CHAPTER 4

FERRITE: STRUCTURE, PROPERTIES AND APPLICATIONS

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Abstract

Ferrites are the unique magnetic materials that exhibit both electrical and magnetic properties and hence are commercially, scientifically important magnetic materials. The brief introduction of the ferrite material is explained herein. The introduction of the various types of magnetism and accordingly the types of magnetic materials are discussed in this chapter. The chemical composition of ferrite including spinel type, garnet type and hexagonal type is given in this chapter. The classification of spinel ferrite based on occupancy of cations is also presented. The properties and applications of ferrite are briefly summarized
4.1: INTRODUCTION TO FERRITE

Ferrites are the important class of ceramic magnetic oxides materials which show the property of electrical insulator and magnetic conductor with large number of applications in various fields. Ferrite belongs to a class of ferromagnetic material as proposed by L. Neel [1]. Iron oxide (Fe₂O₃) and metal oxides (MO) of cobalt, nickel etc divalent metal ions constitute ferrite material. Ferrite materials are being studied since last seven to eight decades. The story of ferrites began in 1949 with the search for ferromagnetic materials of unusually high resistivity to obtain reasonable eddy current losses [2]. When a ferromagnetic material is immersed in an alternating magnetic field, eddy currents are generated in it, which dissipate energy. These losses can be minimized by lamination of the ferromagnetic core to restrict the eddy current path. Since, eddy current losses in ferromagnetic materials are inversely proportional to the resistivity, they can be minimized by the use of magnetic materials of high resistivity.

Ferrite crystallizes with a cubic spinel structure, cubic garnet structure and hexagonal structure. All these types of ferrites possess different chemical formula and are equally important from the point of view of their applications.

Ferrites are classified into soft ferrites and hard ferrites depending on their properties. The high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high permeability, etc
are the important electrical and magnetic properties of ferrite. These several properties of ferrite make them useful in numerous applications including antenna rod, transformer core, memory chips, telecommunication, automobile etc. Because of their extremely low eddy current and dielectric losses they are used at high frequency applications (Switch mode power supply, RF transformers, inductors etc) [3]. The properties of ferrites are sensitive to various factors such as method of preparation, preparative conditions and nature of substituent’s [4]. The variation in these parameters can lead to a modification in the properties of ferrite.

Usually, the ferrites are prepared by ceramic technology using high purity metal oxides. Though, the method has some drawbacks, it is used commonly to produce bulk material. With the advent of nanotechnology, the ferrites have been prepared in nanosize form using different chemical methods. The properties of these nanosized ferrites are found to be very interesting and superior to that of their bulk counterpart [5]. On account of their properties, nanosize ferrites find applications in the field of drug delivery, hyperthermia, sensors, catalyst etc. [6]

In the light of the importance of nanosize ferrite, the research on these materials has been tremendously increased in the recent years. The new synthesis methods have been developed to obtain nanosize particles. Apart from synthesis methods, synthesis parameters (pH,
fuel, annealing temperature) play an important role in governing the properties of nanosize ferrite. Thus, the synthesis methods and synthesis parameters have become the subject of interest to the scientist and technologist as they bring variation in properties. In the present chapter, the crystal structure, properties and applications of spinel ferrite has been discussed.

4.2: CLASSIFICATION OF MAGNETIC MATERIALS

The classification of magnetic materials is based on the susceptibility value and the behavior of magnetic material under the influence of external magnetic field. A brief description of various types of magnetic materials is given below [7-9].

It is evident from experiments that complexes of the elements of the first transition series obey the Curie law (that is for these complexes molar magnetic susceptibility is inversely proportional to the absolute temperature). The complexes which do not obey Curie law \( \chi = \frac{C}{T} \), for such complexes it is found that they obey Curie-Weiss law \( \left( \chi_m = \frac{C}{T-\theta} \right) \), where, \( C \) is Curie constant and \( \theta \) is paramagnetic Curie temperature (which is slightly greater than \( T_c \)). Curie-Weiss law suggest that their exist magnetic interaction between discrete molecules in condensed phases or in magnetically dilute system. Paramagnetic and diamagnetic materials belongs to magnetically
dilute system, whereas ferromagnetic, anti-ferromagnetic and ferrimagnetic materials belongs to magnetically non-dilute system.

*Figure 4.1:* Paramagnetism, diamagnetism, ferromagnetism, anti-ferromagnetism and ferrimagnetism in the absence and presence of magnetic field.
The origin of magnetism lies in the orbital and spin motion of electrons. The magnetism occurs due to interaction of electrons with each other. Some of the materials exhibit collective interaction of atomic magnetic moments, where as some of the materials do not exhibit collective interaction between atomic moments. The magnetic behavior of materials can be classified into six groups namely diamagnetism, paramagnetism, ferromagnetism, ferrimagnetism, anti-ferromagnetism and super-paramagnetism.

Figure 4.1 represents paramagnetism, diamagnetism, ferromagnetism, anti-ferromagnetism and ferrimagnetism in the absence and presence of magnetic field. Fig. 4.2 represents the variation of magnetism as a function of temperature for the different class of magnetic material.

**Figure 4.2:** Variation of $1/\chi$ as a function of temperature for different class of magnetic material
**Diamagnetic Material**

These substances do not contain any unpaired electron. The small circulating current produces a magnetic effect which opposes the external magnetic field hence these are repelled by the magnetic field. In the absence of magnetic field the atoms of the diamagnetic material have known net magnetic moment. Under the influence of external applied field, the motion of spinning electron produces magnetization. The value of susceptibility for such material is independent of temperature and is negative. Bismuth, copper, quartz, water etc are the examples of diamagnetic materials. All the materials exhibit diamagnetism.

**Paramagnetic Materials**

The paramagnetism property is associated with metal complexes where spin and orbitally derived magnetic moments co-exists. Such materials are called paramagnetic. In these materials there is no interaction between the individual atoms. The substance obeys Curie or Curie-Weiss law. According to Langevin model each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. On the application of external magnetic field there is a slight alignment of these moments which produces low magnetization in the direction of applied field. The susceptibility of such materials is positive (less than 1). Oxygen, tin, aluminum, copper sulphates are the examples of this type of material. When the individual dipoles do not
interact with each other and are distributed in the absence of external applied magnetic field then paramagnetism arises.

**Ferromagnetic material**

In ferromagnetic materials, the electrons spin of each of the atom couple together to form resultant unit cell magnetic moment. The individual magnetic moments are considered together. Ferromagnetism is possible when the atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other. In case result is anti-parallel, then it is a anti-ferromagnetic material. Weiss introduce concept of magnetic domains within the material. Domains are the region where the atomic magnetic moments are aligned. The moment of these domains determines how the material response to a magnetic field. Fe, Co, Ni, Dy, Gd are ferromagnetic at and above room temperature. In these ferromagnetic materials the spontaneous magnetization takes place only below ferromagnetic Curie temperature ($T_c$) above $T_c$ these materials behave like paramagnetic material. For such material, susceptibility is well defined and fallows Curie-Weiss law $\chi_m = \frac{C}{T-\theta}$

**Anti-ferromagnetic material**

In anti-ferromagnetic materials, the transition metal ions are separated usually by small legends such as oxide and halides. In such compounds adjacent metal ions couple with their spins anti-parallel.
There is always equal number of two alignments so that in the absence of magnetic field there is no resultant magnetization. Antiferromagnetic materials show a minimum in a plot of susceptibility verses temperature. The maxima on the curve are called yield point. For anti-ferromagnetic materials the susceptibility is temperature dependent. Above Neel temperature anti-ferromagnetic materials follow Curie–Weiss law and become paramagnetic. Some anti-ferromagnetic materials can be made ferromagnetic by the application of a sufficiently high magnetic field parallel to the spin axis.

**Ferrimagnetic material**

The materials showing ferrimagnetism generally have ion on two sets of lattice sites. These ions have opposed spins arrangement. But unlike anti-ferromagnetic materials they do not cancel each other therefore there is a resultant permanent magnetic moment. Iron oxide (Fe₃O₄) is the best example of ferrimagnetic material. Several oxide magnetic materials have been found to be ferrimagnetic. These materials possess a net resultant magnetization due to the unequal anti-parallel spin moments. Ferrimagnetism is actually a special case of anti-ferromagnetism in which the opposite spins are of unequal magnetization (it has a non zero magnetization). Ferrite is a ferrimagnetic material of great interest from engineering point of view.
Super-paramagnetism

Super-paramagnetism is a unique class of magnetic materials. Super-paramagnetism is exhibited by single domain particles that behaves like ordinary ferromagnetic materials below Curie temperature because of their large magnetic susceptibility and are saturated at moderate magnetic fields. Above Curie temperature super-paramagnetic materials behave like ordinary paramagnetic materials as they display no hysteresis. The whole particle represents as single domain having all atomic moments ordered. The magnetization of the particle is no longer fixed in the direction detected by the particle shape. Application of an external magnetic field to an ensemble of such thermally demagnetized particle results in a much larger magnetic response than would be the case of paramagnet.

Spin Canting

The large surface area of magnetic nano-particles is important in deciding the magnetic properties. Normal co-ordination, in the interior breaks down at the surface to have very different form [10]. Spin structure of such nano-particles is very complicated as compared to the bulk. [11]. Mössbauer spectroscopic technique can be used to investigate spin canting at high magnetic field. The main effect of finite size on magnetic nano-particles is that the broken exchange bonds for the surface atom become dominant. The exchange interactions are mostly anti-ferromagnetic; it crucially depends on the bond length and
bond angle between the metal cations and intervening anions. When some of the exchange bonds are made from the surface, there can be frustration and canted spin order in case of these magnetic nanoparticles.

4.3: FERRITE COMPOSITION

Ferrites are the important class of magnetic materials containing iron oxide and metal oxides in different ratio depending upon their type. On the basis of their crystal structure, ferrites are of three types namely spinel ferrite, garnet and hexagonal ferrite. [12]

Spinel Ferrite

A spinel ferrite is a ferrimagnetic material, containing mostly iron oxide which is derived from magnetite \( \text{Fe}^{2+}\text{O} \quad \text{Fe}^{3+}\text{O}_3 \) represented by the formula \( \text{M}^{2+}\text{Fe}^{3+}_2\text{O}_4 \). \( \text{M} \) is a divalent metal ion like cobalt (Co), nickel (Ni), copper (Cu), manganese (Mn), magnesium (Mg), zinc (Zn), cadmium (Cd) etc. Trivalent \( \text{Fe}^{3+} \) ions can be replaced by trivalent metal ions like \( \text{Al}^{3+}, \text{Cr}^{3+}, \text{In}^{3+}, \text{Ga}^{3+} \) etc. In all cases the ionic radii of the substituting ion should be between 0.5 to 1.0 Å.

Garnet

The second type of ferrite is a garnet having cubic structure with general formula \( \text{R}^{3+}\text{Fe}^{3+}_5\text{O}_{12} \) where, \( \text{R} \) is a rare earth ion (like dysprosium (\( \text{Dy}^{3+} \)), gadolium (\( \text{Gd}^{3+} \)), samarium (\( \text{Sm}^{3+} \)) etc or yttrium (\( \text{Y}^{3+} \)). \( \text{Fe}^{3+} \) can be replaced by trivalent metal ions like Al, Cr, etc.
Magneto-plumbite

Magneto-plumbite is having a hexagonal structure and are represented by the formula $\text{MFe}_{12}\text{O}_{19}$ where, M is a divalent metal ion with large ionic radius like $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, $\text{Pb}^{2+}$.

4.4: SPINEL FERRITE STRUCTURE

Figure 4.3: Spinel structure

Ferrite materials have a crystalline structure similar to that of mineral spinel $\text{MgAl}_2\text{O}_4$, where the divalent ions replaced by Mg and trivalent ions replace $\text{Al}^{3+}$ [13]. The structure of spinel ferrite is a close packed cubic structure of oxygen atoms with eight formula units per unit cell. The spinel structure is shown in Fig. 4.3. The white circles in this
Figure represent the oxygen ions, and the black and hatched circles represent the metal ions. The radius of oxygen ion is of the order of 1.32Å which is much greater than that of metal ions, which is in the range of 0.6 to 0.8Å, hence the oxygen ions in this lattice touch each other and form a close packed face centered cubic lattice.

The unit cell of spinel ferrite consists of two sub lattices namely tetrahedral (A) and octahedral [B] sites. Tetrahedral A site is smaller than octahedral B site. Tetrahedral A site is surrounded by four oxygen ions (as shown by the hatched circles) situated at corners of tetrahedron. Octahedral site is surrounded by six oxygen ions (shown by the black circles) situated at corners of an octahedron. In one unit cell there are sixty four tetrahedral sites of which eight are filled and thirty two octahedral sites of which sixteen are filled. From the point of view of valence, it seems reasonable to have the divalent metal ions on (A) sites and Fe$^{3+}$ ions on octahedral [B] sites, because the number of oxygen ions which surrounds tetrahedral (A) and octahedral [B] site are in the ratio of 2:3.

**Classification of Spinel Ferrite**

In spinel lattice, the cations are distributed at tetrahedral (A) and octahedral [B] site depending upon their ionic radii, their electronic configuration and the electrostatic energy of the lattice. On the basis of the occupancy of the cations at tetrahedral (A) and octahedral [B]
sites, the spinel ferrite is classified as normal, inverse and random spinel ferrite.

**Normal Spinel Ferrite**

In this type of spinel ferrite the divalent metal ions are totally occupied at tetrahedral A site and the trivalent ferric ions are totally occupied at octahedral B site. The distribution of cations for spinel ferrite represented by MFe₂O₄ can be written as (M)⁰[Fe₂]⁸ O₄. Zinc and cadmium ions occupy tetrahedral A site and therefore zinc ferrite and cadmium ferrite are the best examples of normal spinel ferrite.

**Inverse Spinel Ferrite**

In this type of spinel ferrite the divalent metal ions totally occupy octahedral [B] site where as the trivalent ferric ions equally occupy tetrahedral (A) and octahedral [B] site. The distribution of cations can be written as (Fe)⁰[MFe]⁸O₄. The examples of inverse spinel ferrite are cobalt ferrite and nickel ferrite.

**Random Spinel Ferrite**

When the divalent metal ions and trivalent ferric ions occupy both tetrahedral and octahedral [B] site, the spinel ferrite is called as random spinel ferrite. The distribution in such type of spinel ferrite can be represented by (M₁₋ₓFeₓ)[Fe₂₋ₓMₓ]O₄, where x is distribution parameter and can vary between 0 and 1. Magnesium and copper ferrite is an example of random spinel ferrite.
When x=0, we get normal spinel, when x=1, we get inverse spinel and when 0<x<1, we get random spinel structure.

4.4 PROPERTIES OF SPINEL FERRITE

Magnetic Hysteresis

![Magnetic Hysteresis Diagram]

**Figure 4.5:** Variation of Magnetic field (B) with applied field (H).

A typical M(magnetization) verses H(field) graph for a magnetic material is shown in Fig. 4.5. Graph exhibits typical curve known as hysteresis. Starting from a demagnetized sample, if field H is increases then magnetization M also increases and reaches a maximum value known as saturation magnetization (Ms). If field is decreased and brought to zero, the magnetization decreases without following the original path. The value of magnetization at which field is zero is called remanence magnetization (Mr). With further decrease in field magnetization decreases and reaches zero value. The point on the
curve where field is negative and magnetization is zero is known as coercive field \((H_c)\). As field decreases the magnetization also decreases and reaches at negative value of magnetization. Further increasing the field the magnetization starts increasing in reverse direction.

The permeability of a magnetic material is given by the slope of the hysteresis curve near its origin \((\mu_0)\). The permeability depends on the state of magnetization of the sample. The maximum value of the permeability is designed as \(\mu_m\). The differential permeability is defined as, the slope of the magnetization curve at the point of intersect.

**Domains**

The concept of domain was introduced by Weiss. The magnetic behavior can be explained on the basis of magnetic domains. Inside a magnetic material, they exists several magnetic domains which are separated by domain walls. Each domain is spontaneously magnetized, the magnetization depends on temperature and type of magnetic material (ferromagnetic or ferrimagnetic). The magnetization of neighboring domains is not parallel. The overall magnetization of the material is then given by the vector sum of the magnetization of all domains. This is zero in the case of a demagnetized material.

Domain structure is a natural consequence of the various contributions to the energy, namely, (i) exchange, (ii) anisotropy, and (iii) magnetism. If the material consists of a single domain, it will show a high value of magnetostatic energy as a result of free poles formed
on the surface. The magnetostatic energy is reduced roughly by half when the domains magnetized in opposite direction. Each subdivision lowers the magnetostatic energy, but creates additional wall energy. The wall energy arises from the fact that on opposite sides of the wall the magnetization is directed in anti-parallel directions, which is contrary to the requirement of the exchange forces, which in case of ferromagnetic materials favor parallel orientation. Thus, the subdivision process continues only as long as the lowering of magnetostatic energy is more than the increase in the wall energy [14].

**Single Domain particles**

The total magnetization energy is a function of the volume of the domain, while the total wall energy is proportional to the area of the domain wall. When the volume is small enough, the energy of a wall created on dividing the particle into two domains may be greater than the reduction in magnetostatics energy. In such a case the single domain becomes stable. In a single-domain-particle, magnetization changes can be brought about by rotation of the magnetic vector against the demagnetizing fields and magneto-crystalline anisotropy.

**4.5: APPLICATIONS OF FERRITE**

Ferrite materials have properties which vary widely, and correspondently their uses cover a considerable range. The magnetostrictive property is used in transducer applications. Ferrite with
narrow hysteresis loops are obvious choices for transformer and inductor core at radio frequencies. Ferrites with approximately rectangular hysteresis loops (square loop materials) are upgrade importance in information storage in switching devices [15].

On the basis of coercivity values the ferrites are grouped into two groups namely soft ferrites and hard ferrites. Hard ferrites have high value of coercivity. Hard ferrites are used in permanent magnets. Hexagonal ferrites like barium ferrite are used for such type of application. They can also be used in transformer core. Barium hard ferrites are used as focusing magnets for TV tubes. Soft ferrites having low value of coercivity are used in transformer and inductors. The soft ferrites are useful at high frequencies, due to their low losses (eddy and dielectric), high resistivity, low value of remanant flux density and high permeability.

Ferrites have application in data storage. The ferrites with rectangular hysteresis loop are used in data storage and are also useful as computer memory devices. Spinel ferrites and garnets are used in microwave application. These ferrites are used as component of electronic filter, microwave devices, magnetic switches and memory elements for computers. For memory and switching devices ferrites are used in the form of thin films.

Magnetic nano-particles of ferrites have some recent applications because of their smaller size and large surface area. In medical field
these magnetic nano-particles of ferrite are used for drug targeting and hyperthermia, separation and magnetic resonance imaging. In environmental science ferrite nano-particles are used in treating polluted waste water from industry. The recent application also includes high density information storage, ferro-fluids, catalyst, sensors etc [16]. The following chart illustrates the applications of ferrite material.

**Application of ferrites**

- **(a) Permanent magnets**
- **(b) Magnetic recording**
- **(c) Computer**
  - Pulse transformer cores
  - Memory cores
  - Substrates for bubble memories
- **(d) Microwave**
  - Reactor cores
  - Power transformer
- **(e) Radio and television**
  - Antenna cores
  - Delay line cores
  - Fly back transformer cores
  - Rotary transformer cores
- **(f) Telecommunication**
  - Low accommodation cores
  - Deflection yoke cores
- **(g) Miscellaneous uses**
  - Ferrite microwave absorbers
  - Rubber ferrites
  - Noise absorber cores
  - Isolators
  - Circulators
  - Magnetic recording heads
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