq -M(u_1 - u_2),$$

whenever $u_1 \geq u_2$ and $L, M > 0$. Then $v(x,t) \leq w(x,t)$ on $J \times \Omega$.
**Corollary 3.1** [17] [Maximal principle] Let

$$\begin{aligned} \frac{\partial^q m(x,t)}{\partial t^q} - k\frac{\partial^2 m(x,t)}{\partial x^2} &\leq 0 \quad on \quad Q_T, \\ m(0,t) \leq 0, m(L,t) &\leq 0 \quad on \quad \Gamma_T, \\ \Gamma(q)t^{1-q}m(x,t)\mid_{t=0} &\leq 0 \quad on \quad \Omega. \end{aligned}$$

Then $m(x,t) \leq 0$ on $Q_T$.
**Definition 3.1** [17] If the functions $v(x,t), \quad w(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the natural lower and upper solutions of (2.3) if

$$\begin{aligned} \frac{\partial^q v(x,t)}{\partial t^q} - k\frac{\partial^2 v(x,t)}{\partial x^2} &\leq f(x,t,v(x,t)), \quad on \quad Q_T \\ \Gamma(q)(t-t_0)^{1-q}v(x,t)|_{t=0} &\leq f^0(x), \quad x \in \Omega \\ v(x,0) \leq A(t), v(L,t) &\leq B(t) \quad in \quad \Gamma_T \end{aligned}$$

and

$$\begin{aligned} \frac{\partial^q w(x,t)}{\partial t^q} - k\frac{\partial^2 w(x,t)}{\partial x^2} &\geq f(x,t,w(x,t)), \quad on \quad Q_T \\ \Gamma(q)(t-t_0)^{1-q}w(x,t)|_{t=0} &\geq f^0(x), \quad x \in \Omega \\ w(x,0) \geq A(t), w(L,t) &\geq B(t) \quad in \quad \Gamma_T. \end{aligned}$$

**Definition 3.2** [17] If the functions $v(x,t), \quad w(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called coupled lower and upper solutions of type I if

$$\begin{aligned} \frac{\partial^q v(x,t)}{\partial t^q} - k\frac{\partial^2 v(x,t)}{\partial x^2} &\leq f(x,t,w(x,t)), \quad on \quad Q_T \\ \Gamma(q)(t-t_0)^{1-q}v(x,t)|_{t=0} &\leq f^0(x), \quad x \in \Omega \\ v(x,0) \leq A(t), v(L,t) &\leq B(t) \quad in \quad \Gamma_T, \\ \frac{\partial^q w(x,t)}{\partial t^q} - k\frac{\partial^2 w(x,t)}{\partial x^2} &\geq f(x,t,v(x,t)), \quad on \quad Q_T \\ \Gamma(q)(t-t_0)^{1-q}w(x,t)|_{t=0} &\geq f^0(x), \quad x \in \Omega \\ w(x,0) \geq A(t), w(L,t) &\geq B(t) \quad in \quad \Gamma_T. \end{aligned}$$

**Theorem 3.4**[17] (i) Let $(v_0, w_0)$ be the coupled lower and upper solutions of (2.3) such that $t^{1-q}v_i^0 \leq t^{1-q}w_i^0$ on $Q_T$.
(ii) Suppose that $f(x,t,u)$ is nondecreasing $u$, on $Q_T$. Then there exist monotone sequences $\{t^{1-q}v_n(x,t)\}$ and $\{t^{1-q}w_n(x,t)\}$ such that $t^{1-q}v_n(x,t) \to t^{1-q}\rho(x,t)$ and $t^{1-q}w_n(x,t) \to t^{1-q}\gamma(x,t)$ uniformly and monotonically on $Q_T$, where $\rho(x,t)$ and $\gamma(x,t)$ are coupled minimal and maximal solutions of (2.3) respectively. Such that $t^{1-q}v_0(x,t) < t^{1-q}\rho(x,t) < t^{1-q}u(x,t) < t^{1-q}\gamma(x,t) < t^{1-q}w_0(x,t)$

**Theorem 3.5**[17] Let all the assumptions of theorem 3.4 hold. Futher, let $f(x,t,u)$ satisfy the one sided Lipschitz condition of the form

$$f(x,t,u_1) - f(x,t,u_2) \leq M(u_1 - u_2),$$

whenever $u_1 \geq u_2$ and $M > 0$. Then the solution $u(x,t)$ of (2.3) exists and is unique.
**Definition 3.3** The functions $v(x,t)$, $w(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the natural upper and lower solutions of (2.4) if

$$\partial_t^{p,q} v - k v_{xx} \leq f(x,t,v) \quad on \quad Q_T.$$
$$v(0,t) \leq A(t), v(L,t) \leq B(t) \quad in \quad \Gamma_T.$$
$$v(x,t)\mid_{t=0} \leq f^0(x) \quad x \in \Omega$$

and

$$\partial_t^{p,q} w - k w_{xx} \geq f(x,t,w) \quad on \quad Q_T.$$
$$w(0,t) \geq A(t), w(L,t) \geq B(t) \quad in \quad \Gamma_T.$$
$$w(x,t)\mid_{t=0} \geq f^0(x) \quad x \in \Omega$$

**Theorem 3.6**[23] (i) Let $f(x,t,u)$ in $C^{2,q}[\Omega \times J \times \mathbb{R}, \mathbb{R}]$ be nondecreasing.
(ii) Let $(v_0, w_0)$ be the upper and lower solutions of (2.4) such that $v_0 \leq w_0$ on $Q_T$.
(iii) Let $f(x,t,u)$ satisfies the one sided Lipschitz condition

$$f(x,t,u_1) - f(x,t,u_2) \geq -M(u_1 - u_2),$$

whenever $u^* \leq u$ and $M > 0$. Then there exist monotone sequences $\{v_n(x,t)\}$ and $\{w_n(x,t)\}$ such that $v_n(x,t) \to \rho(x,t)$ and $w_n(x,t) \to \gamma(x,t)$ uniformly and monotonically on $Q_T$, where $\rho(x,t)$ and $\gamma(x,t)$ are maximal and minimal solutions of (2.4) respectively. Such that $v_0(x,t) < \rho(x,t) < u(x,t) < t^{1-q}\gamma(x,t) < w_0(x,t)$
**Theorem 3.7**[23] Let all the assumptions of Theorem 3.6 hold. Further, let $f(x,t,u)$ satisfy the one sided Lipschitz condition

$$f(x,t,u_1) - f(x,t,u_2) \leq M(u_1 - u_2), \quad M > 0.$$

Then the solution $u(x,t)$ of (2.4) exists and is unique.
Chhetri and Vatsala developed monotone method in [17] for Caputo fractional reaction-diffusion equation with initial and boundary condition for natural lower and upper solutions and type I. Recently, Nanware and Kundgar developed monotone method in [25] for Caputo fractional reaction-diffusion equation initial and boundary condition for type II and type III, which are defined with below.
Now, consider the non-linear Caputo fractional reaction diffusion equations with initial and boundary conditions of the form:

$$^c\partial_t^q u - u_{xx} = f(x,t,u) + g(x,t,u) \quad on \quad Q_T, \tag{3.1}$$
$$u(0,t) = 0, u(L,t) = 0 \quad in \quad \Gamma_T.$$

$$u(x,0) = h(x) \quad x \in \Omega$$

where $\Omega = [0, L]$, $J = (0, T]$, $Q_T = J \times \Omega$ and $\Gamma_T = (0, T) \times \partial\Omega$. Here ${}^c\partial_t^q$ is the Caputo partial fractional derivative with respect to time $t$ of order $q$, $0 < q < 1$. To develop monotone method for the problem, we need to define the following, important results & definitions

**Definition 3.4**[25] Let $v(x,t), w(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$.
(a) $v(x,t)$ and $w(x,t)$ are called the natural lower and upper solutions of (3.1) if the following inequalities are satisfied:

$$\begin{gathered} {}^c\partial_t^q v - v_{xx} \leq f(x,t,v(x,t)) + g(x,t,v(x,t)) \quad on \quad Q_T, \\ v(0,t) \leq 0, v(L,t) \leq 0 \quad in \quad \Gamma_T, \\ v(x,0) \leq h(x) \quad x \in \Omega, \end{gathered}$$

and

$$\begin{gathered} {}^c\partial_t^q w - w_{xx} \geq f(x,t,w(x,t)) + g(x,t,w(x,t)) \quad on \quad Q_T, \\ w(0,t) \geq 0, w(L,t) \geq 0 \quad in \quad \Gamma_T, \\ w(x,0) \geq h(x) \quad x \in \Omega. \end{gathered}$$

(b) $v(x,t)$ and $w(x,t)$ are called the coupled lower and upper solutions of type I (3.1) if the following inequalities are satisfied:

$$\begin{gathered} {}^c\partial_t^q v - v_{xx} \leq f(x,t,v(x,t)) + g(x,t,w(x,t)) \quad on \quad Q_T, \\ v(0,t) \leq 0, v(L,t) \leq 0 \quad in \quad \Gamma_T, \\ v(x,0) \leq h(x) \quad x \in \Omega, \end{gathered}$$

and

$$\begin{gathered} {}^c\partial_t^q w - w_{xx} \geq f(x,t,w(x,t)) + g(x,t,v(x,t)) \quad on \quad Q_T, \\ w(0,t) \geq 0, w(L,t) \geq 0 \quad in \quad \Gamma_T, \\ w(x,0) \geq h(x) \quad x \in \Omega. \end{gathered}$$

(c) $v(x,t)$ and $w(x,t)$ are called the coupled lower and upper solutions of type II (3.1) if the following inequalities are satisfied:

$$\begin{gathered} {}^c\partial_t^q v - v_{xx} \leq f(x,t,w(x,t)) + g(x,t,v(x,t)) \quad on \quad Q_T, \\ v(0,t) \leq 0, v(L,t) \leq 0 \quad in \quad \Gamma_T, \\ v(x,0) \leq h(x) \quad x \in \Omega, \end{gathered}$$

and

$$\begin{gathered} {}^c\partial_t^q w - w_{xx} \geq f(x,t,v(x,t)) + g(x,t,w(x,t)) \quad on \quad Q_T, \\ w(0,t) \geq 0, w(L,t) \geq 0 \quad in \quad \Gamma_T, \\ w(x,0) \geq h(x) \quad x \in \Omega. \end{gathered}$$

(d) $v(x,t)$ and $w(x,t)$ are called the coupled lower and upper solutions of type III (3.1) if the following inequalities are satisfied:

$$
\begin{gathered}
{}^{c}\partial_t^{q} v - v_{xx} \leq f(x,t,w(x,t)) + g(x,t,w(x,t)) \quad on \quad Q_T, \\
v(0,t) \leq 0, v(L,t) \leq 0 \quad in \quad \Gamma_T, \\
v(x,0) \leq h(x) \quad x \in \Omega,
\end{gathered}
$$

and

$$
\begin{gathered}
{}^{c}\partial_t^{q} w - w_{xx} \geq f(x,t,v(x,t)) + g(x,t,v(x,t)) \quad on \quad Q_T, \\
w(0,t) \geq 0, w(L,t) \geq 0 \quad in \quad \Gamma_T, \\
w(x,0) \geq h(x) \quad x \in \Omega.
\end{gathered}
$$

**Theorem 3.8**[25] Assume that
$(i)$ Let $f, g \in C^{2,q}[\Omega, \mathbb{R}]$, $f_u, g_u, f_{uu}, g_{uu}$ exist, are continuous and satisfy $f_{uu}(x,t,u) \geq 0, g_{uu}(x,t,u) \leq 0$ for $(x,t,u) \in \Omega$
$(ii)$ $v_0, w_0 \in C^{2,q}[J, \mathbb{R}]$, $v_0 \leq w_0$ on $Q_T$, and

$$
\begin{gathered}
{}^{c}\partial_t^{q} v_0 - v_{0,xx} \leq f(x,t,w_0) + g(x,t,v_0), \\
v_0(0,t) \leq 0, v_0(L,t) \leq 0, \\
v_0(x,0) \leq h(x)
\end{gathered}
$$

and

$$
\begin{gathered}
{}^{c}\partial_t^{q} w_0 - w_{0,xx} \geq f(x,t,v_0) + g(x,t,w_0), \\
w_0(0,t) \geq 0, w_0(L,t) \leq 0, \\
w_0(x,0) \geq h(x).
\end{gathered}
$$

$(iii)$ $f_u(x,t,u) \geq 0$ on $\Omega$. Then there exist monotone sequences $\{v_n(x,t)\}, \{w_n(x,t)\}$ which converge uniformly to the unique solution of (3.1) and the convergence is quadratic.

**Theorem 3.9**[25] Assume that
$(i)$ Let $f, g \in C^{2,q}[\Omega, \mathbb{R}]$, $f_u, g_u, f_{uu}, g_{uu}$ exist, are continuous and satisfy $f_{uu}(x,t,u) \geq 0, g_{uu}(x,t,u) \leq 0$ for $(x,t,u) \in \Omega$
$(ii)$ $v_0, w_0 \in C^{2,q}[J, \mathbb{R}]$, $v_0 \leq w_0$ on $Q_T$, and

$$
\begin{gathered}
{}^{c}\partial_t^{q} v_0 - v_{0,xx} \leq f(x,t,w_0) + g(x,t,w_0), \\
v_0(0,t) \leq 0, v_0(L,t) \leq 0, \\
v_0(x,0) \leq h(x)
\end{gathered}
$$

and

$$
\begin{gathered}
{}^{c}\partial_t^{q} w_0 - w_{0,xx} \geq f(x,t,v_0) + g(x,t,v_0), \\
w_0(0,t) \geq 0, w_0(L,t) \leq 0,
\end{gathered}
$$

$$w_0(x,0) \geq h(x).$$

$(iii)$ $f_u(x,t,u) \geq 0$ on $\Omega$. Then there exist monotone sequences $\{v_n(x,t)\}, \{w_n(x,t)\}$ which converge uniformly to the unique solution of (3.1) and the convergence is quadratic.

# 4 Monotone Method For System of Fractional Reaction-Diffusion Equations

In this section monotone method developed by Nanware and Kundgar [21] for system of Riemann-Liouville fractional reaction-diffusion equations with initial and boundary conditions and monotone method developed for system Hilfer fractional reaction-diffusion equations with initial and boundary conditions are considered.

Existence and uniqueness results obtained by Chhetri and Vatsala are extended by Nanware and Kundgar [21] for the system of Riemann-Liouville fractional reaction-diffusion equations with initial and boundary conditions

$$\frac{\partial^q u_i}{\partial t^q} - k_i \frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u_1,u_2) \quad on \quad Q_T. \tag{4.1}$$

$$u_i(0,t) = A_i(t), u_i(L,t) = B_i(t) \quad in \quad \Gamma_T.$$

$$\Gamma(q)t^{1-q}u_i(x,t)\mid_{t=0} = f_i^0(x) \quad x \in \Omega$$

where $i = 1,2, f_i \in C[\Omega \times J_0 \times \mathbb{R}^2, \mathbb{R}]$, $\Omega = [0,L]$, $J = (0,T]$, $Q_T = J \times \Omega$, $k > 0$ and $\Gamma_T = (0,T) \times \partial\Omega$.

**Definition 4.1**[21] If the functions $v_i(x,t) \& w_i(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the natural lower and upper solutions of (4.1) if

$$\frac{\partial^q v_i(x,t)}{\partial t^q} - k_i \frac{\partial^2 v_i(x,t)}{\partial x^2} \leq f_i(x,t,v_1,v_2), \quad on \quad Q_T$$

$$\Gamma(q)(t-t_0)^{1-q}v_i(x,t)\mid_{t=0} \leq f_i^0(x), \quad x \in \Omega$$

$$v_i(x,0) \leq A_i(t), v_i(L,t) \leq B_i(t) \quad in \quad \Gamma_T$$

and

$$\frac{\partial^q w_i(x,t)}{\partial t^q} - k_i \frac{\partial^2 w_i(x,t)}{\partial x^2} \geq f_i(x,t,w_1,w_2), \quad on \quad Q_T$$

$$\Gamma(q)(t-t_0)^{1-q}w_i(x,t)\mid_{t=0} \geq f_i^0(x), \quad x \in \Omega$$

$$w_i(x,0) \geq A_i(t), w_i(L,t) \geq B_i(t) \quad in \quad \Gamma_T.$$

**Definition 4.2**[21] A function $f_i = f_i(x,t,u_1,u_2)$ in $C^{2,q}[Q_T \times \mathbb{R}^2, \mathbb{R}]$ is said to be quasimonotone nondecreasing if
$f_i(x,t,u_1,u_2) \leq f_i(x,t,v_1,v_2)$ if $u_i = v_i$ and $u_j \leq v_j$, $i \neq j$, $i = j = 1,2$.
**Definition 4.3**[21] A function $f_i = f_i(x,t,u_1,u_2)$ in $C^{2,q}[Q_T \times \mathbb{R}^2, \mathbb{R}]$ is said to be

quasimonotone nonincreasing if
$f_i(x,t,u_1,u_2) \geq f_i(x,t,v_1,v_2)$ if $u_i = v_i$ and $u_j \leq v_j$, $i \neq j$, $i = j = 1,2$.
Monotone method for the system of Riemann-Liouville fractional reaction-diffusion equations with initial and boundary conditions(4.1) is developed and existence and uniqueness results for the system of Riemann-Liouville fractional reaction-diffusion equations with initial and boundary conditions (4.1) is obtained [] in the following Theorems.

**Theorem 4.1**[21] (i) Let $f_i = f_i(x,t,u_1,u_2)$ in $C^{2,q}[Q_T \times \mathbb{R}^2, \mathbb{R}]$ be quasimonotone nondecreasing.
(ii) Let $(v_i^0, w_i^0)$ be the coupled lower and upper solutions of (4.1) such that $t^{1-q}v_i^0 \leq t^{1-q}w_i^0$ on $Q_T$.
(iii) Let $f_i(x,t,u_1,u_2)$ satisfies the one sided Lipschitz condition

$$f_i(x,t,u_1,u_2) - f_i(x,t,u_1^*,u_2^*) \geq -M_i(u_i - u_i^*),$$

whenever $u_i^* \leq u_i$ and $M_i > 0$. Then there exist monotone sequences $\{t^{1-q}v_i^n(x,t)\}$ and $\{t^{1-q}w_i^n(x,t)\}$ such that $t^{1-q}v_i^n(x,t) \to t^{1-q}\rho_i(x,t)$ and $t^{1-q}w_i^n(x,t) \to t^{1-q}\gamma_i(x,t)$ uniformly and monotonically on $\overline{Q_T}$, where $\rho_i(x,t)$ and $\gamma_i(x,t)$ are coupled minimal and maximal solutions of (4.1) respectively. Such that $t^{1-q}v_i^n(x,t) < t^{1-q}\rho_i(x,t) < t^{1-q}u_i(x,t) < t^{1-q}\gamma_i(x,t) < t^{1-q}w_i^n(x,t)$

**Theorem 4.2** [21] Let all the assumptions of Theorem 4.1 hold and $f_i(x,t,u_1,u_2)$ satisfy the one sided Lipschitz condition

$$f_i(x,t,u_1,u_2) - f_i(x,t,u_1^*,u_2^*) \leq M_i(u_i - u_i^*), \quad M_i > 0.$$

Then the solution $u_i(x,t)$ of (4.1) exists and is unique.
Monotone method for the system of Hilfer fractional reaction-diffusion equations with initial and boundary conditions deu to Nanware and Kundgar is extended for system by Nanware et.al.[24].
Consider the system of non-linear Hilfer fractional reaction-diffusion equations with initial and boundary conditions of the form:

$$\partial_t^{p,q}u_i - k_i\frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u_1,u_2) \quad on \quad Q_T. \tag{4.2}$$

$$u_i(0,t) = A_i(t), u_i(L,t) = B_i(t) \quad in \quad \Gamma_T.$$

$$u_i(x,0) = f_i^0(x) \quad x \in \Omega$$

where $f \in C[[0,L] \times [0,T] \times \mathbb{R}^2, \mathbb{R}]$, $\Omega = [0,L]$, $J = (0,T]$, $Q_T = J \times \Omega$, $k > 0$ and $\Gamma_T = (0,T) \times \partial\Omega$.

**Definition 4.4**[24] The functions $v_i(x,t)$ & $w_i(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the natural lower and upper solutions of (4.2) if

$$\partial_t^{p,q}v_i - k_i\frac{\partial^2 v_i}{\partial x^2} \leq f_i(x,t,v_1,v_2) \quad on \quad Q_T.$$

$$v_i(0,t) \leq A_i(t), v_i(a,t) \leq B_i(t) \quad in \quad \Gamma_T.$$

$$v_i(x,0) = f_i^0(x) \quad x \in \Omega$$

and

$$\partial_t^{p,q} w_i - k_i \frac{\partial^2 w_i}{\partial x^2} \geq f_i(x,t,w_1,w_2) \quad on \quad Q_T.$$
$$w_i(0,t) \geq A_i(t), w_i(a,t) \geq B_i(t) \quad in \quad \Gamma_T.$$
$$w_i(x,0) = f_i^0(x) \quad x \in \Omega$$

**Theorem 4.3**[24] (i) Let $f_i = f_i(x,t,u_1,u_2)$ in $C^{2,q}[\Omega \times J \times \mathbb{R}^2, \mathbb{R}]$ be quasimonotone nondecreasing.
(ii) Let $(v_i^0, w_i^0)$ be the coupled lower and upper solutions of (4.2) such that $v_i^0 \leq w_i^0$ on $Q_T$.
(iii) Let $f_i(x,t,u_1,u_2)$ satisfies the one sided Lipschitz condition

$$f_i(x,t,u_1,u_2) - f_i(x,t,u_1^*,u_2^*) \geq -M_i(u_i - u_i^*),$$

whenever $u_i^* \leq u_i$ and $M_i > 0$. Then there exist monotone sequences $\{v_i^n(x,t)\}$ and $\{w_i^n(x,t)\}$ such that $v_i^n(x,t) \to \rho_i(x,t)$ and $w_i^n(x,t) \to \gamma_i(x,t)$ uniformly and monotonically on $Q_T$, where $\rho_i(x,t)$ and $\gamma_i(x,t)$ are coupled minimal and maximal solutions of (4.2) respectively. Such that $v_i^n(x,t) < \rho_i(x,t) < u_i(x,t) < \gamma_i(x,t) < w_i^n(x,t)$

**Theorem 4.4**[24] Let all the assumptions of Theorem 4.3 hold and $f_i(x,t,u_1,u_2)$ satisfy the one sided Lipschitz condition

$$f_i(x,t,u_1,u_2) - f_i(x,t,u_1^*,u_2^*) \leq M_i(u_i - u_i^*), \quad M_i > 0.$$

Then the solution $u_i(x,t)$ of (4.2) exists and is unique.

# 5 Monotone Method for Finite System of Fractional Reaction-Diffusion Equations

In this section, some basic definitions are considered and monotone method developed by Nanware and Kundgar [22] for finite system of Riemann-Liouville fractional reaction-diffusion equations with initial and boundary conditions when the function $f(x,t,u)$ is mixed quasi-monotone

Now, we consider the weekly coupled finite system of non-linear Riemann-Liouville fractional reaction-diffusion equations of the type:

$$\frac{\partial^q u_i}{\partial t^q} - k_i \frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u(t)), u(t) = (u_1, u_2, ...u_N) \quad (x,t) \in Q_T, \tag{5.1}$$

$$\Gamma(q) t^{1-q} u_i(x,t)|_{t=0} = f_i^0(x), \quad x \in \Omega,$$
$$u_i(0,t) = A_i(t), u_i(L,t) = B_i(t) on \qquad \Gamma_T$$
$$\Omega = [0,L], J = (0,T], Q_T = J \times \Omega, k > 0,$$

$$\Gamma_T = (0,T) \times \partial\Omega \quad i = 1,2,...,N$$
$$f_i \in C^{2,q}[\Omega \times [0,T] \times \mathbb{R}^N, \mathbb{R}].$$

Where $u_i(x,t) \in C_p^{2,q}$ on $Q_T$, and $u_i(x,t) \in C_p$ on $Q_T$.

In order to develop a monotone method for the (5.1) we use the following generalized concept. For each fixed $i \in \{1,2,...N\}$, let $r_i$, $s_i$ be two nonnegative integers such that $r_i + s_i = N-1$, so that we can split the vector $u$ such that $u = \{u_i, [u]_{r_i}, [u]_{s_i}\}$. Then(5.1) can be written as

$$\frac{\partial^q u_i}{\partial t^q} - k_i \frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}), (x,t) \in Q_T, \tag{5.2}$$
$$\Gamma(q)t^{1-q}u_i(x,t)|_{t=0} = f_i^0(x), x \in \Omega,$$
$$u_i(0,t) = A_i(t), u_i(L,t) = B_i(t) on \quad \Gamma_T.$$

**Definition 5.1** [22] If the functions $v_i(x,t)$, $w_i(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the coupled lower and upper quasisolutions of (5.2) if

$$\frac{\partial^q v_i(x,t)}{\partial t^q} - k_i \frac{\partial^2 v_i(x,t)}{\partial x^2} \leq f_i(x,t,v_i,[v]_{r_i},[w]_{s_i}), \quad on \quad Q_T,$$
$$\Gamma(q)(t-t_0)^{1-q}v_i(x,t)|_{t=0} \leq f_i^0(x), \quad x \in \Omega,$$
$$v_i(x,0) \leq A_i(t), v_i(L,t) \leq B_i(t) \quad on \quad \Gamma_T,$$

and

$$\frac{\partial^q w_i(x,t)}{\partial t^q} - k_i \frac{\partial^2 w_i(x,t)}{\partial x^2} \geq f_i(x,t,w_i,[w]_{r_i},[v]_{s_i}), \quad on \quad Q_T,$$
$$\Gamma(q)(t-t_0)^{1-q}w_i(x,t)|_{t=0} \geq f_i^0(x), \quad x \in \Omega,$$
$$w_i(x,0) \geq A_i(t), w_i(L,t) \geq B_i(t) \quad on \quad \Gamma_T,$$

Furthermore, we say that $v_i(x,t)$ and $w_i(x,t)$ are coupled quasisolutions of (5) if above inequalities are equal.

**Definition 5.2**[22] A function $f_i \in C^{2,q}[[0,L] \times [0,T] \times \mathbb{R}^N, \mathbb{R}]$ is said to be mixed quasimonotone property if for each $i$, $f_i(x,t,u_i,[u]_{r_i},[u]_{s_i})$ is quasimonotone nondecreasing in $[u]_{r_i}$ and quasimonotone nonincreasing in $[u]_{s_i}$.

When either $r_i$ or $s_i$ is equal to zero a special case of the mixed quasimonotone property is defined as follows:

**Definition 5.3**[22] A function $f_i \in C^{2,q}[[0,L] \times [0,T] \times \mathbb{R}^N, \mathbb{R}]$ is said to be quasimonotone nondecreasing (nonincreasing) if for each $i$, $v_i \leq w_i$ and $v_j = w_j$, $i \neq j$ then

$f_i(x,t,v_1,...,v_N) \leq f_i(x,t,w_1,...,w_N)$

$(f_i(x,t,v_1,...,v_N) \geq f_i(x,t,w_1,...,w_N))$.

**Definition 5.4**[22] Let $f_i(x,t,u_1,...,u_N)$ be real valued continuous function defined on $[0,L] \times [0,T] \times \mathbb{R}^N$. We say that $f_i(x,t,u_1,...,u_N)$ satisfies Lipschitz condition if there exists $M_i \geq 0$ such that $\mid f_i(x,t,u_1,...,u_N) - f_i(x,t,u_1^*,...,u_N^*) \mid \leq M_i \mid u_i - u_i^* \mid$

**Theorem 5.1**[22] (i)$f_i \in C^{2,q}[[0,L] \times [0,T] \times \mathbb{R}^N, \mathbb{R}]$ possesses mixed quasimonotone

property and let $(v_i^0, w_i^0)$ be the coupled lower and upper solutions of (5.2) such that $t^{1-q}v_i^0 \leq t^{1-q}w_i^0$ on $Q_T$. Suppose $f_i$ satisfies

$$f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}) - f_i(x,t,u_i^*,[u]_{r_i},[u]_{s_i}) \geq -M_i(u_i - u_i^*),$$

with $M_i > 0$ whenever $v_i^0 \leq u_i \leq u_i^* \leq w_i^0$. Then there exist monotone sequences $\{t^{1-q}v_i^n(x,t)\}$ and $\{t^{1-q}w_i^n(x,t)\}$ such that

$$t^{1-q}v_i^n(x,t) \to t^{1-q}\rho_i(x,t)$$

and

$$t^{1-q}w_i^n(x,t) \to t^{1-q}\gamma_i(x,t)$$

uniformly and monotonically on $Q_T$, where $\rho_i(x,t)$ and $\gamma_i(x,t)$ are coupled minimal and maximal quasisolutions of (5.2) respectively. Furthermore, if $u = (u_1, u_2, ..., u_N)$ is any solution of (5.2) such that $v_i^0 \leq u_i^0 \leq w_i^0$ on $Q_T$, then $v_i \leq u_i \leq w_i$ on $Q_T$

**Theorem 5.2**[22] Let all the assumptions of Theorem 5.1. hold. Further, let $f_i$ satisfy the one sided Lipschitz condition of the form

$$\mid f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}) - f_i(x,t,u_i^*,[u]_{r_i},[u]_{s_i}) \mid \leq M_i \mid (u_i - u_i^*) \mid,$$

for $v_i^0 \leq u_i^* \leq u_i \leq w_i^0$, whenever $M_i \geq 0$ on $Q_T$. Then the quasisolutions $u_i(x,t)$ of (5.2) exists and is unique.

Recently, Nanware and Kundgar developed monotone method in [24] for finite system of Hilfer fractional reaction-diffusion equation with initial and boundary conditions

Now, we consider the weekly coupled finite system of non-linear Riemann-Liouville fractional reaction-diffusion equations of the form:

$$\partial_t^{\alpha,\beta}u_i - k_i\frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u_1,u_2,...,u_N) \quad on \quad Q_T. \tag{5.3}$$

$$u_i(0,t) = A_i(t), u_i(a,t) = B_i(t) \quad in \quad \Gamma_T.$$

$$u_i(x,t)\mid_{t=0} = u_i^0(x) \quad x \in \Omega$$

Where $u_i(x,t) \in C_p^{2,q}$ on $Q_T$, and $u_i(x,t) \in C_p$ on $Q_T$.

In order to develop a monotone method for the (5.3) we use the following generalized concept. For each fixed $i \in \{1,2,...N\}$, let $r_i$, $s_i$ be two nonnegative integers such that $r_i + s_i = N - 1$, so that we can split the vector $u$ such that $u = \{u_i, [u]_{r_i}, [u]_{s_i}\}$. Then(5.3) can be written as

$$\partial_t^{p,q}u_i - k_i\frac{\partial^2 u_i}{\partial x^2} = f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}), (x,t) \in Q_T, \tag{5.4}$$

$$u_i(x,t)|_{t=0} = f_i^0(x), x \in \Omega,$$

$$u_i(0,t) = A_i(t), u_i(L,t) = B_i(t) on \quad \Gamma_T.$$

**Definition 5.5**[24] If the functions $v_i(x,t)$, $w_i(x,t) \in C^{2,q}[Q_T, \mathbb{R}]$ are called the coupled lower and upper quasisolutions of (4.8) if

$$\partial_t^{p,q} v_i - k_i \frac{\partial^2 v_i(x,t)}{\partial x^2} \leq f_i(x,t,v_i,[v]_{r_i},[w]_{s_i}), \quad on \quad Q_T,$$
$$v_i(x,t)|_{t=0} \leq f_i^0(x), \quad x \in \Omega,$$
$$v_i(x,0) \leq A_i(t), v_i(L,t) \leq B_i(t) \quad on \quad \Gamma_T,$$

and

$$\partial_t^{p,q} w_i - k_i \frac{\partial^2 w_i(x,t)}{\partial x^2} \geq f_i(x,t,w_i,[w]_{r_i},[v]_{s_i}), \quad on \quad Q_T,$$
$$w_i(x,t)|_{t=0} \geq f_i^0(x), \quad x \in \Omega,$$
$$w_i(x,0) \geq A_i(t), w_i(L,t) \geq B_i(t) \quad on \quad \Gamma_T,$$

Furthermore, we say that $v_i(x,t)$ and $w_i(x,t)$ are coupled quasisolutions of (5.4) if above inequalities are equal.

**Theorem 5.3**[24] (i)$f_i \in C^{2,\alpha}[[0,L] \times [0,T] \times \mathbb{R}^N, \mathbb{R}]$ possesses mixed quasimonotone property and let $(v_i^0, w_i^0)$ be the coupled lower and upper solutions of (5.4) such that $v_i^0 \leq w_i^0$ on $Q_T$. Suppose $f_i$ satisfies

$$f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}) - f_i(x,t,u_i^*,[u]_{r_i},[u]_{s_i}) \geq -M_i(u_i - u_i^*),$$

with $M_i > 0$ whenever $v_i^0 \leq u_i \leq u^* \leq w_i^0$. Then there exist monotone sequences $\{v_i^n(x,t)\}$ and $\{w_i^n(x,t)\}$ such that

$$v_i^n(x,t) \to \rho_i(x,t)$$

and

$$w_i^n(x,t) \to \gamma_i(x,t)$$

uniformly and monotonically on $Q_T$, where $\rho_i(x,t)$ and $\gamma_i(x,t)$ are coupled minimal and maximal quasisolutions of (5.4) respectively. Furthermore, if $u = (u_1, u_2, ..., u_N)$ is any solution of (5.4) such that $v_i^0 \leq u_i^0 \leq w_i^0$ on $Q_T$, then $v_i \leq u_i \leq w_i$ on $Q_T$

**Theorem 5.4**[24] Let all the assumptions of Theorem 5.3 hold. Further, let $f_i$ satisfy the one sided Lipschitz condition of the form

$$| f_i(x,t,u_i,[u]_{r_i},[u]_{s_i}) - f_i(x,t,u_i^*,[u]_{r_i},[u]_{s_i}) | \leq M_i \mid (u_i - u_i^*) |,$$

for $v_i^0 \leq u_i^* \leq u_i \leq w_i^0$, whenever $M_i \geq 0$ on $Q_T$. Then the quasisolutions $u_i(x,t)$ of (5.4) exists and is unique.

# 6 Conclusion and Future Scope

In this work initially review is done on the study of existence and uniqueness of solutions of fractional reaction-diffusion equations with initial and boundary conditions involving Riemann-Liouville, Caputo and Hilfer type fractional derivative via monotone method.The monotone method for the study of existence and uniqueness results can be applied to prove the existence and uniqueness results for fractional reaction-diffusion equations with different type of conditions.

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# Enhancing Magnetic Performance: A Comprehensive Review of Rare Earth Ion Doping in M-Type Hexaferrites for Modern Technological Advancement.

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**ABSTRACT**

The investigation of magnetic materials for contemporary technology has become a pivotal research area due to rapid societal advancements. M-type hexaferrites, acknowledged as ferrimagnetic materials, display notable magnetic, structural, optical, electrical, and dielectric properties, making them suitable for diverse modern applications. The development of ferrites presents a substantial challenge for material researchers. Currently, the established practice of employing rare earth (RE) materials as dopants proves effective in enhancing the magnetic properties of ferrites. RE ions intricately influence the magnetic characteristics of ferrites. This review explores the impact of RE ions on the magnetic hysteresis loop properties of ferrites, providing a comprehensive overview encompassing chemical composition, RE ratio (x), preparation method, annealing temperature (TS), crystallite size (D), saturation magnetization (MS), remanent magnetization (Mr), coercive force (HC), squareness ratio (SQR), magnetic moment (nB), and anisotropy constant (K) presented in a table. Additionally, the review incorporates a graphical representation of the properties in the M−H loop, aiming to succinctly summarize the doping effect of RE ions in M-type hexaferrites. By addressing pivotal issues, this review imparts valuable insights for researchers involved in future undertakings related to the advancement of magnetic materials and applications.

## INTRODUCTION

Recent investigations into hexagonal ferrites have garnered significant attention within the realm of materials science and technology. Hexagonal ferrites, also known as hexaferrites, represent a class of magnetic ceramics with a hexagonal crystal structure, exhibiting remarkable magnetic properties that make them appealing for a broad spectrum of applications. The renewed interest in hexagonal ferrites stems from their diverse technological uses, including but not limited to applications in permanent magnets, microwave devices, and data storage. The unique combination of magnetic and electrical properties exhibited by hexaferrites has positioned them as promising materials for cutting-edge technologies [1].

In the 1930s, hexagonal ferrite material was discovered in its natural state as lead ferrite, known as magnetoplumbite and represented by the chemical formula $PbFe_{12}O_{19}$. Historically, this compound played a significant role. However, a global effort has been initiated to reduce or eliminate the use of lead in various products, including ferrites, driven by concerns about the environment and health. The U.S. Environmental Protection Agency (EPA) and the European Chemicals Agency (ECHA) guide these endeavors [2]. Due to environmental and health considerations, lead ferrites are being replaced by alternative materials. These alternatives offer magnetic properties similar to or improved from lead ferrites, but without the associated environmental and health risks. This shift reflects a broader commitment to global initiatives promoting the use of safer and more sustainable materials. The push to replace lead-containing materials gained momentum due to the toxicity of lead and its adverse effects on human health and the environment. To replace lead, materials such as Ba (Barium)[3], Sr (Strontium), Mn (Manganese), Zn (Zinc), and others have been employed. These lead-free ferrites have become a popular choice for replacing lead-containing ferrites, exhibiting magnetic properties similar to traditional lead-containing ferrites while being considered eco-friendly.

After the discovery of hexagonal ferrites, scientists and industrial technologists have shown considerable interest in studying these materials, a trend that continues today. In 1951, advancements in gyro magnetic, ferroelectric, and ferromagnetic properties of hexaferrite were made, signifying potential economic implications for specific applications. Presently, extensive theoretical and experimental research is being conducted on the various properties and synthesis of hexaferrite in laboratories.

In recent times, significant attention has been devoted to nanotechnology applications of hexagonal ferrites and the development of orientation and alignment effects in ferrites. These ferrites, as ferromagnetic substances, find extensive applications across diverse technological domains due to their exceptional dielectric traits, favorable magneto crystalline anisotropy, substantial magnetostriction coefficient, and elevated magnetic saturation, among other notable features [4]. Within the realm of electronics, these diligently engineered magnetic materials are prominently utilized for their superior output-to-cost ratios compared to alternative permanent magnets. This makes them well-suited for applications encompassing DC motors, microwave devices, magneto-dielectric properties, and more. Moreover, these materials constitute a significant portion of total magnetic materials manufactured globally. Various types of hexagonal ferrites include M-type $(Sr,Ba)Fe_{12}O_{19}$ [5], W-type $(Sr,Ba)Me_2Fe_{16}O_{27}$, X-type $(Sr, Ba)Me_2Fe_{28}O_{46}$, Y-type (Sr, Ba)2 $Me_2Fe_{12}O_{22}$, Z-type (Sr,Ba)3 $Me_2Fe_{24}O_{41}$, and U-type $(Sr, Ba)_4Me_2Fe_{36}O_{60}$ [6-8]. Among these, M-type hexaferrites like $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ possess a magneto plumbite structure, making them ideal as permanent magnets due to their coercivity and magnetization. They offer the advantages of low manufacturing costs for commercial production and stability. The crystal structure is characterized by close packing of Sr ions and Oxygen with Fe atoms at interstitial positions. M-type hexagonal ferrite stands out as a multifunctional material, exhibiting large magneto crystalline anisotropy, high curie temperature, superior coercivity, chemical stability, corrosion resistance, and moderate remanence (350Mt).

The modification in the crystal structure caused by the doping of the mixture of transition ions and RE ions with differing ionic radii leads to significant changes in a ferrite's magnetic characteristics. Thus, the various properties of RE ions have the potential to be useful for hexaferrites in modulating structural and magnetic behavior. The use of rare earth (RE) elements serves a crucial role in influencing the properties of ferrites, particularly in impeding grain size and modifying magnetic characteristics. This alteration in magnetic properties, influenced by the cationic distribution at elevated temperatures [17], renders these materials well-suited for applications in the hyper-frequency range owing to their robust magnetic properties.

There are 17 rare earth elements, including, $Sc^{3+}$, $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Pm^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Yb^{3+}$, $Lu^{3+}$. When the $RE^{3+}$ ion is introduced into a hexaferrite, it induces a spin coupling effect between $Fe^{3+}$ and $Fe^{2+}$ ions, along with a $3d^{+5}$-$4f^7$ coupling effect between RE and Fe ions, which significantly influences the ferrite's properties. R.H.Kadam et.al successfully synthesized $Y^{3+}$ doped Sr-M-type hexaferrite for reporting the crystal structure and magnetic properties of synthesized specimens. In the present investigation, the atomic and lattice parameters are refined with the help of rietveld software. Turkhanov et.al. synthesized BaM hexaferrite with Al, in substitution by solid state reaction method for controlling the electromagnetic characteristics in these nanohexaferrites. It has been found that the external magnetic fields extensively affect the electromagnetic properties of BaM and SrM hexaferrites. These will occur due to the increase of magneto crystalline anisotropy.

The primary objective of this review is to concentrate on hexagonal ferrites, specifically examining the impact of rare earth elements on barium and strontium as divalent cations (BaM or SrM) and their significant substitutions. Hexagonal ferrites exhibit intrinsic ferrimagnetic properties, closely tied to their crystal structures. While the magnetic characteristics of hexagonal ferrites have been extensively covered by Özgür et al. [10], this review will specifically delve into the practical exploration of the synthesis and magnetic properties of hexagonal ferrites, with a particular emphasis on rare earth doped M-type hexaferrites.

## HEXAGONAL FERRITES

Hexagonal ferrites have been classified according to the configuration of their constituent subunit blocks. SrM demonstrates a hexagonal structure (P63/mmc) composed of R blocks (RSR*S*), where $S = Fe_6 0_8^{2+}$ and $R = MFe_6 0_{11}^{2+}$ [10]. The asterisk (*) signifies a 180° rotation around the crystallographic c-axis. At absolute zero temperature, the magnetization of the unit cell is linked to the $Fe^{3+}$ ion count, evenly distributed between the two blocks. Within the hexagonal R block, five ions occupy an octahedral position (three spin-up and two spin-down moments), and one spin-up moment is

situated on the bipyramidal site. The S block, characterized by a Hexaferritestructure, accommodates 4 out of 6 $Fe^{3+}$ ions in octahedral positions. The octahedral cations display spin-up moments, while the two ions in tetrahedral sites exhibit spin-down moments [11]. Each unit cell encompasses eight spin-up and four spin-down moments, resulting in a magnetic moment of 5μB for each Fe3+ ion at absolute zero. Consequently, the anticipated magnetism of each unit cell amounts to 4 * 5μB = 20μB.

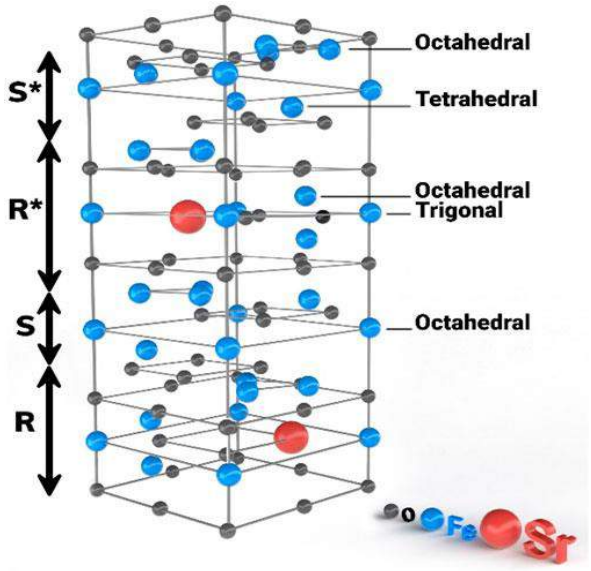


**Fig.1:** Schematic crystal structure of hexaferrites. The cross-section view of (110) and Bond angle surrounded by dashed blue ellipsoids of $SrFe_{12}O_{19}$

## HYSTERISIS LOOP

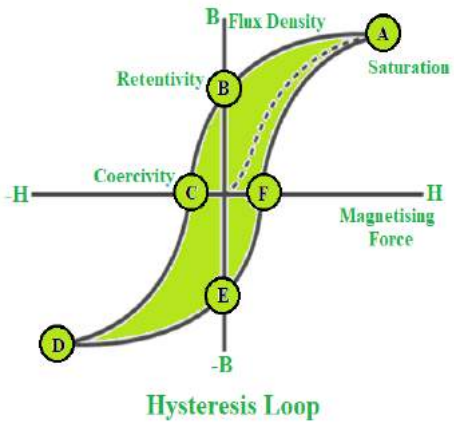


**Fig. 2:** $M_S$,$M_r$ and $H_C$ of a hysteresis loop

In ferromagnetic or ferrimagnetic materials, hysteresis loop characteristics emerge due to the inability to spontaneously demagnetize to zero after being magnetized in a specific direction. The material necessitates the imposition of an opposing magnetic field to attain a zero-magnetization state. This phenomenon is graphically depicted as a loop in the material's magnetization graph, known as a hysteresis loop or MH loop, exemplified in Figure 2. Analyzing the hysteresis loop offers profound insights into diverse fundamental magnetic properties of the material, providing a comprehensive understanding of its magnetic behavior and response to external influences.

## SATURATION MAGNETIZATION

Saturation magnetization ($M_S$)is a property of a magnetic material that represents the maximum magnetic moment per unit volume achievable under the influence of an external magnetic field. When a material is fully magnetized, meaning that all its magnetic domains are aligned, it reaches saturation magnetization.

The formula for saturation magnetization is given by:[12]

$$M_S = \frac{M_r}{V} \quad (1)$$

Where: $M_S$ is the saturation magnetization, M is the total magnetic moment (magnetic dipole moment) of the material, V is the volume of the material.

In simpler terms, saturation magnetization quantifies the maximum magnetic moment a material can achieve per unit volume when exposed to a sufficiently strong external magnetic field. This property is crucial in understanding the magnetic potential of a material and its behavior when subjected to varying levels of magnetic influence.The unit of saturation magnetization is typically expressed in electromagnetic units per unit volume (emu/cm³ or emu/g), depending on the units used for volume.

## REMAMNET MAGNETIZATION

Remanent magnetization (Mr) represents the magnetic polarization that persists in a material even after the removal of an external magnetic field. It is a fundamental characteristic in the examination of magnetic materials and can be calculated using the subsequent formula:[13]

$$M_R = \frac{M_r}{V} \quad (2)$$

Here, $M_R$ denotes the remanent magnetization, $M_r$ stands for the total magnetic moment (magnetic dipole moment) of the material, V represents the volume of the material.

Put simply, remanent magnetization is the magnetic moment per unit volume that endures within a material once the external magnetizing field is no longer present. The formula illustrates the relationship between the total magnetic moment and the volume of the material. This attribute is crucial for comprehending how materials behave in the absence of an external magnetic field, offering insights into their magnetic stability and their ability to retain magnetization over an extended period. The unit of remanent magnetization is commonly expressed in electromagnetic units per unit volume (emu/cm³ or emu/g), depending on the chosen volume units.

## COERCIVE FORCE ($H_C$)

Coercive force ($H_C$) is a measure of the resistance of a magnetic material to demagnetization. It represents the strength of the reverse magnetic field needed to reduce the magnetization of a material to zero after it has been magnetized. In other words, coercive force quantifies the material's ability to retain its magnetization in the presence of an opposing magnetic field.

The formula for coercive force is expressed as follows:[14]

$$H_C = -\frac{H\Delta}{2} \quad (3)$$

Where, $H_C$ is the coercive force, HΔ is the change in applied magnetic field required to demagnetize the material.

The negative sign in the formula indicates that coercive force is a measure of the negative magnetic field strength required to bring the magnetization to zero.

In practical terms, materials with high coercive force are more resistant to demagnetization, making them suitable for applications where stable magnetization is essential. Conversely, materials with low coercive force are easily demagnetized and find applications where frequent magnetization changes are required.

The unit of coercive force is typically expressed in amperes per meter (A/m) or oersteds (Oe), depending on the unit system used.

The squareness ratio, often denoted as \(S_r\), is a measure of how square or rectangular the hysteresis loop is in a magnetization curve. The hysteresis loop represents the relationship between the magnetization and the applied magnetic field for a magnetic material. The squareness ratio is particularly relevant in the study of ferromagnetic materials and is indicative of their magnetic performance.

The formula for the squareness ratio is given by:[13]

$$S_r = \frac{M_r}{M_S} \quad (4)$$

Where, $S_r$ is the squareness ratio, $M_r$ is the remanent magnetization (the magnetic moment per unit volume when the material is fully magnetized), $M_s$ is the saturation magnetization (the maximum magnetic moment per unit volume achievable under the influence of an external magnetic field).

The squareness ratio ranges from 0 to 1, and a higher value indicates a more square-shaped hysteresis loop. A square hysteresis loop signifies that the material has a high remanent magnetization and can retain a significant magnetic moment even in the absence of an external magnetic field. This

property is desirable in applications where a strong and persistent magnetic field is needed. Conversely, a lower squareness ratio indicates a more rectangular hysteresis loop, implying that the material has a lower ability to retain magnetization. This might be suitable for applications where rapid magnetization changes are required.

## MAGNETIC MOMENT ($\mu_B$)

The magnetic moment of a magnetic material pertains to the magnetic strength and orientation of a magnet, which generates a magnetic field. This property is alternatively known as the Bhor magneton number or Bhor magneton. The calculation of magnetic moments in the examined articles employs the formula nB = (Mw × MS) / 5585 [9], where MS represents the saturation magnetization, Mw denotes the molecular weight, and 5585 is the magnetic factor. The magnetic moment is expressed in units of $\mu_B$.

## ANISOTROPY CONSTANT (K)

The anisotropy constant (K) is a parameter in the study of magnetic materials, specifically in the context of magnetic anisotropy. Magnetic anisotropy refers to the dependence of a material's magnetic properties on the direction of magnetization. The anisotropy constant quantifies the energy required to change the direction of magnetization from one preferred axis to another.
The formula for the anisotropy constant is often expressed as:[15].

$$K = -\frac{1}{2}\mu_0 M_s^2 K_1 \quad (5)$$

Where, K is the anisotropy constant, $\mu_0$ is the permeability of free space (a constant), $M_S$ is the saturation magnetization of the material, V is the volume of the magnetic material, $K_1$ is the first-order anisotropy constant (also known as the magnetocrystalline anisotropy constant).

It's important to note that the anisotropy constant is often expressed with negative sign conventionally, indicating that the material has an energy minimum along a specific axis (easy axis) and an energy barrier for magnetization reversal.

## M-H LOOP PROPERTIES OF RE DOPED HEXAFERRITES

The mentioned hysteresis loop properties of all the reviewed article were taken by vibrating sample magnetometer (VSM) at room temperature, and all the samples were hexagonal in shape. The magnetic hysteresis loop properties of RE doped M-type hexaferrite are given below

## SATURATION MAGNETIZATION AND REMANENT MAGNETIZATION OF RE DOPED FERRITES

S S Satpute et al. [9] studied the saturation magnetization of $Y^{3+}$ doped $SrFe_{12}O_{19}$ and observed that the values of $M_S$ for x=0.00 sample was greater than that of yttrium doped samples. In this case, the values of $M_S$ varied between 49.60 emu/g and 35.40 emu/g. They explain that the decreasing nature of $M_S$ and $M_r$ is caused by the substitution of the paramagnetic $Y^{3+}$ ion instead of the ferromagnetic $Fe^{3+}$ ion at the octahedral (B) site and the migration of the $Fe^{3+}$ ion into the tetrahedral (A) site. Chunxiang cao et al.(16) studied the saturation magnetization of $Ce^{3+}$ substituted hexagonal M-type $SrCe_xFe_{12-x}O_{19}$ and observed that Ce substitution has a certain chance to enhance or reduce the $M_S$ and $M_r$ ,even keep the $M_S$ unchanged. Compared with the SrM without substitution, the $M_s$ of Ce- substituted SrM is obiviously greater than those of the former, which is affected not only by the decreasing content of impurity but also by the Ce-substitution. P.Guller et al.[17] studied the magnetic properties of rare earth-doped $BaFe_{12}O_{19}$ and mentioned that the values of magnetic saturation of $Ba_{0.85}$ $(La,Y)_{0.15}Fe_{12}O_{19}$ sintered at $1150^0$C and $1250^0$C were 48.60 emu/g and 52.95 emu/g respectively. Naziya Yasmin et.al [18] studied the magnetic properties of Ce-doped BaM hexaferrite prepared by Sol-gel auto-combustion method sintered at $1250^0$C and mentioned that magnetic saturation, remanence reduces with the exchange of $Fe^{3+}$ ions in spin-up position and enhance with the exchange of $Fe^{3+}$ ions in spin-down position. The predominated values of $M_s$ are observed in range (64.368-40.545). Reduction in $M_s$ and $M_r$ due to split of magnetic co-linearity and spin canting observed due to the increase of Ce-Mn concentration in BaM hexaferrite. M.Almessiere et al. studied magnetic properties of Ce doped SrM Hexaferrites at 300K and 10K with an applied magnetic field of 70kOe, they found typical magnetic hysteresis behavior. Magnetic saturation values correspond to magnetic field 70kOe are respectively 68.56 emu/g at 330K and 102.54 emu/g at 10K which corresponds to sample (x=0.0) and 46.69 emu/g at 300K and 64.34 emu/g at 10K belongs to 0.5 concentration, the variation in the saturation magnetization is due to Ce concentration which influenced by the replacement of magnetic ions of $Fe^{3+}$

by non-magnetic cations and the preferred site occupancy of non-magnetic cations. Furthermore, $Ce^{3+}$ ions mostly generate local strains that possibly produces an environmental disorder or non collinear ferromagnetic arrangement, and the difference in ionic radii between $Ce^{3+}$(1.02Å) and $Fe^{3+}$(0.60Å) enlarges the distance between magnetic ions, which leads to reduce the strength of super-exchange interactions.

## COERCIVITY OF RE DOPED FERRITES

M.Almessiere et.al [19] studied the coercive field ($H_C$) of Ce doped SrM ferrites and observed that the coercive field decreased with increasing Ce content. They explained that their studied ferrites have soft magnetic characteristics, and the decreasing nature of coercivity further supports the soft nature of these samples upon the substitution of $Ce^{3+}$at the $Fe^{3+}$ site, observed that the coercive field initially decreased in x =0.01 sample, after that HC gradually increased from 58.92 Oe to 84.32 Oe with an increasing value of Sc content from x = 0.01 to x =0.05. Naziya Yasmin et al. [18] showed that the value of $H_C$ of $Sm^{3+}$ doped m-type hexaferrite decreased rapidly with an increase in $Sm^{3+}$ content. They mentioned that the increase in crystallite size and magnetocrystalline anisotropy is the reasons behind the increament of coercivity. Khalid mehmood Ur rehman et al. [20] mentioned that the value of HC decreased rapidly from with the increment of Ce content in $Sr_{1-x}Ce_xFe_{12}O_{19}$ material due to the decreasing tendency of $M_S$ and K. Madhav L Ghimire et al. [21] studied the coercive force of Co doped rare earth (La,Pr) and Co-Al substituted M-type $SrFe_{12}O_{19}$ hexaferrites and observed that the coercive force was found to increase with increasing La content, i.e., from 4318Oe to 4761Oe.whereas coercieve force decreases with increase Pr content i.e, from 4651Oe to 3379Oe. The variation of $H_c$ is due to the external factors like crystal structure, morphological features.

## SQUARENESS RATION OF RE DOPED FERRITES

Wu, Ze, Ruonan Zhang et.al [22] studied experiment that the squareness ratio (SQR) of ($H_C$) of Ce doped SrM ferrites was increased from 0.0239 to 0.0334 for x =0.01 to 0.02 of Ce content, after that it decreased to 0.0005 for x =0.3. They explained that the SQR increased due to the predominance of exchange coupled interaction among nanoparticles. On the other hand, magneto static interactions between the nanoparticles reduced the value of SQR for a higher concentration of Ce ion. S.S.Satpute et.al [9] noted that the value of SQR increased gradually from 0.122 to 0.267 with increasing Sc content x = 0.00 to 0.05 in $Y^{3+}$ doped $SrFe_{12}O_{19}$ ferrites. From the hysteresis loop properties of $Y^{3+}$ doped $SrFe_{12}O_{19}$ ferrites. Almessire et.al mentioned that the obtained SQR values for $SrY_{0.5}Ce_{0.5}Fe_{11}O_{19}$ and $SrY_{0.3}Ce_{0.3}Fe_{11.4}O_{19}$ are less than the value of 0.500 suggesting the uniaxial anisotropy for all substituted products.

## SUMMARY AND OUTLOOK

This review serves as an introduction to rare earth-doped ferrites and provides a succinct overview of their magnetic hysteresis loop properties. Utilizing figures, the presentation caters to material science researchers. The examination discloses a reduction in saturation magnetization as rare earth (RE) content increases, linked to compromised sub-lattice interactions and diminished magnetic moments. Remanent magnetization typically diminishes with escalating RE ions. Coercivity trends exhibit correlations with crystallite size, grain size, and densification. Magnetic moment values exhibit a decrease with elevated RE ions, consistent with their paramagnetic nature. Anisotropy constants undergo variations in response to alterations in coercivity and saturation magnetization. Both intrinsic and extrinsic factors influencing hysteresis loop properties encompass chemical compositions, RE ion concentration, preparation method, crystal structure, cation distribution, grain size, morphology, defects, lattice imperfections, porosity, and dislocations. The revealed insights propose diverse applications in memory devices, microwave devices, recording media, and soft magnetic applications for RE-doped Hexaferrites, thus presenting valuable perspectives for future research endeavors.

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# "Exploring Magnetic M-Type Hexaferrite ($MFe_{12}O_{19}$) Nanoparticles: A Comprehensive Overview of Synthesis and Applications"

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## ABSTRACT

Magnetic M-type ferrite materials, vital for biomedical, water treatment, and industrial electronics, are explored comprehensively in this review, focusing on hexaferrites, especially doped nanoparticles. Notably, specific element doping enhances electrical and magnetic properties, ideal for applications like magnetic fields, microwave absorbers, and biomedicine. Doping contributes significantly to customizing hexaferrite nanoparticles' physical properties, and metallic atom substitution augments overall functionality. The review scrutinizes recent advances, emphasizing synthesis intricacies, doping methodologies, and applications, offering insights into selecting metal ferrite nanoparticles based on application requirements. Researchers and practitioners benefit from informed decisions for optimal magnetic ferrite choices in diverse applications.

***Keywords**: M-type hexaferrites, Magnetic properties, Dopants*

## INTRODUCTION

M-type hexaferrite materials, characterized by their hexagonal structures with the chemical formula $AB_{12}O_{19}$ (where A and B represent metal cations at tetrahedral and octahedral positions), are integral in shaping the physicochemical properties of ferrites [1]. Nanocrystalline magnetic materials, particularly those with particle sizes up to 130 nm, have garnered substantial attention across disciplines such as physics, chemistry, biology, medicine, materials science, and engineering. Their distinctive attributes arise from modified reactivity, thermal, mechanical, optical, electrical, and magnetic traits owing to a heightened surface-to-volume ratio [2]. In nanomaterials, the interplay of particle size, morphology, and chemical composition predominantly governs their characteristics and allows for meticulous adjustments based on these parameters. Noteworthy hexaferrites like $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ nanoparticles have risen to prominence due to their thermal and chemical stability, as well as diverse structural, magnetic, optical, electrical, and dielectric properties. These materials find applications in varied technological domains, encompassing photocatalysis, photoluminescence, biosensors, humidity-sensors, catalysis, magnetic refrigeration, and permanent magnets, magnetic drug delivery, magnetic (hyperthermia).

This study elucidates the structural, morphological, and magnetic attributes of M-type hexaferrites ($MFe_{12}O_4$, where M = Ba and Sr) and doped ferrites involving various transition metals ($Zn^{+2}$, $Ni^{+2}$, $Al^{+3}$, $Mn^{+2}$, $Y^{+3}$, $Eu^{+3}$, $Pr^{+3}$, $Sm^{+3}$, $Ho^{+3}$, $La^{+3}$, and $Ce^{+3}$). Synthesis methods encompass Co-precipitation, Hydrothermal, Microemulsion, Sol-gel, Electrochemical Deposition, Microwave-Assisted, and Biosynthesis approaches. The paper aims to explore synthesis methodologies, benefits, drawbacks, and applications of $MFe_{12}O_{19}$ and their metal dopants in various technologies. The review comprises four sections: "Magnetic M-type hexaferrites," covering classification and structural overviews; "Magnetic properties," summarizing magnetic features; "Synthesis methods," detailing methodologies; and "Impact of doping," discussing the effects on ferrite properties. The final section, "Applications of M-type hexaferrites," consolidates major applications in conventional and contemporary technologies.

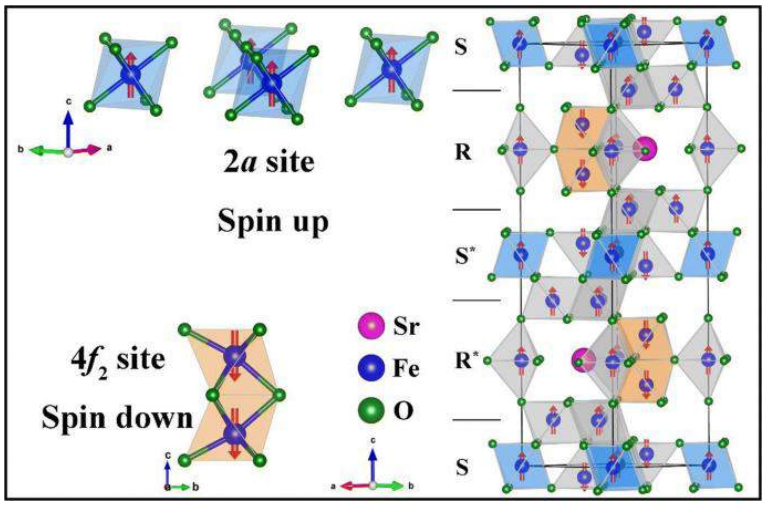


**Fig.1:** shows the distinctive site occupied by the Fe, Sr, and O within the unit cell of the SrM hexaferrite

## MAGNETIC HEXAFERRITE

Recently, magnetic hexa ferrite materials have gained significant attention for their pivotal role in advancing scientific knowledge and understanding of magnetic materials, particularly ferrites [5]. Ferrites, a class of ferrimagnetic ceramics, find application in various electric and optoelectric devices due to their magnetic properties, high electrical resistance, and minimal eddy current losses. Hexa ferrites, represented by the formula $MFe_{12}O_{19}$ (where M is a divalent metal ion and Fe is in the +3-oxidation state), offer diverse physical qualities, low production costs, and excellent chemical stability. The crystal structure of ferrites varies from garnet, hexagonal, to hexa, impacting their properties.
Cation distribution within the crystal lattice leads to three types of hexa: normal, inverse, and mixed, influencing the magnetic properties of hexa ferrites [6]. Strontium ferrite ($SrFe_{12}O_{19}$), known for its high coercivity (Hc), large cubic magnetocrystalline anisotropy, and moderate saturation magnetization (Ms), is considered a hard-magnetic material with applications in magnetic storage, biomedical uses, and industrial purposes. Its essential features, such as high Ms value, visible light absorption capacity, and low bandgap energy, have garnered interest [7]. $BaFe_{12}O_{19}$ NPs, crucial ceramic materials, have distinctive properties and find applications in various fields, including transformer cores, high-speed digital cassettes, radio frequency circuits, and electromagnetic wave absorbers, making them valuable in biomedical diagnostic and therapeutic applications.

Hexa ferrite nanoparticles, like $SrFe_{12}O_{19}$, are noteworthy for high-frequency circuits, radiofrequency transformers, antennas, inductors, and radar-absorbing materials due to their high resistivity and low loss at high frequencies [8]. They also hold potential as catalysts for degrading contaminants and are increasingly relevant in biomedical applications, including magnetic resonance imaging (MRI), drug delivery systems, and hyperthermia treatment of cancer [9]. Research on $SrFe_{12}O_{19}$ NPs has gained attention due to differences in their physical and chemical properties, presenting a wide range of potential applications. Ferrites, with their unique electromagnetic properties, play a crucial role in electronic sectors. Barium hexa ferrite ($BaFe_{12}O_{19}$), a fascinating soft ferrite, has been extensively utilized in applications like MRI, drug delivery, electronic devices, and telecommunications due to its strong magnetic permeability and low losses. Manganese ferrite exhibits a low resistance compared to other hexa ferrites. However, the method used for ferrite preparation, such as sol-gel, can alter the degree of inversion of the crystal structure, influencing the magnetic behavior of zinc ferrite nanoparticles. This underscores the impact of cation distribution on the chemical and physical characteristics of hexa ferrite nanoparticles.

## MAGNETIC PROPERTIES

Nano-scale magnetic materials have garnered significant interest, driven by the growing demand for miniaturized technological devices. A crucial aspect for enhancing the performance of permanent magnetic materials lies in understanding their magnetic properties at the nanoscale. Various factors such as shape, size, surface effects, magnetic anisotropy, and other parameters play a pivotal role in influencing the magnetic characteristics of nanoparticles [10].

Hysteresis, a phenomenon characterized by a lag or phase difference between two related quantities like strain and stress, magnetic field, and magnetic induction, is a notable aspect. The term "hysteresis," derived from the Greek language meaning "to lag behind," encompasses dampening effects observed in properties such as magnetic and mechanical behaviors. Magnetic and mechanical hysteresis are widely recognized forms of dampening, often evident in any magnetic circuit featuring ferromagnetic material. The delay between changes in magnetic flux density and alterations in magnetic field strength gives rise to these phenomena [10]. While the hysteresis mechanism is well-understood, creating an accurate mathematical model based on a comprehensive understanding of the magnetization process remains challenging. Consequently, extensive research spanning decades has been undertaken to develop a hysteresis model applicable for accurate computations in the field of ferromagnetic materials [11]. Examination of hysteresis loops in crucial magnetic structures has revealed significant disparities from fundamental physics concepts associated with ferromagnetism. In hexa ferrites, magnetic interactions are controlled by oxygen ions influencing the spins of metallic cations in octahedral and tetrahedral interstitial sites. The magnetic properties arise from spin interactions with nearby atoms, and three different varieties of interactions ($J_{AA}$, $J_{BB}$, and $J_{AB}$) are governed by the superexchange process. The distance between metallic ions and oxygen directly impacts the magnitude of these interactions. Notably, the A-O-B superexchange interaction holds greater significance compared to A-O-A and B–O–B interactions.

The dominant intra-lattice negative $J_{AB}$ interaction induces uncompensated antiferromagnetic order (ferrimagnetism) between the A and B sub-lattices. In an inverse hexa structure, the magnetic moments of divalent cations at the B sites exclusively contribute to the net moment, canceling out the contribution of iron cations at A sites. The magnetic moments of iron ions at the B sites align antiferromagnetically in a normal hexa configuration. The difference between the contributions of two average sub-lattice magnetic moments provides a basis for calculating the magnetization of hexa ferrite. Subsequently, the resultant saturation magnetization (MS) of the ferrite at T = 0 can be expressed as follows:

$$M_S = \frac{N.d}{M_m}\left[\sum \eta_{B.B} - \sum \eta_{B.A}\right]\mu_{B.B} = \frac{N.d}{M_m}\mu_{eff}$$

In the given context, MM represents the molar mass of ferrite, d signifies its density, N stands for Avogadro's number, and nB,i indicates the quantity of Böhr magnetons (μB) associated with the i site of the unit cell.

Magnetocrystalline anisotropy, a characteristic of magnetic materials, dictates the crystallographic direction in which spontaneous magnetization aligns most energetically. In the case of hexaferrites, the preferred direction of magnetization axis aligns with the stacking direction (111) of the close-packed arrangement. However, Strontium ferrite is unsuitable for high permeability applications due to its significant magnetocrystalline anisotropy and high concentration of Strontium. The magnetic properties of hexaferrites are not solely dependent on their composition; they also hinge on the selection of dopants and synthesis conditions, influencing the magnetic structure. Consequently, intrinsic magnetic properties of the elements comprising hexaferrites play a crucial role in determining physical properties such as magnetic saturation, coercivity, magnetic anisotropy, and magnetostriction.

S S Satpute et al. [12] studied the saturation magnetization of $Y^{3+}$ doped $SrFe_{12}O_{19}$ and observed that the values of $M_S$ for x=0.00 sample was greater than that of yttrium doped samples. In this case, the values of $M_S$ varied between 49.60 emu/g and 35.40 emu/g. They explain that the decreasing nature of $M_S$ and $M_r$ is caused by the substitution of the paramagnetic $Y^{3+}$ ion instead of the ferromagnetic $Fe^{3+}$ ion at the octahedral (B) site and the migration of the $Fe^{3+}$ ion into the tetrahedral (A) site. Chunxiang cao et al. [13] studied the saturation magnetization of $Ce^{3+}$ substituted hexagonal M-type $SrCe_xFe_{12-x}O_{19}$ and observed that Ce substitution has a certain chance to enhance or reduce the $M_S$ and $M_r$, even keep the $M_S$ unchanged. Compared with the SrM without substitution, the $M_s$ of Ce- substituted SrM is obiviously greater than those of the former, which is affected not only by the decreasing content of impurity but also by the Ce-substitution. Naziya Yasmin et.al [14] studied the magnetic properties of Ce-doped BaM hexaferrite prepared by Sol-gel auto-combustion method sintered at $1250^0$C and mentioned that magnetic saturation, remanence reduces with the exchange of $Fe^{3+}$ ions in spin-up position and enhance with the exchange of $Fe^{3+}$ ions in spin-down position. The predominated values of $M_s$ are observed in range (64.36-40.54). Reduction in $M_s$ and $M_r$ due to split of magnetic co-linearity and spin canting observed due to the increase of Ce-Mn concentration in BaM hexaferrite. M.Almessiere et al. studied magnetic properties of Ce doped SrM Hexaferrites at 300K and 10K with an applied magnetic field of 70kOe, they found typical magnetic hysteresis behavior. Magnetic

saturation values correspond to magnetic field 70kOe are respectively 68.56 emu/g at 330K and 102.54 emu/g at 10K which corresponds to sample (x=0.0) and 46.69 emu/g at 300K and 64.34 emu/g at 10K belongs to 0.5 concentration, the variation in the saturation magnetization is due to Ce concentration which influenced by the replacement of magnetic ions of $Fe^{3+}$ by non-magnetic cations and the preferred site occupancy of non-magnetic cations. Furthermore, $Ce^{3+}$ ions mostly generate local strains that possibly produces an environmental disorder or non collinear ferromagnetic arrangement, and the difference in ionic radii between $Ce^{3+}$(1.02Å) and $Fe^{3+}$(0.60Å) enlarges the distance between magnetic ions, which leads to reduce the strength of super-exchange interactions.

Various element-specific techniques, such as Extended X-ray Absorption Fine Structure (EXAFS), X-ray Absorption Near Edge Structure (XANES), Diffraction Anomalous Fine Structure (DAFS), and X-ray Magnetic Circular Dichroism (XMCD), can be employed to ascertain magnetic properties like the inversion degree parameter, which is highly responsive to the local structure. Mössbauer spectroscopy stands out as another crucial characterization method used for assessing magnetic properties and determining the inversion degree of hexaferrites. This technique specifically examines the hyperfine connection between the iron nucleus and the electronic charge of neighboring atoms. Consequently, when preparing and applying hexaferrites, factors such as preparation methods, particle size, shape, and calcination temperature must be carefully considered in light of this characterization approach.

The production of magnetic nanoparticles, commonly integrated into composite materials, involves a dual-step process. Firstly, there is the synthesis of magnetic nanoparticles, followed by the modification of surface functionalities. Various processes can be employed concurrently to generate nanoparticles of diverse sizes. It is well-established that the synthesis procedure has a direct impact on the physical and chemical attributes of the nanoparticles. Since the discovery of magnetic nanoparticles, significant research efforts have been dedicated to developing new preparation techniques and exploring different application scenarios. Presently, the predominant techniques for producing magnetic nanoparticles involve both physical and chemical methods.

In the quest for controlled synthesis encompassing different sizes, compositions, and morphologies of magnetic nanoparticles, the literature has extensively explored numerous synthesis approaches. This section will focus on the most prevalent methods for synthesizing hexaferrite materials, including physical, chemical, and biosynthesis techniques. The various preparation methods for hexaferrite nanoparticles are summarized in Table 1.

**Table. 1:** The various preparation methods for hexaferrite nanoparticles

| Sr.No | Synthesis Via | $M_S$ | $M_r$ | $H_C$ | Application | Reference |
|---|---|---|---|---|---|---|
| 1 | Conventional ceramic technique | 61,49 | 32,24 | 2080<br>1050 | HPMR<br>HLMR | 15, 16 |
| 2 | Coprecipitation technique | 69,60 | 31,36 | 5400<br>860 | PM<br>PM | 17,18 |
| 3 | Sol-gel Technique | 59,61 | 36,36 | 1920<br>5692 | HPMR<br>PM | 19 |
| 4 | Molten-salt Technique | 72,72 | -<br>- | 4650<br>4300 | PM<br>PM | 20 |
| 5. | Hydrothermal Technique | 59,60 | 20<br>- | 1350<br>2300 | HPMR | 21 |

***Conventional Ceramic method** [15,16]**:*** This method involved the mixed ratio of meatal oxides and carbonate powder (precursor) in particular molar ratio, which is used widely in the production of ferrite magnetic materials. If the sample is mixed at the ionic level before the reaction occurrence, then, crystalline structure will exist at lower temperature and this lower temperature can be achieved by the ball milling process, which can be done by two ways one is by dry milling and second one is by wet-milling. Usually, the powders are$\alpha$-$Fe_2O_3$ and Ba or Sr (divalent metals). In case of wet-milling process water, alcohol media is preferred because to improve the milling efficiency the ball powder mass ratio is usually in the range 8-14 and in powder to liquid ratio is 1:1(131).The most of the studies suggested that , firstly the powder are mixed and then milled by the balls which are made of tungsten carbide or stainless steel, zirconia and then finally dried and compressed by pressure application to particular respondent shapes for near full densification (90% of the theoretical density of M-type Hexaferrite).The compact are then sintered at 900 c to 1300 c temperature for few hours, whereas the compaction of the

wet milled powder of M-Type hexaferrite powder at a pressure of 250 MPa and then sintered at 1220 c temperature for 3 hours as a result the density of the pallet will 90% of theoretical density . if the pressure is increased and temperature is lowered the densification will be reduces to 70-80% of the theoretical density

The overall quality of the product was found that it is depend on the Fe: Sr molar ratio of the powder that is Fe:Ba/Sr>12 in the starting material materials in the coexistence of the$\alpha$-$Fe_2O_3$ and Ba or Sr (divalent metals).In detailed investigation it is found that the effect of mola ratio of Fe:Ba/Sr on the quality of the synthesized powders, the optimal ratio of the single phase was found near 11.7 in BaM or SrM

***COPRECIPITATION:*** This method allows for better reaction at molecular level of the starting material and improve the quality of the product because of the homogeneity of the metal hydroxides co-precipitation of NaOH. Adding the base dropwise in the aqueous solution for the precipitation of the metal powders and then, co-precipitated powder is washed and dried. The dried powder is then sintered at temperature lower than conventional SST (solid state route) through that we can obtain the required amount of the M-Type ferrite [17,18]. In variation method, Chloride gas was bubbled through a concentrated NaOH to produce NaCl and NaClO solution to which an particular amount of $Fe(NO_3)H_2O$ was added then $BaCl_2$ .$2H_2O$ was added to the solution at Fe:Ba ratio near 10. Then the solution was left for 24h, then heated for 85 $^0$C for 1 hour. The solution was than filtered and rinsed to remove the residual alcohol and chloride this leads the formation of crystalline Barium/strontium hydroxide and further sintering at 800 $^0$C temperature BaM or SrM Phase obtain.

***SOL GEL METHOD:*** This method is used to manufactured of magnetic powder with controlled particle size distribution. In this method water solution of metal nitrate or metal chlorides solution are mixed under constant stirring, but in the citrate sol gel method, we add appropriate molar ratio of citric solution under constant stirring to maintain the PH value in between 7-9 [19] we add the basic solution drop wise under the constant stirring and the solution gets evaporation at about 80$^0$C and resulting viscous gel is dried and sintered to produce the required hexaferrite phase. There are number of papers are published on improvement of quality of the product and scientists are working in the modification technique to improve the same. SrM -hexaferrite were prepared by this technique after the making some modifying the techniques.

In this variation of the technique SrM ferrite were prepared by dissolving metal chloride in aqueous solution of citric acid with very low PH value and the powders were calcinated at 1000 $^0$C (136), the prepared compound exhibits a low saturation magnetization of 30.61 emu/g, coercivity of 2213 Oe and in previous study suggested that water solution of ferric nitrate was precipitated with the aid of Ammonia, the precipitated compound was than dissolved in Barium carbonate and citric acid by keeping the Fe:Ba=11.6 molar ratio and then benzoic acid and ethylene glycol were added to the transparent solution. The solution was evaporated at 60 $^0$C to produce the viscous gel, which was then dried by heating at 170 $^0$C. The dried gel were placed in the molten furnace and the temperature was set at 1050 $^0$C with heating rate 4.5 $^0$C Min [20]. Another route, firstly the samples were heated at 450 C for 5 hour and once again heated in range 500$^0$C to 1250 $^0$C for 5 Hours with same rate The different phase formation observed in different temperature


**Fig: 2:** schematic diagram of Auto-combution method in case of BaM at low temperature

***AUTO-COMBUSTION METHOD:*** This method is also called as modified Sol-gel citrate method In which self-propagating combustion of the gel takes place on hot plate. In this method the aqueous solution of citric acid and metal nitrate were pre-setappropriate molar ratios and PH of the solution were adjusted in the range of 7-9 by adding basic ammonia solution drop wise. Then a yellow or brown gel is obtained by dehydrating the solution at 80 $^0$C temperature, subsequently heated at 220-240 $^0$C [19] to promote the auto-combustion or self-ignited yielding the foamy powder. This powder was kept for 24 hours for cooling in room temperature. The ferrite powder is then obtained by the grinding and sintering the powder above 600 C temperature

***MOLTEN SALT METHOD:*** This method is also known as salt melt method and this method is used to manufacture or synthesize the M-type ferrite in large scale. The basic or primary procedure is preparation of solution in which barium carbonate and iron oxide is precursor powder are mixed with the stoichiometry ratio with a solvent containing Nacl and Kcl slat mixture [20]. Then heated it temperature at 800 $^0$C to 1100 $^0$C. after heating the mixture the dried sample is crushed and washed with water to get salt out of the dry sample to get the magnetic powder. The number of papers were revealed that magnetic properties of M type or BaM depend on experimental condition, starting reactants, coercivity, solvent composition and purity as well as on heat treatment.

***HYDROTHERMAL METHOD***:

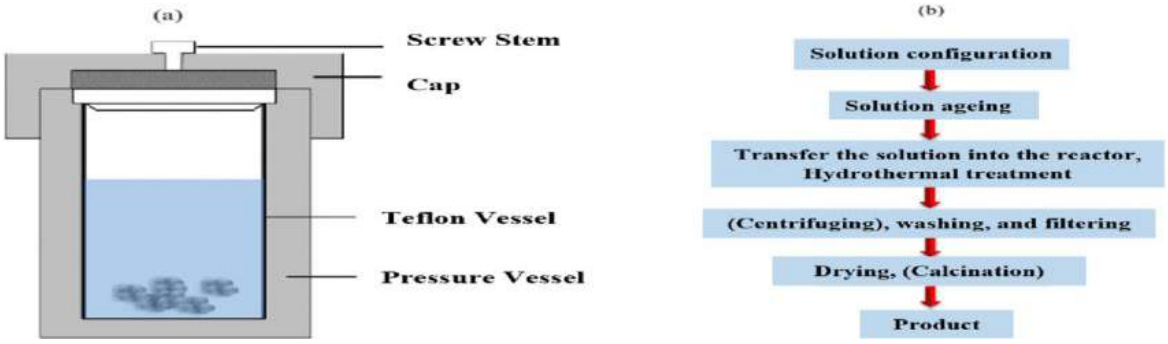


**Fig.3:** Schematic diagram of Hydrothermal method

This method is considered as very useful and accuracy method, the most of the scientist shown a great interest in this method for processing a mono-structural and nanocomposite materials, in this method base aqueous solution of KOH or NaOH plays an important role with addition of with the $OH^- : NO_3^-$ and Fe: Ba ratios in the coprecipitation of aqueous solution of metal nitrate and then, the solution is given a hydrothermal treatment in the range of 150 $^0$C to 290 $^0$C in autoclave .The resulting particles are contains the metal precipitates were filtered and washed and dried in oven, after which the dried powdered sample is sintered in the range of 1100$^0$C to 1200$^0$C. This sintering of dried powder helps us to improve the magnetic characterization which depend upon the several parameters like Fe: Ba ,nitrate ratio , sintering temperature and time duration. In previous studies reported that BaM phase was obtained normally, hydroxide to nitrate ratio > 2 (150) was found to be necessary for formation. But some intermediate iron oxide phase was obtained at low value values of Hydroxide: nitrate and the super magnetic particles (10nm diameter) (153) are obtained at higher value of hydroxide: nitrate values i.e. at 16(151-152) at temperature at 150 $^0$C. Further, the duration of heat treatment was found critical for obtain the Ba / Sr m-type phase. if the sample is prepared at 230 $^0$C with Fe: Ba =8 and $OH^- : NO_3^- = 2$ in which first phase was found α-$Fe_2O_3$ under heat treatments of 10 hour, whereas BaM phase formed in the sample heat treatment for 25 Hours (153).

***PHYSICAL METHODS:*** The predominant physical techniques employed to reduce bulk hexaferrite material into nanoparticles are generally categorized as top-down processes. Notable examples of these physical methods include electrical wire explosions, mechanical milling and laser target evaporation [125–127]. Guo et al. [128] utilized laser ablation on a hexaferrite CoFe2O4 target in an Au NP colloidal solution to synthesize $MFe_{12}O_{19}$ NPs, leading to the formation of Au– Ba/$SrFe_{12}O_{19}$ NPs. While physical methods offer higher production yields, reaching up to 200 g/h, they only account for approximately 10% of the magnetic nanoparticles required for diverse applications [68]. This limitation arises from

challenges in controlling shape and size distributions, along with the relatively high-power consumption associated with physical techniques. The earliest method for synthesizing hexaferrite nanostructures involves mechanical ball milling. In this process, powders (such as oxides, carbonates, and other metal-containing compounds) undergo grinding in high-energy ball mills, followed by heating the mixture to high temperatures to achieve the desired phase of the materials.

The mechanical ball milling procedure is further categorized into two types: dry and wet. The wet approach is particularly effective in producing high-magnetization crystal particles. Figure 12(a-d) illustrates the dry and wet milling procedures before and after milling, respectively. While the ball milling method is straightforward, it presents a drawback as impurities can be introduced during the preparation stage, and both mechanical and chemical factors can influence the crystalline structure of $MFe_{12}O_{19}$. Consequently, the mechanical ball milling process proves ineffective in producing nano-$MFe_{12}O_{19}$ crystals with diverse morphologies.

***APPLICATIONS OF HEXA FERRITES:*** The multifaceted applications of $MFe_{12}O_{19}$, commonly known as hexa ferrites, are elucidated in Figure 4. The properties of ferrite, encompassing its structure, particle size, and shape, exhibit variability contingent on the cation type and synthesis method employed, resulting in a spectrum of applications.

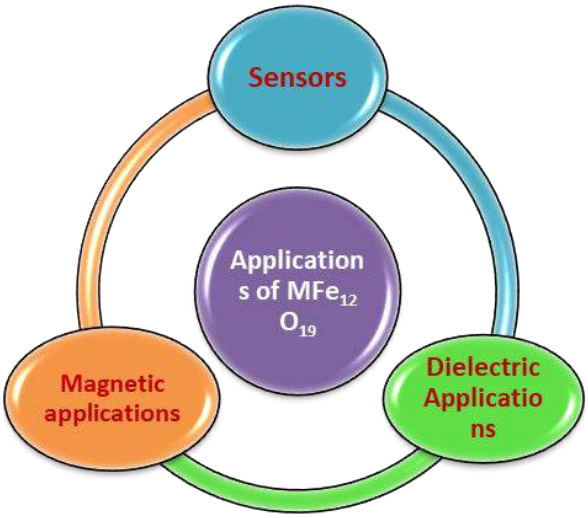


**Fig.4:** Applications of $MFe_{12}O_{19}$

***SENSORS:*** Sensors, electronic devices detecting changes in specific materials within environments, prove invaluable in ferrite nanoparticle-based sensors, known for exceptional sensitivity, low detection limits, and high signal-to-noise ratios [22]. A prominent application involves detecting humidity variations, vital in industrial and residential settings for human comfort, storage regulation, and optimal operating conditions in industries. Ceramic-based humidity sensors, using metal oxides, outperform polymer films with superior stability, thermal capability, mechanical strength, and chemical resistance. Their efficacy in electrochemical humidity sensor applications is notable. Elevated humidity alters electrical properties, increasing conductivity and resulting in a higher dielectric constant. Microstructural properties linked to synthesis influence humidity-sensing efficiency, with $SrFe_{12}O_{19}$ nanoparticles exhibiting heightened sensitivity. Ba/$SrFe_{12}O_{19}$ sensors and actuators, due to their durability and high HC values, find widespread usage. The amalgamation of magnetostriction, stress sensitivity, chemical inertness, and cost-effectiveness sparks interest in magnetostrictive $SrFe_{12}O_{19}$ composites for magnetoelastic sensors. Recognized as a smart material, Ba/$SrFe_{12}O_{19}$ has diverse technological applications, especially in position sensors. For gas sensors, ferrites with single metal ion dopants, mixed ferrite materials, and composites have been studied, comprehensively summarized by A.B.Gadkari et al. [23].

***MAGNETIC APPLICATIONS:*** The magnetization is influenced by the exchange contact variation between tetrahedral and octahedral sites, making it dependent on grain size. In high-density magnetic recording, minimizing media noise requires magnetic particles with nanoscale dimensions to limit exchange interactions between neighboring grains. For achieving high storage density, the particles

must also possess elevated HC values. The magnetic characteristics (MR, MS, and HC) of hexa ferrites depend on their composition, particle size, crystal structure, and cationic distribution between octahedral and tetrahedral sites. Hexa ferrites can exhibit antiferromagnetic, ferromagnetic, and paramagnetic behavior [24].The increase in HC values in hexa ferrites is attributed to factors like spin disorder, spin canting effect, and a rise in surface barrier potential in surface layers. The remarkable and enhanced properties of magnetic nanoparticles, compared to similar bulk materials, arise from the large surface-to-volume ratio of the nanoparticles, leading to the presence of "Significant numbers of atoms at the surface contribute to the distinctive characteristics of nanoparticles. Additionally, the disparity between the low number of coordination surface atoms and the interior atoms in nanoparticles gives rise to various surface effects, including spin canting, spin disorder, and the existence of a magnetically dead layer [25]. Materials exhibiting high coercivity are termed hard materials, whereas those with low coercivity are categorized as soft materials. Soft materials, such as inductor cores, transformers, and microwave devices, are utilized in various electronic applications. Conversely, hard materials, characterized by high coercivity, find applications in the creation of permanent magnets. In general, soft ferrites are characterized by a low coercivity value, allowing for adjustable magnetization. This makes them well-suited for advanced electronic engineering purposes, including transformer cores, high-frequency inductors, and microwave components.

***DIELECTRIC APPLICATIONS:*** The dielectric structure typically comprises highly conductive grains separated by low-conductivity grain boundaries [26]. The dielectric properties of hexa ferrites are intricately influenced by factors such as structural homogeneity, cation distribution, particle size, density, and porosity. Furthermore, the synthesis techniques and thermal treatment parameters, including temperature, time, and heating/cooling rates, significantly impact dielectric properties.

The introduction of a small $Sr^{2+}$ ion at the tetrahedral site in $SrFe_{12}O_{19}$ results in a reduced lattice constant, facilitating electron hopping between $Fe^{3+}$ and $Fe^{2+}$ ions. This Co2+ ion acts as a source of charge carriers, contributing to the enhanced dielectric behavior of $SrFe_{12}O_{19}$. The polarization in $SrFe_{12}O_{19}$ is determined by the low-frequency hopping of charge carriers, accumulating and causing polarization upon reaching grain boundaries, resulting in high dielectric constants. Synthesis method and thermal treatment factors such as temperature, time, or heating and cooling rate play a crucial role in determining these properties. At higher frequencies, the hopping of charge carriers is unable to follow the alternating current-produced field, leading to incomplete polarization and low dielectric constants. The dielectric constant decreases with increasing grain size, creating a smaller grain boundary between microscopic grains. Lower frequencies exhibit large dielectric constants, diminishing as frequency rises. At a specific frequency, the reduction in dielectric constant stabilizes, as dielectric polarization becomes the primary contributor. At low temperatures, charge carriers exhibit limited mobility, unable to align themselves with the applied electric field, resulting in weak polarization and a low dielectric constant. However, elevated temperatures increase the mobility of charge carriers, enhancing polarization and raising the dielectric constant. The interaction between different valence states of elements in nanosized ferrites significantly influences polarization, causing an increase in dielectric constant with rising temperature, as a multitude of charge carriers contribute to polarization.The high dielectric constants observed at high frequencies are attributed to space charge polarization, arising from the inhomogeneous dielectric structure caused by variations in grain size and impurities.

***FUTURE PROSPECTS AND CHALLENGES:*** The last few decades have witnessed a growing interest in nanoscale hexa ferrites due to their distinctive features, including stability in chemical and thermal environments, significant coercivity, elevated anisotropy constant, and Curie temperature, as well as moderate saturation magnetization, high electrical resistance, and minimal eddy current loss. The unique attributes of magnetic hexa ferrites, coupled with potential modifications and functionalizations, open up new avenues for their application in biomedicine, catalysis, water treatment, and energy fields. The evolving trajectory of magnetic hexa ferrite applications is expected to concentrate on fine-tuning essential magnetic properties through adjustments in synthetic methods, leading to precise control over particle size, shape, and crystallinity. The physical and chemical characteristics of hexa ferrites not only hinge on synthesis methods and modifications but also incorporate doping as an effective strategy in preparing non-aggregated and mono-disperse nano sized hexa ferrites.

One notable application of magnetic hexaferrites lies in their role as efficient magnetic materials in magnetic hyperthermia. Despite numerous studies exploring hexaferrite-based materials for hyperthermia, this field is still in its early stages, facing challenges such as the optimization of

nanoparticle size, shape, and magnetic properties, necessitating further investigation. Additionally, the development of effective methods for surface modification of hexa ferrites is a crucial area for future exploration, particularly in achieving magnetic ferrite nanoparticles with anticipated performance in biomedical applications.

**CONCLUSION:** In recent times, there has been considerable attention directed towards $MFe_{12}O_{19}$ materials owing to their distinctive attributes, encompassing stability under mechanical, chemical, and thermal conditions, high coercivity, elevated anisotropy constant and Curie temperature, high electrical resistance, moderate saturation magnetization, and minimal eddy current loss. Among the various synthesis strategies discussed, the efficacy of $MFe_{12}O_{19}$ in numerous applications is largely contingent upon the synthesis processes employed; proficient synthesis methods result in $MFe_{12}O_{19}$ materials that exhibit superior functionality and resilience under the conditions of their synthesis. However, the cost-effective synthesis of substantial quantities of $MFe_{12}O_{19}$with uniform size and shape, particularly for biomedical purposes, warrants further investigation. It is crucial to consider and thoroughly assess the toxicity associated with specific $MFe_{12}O_{19}$ nanoparticles in this context.

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# Structural and Morphological Properties of Graphene Oxide Synthesized Via Modified Hummers Method

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**ABSTRACT**

Two-dimensional (2D) nanomaterials have gained extensive attraction in scientific community due to their excellent and extraordinary properties. Graphene/graphene oxide (GO)/reduced graphene oxide (rGO) are the most applicative and extensively research materials. Herein, we reported the most effective modified Hummer method for synthesis of graphene oxide (GO) and explored its structural and morphological properties. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were employed to study the structural and morphological properties. The XRD results showed that the prepared material is in proper form of GO. The morphological study reveals ultra-thin layers of the GO. Thus, the reported technique is a promising method to synthesize GO.

***Keywords:*** *2D nanomaterials, Graphene Oxide, XRD, FESEM.*

## NTRODUCTION

Exponential growth in technological applications is a boon of nanotechnology. Nanotechnology comprises the manipulation of bulk materials at the nanometer dimension, and study its exceptional and extraordinary properties resulting which further provide the knowledge to use the nanomaterials in tools and technologies [1,2]. Recent days the advancement in nanotechnology resulted the various class of nano dimensional materials such as zero-dimensional (0D), one-dimensional (1D), two dimensional(2D) and three-dimensional (3D) etc. Dimensionality is one of the most fundamental material parameters, different dimension of the same materials exhibits the significant change in physicochemical and optoelectronics properties. Nowadays on of the most familiar and studied material, graphene popularly known as 2D nanomaterial. Owing to the excellent and unique properties of graphene such as electronic, mechanical, optical and thermal properties etc. it employed for the advanced technology [3,4]. Due to the excellent properties graphene and its derivatives such graphene oxide (GO), reduced graphene oxide (RGO) explored for the applications such as sensors, chemical sensors, optoelectronic devices, catalysts, energy storage and conversion devices etc. Regards to this, the easy, ecofriendly, cost-effective, and mass-productive synthesis of graphene derivatives is utmost necessity of the scientific and industrial community [5,6].

In general, graphene is an isolated single layer of carbon atoms hexagons consisting of sp2-hybridized C-C bonding with π-electron clouds. In other hand, graphene oxide has similar layered structure compared to graphite, only differentiate via decorated oxygen-containing groups to carbon atoms. Thus, the graphene oxide expands the interlayer distance and construct the atomic-thick layers hydrophilic. The main elements of the GO are most inexpensive and abundant i.e. carbon, hydrogen, and oxygen etc [7].

Present study reported the synthesis of graphene oxide via modified hummers technique. The prepared GO further explored the structural and morphological behavior by means of XRD and FESEM characterization techniques.

## EXPERIMENTAL

***MATERIAL AND CHARACTERIZATION:*** For the synthesis of GO all chemicals used as AR grade without any further purifications. graphite Flakes, podium nitrate, potassium permanganate, hydrogen peroxide, sulphuric acid (98%), hydrochloric acid (35%) all are purchased form Loba chem, India. The

structural and morphological properties were studied via X-ray diffraction (XRD) and FESEM using a Rigaku Mini flex-II diffractometer with CuKα radiation (λ=1.541 Å) and (S- 4800, Hitachi, Japan).

***SYNTHESIS OF GO:*** Starring materials graphite flakes and $NaNO_3$ mixed in known concentration of $H_2SO_4$ and continuous stirring at (0-5 $^0$C). Then in this mixer known concentration of potassium permanganate was added slowly. Then after 4 h mixture diluted with water and kept under continuous stirring for 2h. further removed the ice bath and mixture stirred again for 2h at 35 $^0$C. After refluxing the mixture brown colored solution prepared then this solution changes to bright yellow by treating with $H_2O_2$. Then the prepared solution purified with distilled water and HCl till forms gel like substance with neutral pH. Lastly via centrifugation and drying at 100$^0$ C, GO powder will get [8].

## RESULT AND DISCUSSION

***STRUCTURAL PROPERTIES (XRD):*** The structural properties and phase purity of the synthesized GO powder studied by using XRD analysis. Fig. 1 shows the XRD pattern of GO in 2θ range 5-90$^0$. The XRD pattern shows the diffraction peak 2θ =12.33$^0$, without any extra unwanted peak. The observed peak corresponds to the (001) plane, which confirmed the hexagonal phase. The observed peak of GO clearly match with the JCPDS card no. 04-0783. Thus, the XRD study elaborate the prepared GO sample using the modified hummers method is consistent for the formation of GO [9].

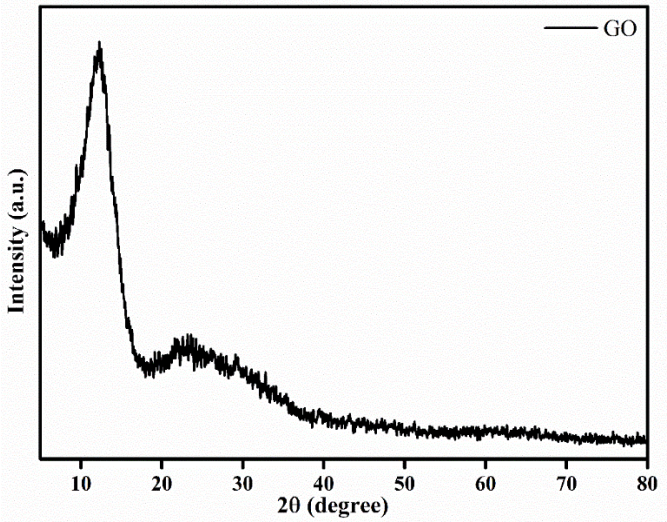


**Fig. 1:** XRD pattern of synthesized GO

***MORPHOLOGICAL STUDY (FESEM):*** Field Emission Scanning Electron Microscopy (FESEM) picturized the surface morphology of the prepared samples. Fig. 2 shows the FESEM micrograph of the prepared GO sample. Generally, graphite has the compactly stalked sheets of graphene. The FESEM image of GO clearly envisaged the well-defined and interlinked three-dimensional exfoliated Graphene sheets [8].

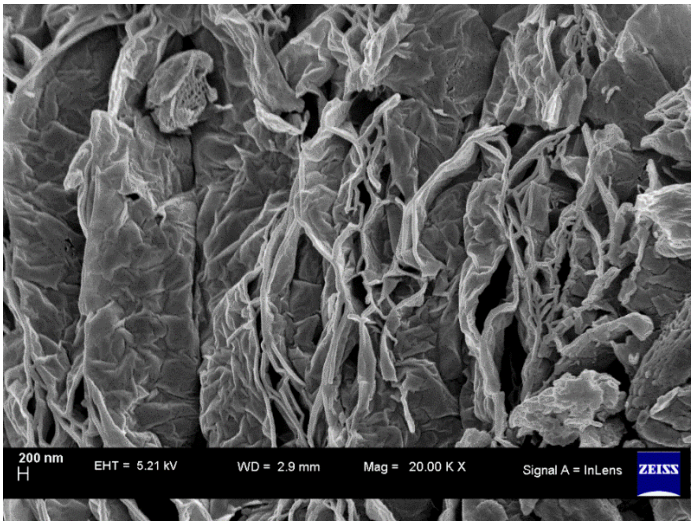


**Fig.2:** FESEM picture of as synthesized GO

## CONCLUSIONS

Summary, in this paper we have successfully prepared the graphene oxide (GO) using modified hummers method. The properties of synthesised GO powder further explored by XRD and FESEM analysis. XRD study revels structural and phase purity of the sample which confirmed that as prepared GO sample in the proper form with excellent purity. The FESEM micrograph provide the surface morphology, which confirmed that the GO sample exfoliated graphene sheets. Thus, the study conclude that the use technique is prominent for the synthesis of GO.

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# Effect of Air Quenching on $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ Nanoferrites synthesized by using Sol gel Auto combustion method

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## ABSTRACT

A nanoparticle of $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ has been synthesized by using sol gel auto combustion method. The synthesized powder was sintered at 1000°C for 10 hours and quenched in air at room temperature. XRD pattern was recorded for the quenched sample to confirm the formation of single phase cubic spinel structure. FTIR was carried out to study the vibrational bands and elastic parameters. FE-SEM study reveals that the synthesized sample is of order of nanometre range. The magnetic parameters were investigated by using VSM technique.

***Keywords:*** *Ferrite material, Quenching, Sol-gel, Ni-Cu-Zn ferrites*

## INTRODUCTION

The cubic spinel ferrite has a chemical formula MFe2O4 where M stands for any divalent metal ion such as magnesium, nickel, copper, zinc etc. The ferrite material has a twin property of magnetic conductor and electric insulator. They are widely used in many electric and magnetic devices due to their excellent electrical and magnetic properties and their magnetic losses [1-2]. The Ni-Cu-Zn ferrite is considered as one of very important magnetic oxide with spinel structure due to their excellent electric and magnetic properties [3]. They are known to be a dominant core material for multilayer chip inductor (MLCI) due its high density, high initial permeability at high frequency and lower sintering temperature [4]. The properties of Ni-Cu-Zn ferrites strongly depend on chemical composition, synthesis technique and conditions which in turn affect the cation distribution among the tetrahedral and octahedral site [5]. From the literature survey, it is found that the set chemical methods provide a better homogeneity and uniformity in particle size and distribution. Among various chemical synthesis techniques sol-gel auto combustion method is known to produce fully crystalline ferrite material [6-7]. Therefore, in present work, an attempt has been made to synthesize Ni-Cu-Zn ferrite composition and study the effect of quenching on its structural and elastic properties.

## METHOD AND MATERIALS

The sample of NiCuZn Ferrite was synthesized by using sol gel auto combustion method. AR grade of Nickel nitrate Ni $(NO_3)_2.6H_2O$, Copper nitrate Cu $(NO_3)_2.3H_2O$, Zinc Nitrate Zn $(NO_3)_2.6H_2O$ and Ferric Nitrate Fe $(NO_3)_2.9H_2O$ and citric acid $C_6H_8O_7$ were used as starting raw materials. The metal nitrates and citric acid was kept in a molar ratio of 1:3 and forms a clear homogeneous solution. The solution was stirred continuously with contact heating at 80°C for 3 hours till it transform into a xerogel. After formation of gel, the stirring is stopped and gel is allowed to burn via auto combustion reaction forming a required loose floppy powder as end product. This synthesized powder was heated at 100°C per 2 hours to remove the water content in the powder. After natural cooling the powder was again heated at 500°C for 4 hours to get the nanocrystalline ferrite powder, final sintering was done at 1000°C for 10 hours, then the powder was quenched in air at room temperature from the sintering temperature 1000°C. The structural characterization was made by using X-ray diffraction method in 2θ range of 20°-80°. The XRD pattern was recorded at room temperature using CuKα λ=1.5406Å radiation. An FTIR spectrum was recorded using FTIR-shimatzu Iraffinity IR spectrometer within the range 300-1000cm$^{-1}$. Surface morphology studied was carried out by field emission scanning electron

micrograph model NOVA NANO SEM-450 with accelerating voltage 20 KV. Magnetic measurement was recorded using VSM with applied field ± 20KOe at room temperature.

## RESULT AND DISCUSSIONS

***XRD analysis:*** Fig. 1 represents the X-Ray diffraction (XRD) pattern of present $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite composition synthesized by using sol-gel auto combustion route and quenched in air medium. The X-ray diffractograms do not point out the occurrence of any unwanted phase. XRD pattern shows the Braggs reflections (220), (311), (222), (400), (422), (511), (440) and (533) which are belong to cubic spinel structure and confirms the complete formation of single phase cubic structure.

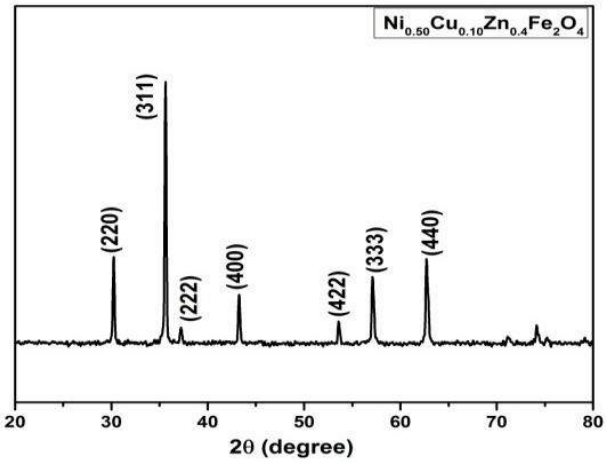


**Fig.1:** XRD pattern of quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite

The structural parameters such as lattice parameter, crystalline size, X-ray density, Bulk density, % porosity, bond length [$d_{AX}$, $d_{BX}$], site radii [$r_A$, $r_B$], tetrahedral edge [$d_{XX}$], shared and unshared octahedral edges [$d'_{XX}$, $d''_{XX}$], hopping length [$L_A$, $L_B$], cation-cation (Me-Me) and cation-anion (Me-O) bond distances, hopping length [La, Lb] and bond angles ($\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$, $\theta_5$) were determined using relations [8-12]. All the obtained values are given in Table 1. From the table it is observed that the crystallite size of the sample lies in order of nano metre range i.e. 32 nm.

**Table 1:** Structural parameters of $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$

| **Composition** | **$Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$** | **Composition** | **$Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$** |
|---|---|---|---|
| Lattice constant a(Å) | 8.3635 | $a_{th}$ | 8.4829 |
| Crystallite size D nm | 32 | b | 2.9569 |
| X-ray density $d_x$ gm/cm$^3$ | 5.39 | c | 3.4673 |
| Bulk density $d_B$ gm/cm$^3$ | 4.79 | d | 3.6215 |
| Porosity(%)P | 11 | e | 5.4322 |
| u | 0.385 | f | 5.1215 |
| dax | 1.9556 | p | 2.0072 |
| dbx | 2.0107 | q | 1.9556 |
| dxx | 3.1935 | r | 3.7447 |
| d'xx | 2.7203 | s | 3.6697 |
| d"xx | 2.9616 | $\theta_1$ | 122.06 |
| La | 3.6215 | $\theta_2$ | 139.63 |
| Lb | 2.9569 | $\theta_3$ | 89.97 |
| ra | 0.563 | $\theta_4$ | 126.34 |
| rb | 0.729 | $\theta_5$ | 71.14 |

***FTIR analysis:*** The FTIR spectrum for quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite composition synthesized by using sol-gel auto combustion route is shown in Fig. 2. It is observed that the FTIR spectra exhibit two major bands in the range 400-700 cm$^{-1}$. The high frequency band $\upsilon_1$ is observed at 542 cm$^{-1}$ and low frequency band $\upsilon_2$ at 392 cm$^{-1}$ and confirms the formation of spinel ferrite structure. The values of $\upsilon_1$and $\upsilon_2$ are given in Table 2. The difference in the positions of high frequency band and low frequency

band is due to the difference in the $Fe^{3+}$-$O^{2-}$ distances for the tetrahedral and octahedral complexes. The Fe-O distance of tetrahedral (A) site is smaller than that of octahedral (B) site [13] which can be explained by the stronger covalent bonding of $Fe^{3+}$ at a site than B site. Using the values of high frequency and low frequency bands, the force constants corresponding to the tetrahedral and octahedral sites are determined by using the formulae [14]. Data on vibrational bands ($\nu_1$ and $\nu_2$), force constants ($K_t$ and $K_0$) and longitudinal modulus (L), shear modulus (G), Bulk modulus (B), Young modulus (E) longitudinal wave velocity ($V_L$) and Transverse wave velocity ($V_T$), Mean wave velocity ($V_m$), Poissons ratio ($\sigma$), elastic moduli corrected to zero porosity ($E_0$, $G_0$, $B_0$, $L_0$, $\sigma_0$), Debye temperatures ($\theta_D$, $\theta_1$) for air quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite composition is represented in Table 2.

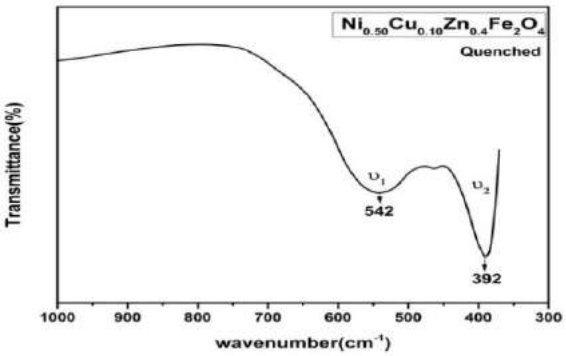


**Fig.2:** FTIR Spectra of quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$

**Table.2:** various elastic parameters

| **Composition $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$** | | **Composition $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$** | |
|---|---|---|---|
| **$\upsilon_1$ ( $cm^{-1}$)** | 542 | **Vs** | 3043.74 |
| **$\upsilon_2$ ($cm^{-1}$)** | 392 | **Vm** | 3379.13 |
| **Kt N/m** | 127.79 | **Lo** | 174.1897 |
| **Ko N/m** | 95.00 | **Go** | 56.6977 |
| **L** | 133.19 | **Bo** | 98.5928 |
| **G** | 44.39 | **Eo** | 142.7326 |
| **B** | 73.99 | **σo** | 0.2587 |
| **E** | 110.99 | **$\theta_D$** | 444.38 |
| **σ** | 0.25 | **$\theta_1$** | 671.54 |
| **$V_L$** | 5271.92 | **$\theta_1$** | 671.54 |

***FE-SEM analysis:*** Fig.3 shows the surface morphology and microstructure of air quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite composition. The grain size is measured by Linear Intercept method [15], the grain size found to be nearly 35 nm which is in close agreement the crystallite obtained from XRD.

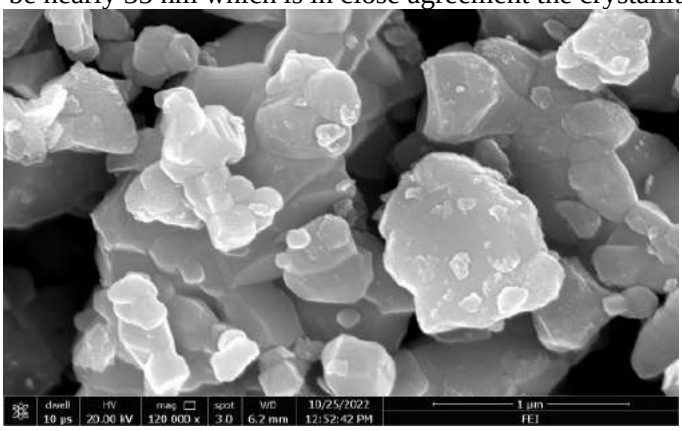


**Fig.3:** FE-SEM micrograph of air quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$

***VSM Analysis:*** The magnetic properties of present air quenched sample is analysed by VSM. Fig.4 indicates the M-H loop of present air quenched ferrite composition. Magnetic properties of ferrite material is dependent on the exchange interaction between metal ions in tetrahedral A site and octahedral B site, In the $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ Nickel having tendency to occupy B site, Zn prefers to A site, Cu prefers B site and Fe ions prefers both site [13,14] but at particular temperature Cu ions transform from its tetragonal structure to cubic phase structure in this transition quenching process plays key role to change the material from ferromagnetic to paramagnetic [16], The saturation magnetization (Ms), coercivity (Hc), remenance (Mr) and cation distribution for composition is given in Table 3

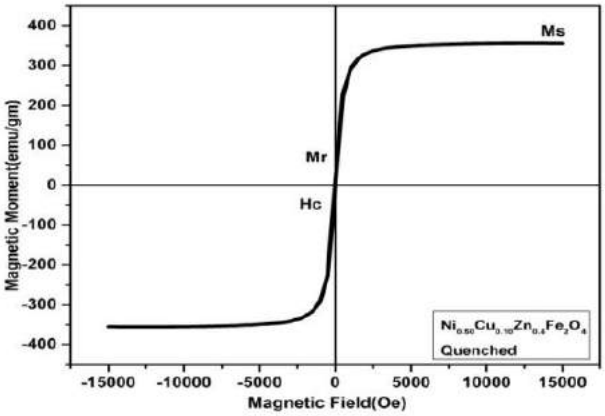


**Fig 4:** M-H curve of $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$

**Table.3**: Magnetic parameters and cation distribution of air quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$

| **Composition** | $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ |
|---|---|
| Ms (emu/gm) | 355 |
| Mr/Ms (emu) | 7 |
| Coercivity Hc (Oe) | 15 |
| Cation distribution | $(Ni_{0.09}Cu_{0.08}Zn_{0.04}Fe_{0.79})_A$ $(Ni_{0.41}Cu_{0.02}Zn_{0.36}Fe_{1.21})_B$ |

## CONCLUSIONS

XRD pattern of air quenched $Ni_{0.50}Cu_{0.10}Zn_{0.4}Fe_2O_4$ ferrite composition indicates the complete formation of single phase cubic structure. FTIR spectrum of this air quenched sample confirms the presence of two vibrational bands. FE-SEM micrograph reveals the morphology of sample and the size of grains lies in order of nanometre range. VSM data represents the values of magnetic parameters of air quenched sample.

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# Synthesis, Characterization and biological utility of Pyrazolone and its derivatives.

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**ABSTRACT**
The synthesis of pyrazolone and its derivatives is achieved by a clean, one-pot, multi-component condensation reaction combining ethyl acetoacetate, hydrazine hydrate, aromatic aldehyde in catalytic amount of MSA. This approach has numerous benefits, including a quick reaction time and an easy work-up process. Compounds were identified via mass spectral analysis, NMR, IR, and chemical transformation. The antibacterial activity of the synthesized compounds was assessed against a specific strain of S. aurous and E. coli.

***Keywords:*** *aryl aldehyde, ethyl acetoacetate, hydrazine hydrate, MSA, pyrazolone etc.*

## INTRODUCTION

Pyrazolone are a class of organic compounds that feature a five-membered ring containing three carbon atoms and two nitrogen atoms. The molecular formula of pyrazolone is $C_3H_3N_2$. This heterocyclic ring structure imparts unique chemical and pharmacological properties to pyrazolone, making them significant in various fields such as chemistry and medicine.Pyrazolone aromatic nature, stability, and adaptable reactivity are among their essential qualities. They can change chemically in a variety of ways, which makes it possible to create different derivatives with unique characteristics. Pyrazolone have been used extensively in the manufacturing of materials, agrochemicals, and pharmaceuticals. Pyrazolone synthesis is achieved using a variety of techniques, such as condensation and cyclization reactions. These techniques increase the variety of compounds that can be produced by incorporating various functional groups onto the pyrazolone ring.In medicinal chemistry, pyrazolone have been recognized for their biological activities and are frequently used as scaffolds for designing drug candidates. Compounds containing the pyrazolone moiety have been investigated for their anti-inflammatory, antiviral, anticancer, and antifungal properties, among others. Pyrazolone also exhibit interesting coordination chemistry, forming complexes with various metal ions. This property makes them relevant in coordination chemistry and catalysis.

The pyrazolonering represent a fascinating class of organic compounds with a broad range of applications, from their roles in synthetic chemistry to their significance in drug discovery and materials science. The diverse properties and reactivity of pyrazolone contribute to their continued exploration and utilization in various scientific and industrial fields.Pyrazolone derivatives, which are created with pyrazolone as the primary core, have garnered more and more interest over time. A five-membered heterocyclic organic molecule with two neighboring nitrogen atoms can be found in the center core. The chemical, pharmaceutical, and agrochemical industries are very interested in pyrazolone derivatives[1,2]. Considered an active scaffold with pharmacological importance, pyrazolone and its derivatives exhibit nearly all pharmacological activity. The pyrazolone moiety's pharmacological potential has been demonstrated by the nucleus's presence in pharmacological agents belonging to various therapeutic categories, including rimonabant, difenamizole, an analgesic; fezolamide, an antidepressant; and celecoxib, a potent anti-inflammatory and antipsychotic.[3] Because of their many characteristics and uses, pyrazolones are a class of chemicals that have been studied. These include pyrazol-3-ol and pyrazolin-5-one. Sulfamazone, propyphenazone, and nifenazone[4] are a few of the exploratory small compounds containing pyrazolone that have been considered as potential therapeutic possibilities. Derivatives of pyrazolone are a significant class of heterocyclic chemicals found in numerous medications and synthetic goods.Based on a review of the literature, pyrazolone derivatives

exhibit a range of pharmacological actions, including, anti-tubercular[5], anti-fungal,[6,7] anti-bacterial,[8] anti-inflammatory,[9] anti-timor,[10] anti-microbial.[11]

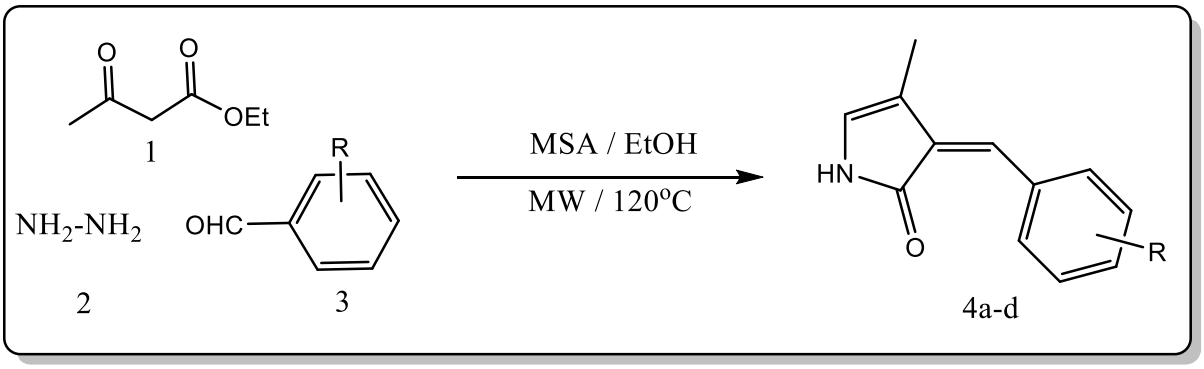
In this study, we have created a sophisticated, effective, simple, and straightforward method for the synthesis of pyrazolone and its derivatives. We do this by employing ethanol as a solvent together with hydrazine hydrate, ethyl acetoacetate, and substituted aryl aldehydes in a catalytic quantity of MSA. In terms of environmentally friendly procedures, the combination of the green technique and the catalyst results in an outstanding product yield. This approach offers many important benefits, including reduced reaction time, solvent-free conditions, atom economy, using a green catalyst, and a more pleasant workup process.

The antibacterial activity of a recently synthesized molecule is the subject of the current antimicrobial study. Using the agar-cup diffusion method, this compound's antibacterial activity was investigated. Both gram positive and gram negative types of bacteria are employed.
*1. Gram positive : S.aureus2. Gram negative : E.coli*

## EXPERIMENTAL

***General:*** The digital melting point device (Veego-VMD) was used to record the uncorrected melting point of the produced chemical. A.R. Grade chemicals were used. Every chemical employed was of A.R. Grade, and it wasn't purified further. Microwave irradiation was carried out in a Microwave Oven, Model No. MS2079 DB DB1QILN (2450 MHz, 1050 W) equipped with Erlenmeyer flask. The compound's melting point was measured in an open capillary tube and might not be accurate. Using an FT-IR spectrophotometer made by Perkin-Elimer, IR spectra were recorded. KBR Pellet. Using chloroform as a solvent, the 1H NMR spectra and mass were recorded using a Perkin-Elimer spectrophotometer. The chemical shift value was reported in parts per million (ppm) with respect to TMS, which served as an internal standard. Antimicrobial activity assessed by means of the Kirby-Bauer technique. Hi-media Laboratories Pvt. Ltd. in India produced nutritional agar for the development of all strains of S. aureus and E. coli, which was the medium utilized for the investigation of the newly synthesized compound's antibacterial effectiveness.

***General Procedure for the synthesis of Pyrazolone and its Derivatives:*** The combination of **1**ethyl acetoacetate (0.01mmol), **2**hydrazine hydrate (0.01mmol), and **3** aryl aldehyde (0.01mmol) in catalytic amount of Methane sulphonic acid (MSA) in an Erlenmeyer flask and irradiated until completion of the reaction in microwave oven.The reaction mixture was poured in crushed ice and filtered, washed with ethyl acetate, the product was recognized as 3-methyl-4-arylidene pyrazolone (4a-d). The crude product was collected and recrystallized in ethanol and dried. The entire product was characterized by physical constant and spectroscopic techniques and compared with the standard method.




**Scheme 1**

## RESULT AND DISCUSSION

As indicated in the scheme 1, we reported a direct method for the synthesis of pyrazolone and its derivatives by one pot condensation of aromatic aldehyde, hydrazine hydrate, and ethyl-acetoacetate.The yield was really high. In order to assess the extent and constraints of the methodology, the reactions were conducted in the absence of a catalyst, and the structures of all newly synthesized pyrazolone derivatives were established using chemical transformation, NMR, IR, and mass analysis.

**Table1:** Synthesis of pyrazolone & its derivatives catalyzed by MSA under M.W. (120oC/300W)

| Product | Name of compound | % yield | Melting Point in $^{O}$C |
|---|---|---|---|
| 4a | (Z)-3-benzylidene-4-methyl-1,3-dihydro-2H-pyrrol-2-one | 94% | 122$^{0}$C |
| 4b | (Z)-3-(4-chlorobenzylidene)-4-methyl-1,3-dihydro-2H-pyrrol-2-one | 89% | 215$^{0}$C |
| 4c | (Z)-4-methyl-3-(3-nitrobenzylidene)-1,3-dihydro-2H-pyrrol-2-one | 87% | 195$^{0}$C |
| 4d | (Z)-3-(4-hydroxybenzylidene)-4-methyl-1,3-dihydro-2H-pyrrol-2-one | 92% | 197$^{0}$C |

**Table 2:** Optimization of catalyst concentration of (4b) under M.W. Irradiation

| Entry | Catalyst mol % | Time, min | Yields % |
|---|---|---|---|
| 1 | No catalyst | 9 | - |
| 2 | 1 | 8 | 76 |
| 3 | 2 | 7 | 89 |
| **4** | **3** | **3** | **95** |
| 5 | 4 | 5 | 85 |
| 6 | 5 | 8 | 70 |

Initially, the mixture of Ethyl acetoacetate, Hydrazine hydrate and substituted aryl aldehydes, (0.01 mol each) was taken in an 50 mL vessel and subjected to microwave irradiation under neat conditions in the absence of catalyst and solvent, and the reaction was failed to get the product under this condition. The reaction was repeated in the presence of catalyst in the range 1-5 mol %. We have optimized the amount of catalyst for the synthesis of (**4b**, Table 1) under microwave irradiation and excellent yield was obtained in only 3 minutes when 3 mol % catalysts are introduced (**Table 2,** entry 4).

A number of approaches have been put forth and modified for the measuring of antibacterial activity. The cup diffusion method[12-14] was used in the current investigation to screen freshly synthesized compounds for antibacterial activity. There are both gram positive and gram negative bacteria among the species, such as S. aureus and E. coli. Agar medium, subcultures, and nutrient broth were prepared in accordance with normal protocol. Sensitivity plates were seeded with 1× 106 CIU ml-1 bacterial inoculims, and each well (diameter of 8 mm) was filled with 0.1 ml of 1000µgml-1 test compound solution in chloroform, resulting in a concentration of 100µgml-1 for each test compound. Using an antibiotic zone scale, the zone of inhibition was measured following a 24-hour incubation period at 370C. The compounds' inhibition zone records made it abundantly evident that compounds (15) and (18) were quite effective against S. aureus and E. coli. Table 3 summarizes the test compound's antimicrobial activity and its ability to suppress the growth of different bacterial species.

**Table 3:** Antimicrobial Activity

| Compounds | Inhibition zone recorded in mm | |
|---|---|---|
| **Microorganisms** | **S. aureus** | **E.Coli** |
| 4a | 11mm | 14mm |
| 4b | 16mm | 13mm |
| 4c | 13mm | 15mm |
| 4d | 12mm | 17mm |

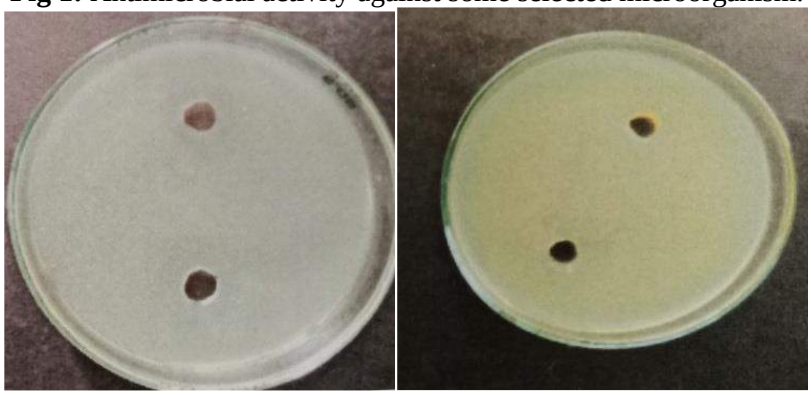
***Composition of Nutrient Agar medium:***

Peptone : 5.0gm

Yeast extract : 1.5gm

Beef extract : 1.5gm
Sodium chloride: 5.0gm
Agar-agar : 15.0gm
Distilled water :1000ml
pH : 6.9-7.1

**Fig 1:** Antimicrobial activity against some selected microorganism.



*S.aureus* *E.Coli*

The quality of media that was employed was bacteriostatic. 28 grams of materials were dissolved in one liter of distilled water to create the nutrient agar medium. It was then autoclaved at 121ºC for 20 minutes, 15 pounds at a time. After cooling to roughly 50ºC, the medium was added to sterile petriplates and allowed to harden. To obtain grass culture, the test bacterial organisms were then planted onto the media plates with 24-hour-old, fresh, active nutrient broth cultures. Using standard quality cork boarers, agar medium was scooped out of a petridish to create the typical 8.0mm diameter cups. Operations are performed in an ultra-clean laminar flow system under aseptic conditions. The test chemicals were dissolved in chloroform while maintaining the solution's initial 1000µg/ml concentration. As a control, chloroform solvent was utilized. These plates were placed in an incubator and incubated for 24 hours at 37ºC. Following incubation, test drug inhibitory effect was monitored on the plates by looking for a clean zone surrounding the cups. By comparing the plate to the antibiotic zone scale, the diameter of the zone of inhibition was determined.

**Spectroscopic characterization.**

**4c) (Z)-4-methyl-3-(3-nitrobenzylidene)-1,3-dihydro-2H-pyrrol-2-one**

Solid: - Melting point = 195ºC

**IR (KBr, $Cm^{-1}$)** : 1354, 1260, 1500, 1607, 670.

**$^1$HNMR (400 MHz, DMSO-d6):**δ 7.2(1H,s), 1.18 (1 H, s), 6.93 (1 H, s), 8.10-8.12 (4H, m).

**4d) (Z)-3-(4-hydroxybenzylidene)-4-methyl-1,3-dihydro-2H-pyrrol-2-one**

Solid: - Melting point = 197ºC

**IR (KBr, $Cm^{-1}$)** : 1354, 1260, 1500, 1607, 670.

**$^1$HNMR (400 MHz, DMSO-d6):** δ 7.45(1H,s), 6.89 (1 H, s), 9.81 (1 H, s), 5.0(1H,s), 6.93 (4H, m).

## CONCLUSION

We have been able to offer an effective method for the synthesis of pyrazolone derivatives in the presence of MSA in our current study. All of the recently synthesized compounds' structures were determined via mass spectral analysis, NMR, IR, and chemical transformations.

Condensation-enhanced pyrazolone synthesis and its derivatives provide high yields of pyrazolone in good quality and purity at a low cost. It is discovered that compound 4d has greater potency against E. Coli while compound 4b has greater potency against S. Aureus. This approach has the noteworthy advantages of being catalyst-free and having an easy workup procedure. The synthesis process used to create these molecules is very easy to use, clean, economical, green, and environmentally friendly.

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# Structural, Optical and Wettability properties of $CoFe_2O_4$ thin film prepared by spray pyrolysis technique

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**ABSTRACT**

Using simple wet chemical spray pyrolysis method at a temperature of 380 °C, nano-structured $CoFe_2O_4$ thin films have been grown on clean glass substrates. Through the use of X-ray diffraction (XRD), UV-Visible spectroscopy, and Contact angle measurement, to take the structural, optical, and surface wettability were investigated. Broad peaks with a single-phase cubic spinel structure and nanocrystalline nature are seen in the XRD examinations. Scherrer's formula was used to compute the crystallite size, for which most intense peak was consider. The large absorption peak seen in UV-Vis spectra exposes the red shift and indicates that the obtained energy band gap. The Contact angle measurement revealed the hydrophilic nature of the thin films under investigation.

***Keywords:*** *Spray pyrolysis, X-ray diffraction, Uv-Vis, thin film, Cobalt Ferrites*

## INTRODUCTION

Now a days the research area of spinel ferrites have attracted incredible attention for the preparation, characterization, development and usages due to its considerable electrical, optical, and magnetic properties. In contrast, spinel ferrites have a high dielectric constant, mechanical strength, chemical stability, a high Curie temperature, and increased magnetic permeability. Because of their exceptional properties, they are frequently used in a wide range of products, including sensors, electronic devices, solar cells, integrated circuits, and energy-saving technology. Because of their wide applications in domains such as industrial, electrical, and biological applications, spinel ferrite thin films drew the attention of many researchers and scientists. Ferrites thin films with high resistivity are used in microwave devices and integrated circuits as insulators, circulators, and gyrators, and are predicted to soon replace surface mounted devices. Ferrite films have been created by spray pyrolysis, pulsed laser deposition, atomic layer deposition, the sol-gel method, RF magnetron sputtering, and other processes. Doping divalent and trivalent metal ions into nickel ferrite thin films improves the material's magnetic and electrical properties, allowing it to be used in memory storage devices, core transformers, and high frequency devices. Spinel ferrites are technologically significant materials with numerous applications, including microwave devices and magnetic storage devices. Spinel ferrite materials with incredible ferrimagnetic and dielectric properties dominate electronics in the modern technological era. Because of their exceptional electric, dielectric, and magneto-optical properties, nanocrystalline spinel ferrites have piqued the interest of scientists working in microelectronics and the medical sciences. Because of their unique features, cubic spinel ferrites with the general chemical formula MFe2O4 (M = divalent metal) have a wide range of applications.

## EXPERIMENTAL

***Synthesis:*** Analytical reagent (AR) grade cobalt nitrate (Co (NO3)3.6H2O) and ferric nitrate (Fe (NO3)3.9H2O) were used as starting material without any further purification. The glass substrate of the size 75 x 25 x 1.45 mm3 was carefully cleaned by sequential treatment with chromic acid, ethanol, and acetone followed by dipping with deionized water in an ultrasonic bath for 30 min, and the same glass plates was used for the deposition. The deposition of the film was carried out using spray pyrolysis technique by optimizing the parameters like spray rate, nozzle to substrate distance, pressure etc. The details of the experimental procedure for the deposition of thin film using spray pyrolysis technique are

already reported in our previous reports. The crystal structure and phase purity of prepared thin film was studied by using X-ray diffractometer (XRD) (Philips) with Cu-K□ radiation in the 2θ range of 20□80□ with wavelength (λ = 1.5406 Å). The contact angle was measured with the help of contact angle meter (Ramehart Instruments Co. USA) equipped with CCD camera.

## RESULTS AND DISCUSSION

***X-ray Diffraction:*** The X-ray diffraction pattern of a cobalt ferrite thin film recorded at room temperature is shown in Fig. 1. The XRD pattern reveals cubic reflections (111), (220), (311), (222), (400), (422) (511) and (440). The spinel structure. The XRD pattern analysis demonstrates that the film has a single-phase cubic spinel structure. The crystallite size was estimated using the XRD pattern's highest strong peak (311). The crystallite size was measured using Debye-formula Scherrer's and found to be... nm, indicating that the film is nanocrystalline. The lattice constant derived from known interplanar spacing (d) and Miller indices was discovered to be in the order.

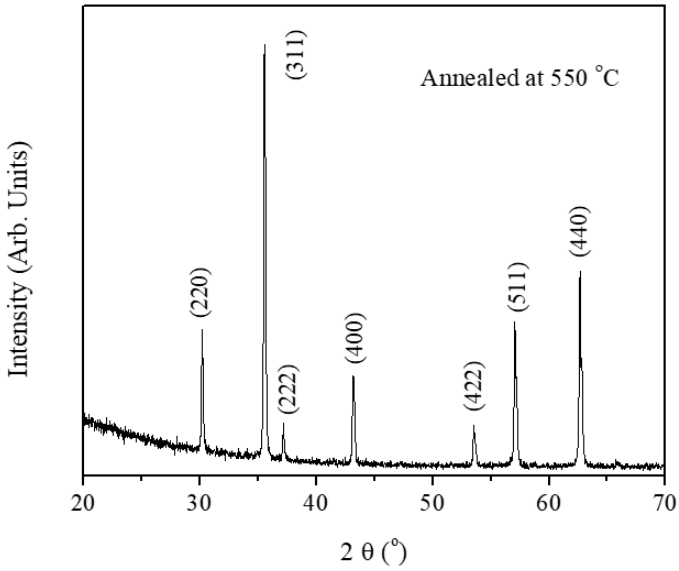


**Fig.1.** X-ray diffraction pattern of $CoFe_2O_4$ (x-0.0) thin films

***Wettability studies:*** The unique hydrophilic surfaces are highly desirable in many important applications such as antifogging, self-cleaning, anti-fouling, water-oil separation etc due to their special wetting behaviour. The present cobalt ferrite thin film, the wettability studies were carried out by contact angle meter. The represents photograph (Fig.2.) of the water droplet on the prepared cobalt ferrite thin film. The contact angle was measured using contact angle meter and it is found to be less than 90° showing the film is hydrophilic in nature. Thus, the prepared cobalt ferrite thin film on account of its hydrophilic nature can be used for antifogging, detergent free self-cleaning, anti-fouling, water-oil separation etc.

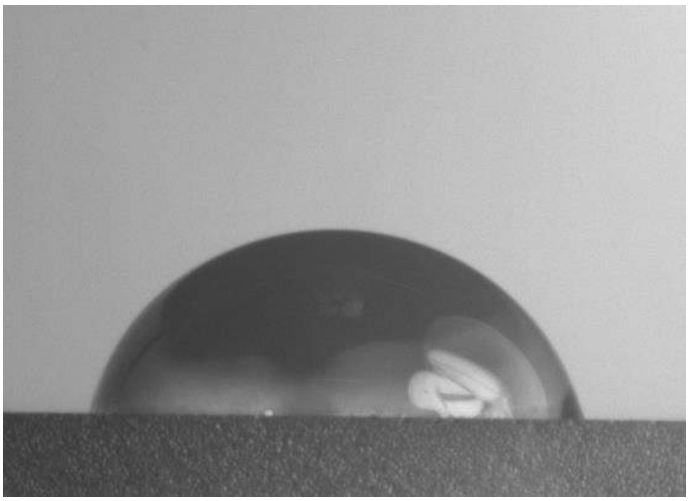

**Fig.2.** Photograph of the water droplet on the prepared cobalt ferrite thin film.

***UV–V is spectroscopy (UV–vis):*** UV–vis spectroscopy technique was employed in the present thin films to understand the optical properties CoFe2O4. The energy band gap is affected by several factors such as lattice parameter, crystallite size, concentration, thickness of films and presence of impurities in films sample. The Tauc relation was estimated to the energy band gap as function of the incident energy and energy band gap. The energy band gap obtained 2.3628 eV in the ferrite materials which can be attributed to the lattice defect, displacement of atom and prebendary diffusion shown in fig. 2.

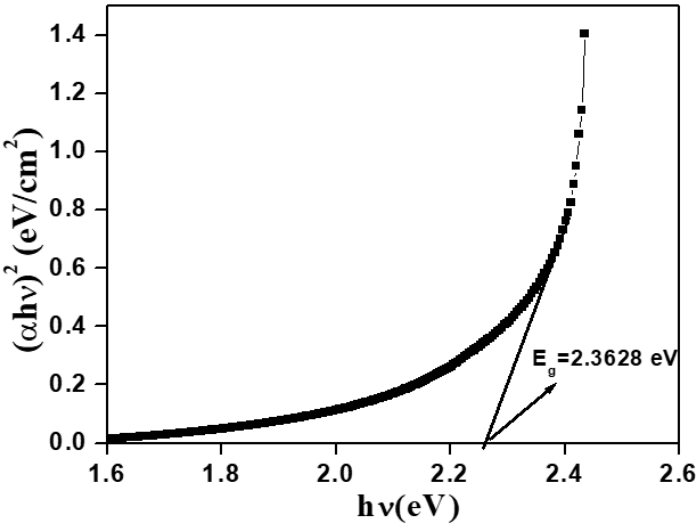


**Fig.2.** Energy band gap for$CoFe_2O_4$ (x-0.0) thin films

## CONCLUSION

Thin films of $CoFe_2O_4$ are deposited on a quartz glass substrate by spray pyrolysis deposition technique. The structural, morphological and optical properties of CFO thin films strongly affected annealing temperature. XRD analysis shows improved crystallinity, and crystallite size with respect to annealing temperature. Uv-Vis Spectroscopy studies confirm that the thin films have direct band gap energy. The unique hydrophilic surfaces are highly desirable in many important applications such as antifogging, self-cleaning, anti-fouling, water-oil separation etc due to their special wetting behaviour.

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# Green synthesis of CuO-NPs from $CuSO_4$ by Using Ixora Coccinea Linn. Leaves Extract

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## ABSTRACT

The strategy for design of new nanometals was developed due to their wide applications in many fields. One of the most important nanometals is copper oxide (CuO-NPs) nanoparticles because of their extensive applications in biotechnology and biomedical fields. copper oxide (CuO-NPs) nanoparticles were usually synthesised by using chemical and physical methods. In the chemical methods, various toxic chemicals are used, which are harmful to the health of living organisms. Therefore, the CuO-NPs were synthesized by using biological methods based on green chemistry for reducing the toxic chemicals. There are various resources for green synthesis of CuO-NPs such as bacteria, fungi, enzyme and plant extracts. The green synthesis of CuO-NPs involves three main steps: the selection of the solvent medium, the selection of environmentally reducing agents, and the selection of non-toxic substances for the stability of CuO-NPs. The biosynthesis of CuO-NPs using plant extract is more favourable than other biological methods because of removing the elaborate process of maintain cell cultures. This research study focuses on green synthesis of CuO-NPs using Ixora Coccinea Linn. leaves extract

***KEYWORDS:*** *CuO-NPs, Ixora Coccinea Linn., green synthesis, nanoparticles,*

## INTRODUCTION

NPs are very small particles having size ranges from 1 to 100 nm and which is undetectable by the human eye; they can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs. NPs can exhibit significantly different physical and chemical properties due to their high surface area and nanoscale size.[1]Humans already make full use of the ceramic matrixes by including natural asbestos nano-fibers more than 4,500 years ago. The Ancient Egyptians were also using NPs more than 4000 years ago based on a synthetic chemical process to synthesize ≈5 nm diameter PbS NPs for hair dye.[2,3,4] Similarly, "Egyptian blue" was the first synthetic pigment which was prepared and used by Egyptians using a sintered mixture nanometer-sized glass and quartz around 3rd century BC.[5]Human dreams and imagination often give rise to new science and technology. Nanotechnology, a 21stcentury achievement, was born out of such dreams. Nanotechnology is defined as the understanding and control of matter at dimensions between 1 and 100 nm where unique phenomena provide novel applications in various filed.[6],[7] Although human exposure to nanoparticles has occurred throughout human history, it dramatically increased during the industrial revolution. The study of nanoparticles is not new. The concept of a ''nanometer'' was first proposed by Richard Zsigmondy, the 1925 Nobel Prize Laureate in chemistry. He invents the term nanometer in a clear and detailed manner for characterizing nanoparticle size and he was the first to measure the size of particles such as gold colloids using a microscope. Modern nanotechnology was the brain child of Richard Feynman, the 1965 Nobel Prize Laureate in physics. During the 1959 American Physical Society meeting at Caltech, he presented a lecture titled, ''There's Plenty of Room at the Bottom'', in which he introduced the concept of manipulating matter at the atomic level.[8]

***Green synthesis of metal oxide-based Nano-particles****:* In the recent years, CuO-NPs, ZnO-NPs and nanocomposites are exciting inorganic materials can be used in various filed because have generated a great deal of interest such as energy conservation, textiles, electronics, healthcare, catalysis, cosmetics, semiconductor, chemical sensing as a catalyst in organic reactions, environmental technology. Nano

particles can be synthesized by various methods (Chemicals, physical and biosynthesis) with multiple properties and large application.[9,10]

***Ethnomedicinal plant*** *: Ixora coccinea Linn.,* (Rubiaceae) commonly known as the flame of the woods, flame of the forest, jungle flame, burning love, scarlet ixora, jungle of Geranium, and red ixora, is one such evergreen shrub [11,12] The plant is supposed to be originally native to India and Sri Lankahowever, today it can be found growing in the tropical and subtropical climates of the world. The plants have also naturalized to Puerto Rico, Florida, and parts of Nigeria.[13] Ixora coccinea are found growing profusely in dry lands where the soil is slightly acidic. The plants are densely branched and normally grow up to a height of 3 m. The stems are grey in color and are about 3 to 4 cm in diameter at the base. The leaves are darkgreen in color and oblong in shape. The inflorescences are terminal, dense corymbs, and contain about 15 to 50 flowers. Each individual flower is tubular with 4 or 5 calyx lobes[14]. The wild varieties of plants produce flowers that are red or red-orange in color. However, plants with white, yellow, salmon, or pink flowers are also prevalent and are now cultivated and marketed in horticultural outlets. Dwarf varieties of these plants are also available and are extensively used in landscaping and as indoor plants. The fruits arefleshy, globose berries, green in color when raw and dark blood red or purplish-black when ripe[15]. The fruits contain 2 seeds that are proportionately large when compared to the size of the fruit[15].

## METHODOLOGY

### *Material and Methods*

***Collection of plants material:*** The leaves of the plant *Ixora coccinea*were collected from region of Buldana District (MS).

***Preparation of plant extracts:*** Fresh leaf of *Ixora coccinea*plant was collected and shades dried. After dry were grinded to fine powder. 10g of leaves powder of *Ixora coccinea*was transfer into 250 ml beaker containing 100 ml distilled water and boiled up to 3 hrs. After cooling, filtered with vacuum suctions pump using whatmann filter paper No.41 and is collected in conical flask, stored in refrigerator to avoid formation of bacteria before its used for bio synthesis.

**Fig.[A]** ***Ixora coccinea***

**Fig.[B] Decantation Process**

**Fig. [C] Filtration of extract**

**Fig. [D]** Centrifuge process for preparing nanoparticles.


**Fig. [E]** Nanoparticles before placing in furnace

**Fig. [F]** Filtration of extract.

### *Green synthesis of CuO NPs*

10 ml of 0.1 M of $CuSO_4$ solution was prepared in 250 ml round bottom flask; 90 ml of leaves extract was added to the copper chloride solution with 30:10(V/V) using separating funnel at $80^0$C for 3 hrs with continuous stirrer using magnetic stirrer for accelerative bio reduction of CuO-NPs. The reddish-brown colour indicated the formation of CuO-NPs. The fully reduced CuO-NPs solution was

centrifuge at 5000 rpm for 5-15 min. The supernant was discarded. The residue was purified with distilled water.

Residue was collected in crucible and then it provides heat treatment/calcinations process at $500^0$C using muffle furnace with ambient air to achieve high purity and fine crystal nanosized CuO particles.

## RESULT AND DISCUSSION

This method of green synthesis CuO-NPs beings by mixing the plant leaves extracts (natural) with $CuSO_4$ solution with biochemical reduction of cupric sulphate salt color change is observed in the solution indicating synthesis of CuO-NPs. In the present work, we develop an eco-friendly, clean, non-toxic, facile chemically preparative method, for the synthesis of CuO-NPs using the extract of *Ixora coccinea.*Project investigation indicates that the extract of *Ixora coccinea* is one of the new approaches in the field of nanosynthesis. To date, there is no report on the green synthesis of CuO-NPs by utilizing the leaves extract of *Ixora coccinea.*

**Fig [I]: Synthesis of $CuSO_4$**

While performing our research we took (**2.49gm** of $CuSO_4$) and obtain yield of nanoparticles is **0.05gm**. Result shows that the obtain nanoparticles are crystalline in nature having a black color. Nanoparticles have low particle momentum and very high mobility. Due to the small size of nanoparticles, they allow for free movement and therefore heat treatment is necessary in furnace which transfers heat. Synthesized CuO-NPs shows magnetic properties.

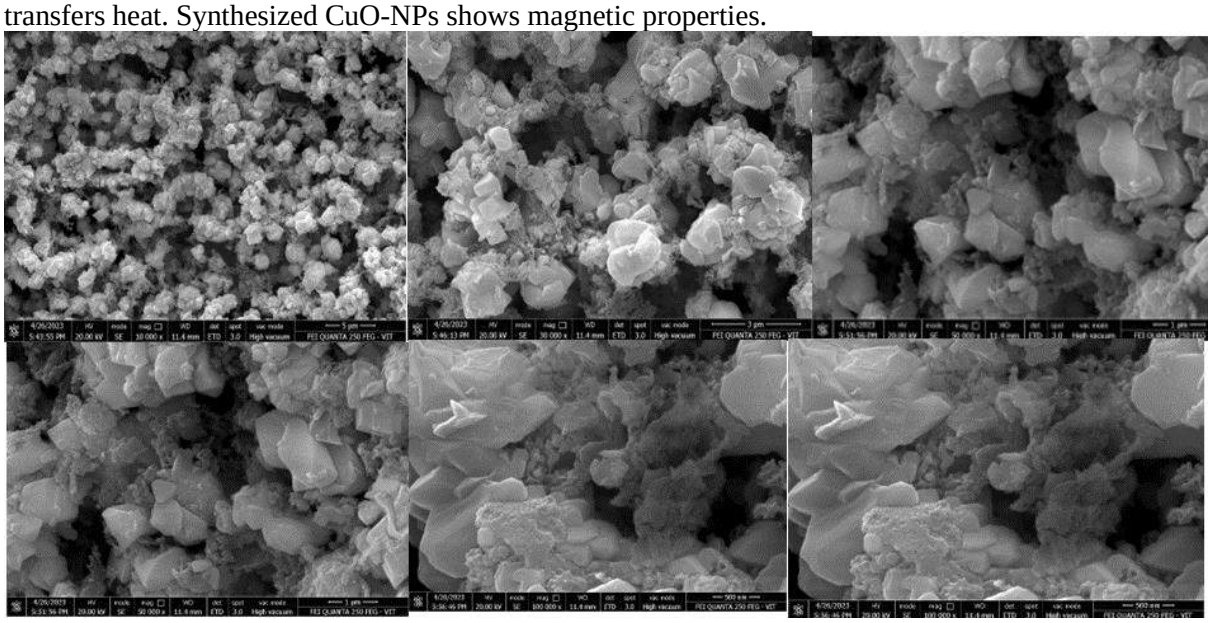

**Fig :Scanning Electron Microscopy (SEM) of CuO-NPs**

## CONCLUSION

The green synthesis of CuO-NPs by using leaves extract of this plant *Ixora coccinea.* is successfully synthesized. The present project work shows that the leaves extract of this plant *Ixora coccinea.* can are efficiently used for CuO-NPs. Physical, chemical and green synthesis methods are available for synthesis of CuO-NPs, but the physical and chemical methods may be toxic and highly reactive and hence it is risk for environment and human health. Therefore, to search an inexpensive, reliable, safe and "Green" method for synthesis of CuO-NPs with controlled size, shape and stability is highly warranted that is no physical or chemical change when it stored. Ixora coccinea extracts have potential to be developed as antimicrobial agents, in particular against S. aureus and S. flexneri. Further

studies on isolation and identification of the active principles and evaluation of possible syner- gism among these constituents for their antimicrobial activity are currently ongoing.

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# Green method for synthesis of ZnO-NPs from $ZnSO_{4.5}H_2O$ by Using Aqueous leaf Extract of Syngonium podophyllum

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## ABSTRACT
*The strategy for design of new nanometals was developed due to their wide applications in many fields. One of the most important nanometals is Zinc oxide (ZnO-NPs) nanoparticles because of their extensive applications in biotechnology and biomedical fields. Zinc oxide (ZnO-NPs) nanoparticles were usually synthesised by using chemical and physical methods. In the chemical methods, various toxic chemicals are used, which are harmful to the health of living organisms. Therefore, the ZnO-NPs were synthesized by using biological methods based on green chemistry for reducing the toxic chemicals. There are various resources for green synthesis of ZnO-NPs such as bacteria, fungi, enzyme and plant extracts. The green synthesis of ZnO-NPs involves three main steps: the selection of the solvent medium, the selection of environmentally reducing agents, and the selection of non-toxic substances for the stability of ZnO-NPs. The biosynthesis of ZnO-NPs using plant extract is more favourable than other biological methods because of removing the elaborate process of maintain cell cultures. This research study focuses on green synthesis of ZnO-NPs using Syngonium podophyllum. leaves extract.*

***KEYWORDS:*** *ZnO-NPs, Syngonium podophyllum. leaves extract, $ZnSO_4.5H_2O$, nanoparticles*

## INTRODUCTION
NPs are very small particles having size ranges from 1 to 100 nm and which is undetectable by the human eye; they can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs. NPs can exhibit significantly different physical and chemical properties due to their high surface area and nanoscale size.[1]Humans already make full use of the ceramic matrixes by including natural asbestos nano-fibers more than 4,500 years ago. The Ancient Egyptians were also using NPs more than 4000 years ago based on a synthetic chemical process to synthesize ≈5 nm diameter PbS NPs for hair dye.[2,3,4] Similarly, "Egyptian blue" was the first synthetic pigment which was prepared and used by Egyptians using a sintered mixture nanometer-sized glass and quartz around 3rd century BC.[5]Human dreams and imagination often give rise to new science and technology. Nanotechnology, a 21stcentury achievement, was born out of such dreams. Nanotechnology is defined as the understanding and control of matter at dimensions between 1 and 100 nm where unique phenomena provide novel applications in various filed.[6],[7] Although human exposure to nanoparticles has occurred throughout human history, it dramatically increased during the industrial revolution. The study of nanoparticles is not new. The concept of a ''nanometer'' was first proposed by Richard Zsigmondy, the 1925 Nobel Prize Laureate in chemistry. He invents the term nanometer in a clear and detailed manner for characterizing nanoparticle size and he was the first to measure the size of particles such as gold colloids using a microscope. Modern nanotechnology was the brain child of Richard Feynman, the 1965 Nobel Prize Laureate in physics. During the 1959 American Physical Society meeting at Caltech, he presented a lecture titled, ''There's Plenty of Room at the Bottom'', in which he introduced the concept of manipulating matter at the atomic level.[8]

***Green synthesis of metal oxide-based Nano-particles****:* In the recent years, CuO-NPs, ZnO-NPs and nanocomposites are exciting inorganic materials can be used in various filed because have generated a great deal of interest such as energy conservation, textiles, electronics, healthcare, catalysis, cosmetics,

semiconductor, chemical sensing as a catalyst in organic reactions, environmental technology. Nano particles can be synthesized by various methods (Chemicals, physical and biosynthesis) with multiple properties and large application.[9],[10]

Syngonium podophyllum, commonly called arrowhead vine, is native from Mexico to Ecuador. It is an evergreen climbing vine that typically grows to 3-6' long. As a house plant, it is typically grown for its attractive ornamental foliage which changes shape as the leaves mature. Arrowhead, (genus Sagittaria), genus of plants of the family Alismataceae, consisting of at least 28 species distributed worldwide, having leaves resembling arrowpoints. Arrowheads are perennial herbs with fleshy rhizomes and frequently with tubers that grow in shallow lakes, ponds and streams.

***Review of literature:*** Recent research trend in green/biosynthesis of nanometals using plant extracts has opened a new era in fast, nontoxic and eco-friendly methods for biosynthesis of metal nanoparticles. Many researchers have reported the green synthesis of metal and metal oxide based nanoparticles by using various parts of plant such as leaf, leaves, flower, stem and roots extracts and their potential applications in various filed.[11,12,13,14]

Plant mediated green/biosynthesis of metal (Ag, Fe, Zn, Au and Cu) and metal oxide (AgO, FeO, ZnO, AuO and CuO) nanoparticles (NPs) is a revolutionary technique that has wide range of applications in catalysis, organic synthesis, inorganic chemistry, electrochemistry, polymer chemistry, physics, life sciences , agriculture, food industry and pharmaceutical industries for the development of medicine.[15]Medicinal plants possess bioactive phytochemicals such as like proteins, vitamins, coenzymes based intermediates, phenols, flavonoids, steroids, terpenoid, alkaloids and carbohydrates. These bioactive phytochemicals contain hydroxyl, carbonyl, and amine functional groups that react with metal ions and reduce their size into nano range.[16]

These molecules not only help in bio-reduction of the ions to the nanoscale size, but they also play a vital role in the capping of the nanoparticles which is important for stability and biocompatibility. Reducing agents such as phenolic compounds, sterols and alkaloids can reduce metal ions into NPs in a single reaction.[17]

Zing oxide nanoparticles have drawn considerable attention from research and scientist in the past 4-5 years due to its wide applications field of the biomedical field as wall as in optics and electronics Znonanoparticals are of great interest due to inexpensive to synthesis, safe and easy method of synthesis. These nanoparticle posses high exciton binding energy of 60 meV and a large bandgap of 3.37eV, and due to this. These shows various semiconducting properties such as high catalytic activity, would healing, anti-inflammatory, ultraviolet filtering properties and extensively used various cosmetics such as sunscreen.[18]

## METHODOLOGY

### Material and Methods

***Collection of plants material***

The leaves of the plant *Arrowhead plant* collected from region of Buldana District (MS).

***Preparation of plant extracts:*** Fresh Leaves of plant were collected and shades dried. After dry were grinded to fine powder. 10g of leaf powder of Arrowhead plant was transfer into 250 ml beaker containing 100 ml distilled water and boiled up to 3 hrs. After cooling, filtered with vacuum suctions pump using whatmann filter paper No.41 and is collected in conical flask, stored in refrigerator to avoid formation of bacteria before its used for bio synthesis.



***Green synthesis of ZnO NPs***: 10 ml of 0.1 M of ZnSO4.5H2O solution was prepared in 250 ml round bottom flask; 90 ml of leaf extract was added to the copper chloride solution with 30:10(V/V) using separating funnel at $80^0$C for 3 hrs with continuous stirrer using magnetic stirrer for accelerative bio reduction of ZnO-NPs. The reddish browncolor indicated the formation of ZnO-NPs. The fully reduced ZnO-NPs solution was centrifuge at 5000 rpm for 5-15 min. The supernant was discarded. The residue was purified with distilled water.

Residue was collected in crucible and then it provides heat treatment/calcinations process at $500^0$C using muffle furnace with ambient air to achieve high purity and fine crystal nanosized ZnO particles.

**Fig. [D]** Centrifuge process for preparing nanoparticles.


**Fig. [E]** Nanoparticles before placing in furnace

**Fig. [F]** Filtration of extract.

## RESULT AND DISCUSSION

This method of green synthesis ZnO-NPs beings by mixing the plant leaf extracts (natural) with ZnSO4.5H2O solution with biochemical reduction of Zinc sulphate salt color change is observed in the solution indicating synthesis of ZnO-NPs. In the present work, we develop an eco-friendly, clean, non-toxic, facile chemically preparative method, for the synthesis of ZnO-NPs using the extract of Arrowhead plant. Project investigation indicates that the extract of Arrowhead plant is one of the new approaches in the field of nanosynthesis. To date, there is no report on the green synthesis of ZnO-NPs by utilizing the root extract of Arrrowhead plant. While performing our project we took (3.4gm of ZnSO4.5H2O) and obtain yield of nanoparticles is **0.06 gm** .result shows that the obtain nanoparticles are crystalline in nature having a black color. Nanoparticles have low particle momentum and very high mobility. Due to the small size of nanoparticles they allow for free movement and therefore heat treatment is necessary in furnace which transfers heat. Synthesized ZnO-NPs shows magnetic properties

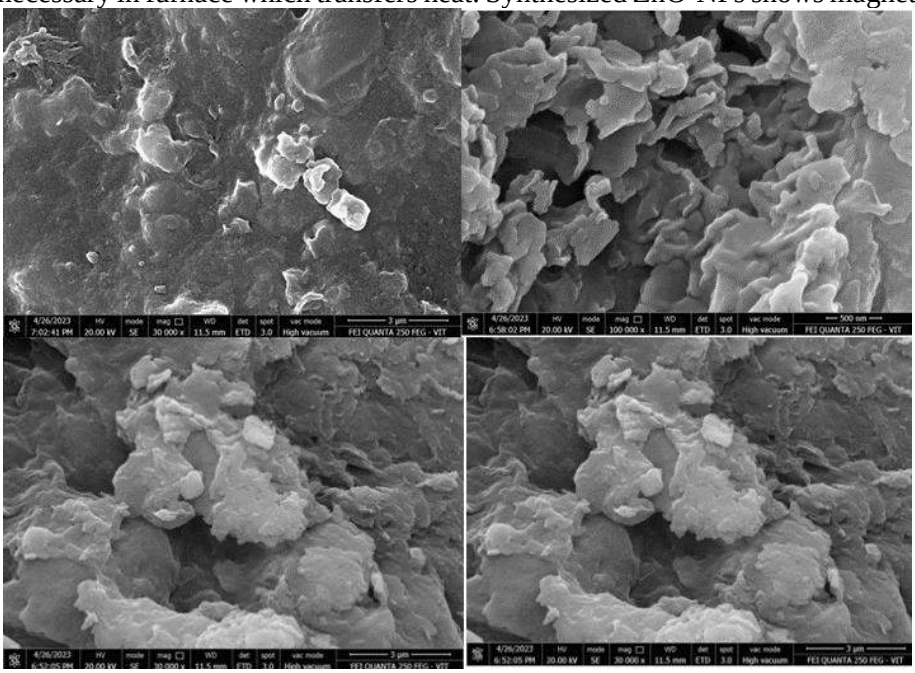

**Fig [G] :** Scanning Electron Microscopy (SEM) of ZnO-NPs

## CONCLUSION

The green synthesis of ZnO-NPs by using leaf extract of this Arrowhead plat is successfully synthesized. The present project work shows that the aqueous roots extract of this plantArrowhead plantcan are efficiently used for ZnO-NPs. Physical, chemical and green synthesis methods are available for synthesis of ZnO-NPs, but the physical and chemical methods may be toxic and highly reactive and hence it is risk for environment and human health. Therefore, to search an inexpensive, reliable, safe and "Green" method for synthesis of ZnO-NPs with controlled size, shape and stability is highly warranted that is no physical or chemical change when it stored.

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# Structural Analysis of Synthesized Ni–Cu–Co Spinel Ferrite Nanoparticles via Sol-Gel Auto Combustion

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## ABSTRACT

The sol-gel auto-combustion method was used to synthesize nanocrystalline spinel ferrites of composition $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \leq x \leq 0.5$) (CNCoF), using high purity metal nitrates and citric acid as precursors. The synthesized sample was sintered at 800 ˚c. for 180 min. The structural properties of the sample were determined using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The XRD pattern confirms phase formation, which is a characteristic of spinel ferrite with most intense (311) peak. The synthesized material having cubic spinel structure, the lattice parameter was found to be 9.32 Å. The average crystallite size of the synthesized samples is 39.85 nm determined by the Scherrer formula. FT-IR of the CNCoF ferrite analyzed in the range of 4000-400 $cm^{-1}$. The absorption bands '$\upsilon_1$' and '$\upsilon_2$' are assigned to the intrinsic stretching vibrations of tetrahedral complexes and octahedral complexes respectively which confirms the formation of a single-phase cubic spinel structure.

***Keywords**: Spinel ferrites, Sol-Gel, Auto combustion Method, X-ray diffraction, FT-IR.*

## INTRODUCTION

Spinel ferrites are a class of magnetic materials that have various applications in information technology, energy storage, and environmental remediation [1]. The properties of spinel ferrites depend on their composition, structure, and morphology [2]. Therefore, it is important to develop efficient and low-cost methods for synthesizing spinel ferrites with controlled characteristics. One of the promising methods is the sol-gel auto-combustion method, which uses metal nitrates and organic fuels as precursors and produces nanocrystalline powders in a single step [3]. The general nature of the spinel ferrite nanoparticles is that their properties can be changed to meet the requirements by varying the synthesis process, precursor pH, catalyst ion substitution, annealing conditions, agglomeration [4][5]. In spinel ferrite, nickel-copper-cobalt ferrite has mixed spinel structure and belongs to the cubic system (fig. 1). It can be described as cubic close packed arrangement of oxygen atoms which forms a unit cell. Layers of oxygen ions contain tetrahedral (A) sites and octahedral (B) sites. It is a magnetic recording material with good performance. In the field of material science, magnetic materials have become a subject of considerable interest in the field of power storage devices [6] and photocatalysis [7].

Recent studies have shown that the physical properties of nanoparticles are significantly enhanced by various processing techniques [8]. Particle size distribution and interparticle spacing have the greatest effect on properties of ferrites [9]. One of the ways to prepare spinel ferrite materials with the required properties is sol–gel auto combustion method.

In this paper, we report the synthesis and characterization of $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \leq x \leq 0.5$) ferrites (CNCoF) by the sol-gel auto-combustion method using citric acid as fuel. We investigated the effects of Ni substitution on the phase formation, crystal structure, lattice parameter, crystallite size, and infrared spectra of the CNCoF ferrites. The results shows that the CNCoF ferrites have a cubic spinel structure with a lattice parameter of about 9.32 Å and an average crystallite size of about 40 nm. The Hoping lengths, as ascertained by Stanley's equation, further contribute to the understanding of the material's structural dimensions, with $L_A$ and $L_B$ values of 4.040 Å and 3.298 Å, respectively. The microstrain of the CNCoF ferrites was calculated by the Williamson-Hall plot and found to be 1.31%, which indicates a low degree of lattice distortion. The FT-IR spectra of the CNCoF ferrites reveal two absorption bands corresponding to the stretching vibrations of the tetrahedral and octahedral metal-

oxygen complexes, confirming the formation of a single-phase spinel structure. The CNCoF ferrites synthesized by the sol-gel auto-combustion method have potential applications in magnetic and electronic devices and photocatalytic degradation of dye pollutants.

## METHODOLOGY

The chemicals used were ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and citric acid ($C_6H_8O_7 \cdot H_2O$), Ammonium Hydroxide ($NH_4OH$) all AR grade were used as received without further purification..

Synthesis of Nickel doped Copper - Cobalt ferrites nanoparticles having the chemical formula $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \leq x \leq 0.5$) (CNCoF) were prepared by sol–gel auto combustion method. The mass of various nitrates calculated by stoichiometric ratio was weighed by a laboratory balance. Metal nitrates and complexing agent were dissolved in distilled water and citric acid was used as fuel for self-combustion and complexing agent. In this study, the molar ratio of citric acid to metal ion was 3:1. The mixed solution of all the chemicals were stirred by using magnetic stirrer until the homogeneous solution was obtained. During the stirring process ammonium hydroxide solution was added drop by drop to obtain pH of 8-9.

The mixed solution was simultaneously heated at 80 ˚C for 180 – 240 min such that formation of wet gel takes place. This wet gel was heated to the 100 – 120 °C temperature to activate combustion. Then, the gel was combusted violently and a large amount of gas was released leads to the formation of ferrite loose powder. The powder was sintered at 800 ˚C for 3.0 h and allowed to slowly cooled down and the powder was ground uniformly in a mortar to obtain the final product. The prepared samples were used for characterization and research. Flow charts of nano ferrite particles prepared by sol-gel auto combustion method with citric acid as complexing agent is shown in (fig 2.)

## RESULTS AND DISCUSSION

### *X-Ray Diffraction (XRD) characterization*

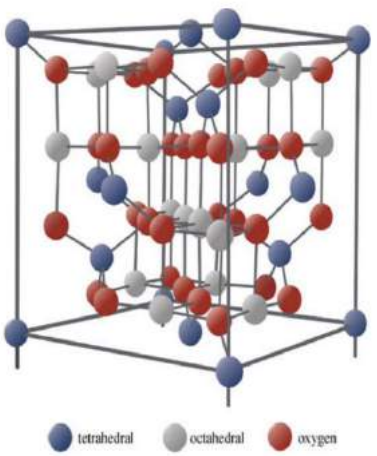
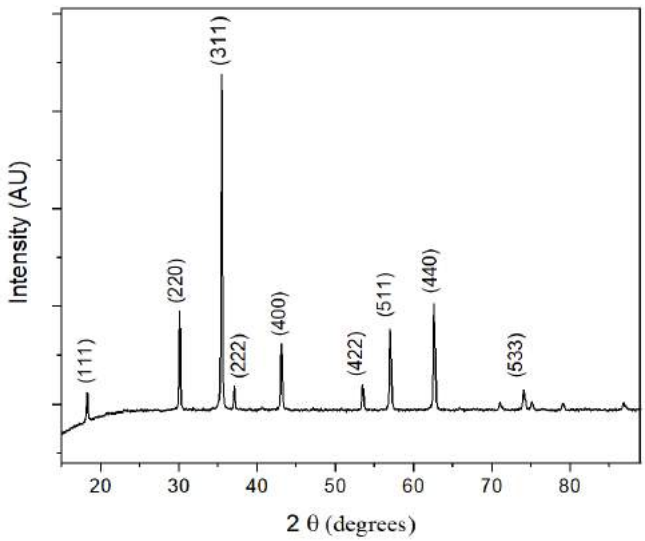



Fig. 1 Schematic representation of spinel




In order to identify the crystal phase formation synthesized materials, utilized X-ray diffraction (XRD) pattern recorded on an X-ray diffractometer Cu (Kα) radiation (λ = 1.5404 Å). The observed XRD pattern well matched with the cubic spinel structure. All the observed XRD peaks positions well matched with the standard patterns of cubic spinel ferrite. The most intense peak (311) observed in 35.45° indicating the synthesized material having high order of crystallinity (fig. 3). The other observed peaks and their peak positions with lattice planes are 18.31° (111), 30.12° (220), 37.11° (222), 43.11° (400), 53.48° (422), 57.014° (511) and 62.6° (440). It shows all the observed peaks well matched with the spinel structure and confirmed that the prepared material is pure spinel phase [10].

Parameters including interplanar spacing (d), lattice constant (a), average crystallite size (D), volume of unit cell ($a^3$), prepared samples are obtained from XRD data are shown in Table 1.

The interplanar distance can be calculated by using Bragg's equation from the relation [11]:

$$n\lambda = 2d\ sin\theta. \quad (1)$$

By using the relationship between cubic lattice constant is determined [12]:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (2)$$

The average crystallite size is calculated using the Scherrer formula [13]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (3)$$

Where, the *'d'* is the distance between the plane, (*h k l*) is the miller indices. *'D'* is the average grain size, *'β'* is the measurement of highest intensity sample diffraction peak (311) half-width (FWHM), 'θ' is the diffraction angle of, 'λ' is the X-ray wavelength (1.5404 Å), the results are also listed in Table 1.

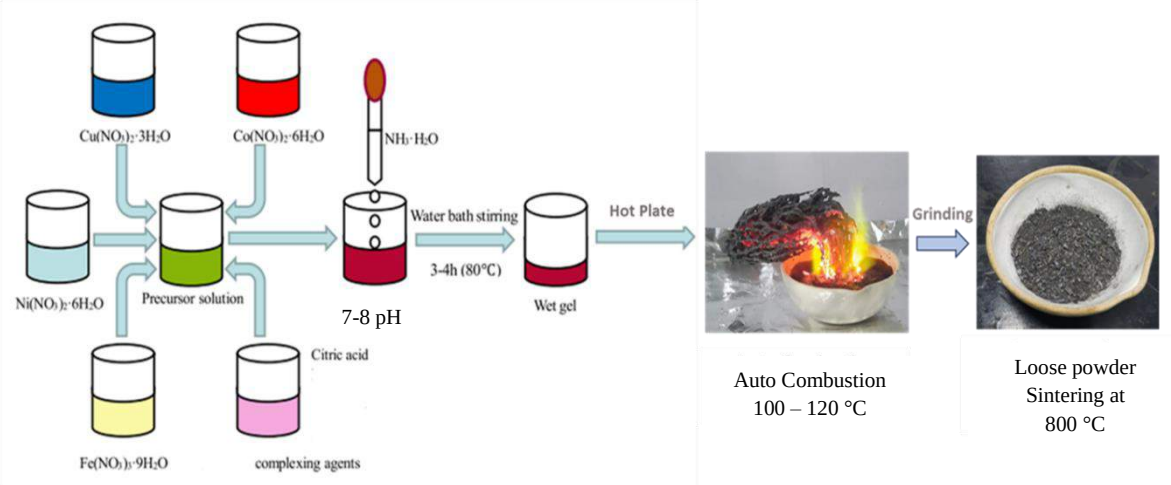



Fig. 2. Flow chart for the synthesis of $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \le x \le 0.5$) nano ferrite particles prepared by sol–gel auto combustion method.

**Table 1:** Parameters obtained from XRD data for $Cu_{0.4}Ni_{0.1}Co_{0.5}Fe_2O_4$ nano ferrite particles.

| Inter planar spacing 'd' (Å) | Sintering Temperature ($^0$) | Lattice constant a (˚A) | Average crystallite size 'D'(nm) | Volume of unit cell 'a3' (Å3) |
|---|---|---|---|---|
| 2.022 | 800 | 9.329 | 39.85 | 811.90 |

The distance between magnetic ions (hopping length) in A-site (tetrahedral) and B-site (octahedral) were calculated using the Stanley's equation [14]:

$$L_A = \frac{a\sqrt{3}}{4} \qquad L_B = \frac{a\sqrt{2}}{4} \qquad (4)$$

The '$L_A$' is tetrahedral hopping length, the position of '$L_B$' octahedral hopping length, 'a' is the lattice constant. The calculated value of different composition of $L_A$ and $L_B$ listed in Table 2.

The microstrain of the CNCoF ferrites was calculated by the Williamson-Hall plot for degree of lattice distortion by following formulas.

$$\beta_{Toal} = \beta_{Sample} + \beta_{Instrument} \qquad (5)$$

Broadening caused by crystallite can be calculated by modified Scherrer equation:

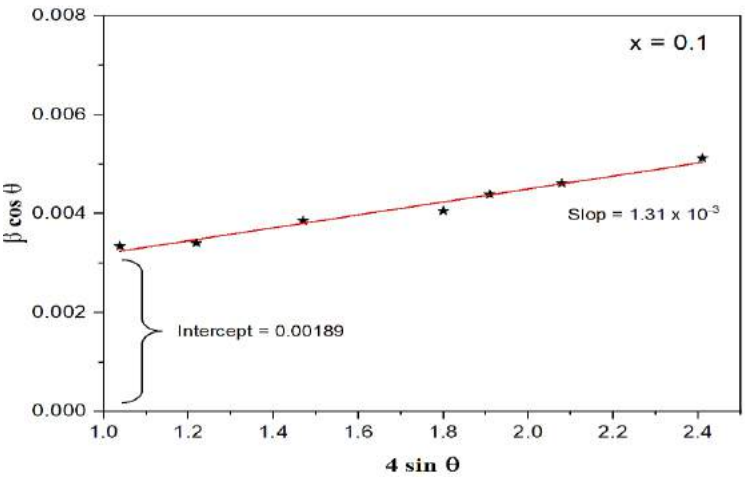



Fig. 4 Williamson–Hall Plot of $Cu_{0.4}Ni_{0.1}Co_{0.5}Fe_2O_4$ ferrite nanoparticles.

$$\beta = \frac{0.9\,\lambda}{D\cos\theta} \quad (6)$$

Broadening caused by microstrain can be calculated by [15]:

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad \text{i.e.,} \quad \beta = \varepsilon\,(4\sin\theta) \quad (7)$$

putting eq (6) and eq (7) to get modified formula,

$$\beta_{Total}\,x\cos\theta = \varepsilon\,(4\sin\theta) + \frac{0.9\,\lambda}{D} \quad (8)$$

β is the total broadening due to strain and size in a particular peak. Fig. 4 show the β cos θ vs. 4 sin θ graph. The slope and y-intercept have been noted from the linear fitted curve, which gives the ε and D of the samples. Where 'ε' is microstrain calculated.

**Table 2**

Various structural parameters of $Cu_{0.4}Ni_{0.1}Co_{0.5}Fe_2O_4$ nano ferrite particles. Crystallite size (D) and strain (ε) estimated by different methods.

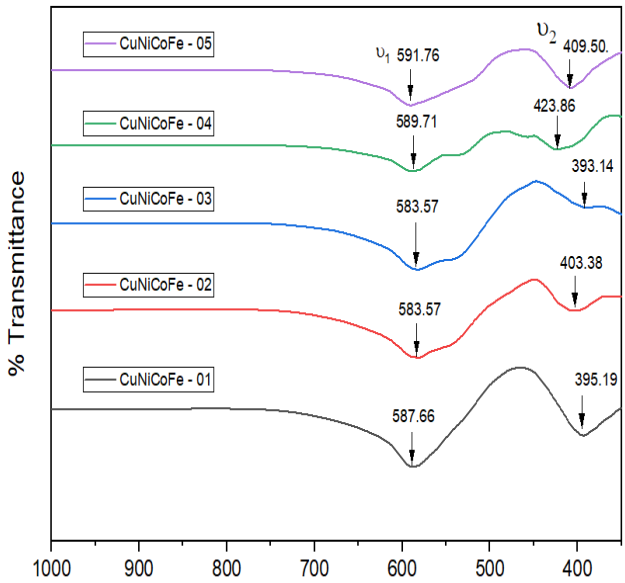
| Molecular weight 'M' (g/mol) | Hopping length | | Crystallite size (D) and strain (ε) | | |
|---|---|---|---|---|---|
| | Tetrahedral site '$L_A$'(Å) | Octahedral site '$L_B$'(Å) | Scherrer method (nm) | Williamson–Hall Method | |
| | | | | D (nm) | ε x $10^{-3}$ |
| 236.07 | 4.040 | 3.298 | 39.85 | 78.24 | 1.31 |

***Fourier Transform Infra-Red Spectroscopy (FT-IR) characterization:*** Figure 5 shows FTIR spectra of copper–nickel –cobalt mixed nanoferrite after sintering at 800 $^0$C. The positions of two strong bands $\upsilon_1$ and $\upsilon_2$ about 570 $cm^{-1}$ and 400 $cm^{-1}$ are related to spinel cubic structure [16]. This was due to the tetrahedral and octahedral complexes, which exhibit $\upsilon_1$ and $\upsilon_2$ absorption bands. High wave number around ($\upsilon_1$ = 580-594 $cm^{-1}$) and low wave number around ($\upsilon_2$ = 390-410 $cm^{-1}$) are designated as tetrahedral complexes ($M_{tetra}$-O) and octahedral complexes ($M_{octa}$-O), respectively [17]. The figure shows a characteristic peak ($\upsilon_1$) at near 585 $cm^{-1}$ for $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$. Therefore, from the FTIR measurements confirmed the formation of the spinel structure sample. The change of absorption peaks $\upsilon_1$ can also be interpreted as the bond-strength and the bond-energy are increased due to the formation of a new chemical bond with $O^{2-}$.

| Sample | $\upsilon_1$ $cm^{-1}$ | $\upsilon_2$ $cm^{-1}$ |
|---|---|---|
| $Cu_{0.5}$ $Ni_{0.0}$ $Co_{0.5}$ $Fe_2O_4$ | 591.76 | 409.50 |
| $Cu_{0.4}$ $Ni_{0.1}$ $Co_{0.5}$ $Fe_2O_5$ | 589.71 | 423.86 |
| $Cu_{0.3}$ $Ni_{0.2}$ $Co_{0.5}$ $Fe_2O_5$ | 583.57 | 393.14 |
| $Cu_{0.2}$ $Ni_{0.3}$ $Co_{0.5}$ $Fe_2O_6$ | 583.57 | 403.38 |
| $Cu_{0.1}$ $Ni_{0.4}$ $Co_{0.5}$ $Fe_2O_6$ | 587.66 | 395.19 |

**Table 3**

Frequency bands $\upsilon_1$ of the samples.




FT-IR spectra of $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \le x \le 0.5$) (CNCoF) ferrite nanoparticles prepared using Cu - Ni

In Table 3, the wave number is used to indicate the position of the absorption band. As can be seen from the table, the position of the tetrahedral band changes as the Concentration of nickel in the structure changes.

## CONCLUSION

The $Cu_{0.5-x}Ni_xCo_{0.5}Fe_2O_4$ ($0.0 \leq x \leq 0.5$) (CNCoF) nano-particles have been prepared successfully by sol-gel auto combustion technology with citric acid as complexing agent. The distinctive cubic spinel structure confirmed through X-ray diffraction (XRD) and their average crystallite size of the sample is 39.85 nm. Fourier transform infrared (FT-IR) spectroscopy has been utilized for confirming the metal-oxygen-metal bonds of the prepared materials.

The meticulous examination of lattice parameters, average crystallite size, hoping lengths, and microstrain offers a comprehensive understanding of the structural dimensions and imperfections within the nanocrystalline CNCoF. The vibrational characteristics revealed by FT-IR spectroscopy, specifically the ' $\upsilon_1$' and ' $\upsilon_2$' absorption bands, confirm the formation of a single-phase cubic spinel structure in the synthesized ferrites.

This study not only advances the understanding of the nanoscale features of Cu-Ni-Co ferrites but also positions CNCoF as a promising material for various applications. The tailored magnetic and electronic properties, coupled with the distinctive structural characteristics, open new avenues for the utilization of CNCoF in magnetic devices, sensors, and photocatalysis, contributing to the evolving landscape of advanced materials in contemporary research and development.

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# Spectral cauterization of $La^{3+}$ doped Ni-Co Ferrite Synthesized by Sol-Gel Auto Combustion Method

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## ABSTRACT

Lanthanum doped nickel-cobalt Nano ferrite with chemical formula $Ni_{0.5}Co_{0.5}La_xFe_{2-X}O_4$(X=0.00,0.025, 0.050,0.075,0.10) was prepared by a simple soi-gel auto combustion method. To observe the transition phase development of the precursor samples, thermo-gravimetric analysis was carried out. The basic structural properties were determined by X-ray diffraction method and the formation of single-phased spinel ferrite was confirmed. FTIR Spectra that contains two absorption bands in the range from 400 to 600cm$^{-1}$ confirms the formation of the spinel structure.

**Keywords:** *Ferrites, sol-gel auto combustion, TGA/DTA, XRD and FT-IR analysis.*

## INTRODUCTION

The spinel ferrite is one of the most important classes of magnetic oxides. They are applied widely as adsorbents, photocatalysts, in biomedical fields, magnetic hyperthermiaetc. The available methods of spinel synthesis are co-precipitation, hydrothermal, sol-gel auto combustion, and microwave methods.

Spinel ferrites have a general formula $MeFe_2O_4$ (where M=Co, Ni) $NiFe_2O_4$ crystallizer within an inverse spinel structure where $Ni^{2+}$ occupy octahedral sites(B) and $Fe^{3}$+ ions are equally distributed between (A) and octahedral(B) sites. $CoFe_2O_4$ and $NiFe_2O_4$ have partially inverse spinel structure. It is important to highlight that both type of structure and the corresponding properties of those spinals could be altered by doping with rare earth ions such as Lanthanum which can displace a part of $Fe^{3}$+ ions in $MeFe_2O_4$ host lattice, thereby resulting in important modifications of structure and magnetic properties of ferrites.

The influence of doping by $La^{3+}$ on the structure and properties of spinel ferrites is of great interest to scientists Albayati *et al*. studied the dielectric properties of $NiLa_xFe_{2-x}O_4$ synthesis using the sol-gel auto-combustion method. It was found that the dielectric constant increases with the increase of La-ion concentration. The effect of $La^{3+}$ doping on the evolution of microstructure complex permeability permittivity and microwave absorption of NiCoFe ferrite prepared by sol-gel method it was found that with the $La^{3+}$ doping the lattice parameters increased gradually alongside a change in particle shape and size.

This study aims to synthesize $Ni_{0.5}Co_{0.5}La_xFe_{2-X}O$ via sol-gel using various fuel, among them citric acidwas used as a reducing agent and fuel in the sol-gelsynthesis forferrites. The structure, morphology, and thermal stability of ferrites were characterized by TGA/DTA, XRD, and FTIR techniques.

## EXPERIMENTAL

The $Ni_{0.5}Co_{0.5}La_xFe_{2-X}O_4$(X=0.00, 0.025, 0.050, 0.075, 0.10) ferrites were prepared by sol-gel auto combustion methods from metal nitrates$(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_2.9H_2O$, $La(NO_3)_2.6H_2O$, $C_6H_8O_7$ and ammonia solution as the starting material. All the materials were of AR grade and used them without further purification. At first the metal nitrates were mixed as per stoichiometric ratio using a sensitive electronic balance having a sensitivity of 0.001 mg and completely dissolved in deionized water of volume 50 ml using a magnetic stirrer. Later citric acid solution in deionized water solution with metal nitrate citric acid molar ratio 1:1 and stirred for 10 min. The main purpose of citric acid is to act as fuel and chelating agent. Here the oxidizers to fuel ratios were fixed

to 1:1 using propellant chemistry, as this ratio provides the maximum energy for the combustion process. Further, the above-mixed solution was stirred continuously for 30 min to obtain a homogenous clear solution using a magnetic stirrer with hot plate slowly increasing the temperature up to $80^0$C. Meanwhile, the 25% $NH_3$ solution was added slowly drop-wise until the pH value of mixed metal nitrates and critic acid solution reaches to 7. Later solution was continuously stirred with a rotation speed 500 r/min [27,33]. A thick sol was formed due to a condensation reaction between the constituent metal nitrates and citrate molecules. The stirring process was continued until the solution completely turned into a gel nearly after 5 hrs. Then the temperature of the hot plate was raised to $110^0$ C. Within a short time, the dried gel gets started burning with flames and finally resulting in the precursor. The product obtained finely ground using agate mortar and pestle to a fine powder. This fine powder socollected readily used for the various characterizations.

The chemical process can be described as follows:

$$0.5Ni(NO_3)_2 + 0.5Co(NO_3)_2 + xLa(NO_3)_3 + (2-x)\ Fe(NO_3)_3 + C_6H_8O_7 \rightarrow Ni_{0.5}Co_{0.5}La_xFe_{2-x}O_4 + 4N_2 + 2nCO_2 + 2nH_2O + nO_2$$

## CHARACTERIZATION TECHNIQUES

Determination calcination temperature of the synthesized samples was decided from simultaneous TG-DTA analyzer, using SDT Q600 V20.9 Build 20, an analyzer in an air atmosphere at a heating rate 10 K/min within a temperature range of 298 to 1100k. The crystal structure was deduced using X-ray diffraction (XRD) method using a diffractometer equipped with Fe $k_\alpha$ radiation. The IR spectra were recorded in the range of 400-800 $cm^{-1}$ on a PerkinElmer infrared spectrometer.

## RESULTS AND DISCUSSION

***Thermogravimetric Analysis:*** The TG-DTA curve of precursor anddecomposition $La^{3+}$ substituted Ni-Co ferrites(X=0.0) precursor as shown in Fig.1. The temperature is around $25^0$C-$110^0$C the first endothermic peak is observed due to the loss of hydrated water molecule 0.7479%. The second exothermic peak located near temperature $110^{0c}$-$250^{0c}$ showed more weight loss of 1.161% can be attributed to the dehydration of coordinated water molecules and metal converted to metal oxide. The third exothermic peak formation of ferrite with liberated of oxygen molecule with loss 0.0821%. No mass loss is observed above 400 K indicates the presence of only $Ni_{0.5}Co_{0.5}La_xFe_{2-X}O_4$ spinel ferrite above this temperature. Therefore, all synthesized precursors were calcinated at 400 K for 4 h.

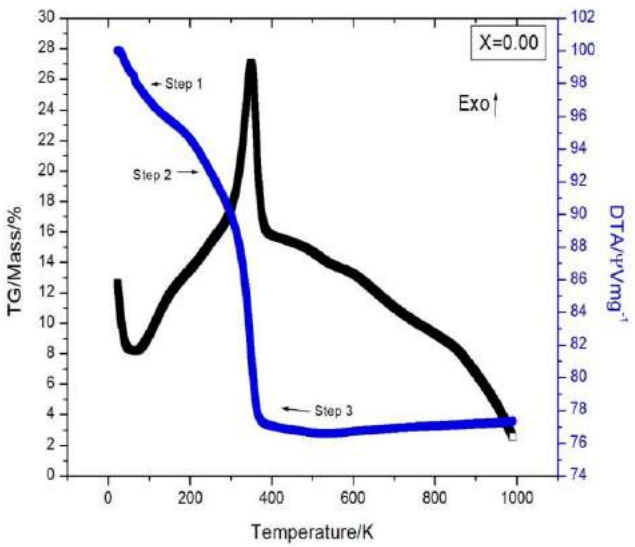


**Fig.1:** TGA-DTA curves of Ni0.5Co0.5Fe2-xLaxO4(X=0.00)

***X-ray Diffraction analysis:*** Fig.2 shows the recorded X-ray diffraction (XRD) patterns of $Ni_{0.5}Co_{0.5}La_xFe_{2-X}O_4$ ferrites synthesis by auto combustion method. The XRD graphs confirms that the prepared ferrites have a single-phased spinel cubic structure with fd-3m space group. Noother extra peaks observed, all these peaks were indexed to (220) (311) (222) (400) (422) (333) and (440) respectively.

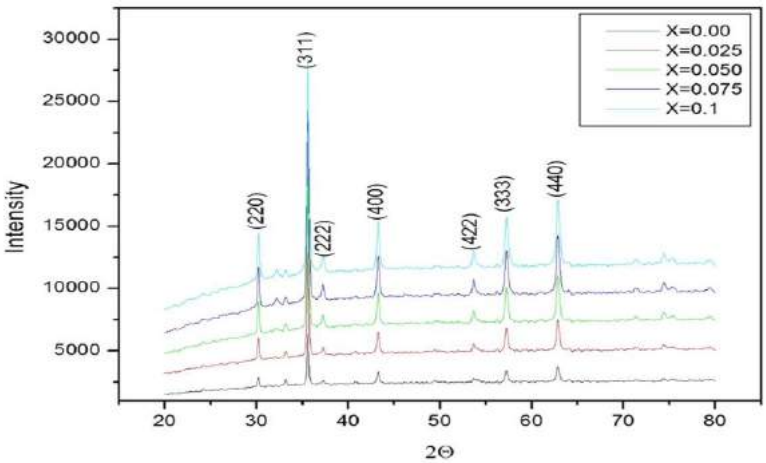


**Fig.2:** XRD patterns of Ni0.5Co0.5Fe2-xLaxO$_4$(X=0.00 -0.1)

Using the XRD data the lattice parameter (a), the interplanar spacing(d), X-ray density(dx), hopping length tetragonal site ($L_A$), and octagonal site ($L_B$) are presented in Table1

The inter-planar distance was calculated using the Bragg law.

$$n\lambda=2d\sin\theta \qquad 1$$

Where n=integer λ=Wavelength of X-ray radiation d=inter planar spacing θ=glancing angle.

The Lattice parameter or lattice constant (a=b=c) is measured using Bragg's equation for all LCF samples by the maximum intense peak(311)

$$a = d\sqrt{h^2 + k^2 + l^2} \qquad 2$$

A=Lattice parameter hkl=miller indices.

The X-ray densities (dx) of all the sample are determined by the following equation.

$$d_X = \frac{8M}{N_A a^3} \qquad 3$$

Where '8' is the number of molecules per unit cell 'M' is the molecular weight of the sample, 'N' is Avogadro's number, and 'a' is the lattice constant.

Hopping Lengths of all the samples are determined by the following equation.

$$L_A = \frac{a\sqrt{3}}{4} \; L_B = \frac{a\sqrt{2}}{4} \qquad 4$$

**Table 1:** Lattice parameter (a), X-ray density ($d_X$), and hopping lengths ($L_A$ and $L_B$) of the series Ni0.5Co0.5Fe2-xLaxO4

| 'X' | 'a' (A) | 'dx' (gm/cc) | '$L_A$' ($A^0$) | '$L_B$" ($A^0$) |
|---|---|---|---|---|
| 0.00 | 8.1134 | 5.27 | 3.6334 | 2.9667 |
| 0.025 | 8.4646 | 5.32 | 3.6328 | 2.9662 |
| 0.050 | 8.4628 | 5.36 | 3.6343 | 2.9674 |
| 0.075 | 8.4621 | 5.48 | 3.6183 | 2.9543 |
| 0.10 | 8.2802 | 5.54 | 3.6158 | 2.9523 |

## CONCLUSIONS

Nickel-Cobalt ferrites doped with small amount of La were prepared by the sol-gel auto combustion method. TGA/DTA analysis shows total mass loss around 30% up to 400 K temperature

The precursors were calcinated at 400 K for 4 h. The XRD pattern clearly indicates the ferrites formed after sintering are belong to single –phase cubic spinel structure.

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# Synthesis and Characterization of Novel ThiazoloPyrimidin-3-ones derived from Benzofuran Pharmacophore

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**ABSTRACT**

*A series of α,β unsaturated ketones (Chalcones) were synthesized by condensation of acetyl-benzofurans and thiophene carbaldehydes in presence of base. These Chalcones further on reaction with thiourea affords thiopyrimidines having benzofuran Pharmacophore. These thiopyrimidines on cyclization with chloroacetic acid yields thiazolo pyrimidin-3-one derivatives. The newly synthesized compounds were characterized using the well-known spectroscopic tools (IR, [1]HNMR, and mass spectroscopy).*

***Keywords:*** *Benzofuran Chalcones, thiopyrimidines, thiazolopyrimidines, thiazolidinone*

## INTRODUCTION

Chalcone is a class of compounds, which has many applications in different fields.α, β-unsaturated carbonyls used as key intermediates for the preparation of number of heterocyclic compounds such as thiazine, oxazines, isoxazoles and pyrazoles. Chalcones can be used as an initial compound for synthesis of lots of compounds[1]. Benzofuran and its derivatives are present as scaffolds in many natural products and biologically active compounds.[2-3] These compounds have attracted much attention in the pharmaceutical and pesticide industries because of their promising antibacterial, antimicrobial, antitumor, and antidiabetic activities.[3,5] Hence, the synthesis of benzofurans has aroused considerable interest and various methodologies have been reported and applied for the synthesis of natural products.[4] Benzofuran derivatives has been used as a dynamic intermediate for the synthesis of variety of value-added heterocyclic compounds. [6-8]

Many benzo[b] furan derivatives are known to exhibit a broad range of biological activities including antiproliferative[9],antiinflammatory[10],antiiral[11],antifungal[12],immunosuppressive[13], antiplatelet[14], antioxidative[15], antifeedant[16] and insecticidal[17] activities[18]. Several thiazolidinedione derivatives of benzofuran pharmacophores showed most potent and efficacious compound as Antidiuretic and Hypolipidemic agents. Anticervical cancer activity of new benzofuran-pyrazol-hydrazono- thiazolidin-4-one has been reported by Hebat-Allah S.et.al. [19]

Various Bis(benzofuran–thiazolidinone)s and bis(benzofuran–thiazinanone)s derivatives as inhibiting agents for chikungunya virus has been reported.[20]

In addition, several reports have pointed out the value of some synthetic benzofuran derivatives having thiazolidinone moiety as antitumor agents[21], recently, using a simple procedure with high yield some new molecules have been developed[22,23]. In the process of new drug discovery, the anticancer and antimicrobial activities of a variety of benzofuran derivatives have been reported. [24,25] In this study, we aimed at designing and synthesizing new compounds with both benzofuran and chalcone units in one molecule, these Chalcones on reaction with thiourea affords thiopyrimidines this on cyclization with chloroacetic acid yields thiazolo pyrimidin-3-one derivatives. Therefore, molecular combinations of the benzofuran system with ThiazoloPyrimidin-3-ones were included in this work.

## MATERIAL AND METHODS

Reagents and solvents were used as obtained from the supplier without further purification. All melting points reported are uncorrected and were determined on a Stuart electric melting point apparatus. TLC was performed on Merk TLC aluminium sheets silica gel. Column chromatography was performed on silica gel 90,200–300 mesh and then used for spectral analysis. IR spectra (in KBr, cm-1) were recorded on Shimadzu spectrophotometer in the range of 400-4000 $cm^{-1}$.$^1$H-NMR spectra were recorded on a Varian 300 MHz with deuterated solvent ($CDCl_3$). Tetramethylsilane (TMS) was used as an internal standard with chemical shifts δ in ppm. LC-MS were obtained using QP 2010 mass spectrometer using EIMS techniques at 70eV.

**Experimental: A) Typical experimental procedure for synthesis of (E)-1-(5-substituted benzofuran-2-yl)-3-(5-substituted thiophen-2-yl) prop-2-en-1-one. Scheme-I(3a-d).**

Flask was charged with mixture 2-acetyl 5-substituted benzofuran (I) (0.011 mole) and 5-substtuted thiophene carbaldehydes (II) (0.011 mole). It was stirred in ethanol (25 mL) and then potassium hydroxide (50%) (10 ml) was added portion wise, keeping the temperature below the $10^0$C throughout the Addition. The mixture was kept for 24 hrs at room temp., after completion of reaction was checked by TLC.(Hexane/Ethyl acetate 7:3). Reaction mixture was poured into crushed ice and the solid obtained was filtered under vacuum. It was washed firstly with sodium carbonate solution and then with water, dried and the product was recrystallized from ethanol to afford the pure product in 72-78 % yield (3a-d). Same procedure is extended for other compounds of this series. Characterization data of synthesized compounds were illustrated in Table-1.

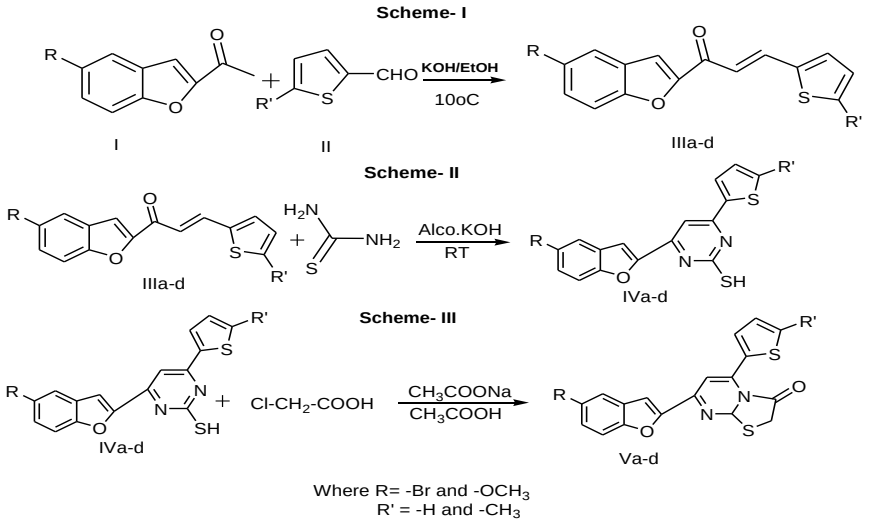
**B) Typical experimental procedure for synthesis of 4-(5-substituted benzofuran-2-yl)-6-(5-substituted thiophen-2-yl) pyrimidine-2-thiol Scheme-II (4a-d).**

Benzofuran chalcones (2 mmol) (3a-d) were condensed with thiourea (2 mmol) in alcoholic KOH in a round bottom flask and the reaction mixture was continuously stirred for about 5-6 hr at room temperature. The progress of the reaction was monitored by TLC. (Hexane/ Ethyl acetate 8:2) and spots were observed by iodine vapor and/or UV light. After completion of reaction, the reaction mixture was cooled, poured into crushed ice with constant stirring and neutralized using 10% $NaHCO_3$.The precipitated product was filtered, dried and recrystallized using ethanol.(4a-d) Yield 62-67 % Same procedure is extended for other compounds of this series. Characterization data of synthesized compounds were illustrated in Table-1.

C) **Typical experimental procedure for synthesis of 7-(5-substituted benzofuran-2-yl)-5-(5-substituted thiophen-2-yl)-2H-thiazolo[3,2-a]pyrimidin-3(8aH)-one. Scheme-III (5a-d).**

A mixture of pyrimidine-2-thiol (4a-d) and monochloro acetic acid was taken in 1:1 molar ratio and dissolved in glacial acetic acid. The sodium acetate (about 1 gm) was added in reaction mixture. The reaction mixture was refluxed for about 3.5 hr. The progress of reaction was monitored by TLC.(Hexane/Ethyl acetate 7:3).On cooling the content was poured on ice, solid obtains was filtered and dried. Product was purified by recrystallization in aqueous acetic acid. (5a-d) Yield 59-62%, same procedure is extended for other compounds of this series. Characterization data of synthesized compounds were illustrated in Table-1.

## REACTION SCHEME:



## RESULTS AND DISCUSSION

**A) Spectral discussion:**

**1) (E)-1-(5-bromobenzofuran-2-yl)-3-(5-methylthiophen-2-yl) prop-2-en-1-one (3b)**

Yield 66 %, Brownish solid (EtOH), M.P. 192°C;

**IR (KBr, *v* cm$^{-1}$):** 3056 cm$^{-1}$ (-CH str. of. Ar), 1648 cm$^{-1}$(C=O str.in ketone), 1589 cm$^{-1}$(C=C str.) 1518 cm$^{-1}$ (C=C str. in Ar), 1134 and 1156 cm$^{-1}$ (C-O-C str) 838 cm$^{-1}$(-CH str.) 744cm-$^{1}$(Ar-H-opb).

**$^{1}$H NMR ($CDCl_3$ in δ ppm):** 2.32 (s, 3H, 5-methyl protons on thiophene ring), 6.86-7.22 (dd, 2H, Ar-protons of thiophene), 6.61 (d,1H,Trans proton of alkene-CH=CH, J= 16.2Hz),7.61 (d,1H, Trans proton of alkene -CH=CH-,J=16.4Hz) 7.21-7.65 (Complex multiplet,3H, benzofuran protons), 7.38 (singlet, 1H, aromatic proton of Furan ring)

**Mass (m/z):**345.54[M]$^{+}$

**2) 4-(5-methoxybenzofuran-2-yl)-6-(thiophen-2-yl) pyrimidine-2-thiol (4c)**

Yield 66 %, faint brown solid (EtOH), M.P. 186°C;

**IR (KBr, *v*cm$^{-1}$):** 2508 cm$^{-1}$ (-SH str.), 1633 cm$^{-1}$(C=N str.in pyrimidine), 1528 cm$^{-1}$ (C=C str. in Ar), 1105 and 1122 cm$^{-1}$ (C-O-C str.), 828 cm$^{-1}$(-CH str.), 721 cm$^{-1}$(Ar-H-opb).

**$^{1}$H NMR ($CDCl_3$ in δ ppm):**

3.68(s, 3H, 5-methoxy protons C-5 on benzofuran ring),7.09-7.21 (dd,3H,thiophene-H), 8.76 (s, 1H, pyrimidine),10.11(s,1H,SH proton),7.28-7.69 (Complex multiplet,3H, benzofuran protons), 7.11 (singlet, 1H, Aromatic proton of Furan ring).

**Mass (m/z):**340.45[M]$^{+}$

**3)7-(5-bromobenzofuran-2-yl)-5-(thiophen-2-yl)-2H-thiazolo[3,2-a]pyrimidin-3(8aH)-one (5a)**

Yield 61 %, brown solid (EtOH), M.P. 179°C;

**IR (KBr, *v* cm$^{-1}$):** 1748 (C=O in thiazolidinone), 1602 cm$^{-1}$(C=N str.in pyrimidine), 1604 cm$^{-1}$ (C=C str. in Ar), 1105 and 1122 cm$^{-1}$ (C-O-C str.), 828 cm$^{-1}$(-CH str.), 721 cm$^{-1}$(Ar-H-opb).2966 and 2836 cm$^{-1}$ C-H str.in -$CH_2$)

**$^{1}$H NMR ($CDCl_3$ in δ ppm):**

3.18(s, 2H, -$CH_2$ in thiazolidinone), 7.12-7.33 (dd,3H,thiophene-H), 8.34 (s,1H, pyrimidine), 7.18-7.67 (Complex multiplet,3H, benzofuran protons), 7.02 (singlet, 1H, aromatic proton of Furan ring).

**Mass (m/z):**429.21[M]$^{+}$

**B) Experimental analysis:**

Synthesis of the various pyrimidin-3(8aH)-one derivatives were achieved according to the reactions illustrated in the Scheme. Physical and analytical data of all synthesized derivatives are tabulated in table-I.

Chalcone intermediates were obtained by Aldol condensation of corresponding 2-acetyl -5 substituted benzofuran (I) with different substituted thiophene carbaldehydes (II) according to the reported procedure (26).The condensed heterocyclic compounds 4-(5-substituted benzofuran-2-yl)-6-(5-substituted thiophen-2-yl) pyrimidine-2-thiol (4a-d) were synthesized by treating (E)-1-(5-substituted benzofuran-2-yl)-3-(5-substituted thiophen-2-yl)prop-2-en-1-one(3a-d)with thiourea respectively in ethanoic KOH. These compounds (4a-d) on treatment with chloroacetic acid and sodium acetate in acetic acid as solvent affords 7-(5-substituted benzofuran-2-yl)-5-(5-substituted thiophen-2-yl)-2H-thiazolo[3,2-a]pyrimidin-3(8aH)-ones(5a-d). The structures of all synthesized compounds were confirmed using IR, NMR and Mass spectral data. The IR spectrum of compounds 3a-d exhibited a broad absorption band at 1648-1665 cm$^{-1}$which confirms the presence of ketone group attached to α,β unsaturated linkage. Lowering of frequency of ketone attributed to conjugation to ketone group. In 1H NMR a characteristics band at δ ppm 6.61 and 7.61 indicates the presence of –CH=CH- in α,β unsaturated ketone with trans coupling/configuration with J=16 Hz. This indicates the formation of chalcones in all derivatives. In IR spectrum of compounds 4a-d exhibited a broad absorption band at 2508-2530 cm$^{-1}$and 1633-1645 cm$^{-1}$ proves us the presence of S-H and C=N in discussed molecules. $^{1}$H NMR of these molecules resonates at δ ppm 8.55-8.76 due to presence of aromatic proton in pyrimidine ring. S-H proton shows downfield at δ ppm 10.11 due to more electronegativity of sulphur (deshielding effect). Compounds of series 5a-d shows IR peaks in the region of 1712-1768 cm$^{-1}$ which suggests presence of C=O stretching vibrations in thiazolidinones. The increase in IR stretching frequency of –C=O indicates presence of ring strain in thiazolidinone. Another IR characteristics band observed at 1585-1622 cm$^{-1}$ confirms the existence of -C=N in pyrimidine ring. The $^{1}$HNMR spectrum of compound 5a-d registered a broad singlet at δ3.18-3.25 ppm due to -$CH_2$- protons in thiazolidinone ring. The presence of aromatic proton Ar-H in pyrimidine ring has been exhibited by obtaining singlet at 8.14-

8.46 ppm.The physical and analytical data of the newly synthesized compounds (3a-d), (4a-d) and (5a-d) are tabulated in Table-I

**Table-I**
**Characterization data of synthesized compounds**

| Compound | R | R' | Yield % | Molecular weight |
|---|---|---|---|---|
| 3a | Br | H | 78 | $C_{15}H_9BrO_2S$ |
| 3b | Br | $CH_3$ | 76 | $C_{16}H_{11}BrO_2S$ |
| 3c | $OCH_3$ | H | 72 | $C_{16}H_{12}O_3S$ |
| 3d | $OCH_3$ | $CH_3$ | 74 | $C_{17}H_{14}O_3S$ |
| 4a | Br | H | 63 | $C_{16}H_9BrN_2OS_2$ |
| 4b | Br | $CH_3$ | 67 | $C_{17}H_{11}BrN_2OS_2$ |
| 4c | $OCH_3$ | H | 62 | $C_{17}H_{12}N_2O_2S_2$ |
| 4d | $OCH_3$ | $CH_3$ | 66 | $C_{18}H_{14}N_2O_2S_2$ |
| 5a | Br | H | 59 | $C_{18}H_{11}BrN_2O_2S_2$ |
| 5b | Br | $CH_3$ | 60 | $C_{19}H_{13}BrN_2O_2S_2$ |
| 5c | $OCH_3$ | H | 62 | $C_{19}H_{14}N_2O_3S_2$ |
| 5d | $OCH_3$ | $CH_3$ | 61 | $C_{20}H_{16}N_2O_3S_2$ |

## CONCLUSION

A novel heterocycles containing chalcones, pyrimidine-2-thiol and pyrimidin-3 (8aH)-one having benzofuran moieties has been synthesized. The procedure used was simple and the yield obtained was good to high. IR, $^1$H Nuclear magnetic resonance and mass were used to establish the structure of the newly synthesized heterocycles. We hope that these synthesized derivatives bearing benzofuran pharmacophore will enhance the various biological activity due to varying substituents on benzofuran scaffolds and may be useful in the future for drug development.

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# Oxidant effect on the electrical properties of the polypyrrole synthesised via chemical oxidation method

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**ABSTRACT**

A new era of the novel materials boosts the technological advancement. The diverse types of materials show their own utility according to their exceptional properties. Among the various types of materials conducting polymers gained enthusiastic attention due to the excellent properties especially electrical. As considering the importance of the conducting polymers we reported the synthesis of polypyrrole and study the effect of oxidant on electrical properties. Polypyrrole was synthesised via simple and cost-effective chemical oxidation technique. In short, a fix amount of monomer was taken and different monomer to oxidant ratio (0.75, 1.00) in hydrochloric acid aqueous solution was used. As synthesised polypyrrole further studied by means of XRD and FESEM to explored the structural and morphological properties. The study of electrical properties reveals when the amount of oxidant increases the electrical conductivity decreased considerably.

***Keywords:*** *Polypyrrole XRD, FESEM, Electrical Conductivity*

## INTRODUCTION

Conducting polymers (CPs) are the special class of organic polymers which have the conductivity comparable with metals. Form the last decades CPs gained exponential interest in research community due to its excellent physicochemical and electrooptic properties. Owing to the exceptional properties CPs can be employed for the various technological applications. The different cost-effective and environment friendly synthesis techniques are available for tuned the properties of CPs as per our expectations [1]. Among the various types of CPs, polyaniline (PANI) and polypyrrole (PPY) are the interesting and most studied CPs. Due to the exclusive properties of the PANI and PPY it can be applicable into the fields such as sensors, biosensors, electrochemical devices, anticorrosion coating, optoelectrical devices and solar cells etc [2,3].

For the synthesis of the CPs mostly electrochemical and chemical oxidation are used which provide the desired structural and morphological properties [4]. In chemical oxidative polymerization technique, the properties of CPs can be modify using reacting temperature, reacting time, stirring rate, dopant or oxidant nature and concentration, oxidant/monomer mole ratio (O/M), and electrolyte etc. Especially, the electrical conductivity is the most important parameters and it can be enhanced by changing oxidant/monomer mole ratio (O/M) [5].

In present study we have been reported the synthesis of PPY using the chemical oxidative polymerization technique with different oxidant/monomer mole ratio (O/M). As prepared samples characterised via XRD and FESEM to explored the structural and morphological properties. Along with the main to study the effect on electrical conductivity corresponding to different oxidant/monomer mole ratio (O/M).

## MATERIALS AND METHODS

Pyrrole (monomer) and ammonium peroxydisulfate (Oxidant) used as the leading chemical which was procured from Loba chem, India. Before used pyrrole was distilled under reduced pressure condition. Sulphuric acid ($H_2SO_4$) purchased from molychem, India and all the synthesis process carried out using double distilled water which was produced in laboratory. As synthesised samples

characterised via XRD using a Bruker AXS (D8Advance, Germany) diffractometer and FESEM using (JEOL JSM-6360, USA). Electrical conductivity measured using four probe technique.

## SYNTHESIS OF PPY

Two samples of polypyrrole were synthesised with oxidant/monomer ratio of 0.75 and 1. In short, pyrrole with prescribe concentration was prepared in 1.0 mol/L $H_2SO_4$ and precooled ammonium peroxydisulfate was added to the above mixture drop by drop. The temperature 0-4 $^0$C was maintained during stirring process and after 4 hours of stirring the PPY were collected on a filter and washed with distilled water. Then the acquired product was dried for 80$^0$ in oven.

## RESULT AND DISCUSSION

***XRD AND SEM ANALYSIS:*** Fig. 1 shows the XRD pattern of PPY samples and it revels a broad peak at about 2θ = 24$^0$, which confirmed the amorphous nature of PPY. The structural behaviour of PPY in amorphous nature exhibited due to the low degree of molecular ordering which assigned to the repeated units of pyrrole ring [6]. In both the samples there is no any considerable difference observed, but when the oxidant/monomer ratio increased slight shifting in the broad peak observed.

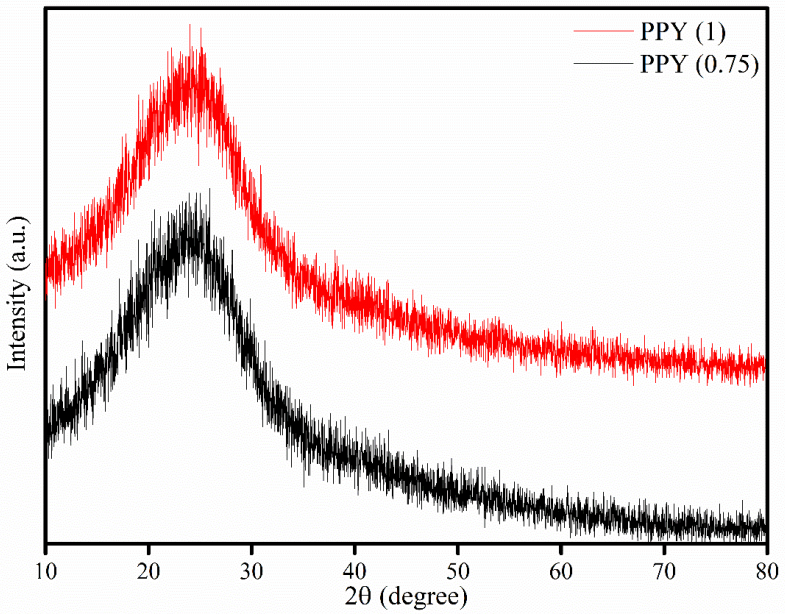


**Fig.1:** XRD spectrum of PPY with different oxidant/monomer ratio

Fig. 2 shows the morphological behaviour of PPY samples which was studied via scanning electron microscopy (SEM). The small ratio of oxidant/monomer (fig. 2(a)) shows the rough aggregated crystal-like morphology it may be due to some chains are unbound with monomer [7]. Whereas when increased the ration of oxidant/ monomer (fig. 2(b)) shows the purely amorphous behaviour due to ordered chains.

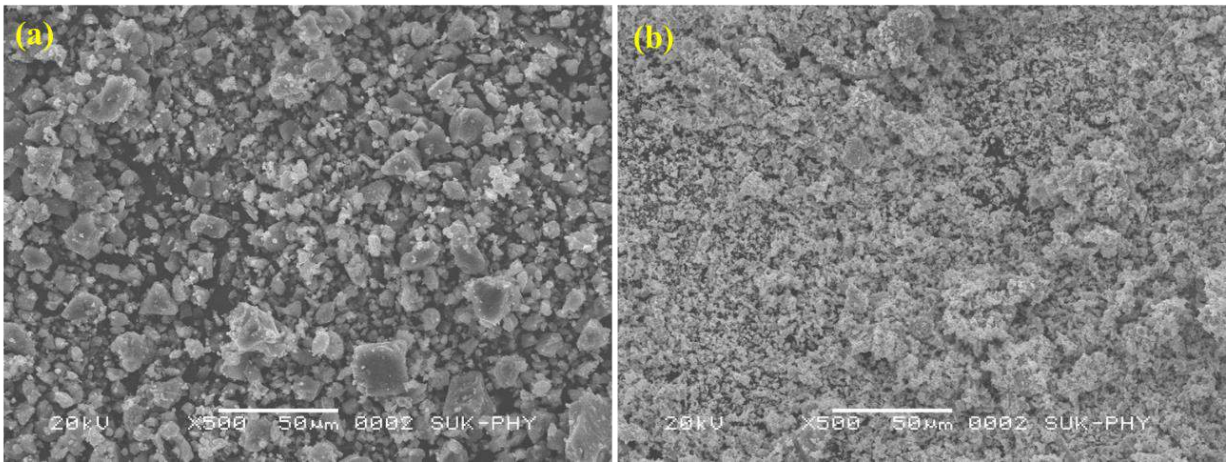


**Fig.2:** SEM micrograph of PPY samples

***ELECTRICAL CONDUCTIVITY (DC):*** Electrical conductivity of the prepared PPY samples were studied via four probe method. The electrical conductivity of the both samples shows considerable compared to the semiconductor. Electrical conductivity of the PPY sample with lower O/M ratio shows sample shows higher than the properties of the sample show 8.2 S/cm, whereas at higher ratio it decreased and show 7.2 S/cm. the electrical conductivity may be decreased due to the ordered chain formation in higher ration of oxidant/monomer ratio.

## CONCLUSIONS

PPY samples with different oxidant/monomer ratio have successfully prepared using chemical oxidative polymerization technique. The structural and morphological properties of the prepared samples confirmed by means of XRD and SEM analysis. The XRD study exhibited the amorphous nature of the prepared samples and which good agreement with the SEM micrograph. The electrical conductivity of the lower oxidant/monomer ration shows higher than when oxidant/monomer ratio increased.

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# The study of Polyethylene terephthalate (PET) irradiated with low-energy $N^+$ ions.

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## ABSTRACT

Polyethylene terephthalate (PET) films were irradiated with $N^+$ ions at low energies ranging from 10keV to 25keV with a constant fluence of 1.98 x $10^{16}$ ions/$cm^2$. The pristine and irradiated films were then characterized using X-ray diffractometer (XRD), Ultra Violet Visible (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopy. The XRD studies and calculations of crystallanity, crystallite sizes, micro-strains and dislocation densities reveal the modifications in the chemical structure and the irradiated polymer surface. It was observed from UV absorbance spectrum that the optical band gap energy decreased significantly from 3.2 eV to 1.51 eV while Urbach energy was increased confirming the creation of disorder produced in the surface of PET due to irradiation. The analysis of FTIR spectra revealed the deviations in the intensities associated with the peaks of C-O, C-H, C=C and C=O bonds. These variations correspond to the molecular bond cross linking and the polymeric chain scissoning in the case of PET.

***Keywords:*** Ion irradiation, PET, Cross-linking, chain scissoning, surface modification.

## INTRODUCTION

Polymer ion-irradiation has attracted researchers recently to achieve desired surface modifications for applications such as in medical implants, microelectronics, optical sensors, automotive industries and many more. Polyethylene terephthalate (PET), developed in the middle 20th century, is a high performance engineering thermoplastic amorphous material which is a low cost flexible, durable, light in weight, naturally transparent, pliable, non-conducting, high impact resistant and corrosion free material. Due to these robust properties, PET has recently proved its perfect candidature in the fields of optical, electronic, medical and space applications[1-3]. Literature survey shows that various research groups have made attempts to study the various properties of irradiated polymers. Structural, physical and chemical properties of polymers can be altered by various methods and techniques such as heat, laser light and oxygen ion irradiations. Alhaddad O. et.all.[4], have studied structural modifications and electrical properties for GaAs infrared pulsed laser beam irradiation on nanocomposite of polyvinyl alcohol (PVA) and nanosize palladium (Pd). Cheng L. et.all.[5], have studied multilayer boron nitride nanofilm as an effective barrier for atomic oxygen irradiation. Zhang Y, et.all., have worked on the effects of atomic oxygen and ion irradiation degradation on multi-polymers [6]. Some studies were performed on irradiations of polymers with electron, SEM electrons, pulsed and continuous electron beam and proton beams. Appadu S. et.all., studied the effects of Electron Beam Irradiation on the Thermal Properties of Scrap Polytetrafluoroethylene [7]. Havranek V. et.all., studied modification of polymethylmethacrylate due to irradiation of the SEM electron beam [8]. Tyutnev A.P. et.all., did theoretical Analysis of the Radiation-Induced Conductivity in Polymers irradiated with pulsed and continuous electron beams [9]. Allayarov S.R. et.all., studied the influence of accelerated protons on the molecular–topological structure of Polyethylene [10]. Gamma rays irradiation and plasma treatment have also been employed for studying the changing behaviour of polymers on irradiations. Chai L. et.all., worked on the influence of gamma irradiation dose on

tribological property of polytetrafluoroethylene. [11]. Nouh S.A. et.all., did structural and optical studies of gamma-irradiated blended, and polyvinyl alcohol PVA, polyethylene glycol PEG, and lignosulfonate LG thin films. The significant difference in colour of the films was observed [12]. Ismail A. M. et.all., studied the structural and optical characteristics of Li ion-doped PVA/PVP solid polymer electrolytes exposed to Gamma irradiation [13]. Mu H. et.all., studied plasma polymer deposition of SiOx coating formed on polyimide film, and its oxygen erosion resistance. A post plasma processing has ensured the uniformly transparent and even superhydrophylic or superhydrophobic surfaces of polymer [14]. The researchers, such as Thorat A.B. et. all., reported the effects of low energy Ar+ ion irradiation on polycarbonate[15]. Molybdenum trioxide films were irradiated with nitrogen ion with 40 KeV at the ion fluence of 2.16 x $10^{16}$ ions/$cm^2$ for the study of optical device applications [25]. Antimicrobial activity for polymers irradiated with different energies was studied in the case of Fe heavy ions 120 MeV [17]. According to our knowledge, no previous research has been conducted on the low energy Nitrogen ion irradiation on PET with constant fluence. The properties of PET can be further enhanced by ion irradiation lead modifications. Hence the objective of the current study has been to disclose the effect of low energy Nitrogen ion irradiation with constant fluence on the various physical parameters of PET material. The research was motivated by a number of applications where radiation enhanced surface modifications might play an important role for polymers. We chose the low energy 10-25 KeV $N^+$ ions irradiation as there is no thorough study reported at this energy range and fluence of $N^+$ ions.

## METHODOLOGY

***Materials:*** The high purity PET (Sigma Aldrich make) thin sheets of 1 mm thickness was considered for irradiation purpose. The sheet was cut in a size having surface area of 10mm x 10mm. Four such selected samples were made dust free using distilled water and methanol. They were then placed in the experimental chamber for irradiation.

***$N^+$ Ion source for irradiation:*** The ion beam irradiation facility (indigenously developed at Department of Physics, Savitribai Phule Pune University). Experimental setup for ion irradiation consists of a Vacuum system, experimental chamber, PIG gaseous ion source, linear acceleration tube and high voltage power supply. After placing the samples properly in the irradiation compartment it was evacuated at the pressure to 4.2 x $10^{-6}$ torr. Irradiating source consists of $N^+$ ions at low ion energies ranging from 10 keV to 25 keV with the constant ion fluence of 1.98 x $10^{16}$ ions/$cm^2$. N+ ion was chosen to reduce the complications arising due to other ion irradiations. Four samples were irradiated one after the other by manual rotations of $90^0$. The ion fluence was kept constant at the value of 1.98 x $10^{16}$ ions/$cm^2$ throughout the experiment.

***Material characterization:*** The PET films before and after ion irradiations were characterized using different techniques. The analysis of structural property of PET was done with X-ray Diffractometer (BRUKER D-8 ADVANCE) with Cu Kα (λ = 1.54180 Å) radiation. To compute the band gap values and record the absorption spectra UV-Visible-NIR (JASCO, V-670) Spectrophotometer having of 200 nm to 800 nm wavelength ranges was employed. FTIR analysis was done to study the chain scission occurred due to the irradiation process. Monte Carlo simulation studies were carried out using SRIM-2013 programming for the computation of displacement of atoms (DPA) and sputtering yield to support the modifications occurred in the energy gap of PC when exposed to incident low energy $N^+$ ions.

## RESULTS AND DISCUSSION

The analysis on pristine and irradiated PET samples was done to compare and study the changes observed in the XRD, UV-visible and the FTIR measurements. The Monte Carlo simulation Code with SRIM-13.00 Software is used to estimate the DPA and sputtering yield in the material.

***XRD. Analysis:*** An XRD spectrum was used for analysing the structure of PET film and is shown in Fig.1. It shows that the pristine sample exhibits the amorphous phase. But there is a change in the intensity peaks before and after irradiation, being most prominent at 25 keV. The peak was more intense for the pristine and 10 keV to 15 keV irradiated films. The intensity of the peak was dropped for the 20 keV irradiated film due to the decrease in crystallinity. For 25 keV ion irradiation the intensity drop was the largest with slight shift in the peak position suggesting the modifications occurred in the surface of the polymer due to irradiated energy tending towards more disordered state. This may be due to the incoming low-energy $N^+$ ions would have been completely stopped in the samples. Hence the chemical

structure of latent tracks around Bragg peak should be far from that in plateau region. Thus, we are having surface modification because the rear of samples are less affected compared to the front

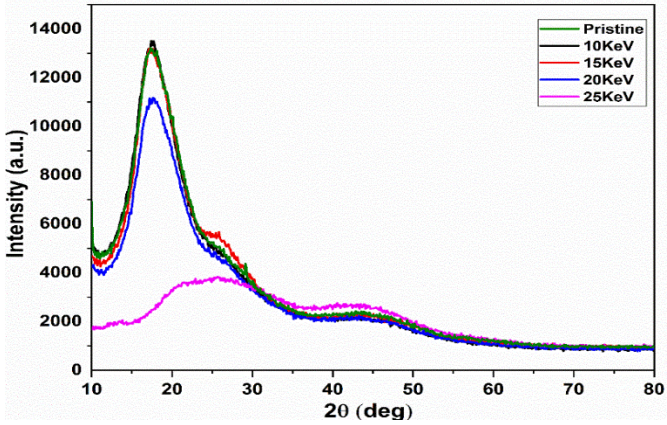


**Fig. 1** X-ray diffraction pattern of PET films for various irradiated energies.

Crystallite sizes were calculated using Scherer's formula [18].

$$D = \frac{0.9\,\lambda}{\beta\, Cos\,\theta}$$

Crystallite sizes slightly increased with increasing irradiation energy from 0 to 10 keV and then decreased for 15 to 25 keV which suggest that due to the shot $N^+$ ions at very high fluence there must have occurred the completely overlapping tracks due to the multi-hits of secondary electrons and the molecular structure of PET is affected. Further the increase in the lattice micro-strains for irradiated samples reveals the modifications in the chemical structure of polymer surface. The crystal lattice at the impinged surface is elastically distorted or strained and such elastic fields causes the broadening of the diffraction peaks as seen in the case of 25 keV irradiation where the micro-strain is found to be maximum while the interplanar spacing is reduced. Micro-strains and dislocation densities were calculated using [18].

$$\eta = \frac{\beta}{4\tan\theta}\ , \quad \delta = \frac{1}{D^2}$$

The calculated experimental values are furnished in table 1.

**Table 1:** crystallite size D, micro-strain η, dislocation density δ and the interplanar spacing d.

| $N^+$ ion Energy (keV) | 2θ (degree) | Crystallite size D (Å) | Micro-strain η | Dislocation density δ ($Å^{-2}$) | Interplanar spacing d (Å) |
|---|---|---|---|---|---|
| Pristine | 17.50 | 7.7073 | 0.2950 | 0.0168 | 4.829 |
| 10 | 17.53 | 7.7287 | 0.2960 | 0.0167 | 4.875 |
| 15 | 17.55 | 7.3625 | 0.3040 | 0.0184 | 4.769 |
| 20 | 17.56 | 7.2381 | 0.3093 | 0.0190 | 4.755 |
| 25 | 25 | 2.5889 | 0.5768 | 0.1492 | 3.176 |

***UV Spectra Analysis:*** UV Visible spectra of 10-25 keV $N^+$ ions irradiated PET films are shown in Fig. 2. It can be detected that the PET has absorption edge at 285 nm. This is corresponding to the transition to higher energy or shorter wavelength indicated by n-π*, and is in good agreement with the previously reported values [18]. For irradiated samples it is observed that, with the increase in $N^+$ ion irradiation energy the absorption band gets red shifted. These effects may be attributed to structural changes or rearrangements including the formation of free radicals and breaking of covalent bonds.

***Energy Band gap calculation of PET:*** The energy for the optical band gap (Eg) is computed with the extrapolation of the linear portion in the graph of the absorption spectra of ($\alpha h^2$) versus photon energy (hυ) [19] as shown in the Fig. 3. Energy gap for the pristine PET is found to be 3.09 eV and it show the decrease (table 1) from 1.71 eV to 1.52 eV as the irradiated energy is incremented above 10 KeV up to 25 KeV respectively keeping the ion fluence constant at 1.98 x $10^{16}$ ions/$cm^2$. The band gap energy of a material depends on atomic or molecular structure, bonding type, temperature and doping in the material. As a result of ion irradiation, defects or vacancies are introduced in the material, resulting in bond breaks and thus causes a change in the band gap energy of the material. The decrease in Energy

band gap is attributed to the irradiation effect of the $N^+$ ion beam on PET sheets where free electrons are produced in addition to the free radicals and ions giving rise to the process of cross-linking and chain scissoning.

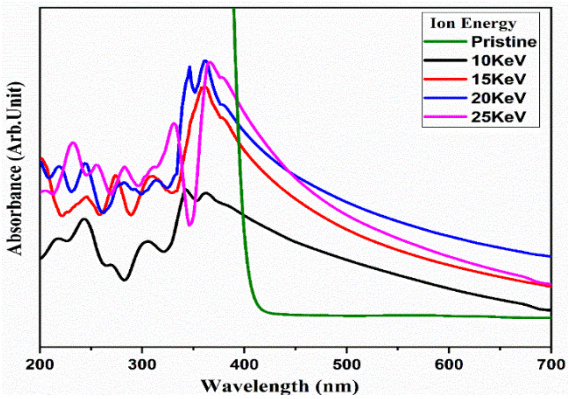


**Fig.2** UV-Vis absorbance Spectra of PET films for various irradiated energies.

This generates the carbon clusters where the number of carbon atoms are calculated using the relation [20].

$$N = \left(\frac{34.3}{Eg}\right)^2$$

The Urbach energy, Eu, which is governed by the structural disorder and passivation at the surface, is calculated from the relation [21]

$$\alpha = \alpha_o \ \exp\left(\frac{h\upsilon - Eg}{Eu}\right)$$

It is seen that as the optical band gap energy decreased significantly from 3.09 eV to 1.52 eV the Urbach energy increased confirming the creation of disorder produced in the surface of PET due to irradiation. The experimental values of Energy gap Eg, Urbach's energy Eu and number of carbon atoms are furnished in table 2.

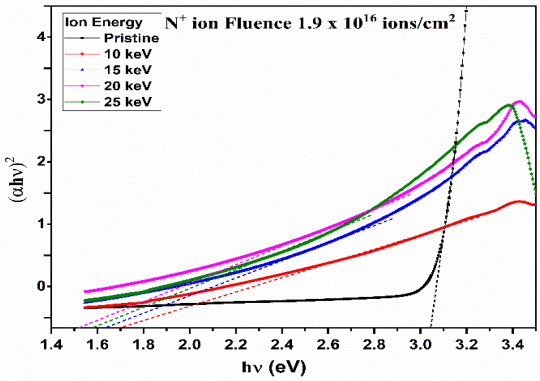


**Fig. 3.** Band gap calculation using Tauc's plot for PET films before and after irradiation.

The Tauc method was employed for calculating band gap [22]. It is seen that as the irradiation energy is increased the band gap decreases from 3.09 to 1.52 eV and the Urbach energy increases from 0.9732 to 1.1318 eV confirming the inverse relation between the two quantities and the number of carbon atoms increase from 123 to 509. These quantities quantify the structural disorders in the PET sheet

**Table 2:** Band gap, Urbach energy and number of carbon atoms of PET films for various ion irradiation energies.

| $N^+$ ion Energy (keV) | Band gap energy $E_g$ (eV) | Urbach energy $E_u$ (eV) | Number of carbon atoms N |
|---|---|---|---|
| Pristine | 3.09 | 0.9732 | 123 |
| 10 | 1.71 | 1.0798 | 402 |
| 15 | 1.64 | 1.0087 | 437 |
| 20 | 1.59 | 1.0134 | 465 |
| 25 | 1.52 | 1.1318 | 509 |

***FTIR Analysis**:*

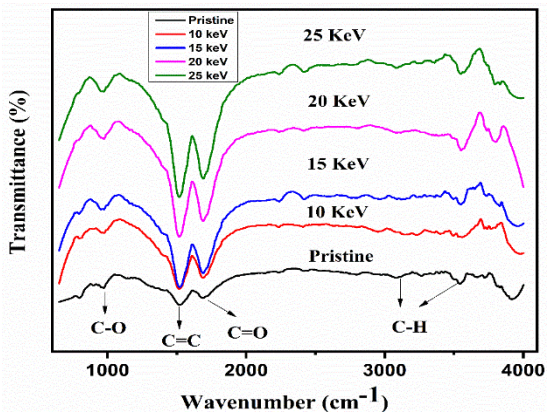


**Fig. 4** FTIR Spectra of PET films irradiated with various ion energies.

Fig.4 shows the FTIR Spectra (ATR method) of PET films irradiated with various ion energies. The analysis done in FTIR spectra shows a slight change in some transmittance peaks of irradiated films as compared to those in the pristine film. PET shows its characteristic peaks at 950 $cm^{-1}$ for C-O, 1434 $cm^{-1}$ for C=C, 1670 $cm^{-1}$ for C=O, 2995 $cm^{-1}$ for C-H bonds [23]. Post irradiation the intensities are reduced around 1500 $cm^{-1}$ region corresponding to the breaking of C=C, C=O bonds and at 2995 $cm^{-1}$ bending of C-H bond. This indicates that the process of chain scission has occurred due to the irradiation process and PET is slightly altered chemically at the surface [24].

***The Monte Carlo simulation study with SRIM-2013 programming.***

***DPA Analysis:*** The Monte Carlo simulation Code with SRIM-13.00 Software was used to estimate the stopping energy and the range of ions projected in the material [25] to support the experimental findings of the present work. The dislocation of the target PET material atoms due to bombarding of incident $N^+$ ions creates vacancies by breaking the O-C-O, C-O and C=O bonds. The software also estimates the vacancies created per unit ion in PET material and helps to calculate the ratio of displaced atoms DPA per unit volume to the total atoms in the same volume as shown in fig.5. The $N^+$ ion energy, incident angle of ions, material elemental composition of PET, and atomic density of PET material are the requisites used in SRIM-13.00 for finding out the DPA due to incident ion bombardment in the PET material. The peak shows the maximum DPA value in PET material for the particular energy at the depth reached by the $N^+$ ion. As the energy of the incident ion is increased the depth increases with decreasing DPA value.

With the increase in the ion energy from 10 to 25 keV, it is observed that the max DPA value varies from 52.82 to 42.49, i.e., 19.55%. This observed fact about DPA changes is correlated with the damages occurred in the surface of the PET material.

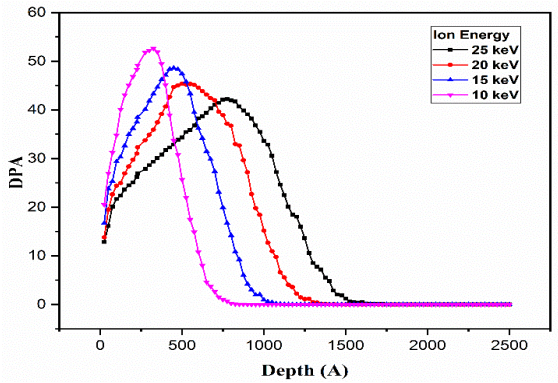


**Fig. 5** DPA as a function of depth of $N^+$ ion energy in PET at constant ion fluence.

***Total sputtering yield:***

As $N^+$ ions are incident on PET sheet, many atoms from the material are sputtered out. These sputtered atoms per incident ion constitute the sputtering yield and the sputtering yield as a function of incident energy is estimated using the Monte Carlo simulation Code with SRIM-13.00 Software as shown in the figure 6. Table 3 shows the total sputtering yield for individual atoms corresponding to the irradiation energies in PET material.

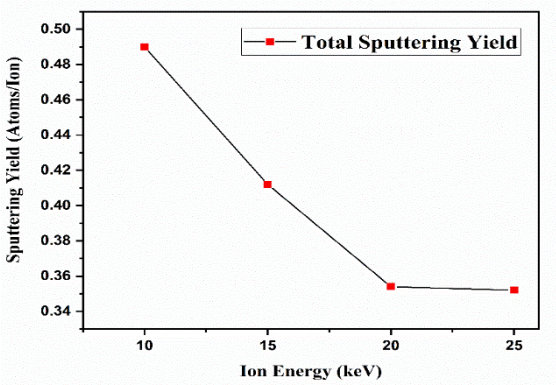


**Fig. 6:** The total sputtering yield in PET material as a function of $N^+$ ion energy at constant ion fluence.

With the increase in the ion energy from 10 to 25 keV, it is observed from fig.6, that the sputtering yield varies from 0.491 to 0.351, i.e., 28.51% change in sputtering yield has been observed. These changes are correlated with the roughness occurred in the surface of the PET material.

**Table 3.** The sputtering yield of H, C and O atoms for incident $N^+$ ion is tabulated below.

| Ion Energy (KeV) | Projected Range (Å) | Sputtering Yield (Atoms/Ion) | | | |
|---|---|---|---|---|---|
| | | H | C | O | Total |
| 10 | 399 | 0.29 | 0.13 | 0.06 | 0.49 |
| 15 | 584 | 0.26 | 0.1 | 0.05 | 0.41 |
| 20 | 767 | 0.23 | 0.08 | 0.03 | 0.35 |
| 25 | 948 | 0.22 | 0.09 | 0.04 | 0.35 |

The dominant band gap change was observed at 10 keV ion energy, it change can be attributed to the maximum displacement of atoms due to nuclear energy loss. The calculations performed using SRIM-2013 was in good agreement with our findings on band gap energy.

***Energy Loss and the projected range:***

The projected range of $N^+$ ion penetration depth with different irradiating energies is calculated using SRIM-2013 programming [25]. The incident nitrogen ion with energy 10 to 25 KeV penetrates in the target PET material up to the depth of 399 to 948 Å respectively as shown in table 3. Due to its energy the incident ion will interact with the atoms in the target material. As ion energy is increased from 10 KeV to 25 KeV, initially the nuclear energy loss is dominant over the electronic energy loss, therefore, DPA value for 10 KeV ion energy is recorded maximum, whereas for 25 KeV it is seen minimum. Also, the sputtering yield shows maximum for 10 KeV $N^+$ ion energy and exhibits decreasing tendency thereafter.

## CONCLUSIONS

Effect of $N^+$ ion energy variation from 10 to 25 KeV with constant fluence of 1.98 x $10^{16}$ ions/$cm^2$ were studied on PET material in the form of thin sheet. It was observed that after $N^+$ ion irradiation the variation occurred in the chemical, structural and electronic properties (band gap energy) of the PET sheet. The XRD studies show that as the irradiation energy increased the crystallite size decreased from 7.5 to 2.5 Å, interspacing distance decreased from4.8 to 3.1 Å whereas the microstrain and dislocation density increased from 0.29 to 0.57 and 0.01 $Å^{-2}$ to 0.14 $Å^{-2}$ respectively. This confirms the destruction of chemical bonds at the surface of PET. UV-Vis absorption studies show that the optical band gap decreases from 3.09 to 1.52 eV and the Urbach energy increases from 0.9732 to 1.1318 eV confirming the inverse relation between the two quantities and the number of carbon atoms increase from 123 to 509. This is due to the increased carbon clusters at the surface of PET. These quantities quantify the structural disorders in the PET sheet. These results are also supported by the DPA and Sputtering yield analysis done using SRIM-2013 software. This simulation analysis was attempted for

the first time for PET material. The FTIR analysis show that the intensities are reduced around 1500 $cm^{-1}$ region corresponding to the breaking of C=C, C=O bonds and at 2995 $cm^{-1}$ bending of C-H bond. This indicates that the process of chain scission has occurred due to the irradiation process at the surface of PET. These modifications are attributed to the cross-linking, chain scissoning carbonization occurred due to bond breakage of O-C-O, C-O and C=O and are also supported by the XRD studies. The results before irradiation are in agreement with the literature but after $N^+$ ion irradiation the physical and chemical parameters at the surface of the PET changed confirming the surface modifications due to the newly attempted interactions between low energy 10KeV to 25KeV $N^+$ ions and the PET constituents.

## ACKNOWLEDGEMENT

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# Nanomaterials

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**ABSTRACT**

*Nanomaterials (NMs) are becoming increasingly important in technological applications because to their adjustable chemical, physical, and mechanical characteristics, as well as their superior performance when compared to bulkier alternatives. This paper summarizes the main types of NMs and offers an overview of nanoparticle (NP) production methods and functionalization via covalent or noncovalent interactions utilizing various methods. It focuses on the methodologies used to characterize NPs and examines their physical and chemical characteristics. Because of their unique features, NMs have a wide range of uses and have become an integral part of our daily life. Thus, this study emphasizes research efforts into the destiny and behavior of several kinds of (NMs) in the environment.*

## INTRODUCTION

Nanotechnology is an interdisciplinary field that allows us to create new materials with novel, intriguing, and valuable features. These novel materials are nanomaterials derived from nanoparticles. Nanoparticles are extremely small particles with extraordinary capabilities that may deliver medications directly to the human body, strengthen materials, and convert solar energy more effectively. Nanoparticles have unique features and behave differently from traditional, bigger building pieces of substances. From a scientific point of view, these interesting new properties are not so much the results of the fact that nanoparticles are small, but that a particle consisting of a relatively limited number of molecules behaves and interacts differently with its surroundings for fundamental physical reasons. Nanoparticles and nanomaterials have gained prominence in technological advancements due to their adjustable physicochemical properties, such as melting point, wettability, electrical and thermal conductivity, catalytic activity, light absorption, and scattering, which result in superior performance over bulk counterparts. Properties (electrical conductivity, color, chemical reactivity, elasticity, etc.) may be changed by varying the form, size, and internal order of nanostructures.

Some nanoparticles exist naturally, but engineered nanomaterials (EN) are particularly interesting since they are created for and are already in use in a wide range of commercial goods and processes. Sunscreens, cosmetics, sports goods, stain-resistant apparel, tires, electronics, and a variety of other daily objects include them. They are also employed in medicine for diagnostics, imaging, and medication delivery.

Engineered nanomaterials are resources created at the molecular (nanometer) level to take use of their small size and new features that are not often found in their traditional, bulk equivalents. Nanoscale materials can have altered characteristics due to increased relative surface area and novel quantum phenomena. Nanomaterials have a substantially higher surface area to volume ratio than traditional materials, which can lead to increased chemical reactivity and reduce their strength. At the nanoscale, quantum effects can play a significantly larger role in influencing material properties and features, resulting in unique optical, electrical, and magnetic behaviors.

## INTRODUCTION OF THE NANOMATERIALS

***Definition of Nanomaterials:***

Nanoscale materials are described as substances with at least one dimension smaller than around 100 nanometers. A nanometer is one millionth of a millimeter, or roughly 100,000 times smaller than the diameter of a human hair. Nanomaterials are interesting because they exhibit unique optical,

magnetic, electrical, and other characteristics. These emerging features have the potential for significant implications in electronics, medicine, and other sectors.

***History of Nanomaterials***

Nanotechnology involves synthesizing ultrafine particles with dimensions of billionths of a meter, allowing us to manipulate materials and devices at atomic and molecular levels. Over the last two decades, reports of colloids and nanoparticles created by nature have been reported.

Nanomaterials have a long history, dating back to the big bang and originating from early meteorites. They have evolved into various forms, including seashells, skeletons, and nanoscaled smoke particles. Michael Faraday created colloidal gold particles in 1857, and nanostructured catalysts have been studied for over 70 years. In the early 1940s, precipitated and fumed silica nanoparticles were used as alternatives for ultrafine carbon black in rubber reinforcements. Nanomaterials have gained interest due to their nanosize, physical, biological, and chemical features compared to bulk materials. They are categorized based on size, chemical composition, form, and source, and are often mass-produced to meet various industries' needs. NMs are formed from synthetic sources and naturally occurring nanoparticles.

***Main differences between nanomaterials and bulk materials***

Nanomaterials are particles with a size range of 1-100 nm in one dimension, such as nanozymes, titanium dioxide nanoparticles, and graphene. Bulk materials, on the other hand, have a size above 100 nm in all dimensions and can be seen through the naked eye, such as plaster, sand, gravel, cement, ore, slag, and salts.

## TYPES AND CLASSIFICATIONS OF THE NANOMATERIALS

As the area of nanotechnology expands fast, a large number of NMs have been developed, and all of these NMs must be distinguished from one another based on their structure, forms, size, and chemical production. Interestingly, NMs may be generically classified into seven groups, as stated below.

***Carbon Nanomaterials***

Carbon nanomaterials are NMs that include carbon and may be synthesized in a variety of forms, including hollow tubes and spheres. Carbon nanoparticles include graphene, fullerenes, carbon black, carbon nanotubes, and carbon onions. (Figure 1.3) [7].

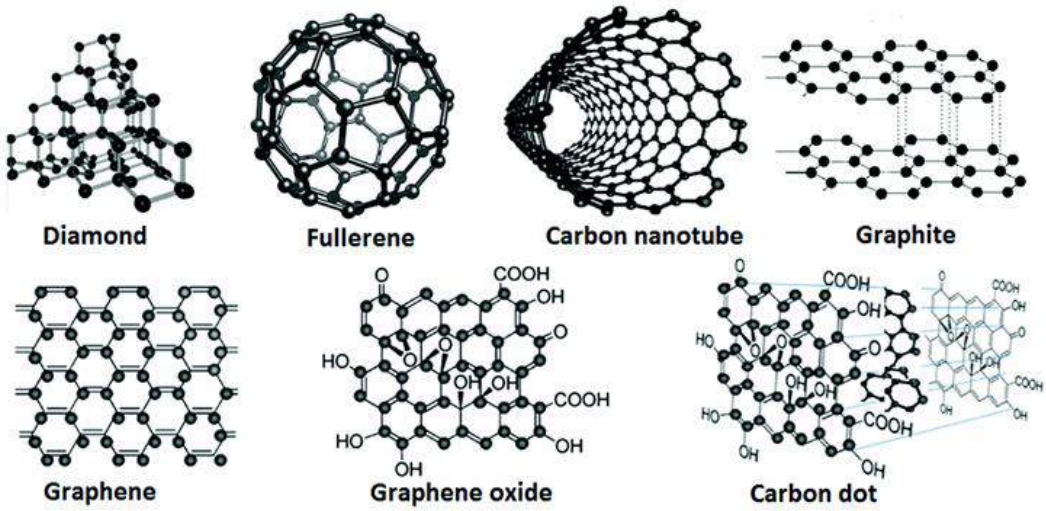


**Figure (1.3): Different Carbon-base nanomaterials [7].**

***Metal and Metal Oxide Nanomaterials***

Metal and metal oxide can also be utilized to create NMs, known as metal and metal oxide nanomaterials or inorganic nanomaterials. Some of these NMs include gold (Au) and silver (Ag) nanoparticles, as well as metal oxide-based nanomaterials such as titanium dioxide (TiO2) and zinc oxide (ZnO).

***Organic Nanomaterials***

This form of NMs is largely composed of organic stuff, with no carbon or inorganic nanoparticles. These organic nanostructures have noncovalent bonds, which are weak and easily

broken. These organic materials are easily manipulated to yield diverse forms of nanomaterials such as liposomes, dendrimers, micelles, and polymers.

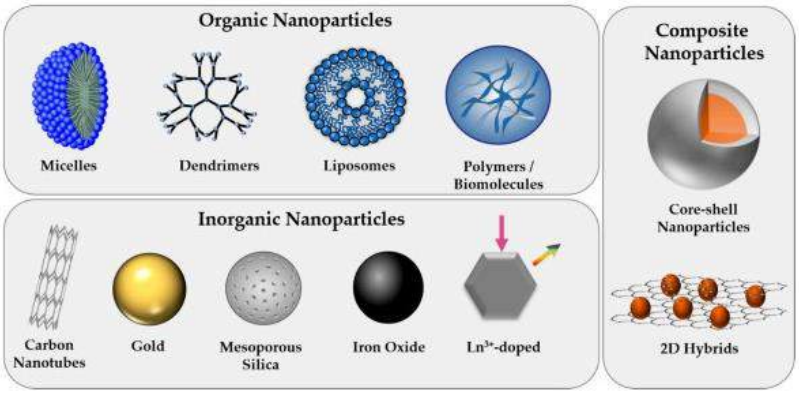


**Fig. Overview of commonly used nanoparticle (NP) types, classified as organic, inorganic, or composite structures**

***Nanocomposites***

Nanocomposites are composed of different types of nanomaterials mixed with various forms of nanowires and nanofibers, as well as larger materials. They can be metal-based, carbon-based, or organic-based nanowires, nanofibers, or any type of ceramic, metal, or polymer bulk materials.

***Ceramic Nanomaterials Nanoceramic***

Ceramic nanoceramics (NMs) are heat-resistant, inorganic, and nonmetallic solids made from nonmetal and metal compounds with dimensions less than 100 nm. They have improved structural, electro-optical, superconductive, ferromagnetic, and ferroelectric capabilities. However, increasing doping concentration can alter the structural and physical characteristics of Ti-doped BiFeO3 nanoceramics, potentially causing deformation and oxygen vacancy removal.

Sobierajska et al. studied the creation of porous hydroxyapatite nanoceramics (ncHAP) with antibacterial properties. They co-precipitated high purity hydroxyapatite and methylcellulose, with surface area and porosity determined by sintering temperature. The study also found that Al2O3-ZrO2 nanoceramics can be synthesized under pressureless and low-temperature conditions, with a homogenous mixture and varying grain size.

***Semiconductor Nanomaterials***

Semiconductor nanomaterials (NMs) have a low bandgap energy of less than 4eV and are made up of various chemicals from groups like ZnO, SiO2, and GaAs. The nanostructure of these materials can change their chemical and physical characteristics due to the quantum size effect or surface area increase. The high electrical conductivity of materials depends on the nanostructure created. NMs are classified into intrinsic semiconductors, which are pure compounds or elements without doping from other metals, and extrinsic semiconductors, which are materials added to other metals to increase their conductivity. Intrinsic semiconductors exhibit negative temperature coefficients of resistance, indicating that increasing temperature decreases resistivity and increases conductivity.

***Polymeric nanomaterials***

Polymeric nanoparticles (NMs) are nanosized solid particles made of natural or manufactured polymers, used in pharmaceutical and medical applications as medication release controls and body sensors. These materials consist of polymeric micelles, which are generated by self-assembly of amphiphilic block copolymers in a specific solvent, such as chitosan polymeric micelles, which are used for drug administration due to their unique properties such as nanosize, stability, biocompatibility, and low toxicity. Polymeric nanoparticles, typically biocompatible and biodegradable, are used to deliver medications to specific locations. The preparation processes for creating polymer NPs include monomer polymerization, ionic gelation of hydrophilic polymers, and polymer dispersion. Dendrimers, smaller than 15 nm and containing 3D-shaped macromolecules, are a novel form of polymeric nanomaterials with properties such as structure, size, and multivalence. Polymeric nanocomposites, composed of different nanofillers and polymers, are designed to have superior qualities and features.

***Classification of Nanomaterials***

Dimensions and Sizes

Nanomaterials, solid particles with various purposes, require classification for optimal use. In 2000, a scientist proposed a classification system based on crystalline shapes and chemical compositions, but

this method was not comprehensive. Researchers developed a new categorization system based on 0 Dimension, 1 Dimension, 2 Dimension, and 3 Dimension nanomaterials. The flow of electrons in nanomaterials determines its categorization, with "0" dimension nanomaterials often locked, while "1" dimension nanomaterials allow electrons to flow freely along the x-axis, typically less than 100 nm. "2" and "3" dimension nanomaterials exhibit superior electron motions along the x-to-y-axis. The ability to anticipate nanomaterials' qualities is the determining factor in their categorization. Gleiter's categorization primarily relies on grain boundaries, while Pokropivny and Skorokhod claimed nanoparticle shapes and dimensionalities are attributed to their features.

***Origin of Nanomaterials***

Nanomaterials can be categorized based on their origin, which refers to the materials used to create them, either naturally occurring nanoparticles or synthetically manufactured nanomaterials.

Natural Nanomaterials

Natural nanomaterials, found in various environments like the hydrosphere, atmosphere, lithosphere, and biosphere, can be created by biological species like bacteria and plants, as well as anthropogenic processes. These naturally occurring nanomaterials are found in rivers, oceans, lakes, rocks, soils, magma, and lava.

***Synthetic Nanomaterials***

Synthetic nanomaterials, produced through biological, physical, chemical, or hybrid processes, offer the ability to produce large quantities in various forms and sizes. They require precise linking or conjugation of compounds or reagents. However, their performance is uncertain due to their unique environmental behavior. Currently, a variety of nanomaterials are developed for various biological applications.

*Synthesis of Nanomaterials: Methods & Characterizations*

Recent decades have seen advancements in nanomaterial synthesis, aiming to produce nanomaterials with defined purposes. Researchers must understand their applications, manufacturing processes for industrial use differ from those for biological or therapeutic purposes. Physical and chemical techniques have been used to enhance nanomaterial performance.

***Methods to Synthesize Nanomaterials***

The two primary methods for synthesizing nanomaterials are "top-down" and "bottom-up," which have been thoroughly described in this text. (Figure).

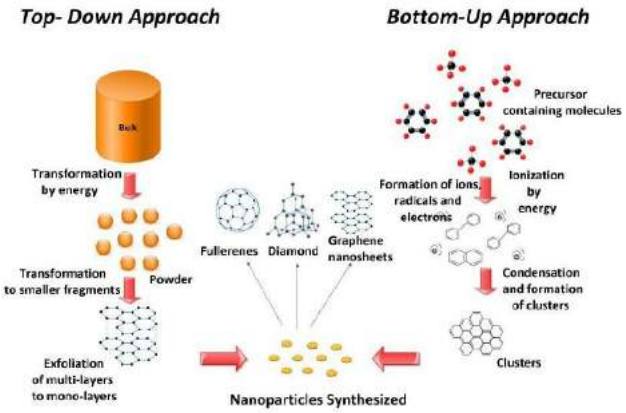


**Figure** Diagrammatic representation of top-down approach andbottom-down approach of making of nanomaterials .

***Production of Nanomaterials by Top-Down Method***

This approach mostly employs solid and state material processing, and it entails breaking down the bulk material into smaller particles using physical processes such as crushing, milling, and grinding. In general, this process is not suitable for producing uniformly shaped nanomaterials, and obtaining very tiny size nanoparticles is extremely challenging even with significant energy utilization. The primary challenge with this approach is a lack of surface structure, which has a substantial influence on the physical characteristics and surface chemistry of nanomaterials. This approach also results in significant crystallographic loss for the treated ***forms.***

***Production of Nanomaterials by Bottom-Up Method***

To manufacture a vast number of materials, this process involves preparing them atom by atom or molecule by molecule. The majority of nanomaterials are produced using this approach. This approach

produces nanomaterials with consistent size, shape, and distribution. It essentially controls the chemical synthesis process carefully in order to prevent unwanted particle development. This approach is crucial for producing and processing nanomaterials with superior particle size distribution and shape. Another essential advantage is that the nanoparticle production procedures are both environmentally benign and cost-effective. There are several methodologies to synthesising nanomaterials, including hydrothermal, combustion synthesis, gas-phase processes, microwave synthesis, and sol-gel processing, which we will discuss below.

***Hydrothermal Method***

The hydrothermal method, typically performed in an autoclave, allows for temperature and pressure control during nanomaterial synthesis. This method, widely used for producing nanoparticles, allows for regulation of material size, particle morphology, crystalline phase, and surface chemistry through temperature, pressure, solvent properties, solution composition, and additives.

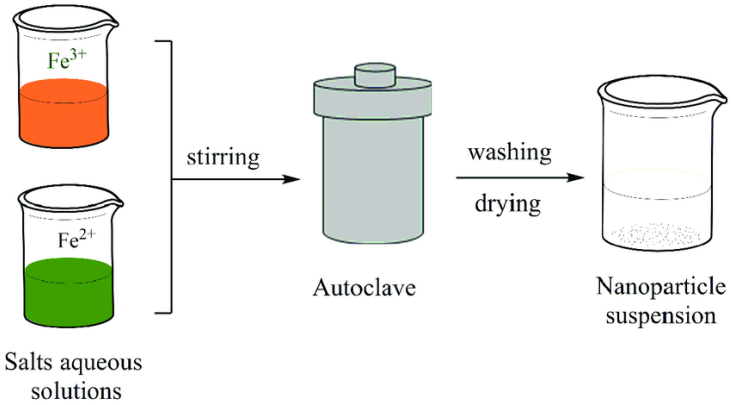


**Figure** () Diagrammatic representation of hydrothermal process nanoparticle production.

***Solvothermal Method***

The solvothermal method, similar to hydrothermal methods, uses solvents other than water and is more effective in synthesizing nanomaterials with good distribution, especially when organic solvents or high boiling points are used. It offers better control for material size and shapes, and can be synthesized with or without surfactants.

***Chemical Vapor Deposition Method***

The chemical vapor deposition (CVD) method is used to create high-performance thin nano-films by treating substrates with volatile precursors. The quality of the deposited materials depends on factors like temperature, reaction rate, and precursor quantity. Sn4+doped TiO2 nanoparticle films were produced using this method, while another doped TiO2 nanoparticle was synthesized using this method. However, this method has limitations, such as higher temperatures and difficulty in scaling up.

***Method of Thermal Decomposition and Pulsed Laser Ablation***

The chemical vapor deposition (CVD) method is used to create high-performance thin nano-films by treating substrates with volatile precursors. The quality of the deposited materials depends on factors like temperature, reaction rate, and precursor quantity. Sn4+doped TiO2 nanoparticle films were produced using this method, while another doped TiO2 nanoparticle was synthesized using this method. However, this method has limitations, such as higher temperatures and difficulty in scaling up.

***Templating Method***

The templating method is a popular method for creating nanomaterials with similar morphology. It uses reactive deposition to create controlled materials by changing template materials' morphology. Various templates have been developed for synthesizing nanomaterials, but it has limitations like complicated procedures and increased manufacturing costs due to contamination risks. Despite these issues, the templating method remains a popular method for nanomaterial production.

***Combustion Method***

The combustion method rapidly heats a redox group-containing solution, producing highly crystalline nanoparticles with large surface areas, reaching temperatures of approximately 650°Celisus for 1-2% of the production time.

*Gas Phase Method*

Thin films can be produced through chemical or physical methods, such as chemical reactions or decomposition of precursors in the gas phase. Physical vapor deposition (PVD) is another technique,

forming films without chemical transition. Electron beam (E-beam) evaporation is a process that produces electrons from a beam of electrons, providing benefits like smoothness and better conductivity compared to the CVD method.

***Microwave Radiation Method***

Microwave radiation can produce nanomaterials quickly and efficiently, without requiring prolonged high temperature calcination. This method also allows for the creation of high-quality rutile rods and TiO2 hollow open-ended nanotubes by reacting anatase and rutile crystals in a NaOH solution.

***Conventional Sol-Gel Method***

The Sol-Gel method is a method used for synthesizing oxide materials, allowing impregnation or co-precipitation of nanomaterials, introducing dopants, and controlling texture formation, chemical reactions, and morphological properties. It allows for high purity nanomaterials scaling up. The process involves hydrolysis and polymerization of precursors, typically inorganic metal salts or metal organic compounds. Factors such as solvent type, water content, acid or base content, precursor type, precursor concentration, and temperature affect the properties of the gel formation. The wet gel can be matured in another solvent, known as aging.

***Methods of detection of Nanomaterials: Techniques and Tool***

Nanomaterials exhibit superior physical, electrical, and chemical properties compared to bulk phase materials. Nanotechnology/biotechnology focuses on synthesizing, characterizing, and applying nanomaterials, which contain tiny particles called nanoparticles. Techniques for characterization include scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy-dispersive X-ray (EDX) spectroscopy, thermal gravimetric analysis (TGA), dynamic light scattering (DLS) analysis, density functional theory (DFT), and zeta sizer.

**Scanning Electron Microscopy (SEM)**

Electron microscopes use electrons to create images, providing better resolution than optical microscopy due to their small wavelengths. Scanning electron microscope (SEM) is a useful technique for obtaining surface topography and chemical composition of specimens. The SEM instrument consists of an electron gun, electron column, chamber, detectors, and vacuum pumps. Primary electrons are focused by electromagnetic lenses, scanning the specimen using electrical coils. Secondary electrons, backscattered electrons, Auger electrons, and X-rays are generated, detected by detectors, producing electronic images or spectra.

**Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) is a powerful tool for obtaining high-quality data on nanomaterials, with the TEM instrument being the microscope used to perform this task. TEM is performed to obtain detailed morphology and structure of the specimen beyond the limits of SEM. The main difference between TEM and SEM is that in TEM, the electron beam is transmitted through a thin specimen, while in SEM, the beam of electrons scans the surface of the sample instead. TEM's power is typically 80-300 kV, which is much higher than SEM's maximum of 30 kV. This power allows TEM to produce better images in terms of resolution.

The wavelength ($\lambda$) of electrons in TEM is related to V, which can be varied according to the relation ($\lambda = h/((2m0eV)1/2)$). By increasing V, we can shorten the $\lambda$ of the electrons and improve the resolution. The $\lambda$ of electrons in TEM is comparable or smaller ($\lambda = 0.00197$ nm at 300 kV) than the size of the atom (~ 0.1 nm), allowing TEM to reveal the finest details of the internal structure of the specimen as small as individual atoms and molecules.

TEM has several modes for collecting data, including bright-field (BF), dark-field (DF), and high-resolution (HR) imaging, known as BF-TEM, DF-TEM, and HR-TEM, respectively. Direct electrons are used to form BF imaging after blocking scattered electrons by objective aperture, while HR-TEM uses the phase of the electrons to acquire detailed structures of the specimens down to the atomic level.

The contrast between BF and DF images is crucial, with bright features appearing dark in BF images and vice versa. TEM images, created by direct or scattered electrons, can be viewed on a fluorescence screen or recorded using a digital camera. TEM images have better resolution than SEM due to the transmission of electrons and the high energy of electrons.

**Fourier Transform Infrared (FTIR) Spectroscopy**

Fourier transform infrared (FTIR) is a technique used to study the molecular bonding of organic/inorganic materials. It uses electromagnetic radiations between the red edges of the visible spectrum at a wavelength of 700 nm to 1 mm. During FTIR, a specimen is exposed to IR radiations,

creating a spectrum. Some radiations are transmitted, while others are absorbed by the specimen. This results in a molecular fingerprint of the specimen, which can provide information on material properties, specimen quality, and the number/ratio of ingredients in a mixture.

***a) Main Components of FTIR Instrument***

The FTIR instrument consists of a source, an interferometer, a sample chamber, a detector, and a computer. The source emits IR energy in the form of a beam, while the interferometer produces a distinctive signal (interferogram) containing all IR frequencies. The sample is mounted in the specimen chamber, and the IR beam enters for specimen interaction. A special-purpose detector gauges the interferogram signal. The computer decodes the interferogram into individual frequencies using the Fourier transform, which is used for identification purposes. The interferogram is then plotted to analyze the signal for identification purposes.

***b) Working of FTIR Instrument***

The Fourier Transform Infrared (FTIR) instrument uses radiation from an IR light source to create an interferogram. The beam splitter divides the radiation into two beams, which are then reflected from two separate mirrors. The IR beam then enters the specimen chamber, and the interferogram contains information about each IR frequency falling on the specimen. The beam is either passed through or bounced off the specimen surface, depending on the analysis requirement. A desired range of IR frequencies representing a distinctive property of the specimen is absorbed. The interferogram signal is detected by a special purpose detector and decoded in a computer using Fourier transformation. The FTIR spectrum is then available for manipulation and exposure, allowing for the analysis of various materials. FTIR spectrocopic characterization can be used to analyze various materials.

**X-Ray Diffraction (XRD)**

X-ray diffraction (XRD) is a non-destructive method used to study the structure of materials at the molecular and atomic level. It is particularly effective for investigating crystalline, polycrystalline, and non-crystalline materials. XRD involves the elastic scattering of X-rays by atoms of the materials, with the principle being based on the interference of scattered waves. The amplitude of the scattered waves depends on the difference in the distance traveled by the waves, known as path difference. Constructive interference occurs when two waves superimpose in a phase, while destructive interference occurs when two out of phase waves merge, resulting in the difference of two intensities. The XRD pattern is plotted between intensity and scattering angle, and analyzed using Bragg's law. The XRD line patterns of over 60,000 different crystallographic phases are available in the electronic database JCPDS, which includes three strong characteristics lines of the existing phase. XRD technique applies to specimens of powders, thin films, and solids.

***Main Components of XRD Instrument***

The XRD instrument consists of an X-Rays Tube, a collimator, a sample stage, a detector, and a computer. The tube produces X-rays by colliding electrons with a metallic target, while the collimator makes the rays parallel. The sample stage is used to place specimens, and the X-rays are detected using a counter. The collected data is then plotted on a computer.

***Working of XRD Instrument***

X-ray diffractography (XRD) is a method used to study the structure and properties of materials by analyzing the scattering angle of a collimated beam of X-rays directed towards a sample. The angle formed by the incoming beam with the specimen's surface is θ, which determines the diffracted beam's angle. The diffracted beam is detected by a detector and sent to a computer for XRD pattern creation.

For a given specimen, consider several periodic lattice planes (atomic layers) separated by d. According to Bragg's Law, constructive interference occurs when the path difference is an integral number of wavelengths. This law states that a constructive interface occurs when $2d \sin \theta = n \lambda$ is satisfied.

For wider interparticle distances, the scattering angle 2θ is lower, indicating that planes with wider d appear earlier in XRD patterns. The angle of the incident beam is varied to obtain all possible reflections for a given sample. The angle of every single crystallographic phase can be determined by comparing the data with standard line patterns available in the Powder Diffraction File (PDF) database.

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# SYNTHESIS , CHARACTERIZATION AND ANTIMICROBIAL PROPERTIES OF NOVEL FLAVONE DERIVATIVES

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## ABSTRACT

Chalcones were synthesized by the condensation product of DHA in combination with aromatic aldehydes in presence of strong base. It was found that the synthesized chalcones were having prominent role in modern coordination chemistry. The chalcone synthesized by base catalyzed condensation of 3-acetyl-6-methyl-2H-pyran-2,4-(3H) dione (DHA) with different aromatic aldehyde. These chalcones were used for synthesis of derivatives i.e. flavones. The synthesized compounds were characterized by IR, $^{1}$HNMR and mass spectral analysis. The derivatives were further used for the estimation of its biological properties. It was found that the derivative possesses efficient antimicrobial properties. From the study it was found that the synthesized compounds are efficient for further research work.

***Keywords :*** *Chalcone , Flavone , IR, $^{1}$HNMR Mass Spectroscopy, Biological Properties*

## INTRODUCTION

Chalcones are the special ligand molecules that used for the synthesis of complexes with desired properties. The complexes are having variations in physical, chemical and biological properties. The existence of the α, β-unsaturated ketone moiety in chalcones is a common part found in a large number of biological active compounds[1], Therefore, chalcone derivatives from nature or synthetic origin exhibit diverse pharmacological activities, such as antimicrobial[2], antitumor[3], anticancer[4], radical scavenger[5] and inhibitor of topoisomerase I.[6]

Flavanones are important naturally occurring organic compounds possessing a wide range of biological activities used in the treatment of various diseases [7]. Different methods are used for the synthesis of flavones, includes Allan- Robinson synthesis, synthesis from chalcones and via intramolecular witting reaction [8]. The most common method used involves Baker- Venkatramn arrangement. In this method 2- hydroxy acetophenone are converted to benzoyl ester, which in presence of base (pyridine / KOH) form 1,3 diketones. The diketones are further cyclized under strong acidic condition to afford the flavones [9]. In recent development of such dehydrative cyclization it includes the use of Amberlyst15, CoIII (sulpr)OH, FeCl3, Br2/CHCl3, EtOH/HCl, clay, NaOAc/AcOH and H2SO4 under microwave irradiation [10]. Prenylated flavanone is a unique class of naturally occurring flavonoids characterized by the presence of a Prenylated side chain in the flavonoid skeleton. It was reported that one phenolic group and certain degree of lipophilicity are required for the activity of the flavonoids Substitution of the flavonoid ring system with prenyl groups would increase their lipophilicity and consequently enhance their interaction with cellular membranes [11]. 4′ ,5,7-Trihydroxy-3′ -prenylflavanone has been isolated for the first time in 1989 from the chloroform extract of the stem bark of Erythrina eriotriocha. The chemical and pharmaceutical industries are always under the pressure to find out environmental friendly organic reaction methodologies. Microwave irradiation is used for a variety of organic reactions due to their use in a rapid and cleaner synthesis of organic compounds [12].

Flavones are a class of flavonoid based on the backbone of 2-phenyl chromene-4-one(2-phenyl-1-benzopyrane-4-one ).They are polyphenolic compound which constitute one of the most numerous & ubiquitous group of plant metabolites, flavonoids are generally present as glycosylated conjugates in fruit, vegetables & other plant products consumed in a normal diet [13].

The immediate family members of flavonoids include flavones, flavanones, flavanols, anthocynidins and catechins. Luteolin is a flavonoids more specifically, it is thought to play an important role in the human body as an antioxidant, a free radical scavenger, an agent in the prevention of inflammation, a promoter of carbohydrate metabolism, and an immune system modulator. These characteristics of lutelin are laso believed to play an important part in the prevention of cancer multiple research eexperiments describe luteolin as a biochemical agent that can dramatically reduce inflammation and the symptoms of septic shock [14]. Luteolin is most often found in leaves, but it is also seen in rinds, barks,clover,blossom and ragweed pollen. It has also been isolated from salvia tomentosa. Dietary sources include celery, green pepper, perilla and camomile tea. Flavonoids have the same basic skeleton and the key feature which distinguishes one structural type from the other is the oxidation level of the various carbon in the heterocyclic ring, chromanones and flavones are integral part of humen diet have been reported to exhibit a wide range of biological effects. They also demonstrate, antibacterial, abortionist, cytotoxic, antimicrobial, antimalarial & antihypertensive activities[15].

## RESULT AND DISCUSSION

The chalcones of DHA were synthesized by claisen-schmidt condensation and characterized as good to excellent yield. The structures of all the compounds were established from IR, $^1$HNMR and mass spectral analysis is mentioned above. The IR spectrum of chalcones gives a broad band for OH group at (3000-3125 cm$^{-1}$) sharp and strong bands were observed at 1700-1750 cm$^{-1}$ for lactone carbonyl group. Another sharp band was observed at 1598-1650 cm$^{-1}$ due to the presence of carbonyl group and carbon- carbon band of α, β-unsaturated chalcone system.

The structure of synthesized compounds were converted to the corresponding flavones (MBFI to MBFV) by oxidative cyclisation of chalcones. All these flavones did not gave violet colouration with ferric chloride solution and pink colouration with conc. Sulphuric acid. The IR spectra of flavones shows absences of band in the region 3000-3100 cm$^{-1}$ (OH group). The $^1$H NMR Spectra showed singlet at δ 6.2 – 6.8 due to COCH proton and absence of singlet in the region δ 15-16 due to proton of hydroxyl group. In conclusion, we have reported that the synthesized chalcones derivatives using DHA (3-acetyl-6-methyl-2H-pyran-2,4-(3H) dione possessing good to moderate biological properties. These compounds will be having application in pharmaceutical, agriculture, medical field for drug development.

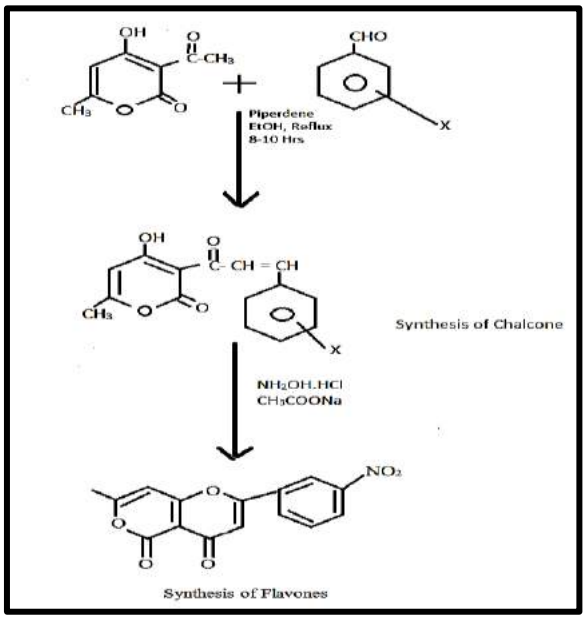



**Fig. 1:** Schematic representation of synthesized chalcone and flavone

## MATERIAL AND METHODOLOGY.

### Synthesis of substituted 3-Cinnamoyl-4-Hydroxy-6- Methyl-2-Pyrones (MBCI-V)

10 mmol solutions of dehydroacetic acid and the10 mmol of aromatic aldehyde were taken and in to that 8-10 drop of piperedine was added as a catalyst. The solutions was dissolved in 30 ml of ethanol solvent, the reaction mixture was then refluxed for a reaction time of 12-15 hrs. After reaction

the compounds were checked by TLC. Then the mixture were filtered, dried and recrystallized with suitable solvent i.e. chloroform.

The characterizations were carried out further of synthesized compounds. Melting points were determined in open capillary and are uncorrected. IR spectra were recorded on FT-IR spectrometer using potassium bromide pellet as standard, $^1$HNMR were determined on a New AVANCE-500 MHz spectrometer against TMS as internal standard. The mass analysis was also carried out using Shimazu -machine. Purity of compounds was checked by thin layer chromatography (TLC).

**General method for the synthesis of Flavones:**

A solution of substituted 2-hydroxy chalcone was dissolved in DMSO (Dimethyl sulfoxide) a catalytic amount of iodine was added and the reaction mixture was refluxed for 2 to 3 hrs till the starting material had completely undergone conversion .Reaction was monitored by TLC, the reaction mixture was cooled at room temperature and sodium thiosulphate solution (10%) was added to decompose excess of iodine. The solid so obtained was filtered and dried. The dry solid on crystallization from alcohol afforded flavone. The M.P. and Yield are listed in table. The structures of flavones were confirmed by spectral analysis (IR, $^1$HNMR and mass).

**Characteristic Test:**

The compound does not give violet coloration with $FeCl_3$ solution and Wilson test was negative.

**Synthesis of flavones**

A solution of 1-(4-hydroxy-6-methyl-2-oxa-2H-pyran-3-yl)-3-(2-fluorophenyl)-2-propenone (0.001mol) and a crystal of iodine was added to it .The reaction mixture was refluxed for 1-2 hrs,the completion of reaction was checked by TLC. After completion of the reaction, the mixture was cooled at room temperature and diluted with water; the excess of iodine was decomposed with saturated sodium thiosulphate solution. The solid thus obtained was filtered & washed with cold water & recrystallized from ethanol to get product name

Similarly other compounds of the series were also synthesized by same procedure. The physical data of synthesized compounds are listed in table no. 1 and 2.

**Spectroscopic data of synthesized Flavone derivatives (MBFI-MBFV)**

**MBFI : 7-methyl-2-(3-nitrophenyl) pyrano [4,3-b] pyran-4,5-dione**

**IR** (KBr, cm-1); 1650 (C=O), 1722(C=O Lactone), 2990 (C-H str. Of –CH3)

**$^1$HNMR** (CDCl3, δ/ ppm): 2.2 (3H, s, CH3), 6.5 (1H, s, COCH), 6.0 (1H, s, pyran ring), 6.8 to 8.4 (4H, m, Ar-H )

**Mass** (m/z): (M+1) 300.

**MBFII : 7-methyl-2-(3,4,5-trimethoxyphenyl) pyrano [4,3-b] pyran-4,5-dione**

**IR** (KBr, cm-1); 1648 (C=O), 1716 (C=O Lactone), 2950 (C-H str. Of –CH3)

**$^1$HNMR** (CDCl3, δ/ ppm): 2.0 (3H, s, CH3), 3.8-4.2 (9H, s, 3X$OCH_3$), 6.2 (1H, s, COCN) 6.0 1H, s, pyran ring), 6.4 to 8.4 (2H, m, Ar-H )

**Mass (m/z):** (M+1) 345.

**MBFIII : 7-methyl-2-(3-methoxyphenyl) pyrano [4,3-b] pyran-4,5-dione**

**IR** (KBr, cm-1); 1658 (C=O), 1720 (C=O Lactone), 2978 (C-H str. Of –CH3)

**$^1$HNMR** (CDCl3, δ/ ppm): 2.3 (3H, s, CH3), 3.9 (3H, s, OCH3), 6.8 (1H, s, COCH), 5.9 (1H, s, pyran ring), 6.8 to 8.2 (4H, m, Ar-H )

**Mass (m/z):** (M+1) 283.

**MBFIV : 7-methyl-2-(3,4-dimethoxyphenyl) pyrano [4,3-b] pyran-4,5-dione**

**IR** (KBr, cm-1); 1651 (C=O), 1720 (C=O Lactone), 2950 (C-H str. Of –CH3)

**$^1$HNMR** (CDCl3, δ/ ppm): 2.1 (3H, s, CH3), 3.9-4.2 (6H, s, 2X$OCH_3$), 6.8 (1H, s, COCH), 6.0 (1H, s, pyran ring), 6.4 to 8.2 (4H, m, Ar-H )

**Mass (m/z):** (M+1) 315.

**MBFV : 7-methyl-2-(2-florophenyl) pyrano [4,3-b] pyran-4,5-dione**

**IR** (KBr, cm-1); 1668 (C=O), 1722 (C=O Lactone), 2990 (C-H str. Of –CH3)

**$^1$HNMR** (CDCl3, δ/ ppm): 2.2 (3H, s, CH3), 6.6 (1H, s, COCH), 6.0 (1H, s, pyran ring), 6.3 to 8.2 (4H, m, Ar-H )

**Mass (m/z):** (M+1) 273.

**Biological Activity**

The synthesized compounds were tested in *in vitro* for antimicrobial activity against bacterial isolates like *S. aureus*, *E. coli* and *Salmonella Typhi* and fungi species like *Fusarium oxysporum*, *Candida albicans* and *Aspergillus flavus.* The concentrations of compounds were taken as 150 µg/ml each. The antimicrobial activity was checked by agar plate diffusion method . The concentrations used for activity was confirmed after estimating the MICs of each compound. The solvent used for assay was dimethyl sulfoxide (DMSO) which further diluted with water. Nutrient agar and PDA (Potato Dextrose Agar) was used as the growth medium for the bacterial and fungal species respectively. DMSO was used as a negative control. The results were compared with standard drug penicillin for antimicrobial activity by measuring the zone of inhibition in mm using 150 µg/mL were mentioned in table no.3. Antimicrobial activity was measured as a diameter of zone of inhibition (mm) .

**Table 1: Percentage yield and melting point of substituted 3-Cinnamoyl-4-Hydroxy-6- Methyl-2-Pyrones.**

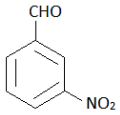
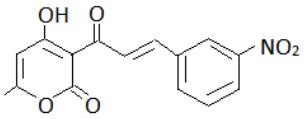
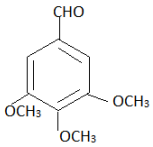
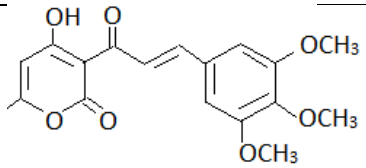
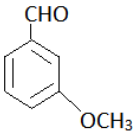
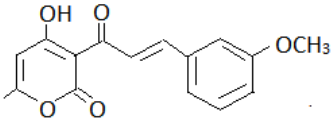
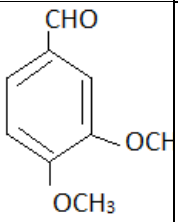
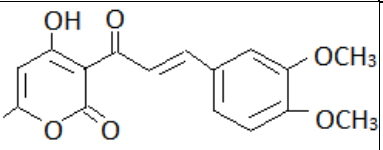
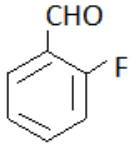
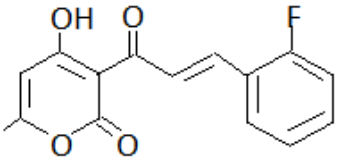
| Entry | X | Product | | Yield % | Melting point ºC |
|---|---|---|---|---|---|
| 1 |  | MBCI |  | 70 | 190 |
| 2 |  | MBCII |  | 80 | 198 |
| 3 |  | MBCIII |  | 85 | 195 |
| 4 |  | MBCIV |  | 80 | 176 |
| 5 |  | MBCV |  | 84 | 160 |

**Table 2 :** Physical data of Flavones derivation (MBFI-MBFV)

| Compounds | Molecular Formula | M. P (ºC) | Yield % |
|---|---|---|---|
| MBF I | $C_{15}H_9O_6N$ | 210 | 85 |
| MBF II | $C_{18}H_{16}O_7$ | 250 | 88 |
| MBF III | $C_{16}H_{12}O_5$ | 212 | 65 |
| MBF IV | $C_{17}H_{14}O_6$ | 205 | 80 |
| MBF V | $C_{15}H_9O_4F$ | 260 | 79 |

**Table 3.** Antimicrobial activity of Flavones

| **Compound** | **Bacteria** (Zone of Inhibition in mm) | | | **Fungi** (Zone of Inhibition in mm) | | |
|---|---|---|---|---|---|---|
| | **A** | **B** | **C** | **D** | **E** | **F** |
| MBF I | 14 | 19 | **21** | 13 | 16 | 14 |
| MBF II | 15 | 17 | 19 | 15 | 17 | 12 |
| MBF III | 18 | 15 | 18 | 18 | 15 | 18 |
| MBF IV | 19 | 18 | 18 | 12 | 18 | 17 |
| MBF V | 14 | 20 | 16 | 14 | **20** | 19 |
| Penicillin* | 11 | 10 | 12 | 10 | 12 | 13 |

***standard, A-** *S. aureus* **, B-** *E. coli* **, C-** *S. Typhi* **, D-** *Fusarium oxysporum***, E-** *Candida albicans* **, F-** *Aspergillus flavus.*

## ACKNOWLEDGEMENT

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# SPECTRAL ANALYSIS OF NEWLY SYNTHESIZED TERPOLYMER FROM O-AMINOPHENOL, OXAMIDE AND FORMALDEHYDE

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**ABSTRACT**
o-APOF terpolymers were meticulously synthesized through a condensation reaction involving o-Aminophenol (o-AP), Oxamide (O), and Formaldehyde (F). This intricate process took place in the presence of an acidic catalyst, where molecular ratios were systematically altered to explore diverse compositional variations. Utilizing a diverse range of spectroscopic techniques such as Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR), and UV-VISIBLE spectroscopy, the probable structures of newly synthesized polymers were successfully identified.

**KEYWORDS :** - o-Aminophenol, Oxamide, Formaldehyde, terpolymer, spectral analysis.

## INTRODUCTION

The synthesis of terpolymers, a fascinating endeavour at the intersection of organic chemistry and material science, has recently unfolded with intriguing possibilities. Terpolymers are important due to their ability to offer tailored properties through the combination of three different monomers. This versatility enables their use across various industries, including pharmaceuticals, electronics, and adhesives [1-5]. Terpolymers can be fine-tuned to optimize performance, making them valuable in composite materials and biomedical applications [6-7]. Their environmentally friendly attributes and contribution to research advancements in polymer science further enhance their significance in addressing diverse industrial and societal needs [8-9]. The significance of formaldehyde in terpolymers extends to applications in areas like adhesives, coatings, and materials requiring high durability [10-11]. The controlled integration of formaldehyde in terpolymer design allows for the customization of specific properties, making these materials adaptable to a range of industrial and technological needs. Moreover, the study of terpolymers involving formaldehyde contributes to advancing our understanding of polymer chemistry, offering insights into novel synthetic pathways and potential applications in various fields. Unlocking the potential of innovative materials, this research delves into the synthesis and characterization of terpolymers crafted from o-Aminophenol, Oxamide, and Formaldehyde. Through a comprehensive analysis using NMR, IR, and UV-VISIBLE spectroscopy, we aim to unveil the molecular intricacies and potential applications of these recently synthesized polymers.

## EXPERIMENTAL

***MATERIALS :*** o-Aminophenol (o-AP), Oxamide (O), and Formaldehyde (F) were utilized in their commercially obtained form for the experiment. Analytical-grade chemicals and solvents were exclusively utilized for all experiments.

***SYNTHESIS:*** A blend comprising o-aminophenol (1.091 g, 0.1 mol), oxamide (0.8807 g, 0.1 mol), and formaldehyde (7.5 mL, 0.2 mol) was subjected to heat in an oil bath at 130 $^0$C for 5 hours, intermittently agitated. The reaction took place in the presence of 200 mL of 2M hydrochloric acid (HCl) serving as a catalyst. The isolated o-APOF copolymer underwent washing with hot water and methanol to eliminate any remaining unreacted monomers. The resulting resinous product was washed with cold water, air-dried, and subsequently powdered. This powder underwent further washing with hot water and subsequent drying. The dried resins were subjected to extraction using diethyl ether, followed by petroleum ether. This process aimed to remove any potential presence of o-aminophenol-

formaldehyde copolymer along with the (o-APOF) copolymer. To purify the resin, it was dissolved in 8% NaOH, and reprecipitation was achieved by the gradual addition of 1:1 (v/v) HCl. Continuous and rapid stirring was employed throughout the process to prevent lump formation. The reprecipitation process was repeated twice to ensure thorough purification of the resin. The obtained copolymer resin, o-APOF-1, underwent filtration, followed by washing with hot water. Subsequently, it was air-dried, powdered, and stored under vacuum conditions using anhydrous $CaCl_2$.

Various resin samples, namely o-APOF-2, o-APOF-3, and o-APOF-4, were synthesized using different molar ratios of o-aminophenol, oxamide, and formaldehyde, specifically (2:1:3), (3:1:4), and (4:1:5). The synthesis details, along with the respective colors and melting points, are documented in Table 1 and the reaction route is given in fig.1.

**Table 1:** Terpolymer abbreviations, yield, and ratio

| Abbreviation | Reactants | | | Molar Ratio | Catalyst 2M HCl (ml) | Reflux temp. ±2K | Yield % | M. pt. |
|---|---|---|---|---|---|---|---|---|
| | o-Amino-phenol (mole) | Oxamide (mole) | Formaldehyde (mole) | | | | | |
| o-APOF-1 | 0.1 | 0.1 | 0.2 | 1:1:2 | 200 | 403 | 66 | 280 |
| o-APOF-2 | 0.2 | 0.1 | 0.3 | 2:1:3 | 200 | 403 | 74 | 325 |
| o-APOF-3 | 0.3 | 0.1 | 0.4 | 3:1:4 | 200 | 403 | 79 | 380 |
| o-APOF-4 | 0.4 | 0.1 | 0.5 | 4:1:5 | 200 | 403 | 90 | 430 |

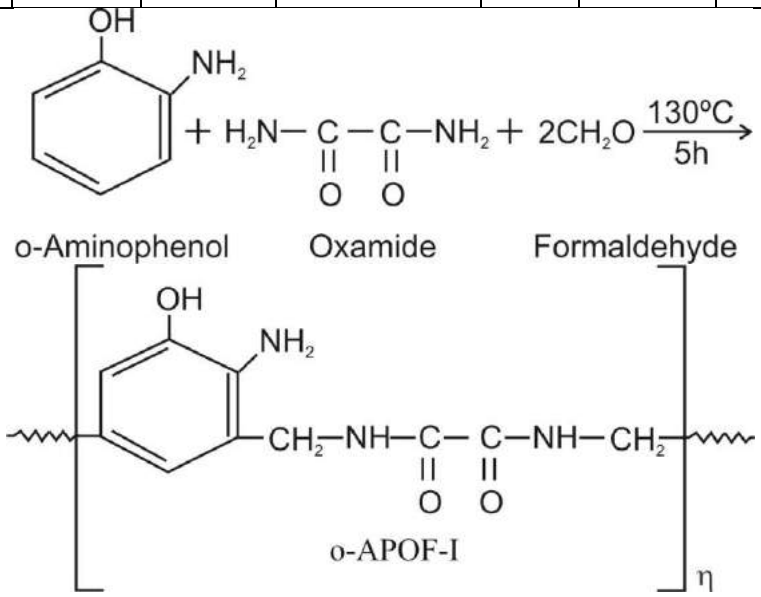


**Fig. 1** : Reaction scheme of the o-APOF terpolymer

## CHARACTERIZATION:

The FT-IR spectra of the synthesized terpolymers were obtained using a Perkin Elmer spectrophotometer. The scans were conducted in KBr pellets to facilitate the identification of linkages and functional groups present in the terpolymer. The $^1$H NMR spectra of the terpolymer resin were acquired using a BRUKER AVANCE II 400 NMR spectrometer, with DMSO as the solvent. Additionally, UV-VIS spectra of the terpolymer resin were recorded at room temperature using a UV-VIS-NIR Spectrophotometer Lambda 750, covering the wavelength range from 190 nm to 3330 nm.

## RESULTS AND DISCUSSIONS

**Spectral studies: -** IR spectral analyses reveal the uniformity in spectra among all o-APOF Copolymers, with Figure 2 illustrating the FT-IR spectrum of the prepared terpolymer resin samples. The broad absorption band in the 3399-3415 cm-1 range signifies the stretching vibration of phenolic

hydroxyl groups. Notably, the strong band in the 1620 to 1654 cm-1 range corresponds to the stretching vibrations of carbonyl groups (>C=O) in both acid and oxamide molecules. The presence of methylene bridges in the polymer chain is suggested by bands at 870, 1097, and 1311 cm-1, while sharp peaks at 1441 cm-1 indicate aromatic skeletal ring breathing modes. Additionally, a broad band around 3000 cm-1 in o-APOF copolymer resins is attributed to the –NH- of the oxamide unit.

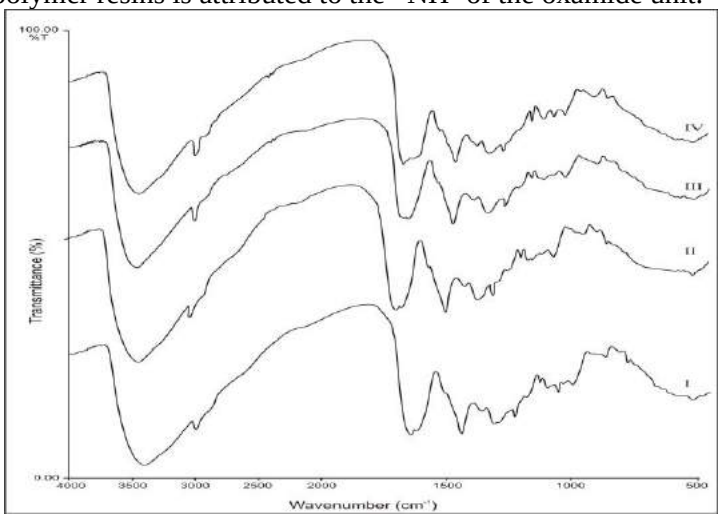


**Fig. 2 :** Infra-Red spectra of o-APOF terpolymers

Fig. 3 illustrates the $^{1}$H NMR spectrum of the prepared terpolymer resins. The spectra reveal distinctive features: the intense signals within the 8.2 to 8.4 ppm range are attributed to phenolic hydroxy protons, indicating intermolecular hydrogen bonding with the carbonyl group. A weak, unsymmetrical multiplate signal between 6.9 to 7.5 ppm corresponds to aromatic protons. The amido proton of the Ar-CH2-NHCO moiety is identified by a prominent peak at 4.6 to 4.9 ppm, while the methylene proton of the Ar-CH2-NH moiety appears in the 4.2 to 4.4 ppm range. With the exception of o-APOF-1 and o-APOF-2, o-APOF-3 and o-APOF-4 exhibit a singlet signal around 3.9 ppm. The aromatic amine is designated by a signal in the 2.6 to 2.8 ppm range.

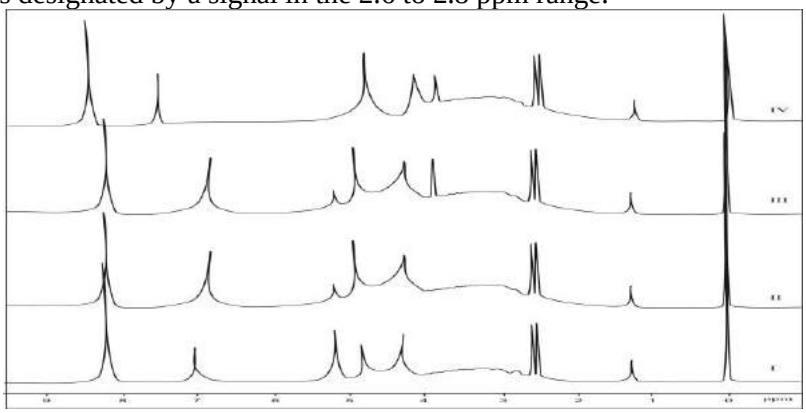


**Fig. 3 :** NMR Spectra of o-APOF terpolymers

Fig. 4 displays the UV-VIS spectra of the terpolymer resins. All terpolymers exhibit characteristic absorption bands at 260-280 nm and 297 nm, indicating the presence of a conjugated ketonic carbonyl group with a double bond in conjunction with the aromatic nucleus. The former, more intense band is attributed to p → p* transition, while the latter, less intense band may arise from n → p* electronic transition. The bathochromic shift towards longer wavelengths (280 and 297 nm) is attributed to conjugation effects, and the presence of phenolic hydroxy groups (auxochrome) leads to higher εmax values, indicating a hyperchromic effect. The increasing order of $\varepsilon_{max}$ values in o-APOF copolymer resins (o-APOF-1 < o-APOF-2 < o-APOF-3 < o-APOF-4) suggests the introduction of more chromophores (carbonyl groups) and auxochromes (phenolic-OH groups) in the repeated unit of the copolymer resins.

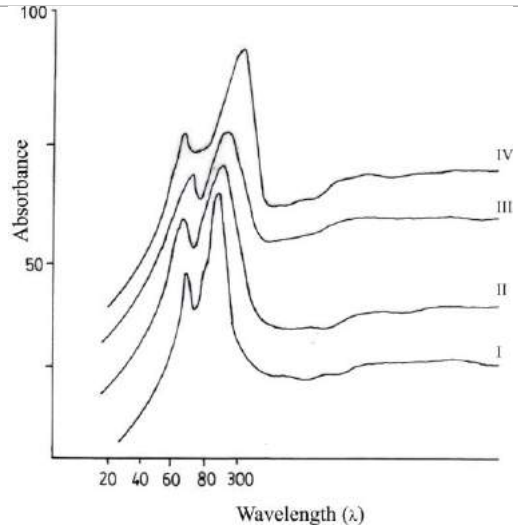


**Fig. 4 : UV-Visible Spectra of o-APOF terpolymers**

## CONCLUSION

The synthesized o-APOF terpolymers exhibited consistent structural features across FT-IR, $^{1}$H-NMR, and UV-VIS spectra. The presence of intermolecular hydrogen bonding and conjugation effects was evident from distinct peaks and shifts. The increasing $\varepsilon_{max}$ values in the UV-VIS spectra, correlated with the introduction of more chromophores and auxochromes, further elucidate the copolymer series' structural variations. This comprehensive analysis enhances our understanding of o-APOF terpolymers, underscoring their potential applications in diverse scientific and technological domains.

**ACKNOWLEDGEMENTS** Authors are thankful to the Director, SAIF, Panjab University, Chandigarh for providing spectral analysis.

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# Preparation and characterization of Pure ZnO and Cu doped ZnO nanoparticles

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**ABSTRACT**

Herein, we presented the synthesis of pure and Cu (5 %) doped ZnO nanocrystals using co-precipitation method. As synthesised nanoparticles were characterised by means of powder X-ray diffraction (XRD) and Ultraviolet visible (UV-vis.) spectroscopy to explored the structural and optical properties. The XRD results reveals that as prepared samples ZnO and 5 % Cu doped ZnO nanoparticles are with wurtzite phase. The average graine size were calculates using Scherrer formula and it shows 26.0 and 32.5 nm for ZnO and 5 % Cu doped ZnO nanoparticles. The UV-vis. absorption study explored the optical properties as well as using tauc's plot calculate the energy bandgap. The energy bandgap decreases from 3.93 eV to 3.75 eV of pure ZnO nanoparticles when Cu (5 %) doped.

***Keywords:*** *Nanoparticles, Co-Precipitation, XRD, UV-Vis. Spectroscopy.*

## INTRODUCTION

Materials science provide the diverse types of materials with excellent physicochemical and optical properties. Form the last century nanotechnology a very exciting technology attracts to the research community due to the vast scope [1]. Nanotechnology provides the nano dimensional materials and explore its size, shape, and morphology dependent properties. Nanotechnology gives the idea about the synthesis techniques of nanomaterials as well as provide the satisfactory explanation of size dependent properties [2]. Nowadays different types nanomaterials found to be investigated with different shape and size. However, metal oxide nanoparticles gained exceptional attraction due to their extraordinary properties [3]. Among the various types of metal oxide nanoparticles zinc oxide (ZnO) shows the excellent properties. ZnO nanoparticles are very easy to synthesised as well as it is nontoxic, ecofriendly with environment [4]. ZnO nanoparticles have the exceptional physical, optical, morphological properties, therefore it can be employed in the applications such as gas sensors, photocatalysis, antibacterial activity, solar cell, fuel cells, photovoltaics, etc. The structural, optical, magnetic, and electrical properties of the ZnO nanoparticles can be enhanced by doping the transition metals such as Cu, Mn, Al, Co, Fe etc. Especially Cu doping can be tuned the properties of ZnO considerably [5].

Thus, in present work we presented the synthesis of ZnO and Cu doped ZnO nanoparticles. As synthesised nanoparticles characterised via XRD and UV-vis. spectroscopy to explored the structural and optical properties.

## EXPERIMENTAL

All chemicals used in present study were analytical reagent grade and used as purchased. Zinc chloride, copper chloride ($CuCl_2$), and precursor sodium hydroxide (NaOH), was procured from Loba chem, India and used for synthesis the pure ZnO and Cu doped ZnO nanoparticles. Pure ZnO prepared by chemical co-precipitation method using zinc acetate (0.5M) and sodium hydroxide (1M) and Cu doped ing $Zn_{1-X}CXO$ (X=0.0, 0.2, 0.3, 0.4) concentrations was used.

## RESULT AND DISCUSSION

**XRD study (Structural properties):** The structural properties and phase purity of pure ZnO and Cu doped ZnO nanoparticles characterized via XRD characterization. Fig 1. Shows XRD pattern of pure ZnO and Cu doped ZnO nanoparticles. It reveals that the prepared nanoparticles are in high purity without any unwanted peak in pure ZnO [6]. As doping of Cu entity in ZnO there is no any extra peak observed concerned to the Cu this means a small amount of Cu not merely changed the structural properties of ZnO nanoparticles.

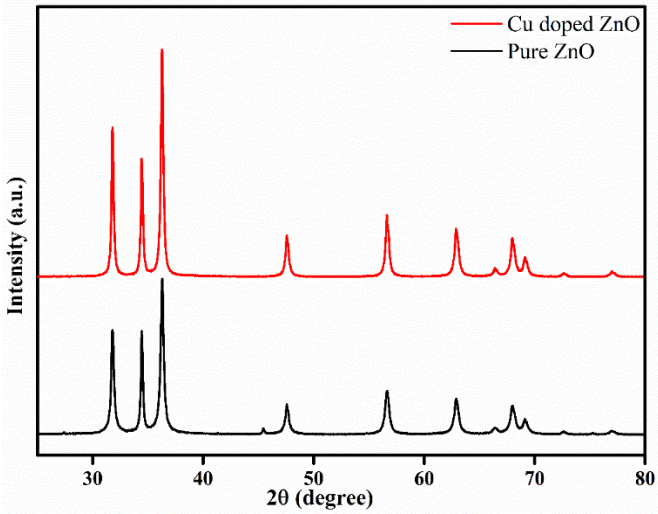


**Fig. 1:** XRD pattern of Pure ZnO and Cu doped ZnO nanoparticles

Table1 shows the crystallographic parameters of as synthesised pure ZnO and Cu doped ZnO nanoparticles. The average graine size were calculates using Scherrer formula and it shows 26.0 and 32.5 nm for ZnO and 5 % Cu doped ZnO nanoparticles. The grain size of the pure ZnO nanoparticles increased when the Cu incorporated.

**Table No. 1 Crystallographic parameters**

| | | |
|---|---|---|
| Crystal system | | Hexagonal |
| Space group | | P63mc |
| Space group number | | (186) |
| JCPDS card no. | | 96-230-0115 |
| a = 3.2190 (Å), | b = 3.2190 (Å), | c = 5.1490 (Å) |
| Alpha = $90^0$, | Beta = $90^0$, | Gamma = $120^0$ |

**UV-Vis. study (Optical properties):** Pure ZnO and Cu doped ZnO nanoparticles were characterized via UV–Vis. spectroscopy for analysis the optical features. Fig 2 (a) shows the absorption spectrum of pure and Cu doped ZnO nanoparticles. Spectrum shows the slight red shift in the absorption edge when Cu doped in ZnO nanoparticles. Fig 2(b) shows the tauc's plot which provide the band gap of pure ZnO and Cu doped ZnO nanoparticles. The bandgap decreased when Cu cations incorporated in the pure ZnO nanoparticles from 3.93 eV to 3.75 eV [7].

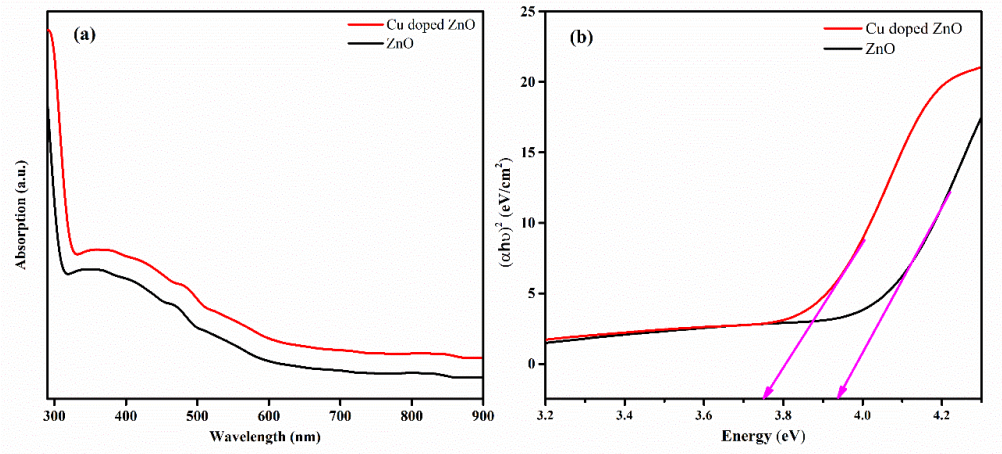


**Fig. 2(a)** UV-Vis. Absorption and 2(b) bandgap of pure ZnO and Cu doped ZnO nanoparticles

## CONCLUSION

In short, pure ZnO and Cu doped ZnO nanoparticles have been successfully synthesised using chemical coprecipitation technique. The structural properties of the synthesised samples studied via XRD characterization and it shows that the samples are in pure form without any external impurity. As well as the average particle size of ZnO nanoparticles increased from 26.0 and 32.5 nm when Cu doped in pure ZnO nanoparticles. Optical bandgap decreased from 3.93 eV to 3.75 eV when Cu doped in the pure ZnO nanoparticles.

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# Unveiling Nuclear Mysteries Comprehensive Insights into Structure and Shape Transitions with the Interacting Boson Model (IBM-1)

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**ABSTRACT**

This study delves into the intricacies of nuclear structure and shape transitions through a comprehensive examination employing the Interacting Boson Model (IBM). Developed by Arima and Iachello in the mid-1970s, the IBM serves as a bridge between the shell model and collective model in nuclear physics. In this model, even-even nuclei are defined as systems of N bosons, incorporating angular momentum zero (s-boson) and two (d-boson). The dynamical symmetry inherent in IBM, characterized by the unitary group U(6), provides a foundation for understanding collective nuclear properties across a range of medium and heavy nuclei

**Kewords:** *Quadrupole electrical transitions,B(E) transitions,Potential applications, Energy levels,Energy production,Material properties,Engineering applications*

## INTRODUCTION

The Interacting Boson Model(1, 2 & 2a) is An essential step to comprehend the nuclear structure which were first proposed by Arima and Iachello (1975-1976)in which an even-even nucleus is defined as a system of N bosons capable of occupy two levels, one with angular momentum constrained to zero (s-boson), and one with angular momentum two (d-boson), which could be affected by interactions between one or more bodies.

In the Interacting Boson Model(2b), The shell model and the geometrical (or collective) model, which were the two most popular paradigms in nuclear physics at the time, were integrated in this model. The IBM links the fermionic characteristics of the shell model to the bosonic behavior of the geometric model, placing it in the middle of these two complimentary approaches.The pairing property of short-range residual interactions is used to accomplish this. When the shell is more than half full, missing nucleons leave holes or vacancies that behave much like bosons.

The notion of dynamical symmetry (3) is fundamental, It offers a basic Hamiltonian that describe collective nuclear properties of several medium and heavy variety of nuclei and is based on approaches from algebraic group theory that are rather broad.

IBM-1 is the name of the model that does not distinguish between neutrons and protons. The IBM treats an even-even nucleus as a closed-shell core that is inert with valence nucleons or holes outside of the core. The total number of bosons in the IBM (3) is an invariant since the total number of valence nucleons is a conserved quantity.

A six-dimensional space(3.. and 3.) is defined by IBM-1 and is characterized in terms of the unitary group U(6). Three dynamical symmetry limits harmonic oscillator U(5), deformed rotator SU(3), and asymmetric deformed rotor O(6) are produced by various reductions of U(6).

Mohammed Abdul Ameer and Mushtaq A. H. Al-Shimmary(7) have been used the Interacting Boson Model (IBM-1 to calculate the energy levels, B(E2) transition probabilities, and electric quadrupole

moment $Q_{2_1^+}$ for the 180-190W isotopes in the SU(3)-O(6) transition zone have been investigated. The outcomes For all isotopes, were good agreement with experimental dataHossain and others (7a) used the interacting boson model-1 to study the nuclear structure of the yrast bands of the 180Hf, 182W, and 184Os nuclei which have for N = 108 neutrons. These nuclei's systematic yrast level, electric decreased transition probabilities $B(E_2)\downarrow$ deformation, and quadrupole moments were have computed, and the results had compared to the data from available experiments.For these nuclei, $R_{4/2}$ the ratio of the excitation energies of the first $4^+$ and first $2^+$ excited states was also investigated. Additionally, we had carefully compared the yrast leve l

$$R = \frac{(E2{:}L^+\rightarrow(L-2)^+)}{(E2{:}2^+\rightarrow 0^+)} \qquad (1)$$

of several low-lying quadrupole collective states to the available experimental data in order to quantify the evolution. Calculations have also been made for the related quadrupole moments and deformation parameters.Additionally, they examined the inherent quadrupole moments, deformation parameters, and systematic $B(E_2)$ values for these nuclei. For even atomic numbers $Z = 72, 74, 76\ and\ N = 108$ nuclei, the moment of inertia as a function of the square of the rotational energy has shown the nature of the back-bending features. The outcomes of these computations were in good accord with the pertinent experimental data that was available. For N = 108 nuclei, the analytical IBM-1 computation of the yrast levels and B(E2) values of even-even Hf, W, and Os had done in the SU(3) character space.Muyasser Fatehi Fadil and Imad Mamdouh Ahmed (7b) have investigated The Collective Properties of Even-Even 164–174W Isotopes, the Calculations of the 164–174W isotopes' ground states bands (GSB) and negative parity bands (NPB) have been performed. This was accomplished using the Bohr-Mottelson (BM), Interacting Boson Approximation-1 (IBM-1), and Interacting Vector Boson Model (IVBM).The primary information regarding the characteristics of the nucleus has been provided by the principal excited state $E_{2_1^+}$ and the ratio of the secondary the primary excited state $R_4^2 = \frac{E_{4_1^+}}{E_{2_1^+}}$ .To determine the ground state attribute of each nucleus, the ratio of gamma energy over spin $E_J$ of each state as a function of angular momentum $(J)$ (E-GOS) has been evaluated. In order to determine numerically the characteristics of the ground state band of all states and all nuclei, the ratio of energies of $(J + 2)$ and $(J)$, states as a function of the angular momentum $(J)$, has been studied. It is discovered that the $\Delta J = 1$ staggering between the ground state band and the octupole band exhibits a beat pattern as a function of angular momentum $(J)$.The approaches demonstrated the transitional $U(5) - O(5)$ properties of $W^{164-166}$ the universal $U(5) - O(6) - SU(3)$ qualities of 168W, and the transitional $O(6) - SU(3)$properties of $W^{170-172}$, while $W^{174}$ demonstrated the SU(3) properties.

**Theoretical Basis:**

The Interacting Boson model(3.), which can explain the shifting low-lying collective characteristics of nuclei across the whole main shell with a straightforward Hamiltonian, has become to be one of the most often used theoretical models. In IBM-1, a system of interacting s- and d-bosons (L = 0) was used to characterize the low-lying collective characteristics of even-even nuclei.

The model's six-dimensional unitary group U(6) has an underlying structure that results in a straightforward Hamiltonian that can describe the three dynamical symmetries U(5), SU(3), and O(6). The broadest IBM Hamiltonian(3.. and 3.) is denoted by:

$$\hat{H} = \epsilon_s(s^\dagger . s^\smile) + \epsilon_d(d^\dagger . d^\smile) + \sum_{L=0,2,4} \frac{1}{2}(2L+1)^{\frac{1}{2}} C_L \left[[d^\dagger \times d^\dagger]^L + [d^\smile \times d^\smile]^L\right]^{(0)}$$
$$+ \frac{1}{\sqrt{2}} v_2 \left[[d^\dagger \times d^\dagger]^{(2)} \times [d^\smile \times s^\smile]^{(2)} + [d^\smile \times s^\dagger]^{(2)} \times [d^\smile \times d^\smile]^{(2)}\right]^{(0)}$$
$$+ \frac{1}{2} v_0 \left[[d^\dagger \times d^\dagger]^{(0)} \times [d^\smile \times s^\smile]^L + [d^\smile \times s^\dagger]^{(2)} \times [d^\smile \times d^\smile]^{(2)}\right]^{(0)}$$
$$+ \frac{1}{2} u_0 \left[[s^\dagger \times s^\dagger]^{(0)} \times [s^\smile \times s^\smile]^{(0)}\right]^0 + u_2 \left[ + [d^\dagger \times s^\dagger]^{(2)} \times [d^\smile \times s^\smile]^{(2)}\right]^{(0)} \qquad (2)$$

Where:

$(s^\dagger, d^\dagger)$ are the creation operators for s-bosons and d-bosons, respectively

$(s^\smile, d^\smile)$ are an annihilation operators for s-bosons and d-bosons, respectively

This Hamiltonian contains two one-body terms specified by the parameters $\epsilon_s\ and\ \epsilon_d$ and seven two-body terms specified by the parameters $C_L\ (L = 0,2,4)$ , $v_L\ (L = 0,2)$ , $u_L\ (L = 0,2)$.

Where:

$\epsilon_s$ *and* $\epsilon_d$ are the single-boson energies .

Hamiltonian operator function according to IBM-1(2,2b, 2a and 7) is written as a multipole expansion in terms of creation and annihilation operators and the one in which it is simplest to comprehend the significance of each component in shaping the ultimate shape of the nucleus under investigation. The numerous boson-boson interactions are bundled in this parametrization so that the Hamiltonian has the form as follows:

$$\hat{H} = \epsilon\hat{n}_d + a_0\left(\hat{P}\hat{P}\right) + a_1\left(\hat{I}\hat{I}\right) + a_2\left(\hat{Q}\hat{Q}\right) + a_3\left(\widehat{T_3}\widehat{T_3}\right) + a_4\left(\widehat{T_4}\widehat{T_4}\right) \quad (3)$$

Where:

$\epsilon = \epsilon_d - \epsilon_s$ is the boson energy.

The operators :

$\hat{n}_d = \left(\hat{d}^\dagger\hat{\tilde{d}}\right)$ is the boson number operator

$\hat{P} = \frac{1}{2}\left(\hat{\tilde{d}}.\hat{\tilde{d}}\right) - \frac{1}{2}\left(\hat{\tilde{s}}.\hat{\tilde{s}}\right)$ is the pairing bosons operator

$\hat{I} = \sqrt{10}\left[\hat{d}^\dagger\hat{\tilde{d}}\right]^{(I)}$ is the angular momentum operator

$\hat{Q} = \left[\left(\hat{d}^\dagger \times \hat{\tilde{s}}\right) + \left(\hat{s}^\dagger \times \hat{\tilde{d}}\right)\right] - \frac{1}{2}\sqrt{7}\left(\hat{d}^\dagger \times \hat{\tilde{d}}\right)^{(2)}$ is the quadrupole operator

$\widehat{T_3} = \left[\hat{d}^\dagger \times \hat{\tilde{d}}\right]^{(3)}$ is the octupole operator

$\widehat{T_4} = \left[\hat{d}^\dagger \times \hat{\tilde{d}}\right]^{(4)}$ is the hexadecapole operator

The parameters $a$Type equation here., $a_0, a_1, a_2, a_3, a_4$, are express the strength of the interaction of the pairs, angular momentum, electric quadrupole, octaloupole, hexadecpole among the bosons, respectively.

The basis(3) for the vector representation of the U(6) group is the one s-boson and the five d-boson creation operators designated as $\{s^\dagger, d^\dagger, \upsilon\}$, v $\{\upsilon = -2, -1, 0, 1, 2\}$. As a result, using the second quantization technique, the 36 generators of the U(6) group can realize the model Hamiltonian.

**Nuclear Shape Transition:**

Phase transitions (3a MAX) are the structural adjustments to a physical system's characteristics. As some of the control parameters that restrict the system are changed, phase transitions may take place. Gilmore et al. discovered a control parameter called g that occurs in the quantum Hamiltonian that represents the system in phase changes known as ground state energy phase transitions.

quantum phase transitions depend on the symmetry that is hidden in the model hamiltonian, Symmetry ideas (3a) include pairs of symmetries since they act as benchmarks and, It is simple to compute the nuclei concatenation in such a phase transitional area.

Typically, a change in one parameter determines where they fall along the appropriate leg of the symmetry triangle. The ratio of the coefficients in the Hamiltonians of the two symmetries that conquer the triangle's apexes at the termini of the transition leg is typically used to determine this value. The transitional zones and the three dynamical symmetries are shown in the Casten triangle.

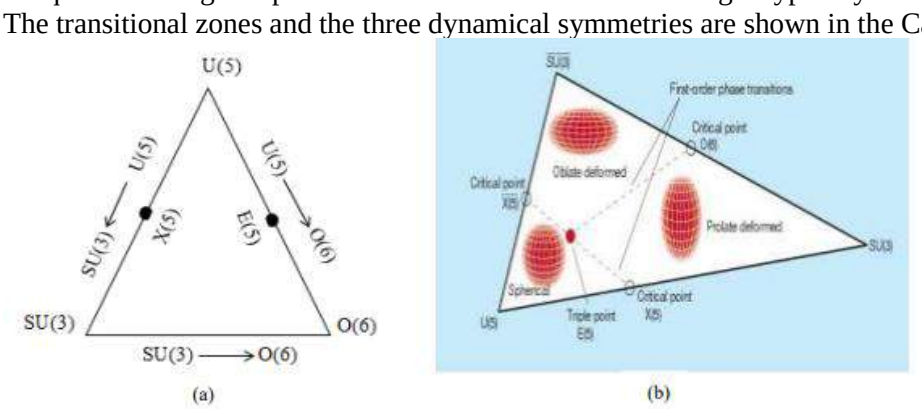


FIGURE 1. The Casten triangle (3a)

According to the three limiting symmetries (4) of the geometric collective model (GCM), namely: spherical vibrator, axially symmetric deformed rotor, and -unstable, there are three potential phases known as U(5), Su(3), and O(6).

Transition points and their crucial symmetries,

According to the three limiting symmetries(4), (3a) of the geometric collective model (GCM), namely: spherical vibrator, axially symmetric deformed rotor, and -unstable, there are three possible phases designated as U(5), Su(3), and O(6) respectively.

Also specified, are first-order phase transitions that there is a "transition between a spherical nuclear form and a prolate or oblate deformed one .a nuclear triple point exists that symbolizes the second-order. So the critical points of the phase transitions from spherical vibrator to unstable rotor, from spherical vibrator to axial symmetric rotor, from axially deformed shapes to triaxially deformed shapes, and for the transition from prolate to oblate nuclear shape were each described by the critical point symmetries E(5), X(5), Y(5), and Z(5), respectively .

Because the majority of nuclei (3a), share characteristics between these limitations, which are referred to as the phase of transition, and due to the fact that are so few nuclei that can be described by these limits, the limits can be easily examined. So the transition region can be classified into four groups.

Class A: U(**5**) → **S**(**3**)

Below the Hamiltonian operator for this nucleus, which exhibits behaviors in the transition area between the vibrational and rotational limits.

$$\hat{H}^{(\mathrm{I+II})} = \epsilon\widehat{n_d} + \alpha_1\hat{L}.\hat{L}+\alpha_2\hat{Q}.\hat{Q} \qquad (3)$$

The characteristics of the nuclei in this region are determined by the ratio $\epsilon\hat{d}/_{\alpha_2}$. As a result, as the ratio increases, the properties approach the $U(5)$ limit, while as the ratio decreases, the properties approach the $SU(3)$ limit.

Class B: SU(**3**) → **O**(**6**)

In the transition area, the nuclei have properties between the rotational limit and the $\gamma-$ unstable limit, and the Hamiltonian is

$$\hat{H}^{(\mathrm{II+III})} = \alpha_0\hat{P}.\hat{P} + \alpha_1\hat{L}.\hat{L}+\alpha_2\hat{Q}.\hat{Q} \qquad (4)$$

The characteristics of the nuclei in this region are determined by the ratio $\alpha_0/_{\alpha_2}$ . As a result, as the ratio increases, the properties move closer to the $\mathrm{O}(6)$ limit, while as the ratio decreases, they become closer to the $\mathrm{SU}(3)$ limit.

Class C: U(**5**) → O(**6**) (3a) and (3aa),

The transitional area of the nuclei shows properties between the vibrational limit and the $\gamma-$ unstable limit, and the Hamiltonian is :

$$\hat{H}^{(1+\mathrm{III})} = \epsilon\widehat{n_d} + \alpha_0\hat{P}.\hat{P} + \alpha_1\hat{L}.\hat{L}+\alpha_3\widehat{T_3}.\hat{T}_3 \qquad (5)$$

The ratio $\epsilon\hat{d}/_{\alpha_0}$ determines this limit's characteristics

Class D: U(**5**) → **S**(**3**) → **O**(**6**)

The Hamiltonian operator is given below, and the nuclei of this class contain the characteristics of the three limits.

$$\hat{H}^{(1+\mathrm{II+III})} = \epsilon\widehat{n_d} + \alpha_0\hat{P}.\hat{P} + \alpha_1\hat{L}.\hat{L}+\alpha_3\widehat{T_3}.\hat{T}_3 + +\alpha_4\widehat{T_4}.\hat{T}_4 \qquad (6)$$

**ENERGY RATIOS:**

The analytical solvable dynamical symmetries SU(3) and O(6) with schematically descriptions – soft nuclei are used to describe axial symmetric rotations and spherical vibrators in IBM. The unstable region γ –soft, from the ratio between

$$\frac{E_{8_1^+}}{E_{2_1^+}}, \frac{E_{6_1^+}}{E_{2_1^+}} \text{ and } \frac{E_{4_1^+}}{E_{2_1^+}} \qquad (7)$$

as in Table (1) Some ratios between the ground energy levels $8^+, 6^+$ *and* $4^+$ with the first excited state $2^+$ to match the three limits as exposed in Table (1).

.

TABLE 1. Typical energy levels ratios for each limits (6)

| **Limit** | $\frac{E_{4_1^+}}{E_{2_1^+}}$ | $\frac{E_{6_1^+}}{E_{2_1^+}}$ | $\frac{E_{8_1^+}}{E_{2_1^+}}$ |
|---|---|---|---|
| **SU(5)** | 2 | 3 | 4 |
| **O(6)** | 2.5 | 4.5 | 7 |
| **SU(3)** | 3.33 | 7 | 12 |

The potential energy surface (PES) :(4a)(4a.) ,

The nucleus can take on a final shape by The potential energy surface (3aa), The three Euler angles, $\beta$ *and* $\gamma$ (3a), are well-known geometrical values as five traditional variables for the IBA-1.

The Gilmore approach relies on the idea of intrinsic or coherent states in order to compute the upper and lower bounds of any operator's expectation values.

The bosonic a potential energy surface (PES) 4a of the nucleus (4a) and (4a.) is determined by the expected value of the total Hamiltonian in the intrinsic coherent state and generates a function of shape variables β and γ

The PES can be expressed using the intrinsic parameters and the Hamiltonian's parameters as a function of $\beta$ *and* $\gamma$, stated in terms of the Hamiltonian (3a) as following:

$$E(N,\beta,\gamma,\chi) = \langle N\beta\gamma|H|N\beta\gamma\rangle \qquad (8)$$

$$= g_1 \frac{N\beta^2}{1+\beta^2} + \frac{N(N-1)}{(1\_\beta^2)^2}[g_2\beta^2 + g_3\beta^3 cos3\gamma + g_4\beta^4] + C \qquad (9)$$

The energy surface only includes minima at $\gamma = 0°$ *and* $60°$ ' because, as one can see, $\gamma$ only appears in the term in $cos3\gamma$. There are no asymmetric minima.

Where:

The coefficients g are generated by linearly combining the model parameters.

$\epsilon, k_3 k_4$ namely

$$g_1 = \lambda + \left(2\chi^2 - \frac{\tau}{2}\right)k_4, \quad g_2 = 8k_4, \qquad g_3 = -8\sqrt{\frac{4}{7}}\chi k_4, \qquad g_4 = \frac{4}{7}2\chi^2 k_4$$

$$C = 10Nk_4 \quad , \qquad \lambda = \epsilon + 6k_3$$

## CONCLUSION

In conclusion, this research presents a comprehensive exploration of nuclear structure and shape transitions using the Interacting Boson Model (IBM). Through a meticulous examination of the IBM-1 variant within the SU(3)-O(6) transition zone, the study successfully aligns theoretical predictions with experimental data, affirming the model's efficacy in describing collective nuclear properties. The theoretical foundation, grounded in the dynamical symmetry of IBM characterized by U(6), provides a robust framework for understanding the behavior of medium and heavy nuclei. The delineation of phase transitions through the Casten triangle, exemplifying U(5), SU(3), and O(6) symmetries, enriches our comprehension of nuclear structure evolution. Furthermore, the identification of distinct transition classes (A, B, C, D) and the application of analytical solvable dynamical symmetries (SU(3) and O(6)) contribute to a nuanced understanding of axial symmetric rotations and spherical vibrators. Energy ratios emerge as crucial indicators of transitional properties, facilitating a refined classification of nuclear behavior. The exploration of the potential energy surface (PES) serves as a pivotal conclusion, offering insights into the final shape of nuclei through shape variables β and γ. The expression of the PES in terms of intrinsic parameters and Hamiltonian coefficients contributes to our understanding of the expected values and behavior of nuclear structures. In essence, this research not only validates the applicability of the IBM in describing nuclear phenomena but also advances our knowledge of nuclear structure and shape transitions. These findings hold significance for the broader field of nuclear physics, providing a solid foundation for further investigations and contributing to the collective body of knowledge in this domain.

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# A Green Synthesis of Honey Mediated Cobalt Chromite Nanoparticles and Their Expeditious Heterogeneous Catalytic Role for the Synthesis of 5-Aryl-4-Phenyl-1,2,4- Triazolidine-3-Thiones

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**ABSTRACT**

A new and environmentally friendly method for the simple synthesis of 5-aryl-4-phenyl-1,2,4-triazolidine-3-thiones has been revealed. It involves the reaction of phenyl hydrazine hydrate, isothiocyanate and various substituted aromatic aldehydes/cyclic ketone/isatins with heterogeneous honey-mediated cobalt chromite nanoparticle catalyst. In this context, firstly cobalt chromite nanoparticles were synthesized using honey as a natural precursor through a bio-derived approach. The benefits of this protocol are an easy workup using inexpensive precursors. The textural characteristics of the as synthesized chromite nanoparticles were examined via UV, XRD, FESEM, FTIR, EDX mapping, and VSM studies. Furthermore, $CoCr_2O_4$ nanoparticles were applied as a catalyst for the facile and one-step formation of 5-aryl-4-Phenyl-1,2,4-triazolidine-3-thiones and high yield makes the present method attractive, sustainable and economical and use of present methodology for synthesis of biologically potent molecules.

***Keywords***: *Cobalt chromite, Nanoparticles, Hydrazine hydrate, triazolidine-3-thiones*

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# Enhanced dielectric properties of lead-free Zn substituted $BaTiO_3$ based ceramic

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## ABSTRACT

Lead-free $BaTiO_3$ (BTO) ceramic is the first artificial polycrystalline ferroelectric material which is widely used material due to its high ferroelectric and dielectric properties and can be utilized for various applications. In this present work, synthesis and characterization of Lead-free $Ba_{1-x}Zn_xTiO_3$ (for x=0,0.03, 0.05 & 0.07) ceramic was studied with structural, morphological, and dielectric properties by the hydroxy coprecipitation method. The X-ray diffraction (XRD) pattern of the corresponding samples confirms the formation of a pure perovskite structure with a tetragonal crystal structure. From the SEM image, it is found that the average grain size of corresponding samples increases with increasing Zn dopant. EDS shows the presence of all the elements Ba, Zn, Ti, and O in all samples confirming the phase purity of all samples. The dielectric properties of Zn-substituted $BaTiO_3$ exhibit mild relaxor behavior with an increased dielectric constant at the Curie temperature (Tc) for different frequencies as a function of temperature. It is also observed that the Curie temperature (Tc) of $BaTiO_3$ increases with an increase in Zn concentration at a frequency of about 1KHz. The variation of dielectric loss tanδ as a function of temperature for different frequencies gives significant results. From the dielectric properties as a function of frequency, it is observed that the dielectric constant increased with increasing Zn concentration.

***Keywords**: Hydroxide Coprecipitation Method, XRD, SEM, EDS, Dielectric Properties.*

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# In vitro Magnetic Hyperthermia Studies of Super Paramagnetic Zinc Spinel Ferrite Nanoparticles

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**ABSTRACT**

Recently, magnetic nanomaterials in particular spinel ferrite nanoparticles were emerged as an active nanoplatform for the biomedical applications due to their easy control, stability, low toxicity and biocompatibility. The present work focuses on in vitro magnetic hyperthermia studies of super paramagnetic zinc spinel ferrite nanoparticles($ZnFe_2O_4$) prepared by wet chemical sol-gel auto combustion method. The prepared nanoparticles were well characterized by the standard technique for structural, morphological, magnetic and dispersibility investigations. To know the capability of prepared nanoparticles for effective use in magnetic hyperthermia applications the in vitro magnetic hyperthermia analysis was performed. To confirm the non-toxicity of the prepared nanoparticles, the reactive cell viability analysis was performed for appropriate cell line assay. The present outcomes demonstrate that magnetic hyperthermia therapy induces the significant bio-heat production that is accountable for the killing of the cancer cells via self-apoptosis.

***Keywords:*** *Zinc ferrite, Magnetic hyperthermia, In vitro, Super Paramagnetism*.

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# Nickel- zinc ferrite thin film for supercapacitor application.

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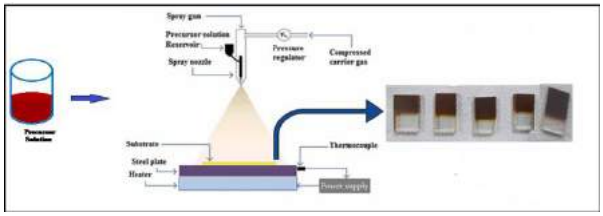
## ABSTRACT

The nickel–zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$ where x= 0.0, 0.25, 0.50, 0.75 and 1.0 thin films have been successfully deposited on FTO substrates using spray pyrolysis technique. The annealed thin film was characterized by using X-ray diffraction (XRD) analysis revealed that annealed films exhibit spinel cubic structure with space symmetry Fd-3m. From XRD, the average crystallite size is 15-30 nm calculated by Debye Scherrer's formula of the $Ni_{1-x}Zn_xFe_2O_4$ thin film. The FESEM study the morphology having grain size is 8 – 28 nm. The UV-Visible spectra give the absorption peak. The highest band gap is 1.82 eV calculated by using Tauc plot. Raman spectra shown the strong vibrational mode above approximately 600 $cm^{-1}$. The electrochemical supercapacitor study of $Ni_{1-x}Zn_xFe_2O_4$ thin films has been carried out in 3 M LiCL electrolyte.

***Keywords:*** *Spray pyrolysis, thin films, crystal structure, morphology, Optical properties, Raman, cyclic voltammetry, supercapacitor.*

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# Highly Sensitive Electrochemical Sensor for Detection of Aspartame Using a Modified Carbon-based Electrode

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**ABSTRACT**

This study presents the development of an electrochemical sensor for detecting aspartame, utilizing a carbon rod extracted from discharged zinc-carbon batteries. The electrode was meticulously modified with Co3O4 nanodiamonds (NDs), Ni-Metal-Organic Framework (Ni-MOF), and an ionic liquid (1-butyl-3-methylimidazolium methyl sulfate) dispersed in ethanol. The resulting Co3O4 NDs/Ni-MOF/IL/graphite electrode exhibited a surface area of 32.98 $mm^2$, showcasing exceptional electrocatalytic activity**.** Cyclic Voltammetry (CV) analysis in a phosphate buffer solution at pH 2.0 revealed that the modified electrode could efficiently oxidize aspartame at a potential of 1.75 V, with a distinctive anodic peak observed at 0.4 V. Characterization techniques, including Field Emission Scanning Electron Microscopy (FE-SEM), X-ray Photoelectron Spectroscopy (XPS) and optical profilometry confirmed the successful integration of Co3O4 NDs, Ni-MOF, and the ionic liquid onto the graphite electrode, ensuring structural integrity**.** Comparative studies with a bare electrode demonstrated that the sensitivity and detection limits of the modified electrode were eight-fold greater. The concentration analysis of powder and tablet samples yielded concentrations of 36 µM and 60 µM, respectively. The developed sensor exhibited a high level of sensitivity and detection capabilities, positioning it as a reliable tool for efficient aspartame detection across diverse matrices. The LOD (Limit of Detection) and LOQ (Limit of Quantification) for the modified electrode were determined to be 0.34µM and 1.05µM, respectively, highlighting its exceptional performance. Furthermore, the obtained correlation coefficient ($R^2$) of 0.997 attests to the accuracy and reliability of the sensor in quantifying aspartame concentrations. The heightened sensitivity and detection capabilities of the modified electrode underscore its potential application in quality control and safety assurance processes, where precise determination of aspartame levels is crucial. Finally, this electrochemical sensor demonstrates remarkable efficiency, offering a promising solution for aspartame detection with implications for various industries and regulatory practices.

***Keywords:*** *Electrochemical sensor, cobalt oxide nanodiamonds, Ni-Metal organic framework, aspartame detection*

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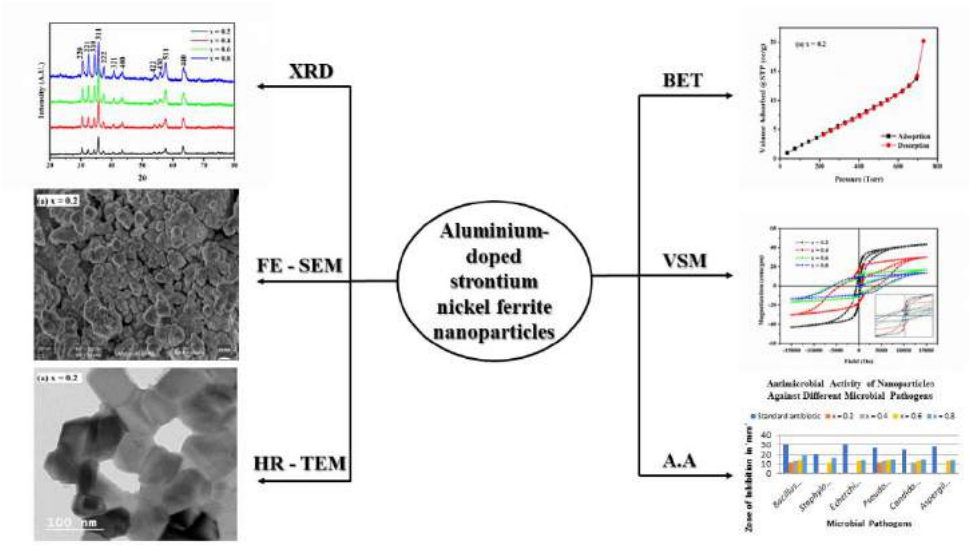
# Exploration of the structural and antimicrobial properties of aluminium-doped nickel-strontium ferrite nanoparticles synthesised by the sol-gel auto combustion route

**Rajkanya M. Bhore[a], Radhakrishnan M. Tigote[a*], Subiya K. Kazi[a], Sanjay R. Chavan[a], Rahul M. Khobragade[b], Gulab Puri[b]**

## ABSTRACT


Sol-gel autocombustion resulted in aluminium-doped strontium co-substitution of nickel ferrite nanoparticles, which have an 84% thermal stability.

The material's optical band gap ranges from 3.62 to 3.75 eV, with its maximum absorption occurring a t approximately 302.57 nm. X-ray diffraction (XRD) was used to investigate the structural characteristics of the Al-Sr-Ni-ferrite particle size, which was found to be between 18 and 25 nm. Field emission scanning electron microscopy (FE-SEM), Brunauer Emmett-Teller (BET), and high-resolution transmission electron microscopy (HR-TEM) confirmed the morphology and surface area, indicating an irregular cubical shape.

In the VSM investigation, the synthesised material exhibits paramagnetic behaviour. Energy dispersive X-ray spectroscopy was used to confirm the presence of every element. A BET adsorption isotherm indicates that the total surface area is between 8.00 $m^2g^{-1}$ and 24 $m^2g^{-1}$. The total pore volume varies from 0.011 $cm^3g^{-1}$ to 0.037 $cm^3g^{-1}$ at P/Po (0.99). Type III with an $H_3$ hysteresis loop is demonstrated by the isotherm, and the average pore width varied between 5.44 and 6.49 nm. A dielectric study revealed that ε and tan δ decreased with $Al^{3+}$ and $Sr^{2+}$ doping. Spinel ferrite has been treated with $Ni^{2+}$ ions to lower loss and dielectric constant. These nanoparticles are effective against both Gram-positive and Gram-negative bacteria as well as fungal diseases. These have antimicrobial qualities.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# Synthesis of zirconium doped lanthanum orthoferrites and their structural features

**Pradip B. Jagtap, Mahesh M. Gurav, Pranjali D. Chaudhari, Shruti G. Mudbikar, Y. D. Mane, Subiya K. Kazi, Radhakrishnan M Tigote***

## ABSTRACT

The zirconium-doped lanthanum orthoferrite nanoparticles were synthesised using the sol-gel process. The nanoparticle samples have an orthorhombic crystal structure, as confirmed by lattice parameter values obtained from x-ray diffraction (XRD). From XRD, it was also confirmed that the crystalline size ranges between 20 and 28 nm. The FE-SEM analysis revealed that the average particle size was 24 nm. X-ray energy dispersive spectroscopy (EDS) confirms that all the constituent elements (La, Zr, Fe, and O) in the nanomaterials were present without any impurities.

***Keywords:*** *sol-gel process, prevoskite, zirconium-doped orthoferrites*

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# Influence of Zirconium Doping on the Structural, Magnetic, and Electrical Properties of Lanthanum Spinel Ferrites

**Rahul B. Bhakte, Shraddha C. Waghmare, Ashwini A. Malkhare, Mahesh M Gurav, Jaishri L. Somwanshi, Subiya K Kazi, Radhakrishnan M. Tigote***

**ABSTRACT**

Nano ferrite Zirconium-doped lanthanum ferrite is synthesised by using the sol-gel auto-combustion method. The structural studies of these ferrites were carried out by X-ray diffraction (XRD), which confirmed the pure spinal cubic structure of ferrites for all concentrations, including crystalline size and lattice parameters. Magnetic properties such as saturation magnetization (Ms), residual magnetization (Mr), and corocetivity (Hc) of the produced spinel ferrite were investigated by using a vibrating sample magnetometer (VSM), and the higher value of saturation magnetization obtained for the sample was 13 emu/g. FE-SEM analysis revealed that the average particle size of synthesised ferrite was 27 nm.

***Keywords:*** *Nanocatalysts, magnetic property, electrical property*

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# Synthesis of Bifeo$_3$ Incorporated PVDF Films and Its Utilization in Piezoelectric Energy Harvesting

**Arijit Ghosal[1], Ashik Ikbal[1], Payal Sengupta[1] and Ruma Ray[1*]**

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The Current paper deals with the synthesis of Bismuth Ferrite $BiFeO_3$ (BFO) Nanoparticles by the method of Sol-Gel reaction by using Bismuth nitrate pentahydrate ( $Bi(NO_3)_3 .5H_2O$ ), Iron nitrate nonahydrate ( $Fe(NO_3)_3 .9H_2O$ ), L-(+)-tartaric acid ($C_4H_6O_6$) and diluted nitric acid ($HNO_3$, 64%) with proper required ratio. The physicochemical properties were evaluated through characterization studies such as X-ray diffraction spectroscopy (XRD), Fourier-Transform Infrared Spectroscopy (FTIR). Refinement Rietveld reveals that BFO Nanoparticles have existence of a distorted rhombohedral perovskite structure (space group- R3c) with lattice parameters $a = b = 5.5740$ & $c = 13.8565$ and $\alpha = \beta = 90°$ & $= 120°$ . We have also made the $BiFeO_3$- (BFO) Polyvinylidene Fluoride (PVDF) composite films for different weight percentages (3%, 5%, 7% and 10% ) of BFO. We have examined the Crystalinity of those composite films for said weight percentages of BFO. We also have calculated the amount of the electroactive phase (increase significantly ~ 94 %) is carried out of BFO-PVDF composite films for those weight percentages. $BiFeO_3$ has been researched in many application fields, but has rarely been investigated for the energy conversion from mechanical motions to electricity. So we demonstrate the fabrication of a flexible piezoelectric Nanogenerator based on BiFeO3 nanoparticles. This BFO Nanoparticles−PVDF composite device exhibits an output open circuit pk-pk voltage of ∼60V under repeated hand pressing.

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# Electrodeposited $NiCo_2O_4$ thin film for Supercapacitor Application

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**ABSTRACT**

With rapid surge of energy requirement globally, the demand of eco-friendly renewable energy is also growing at exponential pace. The efficient renewable energy system requires state of art storage system in order to function smoothly. So, interest in designing different energy storage system such as supercapacitor are growing among researchers. A good supercapacitor requires an effective electrode material to operate in any adverse condition [1]. In this work, rhombus shaped nanoflakes of $NiCo_2O_4$ is successfully deposited on SS-304 substrate via electrodeposition method. The structural properties have been analyzed using XRD, AFM and FE-SEM images revealed the surface morphology of as deposited thin film. Electrochemical activity of the deposited film investigated by using CV, GCD and EIS techniques [2]. CV curves shows pseudocapacitive nature of $NiCo_2O_4$ nanoflakes with good specific capacitance of 266 F/g at current density of 0.5 A/g. From this work we can conclude that inexpensive $NiCo_2O_4$ thin film synthesized by electrodeposition method can serve as a potential candidate for superior supercapacitor electrode.

***Keywords:*** *$NiCo_2O_4$, CBD, Spinel Oxide, supercapacitor, Electrochemical activity*

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# A Hybrid composite of g-C3N4/NiFe2O4/PANI WITH ENHANCED ELECTROCHEMICAL PERFORMANCE FOR ENERGY STORAGE APPLICATION

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**ABSTRACT**

In this work, we report the synthesis of graphitic carbon nitride/ Nickel ferrite/Polyaniline (g-$C_3N_4$/$NiFe_2O_4$/PANI) based hybrid composite by hydrothermal method followed by in situ polymerization. The electrochemical performance of g-$C_3N_4$/$NiFe_2O_4$/PANI as an electrode for supercapacitor application was investigated using cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and Electrochemical Impedance spectroscopic (EIS) techniques. GCD studies revealed that the specific capacitance of g-$C_3N_4$/$NiFe_2O_4$/PANI composite was 770 $Fg^{-1}$ at 1 $Ag^{-1}$ current density

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# *Study on structure, morphology and optical property of co-doped ZnO nanoparticles*

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**ABSTRACT**

ZnO nanoparticles with the size ~ 47 nm to 71 nm were prepared by dual doping of Ag+ and Al3+ ions using sol gel chemical synthesis method. With the continuous growth in the optoelectronic industry, today the demand for novel and highly efficient semiconductor materials is also increasing. We have studied the effect of co-doping (AZO doped with silver) on the $Al_5(ZnO)_{95-X}Ag_X$ (where x=0, 2, 4,and 6%) nanoparticles which was synthesized by most reliable and cost effective sol gel method. Our study will definitely fill the gap between the future prospects of new researchers. We have characterized the materials for X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), EDAS, ultraviolet-visible (UV-Vis) absorption spectroscopy analysis and FTIR. XRD results confirmed the crystallinity and hexagonal wurtzite structure of Ag+ and Al3+ doped ZnO nanoparticles. It is observed that the increase of the Ag dopant ratio reduced the crystallite size. EDS and FT-IR data supported the purity of samples. The optical band gap values showed a blue shift (2.64 eV to 2.81 eV) as the Ag doping ratio increased. The blue shift is discussed in terms of the doping process and induced some transitions on inter bands.

***Keyword:*** *Co-doped Zinc oxide, sol gel, optical band gap.*

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# Spectroscopic and Dielectric Study of Dimethylformamide - Alcohol Binary Liquid Mixtures for Investigation of Molecular Interactions

**Shivraj R. Manegopale[1], Prabhakar B Undre[2]* A. A. Wadodkar[3], Ram H. Kadam[1]**

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**ABSTRACT**

The frequency dependent dielectric relaxation spectra for binary mixture of N, N dimethyl formamide with 1-propanol and 2-propanol at 11 different concentrations at 288 K, 303 K and 308K over frequency range 10 MHz to 20 GHz is studied. The Least squares fit method has employed to obtain the static dielectric constant ($\varepsilon_o$) and relaxation time ($\tau$). Excess permittivity ($\varepsilon^E$), excess inverse relaxation time $(1/\tau)^E$, Kirkwood correlation factor ($g^{eff}$), and corrective Kirkwood correlation factor ($g^f$) have been determined and discussed in terms of the effect of $NH_2$ and $-CH_3$ side group on molecular dynamics and intermolecular hydrogen bonds. Conformational analysis of the formation of hydrogen bond is supported by the Fourier transform infrared spectroscopy and UV-Visible spectroscopy.

***Keywords:*** *Dielectric relaxation, excess dielectric constant, Time Domain Reflectometry, FTIR, UV-Visible spectroscopy, Molecular dynamics*

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# n-n Junction Based Semiconducting $CdO/La_{0.3}Ca_{0.7}MnO_3/Al_2O_3$ Storage Studies for ReRAM Applications

**Nisarg Raval[1], C.M. Panchasara[1], Bharavi Hirpara[1], Sukriti Hans[2], M. Ranjan[2], K.N. Rathod[1,3], Davit Dhruv[1], A.D. Joshi[4], P.S. Solanki[1], N.A. Shah[1,*]**

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The semiconducting n-n junction based $CdO/La_{0.3}Ca_{0.7}MnO_3/Al_2O_3$ (CdO/LCMO/ALO) heterostructures were grown with different thicknesses of the LCMO layer (i.e., 150nm and 200nm) using Chemical Solution Deposition (CSD) method. The investigations on the structural phases using X–ray diffraction (XRD) confirm the single-phase nature of LCMO and CdO without any other impurities. The atomic force microscopy (AFM) was carried out to study the surface morphology for both heterostructures and also quantitative topographic studies of rms surface roughness, granular profile analysis and grain size distribution were undertaken. Also, the temperature-dependent resistivity measurements were performed in order to understand the responsible charge transport mechanism across the interface of CdO/LCMO. The ρ(T) measurements confirm the semiconducting behaviour throughout the temperature range studied which can be understood by Mott type Variable Range Hopping (VRH) model. In order to support and confirm the application side of this prototype device for the data storage purpose, the temperature dependent resistive switching measurements were carried out that shows the sharp set and reset processes at particular voltages and shifting in these voltages were also obtained due to temperature variations. The resistive switching window with a perfect set-reset operations validates the capability of this prototype to be used as a Resistive Random-Access Memory (ReRAM) storage device.

***Keywords***: *n-n Junction; ReRAM; Resistive Switching.*

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# Electroresistance and Field Effect Studies on Manganite-Manganite Composite Structure

**Uday Kareleeya[1], Bhargav Rajyaguru[1,2], Keval Gadani[3], K. Asokan[4], R.J. Choudhary[5], D.M. Phase[5], N.A. Shah[1], P.S. Solanki[1,*]**

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**ABSTRACT**

In this present work, we have successfully fabricated a $LaMnO_{3-\delta}/La_{0.7}Ca_{0.3}MnO_3LaAlO_3$ using low cost and environment friendly chemical solution deposition (CSD) method. The structural characteristics of the LMO/LCMO/LAO metal-insulator-manganite composite structure have been carried out by performing the method of X-ray diffraction (XRD) measurements, specifically the θ – 2θ and φ – scan techniques. The influence of electric field across the electrically polarizable LMO layer and LCMO conducting channel has been investigated using field effect configuration (FEC) coupled field effect studies (FES). Colossal electroresistance (CER) at room temperature is ~ 7000% under 2MV/Cm forward biased control electric field and large CER ~$8.5 \times 10^5$ % under 0.9 Mv/cm reverse biased control electric field. This type of manganite-manganite composite structures are used in the development of spintronic based logic and memory devices.

***Keywords:*** *Electroresistance; Field effect studies; Chemical solution deposition*

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# Field Effect Studies on Swift Heavy Ion Irradiated Manganite Based Thin Films for Device Applications

**C.M. Panchasara[1], Nisarg Raval[1], K.N. Rathod[1,2], R.C. Meena[3], Ambuj Tripathi[3], Davit Dhruv[1], A.D. Joshi[4], P.S. Solanki[1], N.A. Shah[1*]**

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**ABSTRACT**

Monovalent-doped manganites, specifically transition metal oxides, have gained significant interest for various device applications due to their unique electronic, magnetic and transport properties. In the present communication, the structural and electrical transport characteristics of advanced pulsed laser deposited (PLD) $La_{0.85}Na_{0.15}MnO_3$ (LNMO) thin films on single crystalline Nb:$SrTiO_3$ i.e. (SNTO) (*100*) substrate with two distinct film thicknesses i.e. 100 nm & 200 nm have been examined. The structural characteristics of the LNMO were measured using an X-ray diffraction (XRD) measurement at room temperature, which reveals single phase development of the required thin films. One of the thin films is kept in pristine condition, while the other thin films were exposed to $Ag^{15+}$ ions with an energy of ~120 MeV and a fluence of $1 \times 10^{12}$ ions/cm$^2$ at 15 UD Pelletron accelerator at Inter-University Accelerator Centre, New Delhi, India. After Irradiation, one set of the two films was annealed at 600˚C under oxygen environment for 6 h. The resistive switching properties were examined across LNMO/SNTO interface with Ag as electrode in current perpendicular to plane (CPP) geometry at room temperature. The resistive switching effect has been discussed in the context of external electric field induced movement of charge carriers across LNMO/SNTO interface

***Keywords***: *Monovalent doped manganites, PLD, Swift heavy ion irradiation, Field effect studies.*

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# Structural and Electrical properties of Fe doped ZnO nanoparticles using sol-gel methods

**Tanveerhasan Vhora[1], Rujuta Lehru[1], Jaydeep Radhanpura[1], V.S. Vadgama[1], Himanshu Dadhich[2], V.R. Rathod[3], N.A. Shah[1], P.S. Solanki[1]**

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**ABSTRACT**

In this report, Fe doped ZnO nanoparticles, with various doping percentage of Fe were grown successfully using sol-gel method. X - ray diffraction (XRD) measurement reveals the presence of extra phase of $ZnFe_2O_4$ in all samples. AFM image reveal that with increase in Fe doping, grain size gets decreased and grain boundary density gets increased. Dielectric measurements show high dielectric constant is obtained for higher concentrations of Fe doped ZnO samples. Frequency dependent electrical conductivity has been discussed based on Jonscher's power law fit that suggests conduction of charge carrier through correlated barrier hopping (CBH) mechanism. Impedance spectroscopy measurement suggests that for large content of Fe in ZnO system, it's improved dielectric nature of sample, the conduction mechanism identified using equivalent circuit of cole-cole plots temperature dependent dielectric studies revel the enhancement in electrical polarization with increase in temperature. Magnetic dependent dielectric studies show the roles of grain boundary nature and grain density in Fe doped ZnO nanoparticles.

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# Effect of Sintering Temperature on Chemically Grown Nd Doped $LaMnO_3$ Nano Particles

**Amiras Donga [a,b], Hardika Goswami [a,c], Bharavi Hirpara [a], Urvashi Jambukiya [a], Sangita Chavda [a], Keval Gadani [d], Davit Dhruv [a], P.S. Solanki [a], N.A. Shah [a], A.D. Joshi [e]***

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**ABSTRACT**

In this study, the cost-effective Sol-Gel approach was used in this study to synthesized $La_{0.5}Nd_{0.5}MnO_3$ (LNMO) manganites. It has been investigated that the electrical and optical properties of LNMO samples are influenced by the sintering temperature. According to structural study by X-ray diffraction (XRD), the materials are found to be single-phasic in nature without any detectible impurities. The scanning electron microscopy (SEM) measurement was carried out to investigate the variations in grain size with changing sintering temperatures. Moreover, grain size grows as sintering temperature rises because of the agglomeration effect. Utilizing energy dispersive X-ray spectroscopy (EDX), the chemical composition of the synthesized materials' component constituents has been investigated. To examine the electrical properties of the materials. The dielectric and resistivity measurements were performed. Throughout the frequency range studied, it can be observed that dielectric constant increases with increase in sintering temperature. Maxwell–Wagner mechanism and Koop's theory has been used to study the dielectric behavior. Here, using different applied constant DC currents, we also investigated the behavior of temperature-dependent resistivity for all the sintered samples. The resistivity of all the nanostructured LNMO manganite samples reduces as temperature increases over the temperature range, indicating a negative temperature coefficient for the materials and, consequently, a semiconductor behavior for all the samples. Optical measurements were performed using UV-Vis (UV-visible) spectroscopy. The nature of energy band gap with sintering temperature of the nanostructured LNMO was calculated using Tauc's law, where band gap increases with increase in sintering temperature. The stretching mode involving the internal motion along the length of the Mn–O bonds is depicted in Fourier Transform Infrared Spectroscopy (FTIR) recordings made at ambient temperature. This has been correlated with a characteristic vibration of the $ABO_3$ perovskite.

***Keywords:*** *Manganite, Sol-Gel, Dielectric, Resistivity*

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# Phytochemical screening of pods of Acacia Farnesiana (L.) wild from Mimosaceae family

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**ABSTRACT**

Phytochemical study of pods of Acacia Farnesiana (L.) wild was studied from Family Fabaceae and sub family Mimosaceae was studied. The plants belonging to Fabaceae family are mostly herbs; some of them are shrubs and trees found in both temperate and tropical areas. The plant is medium sized shrub with many branches. It is a drought hardy, fire resistant species that does not tolerate frost. The pods of the plant are used for medicinal purposes in cough and cold. The mature pods are swallowed by removing the seeds inside from it. This part of the pods was used for screening purpose.

The matured pods of were collected and shade dried. The seeds from the pods were removed and the pods were grind for fine powder. The powder sequentially extracted with ether, ethyl acetate, chloroform and methanol. The extracts were collected and the solids and viscous liquids from the each solvent kept for further purposes.

The Phytochemical study of the seeds of Acacia Farnesiana (L.) wild reported non protein amino acids. Flavonoids, triterpenoids, glucosides and various fatty acids are the reported phytochemicals from the species. Nonacosane, tricoantane, Gallic acid, Stearic acid, Palmitic acid and Flavonoids were observed from the pods.

***Keywords:*** *Phytochemicals, Pods, Acacia Farnesiana, Flavonoids, Tri terpeonoids, Glucosides, Nonacosane, Palmitic acids.*

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# Structural And Electrical Properties of $La_{0.85}Na_{0.15}MnO_3$: ZnO Composites

**N. A. Chondagar [1], Hardika Goswami[1], Keval Gadani[2], Alpa Zankat[1], N. A. Shah and P. S. Solanki[1].**

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**ABSTRACT**

In this communication, nanostructured Na-doped $LaMnO_3$ manganite was successfully synthesized using low cost, easy, environment friendly and acetate precursor- based sol-gel method. ZnO was synthesized using solid state reaction that shows particle size in micron size. ZnO is known for high insulating nature and wide band gap. In the present work, different weight ratio of $La_{0.85}Na_{0.15}MnO_3$ (LNMO) and ZnO powders were employed to prepare their composites. X–ray diffraction (XRD) measurement reveals the dual phase nature of pure ZnO and pure LNMO as well as their composites. For electrical properties, frequency dependent dielectric constant, conductivity, impedance, resistance and reactance was performed using LCR meter and understood in detail. To investigate the electrical nature of all studied composites, dielectric behaviour has been understand using cole-cole and universal dielectric response model and ac conductivity by Jonscher's power law mechanism.

***Keywords**: Nano, solgel, Conductivity.*

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# Rietveld analysis of XRD pattern of $Ba_{0.5}Sr_{0.5}Y_{1.0}Fe_{11-x/2}Ti_{x/2}O_{19}$ hexaferrite ferrite.

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**ABSTRACT:**

Barium hexaferrite (BHF) is a promising material for technological applications. Hence, the large production of BHF for industrial application needs attention. Therefore, the effect of annealing temperature on the crystal structure, morphology, and magnetic properties of barium hexaferrite has been explored in this article. The $BaFe_{12}O_{19}$ (BHF) was prepared by the sol–gel method ans annealed at. 900 °C. $Ba_{0.5}Sr_{0.5}Y_{1.0}Fe_{11-x/2}Ti_{x/2}O_{19}$ (x=0.0, 0.25, 0.5, 0.75, 1.0) were prepared using Sol Gel Auto Combustion technique using $C_6H_8O_7$ as a fuel. The synthesized $Ba_{0.5}Sr_{0.5}Y_{1.0}Fe_{11-x/2Tix/2}O_{19}$ hexaferrite nanoparticles were characterized by XRD. X-ray diffraction with diffractometer CuKα radiation analysis and Rietveld refinement of the samples were studied and showed a single phase of hexagonal structure with SP63/mmc space group. Lattice parameters, cell volume, crystallite size and x-ray density were determined. it is observed that the lattice constant decreases with increasing x. The hexagonal structure was represented by using Powder Cell program showing the atomic positions of Sr, Y, Ti and Fe ions.

***Keywords:*** *M-type hexaferrite, XRD analysis, Rietveld refinement*.

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# Role of 200Mev $Ag^{+15}$ swift heavy ion irradiation induced defects across mixed valent manganite based thin films

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## ABSTRACT

Defect induced modifications in the transport and electrical properties of $La_{0.5}Gd_{0.2}Ca_{0.3}MnO_3/Al_2O_3$ thin films were investigated. In the present communication, mixed valent $La_{0.5}Gd_{0.2}Ca_{0.3}MnO_3/Al_2O_3$ (LGCMO/$Al_2O_3$) manganites based thin films with 100nm thickness were successfully synthesized by pulsed laser deposition (PLD) technique. Films were irradiated by 200MeV $Ag^{+15}$ swift heavy ion (SHI) irradiation having different ion fluencies (i.e. $1\times10^{11}$ and $1\times10^{11}$ions/cm$^2$) in order to create defects across LGCMO/$Al_2O_3$ film. Modifications due to irradiation in structural, microstructural, electrical and transport properties have been studied for pristine and irradiated thin films. X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements were performed to understand the structural and morphological properties, respectively. XRD measurement reveals single crystalline growth of LGCMO film over single crystalline $Al_2O_3$. Resistance (R), impedance (Z) and reactance (-X) behaviors with applied frequency have been studied. Resistivity behaviors for different applied temperatures (R–T) have been studied and theoretically fitted using various models and mechanisms for better understanding of charge conduction mechanisms across pure and irradiated LGCMO/$Al_2O_3$ thin films.
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***Keywords:*** *Swift heavy ion, XRD, AFM*

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# Investigations on structural, microstructural and electrical properties of $Cu_{1-x}Cd_xO$ Oxides

**Drashti Amrutiya [1], Rajal Pandya [2], Hemani Patel [2], Y.N. Jani [2], M.J. Keshvani [2] N.A. Shah [1], P.S. Solanki [1,a)]**

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**ABSTRACT**

In this present communication, $Cu_{1-x}Cd_xO$ (CCO) (x=0.0, 0.15 and 0.2) nanoparticles have been successfully synthesized via low coat sol-gel route. Effect of Cd dopant in CuO nanoparticles significantly modifies structural, microstructural and electrical properties. X-ray diffraction (XRD) measurement was performed to understand the structural property which reveals single phasic nature of all three samples understudy (i.e., CCO0, CCO1.5 and CCO2). Upon addition of Cd ion lattice parameters and unit cell volume is decreased. Williamson-Hall (W-H) plots show that particles size increases by addition of Cd ion across CuO lattice. Substitution of Cd at CuO lattice significantly modifies its electrical properties, conductivity and impedance behaviors that can be understood using various theoretical mechanisms.

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# Effect of Sintering Temperatures on the Structural, Morphological, Optical and Electric Properties of Zinc Oxide

**Himitri Trivedi[1], N.A. Chondagar[1], Apexa Maru[1], M.V. Parmar[1], V.R. Rathod[2], R.K. Trivedi[2], N.A. Shah[1], P.S. Solanki[1,*]**

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**ABSTRACT**

Zinc oxide (ZnO) powder was prepared by solid state reaction. The effect of sintering temperature on zinc oxide (ZnO) has been investigated in the temperature range of 600-1000 °C. ZnO oxides are owing to their distinct physical properties have gained importance for the futuristic applications. X-ray diffraction (XRD) technique have been carried out for all the samples to investigate crystal structure, which has clearly showed the wurtzite hexagonal structure of ZnO. ZnO has been also characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectroscopy and UV-Vi's spectroscopy. The frequency dependent behaviours of electrical properties of ZnO with different sintering temperatures have been studied to understand the conduction mechanism. At last, the efforts has been made to examine the current challenges and future scope of the low cost synthesis and applications of ZnO metal oxides.

***Keywords***: *Zinc Oxide; Electrical properties; Conduction mechanism*

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# Investigations on Structural and Electrical Properties of $YMnO_3$ Based Mixed Valent Manganites

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**ABSTRACT**

Rare-earth manganites, being suitable for varied technological applications, have been an intriguing subject of interest since the exhibition of its extraordinary resistance behaviours. This current piece of research, here, reports the effect of doping of divalent alkaline cations Sr and Ca at Y–site on the structural and electrical properties in pure $YMnO_3$. The pure $YMnO_3$, $Y_{0.9}Ca_{0.1}MnO_3$ and $Y_{0.9}Sr_{0.1}MnO_3$ samples were prepared by solid state reaction (SSR) method. The structural and electrical properties were studied by X–ray diffraction (XRD), frequency dependent dielectric, ac conductivity and impedance studies. Impedance spectroscopy has been performed in order to understand the role of doping in collective behaviour of resistance and reactance for all the three compounds. The charge transport across the lattices of doped mixed valent manganites has been understood by performing I–V characteristics and their fitting of Simmon's model has been discussed for the non–linear curves. The effect of ionic radius induced disorder is also discussed in detail for all the measurements showcased thoroughly.

***Keywords:*** *Solid state reaction; Dielectric; Conductivity; Impedance*

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# Effect of annealing temperature on Structural and Magnetic Properties of Cobalt ferrite synthesis by Microemulsion Technique.

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**ABSTRACT**

Microemulsion methods have been used to prepare a wide range ferrite nanoparticle with low size distribution. Nanocrystalline cobalt ferrite syntheses using a microemulsion technique were characterized by X-ray diffraction, Transmission electron microscope (TEM), vibrating sample magnetometer and SQUID magnetometers. A transmission electron microscope confirmed nanocrystalline in the range 4 to 12 nm depending on the annealing temperature. The crystalline size increase with increase in annealing temperature, while the coercivity and saturation magnetization increase with increase in crystalline size. SQUID magnetometers results are presented in the paper.

***Keywords***: *Nanocrystalline Ferrites, Microemulsion, TEM, VSM, SQUID.*

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# Studies on Ac conductivity and Dielectric properties of Fe doped ZnO nanoparticles

**M. V. Parmar[1], Himitri Trivedi[1], Apexa Maru[1], V.R. Rathod[2], Rujuta Leharu[1], Jaydeep Radhanpura[1], V.S. Vadgama[1], Himanshu Dadhich[3], N.A. Shah[1], P.S. Solanki[1]**

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**ABSTRACT**

In the present communication, $Zn_{1-x}Fe_xO$ (x = 0.10, 0.15 and 0.20) nanoparticles, with various concentrations of Fe in ZnO, were successfully synthesized using sol-gel method. The dielectric studies have been performed at different magnetic fields (0.0T, 0.5T, 1.0T) and temperatures range 100-400K in the frequency range 1 kHz–2 MHz and the a.c. conductivity and dielectric properties of Fe doped ZnO. It is found that a.c. conductivity $\sigma_{ac}(\omega)$, and dielectric loss factor ($\varepsilon''$) depend on frequency and temperature. The ac conductivity has been analysed to determine the barrier height Wm. Frequency dependent electrical conductivity has been understood on the basis of Jonscher's universal power law that suggests a conduction of charge carrier through correlated barrier hopping (CBH) mechanism. The ac conductivity was found to be reduced for the larger amount of Fe doping due to the presence of extra phase in the materials. The impedance spectroscopy shows that the larger amount of Fe doping reduced the value of impedance at 1.0 T magnetic field. Also, the activation energy and resistivity were found to be deceased at larger amount of Fe contant.

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# A review of recent research on the applications of multifunctional composite materials with different properties

**Pramod D. Mhase[1], Varsha C. Pujari[2], Sunil M. Patange[3]**

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**ABSTRACT**

High-performance composites that absorb microwaves and incorporate ferrite have attracted substantial interest in recent years, owing to the fast evolution of electronic technology and the expansion of communications. These composites should have thin walls, be light in weight, have a wide absorption bandwidth, and have a high absorption intensity. These composites are typically effective in achieving desirable dielectric and magnetic characteristics. Depending on the intended usage, composites can be produced to fulfill structural, mechanical, and chemical characteristics. A nanocomposite material is made up of multiple phases with changing dimensions. When material dimensions are lowered to the nanoscale, phase interfaces are formed, and these interfaces are critical for enhancing the material's properties. The surface area to volume ratio of the reinforced material used in the construction of nanocomposites has a direct influence on understanding the relationship between structure and property. This article provides a historical overview of the research undertaken by many scientists and engineers on nanocomposite materials and continuous systems constructed of them. These materials may be more appropriate for industrial applications that demand considerably improved material properties. Designers in the automotive, mechanical, and aerospace sectors are progressively substituting these materials for standard composite materials as component parts. The goal of current review is to determine the optimal raw material and processing method for producing a certain type of nanocomposites, as well as their applications, advantages, and limits. Current constraints and the continued development of nanotechnology prevent the worldwide shift from the macro to the nanoscale.

**Keywords:** Nanocomposite, Processing, Structure, Application, Technique

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# Effect of nanoparticles on sensing characteristics of composite manganites

**Himanshu Dadhich[1,2], Hardik Gohil[2], Keval Gadani[3], Hetal Boricha[2], Bhargav Rajyaguru[2,4], Nisarg Raval[2], V.R. Rathod[5], K. Asokan[6], N.A. Shah[2], P.S. Solanki[2,*]**

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**ABSTRACT**

In this study the effect of weight concentrations of LMO nanoparticles present in polycrystalline LCMO matrix in the electrical transport properties. Structural studies have been carried out using TEM measurements. The hysteretic nature of the materials has been understood on the basis of phase separation scenario which is affected by temperature, thermal cycle, current and the amount LMO content present in the composite. The variation in EPIR values have been discussed on the basis of formation of conducting filamentary paths due to magnetic fields and applied voltages.

***Keywords:*** *composites, Phase separation, Magnetoresistance, Oxides.*

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# Doping strategies used during synthesis of M type hexaferrites to enhance various properties and applications: a comprehensive review

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**ABSTRACT**

This review study investigates recent improvements in doping strategies to improve M-type hexaferrite applications in depth. These one-of-a-kind materials have piqued the curiosity of a wide range of technical sectors. The major theme of this article is the structural properties of M-type hexaferrites for their technological applications in various field such as permanent magnets, high-density storage media, EMI shielding, photocatalysis for wastewater treatment etc. Because of its magnetic anisotropy, high magnetization, and high coercivity, M type hexaferrite is a popular material for use in magnetic devices. This review study provides a summary of M type hexaferrite production techniques, crystal structure, magnetic properties, and numerous uses. The impact of experimental method of synthesis processes used to prepare M-type hexaferrites on the different parameters investigated in this review study. The synthesis processes, sintering temperature and time duration, as well as the kind of substituted ions, all influences the crystallite size and structural properties of hexaferrites which discussed here. This study also highlights current advancements and applications in m type hexaferrites, including their magnetic characteristics with doped and undoped M type hexaferrites.

**Keywords:** Crystal structure, M-type hexaferrite, Doping, Synthesis approaches, Properties, Applications

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# Prevention of appraisal activity of essential oils against pathogenic fungi of *Trigonella foenum-graecum* L.

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**ABSTRACT**

The in vitro antifungal activity of eghit essential oil was evaluated and suppressed the mycelial growth for their botanical fungi toxicants on pathogenic fungi *Trigonella foenum-graecum*. The antifungal effect of essential oil namely Groundnut oil, Coconut oil, Soybean oil, Castor oil, Sunflower oil, Eucalyptus oil, Clove oil, Mustard oil and Control were selected. The inhibitory effect was tested by food poisoning technique and determined minimum inhibitory concentration (MIC). Due to the presence of bioactive molecules the essential oil showed significant inhibition in different concentrations. Musteard oil showed 100% reduction of radial growth of *Alternaria alternata* 100% conc. In some extent, Clove oil and Mustard oil is also showed significant reduction of *Fusarium oxysporum* at 88.88% conc.

**Keywords**: *Trigonella foenum-graecum*, Antifungal activity, essential oil.

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# Structural influence on the antimicrobial and anticancer activities of $TeO_2$ doped on iron borophosphate glass materials by the sol-gel route

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**ABSTRACT**

Glass in the system Tellurium doped iron borophosphate was prepared by sol-gel method. Their optical, structural and electrical properties were investigated. Results obtained from UV–Visible spectrum predicted that the optical band gap energy decreased from 4.97 to 4.94 eV. X-ray diffraction reveals that BCC structure having crystalline size from 9.77 to 26.68nm. The distinct rounded or courous and porous morphological structure of synthesized glass was examined using FE-SEM. The elemental detection is analysed with the help of Energy Dispersive X -Ray Spectroscopy. According to dielectric studies synthesized glass material shows low dielectric loss as well as dielectric loss tangent (tan δ) decreases at high frequency. And hence it acts as a good conductor. Synthesized glass material shows good biological activity. Based on the results of antimicrobial studies the present glass system may be used in various medical field applications.

***Keywords:*** *Sol-gel, Band gap, Morphological structure, rounded or courous and porous, antimicrobial.*

***

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# Synthesis and Antimicrobial Study Of Novel Substituted Thiazolo [3,2-α] Pyrimidine Derivatives

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**ABSTRACT**

A series of novel substituted thiazolo [3,2-α] pyrimidine derivatives were synthesized by starting material 2-acetylnaphtho[2,1-b] furan (1) has been synthesized by literature (Stoermer & Schaffer) method. It is then converted in to a series of substituted chalcones (2 a-e) were prepared by Claisen-Schimdt condensation with substituted aromatic aldehyde. These Chalcones on reaction with thiourea in presence of ethanol and HCL gave their corresponding thiopyrimidine derivative (3 a-e) subsequent treatment with 2-bromopropionic acid and anhydrous sodium acetate yields, 5-(4-substitutedphenyl)-2-methyl-7-( naphtho [2,1-b] furan-2-yl) 2H-thiazolo(3,2-α) pyrimidine-3(5H)-one (4 a-e).

The antimicrobial screening was done on the compounds in order to test their antibacterial and antifungal activities.

***Keyword:*** *Chalcone, Thiopyrimidine, Thiazolopyrimidine derivatives, biological activity.*

***

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# Synthesis and characterization of Lanthanum doped ferrites by using Sol gel method

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**ABSTRACT**

Currently, Lanthanum doped ferrite nanoparticles were synthesized by using sol gel method. The synthesized nanoparticles are nanocrystalline in nature and their other properties has been studied such as optical, structural, morphological properties and application in degradation of dyes. The optical properties of synthesized nano material were studied using UV – Visible spectrometer with the maximum wavelength at 266 nm. And using the X-Ray diffraction method, the particle size was calculated as 19 nm. The morphology of material is studied by using FE - SEM and elemental composition detected by EDS. The synthesized nanoparticles degraded dye within 180 min.

***Keywords:*** *$CoO_3$ Nanoparticles, Sol-Gel method.*

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# The preparation, structural characterization, and electro-magnetic properties of nanocrystalline $Li_{0.5}Al_xFe_{2-x}O_4$ spinel ferrite, synthesized through the sol-gel route

**Vithal Vinayak**

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**ABSTRACT**

The impact of substituting $Al^{3+}$ ions in lithium ferrite, with the chemical formula $Li_{0.5}Al_xFe_{2-x}O_4$ (x = 0.00, 0.02 and 0.04), is explored in terms of its structural, electrical, dielectric, and magnetic properties. The synthesis of the sample involved the sol-gel route, utilizing nitrates as raw materials and citric acid as a fuel. To enhance crystallization, the prepared powder annealed at 500 °C for 4 hours. XRD patterns confirmed the formation of a spinel structure, while Raman spectra recorded between 200-800 $cm^{-1}$ supported the validation of a cubic structure. The DC electrical resistivity, assessed via the standard two-probe technique across various temperatures, revealed the semiconducting nature of the prepared material. Parameters such as activation energy, drift mobility, charge carrier concentration, diffusion coefficient, and Curie temperature were derived from the Arrhenius plot. Additionally, dielectric constant and dielectric loss tangent were examined as functions of frequency at room temperature, demonstrating a decrease with increasing frequency. Furthermore, magnetic properties were studied through M-H loops at room temperature and deduced various magnetic parameters.

***Keywords:*** *XRD pattern, Raman spectra, Arrhenius plot, M-H loop*

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# Synthesis, characterization and improved magnetization of $Y^{3+}$ doped nanocrystalline $NiFe_2O_4$ ferrite

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**ABSTRACT**

This work investigates the crystal chemistry and single-phase synthesis of heavily $Y^{3+}$ doped nanocrystalline $NiFe_2O_4$, primarily focusing on enhancing magnetization properties. The sol-gel route was employed to achieve single-phase formation of $Y^{3+}$ doped nanocrystalline $NiFe_2O_4$, resulting in a material with significantly improved magnetization characteristics. The as-prepared samples underwent characterization through TG-DTA in an air atmosphere within the temperature range from room temperature to 800 °C. Subsequently, the annealed samples were subjected to analysis using XRD, FESEM, TEM, and FTIR. Magnetic measurements were conducted at room temperature using a pulse field hysteresis loop tracer. The XRD pattern revealed a consistent single-phase cubic structure maintained throughout the $Y^{3+}$ substitution. FTIR spectra exhibited absorption bands corresponding to tetrahedral and octahedral sub-lattices. FESEM micrographs depicted a spherical grain nature, with an average grain size within the range of 27 to 33 nm. M-H loops were utilized to deduce saturation magnetization and coercivity, with an observed increase in saturation magnetization attributed to exchange interaction, further enhanced by $Y^{3+}$ substitution. The single-phase crystal structure played a crucial role, as the absence of secondary phases prevented magnetization degradation. The results indicated improved magnetization and coercivity with $Y^{3+}$ substitution, making $Y^{3+}$ doped nickel ferrite potentially applicable in permanent magnets and recording media.

***Keywords***: *Sol-gel, XRD pattern, Cubic structure, TEM, Saturation magnetization*

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# Diamagnetic indium ($In^{3+}$) doped $Ni_{0.65}Zn_{0.35}Fe_{2-x}In_xO_4$ nanocrystalline ferrites: Evaluating its structure, morphology and electro-magnetic properties

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**ABSTRACT**

Ni-Zn spinel ferrite doped with Indium ($In^{3+}$), featuring the chemical formula $Ni_{0.65}Zn_{0.35}Fe_{2-x}In_xO_4$ (x = 0.00, 0.04, 0.08), was synthesized via the nitrate-citrate route. A comprehensive investigation of its structural, morphological, magnetic, Mössbauer, and electrical properties was conducted using diverse analytical techniques, including XRD, FTIR, FESEM, TEM, VSM-SQUID, and Mössbauer spectrometry. The Rietveld analysis of XRD patterns exhibited distinctive Bragg peaks, affirming the exclusive presence of a single-phase cubic spinel structure, with an average particle size ranging from 22 to 33 nm. FTIR analysis revealed tetrahedral and octahedral configuration modes with cubic symmetry. FESEM affirmed the creation of spherical, dense, and agglomerated nanoparticles, while TEM images depicted nanoparticles with an average particle size of 23 nm. The SAED pattern corroborated the polycrystalline nanostructure of the sample. Magnetic measurements carried out at 300 K and 5 K. The magnetic studies indicated an increase in saturation magnetization with In3+. This trend was attributed to the disparity in magnetic moments between In3+ and Fe3+ ions, elucidated based on exchange interaction. Field cooled and zero field cooled spectra mirrored the M-H results. Mössbauer spectra exhibited normal Zeeman splitting, featuring sextets indicative of the formation of a ferromagnetic phase, thus reinforcing the observed magnetic properties.

***Keywords***: *Nitrate-citrate route, cubic structure, saturation magnetization, FC-ZFC, hyperfine field*

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# Investigation on magnetic properties of Mg-Mn Substituted Cd-Ferrite Nanoparticles

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**ABSTRACT**

In the present work, the synthesis and characteristics of the Mg-Mn substituted cadmium ferrite nanoparticles using sol-gel auto-combustion method to characterized by super paramagnetic, narrow-sized, and small-diameter nanoparticles. Synthesized samples were found to be single-phase in the structural investigation utilizing X-ray diffraction (XRD) patterns and the cubic-spinel structure were validated by the Rietveld refined XRD patterns. Images from transmission electron microscopy (TEM) were used to examine the produced samples' particle size and distribution. M-H plot obtained by Vibrating Sample Magnetometer (VSM) analysis indicates the superparamagnetic nature of the sample. All the results predict the prepared sample is the capable material for various applications.

***Keywords:*** *XRD, Sol-gel Auto-combustion, VSM, Nanoparticle, TEM*

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# Synthesis of Substituted Pyrazoles using Ionic Liquid

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**ABSTRACT:**

Pyrazoles are well known five-membered nitrogen containing heterocyclic compounds possessing diverse bioactivities and are used extensively in pharmaceutical industry. Removing organic solvents in chemical synthesis is important in drive towards benign chemical technologies. Here we have used ionic liquid as green solvent for the synthesis of substituted pyrazoles and the method gave us a excellent yields.

***Keywords:*** *Ionic liquid, Pyrazole, Synthesis etc.*

***

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# Effects of pesticides and chemical fertilizers on some soil properties and accumulation of heavy metals in the soil.

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**ABSTRACT**

This research has been done in order to evaluate long term effects of pesticides and chemical fertilizers usage on soil properties and heavy metals accumulation. In this research, soil samples are collected from 0-30 cm depth both in summer and winter and at least we compared the obtained results with the results of control soil (pasture soil) which was adjacent to the network. In this study, some factors such as EC, pH, nitrogen percentage, organic matter, soil texture, bulk density, soil hydraulic conductivity and also concentrations of some heavy metals such as cadmium, arsenic, and mercury were measured using recommended reference methods. The results showed that soil physical characteristics such as bulk density were changed in long-term and it was increased compared to control soil. The heavy metals accumulation in soil was highly affected and the concentration of some metals such as cadmium has reached a limit beyond the standard for agricultural purposes. The results also showed that the concentration of other metals is not beyond the standard. In this context, given the state of the soil and gained results, considering pesticides and fertilizers management is essential and it requires planning to reduce or replace pesticides and fertilizers usage.

***Keywords:*** *pesticides and fertilizers, pollution, soil characteristics, heavy metals.*

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# Multi-Component Green Synthesis of 1, 4- Dihydropyridine (DHP) using Nanocatalyst

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**ABSTRACT**

In recent years nanotechnology plays pivotal role in every filed of science. Nanocatalyst started to restructure the use of catalyst in multi component synthesis of N- containg heterocyclic compounds. Activity of nanocatalyst is due to its high surface area, high surface to volume ratio, shape, size, inner structure. Organic chemist started to use various types of nanocatalyst for synthesis of N-containg heterocyclic compounds and this nanocatalyst gives good yields. Single metal, Bimetallic, Nanocomposities, Nanocatalyst Supported with biopolymers, Functionalized nanocatalyst, Oxides and mixed oxide, magnetic nanocatalyst these are some types of nanocatalyst used for synthesis of N-containg heterocyclic compounds synthesis. In this review we focus on synthesis of 1, 4-dihydropyridine (DHP) by using various nanocatalyst. 1, 4-dihydropyridine (DHP) is very important scaffold in drug synthesis. This heterocyclic compounds are generally used as Antihypertensive agents. Synthesis by using traditional synthesis creates environmental problems that is use of high temperature, toxic solvent, and toxic catalyst. Using various nanocatalyst in synthesis gives some environmental benign protocols. In this mini review we discuss some synthetic routes of 1, 4-dihydropyridine (DHP) using nanocatalyst in recent years. Scope, applications and how this nanocatalyst helps in 1, 4-dihydropyridine (DHP) synthesis is also disused.

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# Solvent Free Synthesis of Novel Chromonyl Chalcones and Pyrazolines having Benzofuran Pharmacophore

**Suryawanshi Venkat[1], Fulsure Shrushti[1], Bhosle Priyanka[1], Nagade Akash[1], Kamble Kunal[1], Surwase Vishal[1], Salunke Vikas*[1]**

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**ABSTRACT**

The synthesis of biologically important Chromonyl Chalcones and Pyrazolines having benzofuran moiety, via an eco-friendly green approach under solvent-free heating method has been discussed. Herein, Chromonyl Chalcones prepared from 3-formylchromone and 2-acetyl-5-substituted benzofuran by Claisen Schmidt condensation reaction. These Chalcones further on reaction with hydrazine hydrate/phenyl hydrazine affords pyrazoline derivatives. The structures of novel compounds were established by FTIR, $^{1}$HNMR and mass spectroscopic techniques.

***Keywords:*** *Chromonyl Chalcones, Benzofuran, Pyrazoline, Solvent free synthesis.*

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# Computational Approach for Application of Fractional Differential Equations

**J.N. Pawar[1], Dr. V. B. Kulkarni[2], Dr. J. A. Nanaware[3]**

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**ABSTRACT**

This paper presents approximate analytical solutions for systems of fractional differential equations using computational method. The fractional derivatives are described in the Caputo sense. The application of differential equations of integer order, is extended to derive approximate analytical solutions of systems of fractional differential equations. The solutions of our model equations are calculated with easily computable components. Some examples are solved as illustrations, using computation. The numerical results show that the approach is easy to implement and accurate when applied to systems of fractional differential equations. The method introduces a promising tool for solving many fractional differential equations. The two methods in applied mathematics can be used as alternative methods for obtaining analytic and approximate solutions for different types of differential equations. In these schemes, the solution takes the form of a convergent series with easily computable components. This paper presents a numerically as well as computational comparison between the two methods for solving systems of fractional differential equations. This results show that the two approaches are easy to implement and accurate when applied to differential equations of fractional order. The use of fractional calculus may be seen all throughout the world. We present a fractional order expressive finite difference technique for the time fractional wave equation in this study. We further show that the model is unconditionally stable and convergent. The numerical fix of the test issue is achieved using Python Programme and visually shown as a component of the scheme.

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# Hydrogen-bonding interaction in cyanamide oligomers using Density functional theory method

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**ABSTRACT**

Hydrogen-bonding interaction in cyclic and ladder oligomers of cyanamide is studied using density functional theory (DFT) method. Among different levels of theory used, the geometrical parameters for cyanamide monomer at B3LYP/aug-cc-pvdz level are in excellent agreement with the experimental determinations. Cyclic structures are found to be more stable than the ladder structures. Hydrogen bonds in cyclic trimer to pentamer are stronger than those in ladder structures. Many-body analysis technique is used to study the nature of interaction between different molecules in these oligomers and contribution of individual many-body term to the binding energy of a complex. In cyclic structures not only total two-body energies but higher-body energies also contribute significantly to the binding energy of respective complex, whereas in ladder structures only total two-body energies contribute significantly and higher body energies are negligible.

***Keywords:-*** *Hydrogen bonding; Binding energy; Cyanamide oligomers; DFT Method.*

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# Structural and Magnetic properties of Zn substituted $CoCr_2O_4$ spinel synthesized by using Sol – Gel Method

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**ABSTRACT**

The structural properties of $Zn_xCo_{1-x}Cr_2O_4$ (x =0, 0.25, 0.5, 0.75 and 1) spinel was synthesized by sol – gel method using moringa oleifera gum solution have been studied. Particle size, lattice constant are measured from x – ray diffraction pattern. The XRD pattern indicates the formation of single phase cubic spinel structure. The Magnetic parameters such as coercivity and saturation magnetization of Zn substituted CoAl2O4 are measured from vibrating sample magnetometer. All samples shows magnetic behaviour.

***Keywords****: Sol - Gel; Moringa Oleifera ; XRD; VSM.*

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# Estimation of concentrations of Cd and Cr from the untreated and treated sewage water fed ponds of Main Campus of CHRIST(Deemed to be University), Bangalore, Karnataka, India.

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**ABSTRACT**

Assessment of Cd, Cr from the untreated and treated sewage water fed ponds at MU (Main campus Untreated sewage water), MT (main campus Treated water) present in CHRIST (Deemed to be University), Bangalore, Karnataka, India. Study was to assess the water characteristics and the effect of water treatment process using the tertiary treatment process. Heavy metals like Cd, Cr of sewage water, were examined on a monthly basis for the time period of November 2019-November 2020 from the treated and untreated sewage water ponds of CHRIST (Deemed to be University) campuses. During the analysis, waters of treated sewage samples showed a larger difference and more suitable for daily usage when compared to untreated sewage water samples which were heavily loaded with pollution. As per Two Way ANOVA there was highly significant variation in physico-chemical parameters between the untreated and treated sewage water samples($P<0.01$).

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# Synthesis and characterisation of Nickel Molybdenum ferrite for Energy Storage Devices

**Nilesh Chaudhari[1], Yogesh More[2], S.M.Rathod*[3]**

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**ABSTRACT**

Nickel molybdenum ferrite, a promising magnetic material, has been synthesized through the sol-gel method and comprehensively characterized using various analytical techniques. X-ray diffraction (XRD) analysis revealed the crystalline nature and crystal structure of the synthesized ferrite [1]. Vibrating sample magnetometry (VSM) was employed to investigate the magnetic properties of the material, unveiling its ferromagnetic behaviour with a notable saturation magnetization [3].

Ultraviolet-visible spectroscopy (UV) provided insights into the optical properties of the nickel molybdenum ferrite, revealing its wide band gap and potential for optoelectronic applications. Furthermore, Fourier-transform infrared spectroscopy (FTIR) was utilized to explore the vibrational modes and chemical bonding within the material, offering valuable information regarding its structural composition and functional groups.

This multi-faceted study sheds light on the structural, magnetic, optical, and chemical characteristics of nickel molybdenum ferrite, paving the way for its potential use in diverse technological applications, including magnetic storage, sensing, photovoltaic devices and energy storage application like super capacitor .

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# Preparation and Characterization of Lanthanum Selenide Thin Films

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**ABSTRACT**

Thin films of lanthanum selenide were prepared using spray pyrolysis technique in non- aqueous medium. The parameters were optimized. The films were characterized by X-ray diffraction and optical absorption. XRD study shows that the materials are in polycrystalline nature. Optical absorption studies reveal that the band gap found to be 2.8 eV.

***Key words***: *Lanthanum Chalcogenides, lanthanum selenide, Thin Films*

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# Highly Sensitive Electrochemical Sensor for Detection of Aspartame Using a Modified Carbon-based Electrode

**Manju Manuel[1], Suvardhan Kanchi[*]**
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**ABSTRACT**

This study presents the development of an electrochemical sensor for detecting aspartame, utilizing a carbon rod extracted from discharged zinc-carbon batteries. The electrode was meticulously modified with Co3O4 nanodiamonds (NDs), Ni-Metal-Organic Framework (Ni-MOF), and an ionic liquid (1-butyl-3-methylimidazolium methyl sulfate) dispersed in ethanol. The resulting Co3O4 NDs/Ni-MOF/IL/graphite electrode exhibited a surface area of 32.98 $mm^2$, showcasing exceptional electrocatalytic activity**.** Cyclic Voltammetry (CV) analysis in a phosphate buffer solution at pH 2.0 revealed that the modified electrode could efficiently oxidize aspartame at a potential of 1.75 V, with a distinctive anodic peak observed at 0.4 V. Characterization techniques, including Field Emission Scanning Electron Microscopy (FE-SEM), X-ray Photoelectron Spectroscopy (XPS) and optical profilometry confirmed the successful integration of Co3O4 NDs, Ni-MOF, and the ionic liquid onto the graphite electrode, ensuring structural integrity**.** Comparative studies with a bare electrode demonstrated that the sensitivity and detection limits of the modified electrode were eight-fold greater. The concentration analysis of powder and tablet samples yielded concentrations of 36 µM and 60 µM, respectively. The developed sensor exhibited a high level of sensitivity and detection capabilities, positioning it as a reliable tool for efficient aspartame detection across diverse matrices. The LOD (Limit of Detection) and LOQ (Limit of Quantification) for the modified electrode were determined to be 0.34µM and 1.05µM, respectively, highlighting its exceptional performance. Furthermore, the obtained correlation coefficient ($R^2$) of 0.997 attests to the accuracy and reliability of the sensor in quantifying aspartame concentrations. The heightened sensitivity and detection capabilities of the modified electrode underscore its potential application in quality control and safety assurance processes, where precise determination of aspartame levels is crucial. Finally, this electrochemical sensor demonstrates remarkable efficiency, offering a promising solution for aspartame detection with implications for various industries and regulatory practices.

***Keywords:*** *Electrochemical sensor, cobalt oxide nanodiamonds, Ni-Metal organic framework, aspartame detection*

***

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# Optical and Dielectric Properties of conducting Polymer PANI/ $NiSo_4$ and its Nano Composites

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**ABSTRACT**

The Conducting polymer of PANI and its composites with $NiSO_4$ at various weight percentages as wel as different molarities due to their properties and applications in various fields nanomaterials gain a lot of importance. The properties such as dielectric permittivity, dielectric loss and AC conductivity of PANI/NiSO4 composites have been studied as function of frequency in the range of 5 Hz to 35 MHz at room temperature. Polyaniline is the only conducting polymer whose electrical properties can be controlled suitably by charge-transfer doping. The conducting polymer of PANI and its composites have been characterized using X-Ray diffractometer. The size of particles in Polyaniline is around 0.3 nm, the size of particles in NiSO4 is around 0.4 nm and in composite of PANI/NiSO4 is around 0.1 nm. The band gap energy of nano composite can be calculated for PANI is 2.77 eV and Nickel Sulphate (NiSO4) is n-type semiconductor and has wide band gap of energy (4.8 eV),

***Keyword:*** *XRD, UV-VIS spectroscopy, and AC conductivity.*

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**SHRIKRISHNA EDUCATION SOCIETY, GUNJOTI**

Established in 1927, Shrikrishna Education Society is a venerable institution in the region, founding Shrikrishna Mahavidyalaya, Gunjoti in June 1991. The college offers Arts and Science courses at both undergraduate and postgraduate levels, affiliated with Dr. Babasaheb Ambedkar Marathwada University, Chhatrapati Sambhajinagar. Operating under the motto "Education for Deprived," the institution focuses on students below the poverty line and girls in the region who face financial barriers to higher education in urban areas The College boasts 24 qualified regular faculty members, including 15 Ph.D. supervisors, along with 6 contractual faculties and 16 non-teaching staff. It holds permanent affiliation with Dr.B.A.M.U. Ch. Sambhajinagar recognized under 2(f)-12(B) of the University Grants Commission. The institution offers well-equipped laboratories, research centres, and computerized facilities in the Library and Office. A functional website provides comprehensive information about the college. Having received reaccreditation from NAAC with a B++ Grade, the college earned an A grade in the academic and administrative audit conducted by the affiliated university. It is dedicated to promoting quality higher education in rural areas, with a particular emphasis on empowering female students.

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