ELECTRICAL AND MAGNETIC TRANSPORT PROPERTIES OF DOPED NANOFERRITES

ABSTRACT

THESIS

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INTRODUCTION

Low dimensional materials have emerged as a promising candidates form the fundamental point of view to more advanced applications. In fact, the nano-sized materials often exhibit remarkable properties which are drastically contrasting as compared to those possessed by their bulk counterparts. This is due to the fact that as the dimensions of particle approach the nano-scale, the number of atoms residing on the surface of the particle increases and at a few nanometer size, 80-90% of atoms occupy the boundary of the grain. This surprisingly enhances the active sites within the system. Another reason is that low dimensional materials do not have inertia due to negligible mass of constituent particle and hence the kinematics and dynamics of nano-scaled systems is independent of gravitational influences. Apart from that, in low dimensional regime, the behaviour of particle is governed by the laws of quantum mechanics.

Since the last two decade there has been a growing interest in the development and fabrication of magnetic nanomaterials because of discovery of astonishing new phenomena, with potential applications in the fields of information technology, telecommunication, medicine, high frequency material, magnetic core materials and sensing applications. The nano-sized magnetic materials are generally composed of ferro/ferri/antiferro magnetic particles. The size, shape and distribution of the particles play an important role in determining their properties.

In the present thesis, synthesisization and characterization of nano-structured sytems having composition Mg(Cr_{0.5-5Al_{0.5}})_{2}Fe_{2-x}O_{4}, Fe_{2-x}Cr_{2}O_{3}, and Bi_{1-x}Al_{2x}Fe_{1-x}O_{3}, has been carried out. The synthesisization has been done by normal and modified solution combustion techniques. The so prepared materials were investigated broadly for structural analysis, optical band gap measurement, a.c. and d.c. electrical transport properties, dielectric studies, sensing behaviour, and magnetic properties.

CHAPTER 1

Chapter 1 consists of detailed introduction and scope of spinel ferrites along with a brief highlight to perovskite materials. This chapter deals with a general introduction of fundamentals of magnetism followed by a discussion of some
important issues on nanomagnetism like, single domain theory, superparamagnetism, magnetic anisotropy mechanisms and ferrites along with their structural and microstructural/nanostructural aspects. It has also been described how the nature of atoms sitting on Tetrahedral (A) and Octahedral (B) sites in spinel as well as perovskite systems alters its magnetic and electric properties. Further the influence of reduction of grain size on the magneto-electric properties has also been elaborated.

CHAPTER 2

Chapter 2 deals with the synthesis techniques of nano-materials with emphasis on the solution combustion technique which has been adopted throughout this thesis. This chapter further elaborates the detail of material characterization techniques employed to test the material for their structural, microstructural, electrical and magnetic properties.

CHAPTER 3

In this chapter, Aluminum doped Bismuth Ferrite (BFO) nanopowders (grain size 13–20 nm) having composition Bi$_{1-x}$Al$_{2x}$Fe$_{1-x}$O$_3$ ($x = 0.00$, $0.025$, $0.05$, $0.10$, $0.15$, $0.20$, $0.25$ and $0.30$) were successfully synthesized by solution combustion method using citric acid as fuel at a temperature as low as 200 °C. The as-prepared samples were examined by powder XRD for phase identification and crystallite size determination. The X-ray patterns suggest that Al$^{3+}$ ions have been successfully doped in the BiFeO$_3$ matrix and crystallite size varying from 13.0 nm to 19.6 nm. FT-IR analysis was carried out to identify the various chemical bonds present within the system. FT-IR measurements confirmed perovskite nature of the samples. The d.c. resistivity as a function of temperature was measured by standard two probe setup. All samples exhibit metal insulator transition temperature ($T_{MI}$) at 325 K. The resistivity is increasing with Al$^{3+}$ concentration and follows the Arrhenius behavior. The activation energies calculated from the slopes of ln($\rho$) versus $10^3/T$ plots are in the range 0.54–0.73 eV. Activation energy was found to increase with doping. The optical band gap was calculated from the UV–Visible absorbance spectra using classical $Tauc$ relation which was found to vary from 2.78 eV to 2.93 eV for different Al$^{3+}$
concentrations. Optical band gap was observed to vary from 2.78 eV to 2.93 eV on increasing the dopant concentration from 0.00 to 0.30, which is higher compared to bulk BFO (1.82 eV). Higher values of band gaps for these ceramics are quite compatible with their high resistivity. It was observed that Al$^{3+}$ concentration influences the structural and dielectric properties of the material. Dielectric relaxation was investigated over a wide range of frequency and temperature. Relaxation peaks were obtained in low as well as high frequency regions for all samples which are explained on the basis of Debye-type relaxation model. The replacement of Fe$^{3+}$ and Bi$^{3+}$ by Al$^{3+}$ ions in the BFO system creates oxygen vacancies and hence Schottky barriers, which are responsible for the anomalous behaviour in the dielectric properties. Debye relaxation model and Maxwell–Wagner charge carriers hopping were utilized in overall estimation of the dielectric behaviour of the system. The values of dielectric constant and loss tangent were found to decrease with the increase in frequency, while these parameters increase with the increase in temperature as well as dopant concentration. The a.c. conductivity has a general decreasing trend as a function of composition while it increases with the increase in frequency. The temperature dependence of a.c. conductivity and relaxation time follow well-defined Arrhenius behaviour. The calculated values of activation energies are in the order of 0.54 eV–0.73 eV (<1.0 eV) which are indicative of the conduction by means of space charge carriers and $O^{2-}$ vacancies. The frequency and temperature dependence of dielectric spectra shows dispersion and relaxation which has been justified on the basis of Debye-relaxation model and Maxwell-Wagner type charge carrier hopping. Relaxation time was evaluated from the fitted Cole-Cole model. The a.c. conductivity has been accounted on the basis of charge imbalance caused by the oxygen non-stoichiometry and lattice defects (pores) created by the foreign impurity atoms (dopant). The plots of relaxation time and the a.c. conductivity as the function of inverse absolute temperature follow the famous Arrhenius expression. Magnetic data shows that the material exhibits ferromagnetic behaviour which ultimately switched to antiferromagnetic nature at higher doping. Strong saturation at the applied field of 10 KOe is observed for undoped sample which ceases to saturate at this field for higher doping and ultimately becomes linear with the applied field at extreme doping. Coercive force and remanent magnetization become extinct at higher doping thereby confirming the superparamagnetic nature of particles.
CHAPTER 4

In this Chapter, we have shown that a combination of Al$^{3+}$ and Cr$^{3+}$ ions can be incorporated in the lattice system of MgFe$_2$O$_4$ which alters the electrical and magnetic behaviour of the material. We have successfully synthesized Chromium (Cr$^{3+}$) and Aluminium (Al$^{3+}$) co-doped nano-scale (9 nm – 17 nm) spinel magnesium ferrite of the composition Mg(Cr$_{0.5}$Al$_{0.5}$)$_2$Fe$_{2-x}$O$_4$ (for x = 0.00, 0.10, 0.15, 0.20, 0.25, 0.30) utilizing inexpensive materials and very easy one step sol-gel combustion technique using urea as fuel. The so prepared nano-sized powders were characterized by powder XRD for confirmation of phase-purity and crystallite size determination. The FT-IR spectroscopy was carried out to confirm the various bonds present in the system and also to detect traces of impurity materials as by-products of the reaction. Morphological studies were carried out by atomic force microscopy (AFM) and FE-SEM which revealed the reduced particle size and enhanced porosity with doping. Response of the sensor was measured by Keithley source meter interfaced with the computer. There is three order of magnitude reduction in the dielectric constant in the nano version of the material. Apart from that, the measured values of tanδ in the present study are in the range 0.10 – 1.80 which are almost 6 times lower as compared to that of bulk MgFe$_2$O$_4$. Complex impedance spectroscopy of the material reveals the existence of grain and grain-boundaries up to x = 0.150 beyond which only the insulating grain boundaries become effective. Along with the actual impedance plots, the Z-View fitted data of the same has also been provided for the sake of convenience. Cation distribution scheme and hence a general expression for magnetic trend was approached by considering the magnetic M–H data from VSM. Unusually high room temperature magnetism and abnormal coercive behaviour was observed which has been explained on the basis of various competing factors arising due to non-stoichiometry, low dimensionality, and doping. Composition dependent impedance analysis reveals the existence of insulating grain boundaries around relatively conductive grains. Magnetic analysis exhibits unusual magnetic behaviour which has been explained on the basis of the various interacting parameters arising due to low dimensionality of the grains and lattice defects due to dopant species. Scheme of cation distribution in tetrahedral (A) and octahedral (B) sites has been devised by the analysis of magnetic data. The cation distribution scheme was further utilised to suggest a general expression for the trend of magnetization between the given limit of doping. Further, the material was tested for LPG and humidity sensing
properties. It was found that the sensor exhibits fast and intensive response at relatively low operating temperature (120 – 130 °C at 85 % (RH) and 60 – 70 °C at 400 ppm LPG). The humidity response time was observed to be in the range 50 – 60 sec. while the same for LPG was measured to be in the range 40 – 50 sec. The various steps of humidity sensing mechanism have been explained in detail on the basis of Grothuss chain mechanism. The Nano-structured MgFe$_2$O$_4$ is itself a good sensing material. Replacing Fe$^{3+}$ by a combination of 0.5 Cr$^{3+}$ _0.5 Al$^{3+}$ significantly enhances its sensing properties due to creation of nano-structure, pores and defects. The MgFe$_2$O$_4$ is partially inverse spinel. Replacing octahedral Fe$^{3+}$ ions by a combination of Cr$^{3+}$ _Al$^{3+}$ ions affects the Fe$^{2+}$ ↔ Fe$^{3+}$ hopping conduction scheme. Apart from that, the combination of Cr$^{3+}$ _Al$^{3+}$ together with the Mg$^{2+}$ ions on octahedral site introduces more electrons in the system. Doping also favours the creation of the cation vacancies which allow the dissociation of oxygen in their vicinity. All these phenomena are conductivity enhancing factors and hence the sensing behaviour of the material. Thus we conclude that the spin coated films of Cr$^{3+}$ and Al$^{3+}$ doped nano-sized MgFe$_2$O$_4$ materials offer good sensing response towards both humidity as well as LPG.

CHAPTER 5

In this chapter, Chromium doped Gamma Ferrite nanopowders (25.6–16.9) of the composition (Fe$_{2-x}$Cr$_x$O$_3$ for x=0.00, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10) were successfully synthesized by a modified solution combustion method using citric acid as fuel at a temperature as low as 150 °C. The so prepared samples were examined by powder XRD for phase identification and crystallite size determination. FT-IR analysis was carried out to identify the various chemical bonds present inside the system. Magnetic examinations were performed in terms of magnetic susceptibility, hysteresis plots and magnetic permeability. A decrease in the blocking temperature with the increase of dopant concentration was observed which is explained on the basis of Néel's relaxation theory. A simple model has been suggested to explain the behaviour of hysteresis trends as the function of dopant concentration. The powder XRD confirms the phase purity of the material. The FT-IR studies of the samples in the range 4400–400 cm$^{-1}$ provide an insight about the chemical bonding of the system. Microstructural imaging through TEM and FE-SEM confirms the continuous reduction of grain size with Cr$^{3+}$ doping. A continuous decrease in blocking
temperature (378–260 K) as well as the crystallite size (25.61–16.91) was observed with the dopant concentration which is explained on the basis of Neel’s theory. Magnetization analysis revealed that the room temperature saturation magnetization first increases with the dopant concentration up to \( x = 0.07 \) beyond which it falls off rapidly. This behaviour has been explained on the basis of Neel’s theory of antiferromagnetism. The complex permeability measurements revealed the significant enhancement in permeability after \( \text{Cr}^{3+} \) doping thus making this material a cheaper alternative of inductive material for applications in magnetic cores and Multi-layer Chip Inductor (MLCI). Real permeability shows unusual behaviour (enhancement of permeability with reduction of grain size). This has been explained on the basis of Random Anisotropy Model (RAM). The grain diameter in the present case is smaller as compared to the ferromagnetic exchange length thus making this material to deviate from the normal behaviour. The temperature variation plots of real permeability reveal an interesting feature that the permeability at 20MHz and 25MHz is approximately independent of temperature and for \( x = 0.09 \) there is a little variation in permeability with temperature which a feature desirable in applications where the permeability should not vary significantly with changes in temperature, for example, magnetic components in telephone and transmission lines which can be subject to changes in temperature. It was observed that permeability attains highest value at all temperature and frequencies around the dopant concentration of \( x = 0.07 \) which is also supported by the values of saturation magnetization being highest at the same dopant concentration. Optical characterization revealed dual band gaps falling within the visible energy spectrum, thus making this material a promising candidate for single junction photovoltaics with enhanced power conversion efficiency.

CHAPTER 6

This chapter describes the scope of the work, its applicability to the real world, its importance and the future plans.
Dedicated

To

My parents
and
teachers
CERTIFICATE

This is to certify that the work presented in this Ph.D. thesis entitled, "Electrical and magnetic transport properties of doped nanoferites", is the original work of Mr. Ali Jawad, carried out under my supervision.

S.S.Z. Ashraf
(Supervisor)
CANDIDATE'S DECLARATION

I, Ali Jawad, Department of Applied Physics certify that the work embodied in this Ph.D. thesis is my own bona fide work carried out by me under the supervision of Dr. S.S.Z. Ashraf at Aligarh Muslim University, Aligarh. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree.

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and in the body of the thesis. I further certify that I have not willfully lifted up some other's work, para, text, data, results, etc. reported in the journals, books, magazines, reports, dissertations, theses, etc., or available at web-sites and included them in this Ph.D. thesis and cited as my own work.

Dated: 10-09-2013

(Signature of the candidate)

(Ali Jawad)

Certificate from the Supervisor

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor: ...........................................

Name & designation: S.S.Z. Ashraf, Assistant Professor.
Department: Applied Physics, Z.H.C.E.T, AMU, Aligarh

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Praise to Allah, the Lord of the worlds, who says in his Glorious Book, “There has come to you from Allah a Light and a plain Book”, and peace and blessings of Allah be upon the noblest of the Prophets and Messengers, our Prophet Muhammad who has said, “you should insist on acquiring knowledge even if you have to travel up to china.” And seek knowledge from cradle to grave.”

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CHAPTER 1

INTRODUCTION: OVERVIEW OF MAGNETISM AND NANO-MAGNETISM
1.1. Prelude

Spinel ferrites of the formula $\text{MeFe}_2\text{O}_4$ ($\text{Me} = \text{divalent metal}$) have been considered to be an important new class of atomically engineered magnetic materials since about half a century. They were distinguished for a range of properties that had virtually no counterpart in existing metal magnetic materials, and it was not long before full-fledged research and development efforts were underway. Today ferrites are employed in a wide range of applications both in research as well as in industry, and have contributed significantly to material advances in electronics. Research, too, continues apace, and the dedicated efforts to the field are yielding many highly intriguing results. New, high-performance products are appearing one after another, and it seems as if we have only scratched the surface of the hidden possibilities of these fascinating materials. The dependence of electrical, dielectric and magnetic properties on the crystal structure of materials is a very interesting phenomenon in condensed matter science, which has been investigated intensively over the last century. The magnetic properties of materials are mainly determined by their structure and the various magnetic interactions between neighboring atoms. Recently, there is a renewed interest to understand what happens when the physical dimension of a bulk magnetic material is reduced to the nanoscopic regime so as the size to be comparable to or smaller than a magnetically critical size such as the magnetic domain wall width in nanoscopic regime. This would lead the magnetic particle to possess only a single-domain and show superparamagnetic behavior. The magnetization reversal can be agitated by thermal fluctuation and becomes sensitive to the size and shape of the magnetic nanoparticles, which differs dramatically from the magnetic properties of their bulk counterparts. The potential of using these novel size and shape dependent magnetic properties in new technological applications has been demonstrated in many new as well as traditional fields, such as ultrahigh density magnetic data storage, giant magnetoresistance (GMR) sensor, magnetocaloric refrigerator, magnetoelectrics, magnetic resonance imaging (MRI) contrast enhancement agents, magnetically guided target-specific drug delivery systems, cells, DNAs and genes sorting and delivery, and ferrofluids [1-17].
This chapter deals with a general introduction to fundamentals of magnetism followed by a discussion of some important issues in nanomagnetism like, single domain theory, superparamagnetism, magnetic anisotropy mechanisms and ferrites along with their structural and micro/nanostructural aspects.

1.2. Magnetic materials

Intense interest has been generated over the past two decades in the growth and properties of bulk and fine-grain magnetic materials both from a fundamental point of view and applications. We are in the era where technologically and commercially important materials are evolving much more rapidly than any time in history. New and important applications based on the magnetic properties of the materials have come to prominence, in the last four decades, supplementing such traditional applications as in making of transformer cores. Materials thus continue to play their role as “pace-setter” for the development of civilization, and now the process works on greater pace. Magnetic materials are no exception in this regard, particularly in the context of modern engineering history. The control of microstructure for obtaining optimum magnetic properties are today almost as important as the control necessary for achieving optimum mechanical properties.

1.2.1. Properties of magnetic materials

The electronic motion is the key to the magnetic origin in matter. At the atomic level, there are two types of electron motion, spin and orbital and each has a magnetic moment associated with it. Since, the response of a material to a magnetic field \( H \) is characterized by magnetic induction or the flux density \( B \) and the effect that a material has upon the magnetic induction in a magnetic field is represented by the magnetization \( M \). The equation relating these three magnetic quantities is:

\[
B = \mu_0(H + M)
\]  
......1.1

Also

\[
B = \mu H
\]  
......1.2
Where, \( \mu_0 \) is the universal constant of permeability of free space and \( \mu \) is the permeability of material known as magnetic permeability and is a characteristic of material. From equation (1.1), one can realize that \( \mu_0 H \) is the magnetic induction generated by the field alone and \( \mu_0 M \) is the additional magnetic induction contributed by material. The term magnetization of a material \( 'M' \) may be defined as the processes of converting a non-magnetic bar into a magnetic bar and is measured as magnetic moment per unit volume. The magnetic susceptibility \( '\chi' \) is defined as

\[
\chi = \frac{M}{H}
\]  

\[\text{.....1.3}\]

The relative permeability is given by the ratio of the magnetic permeability of the material to that of free space:

\[
\mu_r = \frac{\mu}{\mu_0}
\]  

\[\text{.....1.4}\]

1.2.1.1. Diamagnetism

All materials are inherently diamagnetic. Materials that have filled electron shell exhibit no net spin magnetic dipole moment or orbital magnetic dipole moment and are classified as purely diamagnetic. However, materials that have unpaired electron shells exhibit other types of magnetism that outweighs the diamagnetic effects. Fig. 1.1 shows the schematic arrangement of magnetic dipoles of a diamagnetic material. Diamagnetic materials have negative susceptibility \( '\chi' \) because the direction of the induced magnetic moment upon exposure to a magnetic field is opposite to the external magnetic field [18]. This explanation is based upon Lenz's law, which states that magnetic field due to the current (of electrons) opposes the change in magnetic field, which induces the current.
Figure 1.1: The diamagnetic dipole arrangement with and without applied magnetic field.

1.2.1.2. Paramagnetism

Paramagnetism is characterized by a positive susceptibility and a magnetic permeability greater than $\mu_0$. Fig 1.2 (a) shows the schematic diagram of atomic dipole configuration for a paramagnetic material. In paramagnetic materials, localized magnetic moments are present but they do not exhibit net macroscopic magnetization in the absence of an applied field. There are two types of paramagnetism; one, in which the magnetic moments are present at sufficiently low concentration such that they are well separated from each other and their spins do not interact; second, in which the paramagnetism can exist when there is interaction between the magnetic moments, but these interactions are so weak that there is no net magnetization when there is no applied field. This type of paramagnetism occurs in ferromagnetic materials above their critical temperature (Curie temperature) [19, 20]. At low temperature, many paramagnetic materials possess a finite magnetization in the absence of an applied field. This spontaneous magnetization is due to the alignment of the permanent dipole moments below a critical temperature. The interaction between dipoles results in what is known as magnetic ordering.
1.2.1.3. **Ferromagnetism**

Ferromagnetism differs from the weaker diamagnetism and paramagnetism in the way that the electrons of neighbouring atoms interact with one another through a process called exchange coupling. Fig. 1.2 (b) shows the schematic diagram of atomic dipole configuration for a ferromagnetic material. Exchange coupling phenomenon caused by exchange fields, results in the magnetic dipole moments of atom being aligned at room temperature despite effect of room temperature energy [19]. The ferromagnetism is strongly temperature dependent and the magnetization of a ferromagnetic material is related to the temperature by:

\[ \chi = \frac{C}{T - \theta} \]

\[ \text{......1.5} \]

where, ‘C’ is the Curie constant and ‘\( \theta \)’ the Curie temperature of the material. The Curie temperature is the temperature above which the exchange coupling ceases to be present. This means that above ‘\( \theta \)’, a ferromagnetic material randomizes due to thermal energy as in paramagnetic materials. Thus ferromagnetic materials have their highest magnetization at 0 K and the magnetization decreases with increasing temperature and at Curie temperature it disappears. Complete alignment of magnetic materials (magnetic saturation) occurs readily for ferromagnetic materials. Most ferromagnetic materials are comprised of magnetic domains. Magnetic domains are regions where the magnetic dipole moments are aligned in one direction. An example of a region would be a single crystal within a polycrystalline sample. Magnetic energy minimization within a material causes the formation of magnetic domains. When domains are arranged such that the north pole of one domain is at the south pole of another and vice versa, the energy is decreased by \( \frac{1}{2} \). Further, application of this theory leads the energy of a material to decrease by \( \frac{1}{N} \) where \( N \) is the number of domains formed. Domain wall is the term used to define the interfacial region between magnetic domains and the application of a magnetic field to a ferromagnetic material which results in domain wall moment. Qualitatively, the domain walls move such that the domains aligned in the direction of an applied field ‘grow’ and domains that are in other directions ‘shrink’. The direction of the magnetic moments within domains that are not aligned in the direction of an applied field may also
begin to rotate at significant field strengths [19]. Nevertheless, the formation of the magnetic domains is energetically unfavorable below a certain size (nano scale), which is different for each material. In this case, a material is classified as single domain. Single domain particles are uniformly magnetized along an easy axis.

Since, ferromagnetic materials are the most interesting magnetic materials in terms of their actual and potential applications, their properties need to be measured quantitatively. The hysteresis measurements reveal interesting magnetic properties in magnetic materials. Applying a d.c. magnetic field causes the alignment of magnetic moments along the applied field within a sample. Initially, as \( H \) increases, \( M \) increases until a saturation point \( 'M_s' \) is reached. When \( H \) is decreased from the saturation point, \( M \) does not decrease to the same value it had when the field was applied. It is higher on the curve of the decreasing field, creating a hysteresis. This effect occurs because the domains that were aligned with the increasing field do not return to their original orientation when the field is lowered. When \( H \) is returned to zero, the material still has a magnetization, known as the remanent magnetization; \( M_r \). In order to remove the remanent magnetization, the direction of the applied field is reversed. This reversed or negative field is called the coercive field [19]. The plot of magnetic induction \( B \) versus applied field \( H \), is called a hysteresis loop (shown in Fig. 1.3) and is somewhat analogous
Figure 1.2 (a–e): Different types of magnetic orderings (a) Paramagnetic, (b) Ferromagnetic, (c) Ferrimagnetic, (d) Antiferromagnetic, and (e) Superparamagnetic.

to the one that occurs in ferroelectrics (in fact, a field $H_c$ has to be applied in the opposite direction to ferroelectrics was given the name due to this similarity).

1.2.1.4. Ferrimagnetism

Ferrimagnetic materials, like ferromagnetic materials have a spontaneous magnetization below a critical temperature known as Curie temperature ($T_c$). Fig. 1.2 (c) shows the schematic diagram of atomic dipole configuration for a ferrimagnetic material. The magnitude of magnetic susceptibility for ferro- and ferrimagnetic material is similar; however, the alignment of magnetic dipole moment is drastically different. The magnetic dipole moments in a ferrimagnetic material are divided into sublattices and are classified as sub-set of antiferromagnetic materials. Each sublattice can be treated as ferromagnetic material and the difference between the magnetic dipole moments for the sublattices results in the net magnetization for the ferrimagnetic materials. The difference between the ferri- and antiferromagnetic materials is that either the magnitude or the number of
moments of the sublattice is different. Fig. 1.5(a-e) shows the behaviour of different kinds of magnetism in response to magnetic field and temperature. Qualitatively, ferrimagnetic materials behave like paramagnetic materials at high temperature:

\[ \chi \sim T^{-1} \]

While at temperature below \( \theta \) they have spontaneous magnetization and are organized into magnetic domains. Magnetic materials that fall into this classification are transition metal oxides like magnetite (Fe\(_2\)O\(_4\)) and mixed ferrites like Co Ferrite (CoFe\(_2\)O\(_4\)), etc.

![Hysteresis Plot](image)

**Figure 1.3:** Typical hysteresis plot for a hard ferromagnetic material.

### 1.2.1.5. Antiferromagnetism

Antiferromagnets are characterized by having a weak magnetic susceptibility of the order of paramagnetic materials. Materials like transition metal compounds and some transition metal oxides (CuCl\(_2\), Co, NiO) are antiferromagnetic. Antiferromagnetic materials are comprised of sublattices of atoms whose magnetic dipole moments are aligned anti-parallel. The anti-parallel alignment of magnetic dipoles in antiferromagnetic materials is the cause of small magnetic susceptibility of an antiferromagnetic material. Fig 1.2 (d) shows the schematic diagram of atomic dipole configuration for a antiferromagnetic material. The temperature above which antiferromagnetic ordering ceases to exist is called the Neel temperature (\( \theta_N \)). Above \( \theta_N \), antiferromagnetic materials have a slight positive magnetic susceptibility comparable to paramagnetic materials. Below \( \theta_N \), however, antiferromagnetic materials have spontaneous
magnetization \((H = 0)\) that causes the magnetic dipole moment of the sub-lattices to align anti-parallel to each other.

1.2.1.6. Superparamagnetism

Superparamagnetic materials belong to a special class of materials that are characterized by having single domain particles that behave like ferromagnetic materials below \(\theta\), which is attributed to their large values of susceptibilities and saturation magnetization along with zero remanence and coercivity. Fig. 1.2 (e) shows the schematic diagram of atomic dipole configuration for a superparamagnetic material. Superparamagnetic particles are uniformly magnetized along an easy axis and thermal energy causes the magnetization to switch between equivalent easy axes through an anisotropy barrier. This switching happens so quickly that the time average magnetic remanence is zero. Superparamagnetic particles align with an applied magnetic field by one of the two mechanisms:

1. Néel rotation or 2. Brownian rotation.

Néel rotation occurs when particles are in a fluid or in solid state and results from the rotation of the magnetic moment of a stationary particle. Brownian rotation only occurs when particles are in a fluid and results from the physical rotation of a particle towards the direction of an applied magnetic field.

\[\text{Figure 1.4: Typical } M-H \text{ plot for a superparamagnetic material.}\]
Figure 1.5: Various classes of magnetism and their behavior towards magnetic field and temperature.

1.2.2. Nanocrystalline magnetic particles

Magnetic nanoparticles are offering exciting opportunities for technologies at the interfaces between chemistry, physics and biology. Their appeal stems not only from their use as single particle, but also from their potential to form self-organized films and solids. Magnetic nanoparticles are useful for a wide range of applications from data storage to medicinal imaging. The nanometer length scale is comparable to an electron’s mean free path. When the size of the particle is less than a characteristic length such as the mean free path, it is possible to see different physical or chemical characteristics than
those exhibited by their larger counterparts. Electrical resistivity, reactivity, melting temperature and optical absorption have all been found to change drastically when the size of the particle approaches the nanometer scale [20]. With this in mind, one can immediately deduce that magnetic properties will be affected by particle size, especially when particle size is of the same scale as the magnetic domains of the material. As a matter of fact, at the nanometer scale, magnetic particles have been found to behave differently from that of bulk magnetic materials. As particle size decreases, remanent magnetization and saturation magnetization decreases. This implies that scaling particles down to the nanometer scale can greatly improve the quality of magnets fabricated from them [20]. When the size of single domain particles decreases below a critical diameter, a new type of magnetism is achieved, called superparamagnetism. When this occurs, the coercivity and remanent magnetization go to zero. For superparamagnetic particles, the net magnetic moment in zero field at $T > 0$ K will average to zero. In an applied field, there will be a net statistical alignment of magnetic moments. This is analogous to paramagnetism, except now the magnetic moment is not that of a single atom, but of a single domain particle containing $10^5$ atoms and hence, the term superparamagnetism, which denotes a much higher susceptibility value than that of paramagnetism [21]. Superparamagnetism can improve the efficiency of systems that are subjected to rapidly alternating ac magnetic fields like transformers and rotating electrical machinery. In a traditional magnet, exposed to an a.c. magnetic field, the magnetic field cycles through its hysteresis loop often cause a loss of efficiency and a rise in temperature. This rise in temperature is due to the frictional heating that occurs when magnetic domains are varying their orientation. The amount of energy loss in each cycle is proportional to the area enclosed by the loop, so a small or non-existent coercivity is desirable [20]. It has also been shown that particle size has a large effect on microwave absorption. Particles of nano meter size greatly improve the absorptive efficiency and broaden the bandwidth [22].
1.2.2.1. Exchange interaction

The fundamental basis for the magnetic behaviour of magnetic materials relies on two mechanisms, exchange interaction and anisotropy. The quantum origin of exchange interaction derives from the combination of electrostatic coupling between electron orbitals and the necessity to satisfy the Pauli Exclusion Principle, leading to spin-spin interactions that favour long range spin ordering over macroscopic range. The spin-spin interaction can be expressed universally in terms of Heisenberg Hamiltonian:

\[ H = -\sum_i J_{ij} S_i \cdot S_j \]

\[ \ldots J \] 

Where, \( S_i \) and \( S_j \) are the spin angular momentum located at \( i_{th} \) and \( j_{th} \) sites of a particular lattice, and the exchange integral \( J_{ij} \) represents the strength of the exchange coupling between the spin angular momentum \( i \) and \( j \). If \( J_{ij} \) is positive, the parallel spin configuration will minimize the total energy of the system and all spins aligned to each other are in the ground state. Therefore, a magnetic material is ferromagnetic. On the other hand, a negative \( J_{ij} \) favours the anti-parallel alignment of spins and consequently gives rise to antiferromagnetic ordering.

The exchange interactions are isotropic relative to any externally fixed spatial direction. In reality, the exchange spherical symmetry is always broken, because the electron orbitals interact with the potential created by the hosting crystal lattice. Since the potential symmetry is characterized by the symmetry of the lattice, the spin orientation along certain spatial direction becomes energetically favourable. The macroscopic behavior of a magnetic material will eventually depend on the spatial direction in which it is measured. Such a phenomenon is called magnetic anisotropy.

There are several causes through which the magnetic anisotropy may occur, including the magnetocrystalline anisotropy, shape anisotropy, magnetostriction and stress anisotropy. In case of magnetic nanomaterials, surface anisotropy and/or other kinds of anisotropy can be of the same magnitude as these usual anisotropies. Brief descriptions of three important magnetic anisotropies responsible for the magnetic properties of magnetic nanomaterials are outlined here.
1.2.2.2. Magnetocrystalline anisotropy

Magnetocrystalline anisotropy depends on spin–orbital coupling and shows various symmetries. The two most common cases are uniaxial and cubic forms. For uniaxial symmetry, the magnetocrystalline anisotropy constant \( K_u \) is given by:

\[
K_u = K_0 + K_1 (\sin \theta)^2 + K_2 (\sin \theta)^4 + \ldots
\]

\[
\ldots \ldots 1.8
\]

Where, \( K_0, K_1, \) and \( K_2 \) are anisotropy constants. While for cubic symmetry, the magnetocrystalline anisotropy constant \( K_c \) is given by:

\[
K_c = K_0 + \frac{K_1 ((\sin \theta)^4 (\sin 2 \phi)^2 + (\sin 2 \theta)^2)}{4} + \frac{K_2 (\sin 2 \theta)^2 (\sin 2 \phi)^2}{16} + \ldots \ldots 1.9
\]

The magnetocrystalline anisotropy is an intrinsic property of the material, independent of grain size and shape. It affects the shape of the hysteresis loop and controls the coercivity and remanence. It is defined as the energy to deflect the magnetic moment in a single crystal from the easy to hard direction. Material having large magnetocrystalline anisotropy energy is called hard magnetic material and shows a large coercivity in hysteresis measurement. A magnetic material with small magnetocrystalline anisotropy energy is referred to soft magnetic material and has a small value of coercivity.

1.2.2.3. Stress anisotropy

There is another effect related to spin–orbit coupling called magnetostriction. This arises from the strain dependence of the anisotropy. Upon magnetization, a previously demagnetized crystal experiences a strain that can be measured as a function of applied magnetic field along the principal crystallographic axis. A magnet will, therefore, change its dimensions when magnetized. The inverse affect or the change of magnetization with stress also occurs. A uniaxial stress can produce a unique easy axis of magnetization if the stress is sufficient to overcome all other anisotropies. The magnitude of the stress anisotropy is described by two more empirical constants known as the magnetostriction constants \( \lambda_{111} \) and \( \lambda_{100} \) and the level of stress.
1.2.2.4. Shape anisotropy

Shape anisotropy is induced from magnetostatic energy and is an extrinsic property. For a prolate spheroid with major axis $c$ greater than the other two and equal axes length $a$, the shape anisotropy constant ($K_s$) is:

$$K_s = \frac{M_s^2 (N_a - N_c)}{2}$$

...J.10

Where, $M_s$ is the saturation magnetization, $N_a$ and $N_c$ are demagnetization factors. For nonspherical magnetic materials such as a long rod, the shape anisotropy can be very predominant.

1.2.2.5. Surface anisotropy

Surface anisotropy is caused by the existence of a surface that represents a discontinuity for magnetic interactions. Such surface effects become more significant as the size of magnetic nanomaterials decreases, or as the number of atoms on the surface layer of a material increases. In order to take into account surface effect, Néel first proposed the surface anisotropy [23]. Recent theoretical studies indicate that spins at surface are dictated by the local crystal field, a lower coordination number and a broken magnetic exchange bond. Thus, surface spins are often canted and/or disordered [24-27]. Judging from the surface effect and often correlated to the nanoparticle size effect, an effective anisotropy constant ($K_{ef}$) which includes the surface anisotropy constant, is used to describe surface effect. For a spherical particle, $K_{ef}$ is given by:

$$K_{ef} = K + \frac{6}{d} K_s$$

...J.11

Where, $K_s$ is surface anisotropy constant, $K$ is magnetocrystalline anisotropy constant, and $d$ is the diameter of the particle. Surface anisotropy generally leads the surface to become magnetically harder than the core of the particle.
1.2.3. Unidomain theory and superparamagnetism

It is well known that a bulk magnetic material comprises of magnetic domains. The magnetization inside each domain is uniform, but varies from domain to domain as they are separated by an interface layer known as the domain wall. By reducing the dimensions of a magnetic material, the sizes of the domains accordingly decrease and their structures may change in terms of domain wall width and wall structure. As far as the energy is concerned, when the size reaches a critical size, the magnetic material possesses only a single domain, since the energy cost for the formation of domain walls becomes energetically unfavorable, the energy gain from the formation of domain walls is higher than the energy reduction by dividing the single domain into even smaller domains. The critical size \((R_c)\) for domain formation has been estimated in Kittel [28, 29], which depends on spontaneous magnetization \((M_s)\), the anisotropy constant \((K)\), and the exchange energy density or constant \((A)\) as given below:

\[
R_c = \frac{36(KA)^{1/2}}{\mu_0 M_s^2}
\]

The critical size for typical magnetic materials is in the range of 10-800 nm. A small magnetic particle less than critical size (\(\leq 40\) nm) prefers to be uniformly magnetized along one of its anisotropy easy axes, and is accompanied by a strong enhancement in coercivity. If the size of magnetic material is below the critical size (up to 20 nm) magnetic materials can only acquire a single domain. On still reduction in size (< 20 nm), the magnetic anisotropy energy further decreases and may become so low as to be comparable to or even lower than the thermal energy \((K_B T, K_B\) being Boltzmann constant). As a result, the energy barrier for magnetization reversal may thermally overcome, and the magnetic moment is thermally fluctuated, like a single spin in a paramagnetic material. Hence, the spins within the particle remain magnetically coupled to each other leading to the formation of a ‘superspin’ with a relative enormous moment per particle. This phenomenon is known as superparamagnetism [30, 31].

In a simple model described by Stoner-Wohlfarth [32] for a non-interacting single domain spherical particle with uniaxial anisotropy in zero magnetic field, the magnetic anisotropy energy is given by an expression:
\[ E_A = KV \sin^2 \theta \] \hspace{1cm} \text{......1.13}

Where, \( E_A \) is the energy barrier, \( K \) the magnetocrystalline anisotropy constant, \( V \) the volume of the particle, and \( \theta \) the angle between magnetization and easy axis of the particle. The dependency of anisotropy energy on \( \theta \) is depicted schematically in Fig. 1.5. Clearly, either \( \theta = 0 \) or \( \pi \) is a direction of minimum energy and these directions are symmetrically separated by an energy barrier as high as \( KV \). The magnetic field can also be a form of energy that can lower the magnetic anisotropy energy barrier for magnetization reversal. When a magnetic field \( H \) is applied along the easy axis, the anisotropy energy will be:

\[ E_A = KV \sin^2 \theta - \text{HM}_{nr} \cos \theta \hspace{1cm} \text{......1.14} \]

Where, \( M_{nr} \) is the non-relaxing magnetization. Superparamagnetism is also characterized by a relaxation time (\( \tau \)) and thus the actual magnetic behaviour depends on the value of measuring time (\( \tau_m \)) in a particular experimental technique. Now, the magnetic anisotropy serves as an energy barrier to the total spin reorientation. In a bi-stable system, the probability for such magnetic moment thermally overcoming energy barrier is proportional to Boltzmann factor derived by Néel as:

\[ \tau = \tau_0 \exp \left( \frac{-KV}{K_B T} \right) \hspace{1cm} \text{......1.15} \]

Where, \( \tau_0 \) is an attempt frequency factor equal to approximately 10\(^9\) seconds, and depends on several factors such as temperature, gyro-magnetic ratio, magnetic field, magnetization, particle size and damping constant, and yet is treated as a constant. At given temperature, if the measurement time is much longer than relaxation time, the moment is rapidly relaxed by thermal fluctuation, and consequently the entire system is in superparamagnetic state. On the contrary, as the measurement time is much shorter than relaxation time, the moment relaxes so slow that it seems to be blocked. The blocking temperature is thus defined as the temperature at which the magnetic moment relaxation time is equal to the measurement time, or the temperature where the moment is
able to overcome the energy barrier into the superparamagnetic state at a certain measurement time.

![Energy Diagram](image)

**Figure 1.6:** Schematic diagram of Stoner-Wohlfarth anisotropy energy barrier for magnetization reversal.

Some typical instrument measurement times are 100 s for DC SQUID, $10^{-7} - 10^{-9}$ seconds for Mössbauer spectroscopy, and $10^{-8} - 10^{-12}$ s for neutron diffraction.

### 1.3. Ferrite materials

In the world of advanced materials, ferrites are most widely used magnets comprising 52% of the world market [33]. The story of ferrites began with the search for ferromagnetic materials of usually high resistivity to obtain reasonable eddy current losses. However, since eddy current losses in ferromagnetic materials are inversely proportional to the resistivity, they can be minimized by using ferrites, having a resistivity up to $10^7$ as compared to $10^7$ of iron, which can reduce the eddy current losses in them to negligible values, even at microwave frequencies [34]. Ferrites are a class of chemical compounds with iron (III) oxide as the main component. These ceramic materials are used in applications ranging from magnetic components to
microelectronics. The most important characteristics of these materials is that besides possessing very good magnetic properties, they also possess a very high dc resistivity [35] unlike ferromagnetic metal and magnetic alloys and hence, are particularly useful at high frequency applications [36]. They have multifarious applications in electronics, microwave and satellite communications.

1.3.1. Crystal structure of $\text{AB}_2\text{O}_4$ spinel ferrites

Ferrites, according to the crystal structure and the magnetic ordering, can be grouped into four different categories [37] namely spinel, garnet, magnetoplumbite and orthoferrites, as listed in Tab. 1.1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>General Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$</td>
<td>($\text{M}^{\text{II}} = \text{Cd, Co, Mg, N}$ and $\text{Zn}$)</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$\text{Ln}_3^{\text{III}}\text{Fe}<em>2\text{O}</em>{12}$</td>
<td>($\text{Ln}^{\text{III}} = \text{Y, Sm, Eu, Gd, Tb, Ho, Er, Tm, and Lu}$)</td>
</tr>
<tr>
<td>Magnetoplumbite</td>
<td>Hexagonal</td>
<td>$\text{M}^{\text{II}}\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>$\text{BaFe}<em>{12}\text{O}</em>{19}$</td>
</tr>
<tr>
<td>Orthoferrites</td>
<td>Pervoskite</td>
<td>$\text{LnFe}_3\text{O}_5$</td>
<td>$\text{Ln}$ = same as garnets</td>
</tr>
</tbody>
</table>

Table 1.1: Different type of Ferrite crystals and their composition.

The structure of spinel ferrites is derived from that of the mineral spinel $\text{MgAl}_2\text{O}_4$. The unit cell consists of eight formula units (8x$\text{MeFe}_2\text{O}_4$), where $\text{Me}$ is the divalent metal ion. The 32 oxygen ions form a face centered cubic (fcc) lattice in which two kinds of interstitial sites are present, namely, (i) 64 tetrahedral sites, surrounded by 4 oxygen (A sites); and (ii) 32 octahedral sites, surrounded by 6 oxygen ions (B sites). Fig. 1.7 shows the unit cell of a spinel structure. The ionic positions are different in two octants sharing a face or a corner and are the same in two octants sharing an edge. Thus, to give a complete picture, it is necessary only to show the positions of the ions in two adjacent octants. Note that each octant contains four oxygen ions (large spheres) on the body diagonals and
lying at the corners of a tetrahedron. The right hand octant contains, in the center a metal ion (small sphere, not shaded) surrounded by the tetrahedral of oxygen ions, this ion is said to occupy an A-site. The left hand octant shows four metal ions (small shaded spheres) surrounded by an octahedron (one of which is shown) formed by six oxygen ions. Such ions are said to occupy B-sites. In a unit cell, there are 64 A-sites, 8 of which are occupied, and 32 B-sites, 16 of which are occupied. The divalent metal ions commonly used in ferrites can be classified roughly into those preferring B-sites (Co, Fe, Ni) and those preferring A-sites (Mn and Zn). In a normal spinel structure, the 8 M$^{2+}$ ions go into the A-sites and the 16 Fe$^{3+}$ ions enter the B-sites. ZnFe$_2$O$_4$ is an example of normal spinel ferrite. On the other hand, if the divalent ions have a preference for B-sites, they will displace eight of the Fe$^{3+}$ ions which will go over into the A-sites. This results in an inverse spinel structure. Examples of inverse spinels are Fe$_3$O$_4$ and CoFe$_2$O$_4$. As two ionic species are then distributed over the octahedral sites a certain degree of randomness may be present, contributing to the line width (loss) of the material.

Figure 1.7: Crystal Structure of a cubic spinel ferrite.
1.3.2. Magnetic interaction

The metallic ions occupy two different crystallographic sites in ferrites, i.e., octahedral (B) sites and tetrahedral (A) sites. Three kinds of magnetic interactions are possible (shown in Fig. 1.8) between the metallic ions, through the intermediate $O^2_-$ ions, by superexchange mechanism, namely, $j_{AB}$, $j_{BB}$ and $j_{AA}$ interactions. Since, the distance between the two ions is large; hence, direct interaction is negligible. It has been established experimentally that these interaction energies are negative, and hence induce an anti-parallel orientation.

In general, the magnitude of the interaction energy between two magnetic ions, $M_1$ and $M_1^0$ depends upon:

a. Bond length (represented by the quantities $l_1$ and $l_1^0$).

b. Bond angle (represented by the term $\theta$ as shown in Fig. 1.8).

The exchange energy is having its maximum value at an angle of $180^\circ$ and it decreases rapidly with increasing bond distance. Gorter [38] investigated the various types of effective magnetic interactions between the various possible configurations of ion pairs with favourable bond lengths and bond angles. Experiments have shown that the values of bond length are smaller and the values of bond angle are fairly high ($\theta \sim 180^\circ$) for A-B interaction, which makes it the strongest interaction among the three interactions. The B-B interaction (bond length is too large for the effective interaction) is weak interaction as compared to the A-B interaction, while the A-A interaction is the weakest of all the interactions for which $\theta \sim 80^\circ$.

Since, it is the only A-B interaction which is predominating, the spins of the ions in A- and B- sites in ferrites are anti-parallel which gives the resultant magnetic moment equal to the difference between those of the A and B-site ions. In general, the value of saturation magnetic moment for the B-lattice ($M_B$) is greater than that of the A-lattice ($M_A$), such that the resultant saturation magnetization ($M_s$) is written as:

$$M_s = M_B - M_A$$

The magnetic features of ferrites closely resemble with ferromagnets. Hysteresis phenomenon is observed in ferromagnetic materials during magnetization cycle. Ferrites have specific Curie temperature.
Figure 1.8: Illustration of Me$^{1}$-O$^{2}$-Me$^{II}$ angles in spinel ferrites.

The mixed ferrites show most interesting characteristics while doped with different non-magnetic/magnetic elements [39-41]. The values of the magnetization and of Curie temperatures can be conveniently varied by suitable variation in composition. If a small concentration of non-magnetic material is increased in the ferrite material, the value of saturation magnetization increases. But at higher concentrations deviations occur due to the weakening of A-B interaction and consequent stronger B-B interaction. Although, an increase in the value of $M_0$ is observed with the substitution of divalent non-magnetic ions, the Curie temperature decreases, as the reduced value of $M_s$ weakens the A-B interaction, which is responsible for the observed ferrimagnetism.
Figure 1.9: Interionic angular configurations for different interaction sites.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>$T_c$ (K)</th>
<th>$M_s$ (300K) (G m$^3$/g)</th>
<th>$K_1$ ($\times 10^5$) (erg/cm$^3$)</th>
<th>Easy axis</th>
<th>Hard axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>860</td>
<td>95.5</td>
<td>-1.2</td>
<td>[111]</td>
<td>[100]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>790</td>
<td>80-94</td>
<td>+18, +30</td>
<td>[100]</td>
<td>[111]</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>550-620</td>
<td>80</td>
<td>-0.25</td>
<td>[111]</td>
<td>[100]</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>860-870</td>
<td>56</td>
<td>-0.68</td>
<td>[111]</td>
<td>[100]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>725-775</td>
<td>20-35</td>
<td>-0.6 (cubic)</td>
<td>[111]</td>
<td>[100]</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>10-15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgFe$_2$O$_4$</td>
<td>605-710</td>
<td>31-62</td>
<td>-0.25-0.45</td>
<td>[111]</td>
<td>[100]</td>
</tr>
</tbody>
</table>

Table 1.2: Magnetic properties of some spinel ferrites.

1.3.3. Perovskite (ABO$_3$) type ferrites

This special category of oxides exhibits the unique properties of having both ferromagnetism and ferroelectricity incorporated in the single crystal. This opens new vistas for their potential applications in the field of transducers, magnetic field sensors.
and information storage industry. Some common examples are BiFeO$_3$, BiMnO$_3$, TbMnO$_3$, TbMn$_2$O$_5$, YMnO$_3$, LuFeO$_4$ and Ni$_3$B$_7$O$_{13}$. Among these oxides BiFeO$_3$ (BFO) is the only material which gives ferroelectricity and antiferromagnetism at room temperature. Due to coexistence of both ferromagnetism and ferroelectricity in the same material, it is expected to exhibit ferromagnetic & ferroelectric properties or a coupling of these two properties in a single material. This increases the current range of applications and moreover interesting physics may be observed. Presently lot of research work is focused on this particular field in different forms like bulk, powder, thin film and nanostructure. A single phase multiferroic material is one that possesses two of the three "ferroic" properties i.e ferroelectricity, ferromagnetism and ferroelasticity. Generally current trend is to exclude the requirement for ferroelastic property. Magnetoelastic coupling describes the coupling between magnetic and electric order parameters. BFO is the only prototype among all other multiferroic oxides which shows both ferromagnetism and ferroelectricity in a single crystal above room temperature. It has ferroelectric Curie temperature $T_C = 1143K$ and antiferromagnetic Neel temperature $T_N = 643K$ [42]. The ions responsible for the production of ferroelectricity and magnetism are Bi$^{4+3}$ and Fe$^{4+3}$ ions. Ferroelectricity is produced due to Bi$^{4+3}$ and antiferromagnetism is due to Fe$^{4+3}$ ions. BFO has rhombohedrally distorted perovskite structure with R3c space group at room temperature (Fig. 1.10).

![Figure 1.10: Unit cell diagram of perovskite BiFeO3 structure.](image-url)
Bi$^{3+}$ ions occupy the corner position, Fe$^{4+}$ ion the body centred position, and O$^{2-}$ ions occupy all face centred position. The lattice parameters are $a = 5.587$ Å, $b = 5.587$ Å and $c = 13.867$ Å with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The hexagonal unit cell contains 6 formula units. Generally ferroelectricity is produced by vacant $d^0$ orbital and ferromagnetism is observed due to partially filled $d^0$ orbital. In BFO, ferroelectricity is produced due to stereo chemical activity of Bi$^{3+}$ ion and ferromagnetism is due to Fe$^{4+}$ ions. Bi$^{3+}$ and Fe$^{4+}$ cations are displaced along the [1 1 1] three-fold polar axis and off centred with respect to the bodycentre of the oxygen octahedron, which in turn gives rise to ferroelectricity. Ferromagnetism is produced due to rotations of adjacent oxygen FeO$_6$ octahedral around the [1 1 1] pseudo cubic direction.

1.4. Epilogue

The focus of the present work is the synthesis of the nano-structured particles of spinel and perovskite type ferrites and to investigate the effect of doping on their structural, electrical, optical and magnetic properties over a wide range of dopant concentration, temperature and frequency. In the present thesis, synthesis and characterization of nano-structured systems having composition Mg(Cr$_{0.5}$Al$_{0.5}$)$_3$Fe$_{2x}$O$_4$, Fe$_{2x}$Cr$_x$O$_3$, and Bi$_{1-x}$Al$_{2x}$Fe$_{1-x}$O$_3$, has been carried out. The synthesis has been done by normal and modified solution combustion techniques. The so prepared materials were investigated broadly for structural analysis, optical band gap measurement, a.c. and d.c. electrical transport properties, dielectric studies, sensing behaviour, and magnetic properties. The objectives of the thesis are:

1. The synthesis of nano-structured Bismuth Ferrite (BiFeO$_3$) both in pure as well as doped form. The doping is performed to simultaneously replace both Fe and Bi by Al atoms so as to see the effect of doping on electrical, dielectric properties, and band gap variation.

2. The synthesis of pure and doped nano-sized powder of Magnesium Ferrite (MgFe$_2$O$_4$) and to see the effect of the replacement of Fe$^{3+}$ ions by a combination of Cr$^{3+}$
and Al$^{3+}$ on electrical and magnetic behaviour of the material. Another point has been to evaluate its potential for gas sensing since MgFe$_2$O$_4$ is a famous sensing materials.

3. The synthesis of Cr$^{3+}$ doped γ-Fe$_2$O$_3$ nano-powders and investigation of its dual band gap structure, initial permeability and M-H characteristics over a wide range of temperature, frequency and dopant concentration.
References


CHAPTER 2

SYNTHESIS
AND
CHARACTERIZATION TECHNIQUES
2.1. Synthesis and fabrication of nanomaterials

In nanotechnology to date, much emphasis is placed on the creation of the nanostructures by means of micro- and atomic manipulations. This research field has been highly respected and promoted by the society, politics, and economies. Rapid progress in this field has been greatly stimulated by more fundamental study on nano and micro-materials. In this respect, the scientists and engineers in different fields of physics, chemistry, materials science, and information technology including experimentalists, theorists, and also researchers doing computer simulations have collaborated to form a new interdisciplinary field. One can come up with a variety of logical approaches for the synthesis of oxide nano-materials. A rational synthesis requires a deep understanding of crystal chemistry, besides thermodynamics, phase equilibrium, and reaction kinetics. The elemental metals can combine with oxygen to form a large number of bulk oxides having variety of crystal geometries. The question is whether we can be able to fabricate similar compounds in nano-structured form? This is million dollar question posing the real challenge both from fundamental as well as industrial point of view for the development of systematic methods for the synthesis of metal-oxide nanostructures. For many years, the problem of synthesization both at laboratory and industrial level has been a subject of focus in literature. [1-4]. Since the last two decades, the interest in this field has grown very much because studies have revealed that reducing the dimensions of a crystal down to some critical value may surprisingly alter the properties of the materials as compared to its bulk counterpart [5, 6]. The effects of size reduction become visible when the mean grain dimensions lay in the range 100nm -10 nm. While investigating the properties of ultrafine materials, it is essential to take into account not only their structure and composition but also dispersion and distribution with size. For example, polycrystalline fine materials with a mean grain size of 300 to 40 nm can be referred to as submicrocrystalline, whereas those with a mean grain size of less than 40 nm can supposed to be nanocrystalline materials. Further, the physical and chemical properties of the variety of nanomaterials are immensely influenced and controlled by the choice of the method of synthesis which plays a crucial role in finally deciding their composition, lattice structure, microstructure and morphology. For instance, the Barium Hexaferrite
(BaFe₁₂O₁₉) can work either as a permanent magnet or as a recording media depending on the morphology (grain size) of the material, which in turn is dependent on the synthesis technique. The most widely practiced method for the preparation of oxide materials is solid-state reaction or conventional ceramic method. A variety of metal oxides, both simple and complex, are synthesized by this ceramic technique which involves the mixing of constituent metal oxides, carbonates, etc., followed by heat treatment and subsequent grinding. Although these methods are used on both laboratory as well as commercial scale, there is an increasing quest for alternate routes to the manufacturing of oxide materials that give far superior properties when compared with those synthesized by conventional ceramic methods. Yet, ceramic methods have their importance and they must not be underestimated because large scale production of a huge number of oxide materials still relies on these techniques. However, the need for alternate synthesis routes for oxide materials has arisen because of inherent problems concerning to: (i) inhomogeneity of the products obtained by ceramic methods, (ii) incorporation of chemical impurities during repeated grinding and heating operations since impurities have a deleterious effect on the high-temperature mechanical behavior of engineering ceramics and on the electrical properties of electro-ceramics, (iii) generally, grains are obtained from conventional routes, which make them unsuitable for coating applications. Non-uniform powder compositions make reproducible component fabrication difficult because of chemical inhomogeneity and voids in microstructure. Greater purity and homogeneity from novel methods can lead to improved physical properties. To overcome these problems, soft chemical routes are now increasingly becoming popular to prepare a variety of oxides including their production at the nano-scale. These techniques make use of simple chemical reactions like coprecipitation, sol-gel, ion exchange, hydrolysis, acid leaching, and so on, at considerably low temperatures compared to the ceramic method. Utilization of precursors, intercalation reactions, electrochemical methods, hydrothermal process, and self-propagating high temperature synthesis (SHS) are some of the other commonly employed processes. There are several books and review articles published over the years on the synthesis of oxide materials [7, 8]. There are a host of well established techniques for the synthesis of nanomaterials to tailor the properties as per
requirement for specific application which are briefly described here along with the used combustion synthesis technique that has been explained in detail. Fig. 2.1 is the photograph of synthesis and fabrication facilities available at Department of Applied Physics, Aligarh Muslim University.

![Image of a laboratory](image)

**Figure 2.1:** Nanomaterials fabrication lab at Department of Applied Physics AMU.

### 2.1.1. Gas phase synthesis

This is the simplest method of producing nanocrystalline powders. The first studies in this topic were carried out in 1912 [9-11] by evaporating gold from a heated tungsten filament at a nitrogen pressure of 0.3 mm Hg (40 Pa), which produced spherical particles with a diameter of 1.5–10 nm (the mean diameter approximately 4 nm) in the condensates. The condensation of vapours of aluminium in H₂, He and Ar at different gas pressures made it possible to produce particles with a size of 20–100 nm [12]. Later, the method of combined condensation of metal vapours in Ar and He was used to produce Au–Cu and Fe–Cu highly dispersed alloys, formed by spherical particles with a diameter of 16–50 nm [13, 14]. Several theoretical features of condensation in supersaturated
vapours, which takes place by means of the formation and growth of nuclei (clusters), were discussed in a review reported in [15].

2.1.2. Plasma chemical technique (PCS)

PCS is a wet chemical technique which is mainly employed to synthesize highly dispersed nanoparticles of a variety of elemental as well as oxide materials [16, 17]. The primary requirement for producing highly dispersed powders by this method is the occurrence of a reaction away from equilibrium and the higher rate of formation of nuclei of a new phase at a low growth rate of this phase. In a typical PCS synthesis, the formation of nanoparticles can be carried efficiently by increasing the cooling rate of the plasma flow in which condensation from the gas phase takes place. PCS technique has been potentially utilized for the phase pure synthesis of highly dispersed nano-powders of nitrides of Ti, Zr, Hf, V, Nb, Ta, B, Al and Si, carbides of Ta, Nb, Ti, W, B and Si, and oxides of Mg, Y and Al [18-21].

2.1.3. Precipitation from colloidal solution

These methods include well known sol-gel and coprecipitation techniques. One conventional method to prepare nanoparticles of metal oxide ceramics is the coprecipitation method [22-24]. This process involves dissolution of salt precursors, usually a chloride, oxychloride, or nitrate, such as AlCl₃ to make Al₂O₃, Y(NO₃)₃ to make Y₂O₃, and ZrOCl₂ to make ZrO₂. The corresponding metal hydroxides usually form and precipitate in water by adding a basic solution such as sodium hydroxide or ammonium hydroxide to the solution. Sol-gel techniques have long been known for the preparations of metal oxides and have been described in several books and reviews [25-31]. The process is generally utilized to prepare metal oxides via the hydrolysis of metal reactive precursors, usually alkoxides in an alcoholic solution, resulting in the corresponding hydroxide. Hydrolysis of metal alkoxides [M(OR)ₓ] involves nucleophilic reactions with water as follows:

\[
M(OR)_y + xH_2O \leftrightarrow M(OR)_{y-x}(OH) + xROH
\]
The mechanism of this reaction involves the addition of a negatively charged hydroxyl group (OH⁻) to the positively charged metal centre (M⁺). A proton is released in this process which is then transferred to the metal alkoxy group followed by the elimination of ROH. After releasing H₂O molecules the hydroxide molecules bind together which results stable viscous gel/network like structure of the metal hydroxide. Heat treatment of this gel-like material yields very fine powder of metal oxide.

2.1.4. Milling and mechanical alloying

This is the top-down process which involves the utilization of mechanical forces to break down coarser material into very fine powders. The basis of mechanical alloying is the mechanical treatment of solid mixtures leading to refining and plastic deformation of substances, acceleration of mass transfer and mixing of the components of the mixture on the atomic level, together with the activation of chemical reaction of the solid precursors [32-34]. During the process of mechanical milling and mechanical alloying the materials may lead to the complete solubility in the solid state of elements characterised by very low mutual solubility in the equilibrium condition [35, 36].

2.1.5. Combustion or fire synthesis (CS)

Among all those methods described in previous sections, the combustion or fire synthesis (CS) is quite simple, fast, and economical. Although CS has been successfully used to make non-oxide materials, its application for synthesis of oxide materials was delayed due to commercial reasons. Apart from that, as it is a solid-state method, it sometimes become difficult to maintain phase purity and to have a control over grain size, homogeneity and distribution. Further, due to its high-temperature course it is not a suitable technique for the preparation of nanocrystalline materials. Thus, to prepare materials at nano-scale by this technique, a low-temperature initiated combustion method was worked out [37, 38]. Such low temperature version of self-propagating combustion process is different from the well-known Pechini (citrate gel process) which relies on external heating at high temperatures to burn away the extra carbon [39]. Combustion process is also different from pyrolysis since once ignited it does not require external
heating and the reaction progresses with the help of heat generated during the combustion of fuel/fuel-system. In general, there are two approaches for the synthesis of nanomaterials by soft routes. In first process, there is chemical breaking of a given bulk material down to nano scale while in the second approach the atom, ions or molecules are chemically assembled leading to building-up nano-sized grains. CS of fine grained oxide materials while appearing to be a breaking-down process is in fact an integrated approach, as the desired oxide products nucleate and grow from the combustion residue. This process is also known as self-propagating high temperature synthesis (SHS). The process essentially requires a combustible mixture of an oxidizer and fuel. The reaction triggers at the point of a certain temperature called ignition temperature. SCS process makes use of extremely exothermic redox chemical reactions between an oxidizer and a fuel. In fact, all SHS reactions are essentially redox reactions; however, the converse is not true. The prerequisite for a reaction to be self-propagating is that the amount of heat evolved should be more than the heat required for initiating the combustion. A redox reaction involves simultaneous oxidation and reduction processes. The classical definition of oxidation is addition of oxygen or any other electronegative element (generally nonmetals), while reduction is addition of hydrogen or any other electropositive element (generally metals). In practice, the term combustion covers flaming (gas-phase), smouldering (solid-gas) as well as explosive reactions. It can be linear combustion or volume combustion. In linear combustion the burning surface recedes from top to bottom in layers, whereas in volume combustion, the entire reaction mixture ignites to burn with a flame. The SHS process pioneered by Merzhanov has been used to prepare a large number of technologically useful oxide materials (refractories, magnetic, semiconductors, dielectric, catalysts, sensors, phosphors, etc.) and non-oxide materials (carbides, nitrides, borides, silicides) by the solid-state reaction between the corresponding metals and nonmetals. The process requires high-purity fine precursors, which ignite at temperatures >1000°C. The process is highly exothermic (4000°C) and self-propagating resulting in coarse products. This process has been successfully employed to prepare hundreds of technologically useful materials [40], including the preparation of oxide materials in recent times. However, being a solid-state reaction it
often does not produce homogeneous products and results in coarse powders. Here, the solution combustion approach is presented to prepare oxide materials of desired composition, structure, and properties.

2.1.5.1. Solution combustion synthesis (SCS)

A refined version of CS is SCS. SCS is a versatile technique for synthesis of nano-structured oxide materials especially at large scale and it has been successfully employed for the production of a variety of fine complex oxide as well as non-oxide powders for different advanced applications, including catalysts, biotechnology and fuel cells. This process was unexpectedly discovered during the reaction between aluminum nitrate and urea. When a mixture of Al(NO$_3$)$_3$·9H$_2$O and urea solution was rapidly heated around 500°C in a muffle furnace, it foamed and ignited to burn with an incandescent flame yielding voluminous white fluffy mass which was later identified as α-Al$_2$O$_3$ [41]. To completely understand the highly exothermic nature of this reaction, the concepts of propellant chemistry were utilized [42]. In the context of propellant chemistry, a solid propellant is composed of an oxidizer like ammonium perchlorate and a fuel like Carboxyl terminated Polybutadiene together with Aluminum powder and some additives in minute quantity. The amount of energy released during a certain combustion process is expressed in terms of the specific impulse ($I_sp$) of the propellant in the form of the ratio of thrust produced per pound of the propellant. It is expressed as given below:

\[
I_{sp} = \psi \left( \frac{T_c}{\text{molecular weight of gaseous products}} \right)^{\frac{3}{2}} \quad \ldots \ldots 2.1
\]

The highest amount of heat $T_c$ (temperature of chamber in the rocket motor) is produced when the equivalence ratio ($\psi = \text{oxidizer/fuel ratio}$) becomes unity. The equivalence ratio of an oxidizer and fuel mixture is expressed in terms of the elemental stoichiometric coefficient.

\[
\psi = \frac{\Sigma (\text{coefficient of oxidizing elements in specific formula}) \times (\text{valency})}{(-) \Sigma (\text{coefficient of reducing elements in specific formula}) \times (\text{valency})} \quad \ldots \ldots 2.2
\]

A mixture of fuel and oxidizer is said to be stoichiometric when $\psi = 1$, fuel-lean when $\psi > 1$, and fuel-rich when $\psi < 1$. Stoichiometric mixtures produce maximum energy. The
oxidizer/fuel molar ratio (O/F) required for a stoichiometric mixture (ψ = 1) is
determined by summing the total oxidizing and reducing valencies in the oxidizer
compounds and dividing it by the sum of the total oxidizing and reducing valencies in the
fuel compounds. In this type of calculation oxygen is the only oxidizing element; carbon,
hydrogen, and metal cations are reducing elements and nitrogen is neutral. Oxidizing
elements have positive valencies and reducing elements have negative valencies. In
solution combustion calculations, the valency of the oxidizing elements was modified and
considered as negative, and the reducing elements as positive, similar to the oxidation
number concept familiar to chemists. Accordingly, the elemental valency of C, Al, and H
is +4, +3, and +1, respectively, and oxidizing valency of oxygen is taken as −2. The
valency of nitrogen is considered to be zero. Based on this concept, the oxidizing valency
of aluminum nitrate and the reducing valency of urea are
\[
\text{Al(NO}_3\text{)}_3 = -15; [\text{Al} = +3, 3\text{N} = 0, 9\text{O} = (9\times-2) = -18],
\]
\[
\text{CH}_4\text{N}_2\text{O} = +6; \ [\text{C} = +4, 4\text{H} = (4\times+1) = +4, 2\text{N} = 0, \text{O} = (1\times-2) = -2].
\]
Assuming the complete combustion of aluminum Nitrate : Urea system, the molar ratio
becomes 15/6 = 2.5. The stoichiometric equation for this reaction can be written as
\[
2\text{Al(NO}_3\text{)}_3(\text{aq}) + 5\text{CH}_4\text{N}_2\text{O(}\text{aq}) \rightarrow \alpha\text{-Al}_2\text{O}_3(\text{s}) + 5\text{CO}_2(\text{g}) + 8\text{N}_2(\text{g}) + 10\text{H}_2\text{O(}\text{g})
\]
Thus, whenever the reaction of aluminum nitrate and urea is carried out in the
molar ratio of 1 : 2.5 the energy released is maximum and the combustion is complete
with no carbon residue. Such type of stoichiometric balance of a redox mixture for a
combustion reaction is fundamental to the synthesis of an oxide material by the solution
combustion method. Tab. 2.1 summarizes a list of useful fuels which are commonly
utilized in the process of SCS.
<table>
<thead>
<tr>
<th>Fuel</th>
<th>Molecular formula</th>
<th>Reducing valencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea (U)</td>
<td>$\text{CH}_4\text{N}_2\text{O}$</td>
<td>+6</td>
</tr>
<tr>
<td>Glycine (G)</td>
<td>$\text{C}_2\text{H}_4\text{NO}_2$</td>
<td>+9</td>
</tr>
<tr>
<td>Hexamethylene tetramine (HMT)</td>
<td>$\text{C}_3\text{H}_8\text{N}_4$</td>
<td>+36</td>
</tr>
<tr>
<td>Carboxyhydrizide (CH)</td>
<td>$\text{C}_2\text{H}_6\text{N}_4\text{O}$</td>
<td>+8</td>
</tr>
<tr>
<td>Oxalic acid dihydrazide (ODH)</td>
<td>$\text{C}_2\text{H}_6\text{N}_4\text{O}_2$</td>
<td>+10</td>
</tr>
<tr>
<td>Malonic acid dihydrazide (MDH)</td>
<td>$\text{C}_2\text{H}_6\text{N}_4\text{O}_2$</td>
<td>+16</td>
</tr>
<tr>
<td>Maleic hydrazide (MH)</td>
<td>$\text{C}_2\text{H}_6\text{N}_4\text{O}_2$</td>
<td>+16</td>
</tr>
<tr>
<td>Diformyl hydrazide (DFH)</td>
<td>$\text{C}_2\text{H}_6\text{N}_4\text{O}_2$</td>
<td>+8</td>
</tr>
<tr>
<td>Tetraformal trisazime (TFTA)</td>
<td>$\text{C}_2\text{H}_6\text{N}_6$</td>
<td>+28</td>
</tr>
</tbody>
</table>

Table 2.1: Some commonly used fuels and their reducing valences.

Fig. 2.2 is the flow chart of the solution combustion synthesis rout adopted in this thesis for the preparation of nano-ferrites.
Figure 2.2: Flow chart showing various steps of SCS process adopted in the present work for the synthesis of materials.
2.2. Calcination

It is a controlled heat treatment process which is frequently employed in materials science studies. In this process, the material under investigation is heat treated in the presence of oxygen below its melting temperature at a constant rate of heating and subsequently cooled at a constant cooling rate. During this process, three major changes occur in the material; i) the volatile impurities (like the traces of carbonaceous material(s) present in the sample are evaporated ii) the crystallinity of the material increase iii) the grain size of the material increases. In the present study, the various samples were calcined between 300 °C – 500 °C at a heating and cooling rate of 5 °C/min. In Fig. 2.3, fire treatment facilities available at Department of Applied Physics, Aligarh Muslim University are shown.

Figure 2.3: Heat treatment facility at Department of Applied Physics, AMU.
2.3. Making the pellet

For certain measurements (like electrical and dielectric), the sample is required in the form of circular discs or pellets. 1-2% of PVA solution is added to 1-1.5 grams of the powdered material and it is pressed in the form of discs of 13 mm diameter by applying a pressure of 5-8 tons. Ring shaped pellets of some materials were formed by the same process for permeability measurements. Fig. 2.4 is the image of torroid shaped core of gamma ferrite material.

![Image of Torroidal Core](image.png)

**Figure 2.4:** Torroidal core of $\gamma$-$\text{Fe}_2\text{O}_3$ material.

2.4. Sintering

To ensure the perfect binding of grains in the material, the pellets were again heat treated followed by slow cooling. Sintering leads to the evaporation of PVA and to restore the oxygen non-stoichiometry. In the present study, the heat treatment of materials was carried out inside a programmable Nabertherm furnace.
2.5. Characterization techniques

2.5.1. Structural characterization

2.5.1.1. Powder X-ray diffraction

The interaction of x-ray radiation with crystalline sample is governed by Bragg’s law, which indicates a relationship among the diffraction angle (Bragg angle), x-ray wavelength, and interplanar spacing [43]. According to Bragg, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Fig. 2.5.

Figure 2.5: Ray diagram illustrating the Bragg’s reflection by lattice planes.

The path differences introduced between a pair of waves traveled through the neighboring crystallographic planes are determined by the interplanar spacing. As the total path difference is equal to \( n\lambda \) (as \( n \) being an integer and \( \lambda \) being the wavelength), the constructive interference will occur and a group of diffraction peaks can be observed that give rise to x-ray patterns. The quantitative account of Bragg’s law can be expressed as:

\[
n\lambda = 2d_{hkl}\sin\theta
tilde{\text{Equation 2.3}}
\]

Where, \( d \) is the interplanar spacing for a given set of \( hkl \), \( \lambda \) is the wavelength, and \( \theta \) is the Bragg angle shown in Figure 2.5.
The intensity of powder diffraction peaks is in principal determined by the structural factor, $F_{hkl}$ as expressed in equation 2.4, which in turn depends on the crystal structures including relative positions of atoms in the unit cell, types of unit cells and other characteristics such as thermal motion and population parameters.

$$F_{hkl} = \sum_{i=1}^{n} g^i t^i(s) f^i(s) \exp [2\pi i(hx^i + ky^i + lz^i)] \quad \ldots .2 .4$$

Where, $f^i(s)$ is the atomic scattering factor, $g^i$ is the population factor of $i^{th}$ atom, $t^i(s)$ is the temperature factor, $hkl$ are the Miller indices, and $xyz$ are the fractional coordinates of $i^{th}$ atom in the unit cell [44]. In addition to the primary structural factors, the intensity of diffraction is dependent on other factors, which are not only relevant to sample effects such as its shape and size, grain size and distribution etc., but also with the instruments including detector, slit and / or monochromator geometry.

Figure 2.6: X-ray diffractometer at Department of Applied Physics, AMU.

For all X-ray diffraction experiments presented in the present investigation, Rigaku Miniflex (Japan) X-ray diffractometer (Fig. 2.6) with Cu-Kα ($\lambda = 0.15406$ nm)
radiation was employed and operated at applied voltage of 45 kV and filament current of 40 mA. The spinel phase identification for all as-synthesized samples reported here was performed by matching the peak positions and intensities in the experimental diffraction patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database [45]. One of the more frequent applications of XRD analysis is to determine the crystalline size and lattice strain in nanocrystalline materials. The peak broadening in x-ray diffraction patterns for nanomaterials is the result of the finite size effect. For a finite size nanocrystal, the number of x-ray radiation reflected from successive lattice planes that add up to produce constructive or destructive interference becomes finite and therefore they cannot reinforce or cancel out completely [46]. Additionally, some other factors such as inhomogeneous lattice strains, variations in the lattice constants from one crystallite to another and structural faults can also yield the broadening of the diffraction peaks.

The size of nanomaterials can be derived from the peak broadening and calculated by using the Scherrer formula (equation 2.5), provided that the nanocrystalline size is less than 100nm.

\[ d = \frac{K\lambda}{(\beta \cos \theta)} \]  \hspace{1cm} \text{......2.5}

Where, \( d \) is the average crystalline dimension perpendicular to the reflecting phases, \( \lambda \) is the x-ray wavelength, \( \theta \) is the Bragg angle, and \( \beta \) is the finite size broadening. \( K \) is a constant close to unity that is related both to the crystalline shape and to the way \( \beta \) is defined, i.e., either as the full width at half-maximum (FWHM) or as the integral breadth i.e. the ratio of the peak area to peak maximum.

2.5.1.2. Fourier transform infra-red (FT-IR) spectroscopy

For the structural elucidation of complex organic and inorganic compounds Infrared (IR) spectrometry has changed dramatically over the past 40 years. The rather newer version of the same, the FT-IR is the preferred method of infrared spectroscopy. The impact of Fourier transform infrared (FT-IR) spectrometers was not recognized until 1973 when Herbert Laitinen demonstrated its importance. Since then the FT-IR
spectrometers have assumed such a position of dominance for the measurement of infrared spectra. In fact, in FT-IR spectrometry, all the resolution elements are measured at all times during the measurement. In addition, more radiation can be passed between the source and the detector for each resolution element. As a result, transmission, reflection, and even emission spectra can be measured significantly faster and with higher sensitivity than ever before. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. Perkin Elmer IR spectrometer used in the present study is shown in Fig. 2.7.

Figure 2.7: PerkinElmer FT-IR spectrometer at Department of Applied Physics, AMU.

There is a glowing black-body source which generates infrared energy in the form of a narrow beam of radiation which is utilized in sample analysis. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector). The beam enters the interferometer where the “spectral
encoding" takes place due to which interferogram signals are generated that later exit the interferometer. The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are unique characteristics of the sample, are absorbed. The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the "percent transmittance." This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself. Fig. 2.8 shows the internal optics of a typical FT-IR spectrometer.

Figure 2.8: Block diagram of a typical FT-IR Spectrometer.
2.5.2. Micro-structural characterization

2.5.2.1. Scanning electron microscope (SEM)

Electron microscopes are scientific instruments that make use of a beam of energetic electrons to examine objects on a very fine scale. Electron microscopes were developed due to the limitations of Light Microscopes which are limited by the wavelength of light. In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria...etc.). This required 10,000x plus magnification which was not possible using current optical microscopes. The first Scanning electron microscope (SEM) debuted in 1938 (Von Ardenne) with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. Scanning electron microscopy (SEM) can provide a highly magnified image of the surface and the composition information of near surface regions of a material [47]. The resolution of SEM can approach a few nanometers and the magnifications of SEM can be easily adjusted from about 10 times to 300,000 times. In SEM, electron beam, accelerated by a relatively low voltage of 1-20 kV, is scanned on the specimen surface. As the electron beam strikes the surface, a large number of signals are generated from (or through) the surface in the form of electrons or photons. These signals emitted from the specimen are collected by detectors to form images and the images are displayed on a cathode ray tube screen. There are three types of images produced in SEM: secondary electron images, backscattered electron images, and elemental X-ray maps. Secondary electrons (SE) are considered to be the electrons resulting from inelastic scattering with atomic electrons and with the energy less than 50 eV. The secondary emission of electrons from the specimen surface is usually confined to an area near the beam impact zone that permits images to be obtained at high resolution. These images, as seen on a cathode ray tube, provide a three dimensional appearance due to the large depth of field of the SEM as well as the shadow relief of the secondary electrons contrast. Backscattered electrons (BSE) are considered to be the electrons resulting from elastic scattering with the atomic nucleus and with the energy greater than 50 eV. The backscattering will likely occur in a material of higher atomic number, so the
contrast caused by elemental differences can be built up. After the primary electron beam collides with an atom in the specimen and ejects a core electron from the atom, the excited atom then decays to its ground state and emits either a characteristic X-ray photon or an Auger electron [48]. The energy dispersive X-ray detector (EDX) can sort the X-ray signal by energy and produces elemental images, so the spatial distribution of particular elements can be detected by SEM. SEM usually has resolution of 1 nm for 1 KV even resolution of 0.6 nm is possible for 5 KV. Schematic diagram of a typical SEM is shown in Fig. 2.9.

Figure 2.9: Schematic diagram of a typical SEM.
In the present thesis, the powdered samples were investigated by field-emission scanning electron microscopy (FESEM), LEO Supra 50 Vp, field-emission SEM, Carl-Zeiss SMT, Oberkochen, Germany. Prior to FE-SEM, the samples were coated with gold by an ion sputter coater (Polaron SC515, Fisons Instruments, UK).

2.5.2.2. Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) has evolved as an important and indispensable tool in exploration of nanomaterials. The complementary imaging, diffraction and spatial resolution microanalysis techniques in TEM provide the information on chemical composition, crystal structure, electronic and/or magnetic structure, size and shape of nanomaterials. The versatility of transmission electron microscopy for the analysis of materials primarily originates from the various interactions when electron beams undergo within the solid specimen as shown schematically in Fig. 2.10.

![TEM Diagram](image)

**Figure 2.10:** Cross-sectional diagrams of a TEM illustrating its various components and their functionality.
For example, the transmitted electrons are used to visualize the internal crystal structure by bright and dark field imaging and orientation and identification of crystals in selected area electron diffractions. The elemental and chemical information can be simultaneously derived from the analysis of the characteristic x-ray radiations. The diffraction physics and the principles of imaging can be found in detail from the literature and TEM textbooks [49-51].

In the present work, all high-resolution TEM studies were performed on JEOL 4000 EX TEM with point-to-point image resolution at 0.18 nm, objective lens (Cs = 1.0 mm, Cc = 1.7 mm) and acceleration voltage at 400 kV, respectively.

2.5.3. Electrical characterization

In the present work, the dielectric, a.c. conductivity and impedance measurements have been carried as a function of composition, frequency (42Hz-5MHz) and temperature (300K-473K) using Agilent LCR (4285 A) impedance meter. The temperature was controlled with accuracy of ±50 mK using LakeShore (Model 340) temperature controller. Fig. 2.11 is the block diagram of LCR meter while Fig. 2.12 is the photograph of actual instrument available at Department of Applied Physics, AMU.

![Figure 2.11: Simplified block diagram of LCR meter.](image)
2.5.3.1. Complex dielectric measurements

For dielectric and a.c. impedance measurements, a very thin paste of silver was coated on the opposite faces of the pellet to make parallel plate capacitor configuration with the ferrite material between the plates serving as the dielectric material. The value of dielectric constant (\(\varepsilon\)) has been calculated using the following relation [52]:

\[
\varepsilon = \frac{C_p d}{\varepsilon_0 A}
\]

……2.6

where \(\varepsilon_0 = 8.854 \times 10^{-12}\) F/m, known as permittivity of free space, \(d\) is the thickness of pellets, \(A\) is the area of cross section of the pellet and \(C_p\) is capacitance of the pellet. The complex dielectric constant has been calculated from the relation:

\[
\varepsilon'' = \varepsilon' \tan \delta
\]

……2.7

Where, \(\varepsilon'\) is the real and \(\varepsilon''\) is the imaginary part of the complex dielectric constant, \(\tan \delta\) is the dielectric loss factor.

Figure 2.12: Temperature dependent impedance LCR meter facility available at Department of Applied Physics, AMU.
2.5.3.2. Dielectric loss (\( \tan \delta \))

Dielectric loss is the amount of energy dissipated during the frequency dependent operation of a material. The energy loss is usually characterized by the dielectric loss factor (\( \tan \delta \)) which is expressed as the ratio of the imaginary part of the dielectric constant to the real part, i.e.

\[
\tan \delta = \frac{1}{\varepsilon \omega \varepsilon_0 \rho}
\]

Where, \( f \) is the frequency of the applied a.c. field and \( \rho \) the resistivity of the dielectric material. The root cause of the dielectric loss is the phase mismatching between the dielectric polarization and applied a.c. field which in turn depends upon the microstructure, impurities and defects present inside the crystal lattice. In many cases, the density of a material also plays an important role in the behaviour of dielectric constant. Low compaction (high porosity) often results in low values of dielectric constant and losses [53].

2.5.3.3. a.c. Conductivity

The overall conductivity of any system can be expressed in terms of the sum of the a.c. conductivity and d.c. conductivity. It is given by the following relation:

\[
\sigma_{\text{tot}} = \sigma_{0}(T) + \sigma(\omega, T)
\]

The first term at R.H.S. of equation 2.9 is frequency independent and it is d.c. conductivity due to the band conduction, while the second term of the equation is frequency dependent which represents the pure a.c. conductivity due to electron hopping between Fe\(^{3+}\) and Fe\(^{2+}\) ions at octahedral sites. In the present thesis, the a.c. conductivity measurements of all the nano-structured samples of ferrite materials (both spinel type as well as perovskite type), as a function of frequency and temperature for different compositions were carried out using the following expression [54]:

51
\[ \sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \] .......2.10

Where, \( \omega \) is angular frequency.

2.5.3.4. d.c. Conductivity and activation energy

Temperature dependent d.c. resistivity was measured by Keithley’s standard two probe set up (Fig. 2.13) using sourcemeter-2400. Activation energy was calculated by the slopes of the plots between \( \ln(\rho) \) (y-axis) and \( 10^3/T \) (x-axis).

Figure 2.13: Keithley’s multi-probe set-up used for the measurement of d.c. resistivity

2.5.3.5. Initial permeability

Initial permeability is very important and desirable parameter from technological point of view. It is a factor which defines how quickly the domains of magnetic material align themselves along the direction of applied field. In the present investigation, the complex permeability measurements of torroid shaped pellets of samples (Fig. 2.14) in the frequency range of 50 KHz – 25 MHz and in the temperature range of 300K – 473K for whole range of dopant concentration were carried out with the help of Agilent LCR (4285 A) impedance meter.
Figure 2.14: Torroidal shaped samples of materials coiled with insulated copper wire.

2.5.3.6. Complex impedance spectroscopy

Bauerle [55-57], first used this technique in 1969 to separate bulk properties from interfacial properties in polycrystalline ceramic materials. In this technique, when plotting the complex impedance diagrams, (Also known as Nyquist or Cole–Cole plot) the imaginary part of the impedance $Z''(\omega)$ is plotted against the real part of impedance $Z'(\omega)$. For an ideal combination of a parallel circuit containing a resistance $R$ and a capacitance $C$, the response is in the form of a semicircle centered on the real axis. The value of $R$ is determined from the diameter of this semicircle, whereas $C$ is calculated from the frequency of semicircle maximum. The technique of Impedance spectroscopy is widely employed for analysis and investigation of the electrical response of a variety of dielectric materials as a function of frequency in variable conditions of temperature and composition. That’s why it has emerged as a powerful technique for unraveling the complexities of materials, whose properties and applications depend on the close control of structure, composition, ceramic texture, dopants (or defects) and dopant distribution, which functions by utilizing the different frequency dependences of constituent components for their separation. The impedance spectroscopy of a material is
based on an idealized circuit model with discrete electrical components. The analysis is mainly accomplished by fitting the impedance data to an equivalent circuit, which is representative of the material under investigation. It has been among the most useful investigation techniques since the impedance of grains can be separated from the other sources of impedance, namely grain boundaries and electrode effects [58]. When the grain boundary resistance is larger than the resistance of bulk, two semicircles are often obtained in Cole-Cole plot. Deviations from ideal semicircles have been attributed to the distribution of relaxation times arising from the micro-structural inhomogeneity or disorder in the samples [59, 60]. A sine wave signal was fed to the input terminal (T₁) of the LCR meter and the sample from the signal generator (SG) terminal. The output (T₀) measured the output signal from the sample, which was voltage drop across a standard resistance of 1kΩ. Fig. 2.8 shows the schematic diagram of the LCR meter. LCR then automatically analyzed the signals from T₁ and T₀ to give phase difference (θ) between the input and out signals, i.e., Z' and Z". The complex impedance plot is obtained after plotting Z" versus Z'. When an a.c. voltage \( V = V₀e^{jωt} \) is applied across the sample, the current that flows across the sample is given by:

\[
i = jωCV = \frac{jω(ε' - jε'')ε₀V}{d} \quad \text{.........2.11}
\]

In fact, the complex impedance plot can be represented in terms of any of the five possible complex formalisms, the permittivity (ε), the admittance (Y), the electric modulus (M), the impedance (Z) and the loss tangent (\( \tan δ \)). These parameters are related with each other [61-63] by the formula:

\[
\tan δ = \frac{ε''}{ε'} = \frac{M''}{M'} = \frac{Y'}{Y''} = \frac{Z'}{Z''} \quad \text{.........2.12}
\]

Whereas the real and imaginary parts of the complex impedance are given by:

\[
Z' = \frac{R_g}{[1+(ω_0 c_g^2 R_g)^2]} + \frac{R_{gb}}{[1+(ω_0 c_{gb}^2 R_{gb})^2]} \quad \text{.........2.13}
\]

and
\[ Z'' = \frac{R_g^2 \omega_g C_g}{[1+(\omega_g^2 C_g^2 R_g^2)]} + \frac{R_{gb}^2 \omega_{gb} C_{gb}}{[1+(\omega_{gb}^2 C_{gb}^2 R_{gb}^2)]} \] \hspace{1cm} \text{…….2.14}

Where, the terms \( R_g \) and \( C_g \) represents the resistance and capacitance of the grain, while \( R_{gb} \) and \( C_{gb} \) represents the corresponding terms for the grain boundary volume [64, 65]. The resistance value for the grain and grain boundary have been calculated from the intercepts on the real part of \( Z \) (\( Z' \)) axis, whereas the capacitance values have been calculated from the frequency peaks of the semicircle arcs. Since the value of \( Z' = -Z'' \) at the maximum, we have:

\[ C_g = \frac{1}{R_g \omega_g} \quad \text{…….2.15} \]

\[ C_{gb} = \frac{1}{R_{gb} \omega_{gb}} \quad \text{…….2.16} \]

Also, the relaxation times \( \tau_g \) and \( \tau_{gb} \) have been calculated from the frequency peaks using the equations:

\[ \tau_g = \frac{1}{\omega_g} = C_g R_g \quad \text{…….2.17} \]

\[ \tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \quad \text{…….2.18} \]

The simplest model to describe a dielectric material filled inside two parallel plates is shown in Fig. 2.15.
Figure 2.15: Schematic presentation of dielectric-filled parallel plate model.

A resistor \( R_s \) follows with the parallel of a resistor \( R_p \) and capacitor \( C_p \). \( R_s \) is the contacting resistance between the dielectric material and the electrode, \( R_p \) is related to the power dissipation inside the dielectric material, and \( C_p \) is the capacitance between the two plates. The impedance analysis of the model is as follows.

\[
Z = R_s + \frac{R_p}{1+j\omega R_p C_p} \quad \text{(2.19)}
\]

Where, \( Z \) is the impedance between 1 and 2 nodes in figure, and \( \omega \) is the angular frequency.

\[
Z = Z_r + jZ_i = R_s + \frac{R_p}{1+j\omega R_p C_p} \quad \text{(2.20)}
\]

Where, \( Z_r \) is the real part, and \( Z_i \) is imaginary part of the impedance \( Z \).

\[
Z = R_s + \frac{R_p}{1+\omega^2 C_p^2 R_p^2} - j \frac{\omega C_p R_p^2}{1+\omega^2 C_p^2 R_p^2} \quad \text{(2.21)}
\]

As \( \omega \to \infty \), \( \text{Mod}(Z) = Z = R_s \)

As \( \omega \to 0 \), \( \text{Mod}(Z) = Z = R_s + R_p \)

\[
Z_r = R_s + \frac{R_p}{1+\omega^2 C_p^2 R_p^2} \quad \text{(2.22)}
\]

\[
Z_i = -\frac{\omega C_p R_p^2}{1+\omega^2 C_p^2 R_p^2} \quad \text{(2.23)}
\]

As \( \omega C_p R_p \to 1 \), \( Z_i = -\frac{R_p}{2} \) which arrives at the minimum position of \( Z_i \) from which we can calculate the values of \( C_p \) and \( R_p \).
\[(Z_r - R_s - \frac{R_p}{2})^2 + Z_i^2 = \left(\frac{R_p}{1 + \omega^2 C_p^2 R_p^2} - \frac{R_p}{2}\right)^2 + \left(\frac{\omega C_p R_p}{1 + \omega^2 C_p^2 R_p^2}\right)^2\]
\[= \left(\frac{R_p}{1 + \omega^2 C_p^2 R_p^2}\right)^2 \left((1 - \omega^2 C_p^2 R_p^2)^2 + (2\omega C_p R_p)^2\right)\]
\[= \left(\frac{R_p}{1 + \omega^2 C_p^2 R_p^2}\right)^2 \left(1 + \omega^2 C_p^2 R_p^2\right)^2\]
\[(Z_r - R_s - \frac{R_p}{2})^2 + Z_i^2 = \left(\frac{R_p}{2}\right)^2\]  

Equation 2.24 clearly describes a circle centered at \((R_s + R_p/2, 0)\) and a diameter of \(R_p\). The imaginary part \(Z_i\) is always less than 0, so it appears as a semicircle at the negative imaginary plane.

When \(\omega C_p R_p = 1\), \(-Z_i\) attains its maximum value and the corresponding angular frequency is denoted by \(\omega_{max}\). So we can write

\[C_p = \frac{1}{\omega_{max} R_p}\]  

From the semicircle in the complex plane, we can locate \(R_s\), \(R_p\), and \(f\) at the maximum \(Z_i\) in order to calculate \(C_p\). However, this method has a major disadvantage that the frequency at maximum cannot always be determined easily. The Bode plots (which plots the logZ and phase angle vs logf) has an important advantage that the region which are dominated by the resistive elements such as \(R_s\) and \(R_p\) has the slope of zero and the region dominated by capacitive elements has a slope of \(-1\) for the ideal case. The elements of the \(R_s\) and \(R_p\) can be determined from the high frequency regions of the Bode plots according to the condition that as frequency approaching to 0, \(Z\) approaches \(R_s\), and when frequency approaches infinity, \(Z\) approaches \(R_s + R_p\). From region dominated by capacitors for which has a slope of \(-1\),

\[\log Z' = -(\log \omega + \log C_p) = -\log 2\pi - \log f - \log C_p\]  

Where \(Z'\) is the fitted line.

As \(\log f = -\log 2\pi \Rightarrow f = \frac{1}{2\pi}, \Rightarrow \log Z' = \log C_p\)

\[\Rightarrow C_p = Z'(\frac{1}{2\pi})\]  

The \(C_p\) value is calculated from the Bode plots.
2.5.4. Optical characterization (UV-Visible photospectrometer)

Based on the Beer-Lambert's laws [66, 67], UV-visible spectroscopy measures absorbance or transmittance of radiation in the ultra-violet and visible region of the spectrum. The spectrophotometer has well been called the workhorse of the modern laboratory. In particular, ultraviolet and visible spectrophotometry is the method of choice in most laboratories concerned with the identification and measurement of organic and inorganic compounds in a wide range of products and processes in nucleic acids and proteins, foodstuffs, pharmaceuticals and fertilisers, in mineral oils and in paints. In every branch of molecular biology, medicine and the life sciences, the spectrophotometer is an essential aid to both research and routine control. Modern spectrophotometers are quick, accurate and reliable and make only small demands on the time and skills of the operator. However, the user who wants to optimise the functions of his/her instrument and to be able to monitor its performance in critical areas will need to understand the elementary physics of the absorption process as well as the basic elements of spectrophotometer design. A simple layout of a typical spectrophotometer along with actual instrument is shown in the Fig. 2.16.

![Figure 2.16: Block diagram of internal optics of a typical UV-Visible spectrophotometer and the actual instrument available at department of Applied Physics, AMU.](image-url)
2.5.5. Magnetic characterization (Vibrating Sample Magnetometer, VSM)

The magnetization measurements and its temperature variation study were carried out using a vibrating sample magnetometer. The vibrating sample magnetometer is most widely used instrument for determining magnetic properties of a large variety of materials: diamagnetic, paramagnetic, ferromagnetic, and antiferromagnetic. This technique was put forward in 1956 by Simon Foner, a scientist of the MIT.EGG Princeton Applied Research (EGG PAR). It has a flexible design and combines high sensitivity with ease of sample mounting and exchange. Powders, bulk and thin films can be studied. Using a vibrating sample magnetometer one can measure the DC magnetic moment as a function of temperature, magnetic field, angle and time. Some of the common measurements which can be done using a vibrating sample magnetometer are: hysteresis loops, DC susceptibility or saturation magnetization as a function of temperature (Curie/ Néel temperature of sample), magnetization curves as a function of angle (anisotropy), and magnetization as a function of time. When a sample of any magnetic material is placed in a uniform magnetic field, a magnetic dipole moment will be induced. Such sample if vibrated with a sinusoidal motion, a sinusoidal electrical signal can be induced in suitably placed pick-up coils. The relative motion of magnetic material with respect to pick up coil produces a sinusoidal electrical signal in the coil (Faraday’s law). The induced signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment of the magnetic material, and relative position with respect to the pick-up coil system. A block diagram of vibrating sample magnetometer is given in Fig. 2.17.
Figure 2.17: Functionality illustration of a VSM by block and schematic diagrams.

The sample is fixed to a small holder located at the end of a sample rod mounted on an electromechanical transducer. The transducer is driven by a power amplifier which itself is driven by an oscillator at a fixed frequency (typically in the range 80 to 90 Hz). So, the sample vibrates along the Z axis perpendicular to the magnetizing field. These vibrations induce a signal in the pick-up coil system which is fed to a differential amplifier. The output of the differential amplifier is subsequently fed into a tuned amplifier and then to an internal lock-in amplifier that receives a reference signal supplied by the oscillator. The output of this lock-in amplifier, or the output of the magnetometer itself, is a DC signal proportional to the magnetic moment of the sample being studied. The electromechanical transducer can move along X, Y and Z directions in order to find the saddle point for calibration of the sample. The saddle point calibration of vibrating sample magnetometer is done by measuring the signal of a pure Ni standard sample of the known saturation magnetic moment placed at the saddle point and at a fixed field.
The basic instrument includes the electromechanical system and the electronic
system (including a personal computer), while the user should select the electromagnet or
superconducting coil system with the appropriate bipolar power supply. The user can also
select a high temperature oven assembly and a liquid Helium/Nitrogen cryostat which
allows the temperature variation study of magnetizations of the samples and finding
Curie temperature/Néel temperature. The VSM used in this work was LakeShore 7305
with liquid Helium/Nitrogen assembly for low temperature measurements and an oven
assembly for measurements above room temperature. The maximum sensitivity of the
instrument is upto $10^{-6}$ emu with selection range from 1000 to 0.0001 emu. The
instrument has absolute accuracy better than 2% with the operating temperature range
from 10 K to 1273 K (with accuracy ±1K). For getting accurate measurements with VSM
a great care should be taken during various measurements and calibrations of the
vibrating sample magnetometer. The sample should not be loosely mounted at sample
holder and the sample should be placed at the centre of pick up coils.
References


CHAPTER 3

STRUCTURAL, ELECTRICAL AND MEAGNETIC PROPERTIES OF Al^{3+} DOPED NANO-SIZED BISMUTH FERRITE AND ITS BAND GAP CALCULATION
3.1. Introduction

Aluminium doped Bismuth Ferrite (BFO) nanopowders (grain size 13–20 nm) having composition Bi$_{1-x}$Al$_x$Fe$_{3-x}$O$_3$ ($x = 0.00, 0.025, 0.05, 0.10, 0.15, 0.20, 0.25$ and $0.30$) were successfully synthesized by solution combustion method using citric acid as fuel at a temperature as low as 200 °C. The as-prepared samples were examined by powder XRD for phase identification and crystallite size determination. The d.c. resistivity as a function of temperature was measured by standard two probe setup which exhibits clear metal to insulator transition for all samples. FT-IR analysis was carried out to identify the chemical bonds present in the system. The optical band gap was calculated from the UV–vis absorbance spectra using classical Tauc relation which was found to vary from 2.78 eV to 2.93 eV for different Al$^{3+}$ concentrations. The activation energies calculated from the slopes of $ln(\rho)$ versus $10^3/T$ plots are in the range 0.54–0.73 eV. Dielectric and electrical properties were investigated as the function of frequency and temperature. All the samples show low frequency as well as high frequency relaxation in their characteristic dielectric spectra which were explained on the basis of Debye-type relaxation model. The incorporation of Al$^{3+}$ ions in the BFO crystal lattice creates oxygen vacancies and hence Schottky barriers which were found to be reflected in the form of anomalous behaviour in the dielectric properties. Debye relaxation model and Maxwell-Wagner charge carrier hopping were found suitable in the overall estimation of the dielectric behaviour of the system. The dielectric constant and loss tangent decrease with the increase of the frequency, while they increase with the increase of temperature and dopant concentration. The a.c. conductivity has a general decreasing trend as the function of composition while it increases with the increase of frequency. The temperature dependence of a.c. conductivity and relaxation time follow well-defined Arrhenius behaviour. The calculated values of activation energies are in the order of 0.5372eV-0.7325eV (<1.00eV) which are indicative of the conduction by means of space charge carriers and O$^{2-}$ vacancies.
BiFeO$_3$ (BFO) is a perovskite material which potentially exhibits simultaneous coexistence of ferroelectric and antiferromagnetic ordering having Curie temperature ($T_c$) 1083K and Neel temperature ($T_N$) 657K [1]. The recent investigations have suggested that this material is very promising material for its possible applications especially in the fields of radio transmission, microwave and satellite communication, digital recording, and permanent magnet applications. Bismuth and its compounds may hold the key for future electronics due to their highly frustrated structures. BFO is not new but in the earlier years of its birth it failed to make any remarkable impact on the then electronic industries due to problem of leakage current that was rooted in non-stoichiometry. The main reason is that the BFO nanopowders synthesized by even established methods are generally plagued by impure phases. In its bulk form, measurements of ferroelectric and transport properties in BFO and its derivatives have been limited by the problem of leakage, mainly due to low resistivity, lattice defects and non-stoichiometry. The properties of BFO can be tailored significantly by chemical substitution at both Bi and Fe sites. There are many reports on the site substituted BFO recipes. Li. et al. investigated the Sr doping on Bi site, resulting the samples being oxygen sub-stoichiometric [2]. Further, they concluded that with the increase of Sr concentration, SrFeO$_3$ phase evolves which leads to diminished magnetization. Similar results were obtained by Khomenko et al with Ca and Ba doped BFO [3]. Lee et al prepared La doped BFO thin films with increased dielectric constant and remanent polarization which they attributed to the increased crystallinity and lattice volume with La doping [4]. Further, La doped BFO ceramics exhibited improved magnetization due to phase transition [5]. Another report confirms the enhancement in multiferroic properties of La doped BFO samples which they attributed to the enhanced magnetoelectric interaction [6]. Al$^{3+}$ doping at Bi site has been investigated for photocatalytic applications by Madhu et al. [7]. In its bulk form, measurements of ferroelectric and transport properties in BFO and its derivatives have been limited by the problem of leakage. It has been established that in BFO, the electrical and magnetic dipole ordering originates in different sublattices. Bi-O orbital hybridization due to the Bi 6s$^2$ lone pair is the origin of ferroelectricity whereas a Fe-O-Fe antisymmetric Dzyaloshinskii-Moriya (DM) exchange interaction is the basis of
magnetic ordering. The dielectric properties of BFO in various forms have also been widely studied in single crystalline, ceramic, and thin film forms [8-10]. Recently, Scott et al related the low temperature dielectric anomaly and their magnetic coupling in ceramic and single crystalline BFO and reported the existence of coupling between FE and AFM order parameters in single crystal and ceramic BFO [11-13]. The polycrystalline BFO samples manifested a decrease in the real part of permittivity ($\varepsilon'$) and loss tangent ($\tan\delta$) when the frequency is increased. Additionally, the presence of slight amounts of non-stoichiometric oxygen in BFO often leads to the presence of $\text{Fe}^{2+}$ and lattice defects thereby resulting in an unwanted increase in the conductivity at room temperature due to hopping mechanism from $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$. The high leakage current in bulk BFO synthesized by solid solution methods also leads to serious dielectric breakdown at fields $<100 \text{ kV/cm}$ which makes them unsuitable for practical devices [14]. To overcome this problem and to get higher resistive material, various approaches have been attempted, such as doping with various rare earth and transition metal ions and a solid solution of BFO with other $\text{ABO}_3$ perovskite materials, but these methods also often result in impure phases. The physical properties of single crystalline materials do change significantly on nano-scale, and it is important to study these size-dependent changes in the material properties to find potential applications for nano-scale devices. Recently, due to the advancements in wet chemical techniques to synthesize these complex oxides, there has been a surge in the studies of BFO on nano-scale [15-17]. The properties of BFO can be tailored significantly by chemical substitution both at Bi as well as Fe sites. The aim of the present study is to investigate the structural, optical, electrical- transport properties and dielectric relaxation behaviour of the BFO samples substituted by $\text{Al}^{3+}$ both at Bi as well as Fe sites.

3.2. Materials and methods

In a typical synthesis procedure, stoichiometric amounts of $\text{Bi(NO}_3)_3\cdot5\text{H}_2\text{O}$ (99.00%, S.D. Fine Chemicals), $\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}$ (98.00%, S.D. Fine Chemicals) and $\text{Al(NO}_3)_3\cdot9\text{H}_2\text{O}$ (95%, Merek Chemicals) were dissolved in minimum amount of double
distilled water. All chemicals were of reagent grade and used without further purification. As Bi(NO₃)₃·5H₂O undergoes decomposition into bismuth oxychloride in water, it was first taken in 15 ml water and kept on stirring. During stirring HNO₃ was added drop by drop until a clear and transparent solution is obtained which confirms the complete dissolution of Bi(NO₃)₃·5H₂O. At this point Fe(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O were added to the solution and kept for further stirring up to complete dissolution. The stoichiometric amount of citric acid (C₆H₈O₇) necessary for the complete combustion of the nitrates was calculated according to propellant chemistry expression:

\[ \psi = \frac{\text{total oxidising valence of oxidising agents (nitrates)}}{\text{total reducing valence of reducing agents (fuel)}} \]

For citric acid, the total reducing valence is F = 18 and for each trivalent nitrate the oxidizing valence is O = 15. So, for complete combustion O/F = 15/18 = 0.833. Thus for each nitrate, the nitrate to fuel ratio becomes 1:0.833. This concludes that for the complete combustion of the system

\[ \{[\text{Bi (NO₃)₃}]_{1-x} + x\text{Al(NO₃)₃}\}:[\{\text{Fe(NO₃)₃}]_{1-x} + x\text{Al(NO₃)₃}\}\text{citric acid} = 1:1:1.666, \]

accordingly the calculated stoichiometric amount of citric acid will be 3.2007 g (taking 0.01 M). Assuming the complete combustion the process may be:

\[ 6\text{Fe (NO₃)₃} + 6\text{Bi (NO₃)₃} + 10\text{C₆H₈O₇} = 6\text{BiFeO₃} + 18\text{N₂} + 60\text{CO₂} + 40\text{H₂O} \]

\[ \{[\text{Bi (NO₃)₃}]_{1-x} + x\text{Al(NO₃)₃}\} + [\{\text{Fe (NO₃)₃}]_{1-x} + x\text{Al(NO₃)₃}\} + 10\text{C₆H₈O₇} = 6\text{Bi}_{1-x}\text{Al}_x\text{Fe}_{1-x}\text{O₃} + 18\text{N₂} + 60\text{CO₂} + 40\text{H₂O} \]

The solution was kept on a hot plate maintained initially at 50 °C for 30 min while stirring continuously with a nonmagnetic stirrer. Soon the water evaporates and a very viscous transparent honey like gel is formed. The as-prepared gel was immediately put inside a furnace preheated at 200 °C. The ignition starts and uniformly propagates through the gel. Huge amount of brown fumes evolve towards the end of the reaction. Whole process completes within 5 min resulting in a fluffy and foamy green mass. This porous mass was ground for 30 min and sintered at 300 °C for 3 hours at a heating rate of 5 °C min⁻¹. One gram quantity of each sample was mixed with 2% PVA and compressed in the form of circular pellets of 13 mm diameter. All pellets were again heated at 200 °C to evaporate the binding agent. The powders were examined for crystallinity, phase
identification and crystallite size determination by X-ray diffraction (Rigaku, Japan) using Cu-Kα radiations (\(\lambda = 0.15406\) nm) in 2θ range from 20° to 70° with scan rate of 2°/min and a step size of 0.02°. UV–vis absorbance was taken using Perkin Elmer spectrophotometer. FT–IR spectroscopy was performed on Perkin Elmer spectrometer using KBr as medium. d.c. resistivity was measured using Keithley’s standard two probe set up. The complex dielectric permittivities, ac conductivity measurements were performed as the function of, frequency (100Hz-6MHz) and temperature (273K-473K) and composition (x=0-0.3) using Agilent-4285A-LCR meter. To perform dielectric measurements, high quality silver paste was applied on the opposite faces of the pellet so as to make good electrical contacts and to configure it in the form of parallel plate capacitor.

3.3. Results and discussions

3.3.1. X–ray diffraction

Powder X-ray diffraction patterns of the synthesized powders, heated in the air at 300 °C for 3 hours are shown in the Fig. 3.1. X-ray patterns reveal the formation of highly crystalline, phase pure rhombohedrally distorted perovskite structure with space group R-3c (161). The powder patterns are in good agreement with the powder data of PCPDF card NO. 86-1518. The powders are phase pure up to \(x = 0.20\) after which a minute impurity phase evolves in the form of \(Bi_2Fe_4O_9\) at \(x = 0.25\) and 0.30. The particle sizes of different samples were calculated using Scherrer’s equation \(D = \frac{0.9\lambda}{\beta\cos\theta}\), where \(D\) is the average estimate of grain diameter, \(\lambda = 1.5406\) Å (characteristic Cu–Kα wavelength of Xrays) and \(\beta\) is the width of the diffraction peak at half of the maximum height for diffraction angle 2θ. The particle size as calculated for different samples ranges from 13.02 nm to 19.64 nm. The decrease in the grain size is also evident from the peak intensities which gradually become lower with the increase of dopant concentration. The lowering of peak intensities increases \(\beta\) and hence a decrease in the particle size. Fig. 3.2 illustrates the TEM images of the powdered samples at 50 nm scale which further
corroborate the results obtained by Scherrer's formulation. In some images particle size seems to be larger as compared to crystallite size which is due to the fact that a grain can be an agglomeration of a few crystallites. The lattice parameters \( a_{\text{hex}} \) and \( c_{\text{hex}} \) of the hexagonal unit cell were calculated using the equation

\[
\sin^2 \theta = \frac{\lambda^2}{3a^2} \left( h^2 + hk + k^2 \right) + \frac{\lambda^2 l^2}{4c^2}
\]

\[
.....3.1
\]

where \( \theta \) is Bragg's angle [18]. The strong peaks (012) and (110) were employed for such calculations. The lattice parameters \( a_{\text{hex}} \) and \( c_{\text{hex}} \), the cell size, the volume of the

![Figure 3.1: Powder X-ray spectra of pure and Al\(^{3+}\) doped BiFeO\(_3\) ceramics confirming the phase formation.](image)

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Figure 3.2(a-h): TEM images of powdered samples confirming a continuous reduction in particle size.
hexagonal unit cell $V$, and the ratio $c/a$ are listed in Tab. 3.1, which are in very good agreement with values reported for related compounds [19-23].

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a_{hex}$ (Å)</th>
<th>$c_{hex}$ (Å)</th>
<th>$c_{hex}/a_{hex}$</th>
<th>Cell Volume</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>5.595</td>
<td>13.862</td>
<td>2.477</td>
<td>373.54</td>
<td>19.64</td>
</tr>
<tr>
<td>0.025</td>
<td>5.581</td>
<td>13.860</td>
<td>2.483</td>
<td>372.62</td>
<td>17.53</td>
</tr>
<tr>
<td>0.050</td>
<td>5.547</td>
<td>13.859</td>
<td>2.498</td>
<td>371.88</td>
<td>16.72</td>
</tr>
<tr>
<td>0.100</td>
<td>5.529</td>
<td>13.851</td>
<td>2.505</td>
<td>370.73</td>
<td>15.57</td>
</tr>
<tr>
<td>0.150</td>
<td>5.518</td>
<td>13.846</td>
<td>2.509</td>
<td>370.02</td>
<td>15.01</td>
</tr>
<tr>
<td>0.200</td>
<td>5.512</td>
<td>13.843</td>
<td>2.511</td>
<td>369.51</td>
<td>14.43</td>
</tr>
<tr>
<td>0.250</td>
<td>5.507</td>
<td>13.838</td>
<td>2.512</td>
<td>369.02</td>
<td>13.65</td>
</tr>
<tr>
<td>0.300</td>
<td>5.502</td>
<td>13.830</td>
<td>2.513</td>
<td>368.57</td>
<td>13.02</td>
</tr>
</tbody>
</table>

Table 3.1: Variation of lattice parameters $a$ and $c$, $c/a$ ratio, cell volume of the unit cell and grain size with composition.

The lattice parameters $a$ and $c$, crystallite size, volume of the unit cell $V$, and the ratio $c/a$ are listed in Tab. 3.1, which are in good agreement with values reported in literature [24-26]. Further, it is evident from Tab. 3.1 that crystallite size, lattice parameter and cell volume decrease with the increase in Al$^{3+}$ concentration which may be attributed to the shortened ionic radius of Al$^{3+}$ (0.053 nm) compared to Fe$^{3+}$ (0.064 nm) and Bi$^{3+}$ (0.074 nm).

3.3.2. FT–IR

The (FT–IR) spectra of all the samples in the wavenumber range 400-1000 cm$^{-1}$ are shown in Fig. 3.3. The spectra in this range are indicative of the perovskite type vibrations. The
two strong absorption bands around 445 cm\(^{-1}\) and 552 cm\(^{-1}\) for all samples are due to O–Fe–O bending vibrations and Fe–O stretching of FeO\(_6\) groups in perovskite structure [27]. Other small peaks in the range 400-600 cm\(^{-1}\) give a clear signature of C–C and M–C–O bonding, thereby indicating the presence of very small amount of carbonaceous materials. The band at 650 cm\(^{-1}\) corresponds to the bending modes of vibrations of Al\(_2\)O\(_3\) and at 630 cm\(^{-1}\) corresponds to the bending modes of vibrations of the oxides of bismuth. Here, as it is evident from the spectra, there is a minor shift in the IR active modes of different samples which is mainly due to the presence of nano-sized grains. This can be attributed to the fact that in the case of nano size grains the arrangement of atoms at the grain boundaries are different from that of the bulk crystals. This leads to the disorders both in the coordination number and bond length and this degradation in crystal symmetry is responsible for the shifting in IR active modes [28]. The IR spectra are in a good agreement of other reports [29-31].

**Figure 3.3:** FTIR spectra of all the samples with different concentration of Al\(^{3+}\) ions.
3.3.3. UV-visible (Band gap calculation)

It is well known that the properties of optical absorption (UV–vis) by semiconductors are relevant to the electronic structure features and hence are the key factors in determining their band gaps [32]. The UV–Vis absorption spectra of all samples are shown in Fig. 3.4, which are in good agreement to the typical BFO UV–Vis absorbance spectra reported elsewhere [33, 34].

The optical energy band gap for different samples was calculated by classical Tauc relation [35] as given below:

\[ a h v = A (h v - E_g)^n \]

where \( A \) is a constant, \( h v \) is the photon energy, \( E_g \) is the energy band gap, \( a \) is absorption coefficient given by \( \alpha = 2.303 \frac{A_b}{t} \), where, \( A_b \) is absorbance and \( t \) is the thickness of cuvette which is 1 cm in the present case. The value of \( n = 1/2, 3/2, 2, \) or 3 depending on the nature of the electronic transition responsible for absorption. The value of \( n = 1/2 \) allows for direct transition, thereby giving direct band gap. The absorption spectrum shows that BFO and its \( \text{Al}^{3+} \) derivatives can absorb considerable amount of visible light making them potentially usable for photochemical reactions. The graphs of \((a h v)^2\) versus \( h v \) for all samples are shown in Fig. 3.5. Extrapolation of linear region of these plots to \((a h v)^2 = 0\) gives corresponding direct energy band gap. It is evident from graphs that the direct band gap for all samples increases with the increase of \( \text{Al}^{3+} \) concentration and varies from 2.78 eV to 2.93 eV. These band gaps are relatively higher as compared to their bulk counterparts, being 1.82 eV for BFO microspheres (20 \( \mu m \)), 2.12 eV for BFO.
Figure 3.4: UV–Vis absorbance of all the samples depicting strong UV absorption over a wide range.
Figure 3.5(0.0-0.3): Plots of $(ahv)^2$ versus $hv$ for all the eight samples.
microcubes (5 \( \mu \text{m} \)) and 2.27 eV for BFO submicrocubes (500 nm) [36], indicating that the band gap increases as the particle size approaches to nano regime. In some of the ternary semiconductors (like \( \text{InAs}_x \text{P}_{1-x} \)) it has been observed that band gap decreases with the increase in lattice parameters [37]. Therefore, increase of band gap in the present study with the Al\(^{3+} \) concentration can also be explained on the basis of the decrease in the lattice parameters which is due to smaller size of Al\(^{3+} \) (ionic radii = 0.053 nm) as compared to Fe (ionic radii = 0.064 nm) and Bi (ionic radii = 0.074 nm).

3.3.4. Electrical transport (d.c. resistivity)

Fig. 3.6 presents the plot of d.c. resistivity as a function of temperature for various samples. The general trend for all samples is almost the same.

![Figure 3.6: d.c. resistivities as a function of temperature for different compositions.](image)

The resistivity increases in the temperature range 275–325 K, reaching maximum at around 325 K, beyond which it gradually decreases at higher temperatures. All samples initially manifest metallic behaviour at low temperature and at higher temperatures, semiconducting behaviour is highlighted. Thus, there is a clear metal to insulator
transition which is a behavior typical to manganites and other perovskites. The metal to 
insulator transition temperature (T_{MI}) in the present case is equal to 325 K thereby 
enabling this material to be potentially useful in the field of low temperature sensing. 
Furthermore, the resistivity increases with the increase in Al^{3+} concentrations for whole 
range of temperature. This may be due to the interactions among various types of carrier 
species (electrons, holes, phonons) in the sample resulting in a strong scattering which in 
turn gives rise to elevated resistivity. The whole plot can be divided into two distinct 
regions, metallic region (below T_{MI}) and insulating region (above T_{MI}). In the metallic 
region, the resistivity can be explained on the basis of the model \( \rho(T) = \rho_0 + \beta T^2 + \gamma T^r \), where \( \rho_0 \) is residual resistivity at \( T = 0 \), \( \beta \) the electron–electron (e–e) scattering 
coefficient and \( \gamma \) the electron–phonon (e–p) or electron–magnon (e–m) scattering 
coefficient. The value of \( r \approx 5 \) and 4.5 for e–p and e–m scattering respectively. In the 
insulating region, temperature causes the excitation of electrons to the conduction band, 
hence the resistivity can be considered as a thermally activated process. There are various 
models which explain the resistivity of insulators in the form of thermally activated 
behavior. Jonker and van Santen [38] suggested the model:

\[
\rho(T) = A \exp\left(\frac{E_0}{K_B T}\right) \\
\ldots...\ldots 3.3
\]

Where, \( E_0, K_B \) and \( A \) are activation energy, Boltzmann’s constant and dependency of 
charge carriers on mobility respectively. A strong coupling between electrons and 
phonons (polarons) is also responsible for the transport mechanism in insulating region 
which is modelled as:

\[
\rho(T) = B T \exp\left(\frac{E_0}{K_B T}\right) \\
\ldots...\ldots 3.4
\]

where \( B \) is a measure of ideal conductivity at elevated temperatures [39]. The polaron 
mediated hopping can also be fitted in the model [40]:

\[
\rho(T) = \rho_0 T^\alpha \exp\left(\frac{E_0}{K_B T}\right) \\
\ldots...\ldots 3.5
\]

Some other reports suggest that the variable range hopping (VRH) model given by

\[
\rho(T) = \rho_0 \exp\left(\frac{E_0}{K_B T}\right)^{1/4} \\
\ldots...\ldots 3.6
\]
best describes the electronic transport in insulating region [41, 42]. Fig. 3.7 shows variation of resistivity with Al$^{3+}$ concentrations at different temperatures which makes it clear that at 325 K, the value of resistivity is highest for all concentrations. In the present study the $ln(\rho)$ has been plotted against $10^3/T$. The plots for all samples show linear trend (Fig. 3.8) which can be best fitted in equation (1) and more or less acceptable by other described models. The activation energies calculated from the slopes of $ln(\rho)$ vs $10^3/T$ plots range from 0.54 eV to 0.73 eV (Tab. 3.2) which suggest that the conduction in the insulating region is due to thermally assisted tunnelling of charge carriers through the grain boundary barrier and transition from donor level to conduction band [43].

<table>
<thead>
<tr>
<th>x</th>
<th>Band gap (eV)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>2.78</td>
<td>0.54</td>
</tr>
<tr>
<td>0.025</td>
<td>2.80</td>
<td>0.58</td>
</tr>
<tr>
<td>0.050</td>
<td>2.84</td>
<td>0.61</td>
</tr>
<tr>
<td>0.100</td>
<td>2.87</td>
<td>0.63</td>
</tr>
<tr>
<td>0.150</td>
<td>2.89</td>
<td>0.66</td>
</tr>
<tr>
<td>0.200</td>
<td>2.90</td>
<td>0.69</td>
</tr>
<tr>
<td>0.250</td>
<td>2.91</td>
<td>0.71</td>
</tr>
<tr>
<td>0.300</td>
<td>2.93</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 3.2: Variation of band gap and activation energy with composition.
Figure 3.7: Variation of resistivity with Al\(^{3+}\) concentration at different temperatures.

Figure 3.8: Variation of \(\ln(\rho)\) as a function of \(10^3/T\).
3.3.5. Dielectric relaxation behaviour

There are varieties of methods which can be potentially employed to give an elaborated insight about the dipolar dynamics of the solid systems. Among these techniques, the dielectric spectroscopy is the most useful tool to investigate the dipolar relaxation processes over a wide range of time and frequency domains. In a broad context, the scope of relaxation covers all types of stress relief in solids, like dielectric, photoconductive, chemical and mechanical to name a few. Among these effects the dielectric relaxation has been the most focused subject of interest due to its technological and industrial importance [44]. As the origin of dielectric behaviour is actually rooted in the charge separation in materials, the nature of the observed behaviour of different varieties of solids can be explained with the help of some very simple and common models. Generally, the dielectric response involves effects from ‘dipolar’ and ‘charge carrier’ behaviours. The former is responsible for the restoration of the zero residual polarization after discharging while the later is associated with partial recovery on discharge but always leaves a finite polarization in the system.
Figure 3.9(a-h): Variation of the log of real part of the complex dielectric response $\varepsilon'$ as a function of log (frequency).
Fig. 3.9(a-h) illustrates the variation of the real part $\varepsilon'$ of the complex dielectric response as the function of frequency (Range 100 Hz - 5 MHz), temperature (Range 273K-473K) and composition ($x = 0.000-0.300$). The dielectric spectra are in good agreement with those reported in literature [45, 46]. The variation of $\varepsilon'$ for different Al$^{3+}$ concentration is different but the trends for a particular dopant concentration are same at different values of frequency. The general and overall trend for all the samples is decreasing with frequency, which a behaviour typical of the ferrites and orthoferrite species [47, 48]. This can be attributed to the fact that $\varepsilon'$ and conductivity have the same root of origin via hopping between $\text{F}^{2+}$ and $\text{Fe}^{3+}$ ions. At low frequencies, the hopping plays in unison with the applied a.c. field, but at the elevated frequencies, the hopping ceases to follow the rapid fluctuations of the field and hence $\varepsilon'$ decreases due to random orientation and chaotic dipolar distribution. occurs at high frequency region. For $x = 0.10$, and $0.15$ the dispersion takes place in the low frequency region. For $x = 0.025$ and $0.20$ the dispersion is observed both in high as well as low frequency regions. The similar type of corresponding relaxation peaks are also observed in the loss tangent spectra shown in Fig. 3.13(a-h). For the sake of convenience, the variation of $\varepsilon'$ with temperature and the variation of imaginary part $\varepsilon''$ with frequency are also shown in Fig. 3.10(a-h) and Fig. 3.11(a-h) respectively.

The shifting of peaks with temperature is suggestive of the thermally activated mechanism of conduction through the defects created by oxygen non-stoichiometry [49, 50]. For the quantitative analysis of the relaxation behaviour, the data was fitted with the Cole-Cole model [51, 52] which is actually Debye model modified by Cole-Cole to make it applicable for non-ideal dielectric systems. The equation is as follows:

$$
\varepsilon' = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{[1 + (\omega \tau)^{1-a}]} 
$$

$$
.........3.7
$$

Where, $\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{[1 + (\omega \tau)^2]}$, $\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{[1 + (\omega \tau)^2]}$

are the real and imaginary parts of complex dielectric constant, $\varepsilon_s$ and $\varepsilon_\infty$ are the dielectric permittivities at frequencies lower and higher than the relaxation frequency, $\tau$ is the relaxation time and $\alpha$ is a measure of the relaxation time distribution.

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Figure 3.10 (a-h): Variation of $\varepsilon''$ with temperature.
Figure 3.11(a-h): Frequency dependency of imaginary part $\varepsilon''$ of dielectric response.
In terms of Cole-Cole formulation, \( \varepsilon' \) and \( \varepsilon'' \) can also be expressed in the following way:

\[
\varepsilon' = \varepsilon_\infty + \left( \frac{\Delta \varepsilon}{2} \right) \left[ 1 - \frac{\sinh(\beta z)}{\cosh(\beta z) + \cosh\left(\frac{\beta z}{2}\right)} \right]
\]

\[3.8\]

\[
\varepsilon'' = \frac{\left( \frac{\Delta \varepsilon}{2} \right) \sinh\left(\frac{\beta z}{2}\right)}{\cosh(\beta z) + \cosh\left(\frac{\beta z}{2}\right)}
\]

\[3.9\]

Where, \( z = \ln(\omega t) \), \( \Delta \varepsilon = \varepsilon_s - \varepsilon_\infty \), and \( \beta = 1 - \alpha \).

By fitting the experimental data with the above model, the values of \( \varepsilon_s, \varepsilon_\infty, \beta, \) and \( \tau \) can be calculated. The least square fitted values of the relaxation times for \( x = 0.00 \) and \( x = 0.30 \) as the function of inverse temperature are plotted in Fig. 3.12 which clearly obey Arrhenius relation

\[
\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)
\]

\[3.10\]

Where, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann’s constant, and \( T \) the absolute temperature.

![Figure 3.12](image)

**Figure 3.12**: Least square fitted values of the relaxation times for \( x = 0.00 \) and \( x = 0.30 \) as a function of inverse temperature revealing the Arrhenius behaviour in charge activation.
3.3.6. Dielectric loss tangent

The variation of loss tangent (\(\tan\delta\)) as the function of frequency and temperature for different dopant concentration is shown in Fig. 3.13(a-h). As it is evident from the figure, the \(\tan\delta\) increases with temperature and has a decreasing trend at elevated frequencies. This can be attributed due to the fact that the dielectric relaxation is a thermally activated process in the material under study. The relaxation peaks observed in the loss tangent spectra can be modelled on the basis of Debye equation for loss tangent given by

\[
\tan\delta = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau_{\tan\delta}}{\varepsilon_s + \varepsilon_\infty(\omega\tau_{\tan\delta})^2}
\]

Where, \(\varepsilon_s\) and \(\varepsilon_\infty\) are static (d.c.) and high frequency a.c. permittivities respectively, \(\tau_{\tan\delta}\) is the relaxation time for loss tangent and \(\omega\) is the angular frequency of applied field.

3.3.7. a.c. conductivity

BFO and its doped species are always plagued by impure phases and thus the anomalies and abnormal behaviour related to the phase defects and grain boundary accumulation is inevitable. Adding external ingredients to the system usually creates oxygen vacancies in the lattice, which lead to fluctuation of valence states of the various metal ions and affecting the overall conductivity of the samples. Conductivity can be described as a sum of the frequency-independent part \(\sigma_0\) and frequency-dependent part \(A.\omega^s\)

\[
\sigma(\omega, T) = \sigma_0 + A(T).\omega^s(T)
\]

Where, \(A\) is pre-exponential factor and \(s\) is the fractional exponent whose value lies between 0-1. In fact, in the case of doped ferrites and ortho-ferrites, the value of \(s\) lies between 0.90 to 0.50 which indicates a hopping process limited by diffusion [53].
Figure 3.13(a-h): Variation of loss tangent ($\tan \delta$) as a function of frequency and temperature for different dopant concentration.
Figure 3.14(a-h): Variation of a.c. conductivity with temperature following the well-defined Arrhenius law.
The variation of a.c. conductivity with temperature is shown in Fig. 3.14(a-h). The a.c. conductivity dependence on temperature obeys well-defined Arrhenius law given by

\[
\sigma_{ac} = \sigma_{\infty}\exp\left(-\frac{E_a}{kT}\right)
\]

Where \( E_a \) is the activation energy of the conductance mechanism and \( \sigma_{\infty} \) is conductivity at infinitely high temperature. Another formalism, such as electric modulus [54], have been employed to study the ion dynamics in solids under a.c. electric field. However, there is a debate on which of these formalisms provides better insights into the phenomena of ion dynamics [55]. The overall behaviour of a.c. conduction is consistent with the universal dynamic response which is a widely observed phenomenon in materials having defects and oxygen non-stoichiometry [56, 57]. Apart from that, the conduction mechanism in BFO ceramics is generally controlled by the presence of charge defects in the form of Bi and O vacancies. The incorporation of foreign impurity (dopant) may suppress or highlight this effect depending upon the nature and concentration of dopant. The effects may be summarized by a set of reactions given below:

\[
\begin{align*}
2Fe^{+3} + O^{-2} &\rightarrow 2Fe^{+2} + V_0^{+2} + \frac{1}{2}O_2 \\
2Bi_2^{+3} + 3O^{-2} &\rightarrow 2V_{Bi}^{-3} + 3V_0^{+2} + Bi_2O_3 \\
2Fe^{+3} + V_0^{+2} + \frac{1}{2}O_2 &\rightarrow 2Fe^{+4} + O^{-2}
\end{align*}
\]

Another factor controlling the electrical properties may be quantum confinement effect [58] which can be defined as the observed change in electronic and optical properties when the particle size is reduced to the order of a few nano-meters (called the excitons Bohr radius). In this case, the charge carrier species and other entities responsible for the transport in the material are confined within a narrow range. In other words, their mobility is arrested. As evident from the above discussion, the particle size gradually decreases with the \( Al^{3+} \) concentration which due to smaller ionic radius of \( Al^{3+} \) (0.053 nm) ion as compared to \( Bi^{2+} \) (0.074 nm) and \( Fe^{3+} \) (0.064 nm), and so more pronounced quantum confinement effect begins to play according to the equation given below:
\[ E_g = E_g^0(R) + \frac{h^2 \pi^2}{2\mu R^2} - \frac{1.786 e^2}{\varepsilon R} - \frac{0.124 e^4 \mu}{h^2 \varepsilon^2} \]

Where, \( \varepsilon \) is the dielectric constant, \( R \) is the particle radius and \( h \) is the Planck constant and \( \mu = (1/m_e^*+1/m_h^*)^{-1} \), \( m_e^* \) and \( m_h^* \) are the effective masses of electron and hole, respectively. Thus the energy required to transport electrical and dielectric effects in the material increases with the reduction of particle size and hence making these effects harder to be highlighted.

The a.c. conductivity of ferrites and ortho-ferrites is usually calculated by the equation \( \sigma_{ac} = \varepsilon \varepsilon_0 \omega \tan \delta \) which can justify the frequency dependence of the a.c. conductivity shown in Fig. 3.15 (a-h). It is evident from the figure that in the low frequency region, there is mild dispersion while in the high frequency region, a vigorous dispersion is observed. These results are consistent with equation \( \sigma(\omega, T) = \sigma_0 + A(T) \omega^{s(T)} \).

The variation of \( \sigma_{ac} \) with frequency can also be attributed to the internal morphology of the material in the form of grain and grains boundaries. At low frequencies grain boundaries are active offering high resistant path while at higher frequencies, the grains come into the picture offering an easy path to the transporting agents in the system.

The decrease of conductivity with composition is also under the influence of porosity. The material becomes more porous with the Al\(^{3+} \) concentration. Pores being non-conductive offer obstacles in the path of charge carriers. Variation of a.c. conductivity with Aluminum concentration is shown in Fig. 3.16 (a-e).
Figure 3.15(a-h): Frequency dependence of the a.c. conductivity revealing mild dispersion in low frequency region and a vigorous dispersion in the high frequency region.
Figure 3.16(a-e): Variation of a.c. conductivity with Al\textsuperscript{3+} concentration at different temperatures.
3.3.8. Magnetic behaviour

In BFO unit cell each Fe$^{3+}$ magnetic moment is coordinated by six Fe$^{3+}$ nearest neighbours having antiparallel moments. Weak ferromagnetism has been reported by magnetic measurements but has not been definitely established [59]. The room temperature magnetization versus magnetic field plots are shown in Fig. 3.17(a-e). initially, the material exhibits ferromagnetic behaviour which ultimately switched to antiferromagnetic nature at higher doping which is obvious by the linear dependency of the magnetization on magnetic field. Strong saturation at the applied field of 10 KOe is observed for undoped sample which ceases to saturate at this field for higher doping and ultimately becomes linear with the applied field at extreme doping. The observed weak ferromagnetic hysteresis loop in undoped and mildly doped samples are mainly due to spin canting and nominally due to magnetic interaction between Fe$^{3+}$ and Fe$^{2+}$ ions. Apart from that, it can also be observed from the plots that the coercive force becomes narrower and remanence magnetization tends to vanish with increase in doping thereby confirming the superparamagnetic nature of the particles. As it is evident from Fig. 3.18(a-b) that for undoped sample the magnetization is higher but it is drastically low for doped samples. This can be accounted mainly by three reasons; one is the replacement of highly magnetic Fe$^{3+}$ ions by non-magnetic Al$^{3+}$ ions, second is the reduced hoping between Fe$^{3+}$ and Fe$^{2+}$[60] and thirdly the incorporation of Al$^{3+}$ ions in BFO lattice improves the cycloidal spin structure which in turn suppresses the latent magnetization which hinders the observation of magnetization. The reduced magnetization with doping can also be a size effect because there may be suppression of spin spiral ordering in confined nano-sized BFO system.
Figure 3.17(a-h): Room temperature M-H plots for various dopant concentration showing the origin of superparamagnetism.
Figure 3.18(a-b): Variation of M with dopant concentration and grain size.

3.4. Conclusions

We have investigated the structural, optical, dielectric, electrical and magnetic properties of nano-structured BFO ceramics heavily doped with Al$^{3+}$ ions on both the Fe as well as Bi sites having composition Bi$_{1-x}$Al$_{2x}$Fe$_{1-x}$O$_3$ (x = 0.00, 0.025, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) synthesized by combustion method. The major findings of the present investigation can be briefed as follows:

i. The X-ray patterns suggest that Al$^{3+}$ ions have been successfully doped in the BiFeO$_3$ matrix and crystallite size varying from 13nm to 19.6 nm.

ii. FT–IR measurements confirm perovskite nature of the samples.

iii. All samples exhibit metal insulator transition at temperature ($T_M$) 325 K.

iv. The resistivity increases with Al$^{3+}$ concentration and follows the Arrhenius behavior.

v. Activation energy was found to increase from 0.54 eV to 0.73 eV with doping.

vi. Optical band gap was observed to vary from 2.78 eV to 2.93 eV on increasing the dopant concentration from 0.00 to 0.30, which is higher as compared to bulk BFO (1.82 eV). Higher values of band gaps for these ceramics are quite compatible with their high resistivity.

vii. It is observed that Al$^{3+}$ concentration influences the structural and dielectric properties of the material.
viii. The frequency and temperature dependence of dielectric spectra shows dispersion and relaxation which has been justified on the basis of Debye-relaxation model and Maxwell-Wagner type charge carrier hopping.

ix. Relaxation time was evaluated from the fitted Cole-Cole model.

x. The a.c. conductivity has been accounted on the basis of charge imbalance caused by the oxygen non-stoichiometry and lattice defects (pores) created by the foreign impurity atoms (dopant).

xi. The plots of relaxation time and the a.c. conductivity as the function of inverse absolute temperature follow the famous Arrhenius expression.

xii. Magnetic data shows that the material exhibits ferromagnetic behaviour which eventually switched to antiferromagnetic nature at higher dopings.

xiii. Strong saturation at the applied field of 10 KOe is observed for undoped sample which ceases to saturate at this field for higher doping and ultimately becomes linear with the applied field at extreme doping.

xiv. Coercive force and remanent magnetization become extinct at higher doping thereby confirming the superparamagnetic nature of particles.
References


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CHAPTER 4

STRUCTURAL, MAGNETIC AND COMPLEX IMPEDANCE PROPERTIES OF Cr$^{3+}$-Al$^{3+}$ CO-DOPED NANO-STRUCTURED MAGNESIUM FERRITE AND ITS GAS SENSING APPLICATIONS
4.1. Introduction

Partially inverse spinel of magnesium ferrite (MgFe$_2$O$_4$) and its doped derivatives have attracted considerable attention due to their wide range of technological applications such as heterogeneous catalyst [1, 2], gas and humidity sensors [3-5], photochemical applications and for creating local hyperthermia (in which tumors are locally heated by the application of alternating magnetic fields) in cancer treatment [6]. Nano-structured MgFe$_2$O$_4$ has shown great importance in modern technological applications. In fact, this material is becoming promising due to its potential use in diverse fields like pharmaceutical products, magnetic drug payload carriers, ferrofluids, as a contrasting agents in magnetic resonance imaging and cancer cell highlighting [7], high-density information storage materials, and magnetocaloric refrigeration. In MgFe$_2$O$_4$, the Mg$^{2+}$ ions are diamagnetic due to which the magnetic coupling between A and B sites is relatively weaker and it mainly originates from the strongly magnetic Fe$^{3+}$ ions.

The incorporation of foreign ions in MgFe$_2$O$_4$ lattice alters the degree of inversion which eventually affects its magnetic, electrical and sensing behaviour. There has been growing focus on designing/fabrication and manufacture of humidity and gas sensing devices since last two decades. There is a surge of reports covering humidity sensors using a variety of materials such as electrolytes, organic polymers and metal oxides. Among them, metal oxides (ceramics) have proved to be the most promising and most studied materials because of the resistive change when exposed to various gases. Oxide sensing materials can be categorized into two types, i.e., ionic and electronic. Ionic type materials utilize some sort of ions for conductivity like H$^+$ conductivity in a humid environment due to capillary condensation of water vapour. The second type exploits the mobility of electrons generated as the product of interaction of gas with the sensing material. In the resistive-type humidity sensors, the electrical response of MgFe$_2$O$_4$ ceramic sensor has been discussed in various reports [8, 9]. The gas-sensitive properties of spinel ceramics were also investigated [10]; for example, MgFe$_2$O$_4$, ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ were studied for oxygen sensing properties [11]. A different type of ceramic sensor based on kaolin and sodium salt of carboxymethyl cellulose in deionized water
has also been investigated, confirming the correlation between pore size volume and conductivity of the sample [12]. The sensing mechanism of these materials is based on the property of changing the conductivity (resistivity) in the presence of a determinate gas [13]. As an effect of an oxidizing reaction of the reducing gas with oxygen from the sensor surface, the formation of the oxygen electrons enhances the conductance of the sensing material. Transition metal oxides appear to be the best candidate for reducing gas sensors [14]. There are many reports on the sensing response of spinel type oxide semiconductors towards both reducing as well as oxidizing gases [15-17]. But a very few reports are there on the LPG sensing properties of MgFe$_2$O$_4$ [18, 19].

In the present study, we have investigated the doped MgFe$_2$O$_4$ for electrical and magnetic properties and have shown its potential as sensing element for two reducing gases, water and liquefied petroleum gas (LPG). What makes this material technologically important is the presence of defects and pores which qualifies it as a gas sensor. A porous and defects-rich structure favours the gas molecules to enter easier into the material and so the resistance modulation by gas adsorption in the material will be larger. Another advantage is high resistivity which can decrease very much when the working temperature is elevated. We attempted to improve the gas sensitivity of MgFe$_2$O$_4$ ferrite by using substitutions and by changing the preparation method. The influence of two ions (Cr$^{3+}$, Al$^{3+}$) which partially substitute Mg and/or Fe in MgFe$_2$O$_4$ ferrite on the microstructure, electronic transport properties and sensitivity to water and LPG was studied. As the MgFe$_2$O$_4$ is an n-type semiconductor (band gap 2.18 eV) [20], the resistance in a reducing gas atmosphere, $R_g$, becomes smaller than the resistance in air, $R_a$.

### 4.2. Experimental

In a typical synthesis procedure, stoichiometric amounts of Mg(NO$_3$)$_2$.5H$_2$O (99.00%, S. D. Fine Chemicals Ltd. Mumbai), Fe(NO$_3$)$_3$.9H$_2$O (98.00%, S. D. Fine Chemicals Ltd. Mumbai), Al(NO$_3$)$_3$.9H$_2$O and Cr(NO$_3$)$_3$.9H$_2$O (95%, both from Merck) were dissolved in minimum amount of doubly distilled water. All chemicals were used
without further purification. The stoichiometric amount of Urea \((\text{NH}_2\text{COH}_2\text{N})\) necessary for the complete combustion of the Nitrates–Fuel system was calculated according to propellant chemistry expression

\[
\psi = \frac{\text{total oxidising valence of oxidising agents (nitrates)}}{\text{total reducing valence of reducing agents (fuel)}} \quad \ldots \ldots 4.1
\]

For Urea, the total reducing valence is \(F = +6\). For a divalent nitrate the oxidizing valence is \(O_d = 10\) and for a trivalent nitrate the oxidizing valence is \(O_t = 15\). Thus in the case complete combustion \(\frac{O_d}{F} = \frac{10}{6}\) and \(\frac{O_t}{F} = \frac{15}{6}\). This concludes that for the complete combustion of the system, (Divalent Nitrate) : (Trivalent Nitrate) : Urea = 1: 2: \(\frac{20}{3}\), accordingly the calculated stoichiometric amount of urea will be 4.00 g (considering 0.01 M for each Nitrate). Assuming the complete combustion, the process can be precisely written as:

\[
3\text{Mg(NO}_3)_2 + 6\text{Fe(NO}_3)_3 + 20\text{NH}_2\text{COH}_2\text{N} = 3\text{MgFe}_2\text{O}_4 + 32\text{N}_2 \uparrow + 20\text{CO}_2 \uparrow + 40\text{H}_2\text{O}
\]

\[
3\text{Mg(NO}_3)_2 + 3(2-x)\text{Fe(NO}_3)_3 + 1.5x \text{Al(NO}_3)_3 + 1.5x \text{Cr(NO}_3)_3 + 20\text{NH}_2\text{COH}_2\text{N} = 3\text{Mg(Cr}_{0.5-x}\text{Al}_{1.5-x}\text{)}\_2\text{Fe}_{2-x}\text{O}_4 + 32\text{N}_2 \uparrow + 20\text{CO}_2 \uparrow + 40\text{H}_2\text{O}
\]

The solution was kept on a hot plate maintained initially at 50 – 60 °C for 20 minutes while stirring continuously with a nonmagnetic stirrer. Soon the water evaporates and a very viscous transparent honey like gel is formed. The as prepared gel was immediately put inside a furnace preheated at 250 °C. The gel reaches at ignition point and a violent reaction starts which uniformly propagates through the gel. Huge amount of brown fumes evolve towards the end of the reaction. The whole process completes within a few minutes resulting in a fluffy and porous mass. This foamy mass was grind for 30 minutes and sintered at 500 °C for 3 hours at heating rate of 5 °C/min. The powders were examined for crystallinity, Phase identification and particle size determination by Xray diffraction (XRD from Rigaku Miniflex Japan) using Cu–K\(\alpha\) radiation (\(\lambda=0.15406 \text{ nm}\)) in 20 range from 20° to 70° with scan rate of 2 °/min and a step size of 0.02°. FT–IR spectroscopy was done by Perkin Elmer spectrometer using KBr as medium. The gas
sensor films of the powders were formed on very thin slide of alumina ceramic. At first Silver electrodes were painted onto the alumina substrate to facilitate the sensing of electrical signals. The very fine powdered samples were mixed with a 2% PVA solution to form thin slurry. PVA in this case serves the dual purpose of a binding agent and a pore forming material. A few drops of this slurry were applied on the electrode painted alumina substrate. The later was rotated in a spin coater at 2500 rpm to generate a very uniform thin film of the sensing material. The average thickness of each film as measured by artificially created step by mounting a strip of cello tape on one extreme of the alumina substrate is of the order of 120 nm [21]. The so prepared film was kept for annealing at 250 °C to evaporate the PVA and water content in the sensing element. Surface morphology of the sensing film was investigated by AFM. The schematic and actual gas sensing elements are shown in Fig. 4.1.

![Schematic diagram and actual image of sensing element.](image)

**Figure 4.1:** Schematic diagram and actual image of sensing element.

Microstructure and surface morphology of the sensing film was investigated by the images recorded on a Veeco Innova Scanning Probe Microscope. The surface morphology as revealed by these micrographs for \( x = 0.00, 0.15, 0.30 \) along with their respective zoomed portions is illustrated in Fig. 4.2.
Figure 4.2: Films morphologies along with zoomed portions as revealed by AFM imaging.
The surface morphology in terms of roughness and particle distribution of the sensing surface was quantified by means of 3D reconstruction of the surfaces using a dedicated AFM-Image processing program. Further, the particle size was estimated by creating line-profiles over two directions (Horizontal, Slant) for each image. The 3D reconstructions and line-profiles are shown in Fig. 4.3. The average particle size as evaluated by the program by means of statistical analysis over line-profiles, is in the range of 10±0.5nm – 18±0.5nm which are approximately in agreement with those calculated by Scherrer’s formula.

![Figure 4.3: 3D reconstructions of film surface showing the surface roughness and grain distribution along with the line profiles along the lines drawn in two different directions on image plane to get an estimation of grain size.](image)

The powdered samples were investigated by Field-emission scanning electron microscopy (FE-SEM), LEO Supra 50 Vp, field-emission SEM, Carl-Zeiss SMT, Oberkochen, Germany. Prior to FE-SEM, the samples were coated with gold by an ion sputter coater (Polaron SC515, Fisons Instruments, UK). Grain size as analyzed by SEM (Fig. 4.4) imaging further strengthens the results obtained from AFM and Scherrer formulation.
Figure 4.4: Scanning electron micrographs of powdered samples: (a) for $x = 0.00$, (b) for $x = 0.15$, (c) for $x = 0.30$.

The gas sensing studies were carried out on these sensing elements in a static gas chamber to sense humidity/LPG in ambient air. The sensing element was kept directly on
a heater in the gas chamber and the temperature was varied from 50 to 450 °C. The temperature of the sensing element was monitored by K-type thermocouple placed in contact with the sensing element. The known volume of the gas (water vapour/LPG) was introduced into the gas chamber pre-filled with Nitrogen (dry air) and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured before and after exposure to LPG using a sensitive digital multimeter (2000, Digital Multimeter, Keithley, U.S.A) interfaced by a PC. The schematic diagram for the humidity sensing setup is shown in Fig. 4.5. Water vapours are generated by heating water inside the chamber. To regulate humidity level, a clamped box filled with CaCl₂ has been provided. The block schematic diagram of the sophisticated LPG sensing setup is illustrated in Fig. 4.6. A known and regulated ratio of LPG and dry air is injected inside the steel gas chamber where it interacts with preheated sensing element. The sensitivity ($S$) was calculated with the following relation [22] owing to the fact that MgFe$_2$O$_4$

![Figure 4.5: Schematic diagram of humidity sensing setup.](image-url)
is a n-type semiconductor whose resistance drops in a reducing gas environment, as compared to its resistance in air.

\[ S = \frac{AR}{R_a} \times 100 = \frac{|R_a - R_g|}{R_a} \times 100 \quad \ldots \ldots 4.2 \]

Where, \( R_a \) and \( R_g \) are the electrical resistance values of the sensor element in air and in the presence of gas, respectively.

Porosity of the samples calculated by using the conventional relation

\[ p = (1 - \frac{d}{d_{hkl}}) \quad \ldots \ldots 4.3 \]

Where, \( d_{hkl} = \frac{8M}{Na^3} \) (X-ray density) and \( d = \frac{m}{V} = \frac{Na^3m}{\pi r^2 h} \) (Experimental density),

\( M \) is molecular weight of the sample, \( N \) the Avogadro's number, \( a \) the lattice parameter and 8 represents the number of molecules per unit cell, while \( m, V, r \) and \( h \) represent the mass, volume, radius and the thickness of the samples, respectively. The complex dielectric permittivities and a.c. conductivity measurements were performed as a function
of frequency (100Hz-6MHz), temperature (273K-473K) and composition (x=0.0-0.3) using Agilent LCR meter (4285A). To perform dielectric measurements, one gram quantity of each sample was thoroughly mixed with 0.8% of PVA solution and then was compressed in the form of pellets of 13 mm diameter by applying a pressure of 4 tons. All pellets were again heated at 400 °C to evaporate the binding agent. High quality silver paste was applied on the opposite faces of the pellet so as to make good electrical contacts and to configure it in the form of parallel plate capacitor. The value of dielectric constant ($\varepsilon$) was calculated using the relation:

$$\varepsilon = \frac{C_pd}{\varepsilon_0 A} \quad \ldots 4.4$$

where, $C_p$ is capacitance of the pellet, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, is permittivity of free space, $d$ is the thickness of pellet between the silver contacts, $A$ is the area of cross section of the pellet. The real and imaginary parts of the complex dielectric permittivity were calculated using the relation:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad \varepsilon'' = \varepsilon' \tan\delta \quad \ldots 4.5$$

where, $\tan\delta$ is the dielectric loss given by

$$\tan\delta = \frac{1}{(2\pi f \varepsilon_0 \varepsilon \rho)} \quad \ldots 4.6$$

4.3. Results and discussions

4.3.1. Structural properties and cation distribution (XRD and FT-IR)

Fig. 4.7 illustrates the Powder Xray diffraction patterns of the synthesized powders, sintered in air at 500 °C for 3 hours which confirm the formation of nearly single phase distorted cubic spinel face-centred lattice belonging to space group Fd3m (227). The peaks were indexed using powder X software and they are well matched with the cubic spinel structure. The powder patterns are in good agreement with the standard
ICDD card NO. 73-2410. Scherrer's equation \( D = \frac{8.91}{\beta \cos \theta} \), was used to get an estimate about the average grain size of the samples, where \( D \) is the average crystallite diameter, \( \lambda = 1.5406 \text{ Å} \) (characteristic Cu-Kα wavelength of X-rays) and \( \beta \) is the width of the diffraction peak at half of the maximum height (FWHM) for diffraction angle \( 2\theta \). The crystallite size calculated for different samples varies from 9.0 nm to 17.0 nm.

![Figure 4.7: Powder X-ray diffraction patterns of the pure and doped material confirming the formation of crystalline spinel phase.](image)

It is evident from XRD spectra that peak intensity decreases while FWHM increases with the increase in dopant concentration, which in turn decreases the crystallite size. The lattice constant \( a = 8.374 \text{ Å} \) for the cubic spinel structure was calculated with an accuracy of 0.0001 nm using least squares fitting. For this purpose the powder diffraction data of the material as obtained in the form of ASCII data was processed in PowderX computer program. The indexing was done on a number of prominent peaks by which a data file containing angular variations plane spacing was created. This data was later
exported to *Microcal OriginLab* computer program to generate least square fitted lattice parameters. The lattice parameter, the crystallite size and hence the grain size decrease with the increase in dopant concentration which can be justified on the basis of the replacement of larger Fe\(^{3+}\) (ionic radii \(\approx 0.064\) nm) by relatively smaller Al\(^{3+}\) (ionic radii \(\approx 0.053\) nm) and Cr\(^{3+}\) (ionic radii \(\approx 0.052\) nm). The variation of lattice constant 'a', % porosity, and density with dopant concentration is shown in Fig. 4.8.

![Graphs](image)

**Figure 4.8:** (a) Decrease in lattice parameters with increase in dopant concentration (b) variation of X-ray and bulk density with increase in dopant concentration, and (c) porosity enhancement with increase in dopant concentration.

It is interesting to note that porosity increases while the particle size decrease. In general, the smaller particle size leads to compaction of the material and hence results in an increase in density (reducing porosity). But in the case of nanoparticles it can be explained on the basis of the fact that behaviour of nanoparticle is independent of the forces of gravity. The increase of pore size with the decrease of particle size is explained in Fig. 4.9. The lattice constant gradually decreases with increasing the dopant concentration, which is in agreement with Vegard's law [23].
Figure 4.9: Artistic illustration of pore expansion with reduced grain size

The initial inference for cation distribution in the system was deduced from the observed X-ray intensity ratios. The final cation distributions deduced by simultaneously considering the Bragg plane ratios and the fitting of the magnetization data at room temperature. In order to determine the cation distributions, X-ray intensity calculations were made using the formula suggested by Buerger [24]. The intensity ratios of the planes considered to be sensitive to the cation distribution parameter $(x)$ were taken to estimate the cation distributions. The distribution is also in accordance with Gorter's report [25]. For low dopant concentration like the one in the study the cations distribute normally. For higher concentration of dopant, $\text{Al}^{3+}$ ions (apart form A site) also occupy B site.

It has been well established that the intensities of the $(220)$ and $(422)$ planes are more sensitive to the cation distribution on tetrahedral sites, while the intensity of $(222)$ planes is very sensitive to the cations on octahedral sites [26]. In order to determine the distribution of cations over the available tetrahedral (A) and octahedral (B) sites in the given nano-structured ceramic system, intensities were calculated using the formula suggested by Buerger [27] as:

$$I_{hkl} = |F_{hkl}|^2 P L_p$$  \[4.7\]

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Where, \( I_{hkl} \) is the relative integrated intensity; \( F_{hkl} = \sum_i f_i e^{2\pi i(hu_n + kv_n + lw_n)} \) the structure factor; \( \rho \) the multiplicity factor; \( I_p = \frac{1 + \cos \theta}{\sin^2 \cos \theta} \) is the Lorentz polarization factor; where \( \theta \) is the Bragg's angle. The intensity ratios of planes \( I_{(220)}/I_{(400)} \), \( I_{(400)}/I_{(440)} \) and \( I_{(422)}/I_{(400)} \) are considered to be sensitive to the cation distribution [28]. The distribution of \( \text{Mg}^{2+}, \text{Fe}^{3+}, \text{Cr}^{3+} \) and \( \text{Al}^{3+} \) cations amongst the octahedral and tetrahedral sites in the \( \text{Mg(Cr}_{0.5}\text{Al}_{0.5})_{2}\text{Fe}_{2}\text{O}_{4} \) was determined from the X-ray intensity ratio calculations. Calculations of intensity for the planes were made for various possible values of the distribution parameter. The value of the distribution parameter was determined by comparing theoretical and experimental intensity ratio of the planes under consideration. Since the relative intensity is \( I \), the multiplicity factor \( \rho \) and Bragg angle are known for each line on the diffraction pattern, therefore we can find the value of \( |F_{hkl}| \) for each reflection. The atom positions can be determined only by the trial and hit method. A set of atom positions is assumed; the intensities corresponding to these positions are calculated and compared with that of observed ones. This process is repeated until a satisfactory agreement is reached.

The cation distribution at A as well as B sites as determined by fitting the room temperature magnetization data and taking into account the Bragg's plane intensity ratios may be presented as given below (Tab. 4.1):

FT–IR spectra in the wavenumber range 2250–250 cm\(^{-1}\) for samples with different dopant concentration are shown in Fig. 4.10. The strong absorption band around 504 cm\(^{-1}\) for all samples correspond to the O–Fe–O stretching vibration mode at tetrahedral site [29-31]. The band around 1627 cm\(^{-1}\) is due to O–H stretching vibration interacting through Hydrogen bonds. The IR dip around 1384 cm\(^{-1}\) can be attributed to the presence of trapped nitrates incorporated from the preparing process. Other small peaks in the range 400-600 cm\(^{-1}\) are due to C–C and M–C–O stretching vibrations, thereby indicating the presence of traces of residual carbonaceous materials formed during the combustion of
<table>
<thead>
<tr>
<th>x</th>
<th>Cation Distribution Scheme</th>
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<tbody>
<tr>
<td>0.00</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{ Fe}^{3+}</em>{0.88})^A \cdot \text{[Mg}^{2+}<em>{0.98} \text{Fe}^{3+}</em>{1.16}]^B \text{O}_4^-)</td>
</tr>
<tr>
<td>0.10</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{Al}^{3+}</em>{0.05} \text{Fe}^{3+}<em>{0.79})^A \cdot \text{[Mg}^{2+}</em>{0.88} \text{Cr}^{3+}<em>{0.05} \text{Fe}^{3+}</em>{1.11}]^B \text{O}_4^-)</td>
</tr>
<tr>
<td>0.15</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{Al}^{3+}</em>{0.075} \text{Fe}^{3+}<em>{0.725})^A \cdot \text{[Mg}^{2+}</em>{0.88} \text{Cr}^{3+}<em>{0.075} \text{Fe}^{3+}</em>{1.085}]^B \text{O}_4^-)</td>
</tr>
<tr>
<td>0.20</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{Al}^{3+}</em>{0.10} \text{Fe}^{3+}<em>{0.74})^A \cdot \text{[Mg}^{2+}</em>{0.88} \text{Cr}^{3+}<em>{0.10} \text{Fe}^{3+}</em>{1.06}]^B \text{O}_4^-)</td>
</tr>
<tr>
<td>0.25</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{Al}^{3+}</em>{0.125} \text{Fe}^{3+}<em>{0.715})^A \cdot \text{[Mg}^{2+}</em>{0.88} \text{Cr}^{3+}<em>{0.125} \text{Fe}^{3+}</em>{1.035}]^B \text{O}_4^-)</td>
</tr>
<tr>
<td>0.30</td>
<td>((\text{Mg}^{2+}<em>{0.12} \text{Al}^{3+}</em>{0.15} \text{Fe}^{3+}<em>{0.69})^A \cdot \text{[Mg}^{2+}</em>{0.88} \text{Cr}^{3+}<em>{0.15} \text{Fe}^{3+}</em>{1.01}]^B \text{O}_4^-)</td>
</tr>
</tbody>
</table>

Table 4.1: Cation distribution scheme for various dopant concentrations as calculated from the magnetic data and Bragg's plane intensity ratios from XRD.

![Figure 4.10: FT-IR spectra of all samples showing various bonding orders present in the material.](image)

Figure 4.10: FT-IR spectra of all samples showing various bonding orders present in the material.
fuel and oxidizer system. As it is evident from the spectra, there is a minor shift in the IR active modes of different samples which is mainly due to the presence of nano-sized grains. This can be attributed to the fact that in the case of nano size grains the arrangement of atoms at the grain boundaries are different from that of the bulk crystals. This leads to disorders both in the coordination number and bond length and this degradation in crystal symmetry is responsible for the shifting in IR active modes [32].

The crystal structure of partially inverted magnesium ferrite may be visualized in the form of a quasi distorted cubic close-packed array of oxygen atoms with metal ions embedded within at specified interstitial locations commonly known as tetra (A) and octahedral (A) sites. It is possible for the divalent ions on A sites to exchange places with trivalent ions on B sites while maintaining the symmetry at the same time. This leads to a state of inversion within the system. Actually, it has been well established by Neel that there exists a strong negative exchange coupling between the atoms on A sites and the atoms on B sites. This results in a spin alignment in which the A moments are all oriented antiparallel to the B moments. In the case of an inverted ferrite the iron moments on A sites just cancel those on B sites, leaving the crystal with a net moment equal to that of the divalent ion. Initially, the magnesium ferrite was reported as completely inverted [33]. But in that case its magnetization must vanish which was contradicted by the observed value in the range 1–2.4 Bohr magnetons [34, 35]. The discrepancy can be resolved if we assume magnesium ferrite a partially inverse spinel.

4.3.2. Composition dependent complex electrical analysis

The electrical behaviour of all the sample compounds were studied over a wide range of frequency employing the a.c. techniques. These techniques enable us to separate the real and imaginary components of the electrical parameters, and hence provides a clear insight to the material properties. Impedance data of materials that have capacitive and resistive components, when plotted in a complex plane, appear in the form of a succession of semicircles representing contribution due to bulk grain, grain boundary and many other interfacial phenomena.
4.3.2.1. Complex dielectric constant

Fig. 4.11 and Fig. 4.12 illustrate the real and imaginary parts of dielectric constant respectively as a function of frequency and composition measured at room temperature. As it is evident from the plots, both $\varepsilon'$ and $\varepsilon''$ have higher values at low frequencies and gradually decrease in the high frequency region. Finally, at much higher frequencies the dielectric constant becomes almost independent of the frequency. Apart from that, the value of dielectric constant is lower at higher dopant concentration or in other words the value of dielectric constant has a lower value for smaller particle size. Similar results have also been obtained by Dube [36]. The room temperature dielectric constant of bulk and un-doped sample as obtained by El-Hiti [37] at 1KHz frequency is of the order of $10^4$ while in the present case of doped and nano-sized material, it is in the range of 50-75. Thus there is three order of magnitude reduction in the dielectric constant in the nano version of the material. In the context of ferrites, the phenomenon of dielectric dispersion can be explained on the basis of Maxwell-Wagner’s double-layer model [38, 39] and Koops phenomenological theory of space charge polarization [40]. According to these models, a dielectric structure can be visualized to be composed of two layers; 1) a fairly well conducting layer of grains, which is separated by 2) a thin layer of poorly conducting grain boundaries. The grain boundary layer is more effective in the picture in lower frequency region while the grains more efficiently play their role at higher frequencies. Generally, the dielectric constant is mainly contributed by the atomic and electronic polarization in ferrite grains. The electron exchange between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ is responsible for the origin of polarization in ferrites. The extent of polarization is determined by the local displacement of electrons in the direction of applied field. The polarization decreases with increasing frequency and at higher frequencies it becomes independent of the applied field which is due to the fact that at these frequencies the electron exchange frequency cannot follow the frequency of applied field [41]. The large value of dielectric constant at lower frequencies is due to the predominance of species like $\text{Al}^{3+}$, $\text{Cr}^{3+}$, and $\text{Fe}^{2+}$ ions, vacancies and defects present at grain boundary. The presence of $\text{Al}^{3+}$ and $\text{Cr}^{3+}$ ions in the system influences the hoping process. Apart from that these ionic species try to create p-type character inside the n-type magnesium ferrite.
grains. Thus the anomalous dielectric behaviour in the present study (considerably small values) can also be attributed to the collective contributions by n-type and p-type carriers to the polarization and hopping frequency.

![Graph showing the variation of real part of complex dielectric constant with frequency.](image)

**Figure 4.11:** Variation of real part of complex dielectric constant with frequency.
Figure 4.12: Variation of dissipative part of complex dielectric constant with frequency.

4.3.2.2. Complex impedance

Real and imaginary parts of complex impedance ($Z'$ and $Z''$ respectively) are shown in Fig. 4.13 and Fig. 4.14 respectively. The impedance of ferrites in general has a decreasing trend with frequency but in present case there is slight deviation from the general trend. The impedance initially increases and attains maximum value around 1KHz beyond which it drops rapidly towards higher frequencies. It can be noticed from the plots that both the real as well as imaginary parameters decrease with the increase in frequency for all compositions which can be attributed to the fact that conductivity increases with the enhanced hopping at elevated frequencies. This unexpected behaviour can be due to the fact that initially the inherent dipolar arrangement in the system is
disrupted by the application of external field with low frequency due to localized defect and vacancies. At frequencies beyond 1KHz the dipolar arrangement is relaxed resulting a steep fall in the impedance of the system. Thus a strong frequency dependency has been observed here in low frequency region ranging from 75 Hz -1KHz which is due to the appearance of resistive grain boundary effect. Further, \( Z' \) decreases with the increase in dopant concentration which is due to reduction in barrier height with doping. Apart from that, the decrease in imaginary part \( Z'' \) is an obvious effect of the increase of \( \omega_{gb} \) in \( Z \). View fitted data (Tab. 4.2) with dopant concentration is in accordance with the simplified model \( Z'' = \frac{1}{i(\omega_{gb}C_{gb})} \).

\[ \text{Figure 13: Variation of real part of complex impedance with frequency and concentration.} \]
Figure 14: Figure 13: Variation of real part of complex impedance with frequency and concentration.

4.3.2.3. Loss tangent

Fig. 4.15 shows the plot of dielectric loss tangent (tanδ) as a function of frequency and composition. The value of tanδ decrease with the increase of frequency which is a normal behaviour [42]. The value of tanδ represents the amount of energy dissipated in a dielectric material due to domain wall resonance and eddy effects. At higher frequencies, the energy dissipation becomes low because domain wall motion is ceased. At lower frequencies, the value of tanδ is higher for higher doping (small grain size) while in the high frequency region the same has low values. It suggests that the present material with higher doping can be more efficiently used for high frequency applications. In the low frequency region, the higher value of tanδ for high doping concentration can be due to inconvenience caused in hoping process by Al^{3+} and Cr^{3+} ions both at A as well as B
sites. It can also be noticed that relaxation peaks appear at higher frequencies confirming the Debye-type relaxation process at these frequencies. Further, there is minor shifting of relaxation peaks towards higher frequency region with doping which suggests that in nano-sized grains, hopping process is more capable of keeping itself in unison with higher frequencies. The measured value of tanδ in the present study is in the range 0.10 - 1.80 which is almost 6 times lower as compared to bulk magnesium ferrite [43].

![Graph showing frequency dependence of loss factor](image)

**Figure 4.15:** Frequency dependence of loss factor showing frequency independent behaviour at higher frequencies.

4.3.2.4. **Nyquist analysis (Grain and grain boundary consideration)**

To evaluate the electrical behaviour of the system, the complex impedance spectroscopy was carried out. This technique is extensively employed to separate the resistive and capacitive components of electrical parameters. Under this technique, when the real and imaginary parts of complex impedance are plotted in a complex plane we
obtain a set of large and small semi circles of varying radii. The smaller semi circle appearing in high frequency region corresponds to the grain contribution while the large semicircle appearing in low frequency region, is the result of grain boundary contribution. This is due to the fact that the grain boundaries being highly resistive in nature are effective at lower frequencies. On the other hand, the grains offer conductive path and hence are effective at higher frequencies [44]. Fig. 4.16 illustrates the Nyquist plots of all the samples. For the sake of convenience, and to evaluate various electrical parameters, the Z-View fitted data for the same is also shown in Fig. 4.17. As it is clear from both figures, both the grains as well as grain boundaries are equally contributing towards the electrical behaviour of the material up to $x = 0.20$ dopant concentration beyond which only highly resistive grain boundaries are the only player in the picture. It has been maintained in literature that resistivity of polycrystalline material generally increases with the reduction of particle size [45, 46] which is due to the fact that in case of small grains, there is more segregation at the surface of the grains that gives rise to insulating grain boundaries. In terms of impedance plots, each semicircular arc can be modeled by an equivalent circuit consisting of a resistor (R) and a capacitor (C) connected in parallel.

Corresponding simulated equivalent circuits derived through data from impedance plots are shown in Fig. 4.18. The real and imaginary parts of complex impedance can be written as follows [47]:

\[
Z' = \frac{R_g}{[1+(\omega g^2 C_g^2 R_g^2)]} + \frac{R_{gb}}{[1+(\omega_{gb}^2 C_{gb}^2 R_{gb}^2)]} \quad \ldots .4 .8
\]

\[
Z' = \frac{R_g^2 \omega g C_g}{[1+(\omega g^2 C_g^2 R_g^2)]} + \frac{R_{gb}^2 \omega_{gb} C_{gb}}{[1+(\omega_{gb}^2 C_{gb}^2 R_{gb}^2)]} \quad \ldots .4 .9
\]

where $R_g$, $R_{gb}$, $C_g$, and $C_{gb}$ are the resistance and capacitance of the grain and grain boundary, respectively, while $\omega g$ and $\omega_{gb}$ are the frequencies at the peaks of the semicircles for grain and grain boundary, respectively. The resistance values are obtained from the circular arc intercepts on $Z'$-axis, while the capacitance values can be derived
from the maximum height of the circular arcs. The values of the above parameters can be calculated from the following expressions:

\[ C_g = \frac{1}{R_g \omega_g} \]  \hspace{1cm} \ldots \ldots \text{(4.10)}

\[ C_{gb} = \frac{1}{R_{gb} \omega_{gb}} \]  \hspace{1cm} \ldots \ldots \text{(4.11)}

\[ \tau_g = \frac{1}{\omega_g} = C_g R_g \]  \hspace{1cm} \ldots \ldots \text{(4.12)}

\[ \tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \]  \hspace{1cm} \ldots \ldots \text{(4.13)}

\textbf{Figure 4.16:} Nyquist plots of all the samples illustrating grain and grain-boundary contributions.
Figure 4.17: Z-View fitted data confirming the grains as well as grain boundary contribution up to x = 0.20 dopant concentration beyond which only highly resistive grain boundaries are dominant.

For x = 0.00 - 0.15

For x = 0.20 - 0.30

Figure 4.18: Simulation of equivalent circuits derived through data from impedance plots.
<table>
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<tr>
<th>x</th>
<th>$R_\text{se}(\Omega)$</th>
<th>$C_\text{se}(F)$</th>
<th>$\tau_\text{se}(\text{Sec})$</th>
<th>$R_\text{g}(\Omega)$</th>
<th>$C_\text{g}(F)$</th>
<th>$\tau_\text{g}(\text{Sec})$</th>
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<td>4.60E+3</td>
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<td>2.48E-6</td>
</tr>
<tr>
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<td>30.5E-12</td>
<td>4.80E-4</td>
<td>1.73E+3</td>
<td>0.43E-12</td>
<td>7.43E-7</td>
</tr>
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<td>50.9E-12</td>
<td>4.89E-3</td>
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</tbody>
</table>

Table 4.2: Various grain and grain boundary parameters as calculated from the Z-View plotted impedance data.

4.3.3. Magnetic analysis (Unusual magnetic behaviour)

From the cation distribution scheme, the general model of magnetization for the present can be established as follows:

$$M_s = 5\mu_B (1.16) + 3\mu_B \frac{x}{2} - 5\mu_B (0.84)$$

$$M_s = \mu_B [5(0.32) + 3 \frac{x}{2}]$$

$$M_s = \frac{\mu_B}{2} [3.2 + 3x]$$  \hspace{1cm} \text{Equation 4.14}$$

This shows that increase in the value of $x$ increases the magnetization.

The room temperature magnetic data in terms of M-H plots is shown in Fig. 4.19. It is evident from the figure that the saturation magnetization increases with the dopant concentration while the coercivity decreases. This is contrary to the usual magnetic behaviour of ferrites. Apart from that, the calculated values of $M_s$ on the basis of the proposed magnetic model range from 43 emu/g -58 emu/g. The actual value of $M_s$ for bulk magnesium ferrite at room temperature is 77 emu/g. But the $M_s$ values as actually
observed from the VSM data are greater as compared to those mentioned above. Now the unusual magnetic behaviour of the material under study can be explained by a systematic approach considering the following points:

i) The doping tries to decrease the particle size.

ii) The reduced grain size tries to increase the coercivity. But in the present case the coercivity decreases with the reduction of particle size.

iii) The cation distribution tries to increase the magnetization with doping.

iv) The larger grains should have higher saturation magnetization.

In the present system all these effects may try to compete with each other and final configuration can emerge as a trade off among all of them. Nevertheless, each and every point of the above statement can be separately considered to reach a satisfactory explanation.

Point (i) is quite explainable as the sizes of dopant are smaller as compared to the replaced atoms. Point (ii) is a factual statement since the coercivity $H_c \propto \frac{1}{D}$ where $D$ represents diameter of particle, and $H_c$ represents coercivity of the sample. But here unusually, $H_c \propto D$. This is because of the fact that as the particle size reduces to nanoregime, the particles tend to become single domain which tries to weaken the local magnetic anisotropy and hence magnetic exchange becomes dominant in the picture, resulting in low coercivity in the nano-magnetic materials. The coercivity in this domain can be fitted in the model [48]:

$$H_c = \frac{K4D^6}{M_sA} \quad \ldots \ldots 4.15$$

Where, $K$ is magnetocrystalline anisotropy, $A$ is exchange energy and $M_s$ is saturation magnetization. This shows some sort of proportionality between coercivity and diameter. Similar results (low coercivity for smaller grains) have also been obtained by Yong Ren et. al., for cobalt nano-rods [49]. Apart from that, if we look at the standard plot of
coercivity versus particle diameter (Fig. 4.20), the picture can be more clear. The coercivity is inversely dependent on the diameter for multi-domain grains while it has a direct dependence on the diameter when the grain diameter lies between single domain and superparamagnetic diameter. On this basis it can be inferred that the grain size in the present study lies between superparamagnetic and single-domain diameter. Point (iii) is clear from the scheme of cation distribution. Point (iv) is again a factual statement which is being violated in the present case. The increase of $M_s$ with the reduction of grain size can be primarily attributed to uncompensated magnetic moments of various magnetic ions present in the system. The fine particles consists of two parts i.e. a surface part whose magnetic moment cannot be turned on entirely along the direction of the applied field but makes an average canting angle with the field and an inner part whose magnetic moment can be along the direction of the magnetic field.

![Graph](image)

**Figure 4.19:** The room temperature $M$--$H$ plots showing unusual magnetic behaviour of the material. Inset shows the variation of coercivity and $M_s$ as a function of dopant concentration.
**Figure 4.20:** Dependence of coercivity on diameter in multi-domain and single-domain regions.

As it is evident from Fig. 4.20 the value of $H_c$ has different modes of variation in single domain and multi-domain regions. In multi-domain region, $H_c$ decreases with the increase in grain size which is normally accepted behaviour. But in single domain region the behaviour is different. In this region $H_c$ has some sort of direct proportionality with the grain size lying between single domain diameter ($d_{sd}$) and superparamagnetic diameter ($d_{sp}$), which is the observed trend. On the basis of this observation, we can conclude that the grain diameter in the present case lies between the $d_{sd}$ and $d_{sp}$. Thus the coercive behaviour in this scenario is different from those of macro-sized materials where the grain size and coercivity have inverse relationship [50]. Further, it has also been established that nano-ferrite particles having even tens of nanometer dimension can be considered to have single domains. But the low coercive field is normally assumed to be originating from multi-domains for bulk materials. This implies that there is a changeover from multi-domain nature to single-domain nature in the sample.

The increase of magnetization with the dopant concentration (i.e. with the reduction of grain size) is due to rearrangement of spins, spin-canting and exchange
interaction caused by the substitution of Cr$^{3+}$-Al$^{3+}$ in MgFe$_2$O$_4$ system both at A- and B-sites. The presence of canted moments in MgFe$_2$O$_4$ has been reported in literature [51, 52]. In fact, the finite size effect of the nanoparticles leads to an interplay among three interactions namely superexchange interaction, magnetcrysalline anisotropy and canting effect. The cumulative outcome of these effects can be manifested in the form of unusual magnetic behaviour of the material.

4.3.4. Sensing properties (Application of the material's electronics)

The mechanism of gas sensing by a semiconducting material involves a number of steps, out of which two main functions are (i) detection of the target gas at the solid-gas interface through a gas/solid interaction which brings about an electronic change of the oxide surface and (ii) transduction of the surface-gas interaction into a readable signal (electrical, magnetic or optical). However, the complete understanding of the precise mechanism behind is not easy because of the complex nature of the porous, polycrystalline sensing bodies comprising nano-sized grains of semiconducting oxides. It was believed earlier that the receptor function is provided by the morphology and surface chemical properties of oxide grains to adsorb or react with the target gas which has been supported by the studies on oxygen adsorptive properties of oxide materials [53]. Apart from that, investigation of grain size effects on the sensor resistance and response [54] as well as of the remarkable effects of several foreign receptors on the work function of oxides [55] have strengthened the concept that a layer of surface charges formed on the oxide grains induces gas-dependent barriers for conduction electrons to penetrate the grain boundaries. The relevance of gas response to the porous structure of gas sensing bodies has been analyzed based on a diffusion-reaction equation [56]. The depth of penetration of the gas into the gas sensing bodies determines how the gas response depends on the chemical and physical properties of a target gas and the nano-porous structure of sensing sites.
4.3.4.1 Humidity sensing

The humidity resistive response in terms of output voltage as a function of % relative humidity and material composition is shown in Fig. 4.21. The percentage sensitivity of the material at 85 % relative humidity as a function of operating temperature of the sensors and composition of the films is shown in Fig. 4.22. It is evident from the figures that the intensity of gas response significantly increases with the increase of both the gas concentration as well as amount of dopant while the response time slightly increases (50 sec to 60 sec). Percentage sensitivity (S) increases with the dopant concentration and the peak sensitivity shifts towards the higher temperature thereby indicating that there is no structural deterioration in the sensing material by increasing the temperature and hence the sensor is thermally stable. The overall mechanism can be explained as follows. As the water vapours come in contact to the highly porous Mg(Cr0.5-Al0.5)xFe2-xO4 under investigation, it percolates deep due to capillary action. The adsorbed water condenses on the surface of the material.

![Graph showing output voltage responses of all samples at different RH levels.](image)

**Figure 4.21:** Output voltage responses of all samples at different RH levels.
and accepts electrons present in the conduction band of the sensing material which results in the formation of hydroxyl ions (OH⁻) and hydronium ion (H₃O⁺). In the next step the H₃O⁺ decomposes to liberate proton. The so formed proton proceeds through the aquatic layers by a process popularly known as Grotthuss chain mechanism (Fig. 4.23), through which protons tunnel from one water molecule to the next via hydrogen bonding that universally exists in liquid-phase water. In fact, in bulk water, proton is the dominant carrier responsible for the electrical conductivity. The conduction is due to the Grotthuss chain mechanism [57], through which protons move by tunnel from one water molecule to the next.

Figure 4.22: Percentage humidity sensitivity (S) as a function of temperature and composition at 85% RH.
Figure 4.23: Grotthuss chain mechanism

Further, it is interesting to note in Fig. 4.22 that %S attains peak value at an operating temperature > 100 °C at which it might be difficult to imagine about condensation of water vapours at normal pressure. But in the case of sensing surfaces rich in nano-sized structures and pores, the condensation occurs through a different mechanism [58]. When water vapours come in contact of the sensing surface at higher temperature, they are dissolved into the lattice and creep into the oxygen vacancies to eventually release protons which proceed through Grotthuss mechanism.

A beautiful and satisfactory picture of interaction of water with the oxide sensing materials has been given by Zhi Chen. et. al [59]. Here we attempt to elaborate what actually happens in the overall sensing process right from the interaction of the water vapour to the generation of response. For the sake of convenience, the sensing material is expressed as a solid solution of the constituent oxides. Further, the various bonding schemes present in the solid solution have also been illustrated to understand the nature of bonding with the interacting water molecules. The first layer of water molecules have a direct contact with sensing material by forming actual chemical bonds. This layer is known as chemisorbed and the process as chemisorptions. The chemisorbed layer is immobile and provides a rigid base to next layers which are physisorbed. As water continues to condense on the ceramic film, extra layers atop the first physisorbed layer accumulate. These layers are less ordered and loosely bound as compared to the
physisorbed layer beneath. Further accumulation of layers weakens the ordering which in turn gives more freedom to protons to conduct through the Grotthuss mechanism. In other words, from the second physisorbed layer, water molecules become mobile and finally almost identical to the bulk liquid water, and the Grotthuss mechanism becomes dominant. This mechanism indicates that sensors based purely on water-phase protonic conduction would not be quite sensitive to low humidity, at which the water vapor could rarely form continuous mobile layers on the sensor surface. The two immobile layers, the chemisorbed and the first physisorbed ones, while cannot contribute to proton conducting activity, but could provide electron tunnelling between donor water sites. The tunnelling effect, along with the energy induced by the surface anions, facilitates electrons to hop along the surface that is covered by the immobile layers and therefore contributes to the conductivity. The whole mechanism as it proceeds in various steps is illustrated in Fig. 4.24.

Figure 4.24: Mechanism of interaction of water vapours with the sensing surface by means of chemisorptions and physisorption in various steps.
4.3.4.2. LPG sensing

The LPG temporal response plots in terms of output voltage at four different gas concentrations (100 ppm, 200 ppm, 300 ppm, 400 ppm) for all the samples have been illustrated in Fig. 4.25. The percentage sensitivity of the material at 400 ppm LPG concentration as a function of temperature and composition is shown in Fig. 4.26. It is evident from the figure that the intensity of gas response increases drastically with the increase of both the gas concentration as well as amount of dopant while the response time decreases (50 sec to 40 sec). Percentage sensitivity (%) increases with the dopant concentration. At a low operating temperature, the response of the sensing material towards LPG is restricted by the dynamics of the chemical reaction since the gas molecules are unable to attain sufficient amount of thermal energy to combine with the surface adsorbed O$_2^-$ and O$^-$ species. During the adsorption of atmospheric oxygen on the surface of the material, a potential barrier is developed which halts the transport of charge carriers. In the operating temperature range 60 °C-75 °C the charge carriers attain enough amount of thermal energy to surpass that of the potential barrier. This significantly increases the electronic concentration which in turn is highlighted in terms of better response of the sensor. Further, the peak sensitivity shifts towards higher temperature with the increase of dopant concentration. This can be attributed to the fact that in the temperature range (60 °C-75 °C), the rate of chemisorptions of oxygen on sensing surface speeds up, as a result of which the availability of adsorbed ionic species (O$_2^-$ and O$^-$) on the surface becomes more which react effectively with LPG molecules. Beyond 75 °C, the process of desorption of oxygen from the sensing surface becomes prominent and hence the sensitivity decreases.
Figure 4.25: Output responses of all samples at different LPG concentrations.

Figure 4.26: Percentage LPG sensitivity ($S$) as a function of temperature and composition at 400 ppm concentration.
Apart from that it also signifies that the sensor becomes thermally more stable at higher temperature with the increase in doping.

The LPG sensing mechanism of the films may be explained as follows: The oxygen molecules from the ambience are adsorbed onto the sensing surface. These molecules have a natural tendency to extract electrons from the conduction band of the sensing material (Mg(Cr0.5_Al0.5)2Fe28O4 in this case) which is due their higher electronegativity and by thermal agitation. This adsorption of atmospheric oxygen on the film surface creates ionic species such as O2- and O− which further react with the LPG constituents. At higher temperatures, oxygen vacancies mobility becomes appreciable and the mechanism of conduction turns into a mixed ionic-electronic motion from the point of view of semiconducting sensing. Further, at elevated temperatures (> 400 °C) irreversible changes (both in microstructure and lattice) occur in the sensing material. Therefore it is not wise to employ the conventional gas sensors at high temperature.

In fact, LPG is a mixture of various gases. The normal components of LPG are propane (C3H8, 58 %) and butane (C4H10, 42 %). Sometime small concentrations of other hydrocarbons (like ethane and pentane) may also be present. The response of the material is the collective response towards the constituent gases. Although the reaction mechanism for LPG is quite complex and proceeds through several intermediate steps which are yet to be fully understood, but the overall reaction of LPG molecules with adsorbed oxygen species may be visualized by the equations (4.16-4.19). Generation of ionic oxygen species on the surface of the sensing element has been depicted in Fig. 4.27. In the first step, both constituent gases react with the adsorbed oxygen species on the surface of the sensing material and form an intermediate complex. This complex being unstable gets immediately decomposed in to H2O and CO2 releasing negative charge and energy. The energy released in this process further facilitates the mobility of charge carriers, thereby increasing the conductivity of the material. In other words the energy released during the decomposition of LPG molecules is sufficient for the trapped electron to jump into the conduction band. Thus, the barrier height goes on decreasing and the
conductivity of the material increases, which could be attributed to the adsorption–desorption mechanism resulting from the electronic defects.

\[ nC_3H_8 + 2nO^- \rightarrow nH_2O + nC_3H_6:O + 2ne^- \]  \hspace{1cm} \ldots 4.16

\[ nC_3H_6:O + 8nO^- \rightarrow 3nCO_2 + 3nH_2O + (8ne^- + \text{energy}) \]  \hspace{1cm} \ldots 4.17

\[ nC_4H_{10} + 2nO^- \rightarrow nH_2O + nC_4H_6:O + 2ne^- \]  \hspace{1cm} \ldots 4.18

\[ nC_4H_8:O + 11nO^- \rightarrow 4nCO_2 + 4nH_2O + (11ne^- + \text{energy}) \]  \hspace{1cm} \ldots 4.19

\[ nO_2 (ads) + ne^- \leftrightarrow nO_2 (ads) \]

\[ 2nO_2 (ads) + ne^- \leftrightarrow 2nO (ads) \]

**Figure 4.27:** Mechanism of production of oxygen species on active surface of the sensing material.

### 4.4. Conclusions

In this chapter, we have shown that Al\(^{3+}\) and Cr\(^{3+}\) ions can be incorporated in the lattice system of MgFe\(_2\)O\(_4\) which alter the electrical and magnetic behaviour of the material. There is three order of magnitude reduction in the dielectric constant in the nano version of the material. Apart from that, the measured values of tan\(\delta\) in the present study
are in the range 0.10 –1.80 which are almost 6 times lower as compared to that of bulk MgFe$_2$O$_4$. Complex impedance spectroscopy of the material reveals the existence of grain and grain-boundaries up to $x = 0.150$ beyond which only the insulating grain boundaries become effective. Along with the actual impedance plots, the Z–View fitted data of the same has also been provided for the sake of convenience. Cation distribution scheme and hence a general expression for magnetic trend was approached by considering the magnetic M–H data from VSM. Unusually high room temperature magnetism and abnormal coercive behaviour was observed which has been explained on the basis of various competing factors arising due to non-stoichiometry, low dimensionality, and doping.

Nano-structured MgFe$_2$O$_4$ ceramics incorporating Chromium (Cr$^{3+}$) and aluminium (Al$^{3+}$) as dopant were successfully synthesized by one step sol-gel combustion technique using urea as fuel. The so prepared powders were examined for structure, electronics, magnetic and sensing. It was found that the sensor exhibits fast and intensive response at relatively low operating temperature (120 – 130 °C at 85 % (RH) and 60 – 70 °C at 400 ppm LPG). The humidity response time was observed to be in the range 50 – 60 sec. while the same for LPG was measured to be in the range 40 –50 sec. The various steps of humidity sensing mechanism have been explained in detail on the basis of Grothuss chain mechanism. The Nano-structured MgFe$_2$O$_4$ is itself a good sensing material. Replacing Fe$^{3+}$ by a combination of 0.5 Cr$^{3+}$–0.5 Al$^{3+}$ significantly enhance its sensing properties due to creation of nano-structures, pores and defects. The MgFe$_2$O$_4$ is partially inverse spinel. Replacing octahedral Fe$^{3+}$ ions by a combination of Cr$^{3+}$–Al$^{3+}$ ions affects the $Fe^{2+} \leftrightarrow Fe^{3+}$ hopping conduction scheme. Apart from that, the combination of Cr$^{3+}$–Al$^{3+}$ together with the Mg$^{2+}$ ions on octahedral site introduces more electrons in the system. Doping also favours the creation of the cation vacancies which allow the dissociation of oxygen in their vicinity. All these phenomena are conductivity enhancing factors and hence enhance the sensing behaviour of the material. Thus we conclude that the spin coated films of Cr$^{3+}$ and Al$^{3+}$ doped nano-sized MgFe$_2$O$_4$ materials offer good sensing response towards both humidity as well as LPG.
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CHAPTER 5

STRUCTURAL, MAGNETIC, COMPLEX PERMEABILITY AND DUAL BAND GAP STUDIES OF Cr$^{3+}$ DOPED NANO-STRUCTURED $\gamma$-FERRITE
5.1. Introduction

Since past decade much attention has been focused on the engineering and investigation of magnetic particles produced at nano scale [1-3]. In this context iron oxide nanoparticles and their doped species remain the ideal candidates because of their potential applications in the field of storage electronics, biomedicines, biotechnology, catalytic reactions, selective removal of harmful cation species from contaminated water via adsorption which can be enhanced by improving the surface area (reducing the grain size), magnetic tunneling barrier for room temperature spin filter devices in spintronics, owing to their remarkable properties such as superparamagnetism, low Curie temperature, high Coercivity and high Susceptibility [4-8]. The biocompatibility and clinical importance (magnetic hyperthermia, magnetic resonance imaging) of nano-sized iron oxide has opened new vistas that can be the basis of future medical industry because their magnetism allows remote manipulation with external fields while they are potentially non-toxic to humans. Among the class of iron oxides, maghemite (γ-Fe₂O₃) is the most studied material exhibiting ferrimagnetic behavior below 1000 K (Néel temperature). Such states are due to the competing character of the exchange integral present in the system.

The γ-Fe₂O₃ is the second most stable polymorph of iron oxide after the antiferromagnetic magnetite (α-Fe₂O₃). The γ-Fe₂O₃ exhibits ferrimagnetic ordering with a net magnetic moment (≈ 2.5 \( \mu_B \)/f.u.) which together with its chemical stability and cost effectiveness led to its wide applications. The strange behavior of γ-Fe₂O₃ can also be attributed to its defective spinel geometry.

5.2. Complex initial permeability

From engineering and technological point of view, initial permeability is a very important and desirable parameter. It is the property, which defines how quickly the domains of magnetic material align along the direction of applied field. For high permeability applications, Ni-Zn, Mn-Zn and their doped variants have been commonly employed [9-11]. There is no report to the best of our survey of literature catering to the
permeability study of $\gamma$-Fe$_2$O$_3$ in pure or in doped form. One report relates the permeability and domain wall motion in case of bulk Fe$_3$O$_4$ (a close relative of $\gamma$-Fe$_2$O$_3$) at low frequencies [12]. There is another report dealing with frequency dependence of $\gamma$-Fe$_2$O$_3$ in which initial permeability values range between 0.2 – 0.4 [13]. The standard initial permeability value of magnetic iron oxide powder is equal to 4.0 [14]. In the present investigation we have shown that Cr$^{3+}$ doped $\gamma$-Fe$_2$O$_3$ has significant permeability and it can be used as high permeability core material and Multi-layer Chip Inductor (MLCI) [15] application in electronic products, such as cellular phones, computers and video cameras. The results obtained in terms of permeability spectra are suggestive of the fact that $\gamma$-Fe$_2$O$_3$ and its doped variants when made in nano-form behave as a high permeability material at ultra high frequencies (5MHz – 25MHz) with permeability showing unusually inverse dependence on the grain dimension.

5.3. Experimental

In the solution combustion synthesis, the combustion of gel takes place in a very uncontrolled manner. It propagates through the volume of the gel in an irregular fashion which leads to incomplete combustion and phase impurities. Further the viscous nature of the gel hinders the free swelling of the oxide foam. Apart from that, the sudden evolution of gases at the point of ignition leads to the eruption of uncombusted gel out of the vessel which causes the loss of valuable material. To avoid these problems the proposed method offers a very simple modification for the preparation of highly phase-pure nanocrystalline $\gamma$-Fe$_2$O$_3$. In the present work Cr$^{3+}$ doped $\gamma$-Fe$_2$O$_3$ powders have been synthesized using metal nitrates as oxidizing agents and citric acid as fuel. Citric acid is chosen for this reaction because it offers ideal conditions for the synthesis of nanopowders, i.e., i) it is water soluble, ii) it has low ignition temperature (< 400°C), iii) it is compatible with Fe(NO$_3$)$_3$ and Cr(NO$_3$)$_3$, iv) it evolves huge amount of gases at the point of ignition and v) is easily available/cost effective. These properties make it ideal and specific for the preparation of $\gamma$-Fe$_2$O$_3$ nanopowder. In a typical synthesis procedure, stoichiometric amounts of Cr(NO$_3$)$_3$.5H$_2$O (99.00%, S. D. Fine Chemicals Ltd. Mumbai), Fe(NO$_3$)$_3$.9H$_2$O (98.00%, S. D. Fine Chemicals Ltd. Mumbai) were dissolved
in minimum amount of doubly distilled water. All chemicals were used without further purification. The solution was kept on stirring up to complete dissolution. Stoichiometric amount of citric acid (C_6H_8O_7) necessary for the complete combustion of the nitrates system present in the solution was calculated according to propellant chemistry expression [16]

\[
\psi = \frac{\sum (\text{Coefficient of oxidising elements in specific formula}) \times (\text{Valency})}{-\sum (\text{Coefficient of reducing element in specific formula}) \times (\text{Valency})} \quad \text{(5.1)}
\]

For citric acid, the total reducing valence is F = 18 and for each trivalent nitrate the oxidizing valence is O = 15. So for the complete combustion O/F = 15/18 = 0.833. This concludes that for the complete combustion of the system, the nitrates to fuel ratio should be = 1 : 0.833, and accordingly the calculated stoichiometric amount of citric acid will be 1.60035 g (taking 0.01 M). Assuming complete combustion, the process is as follows:

\[
6\text{Fe(NO}_3\text{)}_3 + 5\text{C}_6\text{H}_8\text{O}_7 = 3\text{Fe}_2\text{O}_3 + 18\text{N}_2 + 20\text{H}_2\text{O} + 30\text{CO}_2
\]

\[
3\{(2-x) \text{Fe(NO}_3\text{)}_3 + x\text{Cr(NO}_3\text{)}_3\} + 5\text{C}_6\text{H}_8\text{O}_7 = 3\text{Fe}_2-x\text{Cr}_x\text{O}_3 + 18\text{N}_2 + 20\text{H}_2\text{O} + 30\text{CO}_2
\]

The solution was kept on a hot plate maintained at 50°C while stirring continuously with a nonmagnetic stirrer. Soon the water evaporates and a very viscous transparent honey like gel is formed. This gel was dried in a vacuum oven at 40°C for 24 hours. The dried gel was crushed into very fine powder using agate mortar. This powder was taken in a porcelain dish and was kept inside a muffle furnace preheated at 150 °C. The powder immediately ignites in a controlled way without any eruption of the mass outside the vessel. The individual grains of the powder are swallowed like popcorn and a highly porous and fluffy brown colour mass was obtained. This fluffy mass was ground into fine powder and was calcinated at 300 °C for 2 hours at heating rate of 5 °C/Min and cooled with the same rate before further investigation. The powders were examined for crystallinity, Phase identification and particle size determination by Xray diffraction (XRD from Rigaku Miniflex Japan) using Cu-Kα radiations (λ=0.15406 nm) in 2θ range from 20° to 70° with scan rate of 2°/min and a step size of 0.02°. FT-IR spectroscopy was
done by Perkin Elmer spectrometer using KBr as medium. The magnetic measurements were performed using SQUID magnetometer.

Complex permeability measurements in the frequency range of 50 KHz – 25 MHz and in the temperature range of 300K – 473K for all whole range of dopant concentration were carried out with the help of Agilent LCR (4285 A) impedance meter. The inductance was measured by making toroidal coils around ring shaped pellets of the material with the help of the following relations:

For Circular cross section [17]:

\[ L = 0.01595N^2[D - (D^2 - d^2)^{\frac{1}{2}}] \]  \( \ldots \ldots 5.2 \)

Where, \( L = \) inductance (\( \mu H \)), \( d = \) internal diameter of coil winding, \( D = \) Outer diameter of the coil, and \( N = \) number of turns in the coil (\( N = 50 \) in the present case). In case, when \( d << D \), the above relation is reduced to the following form.

\[ L \approx 0.007975 \frac{d^2N^2}{D} \]  \( \ldots \ldots 5.3 \)

For rectangular cross-section [18]:

\[ L = 0.0269451N^2h \ln \frac{d_o}{d_i} \]  \( \ldots \ldots 5.4 \)

Where \( d_i = \) inside diameter of toroid, \( d_o = \) outside diameter of toroid, \( N = \) number of turns, \( h = \) height of toroid. The inductance is related to real (\( \mu'_i \)) and imaginary parts (\( \mu''_i \)) of the (relative) initial complex permeability as given below.

\[ \mu'_i = \frac{L_s}{L_0} \quad \text{and} \quad \mu''_i = \mu'_i tan\delta \]

Where \( L_s \) is the self-inductance of the sample core and \( L_0 = \left( \frac{\mu_0 N^2 S}{d} \right) \) is the inductance of the winding coil in the absence of sample core, \( N \) is the number of turns of the coil, \( S \) is
the area of cross section and $d$ is the mean diameter of the toroid-shaped sample. The relative quality factor ($Q_r$) was calculated by the following relation:

$$Q_r = \left( \frac{\mu'_i}{\tan \delta} \right)$$

5.4. Results and discussions

5.4.1. Structural properties (XRD and FT-IR)

Powder X-ray diffraction patterns of the synthesized samples, sintered in air at 300 °C for 2 hours are shown in the Fig. 5.1. X-ray pattern reveals the formation of crystalline, phase pure distorted cubic spinel structure belonging to space group P4_23 (208). The powder patterns are well matched with the standard powder data (ICDD card NO. 24-0081, JCPDF card NO. 39-1346). There is no evidence of the formation of impurity phases other than $\gamma$-Fe$_2$O$_3$ in the samples. However, the possibility of formation of traces of chromium oxides cannot be completely ruled out although there is no signature in diffraction data. That’s why the effect of other phases (if any) has not been considered in the present investigation. All the peaks of pure as well as doped samples are essentially of $\gamma$-Fe$_2$O$_3$. However, the peaks are shifted to lower values of 2θ in the doped samples which is suggestive of Cr$^{3+}$ ion substitution of Fe$^{3+}$ ions in the $\gamma$-Fe$_2$O$_3$. The crystallite sizes for different samples were calculated using Scherrer’s equation

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $D$ is the average crystallite diameter, $\lambda = 1.5406$ Å (characteristic Cu–Kα wavelength of X-rays) and $\beta$ is the width of the diffraction peak at half of the maximum height (FWHM) for diffraction angle 2θ. It is evident from XRD spectra that peak intensity decreases while FWHM increases with the increase in dopant concentration, which in turn decreases the crystallite size. The decrease in crystallite size and lattice parameter with the increase in Cr$^{3+}$ concentration may be attributed to the
Figure 5.1: Powder X-ray diffraction spectra of Cr⁺³ doped γ-Fe₂O₃ nanopowders.

the reduced ionic radius of Cr⁺³ (0.061 nm) compared to Fe⁺³ (0.064 nm). The variation of lattice parameter with dopant concentration is illustrated in Fig. 5.2. The lattice parameters $a$ and $c$ of the unit cell were calculated using the following equation:

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}$$  \hspace{1cm} \ldots \ldots 5.5$$

Where, $\theta$ is Bragg's angle [19].
Figure 5.2: Variation of lattice parameters with dopant concentration showing continuous decrease.

The crystallite size calculated for different samples varies from 8.35 nm to 10.61 nm which is further confirmed by FE-SEM and TEM images shown in the Fig. 5.3. and Fig. 5.4 respectively. Magnetite (α-Fe₂O₃) can be represented as (Fe₈⁴⁺₃⁻)₈[Fe²⁺².₅⁺]₆ O₃₂, where the brackets ( ) and [ ] indicate tetrahedral and octahedral lattice sites respectively, corresponding to 8a and 16d Wyckoff positions in space group Fd3m.
Figure 5.2: Variation of lattice parameters with dopant concentration showing continuous decrease.

The crystallite size calculated for different samples varies from 8.35 nm to 10.61 nm which is further confirmed by FE-SEM and TEM images shown in the Fig. 5.3. and Fig. 5.4 respectively. Magnetite (α-Fe₂O₃) can be represented as \((\text{Fe}^{3+}_8 \text{Fe}^{2.5+}_{16})_6 \text{O}_{32}\), where the brackets ( ) and [ ] indicate tetrahedral and octahedral lattice sites respectively, corresponding to 8a and 16d Wyckoff positions in space group Fd3m.
The $\gamma$-$\text{Fe}_2\text{O}_3$ structure can be obtained by creating 8/3 vacancies out of the 24 Fe sites in the cubic unit cell of $\alpha$-$\text{Fe}_2\text{O}_3$. In this way, the distorted spinel cubic unit cell of $\gamma$-$\text{Fe}_2\text{O}_3$ can be viewed as having the structure $(\text{Fe}_8^{4+}) [\text{Fe}_{40/3}^{4+} [\text{Fe}_8^{4+}]_3] \text{O}_{32}$ [21], where the symbol [ ] represents the iron vacancies at octahedral sites.

Figure 5.4: Further confirmation of particle size. TEM micrographs of $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ samples: (a) for $x = 0.00$ and (b) for $x = 0.30$.

Figure 5.5: FT-IR spectra of all the samples with different concentration of $\text{Cr}^{4+}$ ions.
The Fourier Transform Infrared (FTIR) spectra in the wavenumber range 4400-400 cm\(^{-1}\) for samples with different dopant concentration are shown in Fig. 5.5. The two strong absorption bands around 437 cm\(^{-1}\) and 585 cm\(^{-1}\) for all samples correspond to the stretching vibration mode of O–Fe–O bond. Bands around 3424 cm\(^{-1}\) and 1624 cm\(^{-1}\) ascribe to the bending mode of vibration for surface hydroxyl groups. The IR dip around 1384 cm\(^{-1}\) can be attributed to the presence of trapped nitrates incorporated from the preparing process. Other small peaks in the range 400-600 cm\(^{-1}\) give a clear signature of C–C and M–C–O bonding, thereby indicating the presence of very small amount of carbonaceous materials. It is evident from the spectra that there is a minor shift in the IR active modes of different samples which can be attributed to the plasmonic effect in the nano-sized grains having grain boundaries. This can be attributed to the fact that in the case of nano size grains the arrangement of atoms at the grain boundaries are different from that of the bulk crystals. This leads to the disorder both in the coordination number and bond length and this degradation in crystal symmetry is responsible for the shifting in IR active modes [22].

5.4.2. Magnetic properties

5.4.2.1. a.c. susceptibility

The variation of a.c. susceptibility as the function of temperature for different samples is presented in Fig. 5.6. The general trend followed by all the samples is same. The value of susceptibility increases with temperature. Attains maximum value at temperature called blocking temperature \(T_b\), beyond which it falls off rapidly. This is the typical characteristic behavior of superparamagnetic relaxation of nanoparticles. Beyond \(T_b\) the single domain magnetic moment of particles becomes thermally agitated and undergoes a state of superparamagnetic relaxation. At low temperatures, due to large magnetic anisotropy, the particles become magnetically frozen and magnetic moments tend to align in the direction of easy axis of magnetization.
Figure 5.6: Variation of a.c. susceptibility as a function of temperature all samples. Decrease of blocking temperature can be clearly observed.

This causes a reduction in magnetic susceptibility below $T_B$. The superparamagnetic relaxation can be best described by the Néel's relaxation model [23], $\tau_N = \tau_0 \exp \left( \frac{K_v V}{k_B T_B} \right)$, where $\tau_N$ is the Néel relaxation time (often called superparamagnetic relaxation time), $\tau_0$ is the relaxation time constant ($\approx 10^{-9}$), $K_v$ is the volume anisotropy, $V$ is particle volume, $K_B$ is Boltzmann’s constant, and $T_B$ is the blocking temperature which can be approximated as $T_B = \frac{K_v V}{25k_B}$. Since $T_B \propto V$ (particle size), the reduction in $T_B$ with the dopant concentration can be justified in the present study.
5.4.2.2. Magnetization

The plots of room temperature magnetization as the function of magnetic field for samples with various dopant concentrations are shown in Fig. 5.7. Plots for all the samples are indicative of superparamagnetic nature of particles, indicating that thermal fluctuations become dominant over spontaneous magnetization at a given field [24] and the net magnetization in absence of an external field becomes zero. Such particles have zero coercivity and high saturation magnetization ($M_s$). Further, the $M_s$ initially increases up to 7% dopant concentration, beyond which it falls off considerably. The values of $M_s$ for some doped samples are relatively higher as compared to their pure and bulk counterparts (74 emu/g for bulk γ-Fe₂O₃). These results can be plausibly explained on the basis of Néel's theory of antiferromagnetism [25]. It has been previously well established that the magnetic behavior of the materials is deeply rooted in the crystal geometry and spin moment interactions among the constituent ions. In his investigation, Néel postulated two separate sublattice magnetizations corresponding to two different sublattices in the case of ferrites having spinel structure. One sublattice belongs to tetrahedral (A) sites and other belongs to octahedral (B) sites. The antiferromagnetic coupling between the two lattice sites determines the final magnetic behavior of the material. The AB interaction is stronger as compared to the AA and BB interaction which can be attributed to large A-O-B angle and small bond length. By carefully examining the interactions involving the AB interaction, Néel successfully explained the ferrimagnetism in ferrites. In one formula unit of γ-Fe₂O₃, there are 8 Fe³⁺ ions on A sites and 40/3 Fe³⁺ ions on B sites. In an ideal case, if A-O-B angle considered is 180° and the effects of thermal agitation are ignored, then the antiferromagnetic AB interaction will yield a magnetization of $5\mu_B \left(\frac{40}{3} - 8\right)$, where $5\mu_B$ is the magnetic moment associated with one Fe³⁺ ion (owing to 5 unpaired electrons). This gives a very large value as compared to the established magnetic moment of γ-Fe₂O₃ ($\approx 2.3 \mu_B$). The spin canting by thermal agitations and non-straight A-O-B angle ($\approx 125^\circ$) is responsible for the reduction of net magnetic moment. The variation of $M_s$ with the doping of less-magnetic Cr³⁺ ($3\mu_B$) suggests that initially the Cr³⁺ ions sit on A sites up to $x = 0.07$ dopant concentration,
beyond which they begin to distribute both on A as well as B sites. To elaborate this, if \((x + y)\) is the number of dopant ions, then net magnetic moment can be represented as:

\[
M = 5C\mu_B\left\{\frac{40}{3} - [8 - (x + y)]\right\} = 5C\mu_B\left\{\frac{16 + (x+y)}{3}\right\}
\]  

\[\text{......5.6}\]

where, \(C\) can be considered as the compensation factor to counter the effect of spin canting. This model explains the increase of magnetization in 0-7 % range of dopant concentration. Beyond 7 %, a fraction of Cr\(^{3+}\) (say \(y\)) begins to occupy B sites. Hence, in this range the model can be written as \(M = 5C\mu_B\left\{\frac{16 + (x+y)}{3}\right\}\), which explains the reduction in magnetization at higher doping. Similar results have been reported in the case of other ferrites [26]. Some other factors contributing to the observed behavior of \(M_s\) may be its size dependency of superparamagnetic nano-sized particles [27] which can be attributed to the surface spin effects. As the particle size decreases, the surface spins lack complete coordination and are likewise disordered. This leads to make them less susceptible to changes in the external magnetic field [28, 29] which explains the reduction of \(M_s\) at higher doping due to reduction of particle size. Variation of various parameters as the function of increasing dopant concentration is enlisted in Tab. 5.1.

![Figure 5.7: Magnetization versus magnetic field plots depicting the superparamagnetic nature of material.](image)
<table>
<thead>
<tr>
<th>x</th>
<th>Lattice parameter (Å)</th>
<th>Crystallite size (nm)</th>
<th>$T_B$ (K)</th>
<th>$\chi_{ac}$ (at $T_B$)</th>
<th>$M_S$ (emu/g)</th>
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</thead>
<tbody>
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<td>0.020</td>
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<tr>
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<td>52</td>
</tr>
<tr>
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<td>330</td>
<td>0.015</td>
<td>65</td>
</tr>
<tr>
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<tr>
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</tr>
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</tr>
<tr>
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<td>16.91</td>
<td>260</td>
<td>0.016</td>
<td>36</td>
</tr>
</tbody>
</table>

**Table 5.1:** Measured/calculated values of different parameters as the function of dopant concentration.

### 5.4.3. Complex permeability studies

One of the most important parameters used in evaluating magnetic materials is permeability. Apart from being the function of the chemical composition and crystal structure, it also has a strong dependency on many other physical parameters such as microstructure, temperature, stress, time after demagnetization etc. Permeability can be defined as a measure of the ability of a material of getting internally magnetized when placed in an external magnetic field or technically up to how much extent the material allows the passage of magnetic lines of force through its volume. More precisely, it gives us an idea of how magnetically conductive a material is. To have a better insight of the magnetic behaviour of a material in terms of quality factor and to deal with high frequency magnetic effects, the complex form of permeability is the most important tool. At low frequencies and in the case of a linear materials, the magnetic field and the auxiliary magnetic field are simply proportional to each other through some scalar permeability whereas at high frequencies these quantities will react with each other with some lag time in the form given below:
\[ H = H_0 e^{j\omega t} \quad B = B_0 e^{(j\omega t - \delta)} \quad \ldots \quad 5.7 \]

Where, \( \delta \) is the phase lag of \( B \) from \( H \). Thus, permeability can be written as:

\[ \mu = \frac{B}{H} = \frac{B_0 e^{(j\omega t - \delta)}}{H_0 e^{j\omega t}} = \frac{B_0}{H_0} e^{-j\delta} \quad \ldots \quad 5.8 \]

This makes permeability essentially a complex quantity. Utilizing Euler's formula [30], the polar form of complex permeability can be translated into rectangular form given below.

\[ \mu = \frac{B_0}{H_0} \cos \delta - j \frac{B_0}{H_0} \sin \delta = \mu' - j\mu'' \quad \ldots \quad 5.9 \]

The loss tangent or dissipation factor is the ratio of the imaginary to the real part of the complex permeability as given below.

\[ \tan \delta = \frac{\mu''}{\mu'} \quad \ldots \quad 5.10 \]

Loss tangent gives a measure of how much power is lost in a material relative to how much is stored. The reciprocal of dissipation is a scale of performance of the magnetic material and it is called quality factor (Q). The Q factor of an inductor is the ratio of its inductive reactance to its resistance at a given frequency, and is a measure of its efficiency. The higher the Q factor of the inductor, the closer it approaches the behavior of an ideal, lossless, inductor. The Q factor of an inductor can be found through the following formula, where \( R \) is its internal (Series Model) electrical resistance and \( X_L = \omega L \) is capacitive or inductive reactance at resonance:

\[ Q = \frac{X_L}{R} = \frac{\omega L}{R} \quad \ldots \quad 5.11 \]
5.4.3.1. Frequency dependency of real and imaginary permeability

Fig. 5.8(a - g) shows the variation of real part of initial permeability ($\mu'_i$) with frequency over a temperature range of 300K - 473K for all compositions. It is evident from the figures that $\mu'_i$ has very low values for pure material but a dramatically high value of $\mu'_i$ is observed in Cr$^{3+}$ doped samples which gradually increases with the increase in dopant concentration. The values of $\mu'_i = 60 - 70$ for doped samples are comparable with those observed in some cases for doped Ni-Zn ferrites [31, 32]. Apart from that, it can also be observed from the plots that at a given temperature, $\mu'_i$ first increases up to a certain frequency at which it attains maximum value and beyond which it declines at higher frequencies. This indicates that the frequency of domain wall motion initially increases with the applied frequency and at a particular frequency it becomes resonating with the field giving rise to a relaxation peak in the $\mu'_i$ spectra. This frequency is called domain wall relaxation frequency ($f_r$). It is also evident from the plots that $f_r$ shifts towards higher frequencies with the increase of temperature which suggests that the thermal effects produced due to temperature contribute towards the easy motion of domain walls and thus making relaxation possible at elevated frequencies. It is the general trend of ferrites that their initial permeability remains almost constant up to certain lower range of frequency after which the initial permeability increases to a maximum value and then decreases rapidly to a very low value. This phenomenon, known as dispersion of initial permeability, is attributed to either domain wall displacements or domain rotation or both of these contributions [33]. The phenomenon can be well modeled with the help of well established models suggested by A. Globus model [34] and Snook [35] given below:

$$ (\mu_s - 1)^{\frac{1}{2}} f_r = \text{Constant} \quad .......5.12 $$
Figure 5.8(a-h): Real part of complex permeability as a function of frequency. Dispersion can be seen for all compositions and temperature.
\[(\mu_s - 1) \mu_r = \frac{2}{3} \mu_0 \mu_r \]

\[\ldots 5.13\]

The value of \(\frac{2}{3} \mu_0 \mu_r\) in some specific cases is known as Snoek constant. For low dimensional single domain ferrite materials, the magnetic behaviour can be well analyzed by Landau-Lifshitz equation [36] given below:

\[\frac{dM}{dt} = -\gamma M \times H\]

\[\ldots 5.14\]

Where, \(M\) is the static magnetization vector, \(H\) is the effective static magnetic field and \(\gamma\) is the gyro-magnetic factor. The frequency dependence of permeability is readily obtained by the linearization of the Landau-Lifshitz equation. To understand the frequency dependence of the permeability, the complex permeability is sometimes expressed in terms of tensor components as given below:

\[\mu_{xx} = 1 + \frac{4\pi M_0 (H_k + (N_x - N_z)M_0)}{(H_k + (N_x - N_z)M_0)(H_k + (N_y - N_z)M_0) - \frac{\omega^2}{\gamma^2}}\]

\[\ldots 5.15\]

\[\mu_{yy} = 1 + \frac{4\pi M_0 (H_k + (N_x - N_z)M_0)}{(H_k + (N_x - N_z)M_0)(H_k + (N_y - N_z)M_0) - \frac{\omega^2}{\gamma^2}}\]

\[\ldots 5.16\]

\[\mu_{zz} = 1\]

\[\ldots 5.17\]

Where, \(N_x, N_y\) and \(N_z\) are the normalized demagnetization factors such that \(N_x + N_y + N_z = 4\pi\), and \(M_0\) is the saturation magnetization.

It can be noted from the above expressions that apart from the size the permeability of a sample containing a few domains depends greatly on its shape also. For a multi-domain sample, the magnetic behavior is determined by the shape of domains in some occasions. The above equations can also be expressed in Lorentzian form as:
\[ \mu(\omega) = 1 + \frac{(\mu_r - 1)}{1 - (\omega_0 \omega)^2} \] .......5.18

Where,

\[ \omega_r = \gamma \{(H_k + (N_x - N_z)M_0)(H_k + (N_y - N_z)M_0)\}^{\frac{1}{2}} \] .......5.19

\[ \mu_s(\text{xx}) = 1 + \frac{4\pi M_0}{(H_k + (N_x - N_z)M_0)} \] .......5.20

\[ \mu_s(\text{yy}) = 1 + \frac{4\pi M_0}{(H_k + (N_y - N_z)M_0)} \] .......5.21

The Lorentzian formulation is also known as Lorentzian dispersion. From the Lorentzian dispersion relation, it is clear that permeability gradually increases with frequency but remains around \( \mu_s \) in the order of magnitude till the resonance is reached. Generally it is seen that slight decrease of the permeability with frequency is usually observed due to the presence of magnetic loss. On the other hand if the damping is low enough, there is an abrupt drop in permeability near the resonance again. Above the resonance, the permeability takes small if not negative, values that is unsuitable for most technical applications. That is why the usefulness of the material for microwave applications can be approximately estimated on the basis of \( \mu_s \) and \( \omega_r \). The static permeability characterizes the performance in the operating frequency band. The resonance frequency is a measure of the cut-off frequency, above which the material is no more significantly permeable.

It is the general trend of permeability spectra that \( \mu'_i \) remains fairly unchanged over a certain frequency range, and it drops rapidly to a very small value at elevated frequencies and there is an increase in \( \mu''_i \) (Fig. 5.9). The imaginary part \( \mu''_i \) appears as a result of the lagging of the domain walls motion with the applied alternating magnetic
field. This type of behavior is analogous to a typical relaxation characteristics. The prime reason of such behaviour may be the irreversible domain wall displacement [37]. As is evident from the figure, the value of $\mu''$ starts with smaller values at low frequencies and abruptly increases around 10–15 MHz, which is quite expected because the 10 MHz is the onset of resonance. The permeability loss arising due to appearance of imaginary part is primarily due to lag of the domain wall motion in relation to the applied alternating magnetic field [38]. Imperfections and defects in the crystal system may lead to an enhanced lagging effect in domain wall motion.
Figure 5.9(a-g): Dissipative part of complex permeability showing loss at higher frequencies.
5.4.3.2. Temperature dependency of real permeability

The permeability is the cumulative outcome of a host of many different factors acting simultaneously in the system under magnetic field. Some are inherent properties depending on chemistry of crystal structure. Some are extrinsic, depending on ceramic microstructure, strains, etc. Most of these parameters are temperature dependent in themselves. Thus, it is not surprising to find wide variation in the shape of the permeability vs. temperature plots. The overall result of all these temperature dependent factors is that the permeability ultimately becomes essentially inverse relation to the magnetic anisotropy constant [39]. A typical permeability versus temperature plot consists of a primary relaxation maxima with a sudden drop near the Neel temperature along with a secondary maxima which is observed at lower temperature. This peak most often occurs close to the temperature where the magnetostriction goes through zero [40]. In the present study, the permeability measurements were taken in the range of 300K-473K which is much below the Neel temperature of γ-Fe₂O₃ (~ 951K) because the insulation of coil wire around the ring shaped pellets could not bear the higher temperature (there was risk of burning). Thus, the primary relaxation maxima is not observed as it is evident from Fig. 5.10(a-g). What is observed in this case is the secondary maxima. An interesting feature which appears common in all the plots is that the permeability at 20MHz and 25MHz is approximately independent of temperature and for x = 0.09 there is a little variation in permeability with temperature which a feature desirable in applications where the permeability should not vary significantly with changes in temperature, for example, magnetic components in telephone and transmission lines which can be subject to changes in temperature [41, 42]

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Figure 5.10(a-g): variation of real part of complex permeability with absolute temperature. It can be seen that permeability at 20MHz and 25MHz is approximately independent of temperature for all samples.
5.4.3.3. Composition /microstructural dependency of real permeability

As it has been observed from Fig. 5.11(a-e), initially, \( \gamma\)-Fe\(_2\)O\(_3\) has very low permeability values (\( \mu'_r \approx 6 \)) which is still slightly higher as compared to the standard data [43, 14]. When Cr\(^{3+}\) is introduced in the system, a very significant leap in the value of \( \mu'_r \) is observed which goes on increasing with the dopant concentration. One factor responsible for this drastic change is the increase of magnetization with the Cr\(^{3+}\) doping as it has been explained in the magnetization section. Another factor giving rise to unusual behaviour of permeability with the grain size can be accounted on the basis of the nano-structured nature of the material as it has been also held by G. Herzer [44] in the case of nano-structured system that permeability increases manifolds in case of nano-sized magnetic material. The interactions between the crystallites of the solid material are very complicated because of domain wall effects [45]. The variation of \( \mu'_r \) as a function of dopant concentration is shown in Fig. 5.11(a-e). It has been well established in the literature [46, 47] that in context of ferrites, the \( \mu'_r \propto \frac{(M_s^2\bar{d})}{K^3} \) where \( M_s \) is the saturation magnetization, \( K \) is the magneto-crystalline anisotropy constant, and \( \bar{d} \) is the mean particle diameter. It is well known that the permeability of polycrystalline ferrite can be described as the superposition of two different magnetizing mechanisms: spin resonance and domain wall motion [48], which can be described as follows:

\[
\mu = 1 + \chi_{\text{spin}} + \chi_{\text{dw}} = 1 + 2\pi \frac{M_s^2}{K} + 3\pi \frac{M_s^2 D}{\gamma y}
\]

\[\ldots\ldots\text{Eq. 22}\]
Figures 5.11(a-e): Variation of real part of complex permeability with Cr$^{3+}$ concentration exhibiting high value of permeability around $x=0.07$. 

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Where, $\chi_{dw}$ is domain wall susceptibility and $\chi_{\text{spin}}$ is intrinsic susceptibility originating from the electronic spin, $M_s$ is the saturation magnetization, $\gamma$ is the wall energy, $D$ is the grain diameter and $K$ is total anisotropy. The factor $\chi_{dw}$ contributes at low frequencies while the factor $\chi_{\text{spin}}$ is active at relatively higher frequencies. The value of initial permeability increases and the loss decreases with the increase of domain motion. It is also known that domain wall motion can be enhanced with more uniformly distributed and bigger grain size as well as with increased sintering density [49]. It means that a material with more uniformly distributed and relatively bigger grains will favour the enhanced initial permeability and low loss. But in the present study the results are contradictory to the above factual statement. This unusual trend can be explained as follows:

The retaining of good soft magnetic behaviour while simultaneously maintaining the low dimensionality of grains seems to be at odd and contrasting to the classical rule of soft magnetic engineering which asserts that a lowering in dimensionality of grain imposes adverse effects on the soft magnetic properties of poly-crystalline magnets [50]. In case of nano-sized grains, there may be deviations from this rule because as a matter of fact, this rule applies only as long as the grain diameter ($D$) is larger than the ferromagnetic exchange length ($L_{ex}$). When $D < L_{ex}$, the magnetocrystalline energy is averaged out because the magnetization cannot follow the easy directions within each individual grain and the initial reversible permeability, $\mu_i$ can be related to $K$ and $D$. The interaction among the grains induces a decrease of the magnetocrystalline anisotropy by a factor depending on the number of grains with size $D$ in an exchange volume ($L_{ex}^3$). Thus, the so good soft magnetic properties are related to the very low values reached for $K$ that are of the order of magnitude of a few J/m$^3$. The lowering of the value of $K$ is due to its random distribution such that the average value is scaled smaller as compared to $D$. The complete picture of the mechanism involved can be given by making use of Random Anisotropy Model (RAM) originally proposed by Alben et al. [51]. The basic idea is given in the sketch given below which starts from an assembly of ferromagnetically coupled grains of size $D$ with magneto-crystalline anisotropies $K_i$ oriented at random.

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The final magnetic behaviour of a cluster of nanocrystalline grains is the resultantant of the interplay between local magnetic anisotropy energy and ferro/ferri- magnetic exchange energy. In case of larger grains, the magnetization follows easy axis and so its magnetization is determined by magnetocrystalline anisotropy constant $K_I$. On the other hand, the exchange interaction tries to make the magnetic moments parallel, thus reducing their chance to align along easy axis. As a result of this the net magnetic anisotropy is averaged out as $<K> = \frac{K}{\sqrt{n}}$ and thus its value reduces. As a consequence, the value of $L_{ex}$ increases according to the relation $L_{ex} = \left(\frac{A}{<K>}\right)^{1/2}$ where, $A$ is the exchange stiffness.

Although the RAM was actually proposed for nanocrystalline ferromagnetic materials, in the present case the variation of permeability spectra with grain diameter following the same trend is in accordance with the RAM model. Thus we can conclude that RAM model can also explain the unusual magnetic behaviour of not only nanocrystalline ferro- magnets but it can also explain the same for nanocrystalline ferrimagnetic materials. In fact, ferrites are special class of ferromagnetic materials. As it is evident from the Fig. 5.11 that permeability attains highest value at all temperature and frequencies around the dopant concentration of $x = 0.07$ which is also supported by the
values of saturation magnetization being highest at the same dopant concentration. In fact, the value of \( \mu'_r \) also very much depends upon the processing technique and the subsequent heat treatment which modulates porosity. This type of behaviour gives rise to resonance character, resulting in the formation of poles creating demagnetizing fields and consequently a reduction in magnetic losses [52].

5.4.3.4. Frequency dependency of relative quality factor

The quality factor is the measure of performance of an inductive material. Fig. 5.12(a-g) illustrates the variation of relative quality factor \( Q_r \) as a function of frequency at different temperatures for all dopant concentration. As evident from figure, \( Q_r \) increases with an increase in frequency, attains a maximum value at certain frequency, beyond which it gradually decreases at elevated frequencies. It can also be noted that value of \( Q_r \) decreases with increase of temperature which can be attributed to the fact that at higher temperature thermally-induced strains are generated within the system which in turn induce imperfections and in-homogeneity in the material. Apart from that, the peak value shifts towards higher frequencies which are in accordance with the shifting of resonance loss peak in the \( \mu'' \) spectra in Fig. 5.9(a-g).
Figure 5.12(a-g): Variation of relative quality factor ($Q_r$) as a function of frequency at different temperatures for all dopant concentrations. Decrease in $Q_r$ with increase of temperature can be due to thermally-induced strains within the system.
5.4.4. Optical analysis (dual band gap structure)

Despite numerous investigations and studies, the optical behaviour of nano-sized \( \gamma \)-Fe\(_2\)O\(_3\) particles has not been well understood till today. The UV-Vis absorbance spectra of all the samples are shown in Fig. 5.13. It is obvious from the UV-Vis spectra that \( \gamma \)-Fe\(_2\)O\(_3\) in nano-structured form is capable of absorbing a wide range of visible spectra. As it can be noted that there are two absorption peaks appeared at two different wavelengths corresponding to dual optical transition at these points which is observed in the form of dual band gap in \((\alpha h\nu)^2\) versus \(h\nu\) plots.

**Figure 5.13:** UV-Vis spectra of all samples showing that the material is capable of absorbing over a wide region of spectrum.
Fig. 5.14(a-g) illustrates \((ahv)^2\) versus \(h\) plots for various compositions. It can be readily observed from these plots that two lines can be tangentially extrapolated on the curves which originate due to the two optical transitions corresponding to two optical band gaps \(BG_{d1}\) and \(BG_{d2}\) observed around 2.60 and 3.80 respectively. Thus, this material can be categorized as the class of multi-band semiconductors which can be potentially useful in the processes to convert optical energy and electrolytic dissociation of water molecules into fuel hydrogen [53]. But until very recently, practical realization of semiconductors with this multi-band structure has not been achieved. Another interesting phenomenon that can be observed from the plots is that \(BG_{d2}\) continuously increases with the \(Cr^{3+}\) doping whereas \(BG_{d1}\) initially decreases with the doping up to \(x = 0.08\) beyond which it becomes constant. This indicates that two different kind of optical transition mechanisms are active in the system which are responsible for the opposite progression of two band gaps. The increase in optical band-gap with the reduction of particle size is the well established common behaviour which can be explained by the quantum size effects of an electron-hole pair confined in a semiconductor nanoparticle [54-57]. The energy gap \(E_r\) of a particle of radius \(r\) is determined by the following equation [58]:

\[
E_r = E_g + \frac{\pi^2 \hbar^2}{2 \mu r^2} - \frac{1.786e^2}{\varepsilon_1 r} - \frac{0.248\mu e^4}{2\varepsilon_1^2 \hbar^2} \quad \cdots 6.23
\]

Where, \(E_g\) is the energy band gap for bulk semiconductor material, \(\hbar = \hbar/2\pi\), \(\hbar\) is the plank constant, \(\mu = \frac{m_e m_h}{m_e + m_h}\) is the effective mass of electron-hole pair and \(\varepsilon_1\) is dielectric constant. It is clear from the above equation that the energy band gap has some sort of
Figure 5.14(a-g): Extrapolations on \((\alpha h\nu)^2\) versus \(h\nu\) plots for various compositions confirming the dual band gap nature of the material.
inverse relationship with the grain diameter. Thus the widening of BG42 with the
reduction of grain size is justified. On the other hand the variation of BG41 is quite
unusual. The trends of the two band gaps variation indicate the different optical
behaviour of the material in different wavelength ranges. In the blue region of visible
spectrum, there is blue shifting (normal trend) while in the red region there is shifting
towards red up to x = 0.08 beyond which the shifting ceases. This is contrary to the
normal phenomenon of quantum confinement. Chun-Mingetal [59] have already reported
band gap narrowing effect for doped oxide nanoparticles. However there is no clear
understanding of this phenomenon. A direct–indirect transition has been proposed by
Rakhshani et.al. [60]. In fact, the wave and electrical behaviour within a few nanometer
or within a nanostructure is entirely different from the one observed in bulk materials.
This difference is not surprising since the structure itself imposes field variations on a
scale that is much smaller than the scale outside the nanostructure. Thus such nonlinear
optical response may be due to joint effect of Fe3+-Fe3+ pair excitations (double
excitons) processes observed in the case of γ-Fe2O3 [61], polaron hopping and non-linear
variations in refractive index and wave vector (and hence the absorption coefficient
\( \alpha(\omega) = \frac{3\pi K(\omega)}{\lambda_0} \)) of the system with wavelength. The optical properties of a material
depend on how the charge carriers inside the material respond to optical fields. When
light shines inside a material, there is optically induced rearrangement of charge carriers,
ions, or group of atoms inside the system. In the present case this optical induction is
wavelength dependent and is prominent at larger wavelengths.

The origin of two direct band gaps in the present case can be best explained by
taking into account the well-established Band Anti-crossing model (BAC). Since past few
years, a new class of semiconductors called highly mismatched alloys (HMAs) have
attracted much attention. The fundamental properties of HMAs are dramatically modified
through the substitution of a relatively small fraction of host atoms or through
introduction of defects. The unusual properties of HMAs are well explained by BAC
model [62-64]. In the present case, there may be oxygen non-stoichiometry in the system
which is responsible for the creation of localized defect states sufficiently close to the
conduction-band edge of the host matrix to undergo a quantum anti-crossing interaction with the extended states of the matrix in the form of the hybridization of extended p-orbital. This interaction produces a splitting of the conduction band into \( B G_{d1} \) and \( B G_{d2} \) levels, with the downward movement (reduction) of the \( B G_{d1} \) leading to the band gap bowing which is commonly observed in the diluted alloys. These results are direct evidence that the nano-sized \( \gamma \)-Fe\(_2\)O\(_3\) synthesized by cost effective and modified sol-gel auto-combustion technique (described in detail in section 2) can be a good alternative of HMAs. Further, as \( B G_{d1} \) and \( B G_{d2} \) fall within the visible energy spectrum, this can be a promising material for single junction photovoltaics with enhanced power conversion efficiency.

The existence of two band gaps and their variation with the dopant concentration was further verified by means of differential plots. For this purpose, the absorbance coefficients \( \alpha \) were calculated from this data leading to the calculation of the band gap \( (E_g) \) by using the relation [65]

\[
\alpha = \sum_i \alpha_i = \sum_i \frac{A_i (h\nu - E_g)^{m_i}}{h\nu}
\]

\[\ldots \ldots \text{5.24}\]

Where, \( m_i \) takes the values \( \frac{1}{2}, \frac{3}{2} \) and \( 3 \) corresponding to allowed-direct, allowed indirect, forbidden-direct and forbidden-indirect transitions respectively [66]. All the other symbols have their usual meanings.

For a specific value of \( i \) the equation may be written as

\[
 a h\nu = A (h\nu - E_g)^m
\]

\[\ldots \ldots \text{5.25}\]

Differentiating w.r.to \( h\nu \) yields

\[
\frac{d \ln (a h\nu)}{d (h\nu)} = \frac{m}{(h\nu - E_g)}
\]

\[\ldots \ldots \text{5.26}\]

Plots of \( \frac{d \ln (a h\nu)}{d (h\nu)} \) versus \( h\nu \) exhibit two discontinuities corresponding to the two band gaps as shown in Fig. 5.15(a-g).
Figure 5.15(a-g): Further confirmation of multiband gap nature of the material through the discontinuities observed in $dln(\alpha hv)/d(hv)$ versus $hv$ plots.

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5.5. Conclusions

The main findings and results of the present study can be summarized as follows:

i. We have successfully synthesized Cr$^{3+}$ doped nano-structured $\gamma$-Fe$_2$O$_3$ by solution combustion technique.

ii. The powder XRD confirms the phase purity of the material.

iii. The FT-IR studies of the samples in the range 4400–400 cm$^{-1}$ provide an insight about the chemical bonding of the system.

iv. Microstructural imaging through TEM and FE-SEM confirms the continuous reduction of grain size with Cr$^{3+}$ doping.

v. A continuous decrease in blocking temperature (378–260 K) as well as the crystallite size (25.61–16.91) was observed with the dopant concentration which is explained on the basis of Neel’s relaxation model.

vi. Magnetization analysis revealed that the room temperature saturation magnetization first increases with the dopant concentration up to $x = 0.07$ beyond which it falls off rapidly. This behaviour has been explained on the basis of Neel’s theory of antiferromagnetism.

vii. The complex permeability measurements revealed the significant enhancement in permeability after Cr$^{3+}$ doping thus making this material a cheaper alternative of material for applications in magnetic cores and Multi-layer Chip Inductor (MLCI).

viii. Real permeability shows unusual behaviour (enhancement of permeability with reduction of grain size). This has been explained on the basis of Random Anisotropy Model (RAM). The grain diameter in the present case is smaller as compared to the ferromagnetic exchange length thus making this material to deviate from the normal behaviour.

ix. The temperature variation plots of real permeability project an interesting feature that the permeability at 20MHz and 25MHz is approximately independent of temperature and for $x = 0.09$ there is a little variation in permeability with temperature which is a feature desirable in applications where the permeability should not vary significantly with changes in temperature, for example, magnetic components in telephone and transmission lines where temperature variations are inevitable.
x. It was observed that permeability attains highest value at all temperature and frequencies around the dopant concentration of $x = 0.07$ which is also supported by the values of saturation magnetization being highest at the same dopant concentration.

xi. Optical characterization revealed dual band gaps falling within the visible energy spectrum, thus making this material a promising candidate for single junction photovoltaics with enhanced power conversion efficiency.
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CHAPTER 6

SUMMARY, SCOPE
AND
FUTURE WORK
6.1. Introduction

Low dimensional materials have emerged as promising candidates form the fundamental point of view to more advanced applications. In fact, the nano-sized materials often exhibit remarkable properties which are drastically contrasting as compared to those possessed by their bulk counterparts. This is due to the fact that as the dimensions of particle approach the nano-scale, the number of atoms residing on the surface of the particle increases and at a few nanometer size, 80-90% of atoms occupy the boundary of the grain. This surprisingly enhances the active sites within the system. Another reason is that low dimensional materials do not have inertia due to negligible mass of constituent particles and hence the kinematics and dynamics of nano-scaled systems are independent of gravitational influences. Apart from that in low dimensional regime, the behaviour of particle is governed by the laws of quantum mechanics. Since the last two decade there has been a growing interest in the development and fabrication of magnetic nanomaterials because of discovery of astonishing new phenomena, with potential applications in the fields of information technology, telecommunication, medicine, high frequency material, magnetic core materials and sensing applications. The nano-sized magnetic materials are generally composed of ferro/ferri/antiferro magnetic particles. The size, shape and distribution of the particles play an important role in determining their properties. In the present thesis, synthesis and characterization of nano-structured systems having composition Mg(Cr0.5_Al0.5)3Fe2_xO4, Fe2_xCr_xO3, and Bi1-xAl2xFe1-xO3, has been carried out. The synthesis has been done by normal and modified solution combustion techniques. The so prepared materials were investigated broadly for structural analysis, optical band gap measurement, a.c. and d.c. electrical transport properties, dielectric studies, sensing behaviour, and magnetic properties.

6.2. A detailed study of Al³⁺ doped Bismuth Ferrite

In this chapter, aluminium doped bismuth ferrite (BFO) nanopowders (grain size 13–20 nm) having composition Bi1-xAl2xFe1-xO3 (x = 0.00, 0.025, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) were successfully synthesized by solution combustion method using citric
acid as fuel at a temperature as low as 200 °C. As-prepared samples were examined by powder XRD for phase identification and crystallite size determination. The X-ray patterns suggest that Al$^{3+}$ ions have been successfully doped in the BiFeO$_3$ matrix and crystallite size varying from 13.0 nm to 19.6 nm. FTIR analysis was carried out to identify the chemical bonds present in the system. FT-IR measurements confirm perovskite nature of the samples. The d.c. resistivity as a function of temperature was measured by standard two probe setup. All samples exhibit metal insulator transition temperature ($T_{MI}$) at 325 K. The resistivity is increasing with Al$^{3+}$ concentration and follows the Arrhenius behaviour. The activation energies calculated from the slopes of ln($\rho$) versus $10^3$/T plots are in the range 0.54–0.73 eV. Activation energy was found to increase with doping. The optical band gap was calculated from the UV–Vis absorbance spectra using classical Tauc relation which was found to vary from 2.78 eV to 2.93 eV for different Al$^{3+}$ concentrations. Optical band gap was observed to vary from 2.78 eV to 2.93 eV on increasing the dopant concentration from 0.00 to 0.30, which is higher compared to bulk BFO (1.82 eV). Higher values of band gaps for these ceramics are quite compatible with their high resistivity. It was observed that Al$^{3+}$ concentration influences the structural and dielectric properties of the material. Dielectric relaxation was investigated over a wide range of frequency and temperature. Relaxation peaks were obtained in low as well as high frequency regions for all samples which are explained on the basis of Debye-type relaxation model. The replacement of Fe$^{3+}$ and Bi$^{3+}$ by Al$^{3+}$ ions in the BFO system creates oxygen vacancies and hence Schottky barriers, which are responsible for the anomalous behaviour in the dielectric properties. Debye relaxation model and Maxwell–Wagner charge carriers hopping were utilized in overall estimation of the dielectric behaviour of the system. The values of dielectric constant and loss tangent were found to decrease with the increase in frequency, while these parameters increase with the increase in temperature as well as dopant concentration. The a.c. conductivity has a general decreasing trend as a function of composition while it increases with the increase in frequency. The temperature dependence of a.c. conductivity and relaxation time follow well-defined Arrhenius behaviour. The calculated values of activation energies are in the order of 0.54 eV–0.73 eV (<1.0 eV) which are indicative of
the conduction by means of space charge carriers and O\(^2-\) vacancies. The frequency and temperature dependence of dielectric spectra show dispersion and relaxation which has been justified on the basis of Debye-relaxation model and Maxwell-Wagner type charge carrier hopping. Relaxation time was evaluated from the fitted Cole-Cole model. The a.c. conductivity has been accounted on the basis of charge imbalance caused by the oxygen non-stoichiometry and lattice defects (pores) created by the foreign impurity atoms (dopant). The plots of relaxation time and the a.c. conductivity as the function of inverse absolute temperature follow the famous Arrhenius expression.

6.3. Simultaneous doping of two cations in MgFe\(_2\)O\(_4\) system

In this Chapter, we have shown that a combination of Al\(^{3+}\) and Cr\(^{3+}\) ions can be incorporated in the lattice system of MgFe\(_2\)O\(_4\) which alter the electrical and magnetic behaviour of the material. We have successfully synthesized chromium (Cr\(^{3+}\)) and aluminium (Al\(^{3+}\)) co-doped nano-scale (9 nm – 17 nm) spinel magnesium ferrite of the composition Mg(Cr\(_{0.5}\_Al_{0.5}\)\(_x\)Fe\(_{2-x}\)O\(_4\) (for \(x = 0.00, 0.10, 0.15, 0.20, 0.25, 0.30\)) utilizing inexpensive materials and very easy one step sol-gel combustion technique using urea as fuel. The so prepared nano-sized powders were characterized by powder XRD for confirmation of phase-purity and crystallite size determination. The FT-IR spectroscopy was carried out to confirm the various bonds present in the system and also to detect traces of impurity materials as by-products of the reaction. Morphological studies were carried out by atomic force microscopy (AFM) and FE-SEM which revealed the reduced particle size and enhanced porosity with doping. Response of the sensor was measured by Keithley source meter interfaced with the computer. There is three order of magnitude reduction in the dielectric constant in the nano version of the material. Apart from that, the measured values of tan\(\delta\) in the present study are in the range 0.10 –1.80 which are almost 6 times lower as compared to that of bulk MgFe\(_2\)O\(_4\). Complex impedance spectroscopy of the material reveals the existence of grain and grain-boundaries up to \(x = 0.150\) beyond which only the insulating grain boundaries become effective. Along with the actual impedance plots, the Z-View fitted data of the same has also been provided for the sake of convenience. Cation distribution scheme and hence a general expression for
magnetic trend was approached by considering the magnetic M–H data from VSM. Unusually high room temperature magnetism and abnormal coercive behaviour was observed which has been explained on the basis of various competing factors arising due to non-stoichiometry, low dimensionality, and doping. Composition dependent impedance analysis reveals the existence of insulating grain boundaries around relatively conducting grains. Magnetic analysis exhibits unusual magnetic behaviour which has been explained on the basis of the various interacting parameters arising due to low dimensionality of the grains and lattice defects due to dopant species. Scheme of cation distribution in tetrahedral (A) and octahedral (B) sites has been devised by the analysis of magnetic data. The cation distribution scheme was further utilized to suggest a general expression for the trend of magnetization between the given limit of doping. Further, the material was tested for LPG and humidity sensing properties. It was found that the sensor exhibits fast and intensive response at relatively low operating temperature (120 – 130 °C at 85 % (RH) and 60 – 70 °C at 400 ppm LPG). The humidity response time was observed to be in the range 50 – 60 sec, while the same for LPG was measured to be in the range 40 – 50 sec. The various steps of humidity sensing mechanism have been explained in detail on the basis of Grothuss chain mechanism. The Nano-structured MgFe$_2$O$_4$ is itself a good sensing material. Replacing Fe$^{3+}$ by a combination of 0.5 Cr$^{3+}$-0.5 Al$^{3+}$ significantly enhance its sensing properties due to creation of nanostructures, pores and defects. The MgFe$_2$O$_4$ is partially inverse spinel. Replacing octahedral Fe$^{3+}$ ions by a combination of Cr$^{3+}$-Al$^{3+}$ ions affects the Fe$^{2+}$ $\leftrightarrow$ Fe$^{3+}$ hopping conduction scheme. Apart from that, the combination of Cr$^{3+}$-Al$^{3+}$ together with the Mg$^{2+}$ ions on octahedral site introduces more electrons in the system. Doping also favours the creation of the cation vacancies which allow the dissociation of oxygen in their vicinity. All these phenomena are conductivity enhancing factors and hence improving the sensing behaviour of the material. Thus we conclude that the spin coated films of Cr$^{3+}$ and Al$^{3+}$ doped nano-sized MgFe$_2$O$_4$ materials offer good sensing response towards both humidity as well as LPG.
6.4. Study of Cr$^{3+}$ doped $\gamma$-Fe$_2$O$_3$

In this chapter, Chromium doped Gamma Ferrite nanopowders of the composition (Fe$_{2-x}$Cr$_x$O$_3$ for $x$=0.00, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10) were successfully synthesized by a modified solution combustion method using citric acid as fuel at a temperature as low as 150 °C. The so prepared samples were examined by powder XRD for phase identification and crystallite size determination. FT-IR analysis was carried out to identify the various chemical bonds present in the system. Magnetic examinations were performed in terms of magnetic susceptibility, hysteresis plots and magnetic permeability. A decrease in the blocking temperature with the increase of dopant concentration was observed which is explained on the basis of Neél's relaxation theory. A simple model has been suggested to explain the behaviour of hysteresis trends as the function of dopant concentration. The powder XRD confirms the phase purity of the material. The FT-IR studies of the samples in the range 4400–400 cm$^{-1}$ provide an insight about the chemical bonding of the system. Microstructural imaging through TEM and FE-SEM confirms the continuous reduction of grain size with Cr$^{3+}$ doping. A continuous decrease in blocking temperature (378–260 K) as well as the crystallite size (25.61nm–16.91nm) was observed with the dopant concentration which is explained on the basis of Neél's model. Magnetization analysis revealed that the room temperature saturation magnetization first increases with the dopant concentration up to $x = 0.07$ beyond which it falls off rapidly. This behaviour has been explained on the basis of Neél's theory of antiferromagnetism. The complex permeability measurements revealed the significant enhancement in permeability after Cr$^{3+}$ doping thus making this material a cheaper alternative of inductive materials which have applications in magnetic cores and Multi-layer Chip Inductor (MLCI). Real permeability shows unusual behaviour (enhancement of permeability with reduction of grain size). This has been explained on the basis of Random Anisotropy Model (RAM). The grain diameter in the present case is smaller as compared to the ferromagnetic exchange length thus making this material to deviate from the normal behaviour. The temperature variation plots of real permeability reveals an interesting feature; that the permeability at 20MHz and 25MHz is approximately independent of temperature and for $x = 0.09$ there is a little variation in
permeability with temperature which a feature desirable in applications where the permeability should not vary significantly with changes in temperature, for example, magnetic components in telephone and transmission lines which can be subject to changes in temperature. It was observed that permeability attains highest value at all temperature and frequencies around the dopant concentration of \( x = 0.07 \) which is also supported by the values of saturation magnetization being highest at the same dopant concentration. Optical characterization revealed dual band gaps falling within the solar energy spectrum, thus making this material a promising candidate for single junction photovoltaics with enhanced power conversion efficiency.

6.5. Scope of the present work

i) BiFeO\(_3\), extreme doping, new properties

As it is well known that synthesis of phase pure BiFeO\(_3\) is a difficult task. Synthesis of doped material is rather challenging. In the present study we achieved control over the synthesis of highly doped material in single phase. The material so prepared exhibited some new and remarkable electronic properties which have implications in futuristic devices.

ii) Mg(Cr\(_{0.5}\_Al_{0.5}\))\(_2\)Fe\(_{2-x}\)O\(_4\): A new material for promising applications.

MgFe\(_2\)O\(_4\) is well known for its sensing applications for humidity. Incorporation of Cr\(^{3+}\) and Al\(^{3+}\) ions on Fe\(^{3+}\) sites alters its properties by inducing its sensing ability towards LPG while retaining the humidity sensing at the same time.

ii) Tailoring the Properties of \(\gamma\)-Fe\(_2\)O\(_3\) by Cr\(^{3+}\) doping: A new candidate for magnetic core material.

\(\gamma\)-Fe\(_2\)O\(_3\) is not known for its permeability applications. When doped with Cr\(^{3+}\) ions, it shows surprisingly enhanced permeability which makes it a cheap alternative as magnetic core material. Apart from that the optical properties of the material can be exploited in the field of photo-catalysis and optoelectronics.
6.6. Future work

In view of the abovementioned findings and conclusions we have plan to further proceed the study of the materials presented in this thesis as follows:

i) To use the nano-sized BiFeO$_3$ and its doped variants in photo-voltaic applications.

ii) To see the variation of photo-voltaic properties of BiFeO$_3$ in the presence of external magnetic and electric fields since these fields change the geometry of the lattice and hence the response towards light.

iii) To estimate the degree of coupling in BiFeO$_3$ system in terms of coupling constants.

iv) To investigate the possibility of the existence of new magnetic and electric states in BiFeO$_3$ and its derived systems to use these materials in ultra-high storage devices.

v) To test the sensitivity of MgFe$_2$O$_4$ and its derived systems for a variety of gases.

vi) To extend the study of MgFe$_2$O$_4$ doped by various ions specially rare-earth cations.

vii) To investigate the temperature dependent magnetic behaviour of MgFe$_2$O$_4$ and to explore the magnetic storage possibilities of the material.

ix) Comparative analysis of $\gamma$-Fe$_2$O$_3$ synthesized by using different fuel systems.

x) To explore the in vitro and in vivo potential of the native and doped $\gamma$-Fe$_2$O$_3$ towards various pathogenic species.

xi) To use $\gamma$-Fe$_2$O$_3$ in magnetic hyperthermia for the treatment of breast malignancies.
Appendix
List of publications in peer reviewed journals


x) **Ali Jawad**, Iqbal Ahmed Ansari, *"Characterizing the image operators"* Physics Bulletin. Vol. 1. No. 06, Department of Physics, Aligarh Muslim University, Aligarh 2006.

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**List of publications in conferences/symposia**


Copies of front pages of papers published in peer reviewed journals
Structural, optical and transport properties of Al\textsuperscript{3+} doped BiFe\textsubscript{3}O\textsubscript{5} nanopowder synthesized by solution combustion method

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ABSTRACT

Aluminum doped Bismuth ferrite (BFO) nanopowders (grain size 13–20 nm) having composition Bi\textsubscript{1-x}Al\textsubscript{x}Fe\textsubscript{2}O\textsubscript{5} (x = 0.00, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3) were successfully synthesized by solution combustion method using citric acid as fuel at a temperature as low as 300°C. As-prepared samples were examined by powder XRD for phase identification and crystallite size determination. The d.c. resistivity as a function of temperature was measured by standard two probe setup which exhibits clear metal to insulator transition for all samples. FTIR analysis was carried out to identify the chemical bonds present in the system. The optical band gap was calculated from the UV–Vis absorption spectra using classical Tauc relation which was found to vary from 2.78 eV to 2.93 eV for different Al\textsuperscript{3+} concentrations. The activation energies calculated from the slopes of ln(\rho) versus 1/T plots are in the range 0.54–0.73 eV.

1. Introduction

BiFe\textsubscript{3}O\textsubscript{5} (BFO) is a perovskite material which potentially exhibits simultaneous coexistence of ferroelectric and antiferromagnetic ordering having Curie temperature (T\textsubscript{c}) 1083 K and Neel temperature (T\textsubscript{N}) 657 K\textsuperscript{[1]}. The recent investigations have suggested that this material is very promising material for its possible applications especially in the fields of radio transmission, microwave and satellite communication, digital recording, and permanent magnet applications. Bismuth and its compounds may hold the key for future electronics due to their highly frustrated structures. BFO is not new but in the earlier years of its birth it failed to make any remarkable impact on the then electronic industries due to problem of leakage current that was rooted in nanostructurization. The main reason is that the BFO nanopowders synthesized by even established methods are generally plagued by impure phases. In its bulk form, measurements of ferroelectric and transport properties in BFO and its derivatives have been limited by the problem of leakage, mainly due to low resistivity, lattice defects and nanostructurization.

The properties of BFO can be tailored significantly by chemical substitution at both Bi and Fe sites. There are many reports on the site substituted BFO recipes. Li et al. investigated the Sr doping on Bi site, resulting the samples being oxygen stoichiometric\textsuperscript{[2]}. Further, they concluded that with the increase of Sr concentration, SrFe\textsubscript{2}O\textsubscript{5} phase evolves which leads to diminished magnetization. Similar results were obtained by Khomchenko et al. with Ca and Ba doped BFO\textsuperscript{[3]}. Lee et al. prepared La doped BFO thin films with increased dielectric constant and remnant polarization which they attributed to the increased crystallinity and lattice volume with La doping\textsuperscript{[4]}. Further, La doped BFO nanocrystals exhibited improved magnetization due to phase transition\textsuperscript{[5]}. Another report confirms the enhancement in multifaceted properties of La doped BFO samples which they attributed to the enhanced magnetoelectric interaction\textsuperscript{[6]}. Al\textsuperscript{3+} doping at Bi site has been investigated for photovoltaic applications by Madhu et al.\textsuperscript{[7]}. To the best of our knowledge no report is available on the transport properties of Al\textsuperscript{3+} doped BiFe\textsubscript{3}O\textsubscript{5} nanopowder. This paper presents the investigation of the optical properties and transport behavior in terms of d.c. resistivity of the BFO samples doped by Al\textsuperscript{3+} at both Bi and Fe sites.

2. Experimental

In a typical synthesis procedure, stoichiometric amounts of Bi(NO\textsubscript{3})\textsubscript{3}•5H\textsubscript{2}O (99.00%, S.D. Fine Chemicals), Fe(NO\textsubscript{3})\textsubscript{3}•9H\textsubscript{2}O (99.00%, S.D. Fine Chemicals) and Al(NO\textsubscript{3})\textsubscript{3}•9H\textsubscript{2}O (98%, Merck Chemicals) were dissolved in minimum amount of double distilled water. All chemicals were of reagent grade and used without further purification. As Bi(NO\textsubscript{3})\textsubscript{3}•5H\textsubscript{2}O undergoes decomposition into bismuth oxychloride...
Exploring the dielectric behaviour of nano-structured Al$^{3+}$ doped BiFe$_{3}$O$_{5}$ ceramics synthesized by auto ignition process

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**Abstract**

Dielectric relaxation and electrical properties of Al doped polycrystalline bismuth ferrite (BAFO) nano-structured ceramics (13–20 nm having composition Bi$_{1-x}$Al$_{x}$Fe$_{3}$O$_{5}$ (0.6 ≤ x ≤ 0.3) were investigated over a wide range of frequency and temperature. Relaxation peaks were obtained in low as well as high frequency regions for all samples which are explained on the basis of Debye-type relaxation model. The replacement of Fe$^{3+}$ and Bi$^{3+}$ by Al$^{3+}$ ions in the BFO system creates oxygen vacancies and hence Schottky barriers, which are responsible for the anomalous behaviour in the dielectric properties. Debye relaxation model and Maxwell-Wagner charge carriers hopping were utilized in overall estimation of the dielectric behaviour of the system. The values of dielectric constant and loss tangent were found to decrease with the increase in frequency, while these parameters increase with the increase in temperature as well as dopant concentration. The a.c. conductivity has a general decreasing trend as a function of composition while it increases with the increase in frequency. The temperature dependence of a.c. conductivity and relaxation time follow well-defined Arrhenius behaviour. The calculated values of activation energies are in the order of 0.54 eV–0.73 eV (<1.0 eV) which are indicative of the conduction by means of space charge carriers and O$^{2-}$ vacancies.

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**1. Introduction**

The class of perovskite-type materials (BiFeO$_{3}$, BiMnO$_{3}$, and TbMnO$_{3}$) have attracted much attention as the dielectric polarization and magnetization have mutual control over one another in such type of materials [1]. BiFeO$_{3}$ (BFO) is the perovskite material which potentially exhibits simultaneous coexistence of ferroelectric and antiferromagnetic ordering characterized by having Curie temperature ($T_{C}$) 1083 K and Neel temperature ($T_{N}$) 657 K [2].

The dielectric properties of BFO in various forms have also been widely studied in single crystal, ceramic, and thin film forms [3–5]. Recently, Scott et al. related the low temperature dielectric anomaly and their magnetic coupling in ceramic and single-crystalline BFO and reported the existence of coupling between FE and AFM order parameters in single crystal and ceramic BFO [6–8]. The polycrystalline BFO samples manifested a decrease in the real part of permittivity ($\varepsilon^\prime$) and loss tangent (tan $\delta$) when the frequency is increased. Additionally, the presence of slight amounts of nonstoichiometric oxygen in BFO often leads to the presence of Fe$^{2+}$ and lattice defects thereby resulting in an unwanted increase in the conductivity at room temperature due to a hopping mechanism from Fe$^{3+}$ to Fe$^{2+}$. The high leakage current in bulk BFO synthesized by solid solution methods also leads to serious dielectric breakdown at fields <100 kV/cm which makes them unsuitable for practical devices [9]. To overcome this problem and to get higher resistive material, various approaches have been attempted, such as doping with various rare earth and transition metal ions and a solid solution of BFO with other ABO$_{3}$ perovskite materials. But these methods also often result in impure phases. The physical properties of single crystalline materials do change significantly on nanoscale, and it is important to study these size-dependent changes in the material properties to find potential applications of such nanoscale materials for devices. Recently, due to the advancements in wet chemical techniques to synthesize these complex oxides, there has been a surge in the studies of BFO on nanoscale [10–12].

There are many reports on the site substituted BFO recipes. Li et al. investigated the Sr doping on Bi site, resulting the samples being oxygen substoichiometric [13]. Further, they concluded that with the increase of Sr concentration, SrFeO$_{3}$ phase evolves which leads to diminished magnetization. Similar results were obtained by Khomchenko et al. with Ca and Ba doped BFO [14]. Lee et al. prepared La doped BFO thin films with increased dielectric constant and remnant polarization which they attributed to the increased crystallinity and lattice volume with La doping [15].
Fabrication of Nano-Structured Mg(Cr_{0.5-Al_{0.5}} x Fe_{2-x}O_{4} Ceramics for Gas Sensing Application

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We have investigated the LPG and humidity sensing properties of chromium (Cr³⁺) and aluminium (Al³⁺) co-doped nano-scale (9 nm–17 nm) spinal magnesium ferrite of the composition Mg₃(Crₓ₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃₋₃_- )

Keywords: LPG Sensing, Humidity Sensing, Grothuss Chain Mechanism, Sol-Gel Combustion, Thin Film Sensor, Spinal Nanoferrites.

1. INTRODUCTION

Partially inverse spinel of magnesium ferrite (MgFe₂O₄) and its doped derivatives have attracted considerable attention due to their wide range of technological applications, like heterogeneous catalysts, gas and humidity sensors, photochemical applications and for creating local hyperthermia (in which tumours are locally heated by the application of alternating magnetic fields) in cancer treatment. Apart from that nano-scale MgFe₂O₄ has great importance for applications in modern technologies. In fact, the uses of this material are remarkable, ranging from pharmaceutical products to magnetic drug carriers, contrast agents in magnetic resonance images, ferrofluid technology, storage of information by high-density magnetic materials and magnetoacorific refrigeration to name a few. In MgFe₂O₄, the Mg²⁺ ions are diamagnetic due to which the magnetic coupling between A and B sites is relatively weaker and mainly originates from the strongly magnetic Fe³⁺ ions. The degree of inversion in MgFe₂O₄ can be affected by the substitution of foreign atoms in the spinel lattice eventually determining the magnetic, electrical and sensing behaviour of the material. Among resistive-type humidity sensors, the electrical response of an MgFe₂O₄ ceramic sensor has been discussed in various reports. The gas-sensing properties of spinel ceramics were also investigated, for example, MgFe₂O₄, ZnFe₂O₄, and CdFe₂O₄ were studied for oxygen sensing properties. A different type of
Complex Impedance and Magnetic Properties of Cr$^{3+}$, Al$^{3+}$ Co-Doped MgFe$_2$O$_4$ Nano-Structured
Ceramics Synthesized by Sol–Gel Combustion Process

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ABSTRACT

We have successfully synthesized Chromium (Cr$^{3+}$) and aluminium (Al$^{3+}$) co-doped nano-scale (9 nm–17 nm) spinel magnesium ferrite of the composition Mg$_{0.5}$Al$_{0.5}$Fe$_{2.5-x}$Cr$_x$O$_4$ (for x = 0.00, 0.10, 0.15, 0.20, 0.25, 0.30) utilizing inexpensive materials and very easy one step sol–gel combustion technique using urea as fuel. Composition dependent impedance analysis revealed the existence of insulating grain boundaries around relatively conducting grains. Magnetic analysis shows unusual magnetic behaviour which has been explained on the basis of various interacting parameters arising due to low dimensionality of the grains and because of lattice defects due to dopant species. A scheme of cation distribution in tetrahedral (A) and octahedral (B) sites has been devised through the analysis of magnetic data. The cation distribution scheme was further utilised to suggest a general expression for the magnetization trend observed between the given doping limit.


1. INTRODUCTION

Since the last decade, nano-structured magnetic materials have received considerable attention due to their novel material properties that are significantly different from those of their bulk counterparts. Nano-structured spinel-type pure as well as doped ferrites have emerged as key materials having promising applications in the field of electronics, magnetic storage and ferro-fluid technologies as well as bio-inspired applications. Partially inverse spinel of magnesium ferrite (MgFe$_2$O$_4$) and its doped derivatives have attracted considerable attention due to their wide range of technological applications like heterogeneous catalysts, gas and humidity sensors, photochemical applications and for creating local hyperthermia (in which tumours are locally heated by the application of alternating magnetic fields) in cancer treatment. Apart from that nano-scale MgFe$_2$O$_4$ has great importance for applications in modern technologies. In fact, the uses of this material are remarkable, ranging from pharmaceutical products to magnetic drug carriers, contrast agents in magnetic resonance imaging. In MgFe$_2$O$_4$, the Mg$^{2+}$ ions are diamagnetic due to which the magnetic coupling between (A) and (B) sites is relatively weaker and it mainly originates from the strongly magnetic Fe$^{3+}$ ions. The structural formula of Mg-ferrite is usually written as (Mg$_{1-x}$Fe$_x$)$_{1-x}$(Mg$_x$Fe$_{2-x}$)$_x$O$_4$, where x represents the degree of inversion. The degree of inversion in MgFe$_2$O$_4$ can be affected by the substitution of foreign atoms in the spinel lattice which in turn determines the magnetic, electrical and sensing behaviour of the material. The magnetic properties of a spinel ferrite are strongly dependent on the distribution of the different cations among (A) and (B) sites. The replacement of atoms from (A), (B), or simultaneously from both the sites can immensely affect the coupling scheme between the ions which leads to entirely altered electrical and magnetic behaviour of the material.

2. MATERIAL AND METHODS

Detail of the synthesis process of the material has been published elsewhere. Only the sol system and the fuel used.
Structural and magnetic properties of Cr$^{3+}$ doped nano-structured $\gamma$-Fe$_2$O$_3$ synthesized by a modified solution combustion technique

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Abstract. Chromium doped gamma ferrite nanopowders (16.91 nm to 25.61 nm) of the composition (Fe$_{2-x}$Cr$_x$O$_3$ for $x = 0.00, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10$) were successfully synthesized by a modified solution combustion method using citric acid as fuel at a temperature as low as 150 °C. The so prepared samples were examined by powder XRD for phase identification and crystallite size determination. The dimensions of particle size as calculated from XRD are in good agreement with those evaluated by transmission electron microscope (TEM). Fourier Transform Infared (FTIR) analysis was carried out to identify the various chemical bonds present in the system. Magnetic examinations were performed in terms of magnetic susceptibility and hysteresis plots. A decrease in the blocking temperature with the increase of dopant concentration was observed which is explained on the basis of Néel's relaxation theory. A simple model has been suggested to explain the behaviour of hysteresis trends as a function of dopant concentration.

1 Introduction

Since past decade much attention has been focused on the engineering and investigation of magnetic particles produced at nano scale [1-3]. In this context iron oxide nanoparticles and their doped species remain the ideal candidates because of their potential applications in the field of storage electronics, biomedicines, biotechnology, catalytic reactions, selective removal of harmful cation species from contaminated water via adsorption which can be enhanced by improving the surface area (reducing the grain size), magnetic tunneling barrier for room temperature spin filter devices in spintronics, owing to their remarkable properties such as superparamagnetism, low Curie temperature, high coercivity and high susceptibility [4-8]. The biocompatibility and clinical importance (magnetic hyperthermia, magnetic resonance imaging) of nano-sized iron oxide has opened new vistas that can be the basis of future medical industry because their magnetism allows remote manipulation with external fields while they are potentially non-toxic to humans. Among the class of iron oxides, maghemite ($\gamma$-Fe$_2$O$_3$) is the most studied material exhibiting ferrimagnetic behavior below 1000 K (Néel temperature). Such states are due to the competing character of the exchange integral present in the system.

$\gamma$-Fe$_2$O$_3$ is the second most stable polymorph of iron oxide after the antiferromagnetic magnetite ($\alpha$-Fe$_2$O$_3$). $\gamma$-Fe$_2$O$_3$ exhibits ferrimagnetic ordering with a net magnetic moment ($\approx 2.5 \mu_B$/f.u.) which together with its chemical stability and cost effectiveness led to its wide application. The strange behavior of $\gamma$-Fe$_2$O$_3$ can also be attributed to their defective spinel geometry.

2 Experimental

In the solution combustion synthesis, the combustion of gel takes place in a much uncontrolled manner. It propagates through the volume of the gel in an irregular fashion which leads to incomplete combustion and phase impurities. Further the viscous nature of the gel hinders the free swelling of the oxide foam. Apart from that, the sudden evolution of gases at the point of ignition leads to the eruption of uncombusted gel out of the vessel which causes the loss of valuable material. To avoid these toward the proposed method offers a very simple modification for the preparation of highly phase-pure nanocrystalline $\gamma$-Fe$_2$O$_3$. In the present work Cr$^{3+}$ doped $\gamma$-Fe$_2$O$_3$ powders have been synthesized using metal nitrates as oxidizing agents and citric acid as fuel. Citric acid is chosen for this reaction because it offers ideal conditions for the synthesis of nanopowders, i.e. (i) it is water soluble, (ii) it has low ignition temperature (<400 °C), (iii) it is compatible with Fe(NO$_3$)$_3$ and Cr(NO$_3$)$_3$, (iv) it evolves huge amount of gases at the point of ignition, (v) easily available/cost effective. These properties make it ideal
Complex permeability and optical studies of Cr\textsuperscript{3+} doped nano-structured γ-Fe\textsubscript{2}O\textsubscript{3} synthesized by auto-combustion technique

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**Abstract**

We have successfully synthesized chromium doped gamma ferrite (γ-Fe\textsubscript{2}O\textsubscript{3}) nanopowders (65\textpm{} 10 nm) of the composition (Fe\textsubscript{2-x}Cr\textsubscript{x})O\textsubscript{3} for x = 0.00, 0.05, 0.07, 0.08, 0.09, 0.10 by a slightly modified solution combustion method using citric acid as fuel at considerably low temperature. The so-prepared powders were extensively studied for complex permeability and optical behaviour. It was found that Cr\textsuperscript{3+} doped γ-Fe\textsubscript{2}O\textsubscript{3} has significant permeability values and can therefore be used as a high permeability core material and in Multi-layer Chip Inductor (MLC) applications in electronic products, such as cellular phones, computers and video cameras. The results obtained in terms of permeability spectra suggest that γ-Fe\textsubscript{2}O\textsubscript{3} and its doped variants when made in nano-form behave as a high permeability material at ultra high frequencies (5–25 MHz) with permeability showing anomalous inverse dependence on the grain dimension. Optical studies of the material confirm the presence of two bands B\textsubscript{1} and B\textsubscript{2} falling within the solar energy spectrum, thereby enabling this material a promising candidate for single junction photovoltaics with enhanced power conversion efficiency. We have also shown that the nano-sized γ-Fe\textsubscript{2}O\textsubscript{3} synthesized by cost effective and modified sol–gel auto-combustion technique can be a good alternative to highly mismatched alloys (HMAs).

**1. Introduction**

From engineering and technological perspective, the initial permeability is a very important and desirable parameter. Permeability can be defined as a measure of the ability of a material of getting internally magnetized when placed in an external magnetic field, or in other words up to what extent the material allows the passage of magnetic lines of force through its volume. It is a property, which shows how quickly the domains of magnetic material align with the direction of applied field. More precisely, it gives us an idea of how magnetically conductive a material is. To have a better insight into the magnetic behaviour of a material in terms of quality factor and to deal with high frequency magnetic effects, the complex form of permeability is the more comprehensive parameter that is used to evaluate magnetic materials. Recent advances in ferromagnetic technology have given rise to a great variety of core materials available for research and commercial applications, such as pure nano-structured iron, Fe-Si, Fe–P, Fe–Si–Al, Fe–Fe–Mo, ferrite stainless steel, and other soft magnetic alloys [3].

For high permeability applications, Ni–Zn, Mn–Zn and their doped variants have been commonly employed [2–4]. Enhanced high frequency permeability has been observed in Mn–Zn ferrite in Ag-Encapsulated polystyrene composite [5]. Apart from these conventional materials, some other materials have also been tested by researchers [6–9]. One group has claimed to obtain high permeability in foisonized remains of microscopical organisms pattern coated with iron by chemical vapour deposition [10]. Recently, a weak permeability has been observed in Fe\textsubscript{2}O\textsubscript{3} (a close relative of γ-Fe\textsubscript{2}O\textsubscript{3}) at low frequencies [11]. But there is no report to the best of our survey of literature where the permeability study of γ-Fe\textsubscript{2}O\textsubscript{3} pure or in doped form has been done. One report relates the permeability and domain wall motion in case of bulk Fe\textsubscript{2}O\textsubscript{3} (a close relative of γ-Fe\textsubscript{2}O\textsubscript{3}) at low frequencies [12]. There is another report dealing with frequency dependence of γ-Fe\textsubscript{2}O\textsubscript{3}, in which initial permeability values range between 0.2 and 0.4 [13]. The standard initial permeability value of magnetic iron oxide powder is equal to 4.0.

Permeability parameter, apart from being the function of the chemical composition and crystal structure, has also a strong dependency on many other physical parameters such as microstructure, temperature, stress and time elapsed after demagnetization. At low frequencies and in case of a linear material the magnetic field and the auxiliary magnetic field are simply proportional to each other through some scalar permeability whereas at high frequencies these quantities relate to each other with some time lag in the form as given below:

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Synthesis, Antimicrobial and Cholinesterase Enzymes Inhibitory Activities of Indeno Imidazoles and X-Ray Crystal Structure of 3a,8a-Dihydroxy-1,3-diphenyl-1,3,3a,8a-tetrahydro-indeno[1,2-d]imidazole-2,8-dione

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Abstract Two indeno imidazoles have been synthesized by the reaction of ninhydrin with diphenylurea and diphenylthiourea. The structures have been determined by spectral analysis. The supramolecular behavior of 3a,8a-Dihydroxy-1,3-diphenyl-1,3,3a,8a-tetrahydro-indeno[1,2-d]imidazole-2,8-dione (1) was thoroughly analyzed and reported using X-ray single crystal technique and concepts. The presence of oxygen and nitrogen atoms led to very interesting supramolecular motifs interactions such as nitrogen–oxygen, nitrogen–nitrogen, oxygen–oxygen, nitrogen–hydrogen, and oxygen–hydrogen. 3a,8a-Dihydroxy-1,3-diphenyl-2-thioxo-2,3,3a,8a-tetrahydro-1H-indeno[1,2-d]imidazol-8-one 2 showed good antibacterial activity against B. subtilis and P. aeruginosa, while 3a,8a-Dihydroxy-1,3-diphenyl-1,3,3a,8a-tetrahydro-indeno[1,2-d]imidazole-2,8-dione 1 only showed antibacterial activity against P. aeruginosa. Both of 1 and 2 were inactive against C. albicans. Derivative 2 demonstrated good cholinesterase enzyme activity unlike derivative 1 which has weak inhibitory activity against these enzymes. Furthermore, 2 was found to be a selective butrylcholinesterase enzyme inhibitor that has potential use for prevention of further neurodegeneration as well for symptomatic treatment of Alzheimer patients.

Keywords Synthesis · Crystal structure · 3a,8a-Dihydroxy-1,3-diphenyl-1,3,3a,8a-tetrahydro-indeno[1,2-d]imidazole-2,8-dione · 3a,8a-Dihydroxy-1,3-diphenyl-2-thioxo-2,3,3a,8a-tetrahydro-1H-indeno[1,2-d]imidazol-8-one · Antimicrobial activity · Cholinesterase enzymes inhibitory activity

Introduction

The area of chemistry that works beyond molecules and focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components is called supramolecular chemistry. Different forces are responsible for the spatial organization and vary from weak (intermolecular forces, electrostatic or hydrogen bonding) to strong (covalent bonding). While traditional chemistry focuses on the covalent bond, supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules. These weak forces can be hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π–π interactions and electrostatic effects. Understanding the non-covalent interactions is crucial to understand many biological processes from cell structure to vision that rely on these forces for structure and function [1–9]. This understanding is important and could
Synthesis, Crystal Structure and ab initio Studies of Cyclohexyl N-Phenylcarbamate

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Abstract Cyclohexyl N-phenylcarbamate, C_{12}H_{15}NO_{2} (I), which is a useful target for biotransformations by fungi, has been synthesized and the structure has been solved by X-ray diffraction. The crystals are triclinic, space group P 1, with a = 5.2581 (2) Å, b = 9.5080 (3) Å, c = 12.6165 (4) Å, \( \alpha = 70.544 (2)^\circ \), \( \beta = 93.695 (2)^\circ \), \( \gamma = 98.447 (2)^\circ \), \( \beta = 219.28, V = 585.96 (3) Å^3, Z = 2 and R = 0.065 \). In the title compound the phenyl ring makes a dihedral angle of 30.68(7)^\circ with the carbamate group. The molecules are linked into infinite chains via N–H–O hydrogen bonds along the c axis. These hydrogen-bonded chains are further linked by weaker C–H···π interactions. Quantum-mechanical ab initio calculations for the free molecule reproduce well the observed bond lengths and valency angles but show that the crystal packing might be responsible for the rotation of the phenyl ring out of the carbamate plane in the solid state conformation.

Keywords Crystal structure · Synthesis · Cyclohexyl N-phenylcarbamate · Ab initio calculations

Introduction

Carbamates are a well known class of compounds which can be prepared by different methods, for example carbamoylation of aromatic nitro compounds [1], by the reaction of isocyanates with alcohols and by the reaction of an amine and an alcohol with phosgene. Previous investigations also report the synthesis of cyclohexyl N-phenylcarbamate by the reaction of cyclohexanol and formamidine in the presence of a catalytic amount of RuCl_{2}(PHPH)_{3} [2]. Here the title compound has been synthesized by the reaction of cyclohexanol and phenylisocyanate in the presence of a catalytic amount of HCl (see Scheme 1 and “Experimental” section for details). Like the synthesis by Kottachi et al. [2], our synthesis avoids the use of highly toxic and corrosive phosgene and does not require a poisonous carbon monoxide atmosphere.

N-Phenylcarbamates of cyclic alcohols are useful targets for biotransformations by fungi [3, 4], namely the microbiological hydroxylation of chemically non-activated hydrocarbon positions involving monoxygenases. Based on earlier knowledge and new results of hydroxylation of N-Phenylcarbamates with the fungus Beauveria bassiana ATCC 7159, Pietz et al. [5] proposed a modification of the distance-models by Fonken et al. [6] and Fournier et al. [7], to exclude distance variations caused by the mutability of the phenylcarbamate function. According to the model by Pietz et al., the regio- and stereochemistry of hydroxylation is determined mainly by the structure of the hydrocarbon moiety, namely by a specific distance from the group that anchors to the enzyme. This corresponds to an optimum distance of 5.5 Å between the oxygen atom directly attached to the carbocyclic part of the substrate and the substituted H atoms. In order to gain insight into the sterical requirements for the substrates of the enzymatic