
CHAPTER-I

CHAPTER - I

FERRITES : AN INTRODUCTION

INTRODUCTION

Ferrites are important magnetic materials as they possess wide range of magnetization, show high electrical resistivity and can be used to propagate high field electro magnetic waves with low attenuation. They have been extensively studied both because of their interesting physical properties and varied industrial applications, Several new applications have been devised during the last few years. Some recently developed applications are mentioned at the end of this chapter.

The studies of ferrites have to be, however, restricted due to the vast nature of the subject. But the understanding of the interrelationship of properties with crystal structure, cation distribution, magnetic interaction and the preparation condition is necessary, because the ferrite exhibit properties that sensitively depend on chemical and thermophysical history which also allows the tailormaking of ferrites for specific applications.

In the following sections a brief survey of historical developments, crystal structure, electrical properties of ferrites etc are given.

1.1 HISTORICAL .

The first magnetic material known to man ^{was a} ~~is~~ lode-stone. References to [^]lode-stone (leading stone) are found in the vedas, the most ancient religious scriptures of the Hindus, dating back to some one thousand years (B.C.) in the platonic dialogues of socrates and in the ancient literature of Chinese. The Chemical formula for lode-stone is $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ (ferrous Ferrite) and it ~~is~~ naturally occurring Ferrite. The ferrites are oxide magnetic materials, essentially mixed crystals of various magnetic oxides, Ferrites are an important class of magnetic materials.

The term ferrite is used for semiconducting oxide magnetic materials with resistivity values in the range 10^{-3} to 10^{+11} ohm-cm. They were developed with the main objective of reducing eddy current losses in inductors and transformers. This work was initiated by Hilpert(1) in the years 1909. However Hilpert's attempts were inadequate to achieve the goal. After some years ferrites were studied in theory by Kato and Takai (2), Foreotier (3), Barth and Posjank (4) from various points of view.

During the second world war, Snoek (5) and his colleagues carried out extensive experimental work on artificial ferrites with particular interest of preparation of ferrites and their

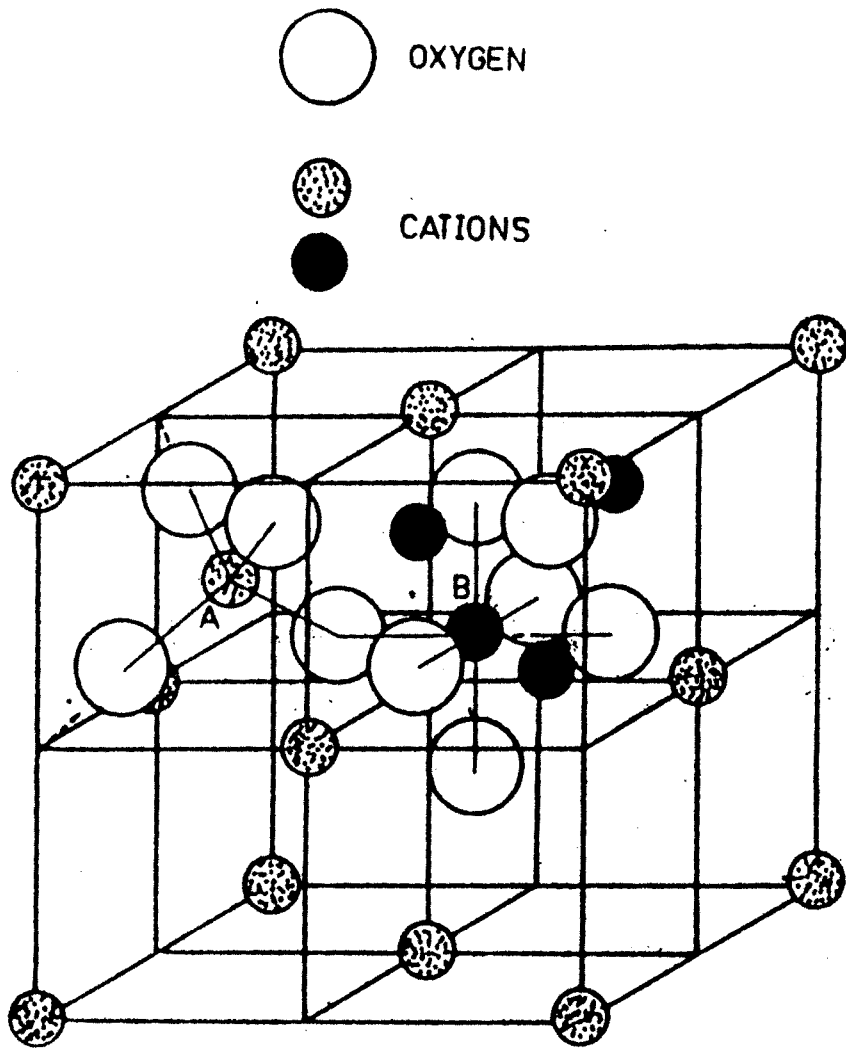
magnetic properties. At the same time Neel (6) put forth his theory of ferrimagnetism, which encouraged the research activities in the field of ferrites. The direct experimental proof of Neel's theory was given by Gorter (7) and Guillaud (8). Gorter measured the magnetization of Mn, Fe, Co, Ni, Cu and Mg ferrites mixed with Zn ferrites with variation of Zinc content, Guillaud et al^y explained the variation of magnetization as a function of temperature for mixed ferrites with varying composition and temperature in ferrimagnetic region. Neel modified the earlier theoretical treatment which could not account for the temperature dependence of Weiss molecular interaction constant as per the experiments (9). The modified theory was confirmed positively by experimental results (10). The direct proof of Neel's model of ferrimagnetism came up only with neutron diffraction studies on magnetite (11) and Zinc ferrite (12).

1.2 CRYSTAL STRUCTURE OF FERRITE

All oxide ferrimagnets have a crystal structure that consists of a basic crystal frame work of oxygen ions with relatively large ionic radii. At the interstices of these ions are located the smaller metallic ions. The different type of oxidic ferrimagnetic materials are distinguished by the type of lattice formed by the oxygen ions.

Ferrites are the semiconducting oxide magnetic materials, possessing Fe_2O_3 as one of the component(13). It has a spinel structure and the general chemical formula $\text{M Fe}_2\text{O}_4$, where M represents a divalent metal ion (M^{2+}) such as Mg, Mn, Fe, Co, Ni, Cu, Zn or a combination of these ions, such as $(\text{Ni}_{0.4} \text{Zn}_{0.6})$, or in some cases a divalent combination like $(\text{Li}_{0.5}^+ \text{Fe}_{0.5})$. The trivalent iron ions (Fe^{3+}) are some times partially replaced by other trivalent ions such as Al^{3+} or Cr^{3+} . The crystal structure of ferrite is analogous to that of the mineral spinel MgAl_2O_4 (Fig.1.2). There are eight molecules of MFe_2O_4 in the unit cell and the lattice parameter 'a' ranges between 8.3 Å and 8.5 Å.¹⁴

As the unit cell contains eight molecules and the unit cell formula becomes $\text{M}_8^{2+} \text{Fe}_{16}^{3+} \text{O}_{32}^{2-}$. The cations occupy interstitial positions. These interstices are of two types the tetrahedral or A site with four ions located at the corners of a tetrahedron as shown in fig.(1.2a) and the octahedral or B site with six surrounding oxygen ions placed at the vertices of an octahedron as shown in fig.(1.2b). There are 96 interstitial positions available between the 32 oxygen ions. Out of the 96 interstitial sites per unit cell 64 are tetrahedral and 32 octahedral. The metal ions occupy 24 interstices out of these 96 interstices. The spinel structure is shown in the fig. 1.1. The distribution of 24 metal ions among A sites and B sites is determined by cation distribution



THE SPINEL STRUCTURE (SCHEMATIC)

FIG. 1-1

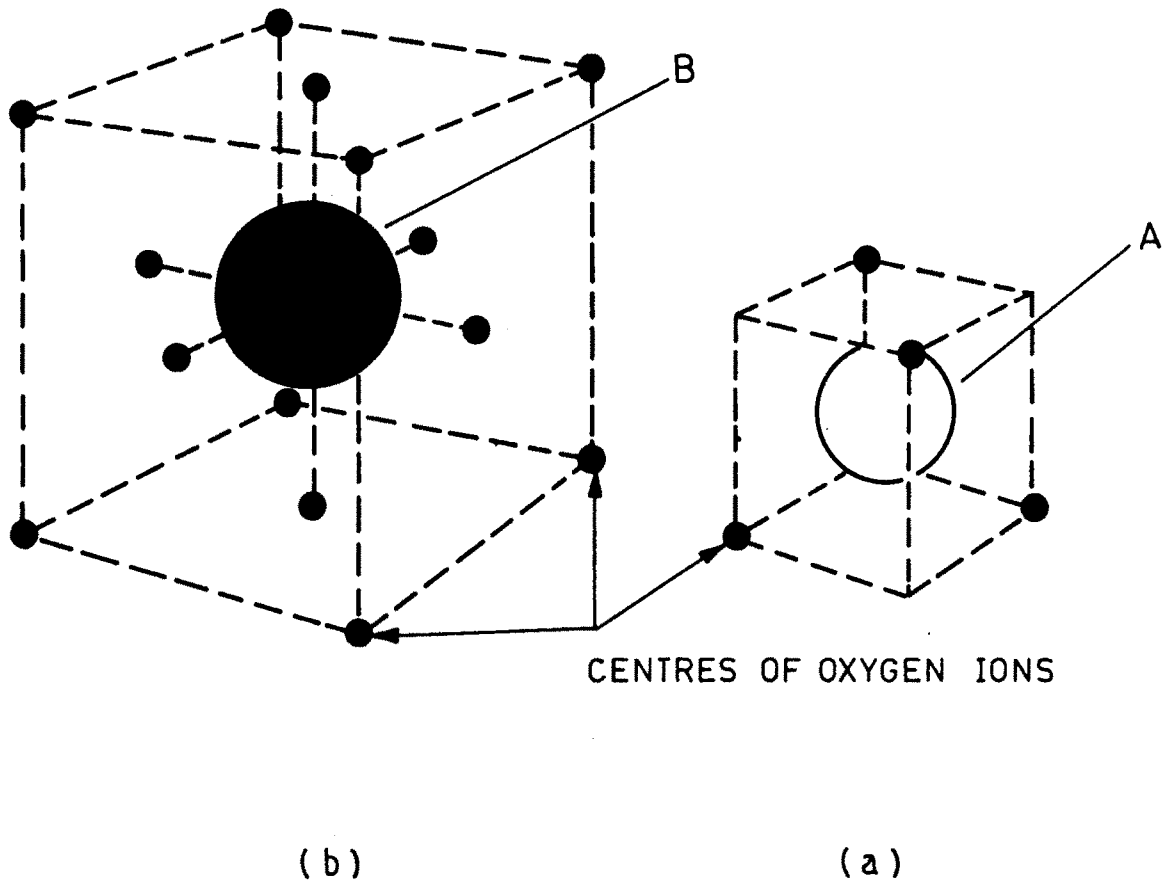


Fig. 1-2

A — Fe ION ON A-SITE .

B — Fe ION OR M (METAL) ION ON B-SITE .

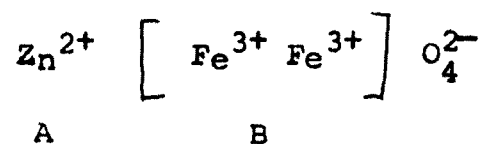
The distribution of cations on A sites and B sites depends upon the relative site preference energies of the respective metal ions present in the ferrite. The classification of ferrites is done on the basis of cation distribution as follows.

- a) Normal spinel Ferrites.
- b) Inverse spinel Ferrites.
- c) Random spinel Ferrites.

1.2.1(A) NORMAL SPINEL FERRITES

In the normal spinel ferrites all the 8 divalent ions (M^{2+}) occupy the tetrahedral sites and all the 16 trivalent ions (Fe^{3+}) occupy the octahedral sites. The normal spinels are nonmagnetic i.e. they do not show ferrimagnetic behaviour.

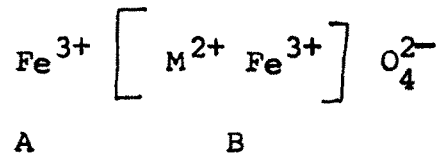
Zinc ferrite ($ZnFe_2O_4$) and Cadmium ferrite ($CdFe_2O_4$) are the ferrites with normal spinel structure. The cation distribution of $ZnFe_2O_4$ can thus be represented as,



1.2.1(B) INVERSE SPINEL FERRITES

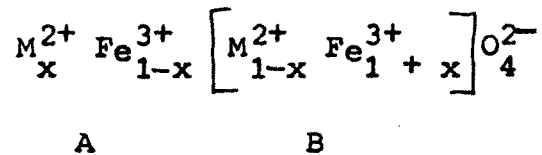
In the inverse spinel the tetrahedral sites are occupied by 8 trivalent ions instead of divalent ions and 8 divalent ions occupy the octahedral sites along with the remaining 8

trivalent ions. In general there is a tendency of large divalent metal ions (M^{2+}) to prefer octahedral positions. The inverse spinels are Ferrimagnetic. The cation distribution may be represented as,



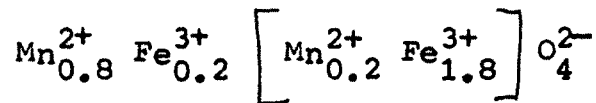
1.2.1(C) RANDOM SPINEL FERRITE

In the random spinel ferrites the divalent (M^{2+}) and trivalent (Fe^{3+}) ions are randomly distributed over tetrahedral and octahedral sites depending on the physico chemical conditions of preparation. In general, the cation distribution for these kinds of ferrites is of the form



The term (1-x) is called the coefficient of inversion.

Manganese ferrite (16) is an example of this type of ferrite.

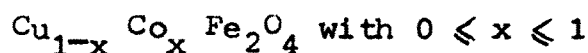


1.2.2 SUBSTITUTIONAL FERRITES

In the spinel structure, both the M^{2+} ions and Fe^{3+} ions can be replaced by other magnetic or nonmagnetic ions. The resulting

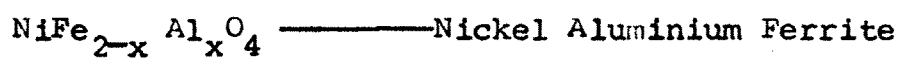
ferrites are called substitutional ferrites. The substitution is possible in two ways.

1. Partial replacement of divalent metal ion by other divalent metal ion (either magnetic or nonmagnetic). For example in copper ferrite (CuFe_2O_4) copper may be substituted partly or completely by cobalt as



It is termed as cobalt substituted copper ferrite or copper cobalt ferrite.

2. In this case the trivalent ions generally nonmagnetic in character e.g. Al Cr or Ga replace partially the trivalent Fe ions.



Thus the resulting substitutional ferrites are equivalent to a solid solution of the two pure end member ferrites.

1.3 PROPERTIES OF FERRITES

The properties of ferrites can be grouped into two categories.

- a) Intrinsic, (b) Structure sensitive.

Saturation magnetisation and Curie temperature are basically the intrinsic properties while permeability, hysteresis and other losses, resistivity and dielectric constant etc. are structure sensitive. The structural aspects like grain size, porosity, impurities and inclusions of non magnetic nature and their size distribution affect the structure sensitive properties (17).

1.3.1 THE D.C. CONDUCTIVITY IN SPINEL FERRITES

Ferrites are semiconducting oxide magnetic materials whose resistivity values lie in a wide range. The high conductivity of $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ has been attributed to the presence of both Fe^{2+} and Fe^{3+} ions (18) on the identical (octahedral) sites in the spinel structure. The electrons move from divalent iron ions to the trivalent iron ions within the octahedral positions. These transitions do not cause a change in the energy state of the crystal.

Verway, Haayman, Romeijn and Oosterhout (19) have shown that the conduction can be increased by mixing a small amount of foreign oxides in high resistivity oxides. In general, the substitution of a cation of low valence state gives rise to P type conduction while the substitution of a cation of high valence state gives rise to n type conduction.

The presence of Fe^{2+} is sometimes desirable (20) as it reduces magnetostriction while it is an hinderence in some cases as it renders the ferrite unsuitable for microwave applications (21).

1.3.2 ELECTRICAL SWITCHING AND MEMORY PHENOMENA

The recently reported electrical properties of ferrites are the switching and memory phenomena similar to amorphous semiconductors (22). Yamashiro(23) has studied CuFe_2O_4 and reported electrical switching and memory phenomena in samples quenched from 800°C and 600°C . Hisatake et al (24) studied lithium ferrites which also showed switching. Patil et al(25) have reported switching as well as memory phenomena in stoichiometric copper ferrite. They attribute electrical switching to Jahn Teller transformation of Cu^{2+} ions at B site of the spinel structure.

1.4 EFFECT OF OTHER FACTORS ON PHYSICAL PROPERTIES

The electrical and the magnetic properties of ferrites also depend on the thermochemical history of the ferrite, which in turn affects the cation distribution. The factors affecting the properties are the impurity, porosity, grain size, heat treatment, oxygen partial pressure etc. Besides any variation in the conditions of preparation like applications of external pressure or external magnetic field, quenching also affects the properties of ferrites.

The electrical properties of polycrystalline ferrites depend upon the conditions of heat treatment during the manufacturing process. This is firstly because the oxygen dissociation pressure increases rapidly (26) above 1200°C and secondly the factors like purity of starting materials, surface conditions, sintering temperature, porosity, grain size, impurities etc. also have a strong influence on the electrical properties. The temperature dependence of electrical resistivity of ferrites can be expressed as

$$\rho = \rho_0 \exp^{\Delta E/KT}$$

Where ΔE is the energy of activation and K is the Boltzman constant.

The surface energy of the particles gives the driving force for the sintering process so that a powder compact grows together and the pores in the compact are filled up with material. This leads to shrinkage of materials (27). The interface between crystallites, the grain boundaries, represents an amount of energy that is reduced by grain growth. The grain boundary energy decreases during the grain growth, as a result the boundaries move towards their centre of curvature. Thus during the sintering process, the change in grain size and the nature of the porosity, affect the electrical properties.

1.5 APPLICATIONS OF FERRITES

The existence of ferrites has been known for centuries (the lodestone, or ferrous ferrite), but little engineering application had been found until the post World War II era. Until that time virtually all magnetic devices used were metals.

Nowadays ferrites occupy an important place in industrial applications, due to their interesting properties such as high electrical resistivity, good magnetic permeability, switching property and almost negligible eddy current losses at high frequencies. The major applications of soft ferrites are high frequency transformer cores, antenna rods, deflection yokes on TV sets, chokes, recording heads etc. Magnetically 'hard' ferrites having high uniaxial anisotropy have equally important area of application in loudspeakers, television sets, telephones, generators etc.

Ferrites find interesting applications in magnetic recording. It is observed that high recording density is obtained when Mn-Zn ferrite head is used for perpendicular recording on Co-Cr thin films obtained by sputtering (27). Normally, magnetised ferrite plates are used for filtering of fast magneto elastic waves (28). In case of Li-Ti-Zn ferrite, the magnetic and dielectric losses are very low. These ferrites are assigned for devices operating at deci, centi,

and millimeter wave lengths (29) Manganese Zinc ferrites with the spinel structure are among the most widely used magnetic materials in electronics (30). Ferrites are found useful in investigation of a ferrimagnetic echo amplifier in the large signal mode (31). It is to be noted that ferrites are absorbers of electromagnetic waves against the conventional radar signals with small relative band width (32).

The large magnetostriction and lower permeability of ferrites can be obtained by the alternate selection and the control of variables in the preparation of ferrites. These are very useful in the accelerometers, mechanical filters, and ultrasonic generators. Ferrites can also be used for magnetically pulsed crystal monochromators on a pulsed neutron source. (32).

1.6 ORIENTATION OF THE PROBLEM

Ferrimagnetic oxides, the ferrites, have advanced to a position of technological prominence in the time period from the late 1940s to the present. These developments have filled demonstrated needs and led entirely to new applications.

Microstructure plays an important role in determining the properties of ferrites e.g. it affects the high power handling ability as well as low power loss in saturated microwave devices. Fine grained ferrites have somewhat low power loss, and are able to handle higher power levels before the onset of

nonlinearities. Ferrite devices such as radio and TV transformers, antennas, computer cores, and magnetic tapes, discs, drums, and recording heads all operate by virtue of the dynamics of the hysteresis loop (34). In most of these cases the motion of magnetic domain walls is important (35). Present knowledge permits a high degree of control of the saturation magnetization of ferrites and fair degree of control of its temperature dependence (36). In ferrites the cation distribution also gets affected by the heat treatment (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). Microwave properties, in particular dielectric and magnetic loss, are also sensitive to the method of fabrication(39).

The hot pressing technique offers a hope for obtaining 100% dense homogeneous ferrites (40). Incorporation of hot pressing may allow better use of the thermodynamic process to improve the orientation problem. Improvement have been made in reducing porosity, in particular, eliminating pores within the grains and also in controlling grain size (41). The decrease in porosity is also effective in reducing the eddy current losses(42) Such property control would lead to better materials for devices using saturated materials because of the resultant ability to control spin wave coupling. For the unsaturated

materials it would promote higher permeability at low frequency on the one hand and lower loss at higher frequencies.

From the above discussion it is clear that the role of microstructure in ferrite technology has been fully recognised. Therefore the modern research workers in the field of ferrites are interested in controlling the properties through microstructure control. Though the large amount of data is available on the processing and characterization of copper containing ferrites, very little seems to have been done on their microstructural aspects, inspite of the fact that their microstructure is an important factor governing their overall behaviour. In the present work it has been proposed to synthesize copper manganese ferrites and study the effect of the microstructure and composition on their properties. The orientation of the problem thus involves.

1. Preparation of copper manganese ferrite with the general formula $Cu_x Mn_{1-x} Fe_2 O_4$.
2. Characterization of the ferrites by XRD.
3. Measurement of Curie temperature and magnetization.
4. Electrical resistivity and I-V characteristics.
5. Study of microstructure by observation with scanning electron microscopy.

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