CHAPTER-I

INTRODUCTION

INTRODUCTION

Ferrites have vast applications from microwave to radio frequencies. They possess very low conductivity, which is one of the considerations for microwave applications. The conductivity greatly influences the dielectric and magnetic behaviour of ferrites. This created considerable interest in many research workers for the development and potential applications of ferrites in the electronic industry. Now a days the study of ferrites has occupied an important place in the realm of electronics technology.

The practical applications of ferrites are now of immense service in every day life, as electronic and magnetic ceramics. Because of their poor electrical conductivity, they have revolutionized the field of high and ultrahigh frequency electronics, with negligible eddy current losses. This is the reason why ferrites have occupied an unique position in this field.

Many parameters play an important role in determining a particular application of material[1]. The quantities such as magnetization, coercivity, conductivity etc are greatly influenced by porosity, grain size and microstructure of the sample. The various experiments on the same sample will give more details about the different mechanisms. With this view in mind the study of magnetization, d.c. conductivity, X-ray diffraction etc of copper ferrite, cobalt ferrite and copper-cobalt ferrite, sintered at different temperatures and timings, have been undertaken.

The following sections include a brief survey of historical developments, crystal structure, properties and applications of ferrites.

1.1 HISTORICAL

Ferrites were first prepared by nature. The naturally occuring mineral magnetite Fe_3O_4 aroused scientific curiosity among the Greeks, centuries before Christian era. Thales of Miletus, about 600 B.C, stated that magnetite attracts iron. He endowed the load stone with a soul in the belief that an inherent living force could account for the observed fact[2]. Gilbert (1540-1603) was the first to apply scientific methods to a systematic exploration of magnetic phenomenon. However it is the 20th Century that physicists have begun to understand why substances behave magnetically. The human interest developed in preparing artificial magnets synthetically to reduce eddy current losses for microwave applications. A good deal of work in this direction was done by Hilpert[3] who laid the foundations of ceramic magnets by fabricating synthetic ferrites at the Bell Telephone Laboratories.

Forestier, in 1928, prepared ferrites by basic precipitation from chloride solutions and subsequent heat treatments[4]. Several Japanese investigators took active part in ferrite preparation in the early 1930[5,6,7]. The strong foundation for improved ferrites at high frequencies was laid by Snoek[8,9] by establishing the importance of an accurate oxygen content and of homogeneous products. Since then number of investigators have developed new ferrite materials for the rapid growth of technical applications. Verwey[9a] established that electronic conductivity in ferrites is mainly due to the exchange of electrons between divalent and trivalent ions. His further study on crystal structure of ferrites proved that ferrites with inverse spinel structure are ferrimagnetic ($NiFe_2O_4$) and normal spinel structure are non-magnetic ($ZnFe_2O_4$).

Neel[10] was the pioneer to introduce the concept of magnetic sublattices to explain the basic theory of spin-spin interactions. Anderson[11] and VanVleck[12] developed the super exchange theory for the extensive study of basic interactions. In the year 1952, Yafet and Kittel[13] extended super exchange theory by incorporating the triangular spin arrangements. Neel's theory was confirmed by Gorter[14] and Guillaud[15] by measuring the magnetization of Mn, Fe, Co, Ni, Cu and Mg ferrites as a function of Zn composition. Morever Guillaud [15] investegated the existance of varying degree of inversion in Mn ferrites sintered at different temperatures. Bertaut[16] confirmed the same by extensive X-ray diffraction studies on Mg and Cu ferrites. In this way cation distribution assumed an importance. Later Smart[17] worked on microwave resonance and magnetization which helped to determine cation distribution. An important investigation on co-relation of observed Curie point with magnetization and cation distribution was carried out by Gilleo[18]. Koops[19] had observed the high conductivity associated with high dielectric constant and also obtained the formula for a.c. conductivity.

1.2 STRUCTURE OF SPINEL FERRITES

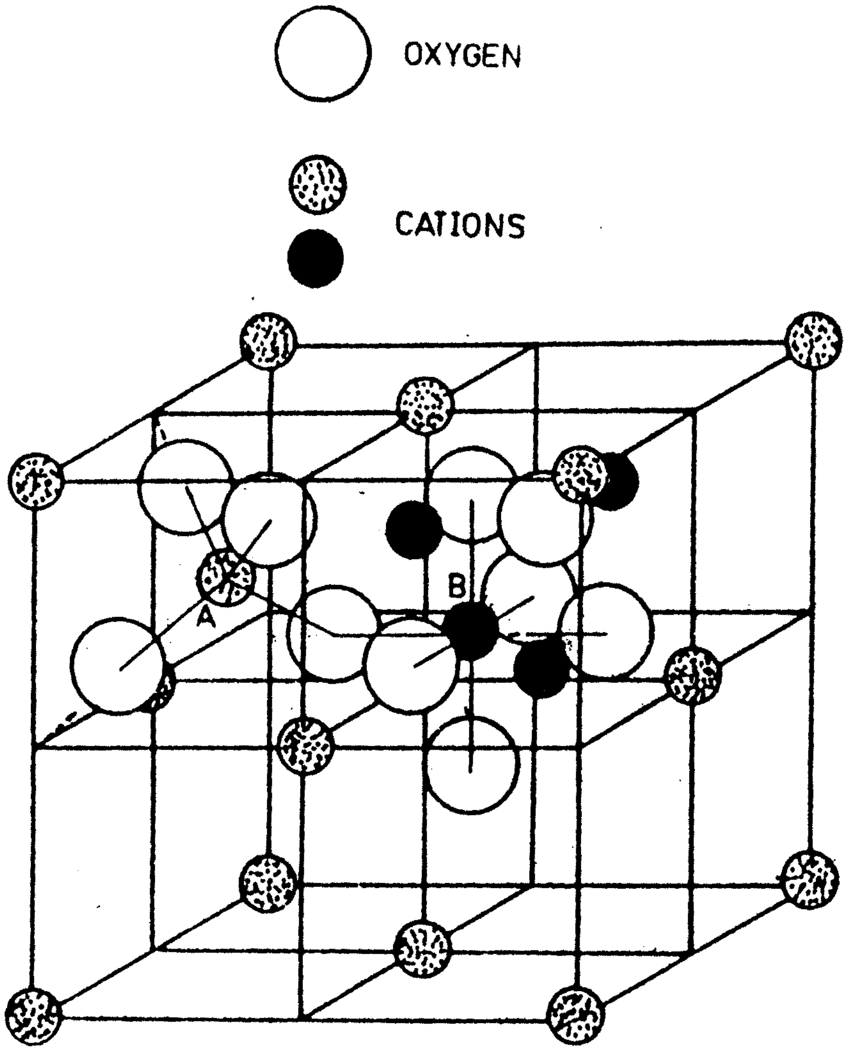
1.2.a Chemical Structure

Spinel is the name of a naturally occuring mineral with chemical formula $MgAl_2O_4$. Ferrimagnetic spinels have the same crystal structure as their mineral, except that the cations are replaced by ions of transition elements. Thus, the general chemical formula for ferrite is $M^{2+}Fe^{3+}O_4^{2-}$ where M is a divalent metal ion of the type Cu, Co, Zn, Mn, Mg, Cd etc.

The oxygen ions being large as compared to metal cations, they form essentially a face centred cubic lattice. The Spinel ferrite unit cell consists of eight molecules of $M^{2+}\ Fe^{3+}\ O_4^{2-}$.

1.2.b Crystal Structure

The structure of spinels was first determined by Bragg in 1915[20] (Fig.1.1) . It is cubic with space group $Fd3m\text{-}O_h^7$ with eight molecules per unit cell of edge length 8A° approximately. The oxygen ions form close packed cube with metal ions occupying the positions of four fold and six fold oxygen co-ordination. Thus cations occupy distinctly different interstitial positions. In one, magnetic ion is surrounded by four oxygen ions and is called A site. Other is



THE SPINEL STRUCTURE (SCHEMATIC)

Fig. 1·1

surrounded by six oxygen ions placed at the vertices of an octahedron and is called B site. The maximum number of possible tetrahedral (A site) and octahedral (B site) sites is 64 and 32 respectively. Only those sites having certain symmetry properties are occupied. Thus in an unit cell 8 A sites and 16 B sites are occupied only[21]. The distribution of these metal ions among A sites and B sites is decided by cation distribution, which depends on site preference energies. The co-ordinates of the ionic positions are as follows

8 positions of four fold oxygen co-ordination at 8a.

$$\begin{bmatrix} 0,0,0, & \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \end{bmatrix} \quad \text{. . . . . face centred.}$$

16 positions of six fold oxygen co-ordination at 16d.

$$\begin{bmatrix} \frac{5}{8}, \frac{5}{8}, \frac{5}{8} & ; & \frac{5}{8}, \frac{7}{8}, \frac{7}{8} \\ \frac{7}{8}, \frac{5}{8}, \frac{7}{8} & ; & \frac{7}{8}, \frac{7}{8}, \frac{5}{8} \end{bmatrix} \quad \text{. . . . . . . face centred.}$$

32 positions at 32e.

$$\begin{bmatrix} uuu, & \bar{u}\bar{u}\bar{u}, & \bar{u}\bar{u}\bar{u}, & \bar{u}\bar{u}\bar{u}, & & \\ \frac{1}{4}-u, & \frac{1}{4}-u, & \frac{1}{4}-u, & \frac{1}{4}-u, & \frac{1}{4}+u, & \frac{1}{4}+u, \\ \frac{1}{4}+u, & \frac{1}{4}-u, & \frac{1}{4}+u, & \frac{1}{4}+u, & \frac{1}{4}+u, & \frac{1}{4}-u, \end{bmatrix} \quad \text{... face centred.}$$

for $u=0.375$, the oxygen ions form a perfect close packed cube. But generally u is slightly greater than the above value. The deviation from perfect close packing is manifested in increase in size of 8 tetrahedral interstices and decrease in size of 16 octahedral interstices.

The complete unit cell can be divided into 8 octants, with identical ionic arrangements in alternate octants. When oxygen parameter increases beyond the ideal value 0.375, oxygen ions move away from their nearest tetrahedral ion neighbour along the (111) direction.

1.3 TYPES OF SPINEL FERRITES

Barth and Posnjak[22] have observed different types of cation distribution in ferrites and classified them accordingly.

1.3.a Normal Spinel Ferrite

In the normal spinel ferrites all divalent metal ions occupy A sites and trivalent iron ions occupy B sites.

i.e. $\left[M_1^{2+}\right] \left[Fe_2^{3+}\right] \quad O_4^{2-}$

e.g. Zinc and cadmium ferrites are having normal spinel structure.

1.3.b Inverse Spinel Ferrite

In inverse spinel ferrites B sites are occupied half by divalent metal ions and half by trivalent iron ions.

$$\left[Fe^{3+}_{x} \right] \quad \left[M^{2+}_{1} \; Fe^{3+}_{2-x} \right] \quad O^{2-}_{4}$$

e.g. Manganese, Cobalt and Nickel ferrites are having completely inverse spinel structure.

1.3.c Random-Spinel Ferrites

In this case divalent metal ions and trivalent iron ions are randomly distributed over A and B sites.

$$\left[M^{2+}_{x} \; Fe^{3+}_{1-x} \right] \quad \left[M^{2+}_{(1-x)} \; Fe^{3+}_{1+x} \right] \quad O^{2-}_{4}$$

where x = coefficient of normalcy

$1-x$ = coefficient of inversion

It has been observed that such a distribution depends upon the physico-chemical conditions of preparation. e.g. the cation distribution in copper ferrites can be expressed as

$$\left[Cu^{2+}_{0.14} \; Fe^{3+}_{0.86} \right] \quad \left[Cu^{2+}_{0.86} \; Fe^{3+}_{1.14} \right] \quad O^{2-}_{4}$$

1.4 SUBSTITUTIONAL FERRITES

Substitutional ferrites are obtained by replacing the divalent metal ions as well as trivalent iron ions by other magnetic or non-magnetic ions in the spinel structure. Hence there are two types of substitutional ferrites.

1.4.a Partial replacement of divalent metal ions by other divalent metal ions, results in one type of substitutional ferrite.

e.g. Cobalt ferrite partially replaced by Manganese.

$Co_{1-x} Mn_x Fe_2O_4$ with $0 \angle x \angle 1$

It may be called either as a cobalt manganese ferrite or manganese substituted cobalt ferrite.

1.4.b Partial replacement of trivalent iron ions by other trivalent metal ions (usually non-magnetic in character) results in another type of substitutional ferrite.

e.g. $NiFe_{2-x} Cr_x O_4$ ..... called Nickel ferrite chromate.

1.5 PROPERTIES OF FERRITES

Ferrites are essentially ionic compounds. At room temperature, their resistivity varies appreciably from 5×10^{-5} ohm-cm to 10^{+11} ohm-cm for magnetic and some nickel and manganese ferrites respectively. Above 1200°C considerable variations in electrical properties, with respect to heat treatment and preparation conditions have been observed in poly-crystalline ferrites[23]. It is due to the fact that above such temperature dissociation of oxygen takes place rapidly.

Electrical properties such as d.c. and a.c. resistivity, dielectric constant, dielectric loss factor mainly depend upon the purity of compound, surface condition, sintering temperature and time, porosity, grain size, physico-chemical history and chemical homogeneity. The dependence of resistivity on temperature obeys the law

$$\rho = \rho_0 \; e^{\frac{\Delta E}{KT}} \qquad \ldots\ldots\ldots \qquad 1.1$$

where ΔE = Activation energy

K = Boltzmann constant

T = Absolute temperature of the sample

ferrites possess extremely high dielectric constant and resistivity in the range of frequency from few Hzs to few MHzs.

The effect of thermochemical history on cation distribution and stochiometry, during sintering process was studied by Economos[24]. The time variation of electrical conductivity as a function of temperature for poly-crystalline copper, nickel and cobalt ferrites, with stochiometric composition is discussed by Rezlescu and Cuciureanu[25]. They interpreted that the cation reordering is the main cause for the time variation of electrical conductivity. This cation reordering takes place more easily at higher measuring temperatures. The mechanism of electrical conductivity in $CuFe_2O_4$ was studied by Mazen[26] on the basis of band picture and hopping model. According to band model the temperature dependence of conductivity is mainly due to variation of charge carriers concentration with temperature. While in the hopping model the change in mobility with temperature constitutes the conduction current by jumping from one iron ion to next.

The magnetic behaviour of $MgFe_2O_4$ and $CoFe_2O_4$ system indicates that such behaviour changes from multidomain to single domain with increasing cobalt content[27]. The nature of magnetic ordering in $CuFe_2O_4$ has been investigated by measuring the magnetic properties of tetragonally distorted crystal. The observed results were explained by a canted magnetic structure in the octahedral sublattice, with Jahn Teller exchange. Maxwell and Wagner[28] suggested that the dispersion in dielectric constant and resistivities is due to inhomogeneous dielectric structure.

Ferrites also exhibit Hall effect and Seebeck effect. As far as their applications are concerned, switching and memory effect are the outstanding characteristics of ferrites. Yamashiro[29] reported switching and memory phenomenon in copper ferrites quenched from 800°C to 600°C. This phenomenon is due to the distortion of crystal structure called Jahn Teller distortion. Dimensional changes occur with magnetization leading to the phenomenon of magnetostriction about the position and valency of the ions in the lattice.

Infrared spectra of several ferrites have been reported by Waldron[30] and he has assigned high frequency band to the tetrahedral group complexes and low frequency band to the octahedral complexes. Josyulu and Sobhanadri[31] have observed variation in intensity, with cobalt concentration, of a small band for infrared spectra of mixed cobalt-zinc ferrites, due to divalent octahedral metal ion-oxygen ion complexes.

1.6 APPLICATIONS OF FERRITES

Ferrites have already found wide applications because of their high efficiency, low cost and small volume. They operate with virtually no eddy current losses. In the design of inductors and transformers, the MQ product of a material has been found to be a useful index of the quality of material. Obviously a material with high MQ product is desirable in inductor design. A high permeability produces larger inductance per turn of coil and reduces leakage of flux. Today commercially available magnetic materials are having highest MQ values. e.g. iron dust (2000); Mn-Zn ferrite (250,000) and permalloy tape (100,000).

Ferrite rods are widely used for antenna cores in broadcast radio receivers. Because of high permeability, the sensitivity of antenna is greatly increased over the normal loop antenna with an air core. In order to make use of intrinsic permeability of ferrite without deleterious demagnetizing effects, the ratio of length to diameter of the rod should be as large as possible.

The largest use of ferrites today is in flyback transformers for television picture tubes. The cores for these transformers must have low loss at high flux densities and high frequencies of the order of 100 Kc, which is the effective flyback frequency used in scanning a television picture tube.

Rapidly growing and potentially large applications of ferrites today is for logic and memory uses in modern digital computers. The rectangularity of hysteresis loop and coercive force are the important factors in these applications. The ideal core has a perfectly rectangular BH[32] relationship and a coercive force so that it could be easily driven from one state of magnetization to other by high speed transistors with only one turn on each core.

The spinel structure is physically flexible, leading to a wide range of physical properties and hence practical applications[33]. Hence spinels are extensively used increasingly for miniaturization.

Many proposals have been made for performing logic and memory functions using a single piece of ferrites with two or more apertures, through which the magnetizing windings are threaded. These devices are easier to wire into a computer system and are capable of performing a wide variety of functions that are not easily accomplished by using individual cores.

The very low loss of certain ferrites has recently permitted the building of a new class of non-reciprocal microwave circuit elements for variety of applications. Power ferrites for high frequency[34] applications have been developed in order to suppress gyromagnetic and dielectric losses by high d.c. resistivity, low magnetic flux density and small core sizes.

Recently piezomagnetic nickel-manganese-cobalt ferrites[35] have been developed for their wide applications in ultrasonics and radio frequency electronics.

In this way ferrites occupy every field in various forms such as filter inductors, I-f transformers, tueners, miniature inductors, loading coils, flyback transformer, miniature transformers, suppression beads, recording heads, memory cores, switching cores, microwave properties for attenuators, circulators, switches, modulators and temperature controls.

1.7 ORIENTATION OF THE PROBLEM

The size of the grains and porosity affect the electrical and magnetic properties of ferrites to a large extent. The modern ceramic technique, therefore deals with the preparation of ferrites with lowest porosity which in turn depends upon the sintering temperature and time, purity of starting materials and applied pressure, while preparing the sample.

Open porosity has a detrimental effect as it enables the material to absorb moisture which greatly increases the dielectric losses. Below the Curie temperature, the crystallites split up into magnetic domains. The mobility of domain walls favours high permeability or low coercivity. This property can be achieved by fault free large crystallites. The coercive force of a ferrite is controlled by the crystallite size. Longer the grinding time and or lower the firing time-temperature, the higher is the coercive force[36]. The remanance is controlled by the density which in turn is a function of the forming conditions as well as firing time-temperature. Hence compromises are necessary to be made in order to effect the greatest (BH) max value, the measure of magnetic quality. The forming pressure has a considerable effect on both ceramic and magnetic properties of permanent ferrites. Morever the effect diminishes as the process of densification progresses.

The studies of Jain[37] on intragranular porosity shows that the initial permeability varies directly with the separation between intragranular pores and coercive force varies inversely as the square root of this distance. The deviation of permeability values from high frequency behaviour, at high sintering temperature is reported by Murthy[38].

Rikukuwa[39] developed the model for the effect of demagnetising field caused by closed pores and grain boundries and established that the demagnetising field is proportional to the magnetic field, whereas that caused by the grain boundries is proportional to the flux density. Thus grain boundry region is important for the control of magnetic properties of ferrites. A survey has been made by Jonker[40] on the importance of ceramic structure and grain boundry condition of electroceramic materials in relation to their applications. The dependence of microstructure on sintering temperature was discussed by Venkataramani and others[41].

Thus the microstructure plays an important role in deciding the properties of ferrites which also enables their tailormaking. The recent developments in the field of ferromagnetism have enabled to synthesize the ferrites having derived properties to suit the needs of any particular electronic device. The present task, therefore, deals with an experimental exercise in understanding a relation between the microstructure and physical properties of some copper, cobalt and copper-cobalt ferrites.

The main aspects of the present work include the following studies at different sintering temperatures and times. viz. 800°C and 900°C and 14 hours, 20 hours and 30 hours respectively.

1) preparation of ferrites
2) X-ray diffraction studies
3) D.C. electrical resistivity measurements
4) Magnetization of ferrites
5) Infrared absorption studies
6) The scanning electron microscopy

The following ferrite compositions have been studied.

$CoFe_2O_4$, $Cu_{0.4}Co_{0.6}Fe_2O_4$ and $CuFe_2O_4$.

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