Investigation on Synthesis, Structural and Electrical properties of Zinc Ferrite on Gamma Irradiation

Santosh Kalunge¹, Ashok V. Humbe², Mangesh V. Khedkar², S. D. More³, A. P. Keche⁴ and A. A. Pandit¹, a)³

¹Department of Physics, Yeshvantrao Chavan College of Arts, Commerce and Science, Sillod, Aurangabad 431 004 (MS), India
²Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431 004 (MS), India
³Department of Physics, Deogiri College, Aurangabad 431 005 (MS), India
⁴Department of Physics, Shri Muktanand College, Gangapur, Aurangabad 431 109 (MS), India

a)Corresponding author email: yccsillod@yahoo.com

Abstract. In the view of magnetic materials application, ferrites are the most attention-grabbing materials therefore in the present work nanocrystalline Zinc ferrite (ZnFe₂O₄) was prepared by sol-gel auto combustion technique. The synthesis was carried out by using citric acid as a chelating agent and nitrates as oxidant. The preparation of zinc ferrite was done at a sufficiently low temperature of 100°C. To get the good crystallinity and ferrite phase formation of prepared nanopowder was sintered at 550°C for 4 hours and then used for structural and electric investigations. Prepared ZnFe₂O₄ sample have been irradiated by a gamma-ray source (⁶⁰Co) to examine the changes that occurred in structural and electrical properties. These changes on gamma irradiation were investigated by X-ray diffraction (XRD) technique and two probe technique respectively. From XRD patterns, it was observed that the lattice constant and average crystallite size decrease after gamma irradiation. DC electrical resistivity after gamma irradiation revealed that the charge carrier concentration and activation energy of zinc ferrite increases whereas drift mobility (µ) decreases.

1. Introduction

Magnetic materials are attracting researchers and scientist's attention due to their novel physicochemical properties. Because of their low cost with unbelievable properties such as good magnetic properties, high resistivity, unbelievable properties, mechanical hardness, and excellent chemical stability have become most attractive magnetic materials. Generally, ferrite materials have a wider range of applications such as in photocatalysts [1], electronics devices [2], electromagnetic technology [3], circulators [4], drug delivery controlled with magnetic materials, transformer core and telecommunication [5-7].

Among magnetic materials, zinc ferrites are the most attention-grabbing material because of their magnetic and insulator properties [8]. Currently, zinc ferrites are vital due to their amazing properties, such as high magnetic permeability, lower eddy current losses, and high resistivity, which makes them...
a potential material for high-frequency applications [9-11]. Ferrite's technological significance lies in its high electrical resistivity, high magnetization, high permeability, and low cost [12-14]. Various researchers have made excellent efforts to develop new ferrite compositions with desirable properties that are useful for high-frequency applications [15-17]. Now-a-days in the field of nanotechnology at nanoscale development, implementation as well as the design of materials and devices whose size and shape can be tailored at the atomic level [18, 19] is being carried out. In the view of applications, modifications, and improvements these magnetic materials are important. At nanoscale, tailoring of the unique characteristics of nanostructured materials can be done by changing their electronic structure. The structural properties can be varied by preparation method, chelating agent, pH of the solution, sintering temperature, etc. Moreover, the properties the properties of magnetic material can be improved by gamma radiation. In order to investigate the effect of radiation on the structural, magnetic, and electrical properties of ferrite materials, fast heavy ions, laser beams, and gamma rays have been used as a source. Gamma radiation can be an effective tool to boost crystal defects and tailor the properties of ferrite in a controlled manner. A lot of scientific focus is thus given to the gamma-irradiation caused formation and alteration of defects leading to tunable structural, electrical, and magnetic properties of ferrites.

It was felt appropriate to examine the impact of gamma irradiation on the structural and electrical properties of zinc ferrite by considering these distinctive effects of gamma irradiation. Therefore, we concentrate on the effect of gamma-irradiation on structural and electrical properties of zinc ferrite prepared by citric acid assisted sol-gel auto combustion.

2 Experimental

2.1 Materials
Zinc ferrite (ZnFe$_2$O$_4$) sample synthesized was through a wet chemical technique sol-gel auto-combustion method by using chemicals such as ferric nitrate (Fe(NO$_3$)$_3$), 9H$_2$O) zinc nitrate (Zn(NO$_3$)$_2$, 6H$_2$O), citric acid (C$_6$H$_8$O$_7$), ammonia (NH$_3$), and distilled water. For the preparation, all required chemicals of AR grade were purchased from Fisher scientific PVT ltd and used as it is received without any further purification.

2.2 Preparation of zinc ferrite
The zinc ferrite nanopowder was prepared by a cost-effective safe sol-gel auto combustion technique at low temperature. In this synthesis citric acid was used as fuel for better combustion. Nitrates of ferric and zinc were dissolved in 200 ml distilled water. Then citric acid dissolved in distilled water was added to nitrate solution in such a way that the ratio of nitrates to fuel was 1:3. The solution was kept for stirring and heating at 80°C to form the gel. The pH of the solution was adjusted at 7 by adding ammonia solution. After getting the viscous gel, the temperature was increased up to 100°C - 120°C for the combustion process. The wet gel burnt in a self-ignition way because of fuel until it completely transforms into loose powder ash. The fluffy powder was obtained with combustion. The prepared fluffy powder was sintered at temperature 550 °C for 4 h using a muffle. The sintered powder was ground using mortar and pestle. For the investigation of the influence of irradiation on structural and electrical properties the prepared zinc ferrite was kept in the gamma radiation chamber. After gamma irradiation both the pristine and radiated sample was characterized by characterization techniques.

2.3 Characterization
ZnFe$_2$O$_4$ (pristine and gamma-irradiated) samples were characterized by X-ray diffraction (XRD) technique to identify the phase of the sample with the confirmation accomplishment of the ferrite structure. The Bruker D-8 X-ray diffractometer with X-ray source: Cu-Kα, having wavelength 1.54439. The XRD pattern has been recorded in a range of 20-80°. The two-probe method using coil loaded copper electrodes associated to Keithley model 614 digital electrometer was employed to measure the DC electrical resistivity of disc-shaped pellets (10 mm diameter and of 2 mm thickness) of the prepared and gamma-irradiated samples. The silver paste has been used to get the good contact with the material.
3 Results and Discussions

3.1 X-ray Diffraction

Figure 1 shows the X-ray diffraction pattern of zinc ferrite nanoparticles synthesized by the sol-gel auto-combustion method recorded at room temperature within $2\theta$ ranges from 20-80°. To ensure that the prepared zinc ferrite possesses the composition of the cubic spinel process, and to investigate the structural variations induced by X-ray diffraction gamma irradiation were reported. The obtained pattern revealed that both samples having hkl planes confirmed the Fd-3m space group and the formation of the spinel structure of prepared samples. There is no impurity peak observed in the obtained pattern. The lattice constant ($a$) values obtained are 8.432 Å and 8.402 Å respectively for unirradiated and irradiated zinc ferrite samples. From these values, it can be observed that the lattice parameter decreasing after irradiation was due to the transformation of $\text{Fe}^{3+}$ ion to $\text{Fe}^{2+}$. For unirradiated and irradiated samples, the measured unit cell volume (V) values are 599 Å$^3$ and 593 Å$^3$ respectively. The unit volume of cells (V) shows decrease in the present ferrite after irradiation. The decrease in cell volume of the present sample is due to a decrease in the lattice constant. Calculated lattice constant values, unit cell volume, average crystallite size, X-ray density, bulk density, the porosity of pre- and post-radiated zinc ferrite are tabled in Table 1. The crystallite size of zinc ferrite before and after irradiation was found to be 23 nm and 20 nm respectively, which is calculated by using following Debye-Scherrer’s formula [20],

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where, $k$ is the constant having value 0.89, $\lambda$ is the X-ray light source wavelength (1.540 Å), $\beta$ is full width at half maximum (FWHM) and $\theta$ is the glancing angle. From the XRD pattern it is cleared that the particle size found to decrease after irradiation. In light of this evidence, it can be inferred that the application of gamma irradiation caused deformity or defects in the synthesized materials crystal structure. A closer look at the peak positions shows a clear difference in the unirradiated and irradiated zinc ferrite peak position. The peak positions of the irradiated samples are shifted to the lower angle ($2\theta$). The slight change of the reflective peaks in the irradiated samples is due to some induced disorder (compressive strain) in the crystal structure resulting from ion migration into interstitial positions. XRD results also reveal that the lattice parameter decreases after irradiation and caused increase in X-ray density.

![Fig. 1: X-ray diffraction pattern of ZnFe$_2$O$_4$ (A) before irradiation and (B) after irradiation.](image-url)
Table 1- Values of ‘Lattice constant (a)’, ‘Unit cell volume (V)’, ‘Average crystallite size (D)’, ‘X-ray density (dX)’, ‘Bulk density (dB)’, ‘Porosity (P)’ of zinc ferrite before and after gamma radiation

|                | ZnFe$_2$O$_4$ | FWHM ($\Theta$) | V       | D (nm) | dx  | dB   | Porosity % |
|----------------|---------------|------------------|---------|--------|-----|------|------------|
| **Before**     | 8.432         | 0.3578           | 599.4   | 23     | 5.342 | 3.638 | 31.90      |
| **radiation**  |               |                  |         |        |      |      |            |
| **After**      | 8.402         | 0.3785           | 593.3   | 20     | 5.361 | 3.617 | 32.53      |
| **Radiation**  |               |                  |         |        |      |      |            |

3.2 DC electrical resistivity

The DC electrical resistivity is the most effective characterization technique for evaluating the mechanism of conduction. Figure 2 demonstrates the DC electrical resistivity as a function of the temperature of the prepared (pristine and gamma irradiated) samples. Before DC electrical resistivity was measured, prepared nanopowder was pressed into a form of circular 10 mm diameter pellet with thickness 2 mm using KBr press. Both the faces of the pallets were coated with the thin layer of silver paste to get good electrical (Ohmic) contact. The effect of temperature on the DC resistivity for both samples was tested using two-probe method in the 300–600 °C temperature range. Using Arrhenius relation, the electrical resistivity ($\rho$) was calculated. The following relationship between DC electrical resistivity concerning the temperature (T in K) [21, 22].

$$\rho = \rho_0 e^{-\frac{E_a}{kT}}$$

Where $\rho_0$ is the resistivity of the induced temperature, $E_a$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. From fig. 2, it was observed that the increase in temperature decreases electrical resistivity which revealed the semiconducting nature. Because of the absorbed gamma dose, the electrical resistivity decreases. This may be explained on the basis that the interaction of ionizing radiation with condensed media gives rise to the output of excess electron and electron deficiency centers, resulting in an increased number of current carriers and thus a decrease in electrical resistivity. Resistivity declines for irradiated sample due to the transfer of ferric ions Fe$^{3+}$ from A sites (tetrahedral sites) to B sites (octahedral sites) as ferrous ions Fe$^{2+}$. The electron exchange interactions between Fe$^{2+}$ and Fe$^{3+}$ are increasing and leading to a reduction in resistivity.

Fig. 2: DC electrical resistivity of zinc ferrite A) before irradiation and (B) after irradiation
Drift mobility of all the samples has been calculated using the equation \[23\]

\[ \mu = \frac{1}{n e \rho} \]

where ‘e’ is the charge on the electron, ‘\(\rho\)’ the resistivity, and ‘n’ is the concentration of charge carriers, which can be calculated from the following equation \[24\],

\[ n = \frac{N_A \rho P}{M} \]

where ‘M’ is the molecular weight, ‘\(N_A\)’ is the Avogadro’s number, ‘\(\rho\)’ the density of the sample, and ‘P’ is the number of iron atoms in the chemical formula of the oxide. From DC electrical resistivity observed that the drift mobility (\(\mu\)) decreases after gamma irradiation. After gamma irradiation, concentration of charge carriers (\(\eta\)) of zinc ferrite increases. The calculated values of activation energy (\(E_a\)), sintered density (\(\rho_s\)), Concentration of charge carriers (\(\eta\)) of drift mobility (\(\mu_d\)) are tabulated in table 2.

| ZnFe\(_2\)O\(_4\) | \(E_a\) (eV) | \(\rho_s\) (gm/cc) | \(n\) (cm\(^{-3}\)) | \(\mu_d\) (cm\(^2\)/V\(\cdot\)s\(^{-1}\)) |
|-------------------|--------------|-------------------|----------------|------------------|
| Before irradiation | 0.304 | 2.44 | 0.12\(\times\)10\(^{23}\) | 2.68\(\times\)10\(^{-9}\) |
| After irradiation | 0.508 | 3.83 | 0.19\(\times\)10\(^{23}\) | 9.33\(\times\)10\(^{-9}\) |

4. Conclusions
The nanostructured zinc ferrite nanopowder was successfully prepared using the sol-gel auto-combustion process. The prepared nanoparticles were irradiated by the source of \(^{60}\)Co gamma-ray. The patterns of XRD have verified the formation of cubic spinel ferrite with space group Fd-3m. After gamma irradiation the lattice parameter, crystallite size decreased. A close analysis of XRD patterns shows the size of crystallite before and after gamma irradiation, which is 23 nm and 20 nm respectively. The results of DC electrical resistivity of zinc ferrite before and after gamma irradiation show the semiconducting existence by Arrhenius reference. Activation energy and charge carrier concentration increase after gamma-irradiation.

Acknowledgement
One of the authors Kalunge, is thankful to Punyashlok Ahilyadevi Holkar University, Solapur for XRD facility and Government Institute of Science, Aurangabad for gamma irradiation facility.

Reference
1. Jadhav, S.A., et al., Magneto-structural and photocatalytic behavior of mixed Ni–Zn nanospinel ferrites: visible light-enabled active photodegradation of rhodamine B. Journal of Materials Science: Materials in Electronics: p. 1-14.
2. Shen, L., et al., Epitaxial Lift-Off of Centimeter-Scaled Spinel Ferrite Oxide Thin Films for Flexible Electronics. Advanced Materials, 2017. 29(33): p. 1702411.
3. Dosoudil, R., et al., Electromagnetic wave absorption performances of metal alloy/spinel ferrite/polymer composites. IEEE transactions on magnetics, 2012. 48(4): p. 1524-1527.
4. Geiler, A. and V. Harris, Atom magnetism: ferrite circulators—past, present, and future. IEEE Microwave Magazine, 2014. 15(6): p. 66-72.
5. Somvanshi, S.B., et al., Hyperthermic evaluation of oleic acid coated nano-spinel magnesium ferrite: enhancement via hydrophobic-to-hydrophilic surface transformation. Journal of Alloys and Compounds, 2020: p. 155422.
6. Patade, S.R., et al., Impact of crystallites on enhancement of bandgap of Mn1-xZnxFe2O4 (1 ≥ x ≥ 0) nanospins: Chemical Physics Letters, 2020. 745: p. 137240.
7. Humbe, A.V., et al., Nanocrystalline Ni 0.70−x Cu x Zn 0.30 Fe 2 O 4 with 0 ≤ x ≤ 0.25 prepared by nitrate-citrate route: structure, morphology and electrical investigations. Journal of Materials Science: Materials in Electronics, 2018. 29(4): p. 3467-3481.
8. Khedkar, M.V., et al., Physicochemical properties of ambient pressure dried surface modified silica aerogels: effect of pH variation. SN Applied Sciences, 2020. 2(4): p. 1-10.
9. Qian, K., et al., The influence of Nd substitution in Ni–Zn ferrites for the improved microwave absorption properties. Ceramics International, 2020. 46(1): p. 227-235.
10. Hou, T., et al., A review of metal oxide-related microwave absorbing materials from the dimension and morphology perspective. Journal of Materials Science: Materials in Electronics, 2019: p. 1-24.
11. Kale, G., et al., l-Ascorbic acid assisted synthesis and characterization of CoFe 2 O 4 nanoparticles at different annealing temperatures. Journal of Materials Science: Materials in Electronics, 2016. 27(2): p. 2151-2158.
12. Birčáková, Z., et al., Magnetic properties of Fe-based soft magnetic composite with insulation coating by resin bonded Ni-Zn ferrite nanofibres. Journal of Magnetism and Magnetic Materials, 2019. 485: p. 1-7.
13. Ikram, S., et al., Tailoring the structural, magnetic and dielectric properties of Ni-Zn-CdFe2O4 spinel ferrites by the substitution of lanthanum ions. Ceramics International, 2019. 45(3): p. 3563-3569.
14. Bharati, V., et al., Influence of trivalent Al–Cr co-substitution on the structural, morphological and Mössbauer properties of nickel ferrite nanoparticles. Journal of Alloys and Compounds, 2020. 821: p. 153501.
15. Zhang, X.-J., et al., Recent progress in microwave absorption of nanomaterials: composition modulation, structural design, and their practical applications. IET Nanodielectrics, 2019. 2(1): p. 2-10.
16. Amiri, M., M. Salavati-Niasari, and A. Akbari, Magnetic nanocarriers: evolution of spinel ferrites for medical applications. Advances in Colloid and Interface Science, 2019. 265: p. 29-44.
17. Bhagwat, V., et al., Sol-gel auto combustion synthesis and characterizations of cobalt ferrite nanoparticles: Different fuels approach. Materials Science and Engineering: B, 2019. 248: p. 114388.
18. Chiang, W.H., et al., Microplasmas for advanced materials and devices. Advanced Materials, 2020. 32(18): p. 1905508.
19. Shu, J.-C., et al., Tailoring MOF-based materials to tune electromagnetic property for great microwave absorbers and devices. Carbon, 2020.
20. Andhare, D.D., et al., Effect of Zn doping on structural, magnetic and optical properties of cobalt ferrite nanoparticles synthesized via. Co-precipitation method. Physica B: Condensed Matter, 2020. 583: p. 412051.
21. Mande, V.K., et al., Effect of γ-radiation on structural, morphological, magnetic and dielectric properties of Zn–Cr substituted nickel ferrite nanoparticles. Journal of Materials Science: Materials in Electronics, 2019. 30(1): p. 56-68.
22. Raut, A., et al., Structural, electrical, dielectric and magnetic properties of Al 3+ substituted Ni-Zn ferrite. Journal of Superconductivity and Novel Magnetism, 2016. 29(5): p. 1331-1337.
23. Kounsalye, J.S., et al. Structural, morphological and dielectric modifications in nanocrystalline Li 0.5 Fe 2.5 O 4 ferrites induced by high energy γ-irradiation. in
Proceedings of the fourteenth biennial DAE-BRNS symposium on nuclear and radiochemistry: book of abstracts. 2019.

24. Humbe, A.V., et al., Impact of Jahn Teller ion on magnetic and semiconducting behaviour of Ni-Zn spinel ferrite synthesized by nitrate-citrate route. Journal of Alloys and Compounds, 2017. 691: p. 343-354.