INVESTIGATION OF STRUCTURAL AND MAGNETIC PROPERTIES OF LANTHANUM SUBSTITUTED Ni-Mg-Cu-Zn FERRITES

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By

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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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SUIJT KUMER SHIL
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The Author
Suji Kumer Shil
ABSTRACT

Polycrystalline Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La_xO_4 (with x = 0.00, 0.025, 0.050 and 0.075) were prepared by conventional solid state reaction technique. Pellet and toroid shaped samples were prepared from each composition and were sintered at various temperatures (T_s) in air for 5 hours. The influences of microstructure, La substitution in place of Fe and T_s on the complex permeability of above mentioned samples are discussed. A possible correlation among T_s, complex permeability and density is also discussed. The Néel temperature (T_N) of the samples is measured from the temperature dependent real part of initial permeability ($\mu'_r$). X-ray diffraction patterns of the samples show the formation of cubic spinel structure. Lattice parameter increases with increasing La substitution. This result is explained with the help of ionic radii of substituted cations. The average grain size slightly decreases with increasing La substitution whereas increases with increasing T_s. Theoretical density ($p_{th}$) and bulk density ($p_b$) both increase with increasing La content. This can be explained on the basis of atomic weight. The $p_b$ increases with increasing T_s up to 1200°C then decreases for a further increase of T_s up to 1250°C. On the other hand porosity has the opposite trend. The $\mu'_r$ decreases with increasing La substitution probably due to the decrease of average grain size. It is also observed that $\mu'_r$ increases with increasing T_s for all ferrites up to 1200°C then decreases for sample sintered at 1250°C. It is expected that there might have a correlation between $\mu'_r$ and permeability. The $\mu'_r$ remains fairly constant in the frequency range up to 10 kHz or greater for parent composition and 1 MHz or greater for La doped compositions. The imaginary part of initial permeability starts raising beyond this frequency which is an indication of dispersion or resonance. At high frequency, the loss factor of all La doped compositions is lower than parent composition and decreases with increasing La substitution. The relative quality factor is found to be maximum in Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{1.925}La_{0.075}O_4 sintered at 1250°C. The T_N was found to decreases with La substitution up to x=0.050 beyond which T_N increases. The decrease of the T_N is due to the weakening of the A-B exchange interaction and vice versa. The magnetization of all samples increases linearly with increasing applied magnetic field up to 0.1 T. Beyond this field, magnetization increases slowly and then saturation occurs. Saturation magnetization decreases with increasing La substitution.
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<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic induction</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>$d_1$</td>
<td>Inner diameter of the toroid shaped sample</td>
</tr>
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<td>$d_2$</td>
<td>Outer diameter of the toroid shaped sample</td>
</tr>
<tr>
<td>$g$</td>
<td>Landé splitting factor</td>
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<tr>
<td>H</td>
<td>Height of the sample</td>
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<td>Magnetization</td>
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<td>$N_A$</td>
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<td>$P$</td>
<td>Porosity</td>
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<td>Intragranular porosity</td>
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<tr>
<td>$P_{\text{inter}}$</td>
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<tr>
<td>$Q$</td>
<td>Relative quality factor</td>
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<tr>
<td>$R$</td>
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<tr>
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<td>Temperature</td>
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CHAPTER 1
INTRODUCTION

1.1 Introduction

Ferrites are ceramic magnetic materials which possess the combined properties of magnetic materials and insulators. They form a complex system of grains, grain boundaries and pores. The term ferrite denotes a group of iron oxides which has the general formula MeO$_2$.Fe$_2$O$_3$, where Me is a divalent metal ion such as Mn$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Mg$^{2+}$, Co$^{2+}$ or Cd$^{2+}$. The typical ferrite is magnetite, Fe$_3$O$_4$ (or FeO.Fe$_2$O$_3$), which has been a well known magnetic oxide. The ferrites were developed into commercially important materials, mainly during the years 1933-1945, by Snoek [1] and his associates at the Philips Research Laboratories in Holland.

Technological advances in a variety of areas have generated a growing demand for the soft magnetic materials in devices. The technological applications of ferrites is influenced by the physical and chemical properties of materials and depends on many factors including the preparation conditions, such as, sintering temperature, sintering time, rate of heating and cooling.

The magnetic ferrites mainly fall into two groups with different crystal structures: cubic and hexagonal. These magnetic ceramics are widely used in electronic industries and information and communication technology. The uses of ferrites in electronic industry and information and communication technology are increasing day by day. The utility, variety, and versatility make these materials very useful and indispensable. But in this millennium, the science and technology are changing very fast. As a result the characteristics and properties of materials used in electronic industries and information and communication technology are changing. So, there is a growing need for developing, controlling and diversification of electronic materials. Ferrites are very conducive to meet this fast changing science and technology.

Ferrites have numerous hidden characteristics and possess unlimited possibilities. The most promising characteristics of these materials are as follows:

- High quality factor, i.e. excellent magnetic and electrical performance.
- Low sensitivity to variation in the ambient temperature.
- Good sensibility with time.
- Satisfactory behavior over the required frequency band.
- Large number of controllable parameters i.e. their electrical and magnetic properties can be controlled by changing the relative percentage of different constituents of the cations.
- Minimum production cost.

Ferrite is also a semiconductor, which means that its electrical resistivity is at least a million times of a metal. This large electrical resistivity means that an applied alternating magnetic field will not induce eddy currents in a ferrite. This property makes ferrites almost ideal materials for high frequency applications, which was first investigated by Hilpert [2] in 1909.

Several facts led Néel to the belief that the ferrites had a magnetic structure distinctly different from any previously recognized materials. It was known that the metal ions in a ferrite crystal occupied two different kinds of position called A sites and B sites in $AB_2O_4$ crystal structure. Néel made the basic assumption that the exchange force acting between an ion on A site and an ion on B site, was negative, as in an antiferromagnetic. There is thus a lattice of A ions spontaneously magnetized in one direction and a lattice of B ions magnetized in the opposite direction. However, in ferrimagnetic, the magnitudes of the A and B sublattice magnetization are not equal. The two opposing magnetic moments do not cancel and a net spontaneous magnetization results. Every magnetic and electric property of ferrites depends on the sublattice distribution of cations.

Among the soft magnetic materials, polycrystalline ferrites have received special attention due to their good magnetic properties and high electrical resistivity over a wide range of frequencies. Spinel type ferrites are commonly used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic losses [3,4] and also used in electrode materials for high temperature applications because of their high thermodynamic stability, electrical resistivity, electrolytic activity and resistance to corrosion [5,6]. Spinel ferrites are also used in the fabrication of multilayer chip inductors (MLCs) as surface mount devices for miniaturized electronic products such as cellular phones, notebook computers, video camera recorders, floppy drives etc [7].
Moreover, these low cost materials are easy to synthesize and offer the advantages of greater shape formability than their metal. Almost every item of electronic equipment produced today contains some ferrimagnetic spinel ferrite materials. Loudspeakers, motors, deflection yokes, electromagnetic interference suppressors, radar absorbers, antenna rods, proximity sensors, humidity sensors, memory devices, recording heads, broadband transformers, filters, inductors etc are fabricated based on ferrites. So ferrites are subject of intense theoretical and experimental investigations [8-18].

The magnetic properties can be changed by the substitution of various kinds of $M^{2+}$ divalent cations ($\text{Co}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}$) or by introducing a relatively small amount of rare-earth ions. Many investigations have been carried out to understand the effect of La substitution on the properties of Ni-Zn ferrite [29,20], Mn-Zn ferrite [21], Mg-Cu ferrite [22]. Sun et al. [19] reported that the permeability of Ni-Zn ferrite decreases with La substitution. On the other hand P. K. Roy et al. [23] reported that permeability of Ni-Cu-Zn ferrite increases with slight substitution of La. So a detailed study is necessary to ensure the La substitutions. Again Hua Su [24] reported that initial permeability of Ni-Cu-Zn ferrite increases with substitution of Mg. On the other hand Ch. Sujatha [25] reported that initial permeability decreases with increasing Mg content. M. A. Gabal [26] also reported improved magnetic properties of Ni-Cu-Zn ferrite with slight substitution of Mg. It is observed that there is not much publish works on Ni-Mg-Cu-Zn ferrite with La substitution. So the purpose of our present investigation is to study the effect of $\text{La}^{3+}$ substitutions for $\text{Fe}^{3+}$ on the structural and magnetic properties of Ni-Mg-Cu-Zn ferrites. For this investigation, $\text{Ni}_{0.12}\text{Mg}_{0.14}\text{Cu}_{0.26}\text{Zn}_{0.50}\text{Fe}_{2}\text{O}_5$ was taken as the nominal composition.

1.2 Objectives:

Ferrites are especially convenient for high frequency uses because of their higher resistivity. The higher frequency response of the complex permeability is therefore very useful in determining the convenient frequency range in which a particular ferrite material can be used. The mechanism of eddy current losses and damping of domain wall motion can be understood from the relative magnitudes of the real and imaginary parts of the complex permeability. The effect of composition on the frequency response is therefore very useful.
The main objectives of the present research are as follows:

- Preparation of various Ni$_{0.12}$Mg$_{0.15}$Cu$_{0.2}$Zn$_{0.3}$Fe$_2$O$_4$ (where $x=0.00, 0.025, 0.050, 0.075$) samples by solid state reaction technique.
- Characterization of crystal structure (X-ray diffraction), density and porosity of the samples.
- Study of surface morphology (grain size).
- Study of frequency dependent complex permeability of the samples.
- Study of temperature dependent permeability and Néel temperature of the samples.
- Study of DC magnetizations of the samples.

1.3 Summary of the Thesis

The summary of the thesis is as follows:

Chapter 1 deals with the importance of ferrites and objectives of the present work.

Chapter 2 gives a brief overview of the materials, theoretical background as well as crystal structure of the spinel ferrites.

Chapter 3 gives the details of the sample preparation.

Chapter 4 gives descriptions of different experimental setup that have been used in this research work.

Chapter 5 is devoted to the results of various investigations of the study and a brief discussion.

The conclusions drawn from the overall experimental results and discussion are presented in Chapter 6.

References


CHAPTER 2
LITERATURE REVIEW

Double oxides of iron and other metals are important members of ferrimagnetic system commonly known as ferrites. The outstanding properties of ferrites are their complex magnetic structure, which can be varied to tailor their magnetic properties for various high frequency applications. In this chapter we describe a brief overview of the ferrites. The basic issue of ferrimagnetism, crystal structure of the spinel ferrites and effect of non-magnetic Zn substitution on the magnetic moments in spinel ferrites are discussed. A few theoretical aspects of complex permeability are also discussed.

2.1 Overview of the Materials

Ferrites commonly expressed by the general chemical formula $\text{MeO}_x\text{Fe}_2\text{O}_3$, where $\text{Me}$ represents divalent metals, first commanded the public attention when Hilpert (1909) focused on the usefulness of ferrites at high frequency [1]. A systematic investigation was launched by Snoek (1936) at Philips Research Laboratory [2]. At the same time Takai (1937) in Japan was seriously engaged in the research work on the same materials [1]. Snoek's extensive works on ferrites unveiled many mysteries regarding magnetic properties of ferrites. He was particularly looking for high permeability materials of cubic structure. This particular structure for symmetry reasons supports low crystalline anisotropy. He found suitable materials in the form of mixed spinels of the type $\text{Me}_2\text{ZnFe}_2\text{O}_4$, where $\text{Me}$ stands for metals like Cu, Mg, Ni, Co or Mn, for which permeability were found to be up to 4000 [1-3]. Hereafter starts the story of Ni-Zn ferrites. Remarkable properties like high permeability, low loss factor, high stability of permeability with temperature and time, high wear resistance, controlled coercive force, low switching coefficient etc have aptly placed Ni-Zn ferrites as highly demandable ferrites to both researchers and manufacturers. Every year great deals of paper are being published on various aspects of Ni-Zn ferrites. A large number of scientists and technologists are engaged in research to bring about improvements on the magnetic properties of Ni-Zn ferrites.

The sintering process is considered to be one of the most vital steps in ferrite preparation and often plays a dominant role in many magnetic properties. Tasaki et al. [4]
studied the effect of sintering atmosphere on permeability of sintered ferrite. They found that high density is one of the factors, which contribute to greater permeability. However, permeability decreased in an atmosphere without $O_2$ at high sintering temperature where high density was expected. This decrease in permeability is attributed to the variation of chemical composition caused by volatilization of Zn. At low sintering temperature a high permeability is obtained in an atmosphere without $O_2$ because densification and stoichiometry plays a principal role in increasing permeability. At high sintering temperature the highest permeability is obtained in the presence of $O_2$ because the effect of decrease of Zn content can then be neglected.

Studying the electromagnetic properties of ferrites, Nakamura [5] suggested that both the sintering density and the average grain size increased with sintering temperature. These changes were responsible for variations in magnetization, initial permeability and electrical resistivity.

High permeability attainment is certainly affected by the microstructure of the ferrites. Roess showed that [6] the very high permeability is restricted to certain temperature ranges and the shapes of permeability versus temperature curves are strongly affected by any inhomogeneity in the ferrite structure.

Rezlescu et al. [7] reported that the sintering behaviour and microstructure of the ferrites samples largely affected by PbO addition. PbO significantly reduced the sintering temperatures, thus energy consumption is minimized and material loss by evaporation is minimized [8].

There are two mechanisms in the phenomenon of permeability; spin rotation in the magnetic domains and wall displacements. The uncertainty of contribution from each of the mechanisms makes the interpretation of the experimental results difficult. Globus [9] shows that the intrinsic rotational permeability $\mu_r$ and 180$^\circ$ wall permeability $\mu_w$ may be written as: $\mu_r = 1 + 2\pi M_s^2 / K$ and $\mu_w = 1 + 3\pi M_s^2 D / 4\gamma$, where $M_s$ is the saturation magnetization, $K$ is the total anisotropy, $D$ is the grain diameter and $\gamma = K\delta_w$ is the wall energy.

Anderson Dias et al. [10] reported that saturation magnetization and remnance for Ni-Zn ferrite increases while the conductivity decreases with sintering temperature and time. They established the relation between microstructure and magnetic properties.
Saturization magnetization and remanent magnetization are functions of relative density. Pores in the grains act as pinning sites at domain walls and above two magnetic parameters increasing with porosity reduction. Coercive field is independent of the density, but highly dependent on the grain size of the samples.

Rezlescu et al. [11] described the effect of two types of substitutions TiO₂ and R₂O₃ (R is rare earth material) on the magnetic and transport properties of a high frequency Ni-Zn ferrite. The substitution of iron with Ti-Ge ions increases the saturation magnetization and decreases the Curie temperature. The R₂O₃ substitution reduced the Curie temperature by weakening A-B interaction. The key point is that the grain size decreases with increasing the ionic radius of R atom. For all samples linear decrease of resistivity with temperature was found.

Chul Sung Kim et al. [12] studied the structure of Cu-doped Ni-Zn ferrite. The lattice parameter increases with Cu content.

Caltun et al. [13] studied magnetic properties of high frequency Ni-Zn ferrites with CoO doped. Upon increasing the Cu substitution, the average grain size decreases and the microstructure becomes more uniform with fewer pores. A change in the hysteresis loop was observed as the frequency changes. The change in shape is significant for the sample with higher Cu content characterized by smallest grain size. As the frequency decreases a slow decrease of the saturation magnetic flux density was observed. Initial permeability was higher for higher Cu content.

2.2 Origin of Magnetism

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. The motion of electrons is equivalent to an electric current which produces the magnetic effects. The major contribution comes from the spin of unpaired valence electrons which produces permanent electronic magnetic moments. The circulating electron produces its own orbital magnetic moment, measured in Bohr magnetons (μₖ), and there is also a spin magnetic moment associated with it due to the electron itself spinning, like the earth, on its own axis (illustrated in Fig. 2.1).
The onset of magnetic order in solids has two basic requirements:

(i) Individual atoms should have magnetic moments (spins),

(ii) Exchange interactions should exist that couple them together.

Magnetic moments originate in solids as a consequence of overlapping of the electronic wave function with those of neighboring atoms. This condition is best fulfilled by some transition metals and rare-earths. The exchange interactions depend sensitively upon the inter-atomic distance and the nature of the chemical bonds, particularly of nearest neighbour atoms. In most materials there is resultant magnetic moment, due to the electrons being grouped in pairs causing the magnetic moment to be cancelled by its neighbor. A number of such magnetic moments may align themselves in different directions to generate a net non-zero magnetic moment. Thus the nature of magnetization produced depends on the number of unpaired valence electrons present in the atoms of the solid and on the relative orientation of the neighboring magnetic moments. The main distinction is that in some materials there is no collective interaction of atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments.
The magnetism in solids can be classified into the following five major groups:

(i) Diamagnetism
(ii) Paramagnetism
(iii) Ferromagnetism
(iv) Antiferromagnetism
(v) Ferrimagnetism

Materials in the first two groups are those that exhibit no collective magnetic interactions and are not magnetically ordered. Materials in last three groups exhibit long-range magnetic order below a certain critical temperature. Ferromagnetic and ferromagnetic materials are usually what we consider as being magnetic (i.e. behaving like iron). The remaining three are so weakly magnetic that they are usually thought of as “nonmagnetc”. The varieties of magnetic ordering are schematically presented in Fig. 2.2.

A brief description of the above mentioned classes of magnetic materials are described below:

2.2.1 Diamagnetism

Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substance are composed of atoms which have no net magnetic moments (i.e., all the orbital shells are filled and there are no unpaired electrons). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative. It obeys Lenz’s law. The other characteristic behavior of diamagnetic materials is that the susceptibility is temperature independent. The typical values of susceptibility on the order of $10^{-6}$ to $10^{-6}$. Most of the materials are diamagnetic, including Cu, B, S, N$_2$ and most organic compounds.
2.2.2 Paramagnetism

Paramagnetic materials possess a permanent dipole moment due to incomplete cancellation of electron spin and/or orbital magnetic moments (unpaired electrons). In the absence of an applied magnetic field the dipole moments are randomly oriented; therefore the material has no net macroscopic magnetization. When a field is applied these moments tend to align by rotation towards the direction of the applied field and the material acquires a net magnetization [14-17]. The magnetic moment can be oriented along an applied field to give rise to positive susceptibility, and the values of susceptibility are very small the order of $10^{-5}$ to $10^{-3}$. O$_2$, NO, Mn and Cr are just a few examples of the paramagnetic materials. The susceptibility of paramagnetic materials is inversely dependent on temperature, which is known as Curie law (Fig. 2.3a).

$$\chi = \frac{C}{T}$$ (2.1)

where $C$ is the Curie constant.

![Diagram](image)

Figure 2.2. Varieties of magnetic orderings (a) paramagnetic, (b) ferromagnetic, (c) ferrimagnetic, (d) antiferromagnetic and (e) super paramagnetic.
2.2.3 Ferromagnetism

A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons intrinsic magnetic moments wanting to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to want to be parallel to each other. Thus even when the applied field is removed, the electrons in the material can keep each other continually pointed in the same direction. Every ferromagnetic substance has its own individual temperature, called the Curie temperature, above which it loses its ferromagnetic properties \([18]\). This is because the thermal tendency to disorder overwhelms the energy lowering due to ferromagnetic order. The susceptibility of a ferromagnetic material does not follow the Curie law, but displayed a modified behavior defined by Curie-Weiss law Fig. 2.3 (b).

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

where \(C\) is a constant and \(\theta\) is called Weiss constant. For ferromagnetic materials, the Weiss constant is almost identical to the Curie temperature \((T_c)\). The elements Fe, Ni and Co and many of their alloys are typical ferromagnetic materials.

Two distinct characteristics of ferromagnetic materials are:

- Spontaneous magnetization and
- The existence of magnetic ordering temperature (Curie temperature)

The spontaneous magnetization is the net magnetization that exists inside a uniformly magnetized microscopic volume in the absence of a field. The magnitude of this magnetization, at 0K, is dependent on the spin magnetic moments of electrons. Spontaneous magnetization is the term used to describe the appearance of an ordered spin state (magnetization) at zero applied magnetic field in a ferromagnetic or ferrimagnetic material below a critical point called the Curie temperature or \(T_c\). This fact led Weiss to make the bold brilliant assumption that a molecular field acted in a ferromagnetic substance below its Curie temperature as well as above and that this field was so strong that it could magnetize the substance to saturation even in the absence of an applied field. The substance is then self-saturating or spontaneously magnetized.
Saturation magnetization is an intrinsic property independent of particle size by dependent on temperature. Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually overcomes the exchange energy and produces a randomizing effect. This occurs at a particular temperature called the Curie temperature \( T_C \). Below the Curie temperature the ferromagnetic is ordered and above it, disordered. The saturation magnetization goes to zero at the Curie temperature.

\[
\frac{1}{\chi} \quad T_N \quad T_C
\]

**Figure 2.3.** The inverse susceptibility varies with temperature \( T \) for (a) Paramagnetic (b) Ferromagnetic (c) Ferrimagnetic and (d) Antiferromagnetic materials. \( T_N \) and \( T_C \) are Neel temperature and Curie temperature respectively.

### 2.2.4 Antiferromagnetism

In antiferromagnetic material adjacent magnetic moments are parallel to each other without an applied field. In the simplest case adjacent magnetic moments are equal in magnitude and opposite therefore there is no resultant magnetization. The natural state makes it different for the material to become magnetized in the direction of the applied field but still demonstrates a relative permeability slightly greater than above a critical temperature known as the Neel temperature the material becomes paramagnetic [17]. The antiferromagnetic susceptibility is followed by the Curie-Weiss law with a negative \( \theta \) as in the inverse susceptibility as a function of temperature is shown in Fig. 2.3 (d). Common examples of materials with antiferromagnetic ordering include MnO, FeO, CoO and NiO.
2.2.5 Ferrimagnetism

Ferrimagnetic material has the aligned magnetic moments are not of the same size; that is to say there is more than one type of magnetic ion. An overall magnetization is produced but not all the magnetic moment may give a positive contribution to the overall magnetization. The magnitude of magnetic moment in one direction differs from that of the opposite directions. As a result a net magnetic moment remains in the absence of external magnetic field the behavior of susceptibility of a ferrimagnetic material also obeys Curie-Weiss law and has a negative $\theta$ as well as in Fig. 2.3(e) while these materials may also demonstrate a relative permeability greater than 1, their temperature dependence are not as consistent as with ferromagnetic materials and can result is some very unusual results. Ferrimagnetism is therefore similar to ferromagnetism. It exhibits all the hallmarks to ferromagnetic behavior like spontaneous magnetization, Curie temperature, hysteresis, and remanence. However ferro and ferrimagnets have very different magnetic ordering. In ionic compounds, such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure. The magnetic structure is composed of two magnetic sublattices (called A and B) separated by oxygen's. The exchange interactions are mediated by the oxygen anions. When this happens, the interactions are called indirect or super-exchange interactions.

2.2.6 Hysteresis Loop

In addition to the Curie temperature and saturation magnetization, ferromagnets and ferrimagnets can retain a memory of an applied field once it is removed. This behavior is called hysteresis and a plot of the variation of magnetization with magnetic field is called a hysteresis loop. Another hysteresis property is the coercivity of remanence ($H_c$) as in Fig. 2.4. This is the reverse field which, when applied and then removed, reduces the saturation remanence to zero is always larger than the coercive force. The initial susceptibility ($\chi_0$) is the magnetization in low fields, on the order of the earth's field (50-100 $\mu$T). The various hysteresis parameters are not solely intrinsic properties but are dependent on grain size, domain state, stresses, and temperature. Because hysteresis parameters are dependent on grain size, they are useful for magnetic grain sizing of natural samples.
2.2.7 Magnetic Domains

In 1907 Weiss proposed that a magnetic material consists of physically distinct regions called domains and each of which was magnetically saturated in different directions (the magnetic moments are oriented in a fixed direction) as shown schematically in Fig. 2.5. Even each domain is fully magnetized but the material as a whole may have zero magnetization. The external applied field aligns the domains, so there is net moment. At low fields this alignment occurs through the growth of some domains at the cost of less favorably oriented ones and the intensity of the magnetization increases rapidly. Growth of domains stops as the saturation region is approached and rotation of unfavorably aligned domain occurs. Domain rotation requires more energy than domain growth. In a ferromagnetic domain, there is parallel alignment of the atomic moments. In a ferrite domain, the net moments of the anti ferromagnetic interactions are spontaneously oriented parallel to each other. Domains typically contain from $10^{12}$ to $10^{15}$ atoms and are separated by domain boundaries or walls called Bloch walls. The formation of domains allows a ferro or ferri-material to minimize its total magnetic energy.
The magnetic energy is composed of several types of energy [19, 20]:

1. **Magnetostatic or demagnetization energy**: The magnetized material behaves like a magnet, with a surrounding magnetic field. This field acts to magnetize the material in the direction opposite from its own magnetization, causing a magnetostatic energy which depends on the shape of the material. This magnetostatic energy can be reduced by reducing the net external field through the formation of domains inside the material.

2. **Magnetocrystalline anisotropy energy**: In some materials, the domain magnetization tends to align in a particular crystal direction (the so-called easy axis). The material is easiest to magnetize to saturation or demagnetize from saturation if the field is applied along an easy axis. The energy difference between aligning the domain in the easy and another direction (hard direction) is called magnetocrystalline anisotropy energy. Anisotropy energy is the energy needed to rotate the moment from the easy direction to a hard direction. For materials with cubic crystalline structure (such as ferrites), the energy is expressed in terms of anisotropy constants and the direction to which the magnetization rotates.

   \[
   E_k = K_1 \sin^2 \theta + K_2 \sin^4 \theta \quad \text{(hexagonal structure)}
   \]

   \[
   E_k = K_f (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_d (\alpha_1^2 \alpha_2^2 \alpha_3^2 + \ldots) \quad \text{(cubic structure)}
   \]

   where, \( K \) is the anisotropy constant, \( \theta \) is the angle between the easy axis and the direction of magnetization, and \( \alpha \)'s are the direction cosines, which are the ratios of the individual components of the magnetization projected on each axis divided by the magnitude of the magnetization. A crystal is higher in anisotropy energy when the magnetization points in the hard direction rather than along the easy direction. The formation of domains permits the magnetization to point along the easy axis, resulting in a decrease in the net anisotropy energy.

3. **Magnetostrictive energy**: In a magnetic field, the material may change its dimensions on the
order of several parts per million. This change in dimension results in what is called magnetostrictive energy, which is lowered by a reduction in the size of the domains, requiring the formation of more domains.

\textit{d) Domain wall energy:} This is energy resulting from the increase or decrease in the width of the walls due to the growth/shrinkage of domains. The magnetization in a domain changes by two mechanisms: rotation of the magnetic dipoles toward the direction of the applied field and change in the domain volume. In the first case, a certain amount of anisotropy energy is needed to rotate the magnetization in a crystal from the easy to another axis. In the second mechanism, the volume of the domain changes, changing its contribution to the bulk magnetization, while the magnetization direction is unchanged. The change in the magnetization intensity of a domain depends on how close its direction is to the direction of the applied field. If the magnetization direction is close, the intensity in the domain increases, whereas if it is far, the intensity decreases.

The domain volume changes due to motion of the domain wall. This movement is originated by a torque that rotates the moments of the domain in line with the field, moving the center of the wall toward the domain opposed to the field. Consequently, the volume of the domains whose direction is favorable is increased whereas the domains with unfavorable direction decrease in volume [5]. In order to explain the fact that ferromagnetic materials with spontaneous magnetization could exist in the demagnetized state Weiss proposed the concept of magnetic domains. The magnetization within the domain is saturated and will always lie in the easy direction of magnetization when there is no externally applied field. The direction of the domain alignment across a large volume of material is more or less random and hence the magnetization of a specimen can be zero.

Magnetic domains exist in order to reduce the energy of the system. A uniformly magnetized specimen as shown in Fig. 2.6 (a) has a large magnetostatic energy associated with it. This is the result of the presence of magnetic free poles at the surface of the specimen generating a demagnetizing field, $H_d$. From the convention adopted for the definition of the magnetic moment for a magnetic dipole the magnetization within the specimen points from the South Pole to the North Pole, while the direction of the magnetic field points from north to south. Therefore, the demagnetizing field is in opposition to the magnetization of the specimen. The magnitude of $H_d$ is dependent on the geometry and magnetization of the specimen. In general if the sample has a high length to diameter ratio (and is magnetized in the long axis) then the demagnetizing field and the magnetostatic energy will be low.
Figure 2.6. Schematic illustration of the breakup of magnetization into domains (a) single domain, (b) two domains, (c) four domains and (d) closure domain.

The breakup of the magnetization into two domains as illustrated in figure 2.6(b) reduces the magnetostatic energy by half. In fact if the magnet breaks down into $N$ domains then the magnetostatic energy is reduced by a factor of $1/N$, hence figure 2.6(c) has a quarter of the magnetostatic energy of Fig. 2.6(a). Figure 2.6(d) shows a closure domain structure where the magnetostatic energy is zero, this is only possible for materials that do not have a strong uniaxial anisotropy, and the neighbouring domains do not have to be at $180^\circ$ to each other.

2.2.8 Structure of domain wall

The introduction of a domain raises the overall energy of the system, therefore the division into domains only continues while the reduction in magnetostatic energy is greater than the energy required to form the domain wall. The energy associated with a domain wall is proportional to its area. The schematic representation of the domain wall, shown in Fig. 2.7, illustrates that the dipole moments of the atoms within the wall are not pointing in the easy direction of magnetization and hence are in a higher energy state. In addition, the atomic dipoles within the wall are not at $180^\circ$ to each other and so the exchange energy is also raised within the wall. Therefore, the domain wall energy is an intrinsic property of a material depending on the degree of magnetocrystalline anisotropy and the strength of the exchange interaction between neighbouring atoms.
The thickness of the wall will also vary in relation to these parameters, as strong magnetocrystalline anisotropy will favor a narrow wall, whereas a strong exchange interaction will favor a wider wall.

![Diagram of a 180° domain wall.](image)

**Figure 2.7. Schematic representation of a 180° domain wall.**

A minimum energy can therefore be achieved with a specific number of domains within a specimen. This number of domains will depend on the size and shape of the sample (which will affect the magnetostatic energy) and the intrinsic magnetic properties of the material (which will affect the magnetostatic energy and the domain wall energy). Ferromagnetic materials get their magnetic properties not only because their atoms carry a magnetic moment but also because the material is made up of small regions known as magnetic domains. In each domain, all of the atomic dipoles are coupled together in a preferential direction. During solidification, a trillion or more atom moments are aligned parallel so that the magnetic force within the domain is strong in one direction. Ferromagnetic materials are said to be characterized by “spontaneous magnetization” since they obtain saturation magnetization in each of the domains without an external magnetic field being applied. Even though the domains are magnetically saturated, the bulk material may not show any signs of magnetism because the domains develop themselves and are randomly oriented relative to each other.

Ferromagnetic materials become magnetized when the magnetic domains within the material are aligned. This can be done by placing the material in a strong external magnetic field or by passing electrical current through the material. Some or all of the domains can become aligned. The more domains that are aligned, the stronger the
Chapter 2

magnetic field in the material. When all of the domains are aligned, the material is said to be magnetically saturated. When a material is magnetically saturated, no additional amount of external magnetization force will cause an increase in its internal level of magnetization. In an unmagnetized sample of material, the domains point in random directions, or form closed loops, so that there is no overall magnetization of the sample. In a magnetized sample, the domains are aligned so that their magnetic effects combine to produce a strong overall magnetism.

2.3 Crystal Structure of Spinel Ferrites

Ferrites have the cubic structure, which is very close to that of the mineral spinel $MgO.Al_{2}O_{3}$ and are called cubic spinel. Analogous to the mineral spinel, magnetic spinel have the general formula $MeO.Fe_{2}O_{4}$ or $MeFe_{2}O_{4}$ where $Me$ is the divalent metal ion [22]. This crystal structure was first determined by Bragg and by Nishikawa [1,21]. Formerly, spinels containing $Fe$ were called ferrites but now the term has been broadened to include many other ferrimagnets including garnets and hexagonal ferrites these need not necessarily contain iron. The spinel lattice is composed of a close-packed oxygen (radius about 1.3 Å) arrangement in which 32 oxygen ions form a unit cell that is the smallest repeating unit in the crystal network. The unit cell of the ideal spinel structures is given in Fig. 2.8. Between the layers of oxygen ions, if we simply visualize them as spheres, there are interstices that may accommodate the metal ions (radii ranging from 0.6 to 0.8 Å). Now, the interstices are not all the same: some which we call $A$ sites are surrounded by or coordinated with 4 nearest neighboring oxygen ions whose lines connecting their centers form a tetrahedron. Thus, $A$ sites are called tetrahedral sites. The other type of sites ($B$ sites) is coordinated by 6 nearest neighbor oxygen ions whose center connecting lines describe an octahedron. The $B$ sites are called octahedral sites. In the unit cell of 32 oxygen ions there are 64 tetrahedral sites and 32 octahedral sites. If all these were filled with metal ions, of either +2 or +3 valence, the positive charge would be very much greater than the negative charge and so the structure would not be electrically neutral. It turns out that of the 64 tetrahedral sites, only 8 are occupied and out of 32 octahedral sites, only 16 are occupied. Thus the unit cell contains eight formula units $AB_{2}O_{4}$, with 8 $A$ sites, 16 $B$ sites and 32 oxygen ions, and total of $8 \times 7 = 56$ ions. A spinel unit cell contains two types of subcells, Fig. 2.8. The two
types of subcells alternate in a three-dimensional array so that each fully repeating unit cell requires eight subcells, Fig. 2.9.

![Diagram showing subcell arrangement](image)

**Figure 2.8.** Two subcells of a unit cell of the spinel structure.

![Diagram showing subcell arrangement](image)

**Figure 2.9.** Unit cell of spinel ferrite divided into eight subcells with $A$ and $B$ sites.

The positions of the ions in the spinel lattice are not perfectly regular (as the packing of hard spheres) and some distortion does occur. The tetrahedral sites are often too small for the metal ions so that the oxygen ions move slightly to accommodate them. The oxygen ions connected with the octahedral sites move in such a way as to shrink the size the octahedral cell by the same amount as the tetrahedral site expands. The movement of the tetrahedral oxygen is reflected in a
quantity called the oxygen parameter, which is the distance between the oxygen ion and the face of the cube edge along the cube diagonal of the spinel subcell. This distance is theoretically equal to $3/8a_0$ where $a_0$ is the lattice constant [1].

2.4 Cation Distribution of Spinel Ferrites

In spinel structure the distribution of cations over the tetrahedral or $A$ sites and octahedral or $B$ sites can be present in a variety of ways. If all the $Me^{2+}$ ions in $Me^{2+}Me^{2+}_2O_4$ are in tetrahedral and all $Me^{3+}$ ions in octahedral positions, the spinel is then called normal spinel. Another cation distribution in spinel exists, where one half of the cations $Me^{3+}$ are in the $A$ positions and the rest, together with the $Me^{2+}$ ions are randomly distributed among the $B$ positions. The spinel having the latter kind of cation distribution is known as inverse spinel. The distribution of these spinels can be summarized as [2, 23-24]:

1) Normal spinels, i.e. the divalent metal ions are on $A$-sites: $Me^{2+}[Me^{2+}_1]O_4$.

2) Inverse spinels, i.e. the divalent metal ions are on $B$-sites: $Me^{3+[Me^{3+}Me^{2+}_2]}O_4$.

A completely normal or inverse spinel represents the extreme cases. Zn ferrites have normal spinel structure and its formula may be written as $Zn^{2+}[Fe^{3+}Fe^{3+}]O_4^{2-}$. On the other hand, Ni ferrites have inverse spinel structure and its formula may be written as $Fe^{3+}[Ni^{2+}Fe^{3+}]O_4^{2-}$. There are many spinel oxides which have cation distributions intermediate between these two extreme cases and are called mixed spinels. The general cation distribution for the spinel can be indicated as:

$$(Me^{2+}_xMe^{3+}_{1-x})(Me^{2+}_1Me^{3+}_{1-x})O_4$$

where the first and third brackets represent the $A$ and $B$ sites respectively. For normal spinel $x=1$, for inverse spinel $x=0$. The quantity $x$ is a measure of the degree of inversion. In the case of some spinel oxides $x$ depends upon the method of preparation.

The basic magnetic properties of the ferrites are very sensitive functions of their cation distributions. Mixed ferrites having interesting and useful magnetic properties are prepared by mixing two or more different types of metal ions. The chemical formula of mixed Ni-Zn ferrite may be written as $(Zn^{2+}_xFe^{3+}_x)[Ni^{2+}_xFe^{3+}_x]O_4^{2-}$ where $0 \leq x \leq 1$. 

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Spinel oxides are ionic compounds and hence the chemical bonding occurring in them can be taken as purely ionic to a good approximation. The total energy involved, however, consists of the Coulomb energy, the Born repulsive energy, the polarization and the magnetic interaction energy. The energy terms are all dependent on lattice constant, oxygen position parameter and the ionic distribution. In principle the equilibrium cation distribution can be calculated by minimizing the total energy with respect to these variables. But the only energy that can be written with any accuracy is the Coulomb energy. The individual preference of some ions for certain sites resulting from their electronic configuration also play an important role. The divalent ions are generally larger than the trivalent (because the larger charge produces greater electrostatic attraction and so pulls the outer orbits inward). The octahedral sites are also larger than the tetrahedral. Therefore, it would be reasonable that the trivalent ions $Fe^{3+} (0.67\text{Å})$ would go into the tetrahedral sites and the divalent ions $Fe^{2+} (0.83\text{Å})$ go into the octahedral. Two exceptions are found in $Zn^{2+}$ and $Cd^{2+}$ which prefer tetrahedral sites because the electronic configuration is favourable for tetrahedral bonding to the oxygen ions. Thus $Zn^{2+} (0.74\text{Å})$ prefer tetrahedral sites over the $Fe^{2+} (0.67\text{Å})$ ions. $Zn^{2+} (0.74\text{Å})$ and $Ni^{2+} (0.74\text{Å})$ have almost the same ionic radius but $Zn$ prefers tetrahedral sites and $Ni$ prefers octahedral sites because of the configuration exception. $Ni^{2+} (0.78\text{Å})$ and $Cr^{3+} (0.64\text{Å})$ have strong preferences for octahedral sites. Hence the factors influencing the distribution the cations among the two possible lattice sites are mainly their ionic radii of the specific ions, the size of the interstices, temperature, the matching of their electronic configuration to the surrounding anions and the electrostatic energy of the lattice, the so-called Madelung energy, which has the predominant contribution to the lattice energy under the constrain of overall energy minimization and charge neutrality.

2.5 Interaction between Magnetic Moments on Lattice Sites

Spontaneous magnetization of spinels (at 0K) can be estimated on the basis of their composition, cation distribution, and the relative strength of the possible interaction. Since cation-cation distances are generally large, direct (ferromagnetic) interactions are negligible. Because of the geometry of orbital involved, the strongest super-exchange interaction is expected to occur between octahedral and tetrahedral cations. The strength of interaction or exchange force between the moments of the two
metal ions on different sites depends on the distances between these ions and the oxygen ion that links them and also on the angle between the three ions. The nearest neighbours of a tetrahedral, an octahedral and an anion site are shown in Fig. 2.10. The interaction is greatest for an angle of 180° and also where the interionic distances are the shortest. Fig. 2.11 shows the interionic distances and the angles between the ions for the different type of interactions. In the A-A and B-B cases, the angles are too small or the distances between the metal ions and the oxygen ions are too large. The best combination of distances and angles are found in A-B interactions.

Figure 2.10. Nearest neighbours of (a) a tetrahedral site, (b) an octahedral site and (c) an anion site.

Figure 2.11. Interionic angles in the spinel structure for the different type of lattice site interactions.
For an undistorted spinel, the $A-O-B$ angles are about $125^0$ and $154^0$ [1-2, 25]. The $B-O-B$ angles are $90^0$ and $125^0$ but the latter, one of the $B-B$ distances is large. In the $A-A$ case the angle is about $80^0$. Therefore, the interaction between moments on the $A$ and $B$ site is strongest. The $B-B$ interaction is much weaker and the most unfavorable situation occurs in the $A-A$ interaction. By examining the interaction involving the major contributor, or the $A-B$ interaction which orients the unpaired spins of these ions antiparallel, Néel was able to explain the ferrimagnetism of ferrites.

2.6 Magnetism in Spinel Ferrite

The magnetic moment of a free atom is associated with the orbital and spin motions of electrons in an incomplete sub-shell of the electronic structure of the atom. In crystals the orbital motions are quenched, that is the orbital planes may be considered to be fixed in space relative to the crystal lattice, and in such a way that in bulk the crystal has no resultant moment from this source. Moreover this orbital-lattice coupling is so strong that the application of a magnetic field has little effect upon it. The spin axes are not tightly bound to the lattice as are the orbital axes. The anions surrounding a magnetic cation subject it to a strong inhomogeneous electric field and influence the orbital angular momentum. However, the spin angular momentum remains unaffected. For the first transition group elements this crystal field effect is intense partly due to the large radius of the 3d shell and partly due to the lack of any outer electronic shell to screen the 3d shell whose unpaired electrons only contribute to the magnetic moment. We have originally defined the magnetic moment in connection with permanent magnets. The electron itself may well be called the smallest permanent magnet [1]. For an atom with a resultant spin quantum number $S$, the spin magnetic moment will be

$$
\mu = g \sqrt{S(S+1)} \mu_B
$$

where $g$ is the Landé splitting factor and $\mu_B$, known as the Bohr magneton, is the fundamental unit of magnetic moment. The value of $g$ for pure spin moment is 2 and the quantum number associated with each electron spin is $\pm 1/2$. The direction of the moment is comparable to the direction of the magnetization (from South to North poles) of a permanent magnet to which the electron is equivalent. Fig. 2.12 illustrates the electronic configuration of $Fe$ atoms and $Fe^{3+}$ ions. $Fe$ atom has four unpaired electrons and $Fe^{3+}$ ion has five unpaired


electrons. Each unpaired electron spin produced 1 Bohr magneton. In compounds, ions and molecules, account must be taken of the electrons used for bonding or transferred in ionization. It is the number of unpaired electrons remaining after these processes occur that gives the net magnetic moment [1]. According to the Hund's rules the moment of Fe atom and Fe$^{3+}$ ion are $4\mu_B$ and $5\mu_B$ respectively. Similarly the moment of Fe$^{2+}$ and Ni$^{2+}$ ion are $4\mu_B$ and $3\mu_B$ respectively.

\[
\begin{array}{cccccccc}
1s^2 & 2s^1 & 2p^6 & 3s^2 & 3p^6 & 3d^6 & 4s^2 \\
\end{array}
\]

Iron atom

\[
\begin{array}{cccccccc}
1s^2 & 2s^1 & 2p^6 & 3s^2 & 3p^6 & 3d^5 \\
\end{array}
\]

Fe$^{3+}$ ion

Figure 2.12. Electronic configuration of atoms and ions

2.6.1 Exchange Interactions in Spinel

The intense short-range electrostatic field, which is responsible for the magnetic ordering, is the exchange force that is quantum mechanical in origin and is related to the overlapping of total wave functions of the neighbouring atoms. The total wave function consists of the orbital and spin motions. Usually the net quantum number is written as $S$, because the magnetic moments arise mostly due to the spin motion as described above. The exchange interactions coupling the spins of a pair of electrons are proportional to the scalar product of their spin vectors [22, 24, 26],

\[ V_g = -2J_s \mathbf{S}_i \cdot \mathbf{S}_j \]  

(2.3)

where $J_s$ is the exchange integral given in a self-explanatory notation by

\[ J_s = \int \psi_i^*(1)\psi_j^*(2) \left[ \frac{1}{r_{12}} + \frac{1}{r_g} - \frac{1}{r_{11}} - \frac{1}{r_{12}} \right] \psi_i(2)\psi_j(2) dv_1 dv_2 \]  

(2.4)
In this expression $r$'s are the distances, subscripts $i$ and $j$ refer to the atoms, 1 and 2 refers to the two electrons. If the $J$ in equation (2.3) is positive, we achieve ferromagnetism. A negative $J$ may give rise to anti-ferromagnetism or ferrimagnetism.

Magnetic interactions in spinel ferrites as well as in some ionic compounds are different from the one considered above because the cations are mutually separated by bigger anions (oxygen ions). These anions obscure the direct overlapping of the cation charge distributions, sometimes partially and some times completely making the direct exchange interaction very weak. Cations are too far apart in most oxides for a direct cation-cation interaction. Instead, super-exchange interactions appear, i.e., indirect exchange via anion $p$-orbitals that may be strong enough to order the magnetic moments. Apart from the electronic structure of cations this type of interactions strongly depends on the geometry of arrangement of the two interacting cations and the intervening anion. Both the distance and the angles are relevant. Usually only the interactions with in first coordination sphere (when both the cations are in contact with the anion) are important.

In the Néel theory of ferrimagnetism the interactions taken as effective are inter and intra-sublattice interactions $A-B$, $A-A$ and $B-B$. The type of magnetic order depends on their relative strength.

The super-exchange mechanism between cations that operate via the intermediate anions was proposed by Kramer for such cases and was developed by Anderson and Van Vleck [23, 24]. A simple example of super-exchange is provided by $\text{MnO}$ which was chosen by Anderson. From the crystal structure of $\text{MnO}$ it will be seen that the antiparallel manganese ions are collinear with their neighbouring oxygen ions. The $\text{O}^{2-}$ ions each have six $2p$ electrons in three antiparallel pairs. The outer electrons of the $\text{Mn}^{2+}$ ions are in $3d$ sub-shells which are half filled with five electrons in each. The phenomenon of super-exchange is considered to be due to an overlap between the manganese $3d$ orbits and the oxygen $2p$ orbitals with a continuous interchange of electrons between them. It appears that, for the overall energy of the system to be a minimum, the moments of the manganese ions on either side of the oxygen ion must be antiparallel. The manganese magnetic moments are thus, in effect, coupled through the intervening oxygen ion. The idea is illustrated in Fig. 2.13.

In Figs. 2.13(a) and 2.13(c) the outer electrons in a pair of $\text{Mn}^{2+}$ ions, and in an intervening $\text{O}^{2-}$ ion in the unexcited state, are shown by the arrows. One suggested mode of
coupling is indicated in Fig. 2.13(b). The two electrons of a pair in the oxygen ion are simultaneously transferred, one to the left and the other to the right. If their directions of spin are unchanged then, by Hund's rules, the moments of the two manganese ions must be antiparallel as shown. Another possibility is represented in Fig. 2.13(d). One electron only has been transferred to the manganese ion on the left. The oxygen ion now has a moment of $1\mu_B$ and if there is negative interaction between the oxygen ion and the right-hand manganese ion then again the moments of the manganese ions will be antiparallel. If these ideas are accepted then the oxygen ions play an essential part in producing antiferromagnetism in the oxide. Moreover, because of the dumbbell shape of the 2p orbit, the coupling mechanism should be most effective when the metal ions and the oxygen ions lie in one straight line, that is, the angle between the bonds is 180°, and this is the case with MnO.

![Diagram](image)

Figure 2.13. Illustrating super-exchange in MnO.
In the case of spinel ferrites the coupling is of the indirect type which involves overlapping of oxygen wave functions with those of the neighboring cations. Consider two transition metal cations separated by an $O$, Fig. 2.14. The $O^2$ has no net magnetic moment since it has completely filled shells, with $p$-type outermost orbitals. Orbital $p$, has two electrons: one with spin up, and the other with spin down, consistent with Pauli’s exclusion principle. The essential point is that when an oxygen $p$ orbital overlaps with a cation $d$ orbital, one of the $p$ electrons can be accepted by the cations. When one of the transition-metal cations is brought close the $O^2$, partial electron overlap (between a $3d$ electron from the cation and a $2p$ electron from the $O^2$) can occur only for antiparallel spins, because electrons with the same spin are repelled. Empty $3d$ states in the cation are available for partial occupation by the $O^2$ electron, with an antiparallel orientation. Electron overlap between the other cation and the $O^2$ then occurs resulting in antiparallel spins and therefore antiparallel order between the cations. Since the $p$ orbitals are linear, the strongest interaction is expected to take place for cation-$O^2$-cation angles close to 180° [2].

2.6.2 Néel Theory of Ferrimagnetism

If we consider the simplest case of a two-sublattice system having antiparallel and non-equal magnetic moments, the inequality may be due to:

1) different elements in different sites,
2) same element in different ionic states, and
3) different crystalline fields leading to different effective moments for ions having the same spin.

The spins on one sublattice are under the influence of exchange forces due to the spins on the second sublattice as well as due to other spins on the same sublattice. The molecular fields acting on the two sublattices A and B can be written as [2, 21-26]

\[
\begin{align*}
\vec{H}_A &= \lambda_{AA} \vec{M}_A + \lambda_{AB} \vec{M}_B, \\
\vec{H}_B &= \lambda_{BB} \vec{M}_B + \lambda_{BA} \vec{M}_A,
\end{align*}
\]

where \( \vec{M}_A \) and \( \vec{M}_B \) are the magnetizations of the two sublattices and \( \lambda \)'s are the Weiss constants. Since the interaction between the sublattices is antiferromagnetic, \( \lambda_{AA} \) must be negative, but \( \lambda_{AB} \) and \( \lambda_{BA} \) may be negative or positive depending on the crystal structure and the nature of the interacting atoms. Probably, these interactions are also negative, though they are in general quite small.

Assuming all the exchange interactions to be negative the molecular fields will be then given by

\[
\begin{align*}
\vec{H}_A &= -\lambda_{AA} \vec{M}_A - \lambda_{AB} \vec{M}_B, \\
\vec{H}_B &= -\lambda_{BB} \vec{M}_B - \lambda_{BA} \vec{M}_A.
\end{align*}
\]

Since in general, \( \lambda_{AA} \) and \( \lambda_{BB} \) are small compared to \( \lambda_{AB} \), it is convenient to express the strengths of these interactions relative to the dominant \( \lambda_{AB} \) interaction.

Let

\[
\lambda_{AA} = \alpha \lambda_{AB}
\]

and

\[
\lambda_{BB} = \beta \lambda_{AB}
\]

In an external applied field \( \vec{H} \), the fields acting on A and B sites are

\[
\begin{align*}
\vec{H}_A &= \vec{H} - \lambda_{AB} (\alpha \vec{M}_A - \vec{M}_B), \\
\vec{H}_B &= \vec{H} - \lambda_{BA} (\vec{M}_B - \beta \vec{M}_A)
\end{align*}
\]

At temperatures higher than the transition temperature, \( T_N \), \( \vec{H}_A, \vec{M}_A \) and \( \vec{M}_B \) are all parallel and we can write

\[
\vec{M}_A = \frac{C_A}{T} [\vec{H} - \lambda_{AB} (\alpha \vec{M}_A - \vec{M}_B)],
\]

(25)
\[ \dot{M}_B = \frac{C_B}{T} [H - \lambda_{ab} (\dot{M}_A - \mu \dot{M}_A)] \]  

(2.6)

where \( C_A \) and \( C_B \) are the Curie constants for the two sublattices.

\[ C_A = N_A g_A^2 S_A (S_A + 1) / 3 K \]

and

\[ C_B = N_B g_B^2 S_B (S_B + 1) / 3 K \]

\( N_A \) and \( N_B \) denote the number of magnetic ions on \( A \) and \( B \) sites respectively and \( S_A \) and \( S_B \) are their spin quantum numbers. Solving for the susceptibility, \( \chi \), one gets [2.21]

\[
\frac{1}{\chi} = \frac{T}{C} \frac{1}{\chi_0} \frac{b}{T - \theta}
\]

\[
\frac{1}{\chi} = \frac{T + (C / \chi_0)}{C} \frac{b}{T - \theta}
\]

(2.7)

where \( C, \chi_0, b \) and \( \theta \) are constants for particular substance and are given by

\[
C = C_A + C_B
\]

\[
\frac{1}{\chi_0} = \frac{1}{C^2} \left[ C_A^2 \lambda_{aa} + C_B^2 \lambda_{bb} + 2 C_A C_B \lambda_{ab} \right]
\]

\[
b = \frac{C_A C_B}{C^3} \left[ C_A^3 (\lambda_{aa} - \lambda_{bb})^2 + C_B^3 (\lambda_{aa} - \lambda_{bb})^2 \right.
\]

\[
- 2 C_A C_B \left[ \lambda_{aa} - (\lambda_{aa} + \lambda_{bb}) \lambda_{ab} + \lambda_{aa} \lambda_{bb} \right] \]

\[
\theta = - \frac{C_A C_B}{C} (\lambda_{ab} + \lambda_{bb}) - 2 \lambda_{ab}
\]

Equation (2.7) represents a hyperbola, and the physically meaning part of it is plotted in Fig. 2.9. This curvature of the plot of \( 1/\chi \) versus \( T \) is a characteristics feature of a ferrimagnet. It cuts the temperature axis at \( T_C \), called the Ferrimagnetic Curie point. At high temperatures the last term of equation (2.7) become negligible, and reduces to a Curie-Weiss law:

\[
\chi = \frac{C}{T + (C / \chi_0)}
\]

This is the equation of straight line, shown dashed in Fig. 2.15, to which the \( 1/\chi \) versus \( T \) curve becomes asymptotic at high temperatures.
Figure 2.15. The temperature dependence of the inverse susceptibility for ferrimagnets.

The ferrimagnetic Curie temperature $T_C$ is obtained from equations (2.5) and (2.6) with $H = 0$ and setting the determinant of the coefficients of $M_i$ equal to zero. This gives

$$T_C = \frac{1}{2} [C_A A_{dd} A_{20} + (C_A A_{dd} - C_B A_{20})^2 + 4C_A C_B A_{20} A_{dd}^2]$$

Equation (2.7) is in good agreement with the experiment, except near the Curie point. The experimental Curie temperature, the temperature at which the susceptibility becomes infinite and spontaneous magnetization appears, is lower than the theoretical Curie temperature [21]. This disagreement between theory and experiment in the region of Curie point is presumably due to the short-range spin order (spin clusters) at temperatures above experimental $T_C$ [2, 21].

The sublattice magnetizations will in general have different temperature dependences because the effective molecular fields acting on them are different. This suggests the possibility of having anomaly in the net magnetization versus temperature curves, Fig. 2.16. For most ferrimagnets the curve is similar to that of ferromagnets, but in a few cases there be a compensation point in the curve, Fig. 2.16(a) [1, 21]. At a point below the Curie temperature point, the two sublattice magnetizations are equal and thus appear to have no moment. This temperature is called the compensation point. Below this temperature one sublattice magnetization is larger and provides the net moment. Above this temperature the other magnetization does dominates and the net magnetization reverses direction.
The essential requisite for Neél configuration is a strong negative exchange interaction between \( A \) and \( B \) sublattices which results in their being magnetized in opposite directions below the transition point. But there may be cases where intra-sublattice interactions are comparable with inter-sublattice interaction. Neél's theory predicts paramagnetism for such substances at all temperatures. This is unreasonable since strong \( AA \) or \( BB \) interaction may lead to some kind of ordering especially at low temperature. In the cases of no \( AB \) interaction, antiferromagnetic ordering may be expected either in the \( A \) or in the \( B \) sublattice. Under certain conditions there may be non-collinear spin arrays of still lower energy.

Figure 2.16. Superposition of various combinations of two opposing sublattice magnetizations producing differing resultants including one with a compensation point (schematic).
2.6.3 Effect of Zinc Substitution on the Magnetic Moments in Spinel Ferrites

$Fe_3O_4$ has ferromagnetic properties because of its inverse structure which leads to the formation of domains. A unit cell of $Fe_3O_4$ contains eight formula units each of which may be written in the form $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}$ [23]. Snoek and his co-workers found that oxides of inverse structure could be artificially produced in which the divalent ions of another element, for example Mn, Ni, Co, Mg or Cu, could be substituted for the divalent $Fe^{2+}$ ions in $Fe_3O_4$. An extensive range of ferrites could thus be made having the general formula $Fe^{3+}[M^{2+}Fe^{3+}]O_4^{2-}$, where arrows indicate spin ordering. Since the trivalent iron ions are equally distributed on $A$ and $B$ sites they cancel each other out magnetically, and the magnetic moment per formula unit is then theoretically the same as the magnetic moment of the divalent ion. The Ni ferrite has a moment of $2.3\mu_B$ compared with a theoretical value of $2\mu_B$ [1]. Zn ferrite is a normal spinel, with $Zn^{2+}$ $(3d^{10})$ ions in $A$ sites have zero magnetic moment; $Fe^{3+}$ ions in $B$ sites have a magnetic moment $5\mu_B$. The cation distribution can be written as $Zn^{2+}[Fe^{3+}Fe^{3+}]O_4^{2-}$, where spin ordering is indicated by arrows. The zero magnetic moment of $Zn^{2+}$ ions leaves trivalent iron ions on $B$ sites with a negative $BB$ interaction between equal ions. Therefore Zn ferrite is not ferromagnetic. Zinc ferrite therefore be expected to be antiferromagnetic and thus to have a Neel point, though measurements show it to be paramagnetic only [1-2, 21, 23].

Magnetic properties can be modified widely by cation substitution. An illustrative case is substitution of Ni by Zn in Co ferrite to form solid solutions $Ni_{1-x}Zn_xFe_2O_4$. The cation distribution can be written as $(Zn^{2+}Fe^{3+})[Ni^{2+}Fe^{3+}]O_4^{2-}$ [2]. $Zn^{2+}$ is diamagnetic and its main effect is to break linkages between magnetic cations. Another effect is to increase interaction distance by expanding the unit cell, since it has an ionic radius larger than the Ni and Fe radii. The most remarkable effect is that substitution of this diamagnetic cation (Zn) results in a significant increase in magnetic moment in a number of spinel solid solutions, Fig. 2.17.
Magnetic moment as a function of Zn content shows an increase for small substitutions, goes through a maximum for intermediate values, decreases and finally vanishes for high Zn contents.

A simple analysis shows that this increase can be expected for an antiparallel alignment. As the Zn content increases, magnetic moments decreases in sublattice A and increase in sublattice B. If the magnetic moment of Fe and Ni are 5 and $-2.3 \mu_B$/ion, respectively, then, per formula unit, the total moment in Bohr magnetons on B sublattice is $2.3(1-x) + 5(1+x)$ and on A sublattice the total antiparallel moment is $5(1-x)$. If the resultant moment per formula unit is $M_z(0)$, then by taking the difference of A and B moments [15],

$$M_z(0) = 2.3(1-x) + 5(1+x) - 5(1-x)$$
$$= x(10 - 2.3) + 2.3$$

A linear relationship is obtained with a slope of 7.7, predicting a moment value of 10$\mu_B$ per formula unit for Zn substitution $x = 1$, as shown by the broken lines in Fig. 2.17. This relationship is not followed over the entire composition range. However, as the Zn content increases, $A-O-B$ interactions become too weak and $B-O-B$ interactions begin to dominate. That is, the average distance between the interacting spins gets
larger. As a consequence, the system becomes frustrated causing a perturbation to the magnetically ordered spins as large number of $B$ sites spins gets non-magnetic impurity atoms as their nearest neighbors.

![Diagram of spin arrangements](image)

**Figure 2.18.** Schematic representation of spin arrangements in $Ni_{1-x}Zn_xFe_2O_4$: (a) ferrimagnetic (for $x \leq 0.5$); (b) triangular or Yafet-Kittel (for $x > 0.5$); and (c) antiferromagnetic for $x \approx 1$.

The $B$ spins are no longer held in place due to this weak anti-ferromagnetic $A-B$ interaction leading to non-collinearity or canting among the $B$ sublattice. Thus for $x > 0.5$ Zn content, instead of a collinear antiparallel alignment, canted structure appears, where spins in $B$ sites are no longer parallel [2, 27], Fig. 2.18. Evidence of this triangular structure has been observed by neutron diffraction [28]; a theoretical analysis showed that departure from collinear order depends on the ratio of the $A-O-B$ to $B-O-B$ molecular field coefficients, $\lambda_{ab}/\lambda_{bb}$ [29]. For high Zn concentration, $B-O-B$ interactions dominant and the ferrite become antiferromagnetic for $x = 1$ [2].

### 2.7 Microstructure

A polycrystal is much more than many tiny crystals bonded together. The interfaces between the crystals, or the grain boundaries which separate and bond the grains, are complex and interactive interfaces. The whole set of a given material’s properties (mechanical, chemical and especially electrical and magnetic) depend strongly on the nature of the microstructure.

In the simplest case, the grain boundary is the region, which accommodates the difference in crystallographic orientation between the neighbouring grains. For certain simple arrangements, the grain boundary is made of an array of dislocations whose number and spacing depends on the angular deviation between the grains. The ionic
nature of ferrites leads to dislocation patterns considerably more complex than in metals, since electrostatic energy accounts for a significant fraction of the total boundary energy [2].

For low-loss ferrite, Ghate [1] states that the grain boundaries influence properties by

1) creating a high resistivity intergranular layer,
2) acting as a sink for impurities which may act as a sintering aid and grain growth modifiers,
3) providing a path for oxygen diffusion, which may modify the oxidation state of cations near the boundaries.

In addition to grain boundaries, ceramic imperfections can impede domain wall motion and thus reduce the magnetic property. Among these are pores, cracks, inclusions, second phases, as well as residual strains. Imperfections also act as energy wells that pin the domain walls and require higher activation energy to detach. Stresses are microstructural imperfections that can result from impurities or processing problems such as too rapid a cool. They affect the domain dynamics and are responsible for a much greater share of the degradation of properties than would expect [1].

Grain growth kinetics depends strongly on the impurity content. A minor dopant can drastically change the nature and concentration of defects in the matrix, affecting grain boundary motion, pore mobility and pore removal [2, 30]. The effect of a given dopant depends on its valence and solubility with respect to host material. If it is not soluble at the sintering temperature, the dopant becomes a second phase which usually segregates to the grain boundary.

Figure 2.19. Porosity character: (a) intergranular, (b) intragranular.

The porosity of ceramic samples results from two sources, intragranular porosity and intergranular porosity, Fig. 2.19. An undesirable effect in ceramic samples is the
formation of exaggerated or discontinuous grain growth which is characterized by the excessive growth of some grains at the expense of small, neighbouring ones, Fig. 2.20. When this occurs, the large grain has a high defect concentration. Discontinuous growth is believed to result from one or several of the following: powder mixtures with impurities; a very large distribution of initial particle size; sintering at excessively high temperatures; in ferrites containing Zn and/or Mn, a low $O_2$ partial pressure in the sintering atmosphere. When a very large grain is surrounded by smaller ones, it is called 'duplex' microstructure.

![Figure 2.20. Grain growth (a) discontinuous, (b) duplex (schematic).](image)

2.8 Theories of Permeability

Permeability is defined as the proportionality constant between the magnetic field induction $B$ and applied field intensity $H$ [2, 25, 31]:

$$B = \mu H \quad (2.9)$$

If the applied field is very low, approaching zero, the ratio will be called the initial permeability, Fig. 2.15 and is given by

$$\mu_i = \frac{\Delta B}{\Delta H}_{(H=0)}$$

This simple definition needs further sophistications. A magnetic material subjected to an ac magnetic field can be written as

$$H = H_a e^{i\omega t} \quad (2.10)$$

It is observed that the magnetic flux density $B$ lag behind $H$. This is caused due to the presence of various losses and is thus expressed as
Here $\delta$ is the phase angle that marks the delay of $B$ with respect to $H$. The permeability is then given by

$$B = B_0 e^{i(\omega t - \delta)}$$  \hspace{1cm} (2.11)

The permeability is then given by

$$\mu = \frac{B}{H} = \frac{B_0 e^{i(\omega t - \delta)}}{H_0 e^{i\omega t}} = \frac{B_0 e^{-i\delta}}{H_0} \cos \delta - i \frac{B_0}{H_0} \sin \delta = \mu' - i \mu''$$  \hspace{1cm} (2.12)

where

$$\mu' = \frac{B_0}{H_0} \cos \delta$$  \hspace{1cm} (2.13)

and

$$\mu'' = \frac{B_0}{H_0} \sin \delta$$  \hspace{1cm} (2.14)

The real part ($\mu'$) of complex permeability ($\mu$), as expressed in equation (2.10) represents the component of $B$ which is in phase with $H$, so it corresponds to the normal permeability. If there are no losses, we should have $\mu = \mu'$. The imaginary part $\mu''$ corresponds to that of $B$, which is delayed by phase angle $90^0$ from $H$ [21, 25]. The presence of such a component requires a supply of energy to maintain the alternating magnetization, regardless of the origin of delay. The ratio of $\mu''$ to $\mu'$, as is evident from equation (2.14) and (2.13) gives

$$\frac{\mu''}{\mu'} = \frac{B_0 \sin \delta}{H_0} \cos \delta$$  \hspace{1cm} (2.15)

This $\tan \delta$ is called loss factor.

The quality factor is defined as the reciprocal of this loss factor, i.e.

$$\text{Quality factor} = \frac{1}{\tan \delta}$$  \hspace{1cm} (2.16)

And the relative quality factor, $Q = \frac{\mu'}{\tan \delta}$  \hspace{1cm} (2.17)
The curves that show the variation of both $\mu'$ and $\mu''$ with frequency are called the magnetic spectrum or permeability spectrum of the material [21]. The variation of permeability with frequency is referred to as dispersion. The measurement of complex permeability gives us valuable information about the nature of domain wall and their movements. In dynamic measurements the eddy current loss is very important. This occurs due to the irreversible domain wall movements. The permeability of a ferrimagnetic substance is the combined effect of the wall permeability and rotational permeability mechanisms.

2.8.1 Mechanisms of Permeability

The mechanisms can be explained as follows: A demagnetized magnetic material is divided into number of Weiss domains separated by Bloch walls. In each domain all the magnetic moments are oriented in parallel and the magnetization has its saturation value $M_s$. In the walls the magnetization direction changes gradually from the direction of magnetization in one domain to that in the next. The equilibrium positions of the walls result from the interactions with the magnetization in neighboring domains and from the influence of pores; crystal boundaries and chemical inhomogeneities which tend to favour certain wall positions.
2.8.1.1 Wall Permeability

The mechanism of wall permeability arises from the displacement of the domain walls in small fields. Let us consider a piece of material in the demagnetized state, divided into Weiss domains with equal thickness $L$ by means of $180^\circ$ Bloch walls (as in the Fig. 2.22). The walls are parallel to the $YZ$ plane. The magnetization $M_z$ in the domains is oriented alternately in the $+Z$ or $-Z$ direction. When a field $H$ with a component in the $+Z$ direction is applied, the magnetization in this direction will be favoured. A displacement $dx$ of the walls in the direction shown by the dotted lines will decrease the energy density by an amount [32, 33]:

$$\frac{2M_z H, dx}{L}$$

This can be described as a pressure $M_z H$ exerted on each wall. The pressure will be counteracted by restoring forces which for small deviations may assume to be $kdx$ per unit wall surface. The new equilibrium position is then given by

$$d = \frac{M_z H, dx}{L}$$

From the change in the magnetization

$$\Delta M = \frac{2M_z d}{L},$$

the wall susceptibility $\chi_w$ may be calculated. Let $H$ makes the angle $\theta$ with $Z$ direction. The magnetization in the $\theta$ direction becomes

$$(\Delta M)_\theta = \frac{2M_z d}{L} \cos \theta$$

and with $H_z = H \cos \theta$ and $d = \frac{2M_z H}{k}$

we obtain

$$\chi_w = \frac{(\Delta M)_\theta}{H} = \frac{4M_z^2 \cos^2 \theta}{KL}$$

(2.18)
2.8.1.2 Rotational Permeability

The rotational permeability mechanism arises from rotation of the magnetization in each domain. The direction of $\mathbf{M}$ can be found by minimizing the magnetic energy $E$ as a function of the orientation. Major contribution to $E$ comes from the crystal anisotropy energy. Other contributions may be due to the stress and shape anisotropy. The stress may influence the magnetic energy via the magnetostriction. The shape anisotropy is caused by the boundaries of the sample as well as by pores, nonmagnetic inclusions and inhomogeneities. For small angular deviations, $\alpha_x$ and $\alpha_y$ may be written as

$$\alpha_x = \frac{M_x}{M_s} \quad \text{and} \quad \alpha_y = \frac{M_y}{M_s}. $$

For equilibrium $Z$-direction, $E$ may be expressed as [32, 33]

$$E = E_0 + \frac{1}{2} \alpha_x^2 E_{xx} + \frac{1}{2} \alpha_y^2 E_{yy},$$

where it is assumed that $x$ and $y$ are the principal axes of the energy minimum. Instead of $E_{xx}$ & $E_{yy}$, the anisotropy field $H_{x}^A$ and $H_{y}^A$ are often introduced. Their magnitude is given by

$$H_{x}^A = \frac{E_{xx}}{2M_s} \quad \text{and} \quad H_{y}^A = \frac{E_{yy}}{2M_s}.$$

$H_{x}^A$ & $H_{y}^A$ represent the stiffness with which the magnetization is bound to the equilibrium direction for deviations in the $x$ and $y$ direction, respectively. The
rotational susceptibilities $\chi_{r,x}$ and $\chi_{r,y}$ for fields applied along $x$ and $y$ directions, respectively are

$$\chi_{r,x} = \frac{M_x}{H_x^A} \quad \text{and} \quad \chi_{r,y} = \frac{M_y}{H_y^A}.$$  

For cubic materials it is often found that $H_x^A$ and $H_y^A$ are equal. For $H_x^A = H_y^A = H^A$ and a field $H$ which makes an angle $\theta$ with the $Z$ direction (as shown in Fig. 2.22) the rotational susceptibility, $\chi_{r,Z}$ in one crystallite becomes

$$\chi_{r,Z} = \frac{M_z}{H^A} \sin^2 \theta$$ \hspace{1cm} (2.19)

A polycrystalline material consisting of a large number of randomly oriented grains of different shapes, with each grain divided into domains in a certain way. The rotational susceptibility $\chi_r$ of the material has to be obtained as a weighted average of $\chi_{r,c}$ of each crystallite, where the mutual influence of neighbouring crystallites has to be taken into account. If the crystal anisotropy dominates other anisotropies, then $H^A$ will be constant throughout the material, so only the factor $\sin^2 \theta$ (equation 2.19) has to be averaged. Snoek [34] assuming a linear averaging of $\chi_{r,c}$ and found

$$\chi_r = \frac{2M_z}{3H^A}$$

The total internal susceptibility

$$\chi = \chi_\text{w} + \chi_r = \frac{4M_z^3 \cos^2 \theta}{KL} + \frac{2M_z}{3H^4}$$ \hspace{1cm} (2.20)

If the shape and stress anisotropies cannot be neglected, $H^A$ will be larger. Any estimate of $\chi_r$ will then be rather uncertain as long as the domain structure, and the pore distribution in the material are not known. A similar estimate of $\chi_r$ would require knowledge of the stiffness parameter $k$ and the domain width $L$. These parameters are influenced by such factors as imperfection, porosity and crystallite shape and distribution which are essentially unknown.
References


CHAPTER 3
SAMPLE PREPARATION TECHNIQUE

3.1 Introduction

A goal common to all the ferrites is the formation of the spinel structure. Nowadays, the majority of ferrite powders are made by the conventional Ceramic process or Solid State Reaction technique. Most of the non-conventional processes are involved in producing the powder by a wet method. Among these methods, some are [1,2]:

1) Co-precipitation
2) Organic precursors
3) Sol-gel synthesis
4) Spray-drying
5) Freeze-drying
6) Combustion synthesis
7) Glass crystallization

In this chapter, we describe the solid state reaction method that is used in this research work.

3.2 Conventional Solid State Reaction Method

In the solid state reaction method, the required composition is usually prepared from the appropriate amount of raw mineral oxides or carbonates by crushing, grinding, and milling. The most common type of mill is the ball mill, which consists of a lined pot with hard spheres or rod inside. Milling can be carried out in a wet medium to increase the degree of mixing. This method depends on the solid state inter-diffusion between the raw materials. Solids do not usually react at room temperature over normal time scales. Thus it is necessary to heat them at higher temperatures for the diffusion length \((2D)\sqrt{t}\) to exceed the particle size, where \(D\) is the diffusion constant for the fast-diffusing species, and \(t\) is the firing time. The ground powders are then calcined in air or oxygen at a temperature above 1000°C. For some time, this process is continued until the mixture is
converted into the correct crystalline phase. The calcined powders are again crushed into fine powders. The pellets or toroid shaped samples are prepared from these calcined powders using die-punch assembly or hydrostatic or isostatic pressure. Sintering is carried out in the solid state, at temperature ranging 1100-1400°C, for times of typically 1-40 h and in various atmospheres (e.g. Air, O₂ and N₂) [3-6]. Fig. 3.1 shows, diagrammatically, the stages followed in ferrite preparation.

The general solid state reaction leading to a ferrite \( \text{MeFe}_2\text{O}_4 \) may be represented as

\[
\text{MeO} + \text{Fe}_2\text{O}_3 \rightarrow \text{MeFe}_2\text{O}_4
\]

where \( \text{Me} \) is the divalent ions. There are basically four steps in the preparation of ferrite:

1) Preparation of materials to form an intimate mixture with the metal ions in the ratio which they will have in the final product,
2) Heating of this mixture to form the ferrite (often called calcining),
3) Grinding the calcined powders and pressing the fine powders into the required shape, and
4) Sintering to produce a highly densified product.

### 3.3 Details of Calcining, Pressing and Sintering

Calcining is defined as the process of obtaining a homogeneous and phase pure composition of mixed powders by heating them for a certain time at a high temperature and then allowing it to cool slowly. During the calcining stage, the reaction of \( \text{Fe}_2\text{O}_3 \) with metal oxide (say, \( \text{MeO} \) or \( \text{Me}_2\text{O}_3 \)) takes place in the solid state to form spinel according to the reactions [7]:

\[
\text{MeO} + \text{Fe}_2\text{O}_3 \rightarrow \text{MeFe}_2\text{O}_4 \quad \text{(Spinel)}
\]

\[
2\text{Me}_2\text{O}_3 + 4\text{Fe}_2\text{O}_3 \rightarrow 4\text{MeFe}_2\text{O}_4 \quad \text{(Spinel)} + \text{O}_2
\]

The \( \text{NiO}, \text{MgO}, \text{CuO}, \text{ZnO} \) and \( \text{La}_2\text{O}_3 \) creeps into \( \text{Fe}_2\text{O}_3 \) as below, to form an intermediate phase:

\[
\text{Fe}_2\text{O}_3 + \text{NiO} \rightarrow \text{NiFe}_2\text{O}_4
\]

\[
\text{Fe}_2\text{O}_3 + \text{MgO} \rightarrow \text{MgFe}_2\text{O}_4
\]

\[
\text{Fe}_2\text{O}_3 + \text{CuO} \rightarrow \text{CuFe}_2\text{O}_4
\]

\[
\text{Fe}_2\text{O}_3 + \text{ZnO} \rightarrow \text{ZnFe}_2\text{O}_4
\]
And lastly

\[(0.12)\text{NiFe}_2\text{O}_4 + 0.18\text{MgFe}_2\text{O}_4 + 0.20\text{CuFe}_2\text{O}_4 + 0.50\text{ZnFe}_2\text{O}_4 + x\text{LaFe}_2\text{O}_4 \rightarrow \text{Ni}_0.12\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_2\text{O}_{x+4}\]
The calcining process can be repeated several times to obtain a high degree of homogeneity. The calcined powders are crushed into fine powders. The ideal characteristics of fine powders are [2]:

1) small particle size (submicron)
2) narrow distribution in particle size
3) dispersed particles
4) equiaxed shape of particles
5) high purity
6) homogeneous composition.

A small particle size of the reactant powders provides a high contact surface area for initiation of the solid-state reaction; diffusion paths are shortened, leading to more efficient completion of the reaction. Porosity is easily eliminated if the initial pores are very small. A narrow size distribution of spherical particles as well as a dispersed state is important for compaction of the powder during green-body formation. Grain growth during sintering can be better controlled if the initial size is small and uniform.

A binder is usually added prior to compaction, at a concentration lower than 5wt% [2]. Binders are polymers or waxes; the most commonly used binder in ferrite is polyvinyl alcohol. The binder facilitates the particles flow during compacting and increases the bonding between the particles, presumably by forming bonds of the type particle-binder-particle. During sintering, binders decompose and are eliminated from the ferrite. Pressures are used for compacting very widely but are commonly several tons per square inch (i.e., up to $10^6 \text{N/m}^2$).

Sintering is defined as the process of obtaining a dense, tough body by heating a compacted powder for a certain time at a temperature high enough to significantly promote diffusion, but clearly lower than the melting point of the main component. The driving force for sintering is the reduction in surface free energy of the powder. Part of this energy is transferred into interfacial energy (grain boundaries) in the resulting polycrystalline body [2, 8]. The sintering time, temperature and the furnace atmosphere play very important role on the magnetic property of ferrite materials. The purposes of sintering process are:

1) to bind the particles together so as to impart sufficient strength to the product,
2) to densify the material by eliminating the pores and
3) to homogenize the materials by completing the reactions left unfinished in the calcining step.

Sintering of crystalline solids is dealt by Coble and Burke [9] who found the following empirical relationship regarding rate of grain growth:

\[
d = k t^n
\]

where \( d \) is the mean grain diameter, \( n \) is about 1/3, \( t \) is sintering time and \( k \) is a temperature dependent parameter. Sintering is divided into three stages, Fig. 3.2 [2, 10].

Stage 1. Contact area between particles increases,
Stage 2. Porosity changes from open to closed porosity,
Stage 3. Pore volume decreases; grains grow.

![Figure 3.2. Schematic representation of sintering stages: (a) greenbody, (b) initial stage, (c) intermediate stage, and (d) final stage.](image)

In the initial stage, neighbouring particles form a neck by surface diffusion and presumably also at high temperatures by an evaporation-condensation mechanism. Grain growth begins during the intermediate stage of sintering. Since grain boundaries are the sinks for vacancies, grain growth tends to decrease the pore elimination rate due to the increase in distance between pores and grain boundaries, and by decreasing the total grain boundary surface area. In the final stage, the grain growth is considerably enhanced and the remaining pores may become isolated.

In Ni-Zn ferrites, the presence of Zn complicates the sintering process because high temperature coupled with low oxygen firing will cause Zn loss. High density is important for high permeability, but so is Zn conservation. Tasaki [1] described two alternative firings to achieve high density:

1) Low sintering temperature excluding \( O_2 \) (Vacuum, argon, nitrogen),
2) High temperature in pure oxygen to reduce Zn loss.
Accordingly, other properties correlated along with density:

1) Lattice constant is greater for $O_2$, smaller for vacuum.
2) Curie temperature is greater for vacuum, smaller for $O_2$.
3) Resistivity is greater for $O_2$, smaller for vacuum.

### 3.4 Preparation of the Present Samples

The $\text{Ni}_{0.12}\text{Mg}_{0.16}\text{Cu}_{0.20}\text{Zn}_{0.30}\text{Fe}_{x}\text{La}_{0.4}O_4$ (for $x = 0.00, 0.025, 0.050$ and $0.075$), samples were prepared by the standard solid-state reaction technique. Powder of NiO (99.9%), MgO (99.9%), CuO (99.9%), ZnO (99.9%), La$_2$O$_3$ (99.9%) and Fe$_2$O$_3$ (99.9%) were used as raw materials. Proper amounts of required powders were mixed thoroughly and then calcined at 950°C for 5 h. The calcined powders were then pressed into disk-shaped and toroid-shaped samples. The samples were sintered at various temperatures 1100, 1150, 1200 and 1250°C in air for 5 h. The temperature rate was 5°C/min for heating and 10°C/min for cooling.

![Figure 3.3.](image)

(a) Disk shaped and (b) Toroid shaped Samples.

### References


CHAPTER 4
EXPERIMENTAL TECHNIQUES

In this chapter, we describe basic experimental techniques to measure the lattice parameters, density, and frequency dependent AC permeability of ferrite samples. We also describe the experimental technique for the measurement of temperature dependent initial permeability. The Neel temperatures of the samples were determined from this temperature dependent initial permeability. DC magnetizations of the samples are also discussed.

4.1 X-ray Diffraction

Bragg reflection is a coherent elastic scattering in which the energy of the x-ray is not changed on reflection. If a beam of monochromatic radiation of wavelength $\lambda$ is incident on a periodic crystal plane at an angle $\theta$ and is diffracted at the same angle as shown in Fig. 4.1, the Bragg diffraction condition for x-rays is given by

$$2d\sin\theta = n\lambda$$  \hspace{1cm} (4.1)

where $d$ is the distance between crystal planes and $n$ is the positive integer which represents the order of reflection. Equation (4.1) is known as Bragg law.

![Fig. 4.1. Bragg law of diffraction.](image)
This Bragg law suggests that the diffraction is only possible when \( \lambda \leq 2d \). For this reason, we cannot use the visible light to determine the crystal structure of a material. The x-ray diffraction (XRD) provides substantial information on the crystal structure.

In the present work, a PHILIPS PW 3040 X’pert PRO X-ray diffractometer was used for the lattice parameter to study the crystalline phases of the prepared samples in the Materials Science division, Atomic Energy Centre, Dhaka. For this purpose, monochromatic Cu-K\(_\alpha\) radiation was used. The lattice parameter for each peak of each sample was calculated by using the formula

\[
a = d \sqrt{h^2 + k^2 + l^2}
\]  

(4.2)

where \(h, k\) and \(l\) are the indices of the crystal planes. To determine the exact lattice parameter for each sample, Nelson-Riley method was used. The Nelson-Riley function \( F(\theta) \) is given as [2]:

\[
F(\theta) = \frac{1}{2} \left[ \left( \cos^2 \theta \sin \theta \right) - \left( \cos^2 \theta \right) \right]
\]  

(4.3)

The values of lattice constant \( a \) of all the peaks for a sample are plotted against \( F(\theta) \). Then using a least square fit method, the exact lattice parameter \( a_0 \) is determined. The point where the least square fit straight line cut the y-axis (i.e. at \( F(\theta) = 0 \)) is the actual lattice parameter of the sample. Using this lattice parameter, \( a_0 \) the theoretical density, \( \rho_\text{th} \) was calculated from the following expression:

\[
\rho_\text{th} = \frac{8M}{N_\text{A}a_0^3} \text{ g/cm}^3
\]  

(4.4)

where \( N_\text{A} \) is Avogadro’s number \( \left( 6.02 \times 10^{23} \text{ mol}^{-1} \right) \), \( M \) is the molecular weight. The porosity was calculated from the relation \( \left[ 100 \left( \rho_\text{th} - \rho_\text{b} \right) / \rho_\text{th} \right] \% \), where \( \rho_\text{b} \) is the bulk density measured by the formula \( \rho_\text{b} = M/V \) [3].

4.1.1 Different Parts of the PHILIPS X’ Pert PRO XRD System

Fig. 4.2 shows the inside view of the X’ pert PRO XRD system. A complex of instruments of X-ray diffraction analysis has been established for both materials research and specimen characterization.
These include facilities for studying single crystal defects, and a variety of other materials problems.

The PHILIPS X' Pert PRO XRD system comprised of the following parts:

(i) "Cu-Tube" with maximum input power of 60 kV and 55 mA,

(ii) "Ni-Filter" to remove Cu-Ka component,

(iii) "Solar slit" to pass parallel beam only,

(iv) "Programmable Divergent slits" (PDS) to reduce divergence of beam and control irradiated beam area,

(v) "Mask" to get desired beam area,

(vi) "Sample holder" for powder sample,

(vii) "Anti Scatter Slit" (ASS) to reduce air scattering background,

(viii) "Programmable Receiving Slit" (PRS) to control the diffracted beam intensity and

(ix) "Solar slit" to stop scattered beam and pass parallel diffracted beam only.
4.2 Study of microstructure

The microstructural study was performed in order to have an insight of the grain structures of different compositions, sintered at different temperatures. The samples were visualized under a high-resolution optical microscope and then photographs were taken.

4.3 Complex permeability measurement

For high frequency application, the desirable property of a ferrite is high permeability with low loss. One of the most important goals of ferrite research is to fulfill this requirement. The techniques of permeability measurement and frequency dependent complex permeability of the present samples are described in sections 4.3.1 and 4.3.2.

4.3.1 Techniques for the permeability measurement

Measurements of permeability normally involve the measurements of the change in self-inductance of a coil in presence of the magnetic core. The behaviour of a self-inductance can now be described as follows. We assume an ideal loss less air coil of inductance $L_0$. On insertion of a magnetic core with permeability $\mu$, the inductance will be $\mu L_0$. The complex impedance $Z$ of this coil [4] can be expressed as follows:

$$Z = R + jX = j\omega L_0 \mu = j\omega L_0 (\mu' - j\mu'')$$

where the resistive part is

$$R = \omega L_0 \mu''$$

and the reactive part is

$$X = \omega L_0 \mu'$$

The RF permeability can be derived from the complex impedance of a coil, $Z$, given by equation (4.5). The core is taken as toroidal to avoid demagnetizing effects. The quantity $L_0$ is derived geometrically as shown in section 4.3.2.

4.3.2 Frequency characteristics of the present samples

The frequency characteristics of the ferrite samples i.e. the initial permeability spectra were investigated using a Wayne Kerr Impedance Analyzer (Model No. 6500B).
The complex permeability measurements on toroid shaped specimens were carried out at room temperature on all the samples in the frequency range 1 kHz - 100 MHz. The real part ($\mu_r'$) and imaginary part ($\mu_r''$) of the complex permeability were calculated using the following relations [5]:

$$\mu_r' = \frac{L_s}{L_0} \quad \text{and} \quad \mu_r'' = \mu_r' \tan \delta,$$

where $L_s$ is the self-inductance of the sample core and $L_0 = \mu_0 N^2 S / \pi \tilde{d}$ is derived geometrically. Here $L_0$ is the inductance of the winding coil without the sample core, $N$ is the number of turns of the coil ($N = 4$), $S$ is the area of cross section of the toroidal sample as given below:

$$S = \tilde{d} \times h,$$

where

$$\tilde{d} = \frac{d_2 - d_1}{2},$$

$d_i = \text{Inner diameter},$

$d_2 = \text{Outer diameter},$

$h = \text{Height}$

and $\tilde{d}$ is the mean diameter of the toroidal sample as given below:

$$\tilde{d} = \frac{d_1 + d_2}{2}.$$

The relative quality factor is determined from the ratio $\frac{\mu_r'}{\tan \delta}$.

4.4 The Néel temperature measurements

The Néel temperature measurement is one of the most important measurements for ferrimagnetic materials. Néel temperature provides substantial information on magnetic status of a substance in respect of the strength of exchange interaction. So, the determination of Néel temperature is of great importance.

Néel temperature was measured from the temperature dependent initial permeability. For this measurement, the sample was kept inside a cylindrical oven with a thermocouple placed at the middle of the sample. The thermocouple measures the temperature inside the oven and also of the sample. The sample was kept just in the middle part of the cylindrical oven in order to minimize the temperature gradient. The temperature of the oven was then raised slowly. If the heating rate is very fast then temperature of the sample may not follow the temperature inside the oven, and there can be misleading information on the temperature of sample. The thermocouple
showing the temperature in that case will be erroneous. Therefore, a slow heating rate was used to eliminate this problem. Also, a slow heating ensures accuracy in the determination of Neel temperature. The oven was kept thermally insulated from the surroundings. The temperature dependent permeability was measured at a constant frequency (100 kHz) of a sinusoidal wave.

4.5 DC Magnetization measurement

The field dependence of magnetization ($M$) measurements at room temperature were made on pieces of the samples using vibrating sample magnetometer.

4.5.1 Vibrating Sample Magnetometer

A vibrating sample magnetometer (VSM) operates on Faraday’s Law of Induction, which tells us that a changing magnetic field will produce an electric field. This electric field can be measured and can tell us information about the changing magnetic field. A VSM is used to measure the magnetic behavior of magnetic materials. VSM is a versatile and sensitive method of measuring magnetic properties developed by S. Foner [3,12] and is based on the flux change in a coil when the sample is vibrated near it. The VSM is designed to continuously measure the magnetic properties of materials as a function of temperature and field. In this type of magnetometer, the sample is vibrated up and down in a region surrounded by several pick-up coils. The magnetic sample is thus acting as a time-changing magnetic flux, varying inside a particular region of fixed area. From Maxwell’s law it is known that a time varying magnetic flux is accompanied by an electric field and the field induces a voltage in pick-up coils. This alternating voltage signal is processed by a control unit system, in order to increase the signal to noise ratio. The result is a measure of the magnetization of the sample.

4.5.2 Principle of VSM

If a sample is placed in a uniform magnetic field, created between the poles of an electromagnet, a dipole moment will be induced. If the sample vibrates with sinusoidal motion, a sinusoidal electrical signal can be induced in suitable placed pick-up coils.
The signal has the same frequency of vibration and its amplitude will be proportional to the magnetic moment, amplitude and relative position with respect to the pick-up coils system. Fig 4.3 shows the block diagram of VSM.

![Block diagram of vibrating sample.](image)

The sample is fixed to a sample holder located at the end of a sample rod mounted in an electromechanical transducer. The transducer is driven by a power amplifier which itself is driven by an oscillator at a frequency of 90 Hz. So, the sample vibrates along the Z axis perpendicular to the magnetizing field. The latter induced a signal in the pick-up coil system that is fed to a differential amplifier. The output of the differential amplifier is subsequently fed into a tuned amplifier and 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. Calibration of the VSM is done by measuring the signal of a pure Ni standard of known saturation magnetic moment placed in the saddle point. The basic instrument includes the
electromechanical system and the electronic system (including a personal computer). Laboratory electromagnets or superconducting coils of various maximum field strengths may be used.

![Vibrating sample magnetometer](image)

Fig. 4.4. Vibrating sample magnetometer.

References


CHAPTER 5
RESULTS AND DISCUSSION

The polycrystalline Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La,O_{4} (x=0.00, 0.025, 0.050 and 0.075) ferrites are studied. All ferrite samples are sintered at various temperatures (1100, 1150, 1200 and 1250°C) for five hours in air. Structural and surface morphology are studied by X-ray diffraction and optical microscopy respectively. The magnetic properties of the ferrites are characterized with high frequency (1 kHz-100 MHz) complex initial permeability and temperature dependent permeability measurements. DC magnetizations of all samples sintered at 1200°C are also studied.

5.1 X-ray diffraction analysis

![X-ray diffraction pattern](image)

**Fig. 5.1.** The X-ray diffraction patterns of polycrystalline various Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La,O_{4} (x=0.00, 0.025, 0.050 and 0.075) sintered at 1200°C
The X-ray diffraction (XRD) was performed to verify the formation of spinel structure of various Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ ferrites, in which Fe$^{3+}$ is replaced by La$^{3+}$. The XRD patterns of these La substituted Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ (with $x = 0.00, 0.025, 0.050$ and $0.075$) ferrites sintered at 1200$^\circ$C in air for 5h are shown in Fig. 5.1. The results indicated that there is formation of spinel structure for each composition. Analyzing the XRD patterns it is observed that the fundamental reflections from the planes (220), (311), (222), (400), (422), (511) and (440) comply with the reported value [1] and no traces of raw materials were found, thereby confirming that the chemical reaction is completed. This also indicated the homogeneity of the prepared samples. From the XRD patterns, a secondary phase LaFeO$_3$ was detected in all La doped samples. It has been established that secondary phase LaFeO$_3$ was formed upon La substitution for Fe in the ferrite. The peak height of LaFeO$_3$ gradually increases with the substitution of La. This indicates that La did not form solid solution with spinel structure or has limited solid solubility. A detailed study on this phase formation behaviour has been described by Roy et al. [2].

5.1.1 Lattice parameters
The values of lattice parameter, ‘a’ obtained from each crystal plane are calculated using the formula, $a = d \sqrt{h^2 + k^2 + l^2}$. The measured ‘a’ values are plotted against Nelson-Riley function $F(\theta) = \frac{1}{2} [\cos^2 \theta/\sin \theta + \cos^2 \theta/\theta]$, where $\theta$ is the Bragg’s angle and straight lines are obtained [3]. The values of lattice parameters ($a_0$) were estimated from the extrapolation of these lines to $F(\theta) = 0$ or $\theta = 90^\circ$ as shown in the Fig. 5.2 and Fig. 5.3 respectively.
Fig. 5.2. The variation of lattice parameter, \( a \), calculated from each plane with \( F(\theta) \) of
\[ \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{1.975}\text{La}_{0.025}\text{O}_4 \]
for (a) \( x=0.00 \) and (b) \( x=0.025 \) sintered at 1200°C.
Fig. 5.3. The variation of lattice parameter, a, calculated from each plane with F(θ) of Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{1.950}$La$_{0.050}$O$_4$ for (a) x=0.059 and (b) x=0.075 sintered at 1200°C.
The lattice constant $a_0$ as a function of La content for various $\text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_x\text{O}_4$ sintered at 1200°C is presented in Fig. 5.4. It is noticed from this figure that the lattice constant increases with increasing La$^{3+}$ content in the various $\text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_x\text{O}_4$ up to $x=0.050$ then decreases. The increase in lattice constant with La content indicates that the present compositions obey the Vegard's law [4] up to $x=0.050$. There exist a correlation between the ionic radius and the lattice constant, the increase of lattice constant is proportional to the increase of the ionic radius [5]. The lattice constant increases because the unit cell has expanded when substituted ionic size is larger. The ionic radius of La$^{3+}$ (1.061 Å) is greater than that of Fe$^{3+}$ (0.645 Å) [6]. When the larger La ions enter the lattice, although the unit cell expands it preserves the overall cubic symmetry. The decrease of lattice constant at $x=0.075$ due to shifting of peaks to the higher angle.

![Fig. 5.4. The variation of Lattice parameter with La content for Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$.](image)
5.2 Microstructures

The optical micrographs of various Ni$_{0.17}$Mg$_{0.16}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2.0}$La$_{x}$O$_4$ sintered at 1100, 1150, 1200 and 1250°C are shown in Fig. 5.5, 5.6, 5.7 and 5.8 respectively. From the micrographs it is observed that the average grain size slightly decreases with increasing La substitution but significantly increases with increasing sintering temperature. The behavior of grain growth reflects the competition between the driving force for grain boundary movement and the retarding force exerted by pores [7]. During the sintering process, the thermal energy generates a force that drives the grain boundaries to grow over pores, thereby decreasing the pore volume and densifying the material. This is the reason behind the increase in grain size with sintering temperature.

![Optical micrographs of various Ni$_{0.17}$Mg$_{0.16}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2.0}$La$_{x}$O$_4$ sintered at 1100°C in air.](image)

Fig. 5.5. The optical micrographs of various Ni$_{0.17}$Mg$_{0.16}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2.0}$La$_{x}$O$_4$ sintered at 1100°C in air.
Fig. 5.6. The optical micrographs of various Ni$_{101}$Mg$_{11}$Co$_{10.5}$Zn$_5$Fe$_{86}$La$_6$O$_{4}$ sintered at 1150°C in air.

Fig. 5.7. The optical micrographs of various Ni$_{101}$Mg$_{11}$Co$_{10.5}$Zn$_5$Fe$_{86}$La$_6$O$_{4}$ sintered at 1200°C in air.
The grain size reflects the presence of more or less grain boundary area. Even porosity may be strongly related to boundaries since it can remove porosity. The uniformity and the average grain diameter can control properties such as the magnetic permeability. When the grain growth rate is very high, pores may be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside the grains. This intragranular porosity is practically impossible to eliminate, leading to poor magnetic and mechanical properties.

Fig. 5.8. The optical micrographs of various Ni$_{0.3}$Mg$_{0.1}$Cu$_{0.2}$Zn$_{0.5}$Fe$_{0.1}$La$_{0.2}$O$_x$ sintered at 1250°C in air.
5.3 Density and porosity

Density and porosity have a great effect on the properties of materials. So study of density and porosity is very essential. Fig. 5.9 shows the variation of bulk density and theoretical density with La content of the samples sintered at various temperatures. It is observed that theoretical density and bulk density both increase with increasing La content. The increase in density with increasing La content can be explained on the basis of the atomic weight. The atomic weight of Fe (55.845 amu) is less than that of La (138.9055 amu). From our previous study, it is confirmed that lattice parameter increases with substitution of La. We know density is equal to mass per unit volume. In this case, with substitution of La atomic weight increases more than volume. Therefore increase in density is expected.

**Fig. 5.9.** Variation of bulk density and theoretical density with La content of the polycrystalline \( \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_x\text{O}_4 \) sintered at various temperatures.
Fig. 5.10 shows the variation of porosity as a function of La content of the samples sintered at 1100, 1150, 1200 and 1250°C respectively. It is found that for all samples porosity decreases with La content. The variation of porosity with La substitution is opposite of variation of density.

Fig. 5.11 shows the variation of bulk density with sintering temperature of polycrystalline Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ for $x=0.00, 0.025, 0.050$ and $0.075$. It is observed that bulk density increases with increasing sintering temperature up to 1200°C then decreases. The increase in density with sintering temperature is expected. This is because during the sintering process, the thermal energy generates a force that drives the grain boundaries to grow over pores, thereby decreasing the pore volume and densifying the material. This decrease in density at higher sintering temperature is attributed to the increased intra-granular porosity resulting from discontinuous grain growth as proposed by Coble and Burke [8].
Fig. 5.11. Variation of bulk density with sintering temperature of polycrystalline Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.30}$Fe$_{2-x}$La$_x$O$_4$.

Fig. 5.12 shows the variation of porosity with sintering temperature of polycrystalline Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.30}$Fe$_{2-x}$La$_x$O$_4$ samples for $x=0.00$, 0.025, 0.050 and 0.075. It is observed that porosity of all samples decreases with increasing sintering temperature up to 1200°C then increases. This variation of porosity with sintering temperature is exactly opposite to the variation of bulk density.
It is known that the porosity of ceramic samples results from two sources, intragranular porosity and intergranular porosity [9]. Thus the total porosity could be written as $P = P_{\text{intra}} + P_{\text{inter}}$. The intergranular porosity mainly depends on the grain size [9]. At higher sintering temperatures the density decreases because the intragranular porosity increases resulting from discontinuous grain growth. When the grain growth rate is very high, pores may be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside the grains. The discontinuous growth of the grain rises with temperature and hence contributes toward the reduction of bulk density. This result agrees with the result for NiZn ferrites [10].
Table 5.1. The lattice parameter, density, porosity, natural resonance frequency and real part of initial permeability of the various Ni$_{0.12}$Mg$_{0.14}$Cu$_{0.20}$Zn$_{0.36}$Fe$_{2.4}$La$_x$O$_4$ sintered at various temperatures with fixed dwell time 5h.

<table>
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<th>$a$(Å)</th>
<th>$T_s$ (°C)</th>
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<th>$P$ (%)</th>
<th>$f_r$ (MHz)</th>
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5.4 Complex permeability

The complex initial permeability is given by $\mu_r^* = \mu'_r - i\mu''_r$, where $\mu'_r$ and $\mu''_r$ are the real and imaginary parts of initial permeability respectively. The real permeability $\mu'_r$ describes the stored energy expressing the component of magnetic induction B in phase with the alternating magnetic field $H$. The imaginary permeability $\mu''_r$ describes the dissipation of energy expressing the component of B at 90° out of phase with the alternating magnetic field. Figs. 5.13, 5.14, 5.15 and 5.16 show the complex permeability spectra for Ni$_{0.12}$Mg$_{0.14}$Cu$_{0.20}$Zn$_{0.36}$Fe$_{2.4}$La$_x$O$_4$ sintered at 1100, 1150, 1200 and 1250°C respectively. It is found that the real ($\mu'_r$) and imaginary ($\mu''_r$) permeability decrease with increasing La$^{3+}$ substitution.
Fig. 5.13. The variation of (a) $\mu'$ and (b) $\mu''$ spectra for Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2.4}$La$_{0.4}$O$_4$ sintered at 1100°C in air.

Fig. 5.14. The variation of (a) $\mu'$ and (b) $\mu''$ spectra for Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2.4}$La$_{0.4}$O$_4$ sintered at 1150°C in air.
Fig. 5.15. The variation of (a) $\mu'_r$ and (b) $\mu''_r$ spectra for $\text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.60}\text{Fe}_{2-x}\text{La}_x\text{O}_4$ sintered at 1200°C in air.

Fig. 5.16. The variation of (a) $\mu'_r$ and (b) $\mu''_r$ spectra for $\text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.60}\text{Fe}_{2-x}\text{La}_x\text{O}_4$ sintered at 1250°C in air.
Fig. 5.17 shows the variation of $\mu'_f$ with La content of the samples. It is found that $\mu'_f$ decreases sharply with La content up to 0.025, with a further increase of La $\mu'_f$ decreases slightly except sample sintered at 1150°C.

The initial permeability of ferrite material depends on many factors like reversible domain wall displacement, domain wall bulging as well as microstructural features viz., average grain size, intra-granular porosity, etc. [11]. In a demagnetized magnetic material, there are a number of Weiss domains with Bloch walls separating two domains. These walls are bound to the equilibrium positions. It is well known that the permeability of polycrystalline ferrite is related to two magnetizing mechanisms: spin rotation and domain wall motion. [12], which can be described as follows:

$$\mu'_f = 1 + \chi_w + \chi_{spin}$$

where $\chi_w$ is the domain wall susceptibility; $\chi_{spin}$ is intrinsic rotational susceptibility. $\chi_w$ and $\chi_{spin}$ may be written as: $\chi_w = 3\pi M_s^2 D / 4\gamma$ and $\chi_{spin} = 2\pi M_s^2 / K$ with $M_s$ saturation magnetization, $K$ the total anisotropy, $D$ the average grain diameter, and $\gamma$ the domain wall energy. The $\mu'_f$ is a function of grain size. As the grain size decreases with La content, the $\mu'_f$ also decreases. The domain wall motion is affected by the grain size and enhanced with the increase of grain size thus the $\mu'_f$ increases. The magnetization caused by domain wall movement requires less energy than that required by domain rotation. As the number of domain walls increases with the grain size, the contribution of wall movement to magnetization increases. Fig. 5.18 shows the variation of $\mu'_f$ with sintering temperature of the samples. The $\mu'_f$ of La substituted samples increases with increasing sintering temperature up to 1200°C then decreases. The $\mu'_f$ increases with increasing sintering temperature because porosity decreases with sintering temperature. The reason behind this is the samples heated at higher temperature contain increasing number of pores within the grain and pore is a hindrance for the domain wall motion which results in decrease in permeability.
Fig. 5.17. The variation of Real part of initial permeability with La content of polycrystalline Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ sintered at various temperatures in air at frequency 1 kHz.

Fig. 5.18. The variation of Real part of initial permeability with sintering temperature of polycrystalline Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ at frequency 1 kHz.
Fig. 5.19. The variation of bulk density and permeability with sintering temperature of Ni$_{x}$Mg$_{0.8}$Cu$_{0.2}$Zn$_{0.5}$Fe$_{5.5}$O$_{4}$ with (a) x=0.00, (b) x=0.025, (c) x=0.050 and (d) x=0.075.

Fig. 5.19 shows the variation of bulk density and permeability with sintering temperature of the samples. It is observed that there is a correlation between bulk density and permeability. As the bulk density increases, permeability also increases. However for sintering temperature >1200°C of La undoped sample, the bulk density decreases although $\mu_i$ still increases. On the contrary, for La doped samples, sintered at temperature >1200°C, bulk density as well as permeability decreases. Therefore it is concluded that the optimum sintering temperature for La doped samples may be around 1200°C.
Increase in $\mu'$ with increase in sintering temperature may be explained as follows. Higher sintering temperatures result in the increase in the density of the specimen which facilitates the movement of the spins as the numbers of pores which impede the wall motion are reduced. Increase in the sintering temperature also results in a decrease in the internal stresses, which reduce the hindrance to the movement of the domain walls resulting thereby in the increased value of $\mu'$ [13].

The $\mu'$ is observed highest for sample Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.20}$Fe$_2$O$_4$ sintered at 1250°C and for La substituted samples sintered at 1200°C, because the microstructure is homogeneous with large grain size and uniform size distribution. Also it is found that the sintered density is highest for these temperatures. All these values are listed in Table 5.1.

Globus et al. [14] have developed an equation correlating static susceptibility $(\mu_s - 1)$ and the resonance frequency, $f_r$ corresponding to the maximum of the imaginary part of the complex permeability $\mu''$ to saturation magnetization, $M_s$ and grain diameter, D as given below:

$$ (\mu_s - 1) = \frac{3M_s^2 4\pi D}{16E_w} \quad (5.1) $$

and

$$ f_r = \frac{16E_w}{\pi\delta D^2} \quad (5.2) $$

where $E_w$ is the wall energy and $E_w = K\delta_w$; where $K$ is the anisotropy energy and $\delta_w$ is the domain wall thickness.

$$ (\mu_s - 1)f_r = \frac{12}{\beta D} M_s^2 \quad (5.3) $$

where, $\beta$ is the domain wall damping factor, $(\mu_s - 1)f_r$ is known as Snoek's product which is constant.

According to the Globus model, the relaxation frequency, the static permeability and their product are microstructure dependent. Large grain size leads to high permeability and low resonance frequency. The smaller the grain size, the higher the $(\mu_s - 1)f_r$ product up to a critical size for which the grains become mono-domain. On the contrary, Snoek's model is only related to spin rotations [14].
\[
(\mu - 1) = \frac{2M_s}{3H_a}
\]

and
\[
\xi = \frac{\gamma}{2\pi} H_a
\]

where \(\gamma\) is the gyromagnetic ratio, \(H_a\) is the anisotropy field and \(M_s\) the saturation magnetization. Thus:
\[
(\mu - 1)\xi = \frac{\gamma}{3\pi} M_s
\]

The \((\mu - 1)\xi\) product depends only on saturation magnetization. As grain size increases, the multi domain grains are obtained which induces in higher permeability values due to the domain wall contribution [15,16]. Also an increase in the density of ceramics not only results in the reduction of demagnetizing field due to reduction of pores but also raises the spin rotational contribution, which in turn increases the permeability [17].

The real part of initial permeability value of all the samples remain independent for frequency until resonance takes place, above which it starts decreasing sharply with simultaneously increase of imaginary part of the permeability. The resonance frequency \(f_r\) corresponds to the maximum of the imaginary part of the permeability \(\mu''\) where magnetic losses can be expressed as the ratio, \(\tan\delta = \mu''/\mu'\). It is observed that as the real part of initial permeability started to decrease, the resonance frequency \(f_r\) (i.e. the frequency at which \(\mu''\) show peak) gets higher. This confirms the Snoek's relation stated as
\[
\mu'_r f_r = \text{constant}
\]

It is observed that the \(\mu'_r\) is almost independent up to 10 kHz or greater for parent composition and 1MHz or greater for La doped compositions and after that decreases sharply. The \(\mu''_r\) starts raising beyond this frequency which is an indication of dispersion or resonance. The dispersions of La doped compositions are at higher frequency compared to parent composition. The dispersion behavior can be explained by Snoek's law that cut-off frequency is inversely proportional with magnetic permeability [18]. The values of resonance frequency, \(f_r\) are listed in Table 5.1.
5.5 Loss factor

Energy loss is an extremely important factor in ferromagnetic materials, since the amount of energy wasted on processes other than magnetization can prevent the AC applications of a given material. The ratio of $\mu''$ and $\mu'$ representing the losses in the material are a measure of the inefficiency of the magnetic system. Obviously this parameter should be as low as possible. The magnetic losses, which cause the phase shift, can be split up into three components: hysteresis losses, eddy current losses and residual losses. This gives the formula $\tan \delta_m = \tan \delta_h + \tan \delta_e + \tan \delta_r$. As $\mu'$ is the initial permeability which is measured in presence of low field, therefore, hysteresis losses vanish at very low field strengths. Thus at low field the remaining magnetic losses are due to eddy current losses and residual losses. Residual losses are independent of frequency. Eddy current losses increase with frequency and are negligible at very low frequency. Eddy current loss can be expressed as $P_e = f^2 / \rho$, where $P_e$ is the energy loss per unit volume and $\rho$ is the resistivity [12]. To keep the eddy current losses constant as frequency is increased, the resistivity of the material chosen must increase as the square of frequency. The ferrite microstructure is assumed to consist of grains of low resistivity separated by grain boundaries of high resistivity. Thicker grain boundaries are preferred to increase the resistance.

The variation of loss factor ($\tan \delta$) with frequency of the polycrystalline Ni_{0.12}Mg_{0.18}Cu_{0.2}Zn_{0.5}Fe_{2-x}La_xO_4 compositions are shown in Fig. 5.20 for different sintering temperatures at (a) 1100, (b) 1150, (c) 1200 and (d) 1250°C respectively. At low frequency, $\tan \delta$ of all the samples is found to decrease with increasing frequency whereas at high frequency increases. It is also observed that at high frequency, $\tan \delta$ of all La doped compositions is lower than parent composition and decreases with increasing La substitution.
Fig. 5.20. The variation of Loss factor with frequency of Ni$_{0.12}$Mg$_{0.88}$Cu$_{0.92}$Zn$_{0.08}$Fe$_{2-x}$La$_x$O$_4$ sintered at (a) 1100°C, (b) 1150°C, (c) 1200°C and (d) 1250°C in air.
5.6 Relative quality factor

Figs. 5.21 show the frequency dependence of relative quality factor (RQ-factor) of the samples sintered at (a) 1100, (b) 1150, (c) 1200 and (d) 1250°C respectively.

![Graphs showing frequency dependence of RQ-factor for Ni_{1-x}Mg_0.16 Cu_{0.2}Zn_{0.5}Fe_{2+}LaO_4 at different temperatures](image)

*Fig. 5.21. The variation of relative quality factor with frequency of Ni_{1-x}Mg_0.16 Cu_{0.2}Zn_{0.5}Fe_{2+}LaO_4 sintered at (a) 1100, (b) 1150, (c) 1200 and (d) 1250°C in air.*
Fig. 5.22. The variation of RQ-factor with La content of Ni_{0.12}Mg_{0.18}Cu_{0.2}Zn_{0.5}Fe_{2-x}La_{x}O_{4} sintered at 1250°C in air.

The RQ-factors were calculated from the quality factor and magnetic loss tangent measured on the coil wound on toroidal samples. The variation of the RQ-factor with frequency showed a similar trend for all the samples. RQ-factor increases with an increase of frequency, showing a peak and then decreases with frequency. This happens at the frequency where the permeability begins to drop. This phenomenon is associated with the ferrimagnetic resonance within the domains [19] and at the resonance maximum energy is transferred from the applied magnetic field to the lattice resulting in the rapid decrease in RQ-factor. In the samples sintered at 1150 and 1200°C, the RQ-factor is found to decrease with La substitution. On the other hand in the samples sintered at 1100 and 1250°C, the RQ-factor shows an irregular variation with La substitution. The highest value of the RQ-factor is found in Ni_{0.12}Mg_{0.18}Cu_{0.2}Zn_{0.5}Fe_{2.05}La_{0.05}O_{4} sintered at 1250°C. It is also observed that the highest value of the RQ-factor of all La doped samples shifted at the higher frequency. At the higher frequency the RQ-factor of all samples increases with increasing La content. Fig. 5.22 shows the variation of RQ-factor at 1MHz with La content. It is observed from those RQ-factor increases with increasing La content.
5.7 Temperature-dependent permeability and Néel temperature

The temperature dependence of initial permeability (μ') is very important in the study of magnetic materials. Since the μ' is directly related to the magnetization and to the ionic structure, the thermal spectra of μ' can be taken as a test of the formation and homogeneity of the ionic structure of the samples. Néel temperature (T_N) of a ferrite is a temperature at which the ferrimagnetic material becomes paramagnetic. T_N gives an idea of the amount of energy taken to break up the long-range ordering in the material. T_N also signifies the strength of the exchange interaction between the magnetic atoms. T_N is the temperature where Hopkinson type of effect is observed with the manifestation of sharp fall of permeability. The real part of initial permeability of the samples as a function of temperature is measured at a constant frequency (100 kHz) of a sinusoidal wave.

![Graph showing temperature-dependent permeability](image)

Fig. 5.23. The temperature dependent μ' of Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La_xO_4 with La content sintered at 1200°C in air.
Real part of the initial permeability ($\mu'_i$) as a function of temperature for $Ni_{12}Mg_{10}Cu_{9.30}Zn_{0.7}Fe_{2.5}La_{0.4}O_4$ sintered at 1200°C is shown in Fig. 5.23. $T_N$ has been taken as the temperature at which a sharp fall of permeability is observed i.e. where $d\mu'_i/dT$ attains its maximum value. The sharpness of the fall of $\mu'_i$ indicates the homogeneity and the single phase of the studied samples, which have also been confirmed by X-ray diffraction by our previous XRD experiment.

It is observed that the $\mu'_i$ falls sharply when the magnetic state of the ferrite samples changes and after that the $\mu'_i$ becomes smaller i.e. the paramagnetic character. The vertical drop of the $\mu'_i$ at the Neél point indicates the degree of homogeneity in the sample composition [15,20]. Further increasing temperature $\mu'_i$ becomes smaller and independent of temperature i.e. paramagnetic behavior. Our samples have showed an excellent degree of homogeneity. Measurement of the $\mu'_i$ as a function of temperature can therefore be used as a material characterization of that composition.

It is revealed from Fig. 5.23 that $T_N$ decreases with La substitution up to $x=0.050$ after that at $x=0.075$ increases. The values of $T_N$ for different samples sintered at various temperatures are given in Table 5.2. The decrease of the Neél temperature is due to the weakening of the $A-B$ exchange interaction. This could be attributed to the increase in distance between the moments of $A$ and $B$ sites, which is confirmed by the increase in the lattice parameter with increasing $La^{3+}$ content up to $x=0.050$. The longest distance between moments leads the $A-B$ interaction to decrease. As the lattice constant decreases at $x=0.075$, the $T_N$ increases. The variation of $\mu'_i$ and lattice constant with La content is shown in the Fig. 5.24.
Fig. 5.24. The variation of $T_N$ and $a_0$ with La content of Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ sintered at 1200°C in air.

Table 5.2. The Néel temperature, $T_N$, of the Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ sintered at various temperatures in air.

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<th>La content, $x$</th>
<th>Sintering temperature, $T_s$ (°C)</th>
<th>Néel temperature, $T_N$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>0.00</td>
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</tr>
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<td>1150</td>
<td>151</td>
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<tr>
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<tr>
<td></td>
<td>1150</td>
<td>110</td>
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<td></td>
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<td>158</td>
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<tr>
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<td>1100</td>
<td>87</td>
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<tr>
<td></td>
<td>1150</td>
<td>109</td>
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<tr>
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<td>147</td>
</tr>
<tr>
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<tr>
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<td>1150</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>145</td>
</tr>
</tbody>
</table>
5.8 DC Magnetization

The magnetic ordering in the simple spinel ferrites is based on the Neel's two sub-lattices (tetrahedral A-site and B-site) model of ferrimagnetism in which the resultant magnetization is the difference between A-site and B-site magnetization, provided that they are co-linear and anti-parallel to each other, i.e.,

\[ M = M_B - M_A \] (5.8)

An intrinsic property such as saturation magnetization \( M_s \) is controlled by the composition whereas an extrinsic property, the microstructure, is in turn governed by the processing techniques. The magnetization of magnetic materials is a structural sensitive static property (intrinsic property), the magnetic field required to produce the saturation value varies according to the relative geometry of the field to the easy axes and other metallurgical conditions of the material.

The magnetization as a function of applied magnetic field, \( M-H \), for various \( \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_2\text{O}_4 \) at room temperature (300K) is shown in Fig. 5.25. The magnetization of all samples increases linearly with increasing the applied magnetic field up to 0.1T. Beyond 0.1T applied field, magnetization increases slowly and then saturation occurs.

![Fig. 5.25. The magnetization, \( M \) versus the applied magnetic field, \( H \) curve for \( \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_2\text{O}_4 \), sintered at 1200°C for 5 h in air.](image-url)
In low field Rayleigh region, magnetization is believed to change entirely by domain wall motion. Between the low-field Rayleigh region and the high field region near saturation there exists a large section of the magnetization curve, comprising most of the change of magnetization between zero and saturation. The main processes occurring here are large Barkhausen jump, and the shape of this portion of the magnetization curve varies widely from one kind of specimen to another. On the other hand, in high field region, domain rotation is predominant effect and this phenomenon obeys fairly simple rules.

Fig. 5.26 shows the magnetic hysteresis curve for Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La_{x}O_{4} with different La content. From this curve it is observed that all compositions exhibit low coercivity values, which is typical of soft ferrite. Fig.5.27 shows the variation of saturation magnetization ($M_s$) and magnetic moment ($\mu_B$) with La substitution. The $M_s$ and $\mu_B$ both are found to decrease with La substitution. This may be due to the presence of nonmagnetic LaFeO$_3$ phase which increases with increasing La substitution [21]. The $M_s$ values of different compositions are enlisted in Table 5.3.

![Graph](image)

**Fig. 5.26.** The Magnetic hysteresis curve for Ni$_{0.12}$Mg$_{0.18}$Cu$_{0.20}$Zn$_{0.50}$Fe$_{2-x}$La$_x$O$_4$ ferrites with different La content sintered at 1200°C for 5 h in air.
Fig. 5.27. The variation of saturation magnetization and magnetic moment with La substitution for \( \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_x\text{O}_4 \) sintered at \( 1200^\circ \text{C} \) for 5 h in air.

The number of \( \mu_B \) per atom for each composition is calculated using the experimental values of \( M \), using following relation,

\[
\eta = \frac{M \times M_s}{N_A \times \mu_B}
\]  

(5.9)

Where \( M \) is the molecular weight of the specimen, \( N_A \) is Avogadro's number, and \( \mu_B \) is \( 9.27 \times 10^{-21} \) emu. From the Fig. 5.28, it is seen that there is a correlation between \( \mu_B \) and \( \mu_J \). As the \( \mu_J \) decreases, \( \mu_B \) also decreases with La substitution. The calculated Bohr magnetons of each composition are enlisted in Table 5.3.
Fig. 5.28. The variation of number of Bohr magneton and real part of initial permeability with La substitution for samples $Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La_xO_4$ sintered at $1200^\circ C$ for 5 h in air.

Table 5.3. The saturation magnetization and Bohr magneton of the $Ni_{0.12}Mg_{0.18}Cu_{0.20}Zn_{0.50}Fe_{2-x}La_xO_4$ sintered at $1200^\circ C$.

<table>
<thead>
<tr>
<th>La content, $x$</th>
<th>Saturation magnetizing field, $\mu_oH_s$ (T)</th>
<th>$M_s$ (emu/g)</th>
<th>$\mu_n$ (expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.9</td>
<td>54.3</td>
<td>2.3</td>
</tr>
<tr>
<td>0.025</td>
<td>0.8</td>
<td>52.4</td>
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</tr>
<tr>
<td>0.050</td>
<td>0.7</td>
<td>48.8</td>
<td>2.1</td>
</tr>
<tr>
<td>0.075</td>
<td>0.4</td>
<td>46.8</td>
<td>2.0</td>
</tr>
</tbody>
</table>

References


CHAPTER 6
CONCLUSIONS

6.1 Conclusions

Ferrites are very important materials for the advancement and development of technology. They possess the combined properties of magnetic materials and insulators which are used in almost every item of electronic equipment produced today. The following conclusions have been drawn from this study:

- X-ray diffraction patterns of the samples show the formation of spinel crystal structure. From the XRD patterns a secondary phase LaFeO$_3$ was also detected of all La doped samples. The peak height of LaFeO$_3$ gradually increases with the substitution of La.

- Lattice parameter increases with increasing La substitution. This increase in lattice constant with La indicates that the compositions obey the Vegard’s law. This result is explained with the help of ionic radii of substituted cations.

- The microstructural study shows that the average grain size slightly decreases with increasing La substitution whereas increases with increasing sintering temperature.

- Theoretical density and bulk density both increases with increasing La content. Bulk density increases with increasing sintering temperature up to 1200°C then decreases. On the other hand porosity has the opposite trend.

- The real part of initial permeability ($\mu'_i$) value decreases with increasing La substitution. It is also observed that real part of initial permeability increases with increasing sintering temperature for all compositions up to 1200°C then decreases. The real part of the initial permeability remains fairly constant in the frequency range up to 10 kHz or greater for parent composition and 1 MHz or greater for La doped compositions after that decreases. The imaginary part of initial permeability value starts raising beyond this frequency which is an indication of dispersion or resonance. This confirms the Snoek’s relation. The dispersions of La doped compositions are at higher frequency compared to La undoped composition.
• At low frequency, Loss factor of all the samples is found to decrease with increasing frequency whereas at higher frequency increases. It is also observed that at higher frequency, Loss factor of all La doped compositions is lower than parent composition and decreases with increasing La substitution.

• The highest value of the relative quality factor (RQ-factor) of all La doped compositions shifted at the higher frequency and at the higher frequency RQ-factor increases with increasing La content. This property describes the application of La doped samples. The RQ-factor is found to maximum in 
\[ \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{1.92}\text{La}_{0.075}\text{O}_4 \] sintered at 1250°C.

• The Néel temperature \((T_N)\) decreases with La substitution up to \(x=0.050\) after that increases. The decrease of the \(T_N\) is due to the weakening of the \(A-B\) exchange interaction and vice versa.

• The magnetization of all samples increases linearly with increasing applied magnetic field up to 0.1 T. Beyond this field, magnetization increases slowly and then saturation occurs. Magnetic hysteresis curve shows that all compositions have low coercivity values, which is typical of soft ferrite. The saturation magnetization \((M_s)\) is found to decrease with La substitution.

6.2 Suggestions for future work

The modern devices are extensively need soft magnetic materials which are used in inductors. From the present investigation, although permeability decreases, RQ-factor increases with La substitution at the higher frequency. It was found that among the 
\[ \text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{2-x}\text{La}_x\text{O}_4 \] ferrites \(\text{Ni}_{0.12}\text{Mg}_{0.18}\text{Cu}_{0.20}\text{Zn}_{0.50}\text{Fe}_{1.92}\text{La}_{0.075}\text{O}_4 \) sintered at 1250°C had the maximum RQ-factor. The applications of these ferrites can be specified if the frequency dependent electrical and dielectric properties are measured. The effects of various sintering aids for getting improved magnetic properties of this sample can be investigated. The effects of Gd or Y substitutions for Fe on the electromagnetic properties of this sample can be investigated.