CHAPTER -II
Composition, crystal structure and properties of ferrite, ferroelectric and composites

2.1 Composition and crystal structure of Ferrite

The term ferrite is derived from the Latin word “ferrum” meaning iron. The ferrite has played the important role in many of the scientific and technological revolution that has completely changed our lives to a great extent during the last 50 years. Therefore magnetic materials such as ferrites have been the subject of tremendous interest to researchers, chemist, physicist and metro-logiest in this century.

Ferrites are mixed metal oxides with iron (III) as the main component. The main feature of these materials is that besides possessing very good magnetic properties, they also possess a very high dc electrical resistivity and therefore are useful in high frequency applications. Ferrite can be classified on the basis of crystal structure they possess, into three important classes namely


The spinel ferrites, known as the ferrimagnetic oxide, have the general form of MeFe$_2$O$_4$, where Me is a divalent metallic ion, such as Fe$^{2+}$, Co$^{2+}$ Ni$^{2+}$ and Zn$^{2+}$. Ionic distribution in this kind of structure is [Me$_{3}\delta$Fe$_{1-\delta}$]$^A$[Me$_{1-\delta}$Fe$_{1+\delta}$]$^B$O$_4$ where $\delta$ is inversion factor and $\delta=0$&1 for the inverse and normal structure respectively. These divalent metallic ions can be distributed on the tetrahedral position (A-site) surrounded by four oxygen ions, or the octahedral position (B-site) surrounded by six oxygen ions in the spinel structure. The composition and distribution of Me ions significantly affect
the electronic and magnetic properties [1] The spinel crystal structure is
determined primarily by the oxygen ions lattice. The radii of oxygen ions are
several times larger than the radii of metallic ions in the compound [2].
Consequently, the crystal structure can be thought of as being made up of
the closest possible packing of layers of oxygen ions, with the metallic ions
fit in at the interstices [3].

The ion packing situation is indicated in Fig.2.1(a) where the solid
line represent the top layer of oxygen spheres while the dotted line represent
the bottom layer of oxygen spheres. A unit cell of the spinel lattice is
represented in Fig. 2.1(b). Two kinds of oxides are available for the cation:
tetrahedral sites surrounded by four oxygen ion situated at corners of
tetrahedron (A site) and octahedral sites surrounded by six oxygen ions
situated at corners of an octahedron [B site]. In a unit cell there are 64
tetrahedral sites of which 8 are filled and 32 octahedral sites of which 16 are
filled [4]. Packing of the ions within the lattice is perfect when the oxygen
parameter $u = \frac{3}{8}$ [5]

The spinel crystal structure is consists of lattice formed by oxygen anions
and metallic cations incorporated within it. The radii of oxygen ions are
several times larger than the radii of metallic ions in the compound.
Consequently, the crystal structure can be thought of as being made up of
the closest possible packing of layers of oxygen ions, and the metallic ions
fits themselves in the interstitial sites available within the oxygen lattice. The
distribution of ions between two types of sites is determined by a delicate
balance of contributions, such as the magnitude of ionic radii, their electronic
configuration and the electrostatic energy of the lattice [6]. Spinel structure of ferrite is as shown in figure below.

![Fig2.1(a)Crystal structure of spinel ferrite](image1)

![Fig2.1.(b) Unit cell](image2)

### 2.2 Classification of Spinel Ferrite:

The unit cell of spinel ferrite has two sites namely tetrahedral (A) and octahedral [B] sites. The metal cations are distributed over the available A and B sites. On the basis of occupancy of cations at A and B sites, the spinel ferrites are classified as normal, inverse and random spinel ferrite.

- **Normal spinel:**

  A compound is called normal spinel when the divalent metal ions occupy the tetrahedral sites while $2\text{Fe}^{3+}$ ions are at octahedral B site. The best examples of normal spinel ferrites are zinc and cadmium ferrites, in which the divalent metallic ions Zn$^{2+}$ or Cd$^{2+}$ are at the A site, while Fe$^{3+}$ ions are at B site like $[\text{M}^{2+}]^A [\text{Fe}^{3+}]^B \text{O}_4^{2-}$

  Examples ZnFe$_2$O$_4$; CdFe$_2$O$_4$ etc

- **Inverse spinel:**

  In inverse spinel ferrite, one trivalent ferric ion Fe$^{3+}$ is at the tetrahedral A site while the remaining trivalent ferric ions Fe$^{3+}$ and the divalent metallic
ions $M^{2+}$ are at the B site. Actually most of the simple ferrites, e.g. Nickel ferrite are of the inverse spinel structure like $(Fe^{3+})^A [M^{2+}Fe^{3+}]^B O_4^{2-}$

Examples MnFe$_2$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$

- **Random spinel:**

The divalent metal ions $M^{2+}$ such as $Mn^{2+}$, $Zn^{2+}$ and trivalent $Fe^{3+}$ ions are distributed at both tetrahedral A site and octahedral B site then the ferrite is termed as random spinel ferrite. The best known example of random spinel ferrite is copper ferrite. The distribution of ions between two types of sites is determined by a delicate balance of contributions, such as the magnitude of ionic radii, their electronic configuration and the electrostatic energy of the lattice [7].

Distribution of ions is as shown $(M^{x^{2+}}Fe_{1-x}^{3+})^A [M_{1-x}^{2+}Fe_{1+x}^{3+}]^B O_4^{2-}$

Examples CuFe$_2$O$_4$, MgFe$_2$O$_4$

2.3 Properties of spinel ferrite:

2.3.1 Magnetic properties of spinel ferrites:

The origin of magnetism in ferrites is due to three main factors:

a) Unpaired 3d electrons

b) Super-exchange between adjacent metal ions

c) Nonequivalence in number of A and B sites in crystal.

In the free-state the total magnetic moment of an atom containing 3d electrons is the sum of the electrons spin and orbital magnetic moment. It is “quenched” by the electronic fields caused by the surrounding oxygen ion about the metal ion. The atomic magnetic moment ($m$) then becomes the moment of the electron spin and is equivalent to ($m=\mu_Bn$) where $\mu_B$ is a Bohr magnetron unit and $n$ is the number of unpaired electrons.
In the oxides the distance between the metal ions is larger than in metals, so it is assumed that the magnetic interactions are of the super exchange type. Here the anion plays the role of an intermediary. In the spinel structure super-exchange will be important for the configurations A -O\(^2\)- B with angle 125\(^0\) and B -O\(^2\)- B with angle 90\(^0\). For other configurations the distance between the oxygen ion and the metal ion is too large to give rise to strong interaction. It is called as the super-exchange interaction. This super-exchange interaction gives rise to spontaneous magnetization.

Neel explained the spontaneous magnetization of these ferrites on the basis of Heisenberg's exchange forces [8]. According to this theory the exchange energy between two adjacent atoms having spin angular momentum is given by

\[ E_{\text{ex}} = -2j_{\text{ex}} S_i S_j \]  

(2.1)

Where \( E_{\text{ex}} \) is the exchange energy, \( S_i \) and \( S_j \) are the total spins of adjacent atoms and \( j_{\text{ex}} \) is the exchange integral which represents the probability of exchange of electron. Thus various factors that determine the magnetic properties of these spinel ferrites are the nature of cations, heat treatment, preparative methods, site preference energy of cations and Madelung energy.

**2.3.2 Hysteresis characteristics:**

For spinel ferrite (ferromagnetic) substances, the intensity of magnetization changes in a complicated and irreversible manner as magnetic field \( H \) is changed, giving rise to the familiar hysteresis curves as shown in Fig 2.2 Only at high fields, when the specimen is said to be saturated, the intensity of magnetization become directly proportional to the field.
In the relationship \( B = H + 4\pi I \), \( I/H \) is of course \( k \), the volume susceptibility. The quantity \( B/H \) is called the permeability, for which the symbol \( P \) will be used. The permeability is related to the susceptibility by

\[
P = 1 + 4\pi k
\]  

(2.2)

All ferromagnetic substances lose their ferromagnetism and become paramagnetic at a characteristic temperature called the Curie point.

![Magnetization curve](image)

**Fig.2.2 Magnetization curve (hysteresis loop) for ferromagnetic material**

When a ferromagnetic body is placed in a magnetic field and then removed, \( B \) may not return to zero as \( H \) becomes zero and that is called remanant magnetization (\( B_r \)). Then body is then said to be permanently magnetized. The magnitude of \( B_r \) under such conditions of permanent magnetization is called the remanence. The field of opposite sign necessary to reduce \( B_r \) to zero is called the coercive force (\( H_c \)). Specific magnetization is the intensity of magnetization divided by density, or \( I/d \).

**2.3.3 The Curie temperature**:

All ferromagnetic materials exhibit a characteristic temperature known as the Curie temperature or Curie point, \( T_c \). This is the critical temperature at which thermal energy is just enough to destroy the spontaneous
magnetization. Thus, the Curie temperature marks the transition point at which a ferromagnetic is converted into a paramagnetic upon heating [9].

**2.3.4. Magnetostriction in spinel ferrite:**

Magnetostriction is the phenomena exhibited by ferromagnetic materials. When these materials are magnetized they undergo small changes in size of dimension. This effect is called magnetostriction.

- **Longitudinal magnetostriction:** In this the fractional change in length to the original length ($\Delta l/l$) is simply a strain and is represented as $\lambda$ it is called Joule Magnetostriction. The value of the strain $\lambda$ measured at magnetic saturation is called the saturation magnetostriction ($\lambda_s$). The value of $\lambda$ is always less than $30 \times 10^{-6}$. In single crystal; the effect of magnetostriction is different in different crystallographic direction and converse of magnetostriction is called Vallari Effect.

- **Transverse magnetostriction:** In this case change in dimension perpendicular to the direction of dimension takes place.

- **Volume magnetostriction:** The above two effect will results in change in volume and hence volume magnetostricition take place [10]

**2.3.5 Electrical properties of spinel ferrites:**

Spinel ferrites materials have low electrical conductivities when compared to other magnetic materials and hence they find wide use at microwave frequencies. Spinel ferrites, in general are semiconductors with their conductivity lying in between $10^2$ and $10^{11}$ Ohm$^{-1}$ cm$^{-1}$. The conductivity is due to the presence of Fe$^{2+}$ and the metal ions (Me$^{3+}$). The presence of Fe$^{2+}$ results in n-type behaviour and of Me$^{3+}$ in p-type behaviour. The conductivity arises due to the mobility of the extra electron or
the positive hole through the crystal lattice. The movement is described by a hopping mechanism, in which the charge carriers jump from one ionic site to the other. In such a process the mobility of the jumping electrons or holes are found to be proportional to $e^{-E/kT}$ where $E$ - the activation energy, $k$- Boltzmann’s constant, $T$ - the temperature in degree absolute.

### 2.3.6 Dielectric properties of spinel ferrite:

The dielectric property of ferrite is important to physicists. These properties are not constant; they can change with frequency, orientation, mixture, and pressure and molecule structure of the material. A material is said to be dielectric if it has the ability to store energy when an external electric field is applied. If an ac sinusoidal voltage source is placed across the same capacitor, the resulting current will be made up of a charging current and a loss current that is related to the dielectric constant. Here we are interested only in the dielectric constant ($\varepsilon'$) of the material and the loss ($\tan\delta$). Dielectric constant ($\varepsilon'$) describes the interaction of a material with an electric field. The relative dielectric constant is given by equation

$$\varepsilon_r = \varepsilon / \varepsilon_0$$

The complex relative dielectric constant is given by

$$\varepsilon_r = \frac{\varepsilon'}{\varepsilon_0} = \frac{\varepsilon - j\varepsilon''}{\varepsilon_0}$$  \hspace{1cm} (2.3)$$

Where $\varepsilon_0$ is the dielectric constant of free space, which is equal to $8.854 \times 10^{-12} \text{ f/m}$. The real part of dielectric constant ($\varepsilon_r$) is a measure of how much energy from an external electric field is stored in a material. The imaginary part of the dielectric constant ($\varepsilon''$) is called the loss factor [11]
2.4 Composition and structure of ferroelectrics

2.4.1 Chemical composition:

The group of compounds which can be described by the general formula ABO$_3$ has the type designation E$_2$I where the B ions of smaller radius are surrounded by the anions in a octahedral form and A ions of larger radius have 12–fold co-ordination with anions. Unit cell is as shown Fig 2.3(a)

2.4.2 Crystal structure of ferroelectrics:

Structure of ferroelectrics is Perovskite. It structures consist of 12 coordinated A$^{+2}$ atoms on the corner, octahedral (O$^-$) ions on the faces and the tetrahedral B$^{+4}$ in the center. The simple cubic perovskite structure of ABO$_3$ and its unit cell is as shown in fig 2.3(a). Depending on ionic radii and polarizibilites, pervoskite family may belong to the cubic, tetragonal, rhombic and monoclinic crystal system. According to the geometric requirement of Goldsmith (1927), pervoskite structure can only be formed when correlation, $r_A + r_B = t\sqrt{2(r_A + r_O)}$ exist between the ionic radii.

Here, the tolerance factor has value $0.85 < t < 1.05$ the ratio of ionic radii is

$0.41 < \frac{r_B}{r_O} < 0.73 \quad \text{and} \quad \frac{r_A}{r_O} > 0.73$ \quad \text{where} \quad r_A, r_B \text{ and } r_O \text{ are radius of } A, B \text{ and } O \text{ atoms respectively}

![Fig2.3(a)](image1) ![Fig2.3(b)](image2)
Tertragonal BaTiO$_3$, $T_c = 120^0^\circ$, Ti-displacement=0.125Å

Ti-O short =1.83Å, Ti-O long= 2.21Å, $Ba^{2+}$ displacement=0.067Å.

BaTiO$_3$ is one of the first simple structures to exhibit compounds with ferroelectric properties and is still probably the most important ferroelectric prototype. Perovskite structure has the curious property that the central tetrahedral B$^{4+}$ atoms do not touch its coordination neighbors in violation of Pauling rule. This allows small displacement of the distortion of the structure and the reduction of symmetry giving rise to ferroelectricity.

The perovskite cubic structure and ferroelectric tetragonal of barium titanate is as shown in fig2.3 (b). In perovskite structure BaTiO$_3$, barium are located at corners, the titanium ion is located at the center and oxygen ions are located at the face center of the cubic lattice cell. Each barium ion is surrounded by 6 oxygen ions and each oxygen is surrounded by 4 barium and 2 titanium ions. Barium titanate is in its tetragonal (ferroelectric) phase at room temperature and will transform into cubic (paraelectric) phase above its Curie temperature ($T_c \approx 120^0^\circ$). In tetragonal ferroelectric two types of domain in boundaries exist at $90^0$ and $180^0$ [12].

2.4.3 Electrical properties:

Ferroelectric semiconductors display a number of properties not inherent in common semiconductors owing to the spontaneous polarization and to the phase transition at Curie temperature [13]. One of these properties is the posistor effect (PTC effect) that shows up a growth in resistivity of a ferroelectric material with temperature when it passes from the ferroelectric phase into paraelectric phase. Ferroelectric materials are bad conductor but
when temperature increases conductivity increases according to relation which is characteristics of semiconductor.

\[ \sigma = Ke^{-E/RT} \]  \hspace{1cm} (2.4)

Where, \( \sigma \) = the conductivity \( K \) = a material constant, \( T \) = the temperature in deg K, \( E \) = the activation energy. It is interest to note that the activity in energy of conductivity of the non-polar paraelectric state (1.75eV=40cal/mole) substantially exceeds that of a crystal in the ferroelectric state (1.15eV=26cal/mole) [14].

### 2.4.4 Dielectric properties of ferroelectrics:

A ferroelectrics has been defined as a dielectric having spontaneous polarization which can be reversed in sign. It must have polar structure with no center of symmetry. In changing the direction of polar axis the structure must pass through an intermediate polar stage and the polar structure is a distortion of this more symmetrical form. The structure of ferroelectric material becomes less distorted as the temperature increases and undistorted at and above a temperature called the Curie point. The dielectric susceptibility (\( \chi_e \)) of a dielectric material is a measure of how easily it polarizes in response to an electric field. The dielectric constant (\( \varepsilon' \)) of the material is defined as the constant of proportionality relating an electric field \( E \) to the induced dielectric polarization \( P \) such that

\[ P = \varepsilon_o \chi_e E \]  \hspace{1cm} (2.4)

where \( \varepsilon_o \) is the dielectric constant of free space.

The susceptibility of a medium is related to its relative permittivity (\( \varepsilon_r \)) by relation, \( \chi_e = \varepsilon_r - 1 \). For vacuum \( \chi_e = 0 \) and electric displacement \( D \) is related to the polarization density \( P \) by relation [15].

\[ D = \varepsilon_o E + P = \varepsilon_o (1 + \chi_e)E = \varepsilon_r \varepsilon_o E \]  \hspace{1cm} (2.4)
Dielectric constant (ε_r) is a combined contribution of four polarization:
atomic polarization (ε_a), ionic polarization (ε_i), dipolar polarization (ε_d) and
space charge (ε_s)[16]. Thus ε_r = ε_a + ε_i + ε_d + ε_s  
\[ \text{(2.5)} \]

All of the useful properties of ferroelectric ceramics are related in
some manner to their response with an electric field, the electrical behavior
of these materials is important to their successful application in dielectric,
piezoelectric, pyroelectric, or electro optic devices. Ferroelectrics are, in
general, characterized by (1) higher dielectric constants (200–10 000) than
ordinary insulating substances. (2) Relatively low dielectric loss (0.1%–7%)
(3) High specific electrical resistivity (>10^{13} \ \Omega \text{-cm}) [17].
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