

XMCD-based Investigation of Magnetic Properties in Optimized Zinc Ferrite

M.Tech. Thesis

By

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**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE**

INDIAN INSTITUTE OF TECHNOLOGY INDORE

May, 2026

XMCD-based Investigation of Magnetic Properties in Optimized Zinc Ferrite

A THESIS

*Submitted in partial fulfillment of the
requirements for the award of the degree*

of
Master of Technology

by
ATANU GHOSH



**DEPARTMENT OF METALLURGICAL ENGINEERING AND
MATERIALS SCIENCE**

INDIAN INSTITUTE OF TECHNOLOGY INDORE

May, 2026



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **XMCD-based Investigation of Magnetic properties in Optimized Zinc Ferrite** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from June 2025 to May 2026 under the supervision of Prof. Rupesh S. Devan and Dr. Ravindra Jangir.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Atanu Ghosh, 16/05/2026

Signature of the student with date
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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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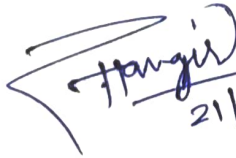
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CERTIFICATE

This is to certify that the dissertation work entitled “XMCD-based Investigation of Magnetic Properties in Optimized Zinc Ferrite”, submitted by Mr. Atanu Ghosh (Roll No. 2402105008) for the partial fulfillment of Master of Technology in Materials Science and Engineering from the Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, M.P., India, is hereby approved as credible work carried out by him during the period from June 2025 to May 2026 under my supervision in the Indus Synchrotrons Utilization Division at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, M.P., India. The work presented has not been submitted or included in any other thesis for any degree/diploma previously. Furthermore, it has been organized and presented in a manner suitable for acceptance towards the partial fulfillment of the requirements for the degree of Master of Technology in Materials Science and Engineering.


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ACKNOWLEDGEMENTS

I sincerely thank Prof. Rupesh S. Devan and Dr. Ravindra Jangir for their encouraging support and guidance throughout my M. Tech. degree. Their suggestions, impressive knowledge, and motivation were the main contributors to the completion of this thesis. Their support also helped me to strengthen my understanding and confidence regarding the synthesis and characterization of the materials and conducting scientific research. I appreciate their patience, supportive behavior, and trust in my ability to do this work at each stage. I also want to thank the members of my thesis committee from the MEMS Department for their constructive comments and suggestions, which were very helpful in improving this research. I am very appreciative of Dr. Velaga Srihari for his help with the characterization of materials, especially with powder and capillary tube X-ray diffraction (XRD). I gained a lot of knowledge with XRD due to his help and support. I also appreciate Mr. Sudip Nath for his help with XMCD, Dr. Ashok Kumar Bhakar for his help with dielectric measurements, and his continued help during my research.

I'm thankful to Dr. Ram Janay Choudhary for his help in VSM experiments and his helpful discussions regarding the properties of the materials. My special thanks are to RRCAT, Indore, for giving me access to the required research infrastructures as well as to the Indus-2 Beamline-11 and Indus-2 Beamline-20, both of which have been instrumental for this work. I also want to extend my appreciation to all my colleagues and lab mates from the Nano-architectures Research Group, IIT Indore, for their encouragement and support, which were key to my work completion. I extend my special gratitude to Ms. Harshada

Jadhav, Ms. Samtham Manopriya, Ms. Ekta Chaudhary, Ms. Ayushi Miglani, Ms. Suman Yadav, Mr. Ajay Patil, Mr. Ankit, Ms. Sheetal Yamalakonda, Mr. Rishav Sharma, Ms. Apurva, and Mr. Prabhat Singh for enriching discussions and for the work atmosphere we built together. I am thankful to Mr. Rishav Sharma for his encouragement, highly appreciated suggestions, and support, which were crucial for the successful completion of the work. I am obligated to my family for their love and support, which uplifted me morally, as well as for their sacrifices and unwavering faith in my abilities. They have motivated me the most and given me the strength to pursue my journey of research.

Atanu Ghosh

Dedicated

To

My Parents

Abstract

In the current research, the effect of non-stoichiometry and aluminum incorporation in zinc ferrite is studied using compositional series of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ and $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ by the conventional method of solid-state reaction route synthesis. Zinc ferrite is a versatile spinel ferrite material that can be tailored in terms of functional properties by tuning the ion distribution and doping of ions. Here, the excess of iron and non-magnetic aluminum doping effects have been examined for studying their role in ion distribution, charge conduction, magnetic interaction, and electronic behavior.

The crystal structure was analyzed by synchrotron X-ray diffraction analysis conducted on BL-11 beamline at the synchrotron facility INDUS-2, RRCAT, Indore. The materials exhibited a pure cubic spinel structure with space group Fd-3m. Lattice parameter variations and diffraction peak shifting suggested incorporation of doped ions in the host spinel lattice.

Diffuse reflectance spectroscopy (DRS) showed the existence of a tunable optical bandgap depending on the composition. The Fe-rich compositions showed a lower bandgap and hopping conduction attributed to high interaction between Fe^{2+} and Fe^{3+} ions. On the other hand, aluminum substitution in the composition increased the optical bandgap as it weakens the Fe 3d-O 2p hybridization. The complex impedance spectroscopy (CIS) showed semiconducting behavior with negative temperature coefficient of resistance (NTCR) behavior. Increasing Fe content slightly improved charge carrier mobility and lowered activation energy. Conversely, Al substitution in

higher concentrations increased electrical resistivity as a result of suppression of hopping electrons between Fe ions. SQUID-VSM magnetic measurements for the various compositions indicated ferrimagnetic ordering due to cation rearrangement and A-B type superexchange effect. Fe excess slightly increased the magnetization, while Al substitution decreased the magnetic ordering due to dilution of the Fe–O–Fe exchange path. In addition, XMCD element-specific measurement confirmed that substitution of Al decreased Fe electronic state, resulting in decreased spin magnetic moments.

Of all the compositions considered, $\text{Zn}_{0.95}\text{Al}_{0.3}\text{Fe}_{1.75}\text{O}_4$ had excellent multi-functional properties with high electrical resistivity and optical bandgap with stable magnetic ordering. As a result, the material can be used in spintronics, high-frequency electronics, sensors, and optoelectronics.

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NOMENCLATURE

Symbol/Notation	Description
a	Lattice parameter
E_a	Activation energy
E_g	Optical band gap energy
f	Frequency
$f_{\max}$	Relaxation peak frequency
f_0	Pre-exponential factor
$F(R)$	Kubelka–Munk function
$h\nu$	Photon energy
k_B	Boltzmann constant
M_s	Saturation magnetization
R	Reflectance
R_G	Grain resistance
R_{GB}	Grain boundary resistance
R_0	pre-exponential resistance factor
T	Absolute temperature
Z^*	Complex impedance
Z'	Real part of impedance
Z''	Imaginary part of impedance
C_G	Grain capacitance
C_{GB}	Grain boundary capacitance

τ	Relaxation time
ω	Angular frequency
χ^2	Goodness of fit parameter
λ	X-ray wavelength
θ	Bragg diffraction angle
ρ	Electrical resistivity
σ	Electrical conductivity
μ_B	Bohr magneton
ZFO	Zinc ferrite
ZFO_95	$\text{Zn}_{0.95}\text{Fe}_{2.05}\text{O}_4$
ZFO_90	$\text{Zn}_{0.90}\text{Fe}_{2.10}\text{O}_4$
ZAFO_95_10	$\text{Zn}_{0.95}\text{Al}_{0.1}\text{Fe}_{1.95}\text{O}_4$
ZAFO_95_20	$\text{Zn}_{0.95}\text{Al}_{0.2}\text{Fe}_{1.85}\text{O}_4$
ZAFO_95_30	$\text{Zn}_{0.95}\text{Al}_{0.3}\text{Fe}_{1.75}\text{O}_4$
ZAFO_95_40	$\text{Zn}_{0.95}\text{Al}_{0.4}\text{Fe}_{1.65}\text{O}_4$
ZAFO_95_50	$\text{Zn}_{0.95}\text{Al}_{0.5}\text{Fe}_{1.55}\text{O}_4$

ACRONYMS

Acronym	Full Form
BL	Beamline
CIS	Complex Impedance Spectroscopy
CPE	Constant Phase Element
DRS	Diffuse Reflectance Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
HRTEM	High Resolution Transmission Electron Microscopy
MEMS	Metallurgical Engineering and Materials Science
MRI	Magnetic Resonance Imaging
NTCR	Negative Temperature Coefficient of Resistance
PVA	Polyvinyl Alcohol
RRCAT	Raja Ramanna Center for Advanced Technology
SQUID	Superconducting Quantum Interference Device
SXRD	Synchrotron X-ray Diffraction
TEM	Transmission Electron Microscopy
UV	Ultraviolet
VSM	Vibrating Sample Magnetometer
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XMCD	X-ray Magnetic Circular Dichroism
XRD	X-ray Diffraction

Chapter 1

Introduction

1.1 Overview

Ferrites are a class of ceramic materials that exhibit both magnetic properties and high electrical resistance. They are generally formed by combining Iron oxide (Fe_2O_3) with other metal ions giving compound of general formula MFe_2O_4 . Most of the ferrites have high electrical resistivity which minimizes eddy current losses and make them suitable for high frequency applications. Some of them exhibit strong magnetic ordering because of the Fe^{3+} ions that are present there [1].

The ferrites are basically so diverse because of their crystal structure. Which is spinel structure. The general formula is AB_2O_4 and the space group is Fd-3m. In this arrangement the oxygen ions form a closed packed structure, and the metal ions occupy the interstitial sites i.e. Tetrahedral (A site) and octahedral (B site). The tetrahedral sites are occupied by 4 oxygen atoms and the octahedral are surrounded by 6 oxygen ions. The distribution of the cations plays a significant role on their properties.

Crystal structure of Spinel Ferrite

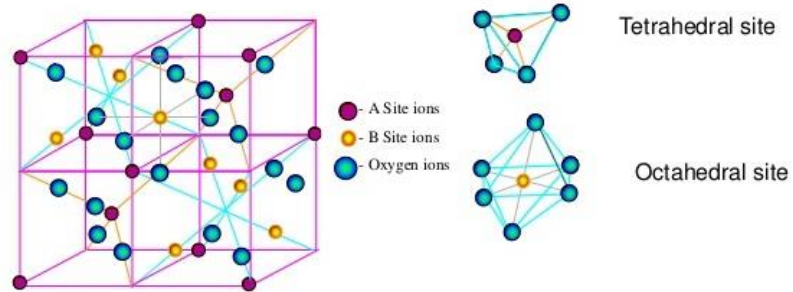


Fig 1: Structure of Zinc Ferrite

Based on how ions are arranged, spinel ferrites can be divided into normal, inverse and mixed spinels [2]. In a normal spinel the divalent cation A^{2+} prefer to occupy the tetrahedral sites, while the trivalent cations B^{3+} occupy the octahedral sites. When the distribution is not perfectly ordered it is called mixed spinels. The magnetic properties in spinel ferrites also take place because of the superexchange interaction between cations located at A and B sites through oxygen ions [3]. Generally the magnitude of the magnetic moments of A and B are in opposite direction. The interaction between A and B results in net magnetic moment. The spinel ferrites have a very flexible structure, which allows different cations to be introduced to the lattice. This makes doping an effective method to change the properties of the material. Because of this combination of tunable structure and multifunctional properties, spinel ferrites can be applied in various fields including magnetic storage devices, biomedical application such as drug delivery, MRI contrast agents, catalysis, sensors etc. Overall the spinel structure along with the ability to modify cation distribution and properties through doping makes it an important class of material for fundamental studies.

Zinc Ferrite (Properties and importance)

Zinc ferrite (ZnFe_2O_4) is a well-known material in the spinel ferrite group and is widely studied due to its simple crystal structure and tunable physical properties. ZnFe_2O_4 crystallizes in cubic spinel structure with space group Fd-3m . In this structure the oxygen ions form a close packed lattice while the cations occupy the interstitial positions. In case of the magnetic properties Zn^{2+} ions are nonmagnetic while Fe^{3+} ions are magnetic. As all the Fe^{3+} ions are present in the octahedral sites in normal spinel structure the super exchange A-B is absent. Thus, the magnetic properties of bulk Zinc ferrite is different from other ferrites. Experimental studies showed that ideal spinel structure is rarely seen in real samples [4]. Synthesis route, experimental conditions, thermal treatment can lead to the structure to become a mixed spinel as some of the Fe^{3+} ions occupy the tetrahedral sites. This distribution introduces A-B super exchange interaction resulting in weak magnetic behavior. The degree of inversion is significantly increased in nanocrystalline samples. Reduction in particle size leads to increased surface area and structural disorder which promotes cation redistribution. The synthesis methods can also influence the cation redistribution and thereby modify the magnetic properties.

ZnFe_2O_4 is a semiconductor with a bandgap in the range 1.9-2.2 eV. The bandgap arises mainly from O2p to Fe3d electronic transitions. The band gap can be modified with doping of other materials. This band gap resizing can help in various optical and optoelectrical applications.

Doping effect on zinc ferrite

Doping can be used to further modify the cation distribution and thus change its physical properties. The electrical and magnetic properties change due to the A-B interaction and doping mechanism between the two sites respectively.

The substitution of divalent cations such as Co^{2+} , Mn^{2+} , Mg^{2+} can increase magnetic properties [5]. The doping of other magnetic ions help in additional magnetic interaction and more A-B super exchange. Trivalent cations such as Cr^{3+} and Al^{3+} primarily change the structural properties. They generally reduce lattice constants and modify exchange interactions. Ga^{3+} and Al^{3+} due to their nonmagnetic nature dilute the magnetic saturation and weakens Fe-O-Fe interaction.

Rare earth ions like Gd^{3+} , Nd^{3+} introduces significant lattice distortion due to their bigger size and this enhance magnetic anisotropy making them suitable for high frequency and magnetic storage applications [6]. In the high oxidation state metals, doping can enhance conductivity due to additional charge carriers.

Optical properties are also influenced by doping [7]. Transition metal dopants introduce localized energy levels within the bandgap which changes optical behavior [8]. For example, Al^{3+} and Ga^{3+} doping generally leads to bandgap widening due to reduced d-d transitions [9]. So, by carefully selecting the dopants zinc ferrite can be tailored for various applications.

Aluminium doping in Zinc Ferrite

Aluminium doping in zinc ferrite has been studied due to tailoring properties due to doping. Due to smaller ionic radius Al^{3+} (0.535 Å) compared to Fe^{3+} (0.645 Å), Al^{3+} substitutes the Fe^{3+} ion easily at the octahedral sites(B), leading to contraction of the lattice parameters [10]. From a magnetic perspective, Al^{3+} is nonmagnetic in nature. the substitution of Fe^{3+} with Al^{3+} weakens dominant Fe^{3+} - O^{2-} - Fe^{3+} super exchange interaction. Because of this there is a observed decrease in saturation magnetization [11].

Aluminium doping also influences the band structure of zinc ferrite. The change in bandgap can be attributed to the reduction in Fe^{3+} d - O^{2-} p hybridization and the decreased availability of the Fe^{3+} states near

conduction band. Widening of band gap enhances transparency and the material becomes much more useful in Optoelectronic applications.

Electrical properties are also affected by the doping of aluminum. Conduction is mainly governed by the electron hopping between Fe^{2+} and Fe^{3+} ions. As Al^{3+} doesn't participate in electron hopping the number of electrons decreases thus decreasing electric conductivity.

Temperature-dependent measurements show that the mobility of charge carriers decreases with increasing Al content. This can be especially useful in power electronics and communication devices.

1.2 Motivation and Research Gap

Despite extensive research on zinc ferrite, significant gaps still exist in understanding the controlled cation distribution on its structural, magnetic and electronic properties.

A major research gap is about the limited understanding of non-stoichiometric doped zinc ferrite. Previous studies have explored substitution with transition and non transition elements, but it was restricted to only single site substitution and in narrow ranges. The effect of doping of Aluminium on electronic structure and element specific magnetization is not understood [12].

There is also a lack of coordination between structural changes and magnetic behavior. Conventional techniques like XRD and VSM show bulk magnetization, but they cannot easily correlate how the change in stoichiometry is affecting the properties.

Motivated by these gaps, the present work focuses on systematic doping of Aluminium in zinc ferrite through 2 compositional series, $Zn_xFe_{3-x}O_4$ and $Zn_{0.95}Al_xFe_{2.05-x}O_4$, to understand cation distribution and non-stoichiometry effects simultaneously. A key motivation is to employ advanced characterization techniques like XMCD along with XRD, VSM, DRS and CIS to form a direct correlation between electronic structure, magnetic behavior, optical properties and electrical transport.

Chapter 2

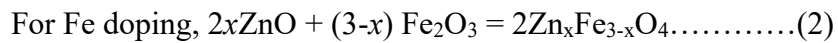
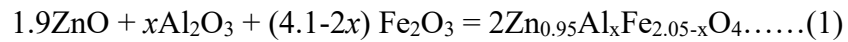
Methodology

2.1 Materials and reagents:

In our study the solid-state method was applied to synthesize the undoped Zinc Ferrite and its non-stoichiometric and doped Al^{3+} variants. The synthesis method started with weighing the samples. The weighed samples were crushed and grinded using mortar and pestle and then it was ball milled using Ethanol. High temperature calcination was done on the ball milled particles for phase formation. Pellets were made using pellet press and then sintering was used for densification. The detailed procedure with figures is presented in the following sections. After that we perform various characterizations for its physical properties.

For synthesis of single phase $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ and $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ high purity ZnO (99.99% purity, Aldrich), Al_2O_3 (99.99% purity, alfa aesar) and Fe_2O_3 (99.99% purity, alfa aesar) served as primary precursors. Stoichiometric proportions were calculated for the general formula, for excess iron doped is $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ (where $x = 1, 0.95, 0.9$ and 0.85) and $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ (where $x = 0.1, 0.2, 0.3, 0.4, 0.5$), the appropriate amounts were calculated using the equation,

For Al doping,



Two synthesis methods were done as part of our work for comparative studies,

Method 1- Fe doped ZFO, i.e. $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ samples a different concentration level ($x = 1, 0.95, 0.9$ and 0.85)

Method 2- Al doped ZFO, i.e. $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ samples a different concentration level ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5)

2.2 Synthesis of ZnFe_2O_4 and its doped variants:

2.2.1 Solid state synthesis method:

The synthesis procedure followed is illustrated in figure. Each step in this process is very important to ensure the synthesis of single-phase polycrystalline samples and repeatability. The procedure for synthesis as follows:

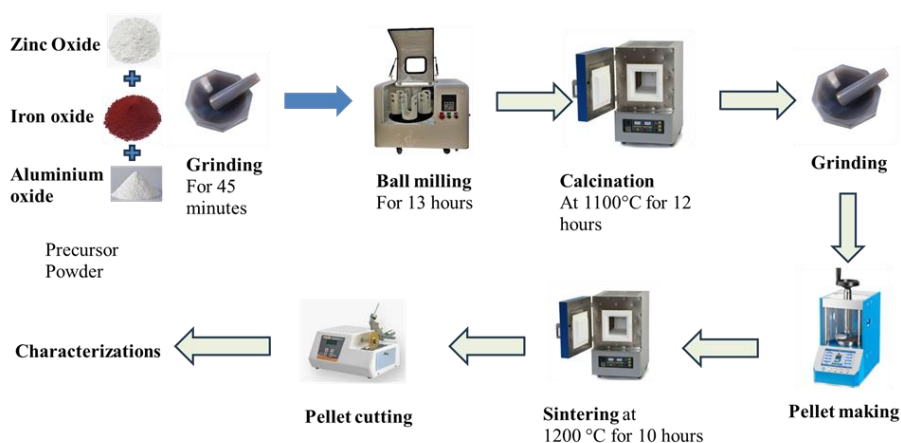


Fig 2: Schematic of synthesis process

a. Manual Grinding:

At first the powders are measured in a weighing balance according to their proper stoichiometric ratio. Then the samples are manually grinded for around 30- 45 minutes for proper mixing of the powders as Aluminium oxide comes in the form of small particles, so they are to be grinded properly. The fine uniform powder is very crucial as it facilitates uniform diffusion when they react at high temperatures.

b. Ball milling:

After the manual mixing of the powder are finished, to further help in the homogenize of the mixture of powders this ball milling is

done. The powder is placed in a ball milling chamber with Isopropyl alcohol present in it. Then 10 zirconia balls are placed in the container, and they are sealed for ball milling. The IPA helps to reduce the agglomeration of the particles and the reduction of excess heat. It also helps the powders to mix uniformly. After placing the container on the ball milling chamber the container is rotated at 180 rpm and the whole setup revolve at 150 rpm. The ball milling is done for 13 hours with each 30 minutes for an alternate cycle. After ball milling the paste is dried at room temperature for around 1-2 hours. After drying the mixture is grinded again for further steps.

c. Calcination:

The grinded powder is then transferred into ceramic crucibles and then was kept for calcinations at 1100 °C for 12 hours with a ramp rate of 4°C/min in a programmable box furnace. The sample was kept at that temperature to allow solid-state diffusion and to form the spinel structure, In this process the Zn^{2+} , Fe^{3+} and Al^{3+} Ions rearrange inside the lattice and improve the crystallinity and phase purity. The dwell time of 12 hours guarantees successful diffusion and no incomplete reaction. After the holding temperature the temperature goes down at a controlled ramp rate of 4°C/ min until 700°C and the controller is switched off and by natural cooling takes place. The calcined material was removed at around 200-300°C and ground into fine powder for further processes.

d. Pellet making and sintering:

After the powder taken from the calcinations process is taken out and grinded 2 drops of binder i.e. Polyvinyl Alcohol (PVA)(2%wt PVA in DI water) is added and then grinded finely for 30 minutes till it again becomes like powder. PVA was added so that the pellet formed doesn't break and get sufficient strength. After grinding the

sample, it is placed inside a die of diameter 15 mm for forming pellet. The die is then sent to a pellet press to form the pellet. It is given a force of 4 tons for 2 minutes for the successful formation of pellet. The force was optimized that the pellet does not break. Uniform pressing results in the pellet in having constant density and reduce the cracks that can be formed during sintering. The pellet is then removed carefully to prevent damage at the edges and is placed inside a crucible.

The pellets were subjected to a pre-sintering step at a temperature of 500°C for 4 hours. This was done so that the binder can be properly evaporated. Then the sintering was done at 1200°C for 10 hours at a ramp rate of 4°C/min. This sintering process was done to promote grain growth and densification. After sintering the pellet was cut with a diamond cutter. The top and bottom portions were cut off as they had contact with external environment. The cut pellets were polished using emery paper and sonicated so that we can get uniform surfaces. The pellets were found to have thickness ranging from 0.64 to 0.68 mm with an average of 0.66 mm. These polished samples were then prepared for various characterizations like they are grinded into powder for SXRD, DRS and the pellets were used for XMCD, VSM and they were coated with silver for complex impedance spectroscopy measurements.

2.3 Characterization techniques:

2.3.1 Synchrotron- Based Powder X-Ray Diffraction (SXRD)

XRD is used to investigate crystal structure, detect different phases and measure lattice parameters in crystalline materials [13]. In this study, XRD was employed to detect the phase changes and lattice parameters changes due to doping of excess Fe^{3+} and Al^{3+} in it. The structural characterization was carried out at BL-11 beam line in the

synchrotron facility (INDUS-2) at Raja Ramanna Center for Advanced Technology, Indore. The synchrotron is equipped with 1.5 T bending magnet and the ring is operated at 2.5 GeV at 200 mA current. The measurements were carried out using a monochromatic X-ray of wavelength in ambient condition. The samples were enveloped in capillary tubes of diameter 0.3mm and length 7 cm to ensure random orientation during measurements. The use of capillary tube ensures a good accuracy of the measured data.

The measurements were carried out using wavelength of 0.6862 Å, which is significantly shorter than conventional sources and allows higher resolution. The capillary rotates which improves particle statistics and gives smooth diffraction pattern. The MAR345 detector was used to get the 2D data of the material. The calibration was done using CeO₂. The calibrated data was the saved and exported for further analysis.

2.3.2 Le-Bail Fitting

Le bail fitting was carried out to extract precise structural information from the XRD data that we got from the samples without knowing the exact structure. This is very useful for doped materials whose structure and positions of atoms are not so well established [14]. We have examined the peaks and indexed based on cubic structure of zinc ferrite with Fd-3m space group.

The fitting was performed using FullProf suite [15]. Automatic background find was used using polynomial; function which took 62 background points. Then next peaks were identified and described using pseudo-voigt profile. Then with taking the structure as cubic (fd-3m space group)

the parameters were refined. Parameters such as u, v, w, x, Asy1, Asy2 etc were refined. The convergence was monitored through R_{wp} which was less than 10% and χ^2 which had a value of around 0.9 which ensured fitting reliability. Refined parameters were noted for the samples and the fitted graphs were plotted in origin.

2.3.3 Diffuse Reflectance Spectroscopy (DRS)

DRS is widely used for finding the optical characteristics of powdered samples. In my case DRS measurements were carried out to investigate the optical properties of Al doped Zinc ferrite and non stoichiometric zinc ferrite. The measurements were done by placing powdered samples in a sample holder and measure the reflectance using the UV radiation over the range of 1200-200 nm. When the light falls on the sample surface, it undergoes multiple scattering and some of the light is absorbed while the rest gets reflected and is detected by the detector present. The reflectance(R) that we get indirectly gives us the absorption characteristics of the sample.

To analyze the optical properties the data is converted into absorption coefficient $F(R)$ using the Kubelka-Munk function which is,

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{C}{k} = \frac{K}{S} \dots \dots (3)$$

Here, C = sample concentration, K= absorption coefficient, S= scattering coefficient, $F(R_{\infty})$ = Kubelka-Munk function, R_{∞} = Absolute reflectance of sample layer, k= Molar absorption coefficient [16].

The optical band gap was measured using the Tauc plot which is $[F(R_{\infty})hv]^n$ versus (hv) plot and extrapolating it we will get the band gap of the material [17]. Any shift was

carefully analyzed as it tells about the electronic structure and cation distribution within the material.

2.3.4 Complex Impedance Spectroscopy (CIS)

CIS measurements were carried out to study the electrical transport properties of pure ZnFe_2O_4 (ZFO), non-stoichiometric ZFO and also comparing to Al doped ZnFe_2O_4 [18]. For this purpose, the cutted pellets were coated with silver, on one side it was fully coated and the other side was coated as a circle with diameter 5 mm. The measurement was performed using 0.66 mm thick pellets of all the compositions including ZFO, ZFO_95, ZFO_90, ZFO_85 and $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ (where $x = 0.1, 0.2, 0.3, 0.4$ and 0.5) using the impedance analyzer (Warren Kerr). Prior to the measurements the pellets were made at 400°C for 30 minutes. The measurements were carried out in the frequency range of 100Hz to 5MHz, across a temperature range of 100K to 480K. The temperature was brought down by using liquid nitrogen. The vacuum pump is used to make vacuum inside the chamber up to 4×10^{-3} mbar.

The impedance data was analyzed in terms of Z' and Z'' components as a function of frequency [19]. The variation of Z'' with frequency was plotted across various temperature to understand the relaxation behavior of the charge carriers. Z'' plots show peaks that shift toward higher frequencies with increasing temperature which shows thermally activated relaxation process. From the f_{max} from the Z'' vs f plot we can get the activation energy of the grains and grain boundary. The cole-cole fitting shows us a clear picture of the contribution of grain and grain boundary towards conduction mechanisms [20]. The fitting is done using Zfit software

with equivalent circuit consisting of both resistance and capacitance.

2.3.5 Vibrating Sample Magnetometer (VSM)

Magnetic Measurements were carried out using SQUID VSM. It is a highly sensitive technique and capable of detecting even small magnetic changes. This instrument can detect extremely small magnetic field due to the combination of Superconducting Quantum interference Device (SQUID) and Vibrating Sample Magnetometer (VSM). M-H curve was recorded and analyzed of the samples [21].

The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. When the sample is moved up and down it produces an alternating magnetic flux in the pick-up coil. The magnetic signal of the sample is obtained via a Superconducting pick-up coil. This device acts as a magnetic flux-to-voltage converter. The magnetization as a function of applied magnetic field is recorded at room temperature for a range from -7T to +7T. We have obtained the required hysteresis curve and got coercivity and saturation magnetization of the samples. The shape of the hysteresis loop can also provide insight on the sample [22]. The effect of Al^{3+} doping is analyzed by comparing the hysteresis loops at various compositions.

2.3.6 X-Ray Magnetic Circular Dichroism (XMCD)

Orbital and spin magnetic moments are invaluable fundamental quantities for understanding the macroscopic magnetic properties of matter. The experiments were

performed using synchrotron beam lines at BL-20 at INDUS-2 in RRCAT, Indore using circularly polarized X-rays at the FeL_{2,3} absorption edges. This technique is element specific and is useful in probing the magnetic properties of the components in a sample [23].

Here, the circularly polarized X-rays are used which have parallel and anti parallel orientation. When the light falls on the sample the absorption differ relative to the orientation of spin and angular magnetic moment. This difference gives the data. The measurements were carried out using total electron yield mode and in a highly vacuum environment.

The absorption spectra were recorded for both left and right circularly polarized X- rays under an applied magnetic field. The XMCD signal was obtained by the difference of the two. Prior to analysis the spectra is normalized and baseline is corrected to get an uniform spectra. The sum rules were applied to extract spin and orbital magnetic moment from integrated XMCD and XAS spectra [24]. The integrals correspond to the parameters p, q and r. Changes in the XMCD signal with aluminum doping were analyzed and related to the spin and orbital magnetic moments of the samples.

Chapter 3

Results and discussions

(Fe-doped $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$)

3.1 Introduction

As discussed in the previous chapters, the doping of aluminum with non-stoichiometric zinc ferrite remains unexplored. Driven by the curiosity of the effect of magnetic Fe^{3+} on the change in physical properties of the zinc ferrite due to non-stoichiometry, we have conducted the following doping. In this chapter, we will talk about the change in properties of materials due to the insertion of Fe at various concentrations into zinc ferrite (ZFO). We completed SXRD to check the limit of phase formation concentration.

3.2 X-Ray Diffraction Analysis

To know about the phase purity and crystal structure of the Fe doped non stoichiometric zinc ferrite[1] $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 1, 0.95, 0.9, 0.85$) SXRD data were recorded using a monochromatic beam of wavelength of 0.6862 Å on BL-11 of Indus 2 in RRCAT, Indore. Figure 3a shows the diffraction pattern of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ 4 compositions and of pure ZnFe_2O_4 (ZFO), which are indexed to a simple cubic Fd-3m space group, consistent with previous reports of pure ZFO.

No secondary diffraction peaks are observed up to ZFO_90, indicating the successful incorporation of Fe^{3+} into the spinel lattice within the solubility limit. For $x < 0.9$ (particularly for ZFO_85), impurity phases of iron are present in the lattice, which can be seen in the graphs due to the solubility limit or phase segregation. Despite the impurities present here, the major diffraction peaks still represent the Fd-3m lattice, showing that there are no structural changes due to the change of doping.

Figure 3b shows magnified images of the minor defect peaks observed at a higher doping.

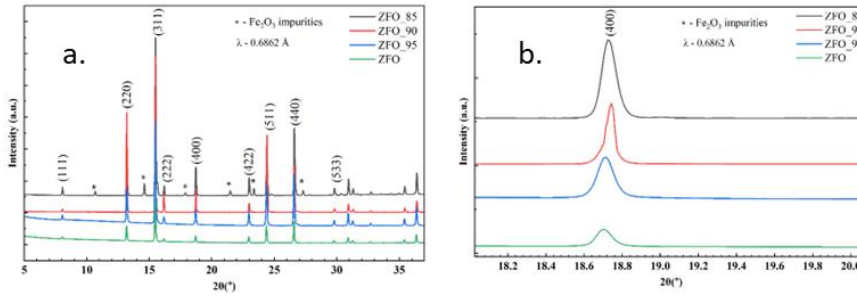


Fig 3: X-Ray diffraction analysis of ZFO_x samples

level. It can be observed from Figure 3b that the peak shifted towards a lower 2θ with increasing Fe^{3+} concentration. A systematic peak shift was observed for the (400) peaks, which can be due to the substitution of larger Zn^{2+} ions ($0.74 \text{ \AA}$) by smaller Fe^{3+} ions ($0.67 \text{ \AA}$), which introduces lattice strain and lattice distortion.

3.3 Le-Bail Fitting Analysis

In order to elucidate the changes in structure resulting from the incorporation of Fe ions, Le-Bail refinement analysis was performed using the FullProf suite of software. In this case, the refinement was accomplished through considering the $\text{Fd-}3\text{m}$ space group for all compositions in the $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ series. The conditions for the Le-Bail refinements are that $\alpha = \beta = \gamma = 90^\circ$, and $a = b = c$. The resulting Le-Bail fit patterns for all compounds are shown in Figure 3.

The Le-Bail refinements yielded χ^2 close to 0.4, thus showing a high degree of reliability. As expected, there was no significant change in structure since no phase transition occurred. Some impurity peaks were detected, but they did not affect the accuracy of the refinement process.

The lattice parameter 'a' for the materials was then graphed against the Fe^{3+} concentration. Figure 4d. illustrates this relationship. As can be seen, there is an inverse relation in the

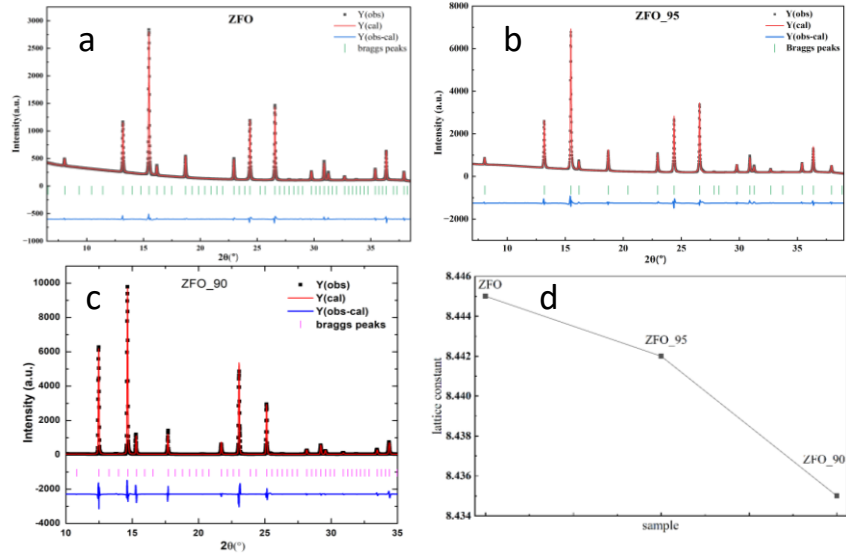


Fig 4: (a-c) Le Bail fitting of samples $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 1.0, 0.95, 0.9$), (d) Variation of lattice parameter as a function of concentration

lattice parameter with respect to the increase in Fe doping due to the substitution of Zn^{2+} by Fe^{3+} .

3.4 Diffuse Reflectance Spectroscopy (DRS)

Optical behavior of the produced samples was investigated through Diffuse Reflectance Spectroscopy (DRS), as per the Kubelka–Munk equation. The figure depicts the spectra of $F(R)$ as a function of photon energy (eV) for each composition. Some notable absorption transitions have been observed in the case of Fe doping in ZnFe_2O_4 . In the case of ZnFe_2O_4 , the charge transfer excitation from O 2p to Fe 3d usually leads to an optical bandgap of about 2.1 eV along with crystal field splitting. Nevertheless, after Fe doping, the absorption edge in ZnFe_2O_4 (ZFO) and Fe-doped ZnFe_2O_4 was observed to be around ~1.95 eV.

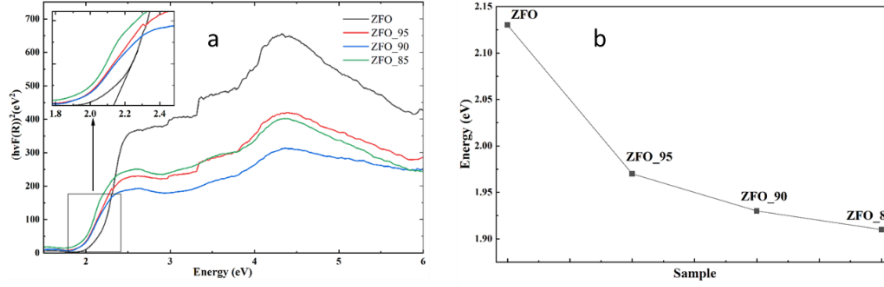


Fig 5: (a) DRS of Fe-doped ZFO with Tauc plot (b) Change in bandgap with concentration.

It can be seen from Figure 5 that the locations of all main absorption peaks are almost constant for both ZFO and Fe-doped samples. Furthermore, a slight shift in absorption edge with increasing Fe concentration was observed, indicating that excess Fe doping introduces additional $\text{Fe}^{2+}/\text{Fe}^{3+}$ related electronic states near the conduction band.

3.5 Complex Impedance Spectroscopy Analysis (CIS):

In order to analyze the effect of temperature and frequency on the electrical behavior of the samples, complex impedance spectroscopy (CIS) analysis was performed for all the samples. CIS analysis was conducted using a frequency range between 100 Hz and 1 MHz and a temperature range between 100 K and 480 K. Complex impedance spectroscopy is an effective analytical method that is frequently utilized in the investigation of electrical properties of materials at various temperatures and frequencies.

Complex impedance spectroscopy is highly efficient in isolating the contribution of bulk, grain boundaries, and electrode effects in a system. However, it is hard to separate long-range transport and localized dipole relaxation mechanisms due to their similarity, which occurs since both mechanisms occur in the bulk and have nearly identical geometrical capacitances. In order to resolve this

problem, the imaginary impedance (Z'') is used to isolate resistive effects like grain boundary effects.

Impedance is a complex quantity, which consists of an imaginary part as reactance Z'' and a real part as resistance Z' .

$$Z^* = Z' + jZ'' \dots\dots(4)$$

CIS is a non-destructive tool that separates the contribution of bulk, grain boundary, and electrode using electrical impedance and electric modulus formalism.

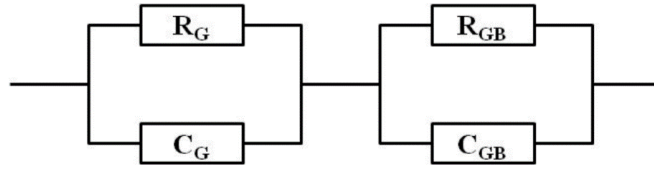


Fig 6: Schematic of equivalent circuit

Here, an equivalent circuit is used to represent the electrical properties corresponding to grain (R_G , C_G) and grain boundary (R_{GB} , C_{GB}) effects in the material.

The impedance (Z^*) of the above circuit is given by

$$Z^* = Z' + jZ'' = \left(\frac{1}{R_G} + j\omega C_G\right)^{-1} + \left(\frac{1}{R_{GB}} + j\omega C_{GB}\right)^{-1} \dots (5)$$

where R_G and R_{GB} are the DC resistances associated with grains and grain boundaries, respectively. C_G and C_{GB} are the capacitances associated with the grains and grain boundaries, respectively. The real part (Z') and imaginary part (Z'') of the complex impedance are:

$$Z' = \frac{R_G}{1 + (\omega R_G C_G)^2} + \frac{R_{GB}}{1 + (\omega R_{GB} C_{GB})^2} \dots (6)$$

and

$$-Z'' = R_G \left(\frac{\omega R_G C_G}{1 + (\omega R_G C_G)^2} \right) + R_{GB} \left(\frac{\omega R_{GB} C_{GB}}{1 + (\omega R_{GB} C_{GB})^2} \right) \dots (7)$$

To understand complete information about the studied material, it is required to measure the value of each component of R and C in the circuit. Impedance formalisms are used to attain these values. Each parallel RC sub-circuit corresponds to the semicircle in the complex plane (Z'' vs Z') or Debye peak in the plot of the imaginary component, i.e., Z'' vs $\log f$. The frequencies corresponding to the maxima of the peak in Z'' plots satisfy the following equation

$$2\pi f_{max}RC = 1 \quad \dots (8)$$

Two semicircles observed in the complex plane (Z'' vs. Z') correspond to the grain boundaries and the grains. The equation mentioned above and the correlation between the grain and grain boundaries can be analyzed using the plots below for all the samples.

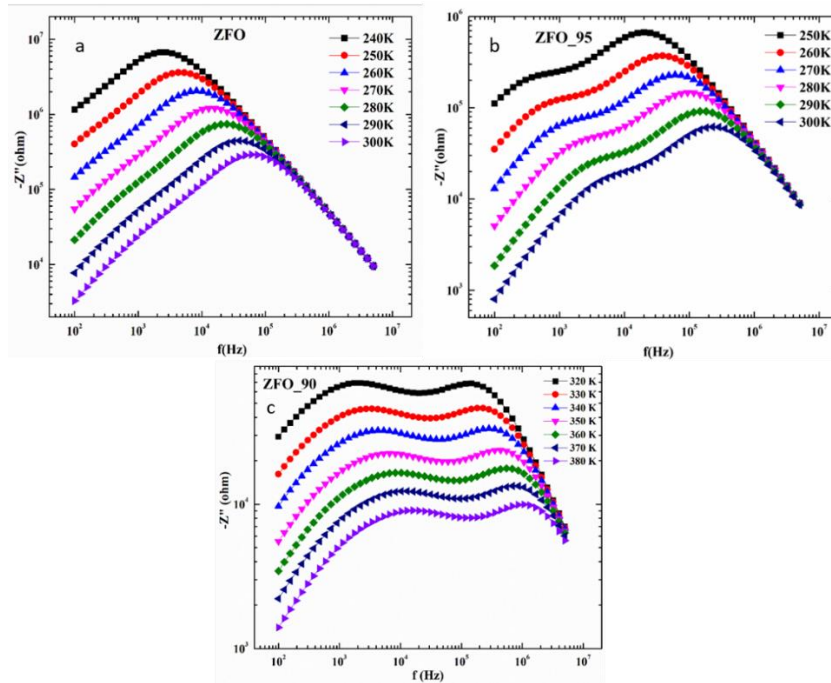


Fig 7 (a-c): Frequency dependent imaginary(Z'') plot for ZFO, ZFO_95, ZFO_90 at various temperature with respect to frequency

The analysis of the Z'' against frequency diagrams (Figure 7) constructed for the first set of Fe-doped Zinc ferrite materials revealed a pronounced development of relaxation processes with the increase in the amount of added iron atoms. The undoped ZnFe_2O_4 sample displayed primarily one relaxation process taking place

within the investigated temperature and frequency ranges due to the dominant role of localized hopping conductivity via grain boundaries. In zinc ferrite, electrons move mostly due to hopping between the Fe^{2+} and Fe^{3+} ions occupying the octahedral B-sites. When iron is doped into zinc ferrite in excess, more iron atoms are formed, which, in turn, causes the formation of additional pairs $\text{Fe}^{2+}/\text{Fe}^{3+}$, resulting in a higher probability of electron hopping. It consequently results in an enhanced charge carrier concentration, providing better electronic conduction. Therefore, new features become observable with respect to the relaxation curves for Fe-doped samples, which additionally have two relaxation peaks because of higher conductivity. One of them can be explained by grain boundary conductivity, while the second one is linked to grain conduction and long-range polaron hopping. Thus, two peaks in the Z'' vs f diagram indicate the occurrence of both localized and delocalized conductivities. The shift in relaxation peaks towards higher frequencies talks about the thermally activated conduction mechanism.

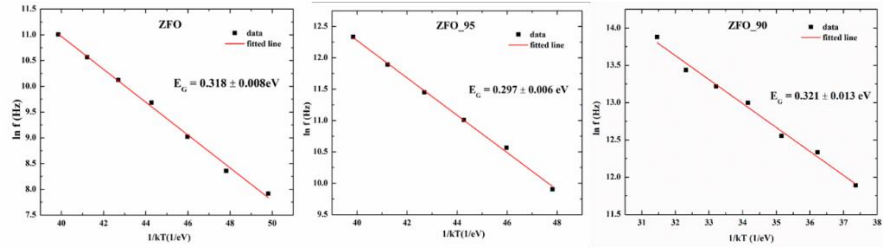


Fig 8: Arrhenius plot of $\ln(f_{\max})$ vs $1/k_B T$ derived from Z'' data

The significant aspect in characterizing conduction mechanisms is the value of the activation energy, which is the minimum energy that must be acquired by the charge carriers to take part in the conduction process. In the current work, the activation energy (E_a) related to the grains and grain boundaries was extracted based on the variation of the relaxation frequency ($f_{\max}$) at different temperatures from the Z'' vs. f graph peak, as seen in Figure 8.

The activation energies were calculated based on the Arrhenius equation:

$$f_{max} = f_0 \exp \left(\frac{-E_a}{k_B T} \right) \dots \dots (9)$$

Here, f_0 is the pre-exponential factor, k_B is the Boltzmann constant, and T refers to the temperature in Kelvin [34]. The values of activation energy were extracted from the slope of the linear fit plot between $\ln(f_{max})$ and $1/T$. The linearity observed in the graphs indicates that the relaxation mechanism is thermally activated.

For the Fe-excess Zinc ferrite samples, the activation energies were evaluated from the temperature-dependent relaxation frequencies calculated using the Z'' versus frequency plot data. The linearity of the Arrhenius curves proves that the relaxation behavior can be attributed to thermally activated conduction in the given temperature region.

The value of activation energy for the undoped $ZnFe_2O_4$ was found to be 0.318 eV. The presence of a small amount of excess Fe results in lowering the activation energy to 0.297 eV in the case of ZFO_95. This indicates higher charge carrier mobility and better hopping conductance in this system. The reason for the decrease in activation energy could be due to the formation of more Fe^{2+}/Fe^{3+} ions, enabling better hopping conduction via them.

In contrast, in the presence of higher Fe content, the activation energy increases to 0.321 eV in ZFO_90.

3.6 Nyquist Plot Analysis

Nyquist plots (Z'' vs. Z') were generated for all compositions within a broad temperature range, as shown in Figure 9. The acquired data show two semicircles for all compositions except for the undoped composition. The semicircle seen at high frequencies is that of the grains, whereas the semicircle seen at low frequencies becomes

more prominent with increasing temperature and represents the effect of the grain boundary. The appearance of these two different semicircles shows that the dielectric relaxation behavior is due to two different effects: bulk grains and grain boundaries.

In order to shed some light on the physical origin of the relaxation and charge transportation mechanism, the Nyquist plots recorded at various temperatures were normalized against the high-frequency arc recorded at the lowest temperature. As can be seen after normalization, all the plots collapse into one plot, revealing that the relaxation mechanism does not change with temperature. Therefore, the observed discrepancy is mainly attributed to the changes in the relaxation time constants due to temperature. It is very clear that there exists a common conduction mechanism for the investigated temperature range. Furthermore, the occurrence of two asymmetric semicircular arcs shows that the relaxation phenomenon is non-Debye in nature. In an ideal Debye relaxation, one relaxation is depicted by a symmetric semicircle with one specific relaxation time constant. However, in this work, the presence of two broadened peaks confirms non-Debye type dielectric relaxation behavior of the samples. In order to explain this phenomenon, an equivalent circuit diagram comprising two constant phase elements (CPEs) was used. In this case, the grain and grain boundary contributions are represented by a resistance-capacitance combination in parallel arrangement.

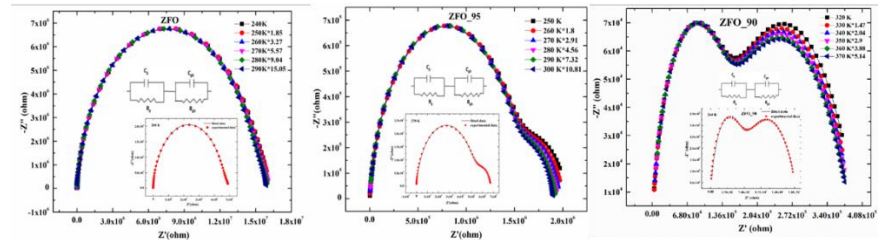


Fig 9: Nyquist plots (Z'' versus Z') for ZFO and Fe-doped ZFO samples at various temperatures, displaying semicircular arcs that correspond to the electrical response of grains and grain boundaries.

In order to get the quantitative data, the value of R_G and R_{GB} was found from the fitted equivalent circuit to the plotted Nyquist diagrams at different temperatures. The calculated R values were then plotted against the graph of $\ln(R)$ vs. $1/k_B T$, and E_a was calculated through the Arrhenius equation.

$$R = R_0 \exp\left(\frac{E_a}{k_B T}\right) \dots \dots (10)$$

The results of the calculated activation energies (E_a) of all the samples are shown in Figure 10.

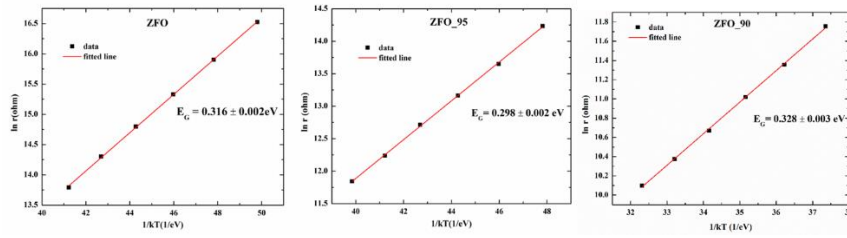


Fig 10: Arrhenius plots of bulk (R_G) resistances, showing $\ln(R)$ vs $1/k_B T$ plot for the samples

An appreciable reduction in the value of activation energy is seen with the increase in dopant concentration up to the optimum value of the doping ratio (5%). This shows an improvement in the mobility of charge carriers for the process of conduction in grains and grain boundaries. However, with further increase in dopant concentration, there is a very small rise in activation energy, which implies that excessive doping can lead to clustering of defects, non-uniformity in composition, or segregation within the grain boundaries. Even at higher doping levels, the activation energy is still significantly lower than that of the undoped specimen.

The values of R_0 were estimated through extrapolation of linear fitted plots to $1/k_B T = 0$ as seen in Figure 10. These values are equivalent to the y-intercepts of the plots in the logarithmic version of the Arrhenius equation. Utilizing these parameters, the bulk resistances were extrapolated for all samples at a wide range of

temperatures, and the variation is shown in Figure 11. A consistent reduction in resistance with temperature increase for all samples was noted, depicting a negative temperature coefficient of resistance (NTCR), which is a clear confirmation of their semiconducting nature.

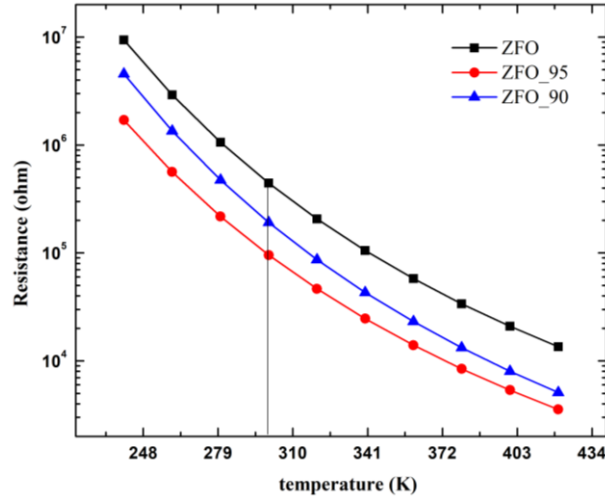


Fig 11: Dependence of bulk resistance on temperature for various samples

The reduction in the activation energy with doping, in conjunction with the NTCR trend, implies a positive effect on the charge carrier mobility. Also, activation energies determined from the Z'' and Nyquist plot fittings were plotted as a function of dopant concentrations.

Using both formalisms, it was observed that the activation energies reduce as the dopant concentration increases up to the optimal dopant concentration. After reaching the optimal dopant concentration, there was a gradual increase in the activation energy for all three formalisms. Such trends may be associated with the saturation of dopants, clustering of defects, compositional disorder, or secondary impurity phases that may act as scattering centers or trap sites and reduce the mobility of charge carriers.

In conclusion, the analysis of activation energy and NTCR behavior of materials reveals that moderate Fe doping is $x = 0.95$ (ZFO_95), due to enhanced carrier conduction by minimizing activation energy, while exhibiting semiconducting characteristics with minimum resistances.

3.7 Vibrating sample magnetometer (VSM)

Magnetic investigations for the study of the effect of Fe concentration in excess on the magnetization were performed at room temperature by the SQUID-VSM method with magnetic fields ranging between -7 T and $+7$ T. Magnetization hysteresis curves of ZFO, ZFO_95, and ZFO_90 samples are presented in Fig 12

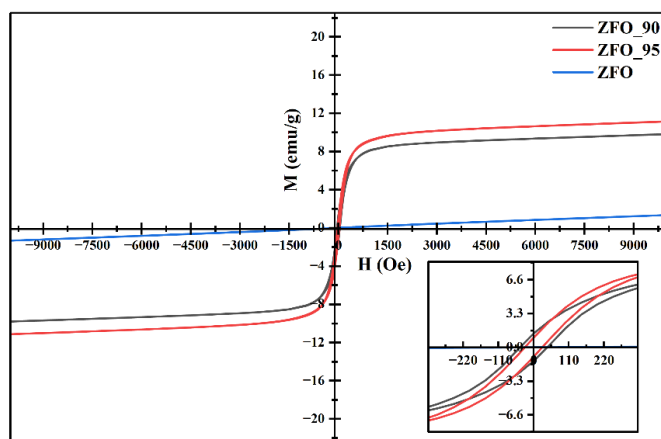


Fig 12: M-H studies of the Fe-doped samples

From the hysteresis curves, it is clear that all synthesized samples exhibit ferrimagnetic properties with narrow hysteresis curves and low coercive fields. Bulk zinc ferrite (ZnFe_2O_4) usually shows antiferromagnetic ordering, with occupation of Zn^{2+} ions at tetrahedral sites and Fe^{3+} ions at octahedral sites. However, in nanocrystalline and non-stoichiometric compounds, redistribution of cations happens such that a few Fe^{3+} ions occupy tetrahedral sites. Thus, ferrimagnetism emerges due to A-B superexchange interaction between tetrahedral (A) and octahedral sites (B).

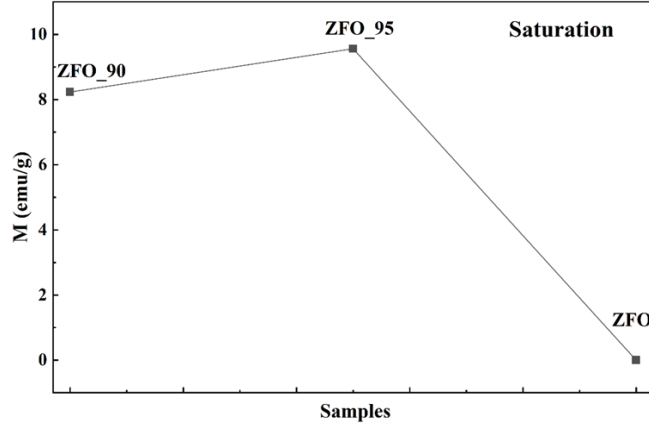


Fig 13: Saturation magnetization trends of the samples

Saturation magnetization (M_s) first increases up to ZFO_95 and then reduces to ZFO_90 samples. For ZFO_95, there is an increase in magnetization, which is because of the excess amount of Fe ions that causes a partial inversion of the spinel structure and an increase in Fe^{3+} ion population in tetrahedral sites (A). Consequently, more super exchange between $\text{Fe}^{3+}(\text{A})\text{-O}^{2-}\text{-Fe}^{3+}(\text{B})$ occurs.

Upon further addition of Fe into ZFO_90, the saturation magnetization drops down. This is probably because of the structural disorder, spin canting effects, and cluster formations of Fe atoms or antiferromagnetic coupling regions. An excess amount of Fe atoms can affect the balance of the magnetic moments of the A- and B-sublattices and consequently lower the magnetization.

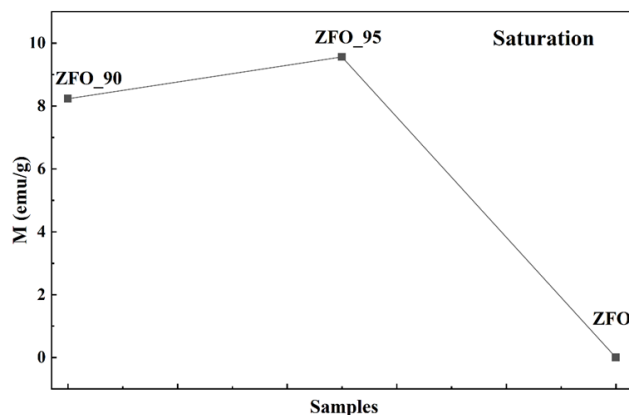


Fig 14: Coercivity of the samples (ZFO, ZFO_90, ZFO_95)

It was noticed that the coercivity showed a decreasing trend with the increment in the Fe atoms' content. The reduction in coercivity shows a soft magnetic nature. This can be attributed to a reduction in magnetic anisotropy, small domain wall pinning, and strong exchange interaction caused by the distribution of Fe atoms in the lattice structure.

The results obtained from the magnetic measurements clearly show that an excess amount of Fe atoms could control the cation distribution and magnetic exchange interactions in zinc ferrite.

3.8 X-ray Circular magnetic Dichroism (XMCD)

In order to get element-specific information about the magnetic properties and electronic configuration of Fe ions in our synthesized materials, XMCD experiments were performed for the Fe L_{2,3} absorption edges using circularly polarized X-rays obtained from the synchrotron radiation source of INDUS-2, RRCAT, Indore, India, operated on the beam line BL-20.

The XAS and XMCD spectra of ZFO_95 are depicted in Figure 15. In this case, characteristic Fe L₃ and L₂ absorption edges were

noticed in the XAS spectra, which can be attributed to the transition of electrons from Fe 2p orbitals to empty Fe 3d orbitals.

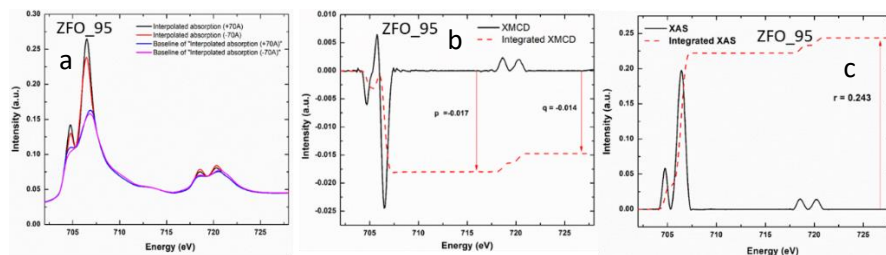


Fig 15: (a) Baseline correction of left and right circularly polarized data in XMCD, (b) XMCD of ZFO_95, (c) XAS of ZFO_95

The XMCD spectra were derived by subtracting the absorption spectra obtained using left circularly polarized X-rays from those using right circularly polarized X-rays under a fixed magnetic field.

The XMCD spectra obtained for the Fe-excess zinc ferrite (ZFO_95) revealed a marked dichroic response, which clearly showed the strong magnetic polarization of Fe ions. The significant intensity of the dichroism spectra confirmed the occurrence of ferrimagnetic ordering due to the redistribution of Fe ions into tetrahedral and octahedral crystallographic positions.

The XMCD measurement thus serves as direct proof of the effects of non-stoichiometric doping on Fe in Zinc ferrite's local electronic structure and magnetic exchange interactions. In addition, the combination of VSM and XMCD measurements shows that an increase in Fe content above stoichiometry significantly improves ferrimagnetic properties in ZnFe_2O_4 .

Chapter 4

Al-doped $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$

(ZAFO_95_x)

4.1 Introduction

The current chapter is focused on study of the structural, optical, electrical, and magnetic properties of non-stoichiometric zinc ferrite compositions $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$, and 0.5) doped by Al^{3+} . The main idea of the present work was to find out how the presence of non-magnetic impurity will affect the crystal structure, cation distribution, charge transfer mechanism, and magnetic properties of excess iron zinc ferrite.

As for the size parameters, it can be mentioned that aluminum ions have smaller radii in comparison with Fe^{3+} and, thus, are likely to occupy octahedral B-sites within the spinel lattice. Thus, lattice contraction and change of the $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ super exchange are expected. What is more, since Al^{3+} ions are non-magnetic and do not participate in electron hopping, substantial changes in magnetic and transport properties of the material were observed.

In order to prove this assumption, the SXRD measurements, Le-Bail refinement, DRS, CIS, VSM, and XMCD analysis were carried out.

4.2 X-Ray Diffraction Analysis

The structural evolution and phase purity of synthesized Al-doped compositions of ZnFe_2O_4 , viz. $\text{Zn}_{0.95}\text{Al}_x\text{Fe}_{2.05-x}\text{O}_4$ ($x = 0.1\text{--}0.5$) were characterized by using monochromatic X-ray diffraction measurements at the BL-11 beam line of INDUS-2 synchrotron facility, RRCAT, Indore, with a monochromatic radiation source of wavelength $0.6862\text{\AA}$.

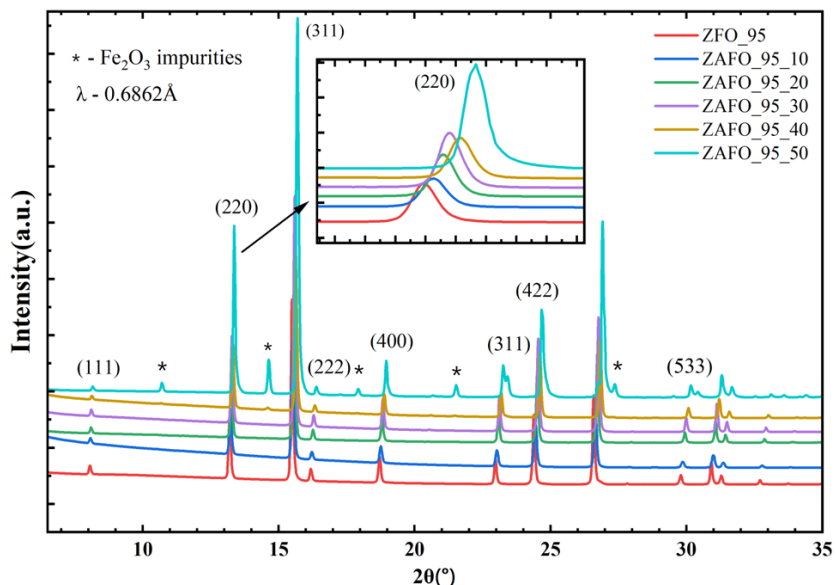


Fig 16: XRD of ZAFO_95_x sample

Fig 16 displays SXRD patterns of various compositions along with that of pure ZnFe_2O_4 . All major diffraction peaks were indexed to the cubic spinel structure with space group $\text{Fd-}3\text{m}$ as expected. The diffraction peaks for (111), (220), (311), (400), (422), (511), and (440) planes indicate the successful synthesis of spinel ferrite phase.

The absence of any other impurity peaks up to $x = 0.3$ suggests that incorporation of Al^{3+} ions in the cubic spinel structure is successfully accomplished below the solubility limit. For higher concentrations of dopants ($x > 0.3$), some impurity peaks corresponding to Fe_2O_3 phases were observed. This may be attributed to partial segregation of the phases due to the limited solubility of the doped ions in the spinel lattice.

The systematic shift towards high 2θ values in the diffraction peaks with increased Al content shows that there is a contraction in the unit cell size because of the substitution of relatively bigger Fe^{3+} ions ($0.645 \text{ \AA}$) by smaller Al^{3+} ions ($0.535 \text{ \AA}$). It further shows that Al ions have successfully occupied the octahedral B sites of the

spinel lattice. Reduced lattice parameter further indicates the increased lattice strain.

4.3 Le-Bail Fitting Analysis

In order to quantitatively assess the structural changes due to Al doping, the Le-Bail refinement analysis has been done using FullProf Suite, taking into consideration the cubic spinel structure with Fd-3m space group for all compositions.

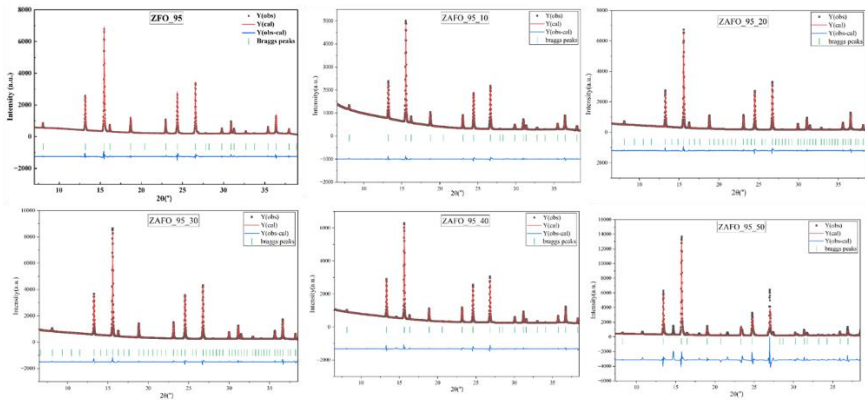


Fig 17: Le-Bail fitting of samples ZFO_95 and ZAFO_95_x (x = 10, 20, 30, 40, 50)

Figure 17 shows the refinement patterns for all compositions. Very good agreement between experimental and refined data was achieved, thus validating the refinement technique employed. All the obtained refinement factors yielded very low Rwp and χ^2 values close to one.

All compositions retained their cubic spinel structure without undergoing any structural phase change despite the presence of very small impurities at high concentrations of dopants. However, these minor impurity phases did not affect the refinement results.

The refinement of the lattice parameters showed a steady decline with an increase in the Al concentration. This observation provides

clear evidence for the successful substitution of Fe^{3+} by Al^{3+} ions. It also conforms to Vegard's Law.

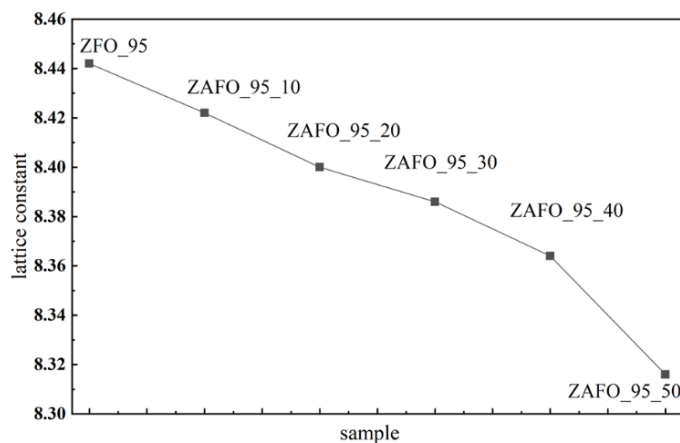


Fig 18: Trends in the lattice constants of the samples

The decrease in the lattice parameter also reflects an increase in lattice distortion and changes in the cation distribution in the lattice, as given in Figure 18.

4.4 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy experiments were conducted to study the optical properties and bandgap tuning of the Al-substituted zinc ferrite compounds.

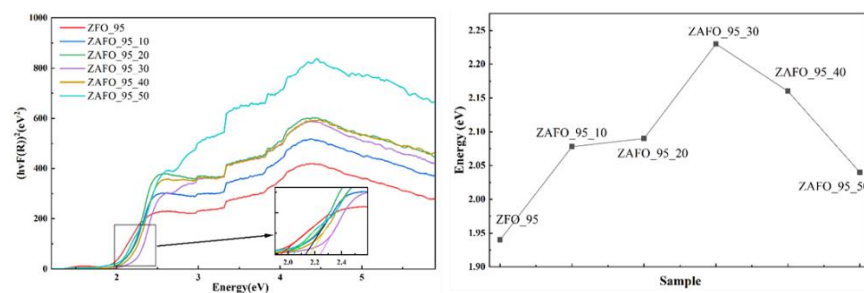


Fig 19: Tauc's plot of the samples ZFO, ZAFO_95_x (x = 10, 20, 30, 40, 50), (b) magnified curve of extrapolated band gap

Figure 19 presents the transformed Tauc's plot as a function of photon energy for all compositions studied. The presence of an

optical absorption edge in the visible range confirmed that the prepared ferrites exhibit semiconductor behavior.

The optical band gaps were calculated using the Tauc relation through the extrapolation of the straight line $[F(R)hv]^2$ versus photon energy (hv). Bandgap values varied systematically with the amount of aluminum substitution.

Undoped $Zn_{0.95}Fe_{2.05}O_4$ composition showed a bandgap of about 1.97 eV. Increasing the concentration of Al resulted in an increase in the bandgap up to ZAFO_95_30 composition, followed by a slight decrease in larger doping amounts.

An increase in the bandgap width is caused by a decrease in Fe 3d–O 2p interaction due to magnetic Fe^{3+} ion substitution with non-magnetic Al^{3+} ions. Because the latter does not have any contribution to d–d transitions, the density of electronic states related to Fe ions decreased at the valence band, leading to the widening of the bandgap.

However, the relatively small reduction in band gap at high doping levels may result from localized states created by defects or secondary impurities, where extra energy levels are introduced within the forbidden energy gap.

This shows the feasibility of tuning the band gap and thus making use of aluminum-doped zinc ferrite in optoelectronic or photocatalytic processes.

4.5 Complex Impedance Spectroscopy (CIS)

The study of electric transport characteristics and relaxation processes was conducted on the basis of complex impedance spectroscopy studies at temperatures from 100 to 480 K and frequencies from 100 Hz to 1 MHz for Al-doped zinc ferrite

samples. The temperature dependence of imaginary impedance (Z'') with respect to frequency is illustrated in Figure 20.

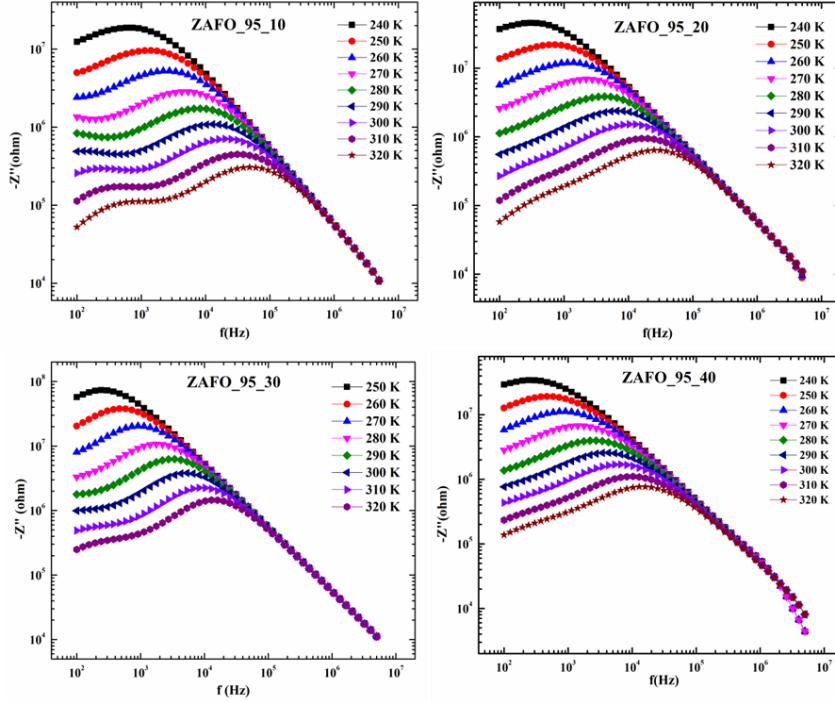


Fig 20: Frequency dependent imaginary(Z'') plot for ZAFO_95_10, ZAFO_95_20, ZAFO_95_30, ZAFO_95_40 at various temperatures with respect to frequency

The dependence of all the compositions on temperature revealed relaxation peaks that were shifted towards higher frequencies as temperature increased. This is indicative of a relaxation process influenced by thermal activation in the material. While the undoped ZFO showed mostly a single relaxation peak attributed to grain boundary-dominated conduction, the doped Al samples showed broader relaxation with altered peak positions as a result of enhanced hopping conduction. The reduction in Z'' with increasing temperature reveals a reduction in the value of resistance, while the charge carrier mobility was increased.

In zinc ferrites, charge carriers are electrons that hop between Fe^{2+} and Fe^{3+} ions at octahedral sites; thus, the introduction of Fe^{3+} ions

with non-conducting Al^{3+} ions leads to reduced hopping conductance. The activation energies were obtained from the Arrhenius plot $\ln(f_{\max})$ vs. $1/k_{\text{B}}T$ following the expression:

$$f_{\max} = f_0 \exp(-E_a/k_{\text{B}}T) \dots (11)$$

Linearity of the Arrhenius plot is indicative of thermally activated conduction for all compositions.

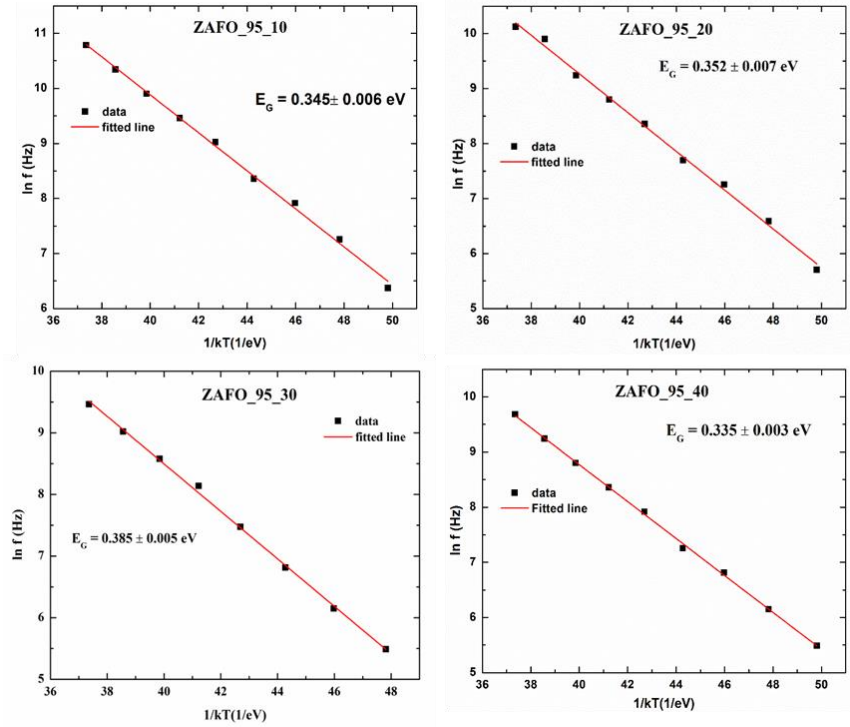


Fig 21: Arrhenius plot of $\ln(f_{\max})$ vs $1/k_{\text{B}}T$ derived from Z'' data

A systematic trend of increasing activation energy was observed with an increase in the concentration of aluminum. At low levels of aluminum doping, the activation energy decreased slightly, implying that the hopping process became easier for the carriers due to local lattice distortion. But with higher aluminum concentration, the activation energy increased due to the inhibiting effect of the Al^{3+} ion on the hopping of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions.

Increasing activation energy in the presence of high concentrations of aluminum signifies localization of the charge carriers.

4.6 Nyquist plot analysis

Nyquist plots (Z'' vs Z') of all compositions at various temperatures are presented in Fig 22

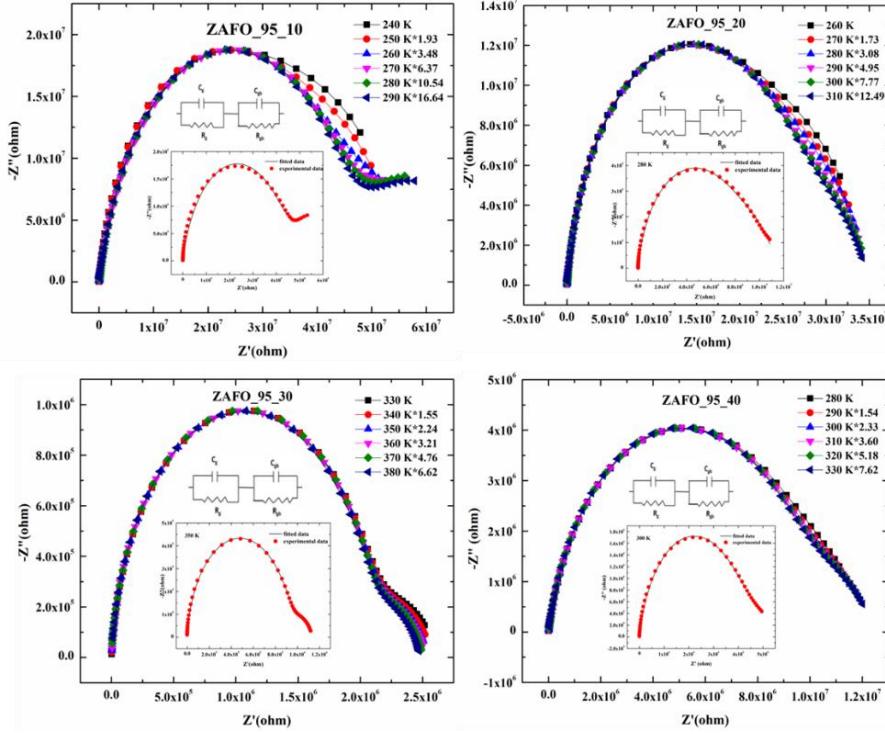


Fig 22: Nyquist plots (Z'' versus Z') for Al-doped ZAFO samples at various temperatures, displaying semicircular arcs that correspond to the electrical response of grains and grain boundaries.

Impedance data showed depression of semicircular arcs, implying non-Debye relaxation behavior. The presence of two semicircles in doped samples indicates two contributions, namely grains and grain boundaries.

The high-frequency semicircle represents the grain contribution, while the low-frequency semicircle is indicative of grain boundary contribution. The higher contribution of the grain boundary implies that it plays an important role in electrical transport phenomena.

Equivalent circuit modeling by a parallel resistor-capacitor model along with constant phase elements (CPEs) gave satisfactory results in fitting the experimental data.

Grain boundary resistance obtained from equivalent circuit modeling decreased with an increase in temperature, which further supports the semiconductor behavior as well as the NTCR effect.

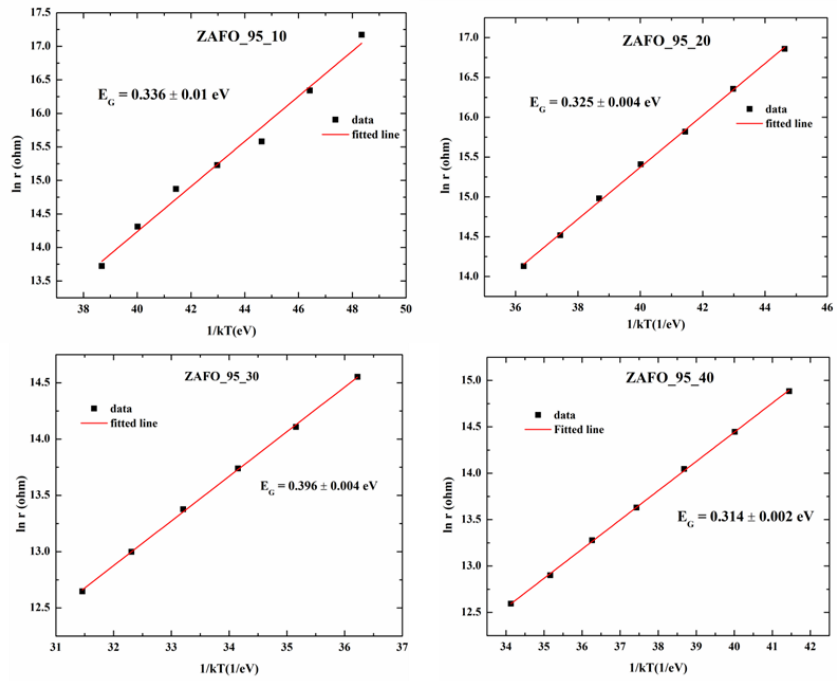


Fig 23: Arrhenius plots of bulk (R_{GB}) resistances, showing $\ln(r)$ vs $1/k_B T$ plot for the samples

Activation energies calculated from Nyquist plots were found to be consistent with activation energies obtained from Z'' plots.

The resistance vs temperature plots of various samples are given in the figure below.

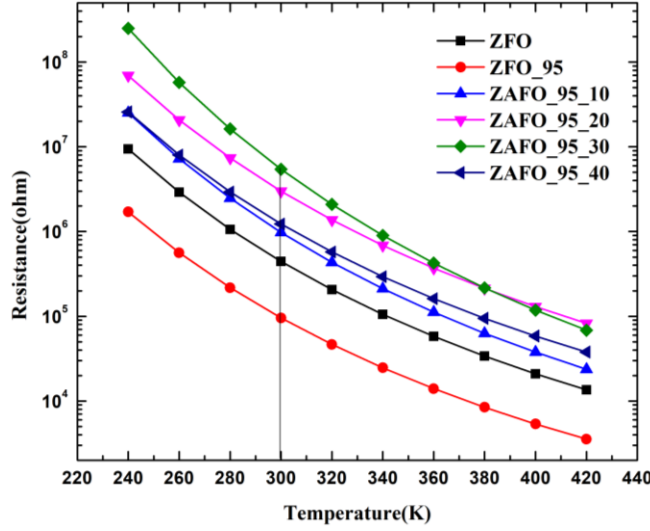


Fig 24: Dependence of bulk resistance on temperature for ZAFO samples

4.7 Vibrating Sample Magnetometer (VSM)

Magnetic hysteresis was measured at room temperature through the SQUID-VSM method to explore the influence of aluminum substitution on the magnetic property.

The M-H hysteresis loop of all compositions is presented in Figure 25

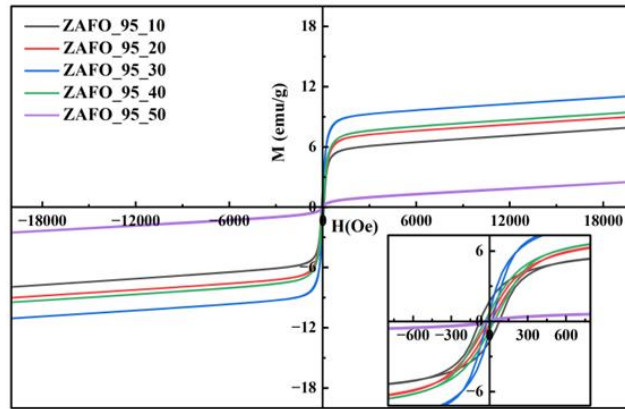


Fig 25: M-H studies of the Al-doped samples

A narrow hysteresis loop shows a soft magnetic property. The saturation magnetization M_s showed a gradual decrease as a result of an increase in Al concentration.

This observation can be explained by substituting magnetic Fe^{3+} ions with non-magnetic Al^{3+} ions, thereby decreasing $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ superexchange interactions and resulting in ferrimagnetic ordering.

Aluminum substitution also affects the cation distribution and magnetic exchange interaction between A and B ions. Decreasing A-B superexchange interactions decreases long-range order and magnetization.

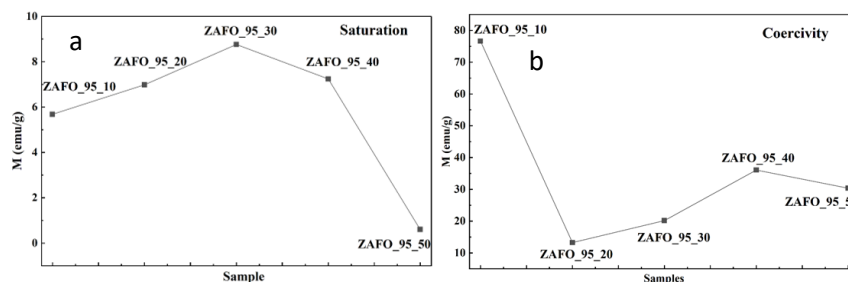


Fig 26: (a) Saturation magnetization of the samples, (b) Coercivity of the samples

Furthermore, the coercive field was found to vary with Al doping concentration due to the influence of magnetic anisotropy, crystallite size, and lattice distortion caused by Al doping.

These results demonstrate the ability of Al to tune magnetic interactions in zinc ferrite.

4.8 X-Ray Magnetic Circular Dichroism Analysis (XMCD)

X-ray magnetic circular dichroism measurements were performed at the Fe $L_{2,3}$ absorption edges to investigate element-specific magnetic behavior of Al-doped zinc ferrite.

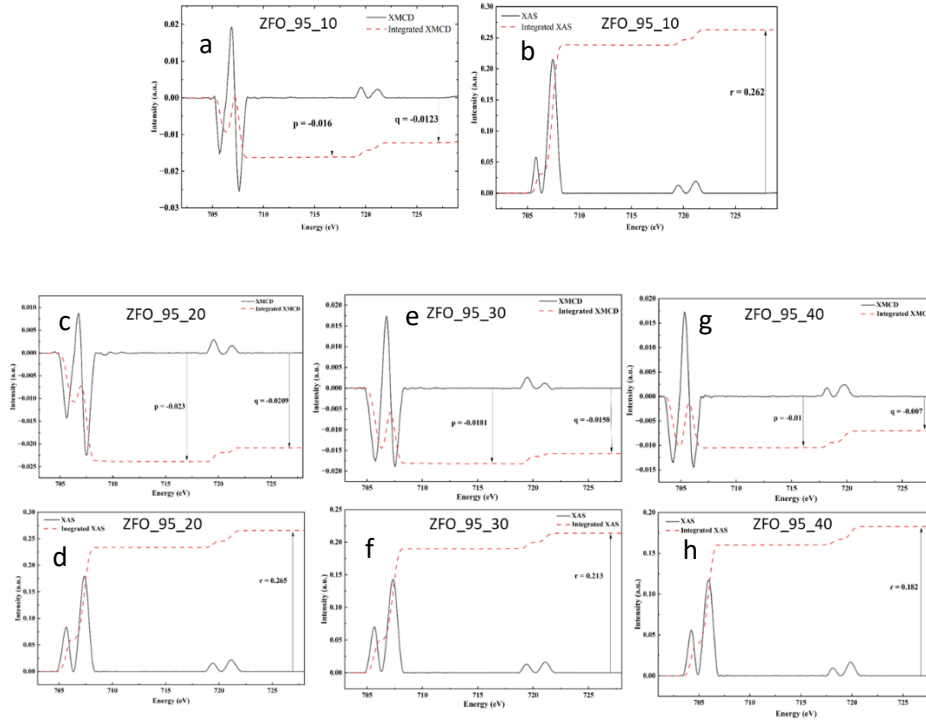


Fig 27: (a, c, e, g) XMCD spectra of Al-doped ZAFO, (b, d, f, h) XAS spectra of Al-doped ZAFO.

The XAS and XMCD spectra for all compositions are shown in Figure 27. The XMCD spectra exhibited characteristic dichroic signals corresponding to Fe magnetic moments. The magnitude of the XMCD signal gradually decreased with increasing Al concentration, indicating suppression of magnetic ordering due to replacement of magnetic Fe^{3+} ions by non-magnetic Al^{3+} ions. Using XMCD sum rule analysis, the orbital and spin magnetic moments were estimated from integrated XAS and XMCD spectra using p, q, and r parameters. The reduction in spin magnetic moment with Al substitution confirms weakening of Fe-related magnetic exchange interactions. The XMCD results strongly support the VSM observations and provide direct evidence of modification in electronic and magnetic structure due to Al doping. The element-specific sensitivity of XMCD further confirms that the reduction in magnetization originates primarily from changes in Fe electronic states and local magnetic environment.

Chapter 5

Conclusion and future scope

Conclusion

In the current study, stoichiometric deviation and aluminum-doped zinc ferrites have been synthesized by employing the traditional solid-state reaction technique to evaluate the effect of an excess of iron and the incorporation of the non-magnetic aluminum element on the physical characteristics of zinc ferrite. The synchrotron X-ray diffraction analysis demonstrated that a cubic spinel structure with the space group of $Fd-3m$ has formed for all major compositions. The progressive shift of diffraction lines towards higher 2θ angles and decrease in lattice parameter with increasing aluminum concentration validated that small-sized Al^{3+} ions had been incorporated in the spinel lattice without altering its crystal structure.

Diffuse reflectance spectroscopy indicated the tuning effect of the optical bandgap through compositional engineering. For the Fe-rich series, a relatively low level of Fe doping resulted in lowering the bandgap energy and electrical resistance owing to improved hopping conduction through Fe^{2+}/Fe^{3+} . However, a high level of Fe concentration resulted in disordering and decreased charge carrier mobility. As depicted in Figure 28, ZFO_95 showed the minimum electrical resistance and appropriate conduction properties among the Fe-doped compositions, thereby being suitable for semiconductor and spintronics applications.

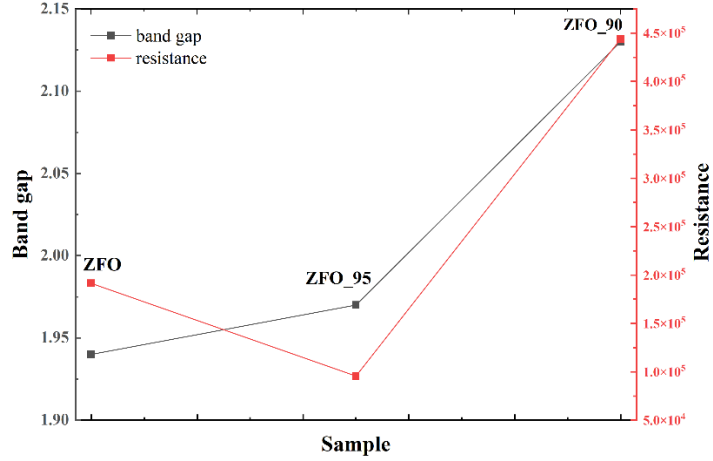


Fig 28: Correlation between bandgap and resistance in Fe-doped ZFO

Impedance spectroscopy analysis revealed semiconducting characteristics with NTCR in all samples. In the Al-doped series, increasing the Al concentration caused an increase in resistance and bandgap. The former results from the inhibition of $\text{Fe}^{2+}/\text{Fe}^{3+}$ hops, while the latter arises from weakening Fe 3d-O 2p hybridization. This trend is illustrated in Figure 29. It can be seen that ZAFO_95_30 had the highest bandgap and resistance, meaning that it behaved as an insulator and hindered the flow of charge carriers effectively.

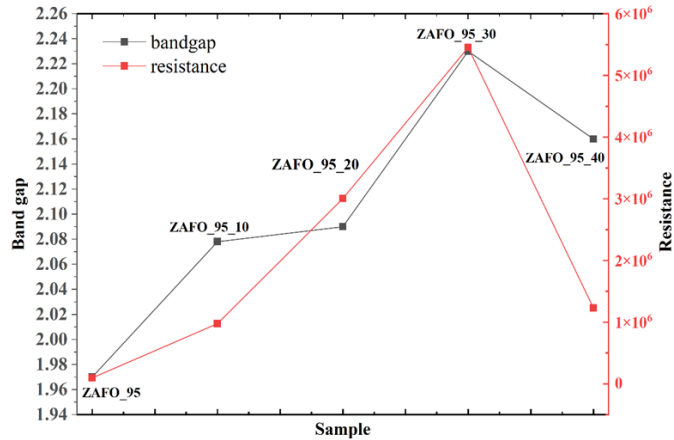


Fig 29: Correlation between bandgap and resistance in Al-doped ZAFO

The magnetic Analysis conducted using SQUID-VSM and XMCD techniques demonstrated that the magnetic ordering is highly dependent on the distribution of cations and dopant content. Fe excess slightly increased

ferrimagnetism by intensifying $\text{Fe}^{\text{A}3+}\text{-O}^{2-}\text{-Fe}^{\text{B}3+}$ super exchange interactions. On the other hand, the introduction of Al^{3+} ions gradually reduced ferrimagnetism due to dilution of the Fe-O-Fe exchange paths. This effect is illustrated in Figure 30. It is evident that the orbital and spin magnetic moments were optimized at around ZAFO_95_20 and ZAFO_95_30, followed by a gradual decrease at higher Al concentrations.

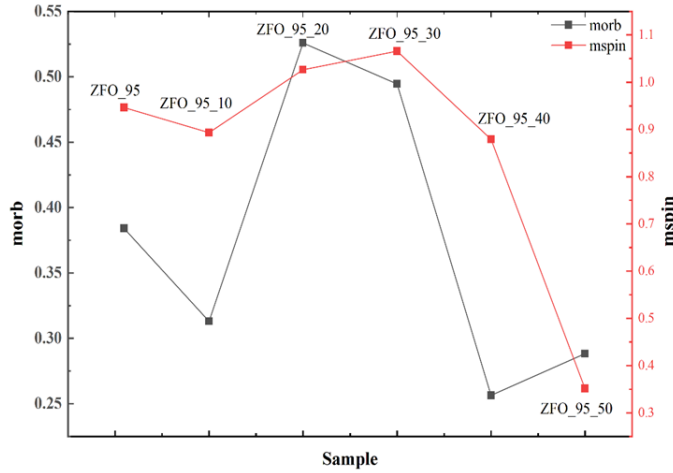


Fig 30: Change in the spin and orbital magnetic moment due to a change in the concentration of Al

Among all prepared compositions, ZAFO_95_30 possessed the highest degree of multifunctional properties including enhanced electrical resistivity, widened optical band gap and stable ferrimagnetic ordering. This composition is positioned near the limit of solubility but remains structurally stable and magnetically ordered. This tunability of properties indicates the possibility of efficient tuning of optical, electrical, and magnetic properties of zinc ferrite by varying Fe content and using Al substitutions in magnetic cores, spintronics, photocatalytic applications, sensing, and high-frequency electronics.

Future Scope

There are various ways that this study can be extended through future research. The detailed EXAFS and XANES analysis can help in the exploration of cationic distribution, coordination, and oxidation state of iron ions in the crystal lattice. XMCD analysis can help in understanding the magnetic order and exchange interaction at lower temperatures.

More advanced studies regarding microstructure can be carried out using TEM/HRTEM in order to understand defect formation, grain boundary structures, and secondary phases developed during the synthesis at higher aluminum concentration levels. DFT calculation can further help in the theoretical understanding of the changes made in the energy band gap, magnetic exchange interactions, and charge transport characteristics.

Due to the multi-functional nature of the optimized composition, i.e., ZAFO_95_30, its practical applications can be analyzed through photocatalysis, dielectric measurements, and high-frequency magnetic losses measurements.

Focusing on the future prospects for further improvement, the researchers can explore the areas of codoping, thin film growth, and nanostructured zinc ferrite system development.

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