CHAPTER — I

INTRODUCTION

1.1 HISTORICAL

Ferrites are ferrimagnetic materials, essentially mixed crystals of various magnetic oxides. The 'ferrites' are an artificial version of load stone (Fe_3O_4), also called ferrous ferrite, the first magnetic material known to man. They consist of oxygen ions in a close packed structure with cations fitted into interstices.

The interest in the study of ferrites stemmed on one hand from academic interest owing to their crystal structure, scope for employing a large number of ingradients, a vast variation in their properties depending upon the preparation techniques and the physical parameters such as grain size, porosity, inhomogeneity etc. and on the other hand, due to their important electrical and magnetic properties. The aim was to develop certain ferrites which will have immediate industrial applications. The simultaneous requirements of optimal electronic and magnetic properties in the advanced electronics microwave, computer technologies have focussed the attention of research workers on ferrites.

Ferrites also assumed importance as magnetic materials possessing a wide range of saturation magnetization from 1500

gauss to 5000 gauss, together with the property of electrical insulation and the fact that the propagation of high field electromagnetic waves through them takes place with low attenuation [1].

In the past, the development of synthetic ferrites was started with an objective of reducing the eddy current losses in inductors and transformers by Hilpert [2] in 1909. However, Hilpert's attempts were inadequate to achieve the goal. Later, Snoek [3] and his colleagues carried out extensive experimental work on the artificial ferrites with particular interest of preparation of ferrites and studies on their magnetic properties. Verwey [4] showed that electronic conductivity of ferrites is due to the exchange of electrons between divalent Fe^{2+} and trivalent Fe^{3+} ions of iron in ferrites. This is hopping mechanism of electrons through ionic lattice. Further studies by Verwey revealed that ferrites with inverse spinel structure are ferrimagnetic whereas those with normal structure are non-magnetic [5]. Here after the concept of cation distribution and ferrimagnetism was evolved. During the same period, Neel's [6] theory of ferrimagnetism, with spin-spin interaction concept, added impetus to the research activity in the field of ferrites. This simple spin-spin interaction mechanism was soon found to be inadequate and the detailed examination of basic interactions was made by Anderson and Van Vleck by proposing a theory of superexchange forces [7].

In 1952, Yafet and Kittel [8], introduced the idea of triangular arrangement of spin in the Neel's two sub-lattice model. By magnetization measurements Gorter and Guillaud [9] gave the experimental supporting to Neel's theory. Then Koops [10] introduced the formula for AC conductivity of ferrites and Gilleo [11] developed the formula which correlated the observed Curie temperature, magnetization and cation distribution.

Guillaud [9] found different values of magnization for magnesium ferrite samples prepared at different tempetatures. He concluded that the specimens were with varying degree of inversion. This was supported by Bertaut's [12] detailed X-ray diffraction studies on Mg-ferrite and Cu-ferrite. Thus cation distribution in ferrite assumed importance. Smart [13] and Gorte [14]also correlated independently the cation distribution found out by microwave resonance and magnetization.

1.2 STRUCTURE OF FERRITE MATERIALS

1.2.1 *CHEMICAL STRUCTURE OF FERRITES*

The term 'ferrite' has been used for semiconducting materals possesing Fe_2O_3 as a basic constituent, regardless of the crystal structure of the material [15].Of late,however,this term is used to indicate ferrimagnetic oxides and is getting restricted [16] to materials with spinel structure having the general chemical formula $M^{2+}Fe_2^{3+}O_4^{2-}$, where M denotes a divalent

metal ion like Cu, Mn, Zn, Ni, Co, Mg, Fe.,and Fe^{3+} a trivalent ion. Actually, MFe_2O_4 is a combination or the solid ionic solution of two oxides MO and Fe_2O_3. The compounds of this type form cubic symmetry similar to that of mineral spinel $MgAl_2O_4$. Ferrites formed with single divalent metal atom are called as single or simple ferrites, e.g. $CuFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ etc. The divalent atoms may be partially replaced by combination of their metal ions e.g. $Co_{0.8}Zn_{0.2}Fe_2O_4$, such ferrites are called mixed or binary ferrites.

1.2.2 *LATTICE STRUCTURE OF FERRITES*

The ferrite is an ionic crystal and its lattice displays cubic symmetry with lattice parameter ranging from 8.3 A^o to 8.5 A^o. The space group is Fd3m – O_h^7 . The unit cell contains 8 molecules and thus the unit cell formula is

$$M_8^{2+}\ Fe_{16}^{3+}\ O_{32}^{2-}\ .$$

The 32 oxygen ions are arranged on a more or less close packed fcc lattice. There are 96 interstices available between these 32 oxygen ions. The oxygen close packed fcc lattice structure is shown in Fig. 1.1. The 96 interstitial sites are divided into 64 tetrahedrally co-ordinated A-sites and 32 octahedrally co-ordinated B-sites.

The metal ions occupy only 24 sites [17]. The distribution

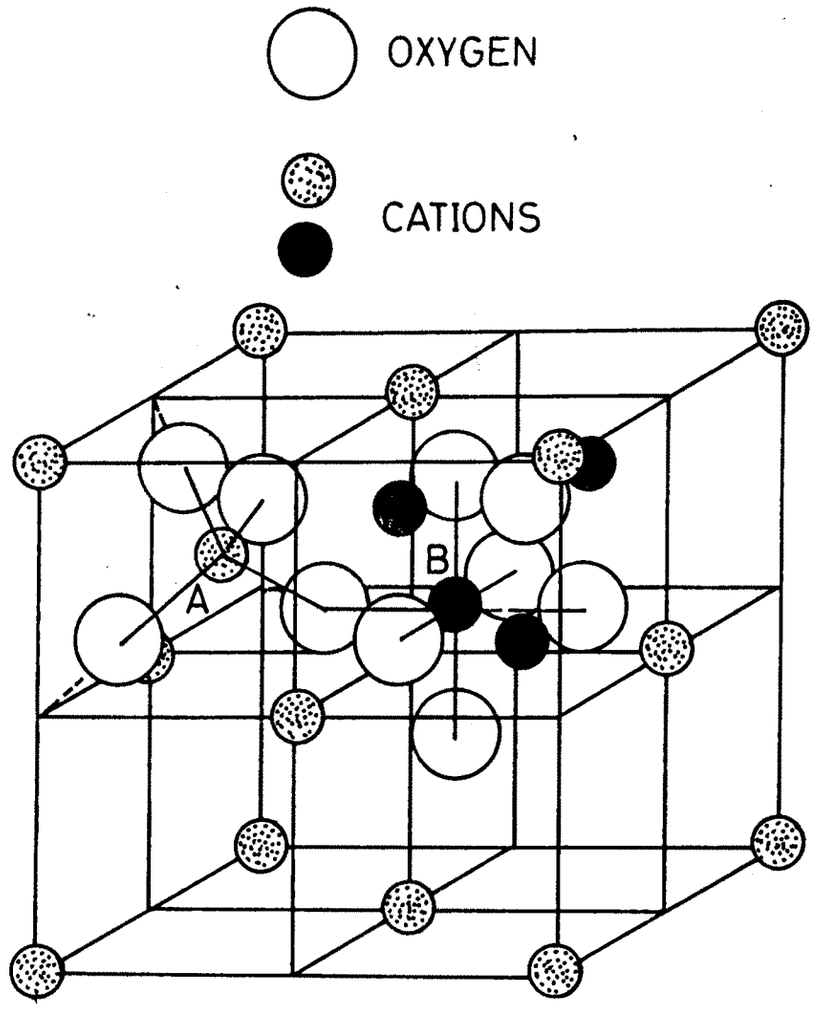

Fig. 1·1 - THE SPINEL STRUCTURE (SCHEMATIC)

24 metal ions among A-sites and B-sites is determined by cation distribution. The distribution of cations on A-sites and on B-sites depends upon the site preference energies of the different ions.

In ferrites every oxygen ion is surrounded by three B-cations and one A-cation. The distances and the angles are as follows :

$$OA = \sqrt{3}\ a\ (u - \tfrac{1}{4}) \qquad OB = a\ (5/8 - u);\ u = 3/8;$$

$$A - O - A = 79^{o}\ 58';$$

$$B - O - B = 90^{o} \text{ and}$$

$$A - O - A = 125^{o}\ 9'.$$

The strength of the interaction is expected to be more in case of smaller metal-oxygen distances and when M-O-M angles are nearing 180°. Thus it can be concluded that A-B interaction is strongest while B-B interaction is weak. A-A interaction interactions are all negative.

1.3 *CLASSIFICATION OF FERRITES*

On the basis of cation distribution, Barth and Posnjak [18] have classified ferrites in three groups. The general formula for cation distribution of a spinel ferrite may be written as

$$M_{x}^{2+}\ Fe_{1-x}^{3+}\ \left[\ M_{1-x}^{2+}\ Fe_{1+x}^{3+}\ \right]\ O_{4}^{2-}$$

where M stands for divalent metal ion and x varies from 0 to 1.

1.3.1 *NORMAL SPINEL FERRITES*

With $x = 1$ we get cation distribution formula

$$M^{2+} \left[Fe^{3+} \; Fe^{3+} \right] O_4^{2-}$$

for normal spinel ferrites. Here the divalent metal ions occupy 8 tetrahedral A-sites while trivalent ferric ions occupy 16 octahedral B-sites (shown in brackets). Examples of ferrites with normal spinel structure are $CdFe_2O_4$ and $ZnFe_2O_4$. The cation distribution of $ZnFe_2O_4$ is thus given by

$$Zn^{2+} \left[Fe^{3+} \; Fe^{3+} \right] O_4^{2-}.$$

The normal ferrites do not show ferrimagnetic behaviour.

1.3.2 *INVERTED SPINEL FERRITES*

When $x = 0$ we get the cation distribution formula

$$Fe^{3+} \left[M^{2+} \; Fe^{3+} \right] O_4^{2-}$$

for inverted spinel ferrites. If $8M^{2+}$ ions on A-sites change their positions with 8 of 16 Fe^{3+} ions on B-sites, then the inverted spinel structure results. This is completely inverted or inverse spinel structure. Ferrites such as Co, Ni, Mg occur in almost completely inverted form. Here there is A-B interaction between dissimilar ions, and inverse spinel ferrites show ferrimagnetic behaviour. Cation distribution of

$CoFe_2O_4$ is given by

$$Fe^{3+} \left[Co^{2+} \; Fe^{3+} \right] \; O_4^{2-} .$$

1.3.3 *RANDOM SPINEL FERRITES*

For $0 < x < 1$ we get cation distribution or random spinel structure. In random ferrites M^{2+} and Fe^{3+} are randomly distributed over A and B sites depending on the physico-chemical conditions of preparation or compositional variation. Such a kind of ferrite is partially inverse. The general formula for partially inverse spinel ferrite is written as

$$M_x^{2+} \; Fe_{1-x}^{3+} \left[M_{1-x}^{2+} \; Fe_{1+x}^{3+} \right] \; O_4^{2-}$$

where x is known as the coefficient of normalcy and (1-x) the coefficient of inversion. Manganese ferrite is partially inverse ferrite with coefficient of normalcy $x = 0.8$; i.e.

$$Mn_{0.8} \; Fe_{0.2} \left[Mn_{0.2} \; Fe_{0.8} \right] \; O_4 .$$

$MnFe_2O_4$ is only 20% inverse.

1.3.4 *SUBSTITUTIONAL FERRITES*

In spinels it is always possible to replace some or all metal or iron cations with alternate cation, in some cases magnetic and in other cases non-magnetic [16]. The resulting

ferrites are called substitutional ferrites.

For example, in $NiFe_2O_4$, Ni may be substituted partly or completely by Cobalt to obtain Nickel Cobalt ferrite

$$Ni_{1-x}Co_xFe_2O_4$$

where $x = 0$ to 1. Part of iron may be substituted by one of trivalent non-magnetic elements like Al, Cr, Ga to obtain Nickel ferrite aluminate

$$NiFe_{2-x}Al_xO_4$$

where $x = 0$ to 2.

The resulting substitutional ferrites are equivalent to a solid solution of two pure end member ferrites. Nickel cobalt ferrite with substitution parameter $x = 0.5$ is thus equivalent to a solution of one part of pure Nickel and one part of pure Cobalt ferrite i.e.

$$2Ni_{0.5}Co_{0.5}Fe_2O_4 = NiFe_2O_4 + CoFe_2O_4 .$$

1.4 *PROPERTIES OF FERRITES*

By nature, the ferrites are semiconductors, but their resistivity varies from 5×10^3 ohm-cm in case of magnetite to as high as 10^{11} ohm.cm in certain nickel ferrites and magnesium ferrites at room temparature [19]. Electrical

properties of polycrystalline ferrites very markedly depending upon the heat treatment given during the preparation process. This is due to rapid increase of oxygen dissociation pressure above 1200°C [20] and microstructural changes. The electrical properties also depend upon extrinsic parameters such as purity of compounds, stoichiometry, surfacecondition, sintering temperature, physico-chemical history during preparation, porosity and density, grain size, chemical inhomogeneity etc.

The temparature dependence of electrical resistivity and its study is a matter of much importance in ferrites. It obeys the law

$$\rho = \rho_0 \exp\left[\frac{\Delta E}{KT} \right] \qquad \ldots(1.1)$$

where ΔE is the energy of activation and K is the Boltzmann constant.

The time variation of electrical conductivity as a function of temperature for polycrystalline copper, nickel and cobalt ferrites, with stoichiometric composition is discussed by Rezlescu and Cuciureanu [21]. They interpreted that the cation reordering is the main cause for the time variation of electrical conductivity. The mechanism of electrical conductivity in $CuFe_2O_4$ was studied by Mazen [22] 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 carrier concentration with

temperature. While in the hopping model the change in mobility with temperature costitutes the conduction current by jumping from one iron ion to next.

The magnetic behaviour of $MgFe_2O_4$ and $CoFe_2O_4$ systems indicates that such a behaviour changes from multidomain to single domain with increasing cobalt content [23]. Maxewell and Wagner [24] suggested that the dispersion in dielectric constant and resistivities is due to inhomogeneous dielectric structure.

Ferrities exhibit Hall effect and Seebeck effect [41]. As far as their applications are concerned switching and memory effect are the outstanding characteristics of ferrites. Yamashiro [25] reported switching and memory phenamena in copper ferrites quenched from 800 °C to 600 °C. This phenamenon is due to the distortion of crystal structure called Jahn-Teler distortion. Dimensional changes occur with magnetization leading to the phenamenon of magnetostriction [42,43].

Infrared spectra of several ferrites have been reported by Waldron [26] and he has assigned high frequency band to the tetrahedral group complexes and low frequency band to octahedral complexes. Josyulu and Sobhanadri[27] 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.

1.5 *APPLICATIONS OF FERRITES*

Ferrites have both the properties of high electrical resistivity and reasonably good magnetic permeability combined together in one. Therefore, they find numerous applications in many fields. In addition to this they have switching property. This proves to be of great advantage from applications point of view.

Ferrites can operate with virtually no eddy current loss at high frequencies where the metal cores made up of extremely thin ribbon or fine particles were found useless. Thus the high frequency applications of soft ferrites are mainly as cores for special transformers or inductors used in radio and TV receivers. Modern electronic technology needs the inductors and transformers on very miniature scale and ferrites can efficiently serve this purpose at higher frequencies. Certain comunication equipment requires broad band transformers where ferrite cores are useful since they respond to some broad band frequencies. In electronics, ferrites are finding interesting application in the manufacture of microwave integrated circuits (MICS) [28]. In such devices discs of ferrites or garnets are introduced in the composite made up of ferrite and nonmagnetic supporting matrix such as alumina. Another application is in

pulse transformers used in some data handling circuits. The Fourier component of a square pulse, cover a wide range of frequencies and if the permeability of core varies with frequency there results the distoration of the pulse shape. In digital computers the ferrite cores are used as the switching and memory elements for transmitting, storing and reading signal pulse in a few microseconds [29]. Ferrites with square loop characteristics of B-H curve are more suitable involving flip-flop changes in computers and memory devices. Ferrites have wide range of magnetization and at the same time the propagation Of high frequency E-M waves takes place with low attenuation. Hence these find applications in various fields such as microwave communications, radars and TVs. Ferrites of lower permeability and large magnetostriction are useful in accelerometers, mechanical filters and ultrasonic generators. Demanding upon the nature of gyromagnetic resonance, ferrites are used as the elements in nonreciprocal microwave devices such as circulators, isolators, modulators, phase shifters, magnetically tuned ferrite loaded resonant circuits,directional couples, filters etc. At present it is rather difficult to manufacture ferrites for high power amplification due to dielectric and magnetization losses and deterioration of permeability [16].

Varied applications of ferrites are being developed now a days. Recently, Saburao Motozawa of Japan used sintered

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$NiFe_2O_4$as granulated material for the purpose of electrolysing water [30]. High buildings are constructed in Japan which produce ghost images in TV receivers. Ferrite absorbers were applied to structures and its effectiveness was confirmed [31]. In Bell laboratories new ferrite Fe-Ni alloy is developed which can replace 2v permendur used in telephone receivers [32]. Research workers in Fujitsu laboratories observed that high recording density is obtained when Mn-Zn ferrite head was used for prependicular recording on Co-Cr thin film obtained by sputtering [33]. For developing accelerating machine for ion synchrotron a ferrite accelerating resonator was proposed by Averbukh [34].

1.6 *ORIENTATION OF THE PROBLEM*

It has been increasingly evident since the early 1950 that the characterization of ceramic materials such as ferrites is a necessary goal to the understanding of their chemical and physical properties. The term 'microstructure' has been the pivot around which characterization has centred.

Microstructure affects structure sensitive properties of the materials. It affects high power handling ability as well as low power loss in saturated microwave devices. Fine grained ferrites have some what low power loss and are able to handle higher power levels before the onset of nonlinearities. Ferrite devices, used in radio, TV and computers, all operate by

virtue of the dynamics of the hysteresis loop [35]. In moat of these cases the motion of magnetic domain walls is important [36], and it is affected and controlled by microstructure. Present knowledge permits a high degree of control of saturation magnetization of ferrites and fair degree of control of its temperature dependence [37]. The initial permeability and hysteresis loop properties of ferrites are strongly influenced by the microstructure of the material and hence the preparation method used [38]. The microwave properties, in particular dielectric and magnetic loss, are also sensitive to the method of fabrication [39].

The tools and techniques of microstructural analysis have naturally expolded in number over last 30 years. The edvent of electron microscopy and electron microprobe analysis, coupled with the more familiar tools of X-ray diffraction and optical microscopy, has developed a much deeper understanding into the complexity of ferrite and ceramic materials. Recent researchers have shown that it is possible to process ferrites having desired properties to suit the requirements of a particular application by controlling their microstructures which can be done in turn by controlling the fabrication methods. Thus microstructure plays an important role in deciding the properties of ferrites which also enable their tailor-making.

Though it has been established that the properties of

ferrites depend to a great extent on their microstructure,exact correlation between the ferrite microstructure and their physical properties has been rarely established. Studies in this direction are rare. In the present work, it is therefore, decided to study ferrites in the light of microstructures obtained with the help of scanning electron microscope.

We have chosen the cobalt-zinc ferrite system for our study as its saturation magnetization is comparatively high and the system is much less studied. We have restricted ourselves to the study of the effect of sintering time and compositional variation on properties of these ferrites.

The orientation of the problem involves the following studies,

[1] Preparation of $Co_xZn_{1-x}Fe_2O_4$ ferrites with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0,

[2] Charactrerization of ferrites by XRD,

[3] Measurement of DC electrical resistivity,

[4] Measurement of magnetization and I.R. absorption studies.

[5] Calculation of porosity, study of microstructure obtained with SEM and to establish correlation between microstructure and properties of ferrites.

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