1.0 Introduction:

The progress of human civilization has been indexed based on the progress in the field of material science. Material science is an extremely interdisciplinary subject involving different branches such as physics, chemistry, engineering, biology, etc. The varieties of subjects such as thermodynamics, crystallography, solid state chemistry, polymer science, biochemistry, etc can be brought under one umbrella of materials science.

New branches are still evolving with the advent of knowledge in materials science. Nanotechnology is one such example. Materials science is one of the oldest forms of engineering and applied science. Understanding the basic aspects of a variety of materials such as their structure and properties are the key issues in materials science. Based upon the fundamental understanding of structure-property relationship, new materials with enhanced performance are currently being developed. Materials can be classified according to their interaction with the surroundings.

a) Functional Materials:

These materials perform a particular function for a specific application depending upon their crystallographic or electronic features.

* e.g. semiconductors, magnetic materials, Catalysis, Sensors and Photocatalysis etc.

b) Structural Materials:

These materials are basically important because of their mechanical properties and their other features are not much relevant.

* e.g. steel, plastic, rubber, etc.

c) Smart materials:

This class of materials respond to their surrounding in a two way manner. They can sense the changes happening in their surrounding and send a feedback signal to take an appropriate action. These materials are also termed as intelligent materials.

* e.g. piezoelectric materials, shape memory alloys, magnetostrictive materials, magneto-rheological fluids, etc.
Magnetic materials around us have simplified engineering efforts in the development of technology in various fields today. Therefore the magnetism and magnetic materials have been known as one of the most demanding disciplines in condensed matter physics. Today applied research is developed to optimize the performance of magnetic materials for industrial applications. New magnetic materials have their better performance and lower cost. These materials have been proved very important components in various instruments due to their diverse physical properties such as structural, magnetic and electrical properties. These materials have been used in audio, video, computer, telecommunications, electronic motors, automotive sensors, medical imaging and diagnosis, energy supply, design of stealthy airplanes and in many other applications [1]. These materials are prepared today by various techniques in different forms. Therefore, it is very essential to know the origin and mechanism of magnetism for every combination and form of the magnetic materials which are used for special applications. There is a wide and endless range of applications of magnetic materials.

1.1 Historical Background of Magnetic Materials:

The first type of magnetic material known was in the form of lodestone; consisting of the ore magnetite (Fe$_2$O$_3$). It is believed that it has been discovered in ancient Greece around year 800 BC. Magnets found their first application in compasses, which were used in the nineth century by the Vikings or perhaps even earlier.

A milestone in the history of magnetism was the work done by William Gilbert in 1600. His work "De Magnete, Magneticisque Corporibus, et de Magno Tellure" described the magnetic properties of lodestone up to that point in time. The later development in magnetic materials was done by Hans Christian Orsted, Andre Marie Ampere, Wilhelm Eduard Weber, Michael Faraday, Pierre Curie, and James Clerk Maxwell. Their work provided the basis of electromagnetic theory in general and for crystal structures.
In 1947, J. L. Snoeck published the book, New Developments in Ferromagnetic Materials [2]. Studies by Snoeck and others at Phillips Laboratories in Netherlands led to magnetic ceramics with strong magnetic properties, high electrical resistivity, and low relaxation losses.

In 1948, L. Neel published his work on ferrimagnetic materials in a pioneer paper [1-2]. In this paper, he interpreted the theoretical magnetic properties of this newly formed oxide material called ferrites. In order to understand magnetism of this material, Neel proposed a new model called Neel model of two interpenetrating sub-lattices with oppositely directed magnetic moments.

In 1952, C. L. Hogan from Bell Labs and in 1956, Neel, Bertaut, Forrat, and Pauthenet, discovered the garnet and hexagonal ferrites to fulfill the needs of many devices. In 1959, J. Smit and H. P. J. Wijn published a comprehensive book on ferrite materials entitled ‘Ferrite’. In the United States, many researchers were engaged in the study of ferrites from 1950 to 1970, and they attained remarkably fruitful results both in the technical as well as fundamental research [1-2].

1.2 Magnetism and it’s Origin:

We know that a bar magnet has a magnetic dipole, consisting of two poles of equal strengths separated by a finite distance. If we try to separate them by cutting magnet into two pieces, we find that two opposite poles of equal strengths appear near the broken ends and each piece becomes a complete magnet with the N-pole at one end and the S-pole at the other end. If we go on breaking the magnet into smaller and smaller pieces, we will find that each piece to be a complete magnet with north and south poles at the two ends. If we were to cut the magnet into atoms, we would still find that each atom is a magnet with two poles. Thus a single magnetic pole cannot be isolated from another. The simplest magnetic structure is a magnetic dipole, consisting of two poles of equal strengths, separated by a finite distance.
Matter is made up of atoms and an atom consists of a positively charged nucleus surrounded by negatively charged electrons revolving in orbits around the nucleus. Every atom has three contributions to the magnetism due to Orbital motion, Spin motion of electrons and Spin motion of nucleus are responsible to form

i) Orbital magnetic momentum of electrons

ii) Spin magnetic momentum of electrons

iii) Spin magnetic momentum of nucleus

The magnetic momentum due to nuclear spin motion is negligible. Hence the magnetic effects in magnetic materials are due to orbital and spin motion of electron which induces a small current in the atom giving rise to its self magnetic moment. A circulating electron is equivalent to a current loop. It is known that the current loop behaves like an atomic magnet or a magnetic dipole with one face acting as a north pole and the other face acting as a south pole. Thus a circulating electron is a magnetic dipole and it possesses a magnetic moment. The electrons also spin about their own axes and possess an additional magnetic moment due to the spinning motion. The total magnetic moment of the electron is equal to the vector sum of the magnetic moments due to its orbital motion and spin motion. The magnetic effects in magnetic materials are due to the atomic dipoles in the materials. Since all these motions of charged particles form closed electric current, they are equivalent to magnetic dipoles. The magnetic moment of an atom is equal to the vector sum of the magnetic moments of all the circulating electrons. Thus magnetism originates from the moving charges in the atoms of any substance. The explanation of three important aspects with respect to magnetic materials is given as

1) Some materials are magnetic even without the application of any magnetic field and become more magnetic when a weak field is applied to them.
2) Some materials lose their initially strong magnetism when heated above a certain critical temperature and become comparatively weakly magnetized.

3) Some materials show a magnetic response in an opposite direction to that of an externally applied field.

4) Some materials show the anti-parallel alignment of the atomic dipole moments whenever kept in an external magnetic field.

1.3 Classification of Magnetic Materials:

On the basis of above explanation, the magnetic materials are classified in five types namely.

- Diamagnetism
- Paramagnetism
- Ferromagnetism
- Antiferromagnetism
- Ferrimagnetism

In order to classify the materials, let us know some distinguishing properties of each of them. An atom is said to be magnetic if it carries the permanent magnetic moment. Every substance is formed from an assembly of atoms which can be either magnetic or non-magnetic. In case of magnetic materials, the direction and sometimes the modulus of the magnetic moment can depend upon the particular environment of each atom. This environment depends upon the nature of the material, temperature and applied magnetic field. The behavior of each material can be explained on the basis of their response to the applied magnetic field and temperature.

I) Diamagnetism:

Diamagnetism is a very weak phenomenon of magnetization of materials arising due to the spin motion and the orbital motion of the electron. When a magnetic field is applied to an atom, the orbital motion of the electrons
gets modified in such a way that a weak magnetic moment opposing the field is induced. According to Lenz’s law, the induced current gives rise to an induced flux opposite to the change in the applied field. This magnetism also exists in substances with magnetic atoms. The diamagnetic susceptibility and hence magnetization both are very small and negative. Antimony, bismuth, mercury, gold and copper are some examples of diamagnetic substances. If a magnetic material is placed in a magnetic field, there may be an increase or decrease of the flux density in the material. Diamagnetic materials reduce the density of lines of force while paramagnetic materials increase the flux density. The circulation of electrons in atoms or molecules produces diamagnetism. For diamagnetic substances magnetic susceptibility is less than zero ($\chi < 0$) i.e. very small in magnitude of the order of $10^{-5}$ and is independent of temperature. However a very strong diamagnetism is present in super-conducting materials with a susceptibility equal to -1.

II) **Paramagnetism:**

Paramagnetism is due to the magnetic moments arising from the individual ions, atoms or molecules which contains an odd number of electrons or because of an inner unfilled electron shell. The magnetic moment in these materials have negligible interaction with each other and can orient themselves freely in any direction. Thus in some materials, the permanent magnetic moments of the atoms or ions are acted upon individually with no interaction among them, this effect is called paramagnetism. However in the presence of the field, the magnetic moment have a tendency to turn towards the direction of the field. If no opposing force acts, complete alignment of the atomic moments will be produced and the specimen as a whole would acquire a very large magnetization in the direction of field. However, thermal agitations of the atoms oppose the tendency and try to keep the atomic dipole moments at random. The result is only a partial alignment in the field direction. Therefore a weak magnetization and a small susceptibility is observed in such materials. An
increase of temperature therefore will decrease the susceptibility. Effectively materials with atoms of unpaired spins are paramagnetic.

III) **Ferromagnetism:**

In these materials the individual moments of the atoms or ions are strongly coupled and are more or less parallel to each other even in the absence of a magnetic field, so called positive exchange interactions. There results a very large macroscopic moment. It is a spontaneous magnetization of small regions of material that exists even in the absence of external magnetic field. Ferromagnetism occurs when paramagnetic ions in a solid, lock together in a small region in which all magnetic moments are along the same direction. Such a region is called domain. Domain is the self-alignment of atoms carrying permanent moments in the same direction. There are number of domains present in the ferromagnetic material. The boundaries between domains having different orientations are called as domain walls. If there is no external magnetic field applied to the sample of ferromagnetic material, the domains are randomly oriented such that the net magnetic moment is zero. When the sample is placed in an external magnetic field, the domains tend to align along the direction of the field giving the net magnetization. If the temperature of the ferromagnetic substance is increased, at sufficiently high temperature the domain structure breaks down and ferromagnetic substance becomes paramagnetic. This temperature is called as Curie temperature $T_c$.

IV) **Anti-ferromagnetism:**

This is a weak form of magnetism similar to that of paramagnetism with a weak and positive susceptibility. There are number of materials that show interesting modifications of ferromagnetic behavior. These materials are characterized by two interlocking sets of atoms, which have the spin lining up character of ordinary ferromagnetic substances. In some materials like MnO, the two sub lattices have identical magnetic moments but opposite in direction. These orientations are due to exchange forces between adjacent atoms to have anti-parallel spin orientations. Hence such materials show very less gross
external magnetism. Such materials are called as Anti-ferromagnetic materials. If they are heated sufficiently, at high temperature, thermal agitation overcomes interaction effects of the material which shows susceptibility similar to that of paramagnetic materials.

V) Ferrimagnetism:

These materials are also called as partially antiferromagnetic materials due to the uncompensated magnetic spin moment. In this case the magnetization arises due to the resultant of two sub lattices. Each sub lattice behaves as an individual ferromagnet within which moments are aligned parallel. These sublattices are alternately arranged to one another. There will be a strong interaction between the two sublattices in the opposite directions so that it results in a total magnetic moment equal to the difference between their individual magnitudes. Below certain temperature materials exhibit spontaneous magnetization. Thus the class of materials with an unequal and opposite spin systems has been named as ferrimagnetism and the materials are so called as ferrites. Above certain high temperature below $T_c$ these materials behaves as paramagnetic in nature due to cancellation of magnetic moments. Also at very high temperature, the thermal variation of the reciprocal susceptibility is almost linear and it shifts away from linear behavior when approaching the Curie temperature. The distinguishing properties of all above magnetic materials such as orientation of spin moments, magnetization and susceptibility with varying magnetic field and temperature are tabulated in Table I below.
### Table I Classification of magnetic materials

<table>
<thead>
<tr>
<th>Type of Magnetism</th>
<th>Susceptibility</th>
<th>Atomic / Magnetic Behaviour</th>
<th>Example/ Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dia magnetism</td>
<td>Small &amp; -ve</td>
<td>No magnetic moment</td>
<td>Au -2.74x10^-6 Cu -0.77x10^-6</td>
</tr>
<tr>
<td>Para magnetism</td>
<td>Small &amp; +ve</td>
<td>Randomly oriented magnetic moments</td>
<td>β-Sn 0.19x10^-6 Sn 21.04x10^-6 Pt 66.10x10^-6</td>
</tr>
<tr>
<td>Ferro magnetism</td>
<td>Large &amp; +ve</td>
<td>Parallel aligned magnetic moments</td>
<td>Fe ~100,000</td>
</tr>
<tr>
<td>Antiferro magnetism</td>
<td>Small &amp; +ve</td>
<td>Anti-parallel aligned equal magnetic moments</td>
<td>Cr 3.6x10^-6</td>
</tr>
<tr>
<td>Ferri magnetism</td>
<td>Large &amp; +ve</td>
<td>Anti-parallel aligned unequal magnetic moments</td>
<td>Ba ~3</td>
</tr>
</tbody>
</table>

### 1.4 Introduction to Ferrites:

This is the fifth class of magnetic materials also known as ferrimagnetic materials. Basically these are the mixed metal oxides with iron oxide as their main components are known as “ferrites”. Ferrites are of great technical importance because they exhibit a spontaneous magnetic moment below Curie temperature. The requirements of electronic and magnetic properties in the
advanced electronics and microwave devices have focused the attention of researchers in ferrites.

Ferrites are the oxides of transition metals which particularly crystallize in the spinel structure and contain to some extent one of the known ferromagnetic elements. The chemical formula for the ferrites may be written as $\text{AB}_2\text{O}_4$, where A is divalent metal ion, B is Fe$^{3+}$ and O is divalent oxygen ion. In spinel structure, the oxygen atoms are closely packed in face centered lattices, into the interstices of which the metal ions are distributed. This class of materials possess a macroscopic moment and an unbalance of the two spins that results from an antiferromagnetic interaction.

In 1948, L. Neel published his work on ferrimagnetic materials in a pioneer paper. In this paper, he interpreted the theoretical magnetic properties of this newly formed oxide material called ferrites. Lodestone (FeO.Fe$_2$O$_3$) is the first naturally occurring ferrite which fulfils the ferrite structure. Ferrites are said to have spinel structure as that of the structure exhibited by natural mineral MgAl$_2$O$_4$ (magnetite) which is the familiar example of ferrite. In order to understand the magnetic properties of these materials, scientist Neel proposed a new model called Neel model of two interpenetrating sub-lattices with oppositely directed magnetic moments. According to this model, the resultant macroscopic magnetic moment is due to two oppositely directed unequal spin moments. The stage was now set for the development of microwave ferrite devices.

In 1952, C. L. Hogan from Bell Labs made the first non-reciprocal microwave devise at 9 GHz that was based on the Faraday rotation effect. Research was completed to improve the properties of the spinel ferrite materials by various cation substitutions. This modified the magnetic properties for different frequency ranges, power requirements, and phase shift applications. In 1956, Neel, Bertaut, Forrat, and Pauthenet discovered the garnet ferrite class of materials. This type of ferrite material has three sub lattices, and is also referred to as rare-earth iron garnets. These materials, although having a magnetization lower than spinel ferrite, possess extremely
low ferromagnetic line width. Another class of ferrite material that was
developed during this time is the hexagonal ferrite. These materials have three
basic sub lattices combined in different numbers in a hexagonal structure. The
high anisotropy fields have been utilized in microwave ferrite devices in the
millimeter range. In 1959, J. Smit and H.P.J. Wijn published a comprehensive
book on ferrite materials entitled Ferrite. Developments have been made on the
magnetic characteristics of ferrite materials. In the United States, many
researchers were engaged in the study of ferrites from 1950 to 1970, and they
attained remarkably fruitful results both in the technical as well as in
fundamental research.

The first international conference on ferrites, ICF, was held in 1970 in
Japan, and, after that more than seven such conferences have been held. These
conferences have contributed greatly to the advancement of the science and
technology of ferrites.

In ICF (3) 1980 Prof. Takai in his opening address pointed out the need
of power ferrite material which can be operated at much higher flux levels than
those operated in telecommunications [3-4].

During last three decades, a remarkable research growth in ferrites has
been found. Researchers have shown that mixed ferrites usually have better
performance than the simple ferrites and show properties and stability
depending on the stoichiometry, nature of the metallic ions in the final mixture,
method of preparation and size of the particles. The technological applications
of the ferrites are in high frequency and pulse transformers, inductances,
deflection coils and in applications in high permeability and low loss at high
frequencies.

Today nano scale ferrites have been attracted large number of
researchers due to their unusual physical and chemical properties than that in
bulk form. It is observed that polycrystalline nano ferrites are widely used for
many technological applications such as in home appliances, electronic
products, communication and data processing devices, radio, television,
microwave and satellite communications. The present work of this project
deals with the synthesis and study of nanocrystalline Mn and Cr substituted lithium ferrites.

1.4.1 Classification of Ferrites:
Ferrites crystallize in four different crystal types depending on their structure, as summarized in Table II

Table II Structure based classification of ferrites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Type</th>
<th>Structure</th>
<th>General Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spinel</td>
<td>Cubic</td>
<td>$A^{II}Fe_{2}O_{4}$</td>
<td>$A^{II} = Cd, Co, Mg, Zn$</td>
</tr>
<tr>
<td>2</td>
<td>Garnet</td>
<td>Cubic</td>
<td>$Ln^{III}Fe_{2}O_{4}$</td>
<td>$Ln^{III} = Y, Sm, Eu$</td>
</tr>
<tr>
<td>3</td>
<td>Magneto-Plumbite</td>
<td>Hexagonal</td>
<td>$A^{II}Fe_{12}O_{19}$</td>
<td>$BaFe_{12}O_{19}$</td>
</tr>
<tr>
<td>4</td>
<td>Pervoskite</td>
<td>Orthorhombic</td>
<td>$A^{III}FeO_{3}$</td>
<td>$LaMnO_{3}, CaTiO_{3}$</td>
</tr>
</tbody>
</table>

1.4.2 Types of Ferrites (Composition dependent)
Depending on chemical composition spinel ferrites are classified into three types,

- Simple spinel ferrites
- Mixed spinel ferrites
- Substitutional spinel ferrites

I) Simple spinel ferrites:
When a divalent ferrous ion in $Fe_{3}O_{4}$ is replaced by other divalent metal ions like Cu, Mn, Mg, Co, Cd, Ni, etc. the resulting ferrite is called as simple ferrite.
e.g. $NiFe_{2}O_{4}$, $CoFe_{2}O_{4}$ and $CuFe_{2}O_{4}$ etc.
II) Mixed spinel ferrites:

When a ferrous ion in $\text{Fe}_3\text{O}_4$ is replaced by two other divalent ions like Co, Mn, Mg, Cu, Cd, Ni, etc. maintaining the stoichiometry of the system as it is, it constitutes mixed ferrites. e. g. $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$, $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ etc.

III) Substitutional spinel ferrites:

When a divalent metal ion or trivalent iron ions are replaced by other magnetic or nonmagnetic ions in the spinel structure, the resulting ferrites are called substitutional ferrites.

1.4.3 The Structure of Spinel Ferrite:

Ferrites are said to have spinel structure. In this spinel structure the oxygen atoms are closely packed in face centered lattices, into the interstices of which the metal ions are distributed. The unit cell of ferrite contains 8 molecules ($8\times\text{FeFe}_2\text{O}_4$). There are 32 divalent oxygen ions, 16 trivalent iron ions and 8 divalent iron ions per unit cell. When the oxygen atoms arrange themselves in fcc structure, there are 8 occupied tetrahedral voids called the A and 16 occupied octahedral voids called the B sites.

The crystal structure can be described by dividing the unit cell into eight octants, with metal ions in every octant as shown in Fig. 1.1. The oxygen ions are arranged in identical manner in all octants. Each octant contains four oxygen ions on the body diagonals and at the alternate corner of a tetrahedron. Each oxygen ion is located at a $1/4$ distance of the body diagonal from alternate corners of the octant. The array of oxygen ions in a whole crystal forms fcc lattice with edge $a/2$. Thus there are such four interpenetrating fcc oxygen lattices.

The positions of metal ions are different in the two octants sharing a face. If we consider two adjacent octants, in one of the octants, an occupied tetrahedral site is located at the centre of four more sites on the corners of the octant. In the adjacent octant, the central site is not occupied. Thus the
occupied tetrahedral sites form two interpenetrating fcc lattices having an edge ‘a’ and are displaced with respect to each other, over a distance ‘a√3/4 in the direction of the body diagonal of a cube. Each tetrahedral ion is surrounded by four other tetrahedral ions which lie at the corners of a regular tetrahedron. There are twelve nearest neighbour octahedral ions for every tetrahedral ion.

Fig. 1.1 Spinel Structure of Ferrite

Each octant contains four octahedral metal ions and these are situated at sites analogous to those of the oxygen ions i.e. at one quarter length of the diagonal from the other ends of the four body diagonals of the octant.
Octahedral metal ions form four interpenetrating fcc lattices with edge ‘a’, and are displaced with respect to each other over a distance \(1/4a\sqrt{2}\) in the direction of the face diagonals of a cube. The environment of an octahedral ion by the other octahedral ions is not cubic as in the case of an individual tetrahedral ion. Each octahedral ion forms part of the two regular tetrahedral of octahedral ions, having the ion under consideration as common one. Each octahedral ion is surrounded by six nearest tetrahedral ions.

Also each oxygen ion is surrounded by one tetrahedral ion (A ion) and three octahedral ions (B ions) as shown in figure 1.2 (a, b). This unit can be considered as a basic component of the spinel lattice. Each A ion belongs to four such units and each B ion to six units. The direction of OA is along the body diagonal of a cube and the directions OB are along the edges of cube [3-4].

There are several ion combinations possible in A and B sites. A wide range of ions may be used such as Ni, Co, Mg, Cu, etc. A combination of two or more can also be used in which we get a **mixed ferrite**.

### 1.4.4 Classification of spinel ferrites on the basis of cation distribution:

Spinel ferrite can be classified on the basis of cation distribution into three groups,

- Normal spinel ferrite
- Inverse spinel ferrite
- Random spinel ferrite

#### a) Normal Spinel Ferrites:

In normal spinel ferrite, all the divalent metal ions occupy A-sites and all trivalent occupy B-sites. The structural formula of such ferrites shows a cation distribution as given below.

\[
[M^{2+}]^A [Fe^{3+} \, Fe^{3+}]^B O_4^{2-}
\]

Where \(M^{2+}\) divalent metal ions located at A site
Chapter I : Introduction

Fe\(^{3+}\) iron ions located at B site.

O\(_4\)^{2-} Oxygen ions at O-sites

This type of ferrites are non-magnetic in nature. The examples of these ferrites are ZnFe\(_2\)O\(_4\) and CdFe\(_2\)O\(_4\) exhibit this type of structure.

b) **Inverse Spinel Ferrites:**

In inverse spinel ferrite, 8 divalent metal ions (M\(^{2+}\)) occupy B-sites and 16 trivalent ion (Fe\(^{3+}\)) are equally divided between A and B sites. The general cation distribution may be written as

\[
[\text{Fe}^{3+}]^A[\text{M}^{2+}\text{Fe}^{3+}]^B\text{O}_4^{2-}
\]

This type of ferrites is magnetic in nature. The examples are Fe\(_3\)O\(_4\), NiFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\) etc.

c) **Random Spinel Ferrites:**

The divalent metal ions [M\(^{2+}\)] and trivalent metal ions (Fe\(^{3+}\)) are randomly distributed over A and B sites depending on their physical and chemical condition of preparation and chemical variation. Such ferrites are partly inverse spinel ferrites.

The general cation distribution formula may be given as,

\[
[M_x^{2+}\text{Fe}_{1-x}^{3+}]^A[M_{1-x}^{2+}\text{Fe}_{1-x}^{3+}]^B\text{O}_4^{2-}
\]

where, x - coefficient of normality

1-x – coefficient of inversion

Examples of these are MnFe\(_2\)O\(_4\) and CuFe\(_2\)O\(_4\) etc.

1.5. **Magnetic Properties of Ferrites:**

In last four decades, magnetic materials due to their versatile magnetic properties and their applications made tremendous interest to physicist, chemists, metallurgists and also the researchers working in the field of materials science. The ferromagnetic and ferrimagnetic materials are
considered to be most important magnetic materials because of their combined electrical and magnetic properties. Ferrites are considered as uncompensated ferromagnetic materials.

The spins apart from the exchange interaction between neighbouring atoms have interaction with lattice atoms. The spin lattice interaction can be seen if all the spins are completely aligned and alignment is rotated relative to the crystal axis, prefered directions of magnetic moments are then observed. The excess work is done in magnetizing a specimen to saturation. Thus hysteresis study of ferrites gives us valuable information regarding saturation magnetization (Ms), coercive force (Hc) and remanence (Mr). Magnetic materials exhibit different kinds of magnetic ordering on the basis of spin orientation. Magnetic materials contain three types of domains such as Multi Domain (MD), Single Domain (SD) and Super paramagnetic Domain (SP). These domain structures change with chemical composition and thermal treatment. Hysteresis studies are useful to explore these domain structures. The variation in shapes of hysteresis with thermal variation are correlated with domain structure. The curie temperature can also be found from the hysteresis loop so obtained.

**Hysteresis:**
The ferrites exhibit all properties similar to ferromagnetic materials. The properties of ferrites can be classified into two categories such as intrinsic and structure sensitive. Saturation magnetization, anisotropy, magnetostriction, and Curie temperature are the intrinsic properties while permeability and hysteresis are very much structure sensitive. The structural aspects such as grain size, porosity, impurities and inclusion of non magnetic ions are very much sensitive to above said properties.

Ferrites are mainly classified into two different categories based on their coercivity value. In general, the coercive force for all ferrites can range from 0.1 Oe to 3 KOe. The ferrites in the coercivity range from 0.1 Oe to 1.5 KOe are termed as ‘soft ferrites’ and the ferrites in the coercivity range from 1.5 KOe to 3 KOe are termed as ‘hard ferrites’. Hysteresis properties mainly depend on the parameters such as crystal structure, cation distribution, chemical composition, sintering atmosphere and condition and final fabrication.

1.6. Dielectric materials:
1.6.1. Introduction:

Electrical circuits use insulator materials in various forms. Capacitors use dielectrics as medium. A dielectric is a nonconducting substance, i.e. an insulator. The term was coined by William Whewell in response to a request from Michael Faraday. The dielectric materials, which are also known as insulating materials, constitute a very important group of electrical (and electronic) engineering materials. Although "dielectric" and "insulator" are generally considered synonymous, the term "dielectric" is more often used to describe materials where the dielectric polarization is important, such as the insulating material between the metallic plates of a capacitor, while "insulator" is more often used when the material is being used to prevent a current flow across it. Dielectrics are the study of dielectric materials and describe how an electric field behaves inside a material. Dielectrics are characterized by dielectric constant, dielectric loss, dielectric strength and resistivity.
Capacitance:

When a voltage is applied across a capacitor, one plate becomes positively charged, the other negatively charged, with the corresponding electric field directed from the positive to the negative. The capacitance $C$ is related to the quantity of charge stored on either plate $Q$ by

$$ C = \frac{Q}{V} \quad \text{--------1.1} $$

where $V$ is the voltage applied across the capacitor. The units of capacitance are coulombs per volt, or farads (F).

Now, consider a parallel-plate capacitor with a vacuum in the region between the plates. The capacitance may be computed from the relationship

$$ C = \varepsilon_0 \frac{A}{l} \quad \text{--------1.2} $$

where $A$ represents the area of the plates and $l$ is the distance between them. The parameter $\varepsilon_0$ called the permittivity of vacuum is a universal constant having the value of $8.854 \times 10^{-12}$ F/m.

If a dielectric material is inserted into the region within the plates (Figure 1.3), then

$$ C = \varepsilon \frac{A}{l} \quad \text{--------1.3} $$

Where $\varepsilon$ is the permittivity of this dielectric medium, which will be greater in magnitude than $\varepsilon_0$. The relative permittivity $\varepsilon_r$ often called the dielectric constant, is equal to the ratio

$$ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \quad \text{--------1.4} $$

which is greater than unity and represents the increase in charge storing capacity by insertion of the dielectric medium between the plates. The dielectric constant is a material property that is of prime consideration for capacitor design.
Figure 1.3 Parallel-plate capacitor (a) when a vacuum is present and (b) when a dielectric material is present

1.6.2. Types of dielectrics:

   Dielectrics are of two types:

   (I) Polar dielectrics

   (II) Non-Polar dielectrics

(I) Polar dielectrics:

   Materials like water, Alcohol, CO₂, NH₃, HCl etc. are made of polar atoms/molecules. In polar molecules when no electric field is applied centre of positive charges does not coincide with the centre of negative charges.
A polar molecule has permanent electric dipole moment in the absence of electric field also. But a polar dielectric has net dipole moment as zero in the absence of electric field because polar molecules are randomly oriented as shown in figure.

In the presence of electric field polar molecules tend to line up in the direction of electric field, and the substance has finite dipole moment.

(II) Non-polar dielectrics:

Materials like N\textsubscript{2}, O\textsubscript{2}, Benzene, Methane etc. are made of non-polar atoms/molecules. In non-polar molecules, when no electric field is applied the centre of positive charge coincides with the centre of negative charge in the molecule. Each molecule has zero dipole moment in its normal state.
When electric field is applied, positive charge experiences a force in the direction of electric field and negative charge experiences a force in the direction opposite to the field i.e., molecule becomes an induced electric dipole.

**1.6.3. Electrical polarization mechanisms:**

The electrical polarization takes place through four different mechanisms (Figure 1.4). They are

1. Electronic polarization.
2. Ionic polarization.
3. Orientation polarization.
4. Space charge polarization.

The net polarization of the material is due to the contribution of all four polarization mechanisms.

\[ P = P_e + P_i + P_o + P_s \]  

\[ \text{--------- 1.5} \]

**1) Electronic polarization:**

This occurs throughout the dielectric material and is due to the separation of effective center of positive charges from the effective center of
negative charges in atoms or molecules of dielectric material due to applied electric field. Hence dipoles are induced within the material. This leads to the development of net dipole moment in the material and is the vector sum of dipole moments of individual dipoles.

2) Ionic polarization

This occurs in ionic solids such as sodium chloride etc. Ionic solids possess net dipole moment even in the absence of external electric field. But when the external electric field is applied the separation between the ions further increases. Hence the net dipole moment of the material also increases.

3) Orientation Polarization

This occurs in polar dielectric material, which possesses permanent electric dipoles. In polar dielectrics the dipoles are randomly oriented due to thermal agitation. Therefore net dipole moment of the material is zero. But when the external electric field is applied all dipoles tend to align in the direction of the field. Therefore, dipole moment develops across the material. This is referred to as orientation polarization ($P_o$). Orientation polarization depends on temperature. Higher the temperature, more the randomness in dipole orientation, smaller will be the dipole moment.

4) Space charge polarization

This occurs in materials in which only a few charge carriers are capable of moving through small distances. When the external electric field is applied these charge carriers move. During their motion they get trapped or pile up against lattice defects. These are called localized charges. These localized charges induce their image charge on the surface of the dielectric material. This leads to the development of net dipole moment across the material. Since this is very small it can be neglected. It is denoted by $P_s$. 
Figure 1.4. (a) Electronic polarization that results from the distortion of an atomic electron cloud by an electric field. (b) Ionic polarization that results from the relative displacements of electrically charged ions in response to an electric field. (c) Response of permanent electric dipoles (arrows) to an applied electric field, producing orientation polarization.

1.6.4. Dielectric constant:

Faraday discovered that the capacitance of the condenser increases when the region between the plates is filled with dielectric. If \( C_0 \) is the capacitance of the capacitor without dielectric and \( C \) is the capacitance of the capacitor with dielectric then the ratio \( C / C_0 \) gives \( \varepsilon_r \) called relative permittivity or dielectric constant. Also for a given isotropic material the electric flux density is related to the applied field strength by the equation \( D = \varepsilon_0 E \), where \( \varepsilon_0 \) is absolute permittivity. In SI system of units, the relative permittivity is given by the ratio of absolute permittivity to permittivity of free space.
\[ \varepsilon = \varepsilon_0 \varepsilon_r, \quad \text{------ 1.6} \]

\( \varepsilon_0 \) is permittivity of free space. \( \varepsilon_r \) is relative permittivity or dielectric constant.

For an isotropic material, under static field conditions, the relative permittivity is called static dielectric constant. It depends on the structure of the atom of which the material is composed.

1. 6.5. **Frequency dependence of the dielectric constant:**

In many practical situations the current is alternating (ac); that is, an applied voltage or electric field changes direction with time, as indicated in Figure 1.5a. Now consider a dielectric material that is subject to polarization by an ac electric field.

![Figure 1.5](image)

**Figure 1.5** Dipole orientations for (a) one polarity of an alternating electric field and (b) for the reversed polarity

With each direction reversal, the dipoles attempt to reorient with the field, as illustrated in Figure 1.5, in a process requiring some finite time. For each polarization type, some minimum reorientation time exists, which depends on the ease with which the particular dipoles are capable of realignment. A relaxation frequency is taken as the reciprocal of this minimum reorientation time. A dipole cannot keep shifting orientation direction when the frequency of the applied electric field exceeds its relaxation frequency and, therefore, will not make a contribution to the dielectric constant. The
dependence of dielectric constant on the field frequency is represented schematically in Figure 1.6 for a dielectric medium that exhibits all three types of polarizations. The absorption of electrical energy by a dielectric material that is subjected to an alternating electric field is termed dielectric loss. This loss may be important at electric field frequencies in the vicinity of the relaxation frequency for each of the operative dipole types for a specific material. A low dielectric loss is desired at the frequency of utilization.

![Figure 1.6 Frequency dependence of several contributions to the polarization](image)

**Figure 1.6** Frequency dependence of several contributions to the polarization

### 1. 6.6. Dielectric loss:

When a material is subjected to an electric field, it dissipates part of the electrical energy which gets converted to heat energy. That part of energy is lost or wasted, as no useful work is done by it. The term ‘power loss’ denotes the average electrical power dissipated in a material during a certain interval of time. In general, power loss in a material is directly proportional to the square of the applied voltage.
When a conductor is connected to a dc voltage \( V \), the power loss in it is given by

\[
P_{ac} = \frac{V^2}{R} = I^2 R
\]

--- 1.7

Where \( R \) is the resistance of the conductor.

When the conductor is connected to an ac voltage of the same effective magnitude as the dc voltage \( V \), the power loss in it is still given a relation

\[
P_{ac} = \frac{V^2}{R} = I^2 R
\]

--- 1.8

The power loss in conductors is also called \( I^2R \) loss or Joules heat. It is seen from the relations 1.7 and 1.8 that in a conductor \( P_{ac} = P_{dc} \)

As distinct from conductors, the power \( (I^2R) \) loss in dielectrics subjected to dc voltages will be very small due to the high resistance of the dielectric materials. on the other hand, the power loss in ac fields will be quite large. The absorption of electrical energy by a dielectric subjected to an alternating electric field is known as the dielectric loss. The dielectric loss caused by an ac field also results in dissipation of the electrical energy as heat in the materials.

1. 6.7. Dielectric strength:

**Dielectric strength:**

In physics, the term dielectric strength has the following meanings:

Of an insulating material, the maximum electric field strength that it can withstand intrinsically without breaking down, i.e., without experiencing failure of its insulating properties.

It is the maximum electric stress the dielectric material can withstand without breakdown. The theoretical dielectric strength of a material is an intrinsic property of the bulk material and is dependent on the configuration of the material or the electrodes with which the field is applied. At breakdown, the electric field frees bound electrons. If the applied electric field is sufficiently high, free electrons may become accelerated to velocities that can liberate additional electrons during collisions with neutral atoms or molecules in a process called avalanche breakdown. Breakdown occurs quite abruptly
(typically in nanoseconds), resulting in the formation of an electrically conductive path and a disruptive discharge through the material. For solid materials, a breakdown event severely degrades, or even destroys, its insulating capability. Dielectric strength increases with the decrease in thickness of the specimen (Directly proportional), decreases with the increase in operating temperature (Inversely proportional), decreases with the increase in frequency (Inversely proportional) and decreases with the increase in humidity (Inversely proportional).

1.6.8 Applications:

Capacitors:

Commercially manufactured capacitors typically use a solid dielectric material with high permittivity as the intervening medium between the stored positive and negative charges. This material is often referred to in technical contexts as the "capacitor dielectric". The most obvious advantage to use such a dielectric material is that it prevents the conducting plates on which the charges are stored from coming into direct electrical contact. More significantly however, a high permittivity allows a greater charge to be stored at a given voltage. This can be seen by treating the case of a linear dielectric with permittivity $\varepsilon$ and thickness $d$ between two conducting plates with uniform charge density $\sigma\varepsilon$. In this case, the charge density is given by

$$\sigma\varepsilon = \varepsilon \frac{V}{d} \quad \text{(1.9)}$$

and the capacitance per unit area by

$$C = \frac{\sigma\varepsilon}{V} = \frac{\varepsilon}{d} \quad \text{(1.10)}$$

From this, it can easily be seen that a larger $\varepsilon$ leads to greater charge stored and thus greater capacitance. Dielectric materials used for capacitors are also chosen such that they are resistant to ionization. This allows the capacitor to operate at higher voltages before the insulating dielectric ionizes and begins to allow undesirable current flow.
Cable insulation:

The term "dielectric" may also refer to the insulation used in power and RF cables. Common materials used as electrical insulations are electrical insulation paper and plastics.

Some practical dielectrics:

Dielectric materials can be solids, liquids, or gases. In addition, a high vacuum can also be a useful, lossless dielectric even though its relative dielectric constant is only unity.

Solid dielectrics are perhaps the most commonly used dielectrics in electrical engineering, and many solids are very good insulators. Some examples include porcelain, glass, and most plastics. Air, nitrogen and sulfur hexafluoride are the three most commonly used gaseous dielectrics.

1.7 Applications of Ferrites:

The research in ferrites in past twenty years is a milestone in the history of development of modern technology and electronics. It is a very important member of family of magnetic materials. The electrical and magnetic properties of ferrites made the ferrite material as an unique substance in the electrical, electronics and magnetic applications.

Phillips Research Laboratories in the Netherlands succeeded in producing a 'soft' ferrite for commercial applications. Primarily, soft ferrites in a few selected shapes and sizes have been used for inductor and antenna applications, 'soft' ferrite has been manufactured into countless sizes and shapes for multipurpose uses. Soft ferrites are used for low signal, memory core, read write heads, transformers and low energy inductor. A large use of these ferrites is in deflection-yoke cores, flyback transformers and convergence coil for television [4-6].

Ferrites are used in high frequency applications due to no eddy current losses at high frequencies. Hence these are used in certain fields such as radar, television, microwave communication, data processing devices, mechanical filters, circulators, broad band transformers, ferromagnetic insulators,
ultrasonic generators, isolators, modulators, phase shifters, directional couplers, tape recorders and in radio etc. Ni, Co and Mg ferrites are used for above applications. These are also used in microwave devices in information processors, in thermo magnetic recorders, in magneto-optical devices and in magnetic holography etc. Mn-Zn ferrites are used for operation upto 500 KHz and Ni-Zn ferrites for high frequency operations upto 100 MHz [5-6].

Modern electronic industries need ferrites in inductors and transformers on miniature scale. Ferrites are used predominately in three areas of electronics Low level applications, Power applications and Electro-Magnetic Interference (EMI) suppression.

In digital computers, the Mg-Mn, Mn-Cu and Li-Ni ferrites are used as the switching and memory elements or logic operation devices, for transmitting, storing and recording the signal pulse in few microseconds. Due to high resistivity of ferrites, they find applications in audio devices such as recording and erasing heads in the tape recorder [6]. Ferrites with large magnetostriction or low permeability are used in accelerators and generators. Hard ferrites are used as permanent magnets for making storage device in computers. They are used in generators, relays, loud speakers, telephone ringers and toys etc. Hard ferrite powders are mixed with plastic materials to form flexible magnets for door closers (refrigerator doors) and other holding devices. Ferrite plating is a new technique used for the preparation of film devices in which heat resistant materials such as plastic is used. Ba ferrite (Ferroxdure) can be used for such applications. Hexagonal ferrites are generally used as permanent magnetic materials for above applications [6-7].

Catalysis is fundamental to life. In fact, without catalysis no form of life could exist. Most of the life supporting reactions in our body are catalyzed by enzymes, which are nature’s catalysts. The global economy is based on catalytic production of chemicals and fuels worth over 10 trillion dollars per year. Catalysis has played a vital role in developing new, environmentally benign technologies to replace stoichiometric synthetic routes often involving toxic and corrosive reagents and associated with generation of waste products.
Catalysis plays a very fundamental role in the oil and chemical industry, allowing the conversion of a wide variety of feedstocks to high value products at lower cost, with minimum generation of byproducts. Catalyst technology not only accounts for the large-scale conversion of oil to gasoline in petroleum industry but also to small-scale synthesis of drugs in the pharmaceutical industries. Almost all chemicals, fuels, polymers and fibers are manufactured by catalytic processes. Thus, the importance of catalysis to society is obviously based on its great economic impact in the production of a broad range of commodity products that improve our standard of living and quality of life. The word ‘catalysis’ was coined by Berzelius in 1836 which is a Greek word, the prefix, ‘cata’ meaning down, and the verb ‘lysein’ meaning to split or break. A catalyst breaks down the forces that inhibit the reactions of the molecules by lowering the activation energy. The widely accepted definition of a catalyst is ‘a substance that changes the rate at which reaction equilibrium is attained, without itself being consumed in the reaction processes. Catalysis is broadly classified into three categories depending on the physical nature of the catalyst employed:

1. **Homogeneous catalysis**: The reactants, products and catalyst are present in the same phase.
   e.g. liquid-liquid system, here the catalyst is mixed uniformly with the reactant, hence the yield and efficiency is very high, but the separation cause the major problem.

2. **Heterogeneous catalysis**: Reactants/products and catalyst are present in separate phases; the catalyst is generally solid and the reactants are either liquid or gas.
   e.g. solid-liquid system, the separation of the catalyst is easy but the efficiency of process mainly depends upon the contact time and contact area of the catalyst.

3. **Biocatalysis or enzymatic catalysis**: It mainly involves all biological and related reactions. *Enzyme catalysis* is also homogeneous in nature and
provides regioselective and stereoselective transformations at ambient reaction conditions with almost no byproduct formation. The enzymes are the most efficient catalysts known to human being, as they are substrate specific, regio/stereo and chemoselective with nearly 100% atom efficiency.

By the consideration of the rigid thermal and structural stability, variable oxidation state, enhanced catalytic activity and better selectivity, the mixed-metal oxides have been used as catalysts in commercial industries for organic transformation reactions. The nanostructure and high surface to volume ratio of the material are the important features of the materials to perform their catalytic activities. Mixed-metal oxides used are of the class of heterogeneous catalysts.

Demand for chemical sensors has been growing at a consistent pace in recent years due to the stringent environmental regulations that are coming into effect to reduce emissions and hazardous pollutants. Semiconductor gas sensors like \( \text{SnO}_2 \), \( \text{ZnO} \) or \( \text{Fe}_2\text{O}_3 \) have been well studied to detect most of the reducing gases and they are considered interesting for their low cost and simple sensing methods. The working principle of gas sensor is based on the change in conductivity that takes place after exposure to gases capable of reacting with chemisorbed oxygen. Nevertheless, there still exist some problems with them, like the poor selectivity or the high working temperature. Hence, there is always a search for a new gas sensor. Detection of various oxidizing and reducing gases is one of the major needs of the industries as well as domestic uses. In order to optimize the performance of these sensors, many other studies were focused on the use of noble metals, metal doped oxides or mixed-oxide/composites and Tb doped YSZ. Transition metal containing \( \text{AB}_2\text{O}_4 \) type spinels are a family of oxides that play an important role in a wide variety of this field.

1.8 Aim of the present Investigations:

Spinel containing transitional metal ions is of great commercial importance. In this class of compounds, the metal ions are capable of possessing one or more oxidation states and they can occupy tetrahedral and
octahedral sites. The physico-chemical properties such as crystal structure, electronic conduction, magnetism are greatly influenced by the cations present in two different interstices. The nanostructure of the material and their high surface area are the basic criteria to perform their catalytic, photocatalytic and gas sensing activities.

Despite the prolific use of various inorganic acid−base catalysts, the process is environmentally hazardous. The use of homogenous catalysts also creates a problem of separation of the catalyst or formation of sludge. This has promoted our research interest in the development of heterogeneous catalyst. Today, metal oxides have been explored for the same purpose but their structural as well as thermal stability remains challengeable. Therefore, in last decades the mixed-metal oxides have been replaced to overcome these problems. Several investigations have also proved their ability to perform the various organic transformation reactions. These reactions are carried out in gaseous phase but our aim is to perform them efficiently in liquid phase.

The demand of gas sensor has been increased to control on the emission of harmful and hazardous gases from the industries and domestic uses. Gas sensing activity is surface phenomenon just like catalysis. Several metals and semiconductor based metal oxides viz. SnO$_2$, ZnO or Fe$_2$O$_3$ has been developed as gas sensors. However, there still exist some problems with them, like the poor selectivity or the high working temperature. Hence, there is always search for a new gas sensor. To keep up this view, following aspects of the present research work are aimed at -

1. Preparation of nanosized mixed-metal oxides.
2. To characterize them by various physico-chemical properties.
3. To carry out mixed-metal oxides catalyzed organic reactions in solvent free or ecofriendly solvents.
4. To test out the gas response towards various oxidizing and reducing gases.
With this objective we have prepared the economically cheap and efficient catalysts as well gas sensors and characterized them by various physico-chemical and surface properties.

We have made an attempt to carry out oxidation of different oximes. These reactions were carried out using different catalysts which include oxidic ferrospinelns of cobalt, copper, zinc, nickel, iron, chromium and manganese metal ions. We have attempted some reactions under solvent-free condition and have also replaced commonly used hazardous chlorinated solvents with less harmful solvent like ethanol. Photocatalytic activity is also studied by using different aqueous dye solutions which are harmful to human beings.

The study of the gas sensing activity of nanostructural ferrospinelns have been carried out at different operating temperatures towards various gases. We have also tested their selectivity for various gases. Gas response as well as recovery time was evaluated to use them commercially as gas sensor. Some of these compounds act as good sensors towards petrol, ethanol, LPG and H₂S gas/vapours.

1.9. Literature survey:

In recent years considerable amount of work has been carried out on substituted ferrites. Lithium ferrites and substituted lithium ferrites have become a subject of interest for many researchers because of their innumerable applications at lower microwave frequencies as non-resonant devices [8]. Especially these ferrites are useful as a replacement for garnets due to their low cost, square ness of hysteresis loop along with superior high temperature performance due to their high Curie temperature [9]. These properties have made them promising candidates for microwave devices.

In 1965, Prince [10] has reported on the sub lattice magnetization of lithium ferrite by neutron diffraction. West et.al. [11] have studied the magnetic properties of dense lithium ferrites and reported relatively large value of remanant induction, rectangular hysteresis loop and ordered increase in resonance line width. Kumar et.al. [12] have investigated the effect of Mg-Ti
and Zn-Ti substitution on electrical magnetic properties on lithium ferrites. They have reported Curie temperature in the range of 200 to 600 °C and saturation magnetization in the range of 1000 to 3500 Gauss. They also reported the lattice parameter values in the range of 0.834 to 0.838 nm, which increase linearly with increase in dopant contents. The initial permeability values obtained for these Li-Mg-Ti series are in the range 20 to 50 and 20 to 250 respectively. Pran Krishnan et.al [13] has reported the Curie temperature of lithium ferrites to be 640 °C. The spin wave line width and high field effective line width, the important microwave relaxation parameters, have been studied by Patton et.al. [14] For Co, Mn, Ti, Al substitutions. They observed that Mn decreases both of them while Co tends to increase. Patton et.al. [15] have reported the magnetic properties of Mn-Ti substituted ferrites. Venugopal Reddy [16] studied the magnetization and Curie temperature of Li-Ni ferrites. Iglesial et.al. [17] have studied the non-stoichiometric Li-Zn-Ti ferrites for microwave applications. They have reported the decrease in saturation magnetization Ms and ferromagnetic line width H with increase in the content of Zn and Ti. They showed that the samples sintered in oxygen atmosphere bear high values of Ms as compared to those sintered in air and in oxygen sintered samples H decreases with increase in dopants without changing appreciably the Ms Values. Gill et.al. [18] have studied the Li-Cr ferrites and their Moss Bauer results. They observed the IR bands in the range 400 to 800 cm⁻¹. Robinson [19] has reported that the spin wave line width of lithium ferrites may be increased by substituting relaxing ions like Co, however, effective line width is also increased. Ruiyum et.al [20] have reported the magnetic and microwave data for Li-Ti ferrites. Mazenet.al. [21] have reported two transition points at 905 and 1030 K while studying the conduction mechanism in lithium ferrites. The first is due to Neel temperature while the second is due to disorder phase change. Manjula et.al. [22] have studied the Li-Ti ferrites and reported the reduction of Curie temperature and saturation magnetization due to non magnetic substitution like Ti. Kumar et.al [23] studied the dielectric and magnetic properties of polycrystalline cobalt
substituted Li-Ti ferrites. Mazen et.al [24] studied both AC and DC conductivities of Li-Ti ferrites. Kuanr et al. have investigated the dispersion observed in electrical properties of Li-Ti ferrites [25]. Effect of anisotropy and volume of pore on spin wave line width in Al substituted Li-Ti ferrite system are also reported [26]. Naik et.al. [27] have reported the variation of AC susceptibility with temperature for some Li-Cu ferrites. They have also reported cation distribution and long range order in the same ferrites using magnetization data [28]. Wafik et.al. [29] have studied the composition dependence of discontinuous magnetization in Li-Ti ferrites. Reddy et.al [30] have carried out thermoelectric power studies on mixed Li-Ti ferrites in the temperature range 300 to 900 K, revealing their n-type nature. The electric conductivity studies of Li-Ni ferrites have also been reported [31]. Raman et.al. [32] have reported the loss of lithium in Li ferrites as a result of heating above 1000°C. Studies on electrical properties of Li-Co ferrites have been reported by Song et.al [33].

Yousif et.al. [34] have carried out Moss Bauer and x-ray investigation of Li-Ti ferrites and proposed a cation distribution for the system. Nogues et.al.[35] reported that all the features of Li-Al ferrites are similar to Li-Ti ferrites and their magnetization can be explained on the basis of canted spin structure. Patil et.al [36] have studied the magnetic properties of Li-Zn-Zr ferrites. The substitution of Zn and Zr are found to lower the initial permeability. Microwave dielectric loss in Li-Zn ferrites has been reported by Raman et.al. [37]. They observed increase in dielectric loss with temperature.

Bogdanovich [38] has studied the influence of porosity on electrical and magnetic properties of lithium ferrites. He has reported that the coercivity increases while conductivity decreases with increase in porosity. Rezlescu et.al. [39] have studied the densification of Li-Zn and Ni-Zn ferrites by non magnetic additives.

Many workers [40-48] have studied the lithium cadmium ferrite system. Radha et.al. [43] have reported the frequency and composition of dielectric behavior of mixed Li-Ti ferrites in the frequency range 0 to 100 kHz. Ravindra
[45] studied the composition dependence of elastic modulii of mixed Li-Cd ferrites. Bellad et.al. [41, 46, 47, 48] have reported many magnetic properties of these ferrites. They have reported highest value of permeability 765 achieved with 60% addition cadmium.

Infrared spectroscopy is extensively used to study the ordering phenomena in spinels. Reddy et.al.[49] have reported four absorption bands for lithium rich samples and only two bands for lower concentration of lithium. The splitting of the main band is attributed to the presence of Fe ions in excess amount. Bellad et.al [47] and Mazen et.al.[49] have reported similar result. The IR technique can be successfully used for suggesting cation distribution and possible formation of Fe ions in the ferrite. Mohan et.al.[50]have studied the IR spectra of Li-Co ferrites. Shaikh et.al [51] have reported IR spectra and saturation and structural dependence of magnetic properties of Li-Cd ferrites. Recently Shaikh et.al. have reported microstructure and magnetic properties of Li-Mg ferrites while Watave et.al.[52] have observed that temperature dependant dielectric properties of Li-Co ferrites. Very recently Jadhav [53] has reported on structural and magnetic properties of Zn substituted Li-Cu ferrites and Radhapiyari Devi et.al.the effect of chromium impurity on DC resistivity of Li-Sb ferrites [54]. Darshane et.al. have studied ZnFeMnO$_4$ – GaCoMnO$_4$ mixed oxides for their electrical as well as magnetic properties [55]. Gas sensing study of zinc ferrite towards petrol vapours was investigated by Hankare et. al. [56] Mulla et. al. [57] studied the H$_2$S sensing activity for the zinc ferrite while nickel ferrite thin films worked as good gas sensor for the detection of LPG gas [58]. Semiconductor based cobalt and zinc ferrite acts as H$_2$S gas sensor [59].
References:


Chapter I : Introduction


