
CHAPTER-I

CHAPTER I

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1.1 HISTORICAL

Though the natural magnet lode-stone was known to man right from the ancient times, the actual interest in the preparation of artificial magnets developed after the phenomenon of magnetism was known. The synthetic ferrites developed later on are essentially mixed crystals of various magnetic oxides combined with divalent metal oxides. They have close packed structures with cations fitted into interstitial positions.

Forestier, in 1928, prepared ferrites by basic precipitation from chloride solutions and subsequent heat treatments (1). Several Japanese investigators took active part in ferrite preparation in the early thirties (2,3,4). The strong foundation for improved ferrites at high frequencies was laid by Snoek (5,6) by establishing the importance of an accurate oxygen content and of homogeneity. Since then number of investigators have developed new ferrites for the rapid growth of technical applications.

Verwey (7) 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 and normal spinel structures are non-magnetic. The theory of spin interaction in ferrites was first proposed by

Neel(8). He introduced the concept of magnetic sublattices. There are two sublattices for the ferrite crystal and there exists a coupling between the atoms in A sites and atoms in B sites. This interaction mechanism was however found to be inadequate and detailed study of basic interaction was made by Anderson and Van-Vleck by proposing a theory of super-exchange forces (9). Yafet and Kittle (10) extended the theory of magnetic sublattice by postulating a "triangular" arrangement of spins. Gorter and Guillaud (11) gave the experimental support to Neel's theory. Moreover, Guillaud established the existence of varying degree of inversion in Mn ferrites sintered at different temperatures. Bertaut(12) confirmed the same by extensive X - ray diffraction studies on Mg and Cu ferrites. Cation distribution assumed importance. Later, Smart (13) worked on microwave resonance and magnetization of ferrites, which helped to determine cation distribution. An important investigation on the co-relation of observed Curie point with magnetization and cation distribution was carried out by Gilleo(14). Koops (15) 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

All oxide spinels crystallize in the structure of a naturally occurring spinel, $M_0Al_2O_4$, except that the cations in the natural spinel are replaced by transition metal ions. The chemical formula of a ferrite is thus $M^{2+}Fe_2^{3+}O_4^{2-}$, where M is a divalent metal ion of the type Cu, Co, Zn, Mg, Mn, Cd etc.

The crystal structure of oxide spinels essentially consists of a basic framework of relatively large oxygen ions. Metal ions occupy the interstitial positions being smaller in size. The spinel ferrite unit cell consists of eight formula units of $M^{2+}Fe^{3+}O_4^{2-}$.

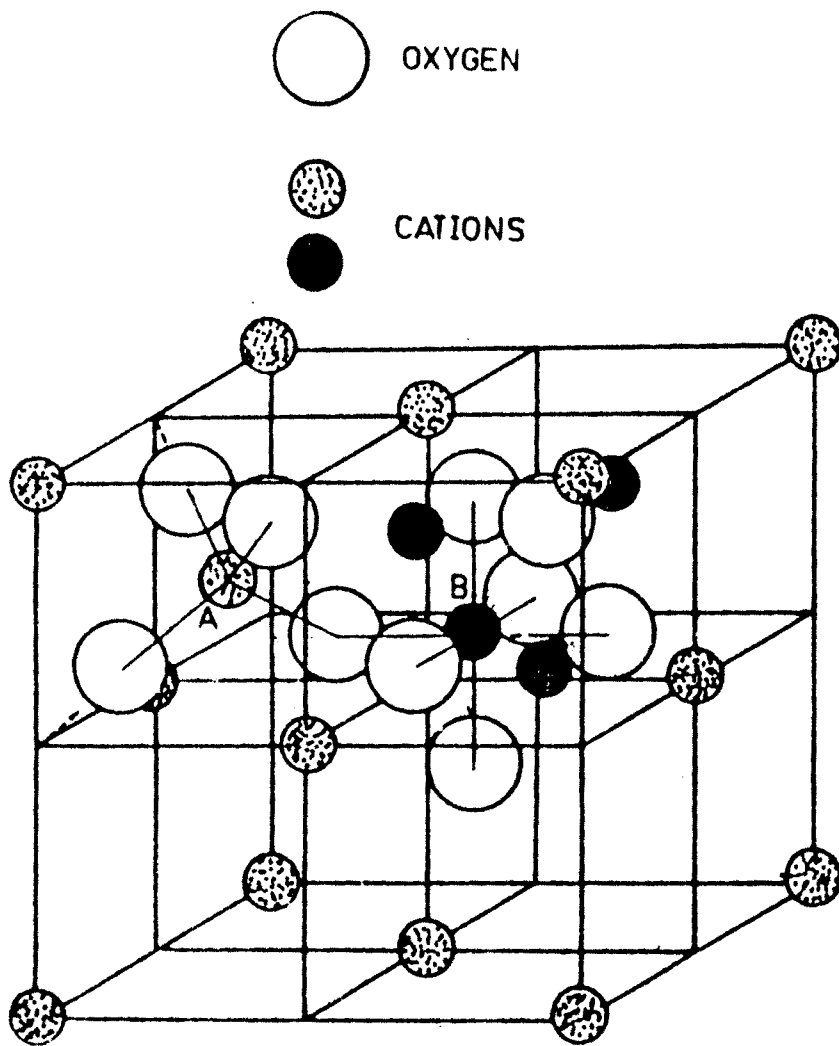
The structure of spinel ferrites was first determined by Bragg in 1915 (Fig 1.1). It is f.c.c. with space group $Fd3m-O_h^7$. The side of the unit cell is approximately $8A^\circ$. Since the unit cell consists of eight formula units of $M^{2+}Fe^{3+}_2O_4^{2-}$, the total unit cell formula becomes $M^{2+}_8Fe^{3+}_{16}O^{2-}_{32}$. The oxygen ions form a close packed cube with metal ions occupying the positions of four-fold and six-fold oxygen coordination. Thus the cations occupy distinctly different interstitial position. When the cation is surrounded by four oxygen ions it is said to occupy an A site and when it is surrounded by six oxygen ions it is said to occupy a B site. The maximum possible number of A and B site in a spinel structure is 64 and 32 respectively. Thus in an unit cell 8A sites and 16B sites are occupied only. The distribution of metal ions among A and B sites depends upon number of factors

including their site preference energies.

The co-ordinates of the ionic positions are as follows
- 8 positions of four fold oxygen co-ordination at 8a

[0,0,0,1/4,1/4,1/4] -----face centered

16 position of six fold oxygen co-ordination at 16d



THE SPINEL STRUCTURE (SCHEMATIC)

Fig. 1.1.

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-
|
| 5/8,5/8,5/8;5/8,7/8,7/8 |
|
| ---- face centered
| 7/8,5/8,7/8;7/8,7/8,5/8 |
|_

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32 positions at 32e

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-
| uuu,   uuū,   ūūū,   ūūū
| 1/4 - u, 1/4 - u, 1/4 - u, 1/4 - u, 1/4 + u, 1/4 + u | face
| 1/4 + u, 1/4 - u, 1/4 + u, 1/4 + u, 1/4 + u, 1/4 - u | centered
|_

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For oxygen parameter $u = 0.375$ oxygen ions form a perfect close packed cube. But generally u is greater than the ideal value. When oxygen parameter increases beyond the ideal value, oxygen ions move away from their nearest tetrahedral ion neighbour along (111) direction. Any deviation from close packing is manifested in the increase in size of 8 tetrahedral interstices and decrease in size of 16 octahedral interstices.

Every oxygen ion is surrounded by 3B cation and 1A cation in ferrites. The angles between them are
 i) A-O-A = $79^{\circ}38'$ ii) B-O-B = 90° and $125^{\circ}2'$ iii)
 A-O-B = 125° and $154^{\circ}34'$ (Fig.1.2). The conclusion is that A-B interaction is strong, while B-B is weak and A-A is weakest.

1.3 TYPES OF SPINEL FERRITES

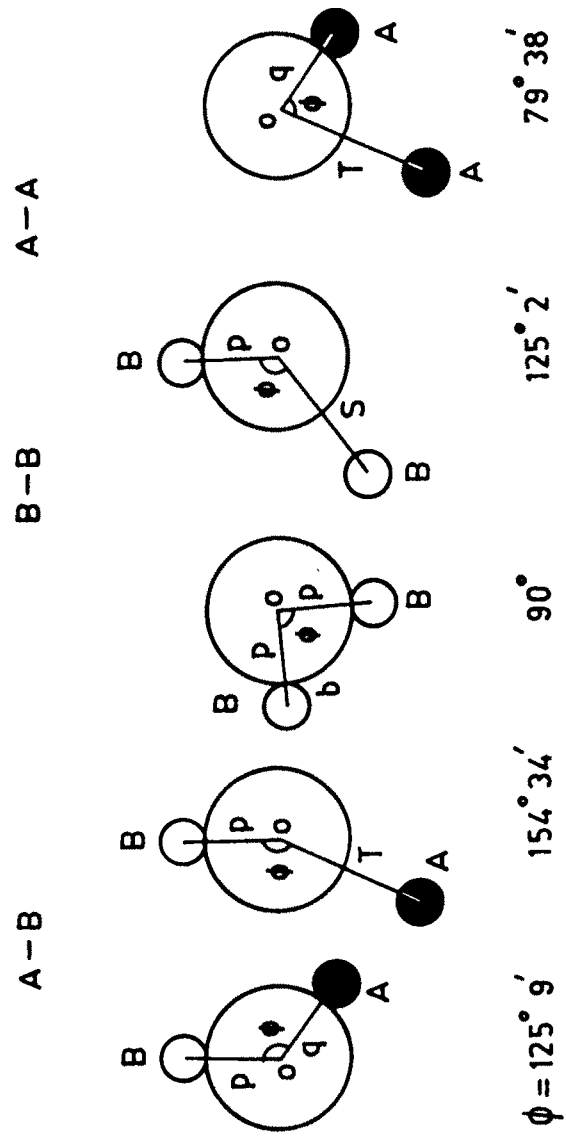
Barth and Posjank(16) have observed different types of cation distribution in ferrites and classified them accordingly.

1.3.a NORMAL SPINEL FERRITES

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



e.g. Zinc and Cadmium ferrites are having normal spinel structures.

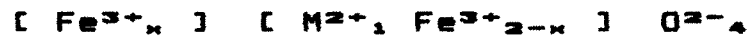


Angle between A-A, B-B & A-B cations in a spinel structure .

Fig.1.2

1.3.b INVERSE SPINEL FERRITES

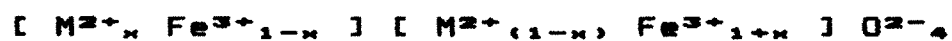
In inverse spinel ferrites B sites are occupied half by divalent metal ions and half by trivalent iron ions.



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

1.3.c RANDOM SPINEL FERRITES

In random ferrites M^{2+} and Fe^{3+} are randomly distributed over the A and B sites depending on the physico-chemical conditions of preparation. Such a kind of ferrite is partially inverse.



where x = coefficient of normalcy, $1-x$ = coefficient of inversion. Manganese ferrite is partially inverse ferrite with coefficient of normalcy 0.8.

1.4 SUBSTITUTIONAL FERRITES

In substitutional ferrites the divalent metal ions as well as trivalent iron ions are replaced by other magnetic or non magnetic ions. The substitution can be done either by replacing divalent ion by other divalent ion or by replacing trivalent iron ions with other trivalent ions.

In the present case magnesium in magnesium ferrite has been substituted partly by Zinc.

1.5 PROPERTIES OF FERRITES

The properties of ferrites can be classified in to two groups (I) Intrinsic and (II) Structure sensitive. The intrinsic properties are saturation magnetization and Curie temperature and structure sensitive properties are permeability, hysteresis and other losses, resistivity and dielectric constant etc. The grain size, porosity, impurities and inclusions affect the structure sensitive properties (17).

The low frequency permeabilities of manganese - zinc ferrites are higher, while the Nickel-Zinc ferrites have much higher resistivities. It is thus convenient to consider the Manganese-Zinc compositions as the high

permeability ferrites and the Nickel - Zinc compositions as low loss ferrites. The substitution of Zinc for manganese affects both the saturation magnetization and the anisotropy. Which has the greatest effect on the permeability. The relation between Zinc content and the saturation magnetization and anisotropy at different temperatures is complex. Since the anisotropy varies rapidly near the Curie point the permeability around the high temperature peak is generally unstable with respect to temperature.

The electric and magnetic properties of the ferrites are influenced by their thermochemical history. It affects cation distribution and stoichiometry of the ferrites (18). The other factors affecting the ferrite properties are the purity and activity of the constituent oxides. Besides, any variation in the procedure of the heat treatment also affects the properties of the ferrites. The marked effects of firing conditions on ferrite properties have been reported by Economos (18,19). The square loop properties of soft ferrites are found to be very much sensitive to the methods of preparation.

The porosity lowers the conductivity, saturation magnetization and the coercive force. The values of these parameters can be enhanced by preparing dense ferrites. Dense ferrites have been prepared by hot pressing technique (20,21,22).

Some ferrites exhibit Hall effect as well as Seebeck effect. Electrical switching is shown by some ferrites. The switching property is due to the distortion of crystal structure. The field quenching or water quenching also shows interesting results. For

example $MgFe_2O_4$ shows a change in M_s on quenching.

The dependence of resistivity of ferrites on temperature obeys the law

$$\rho = \rho_0 \exp [\Delta E/KT] \text{ ----- (1.1)}$$

where E is energy of activation, K is the Boltzmann constant and T is absolute temperature. The straight line graph of $\log \rho$ versus $1/T$ enables the determination of activation energy .

Infrared spectra of several ferrites have been reported by Waldron (23). He has assigned high frequency band to the tetrahedral group complexes and low frequency band to the octahedral complexes. Josyulu and Sobhanadri (24) 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

The ferrites cover a wide range of application. It is due to their typical magnetic and electrical properties. They are particularly used in microwave fields (25) and also in the electronic industry. Ferrites having high permeability over the range of 50

KHZ to 150KHZ are used in filter inductor for band pass filters in telephone circuits and also used for IF transformers in radio circuits.

One of the fastest growing and potentially vast application of ferrite cores is in the field of memory and switching circuits in digital computers (26). The application involves the use of microsecond pulses for transmitting, storing and reading information expressed in binary code.

The interesting application of ferrite is in the manufacture of microwave integrated circuits (27). In such devices discs of ferrites are introduced in the composite made up of ferrite and non-magnetic supporting matrix such as alumina. Another application is in pulse transformers used in some data handling circuits. Ferrites having square loop characteristics are more suitable for flip-flop changes in computers and memory devices. The large magnetostriction and lower permeability of ferrites is used in the accelerometers, mechanical filters and ultrasonic generators. Ferrites are used as the elements in microwave devices such as circulators, isolators, modulators, phase shifters, directional couples, filters etc.

Research workers in Fujitsu Laboratories have observed that high recording density is obtained when Mn-Zn ferrite head is used for perpendicular recording on Co-Cr thin film obtained by sputtering (28). Ferrites are useful in the investigation of a ferrimagnetic echoamplifier in the large signal mode(29). It is to be noted that ferrites are absorbers of electromagnetic waves against the conventional radar signals with small

relative band width (30).

Recently piezomagnetic nickel - manganese cobalt ferrites (31) have been developed for applications in ultrasonics and radio - frequency electronics.

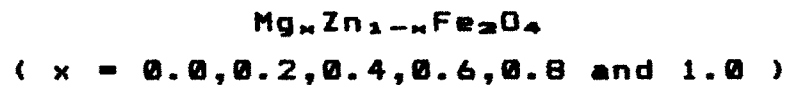
1.7 ORIENTATION OF THE PROBLEM

Ferrite magnetic materials have recently come into prominence because of their interesting physical properties and potential uses in the fields of electronics and computer technology. The recent development in the field of materials science have enabled us to tailor make their properties through their microstructure control. Since the properties of ferrites are very much sensitive to their methods of preparation a precise microstructure control is possible during their preparation stage. In order to find out such a relation between the microstructure and properties, magnesium - zinc ferrites have been studied in the present cases.

The spinel ferrites containing varying amount of zinc has been the subject matter of many recent researchers (32,33). The role of Zn^{2+} ions on the magnetic properties of Mg-Zn ferrites has been recently investigated by Kulkarni et al (33). The infrared absorption studies have been carried by Sobhanadri et al (24) for one such ferrite. The effect of sintering

temperature on the electrical and magnetic properties and microstructure in general have not been so far reported in case of these ferrites. In order to see the effect of changing microstructure on the properties like electrical conduction, magnetization and infrared absorption etc. the following systematic studies on Mg-Zn ferrites have been undertaken.

1. Preparation of Mg-Zn ferrites with the general formula



2. X-ray diffraction studies to calculate the lattice parameters, interplaner distances as well as to confirm the ferrite phase formation.

3. Measurements of electrical conductivity as a function of temperature to propose the conduction mechanism in these ferrites.

4. Magnetization studies to see the effect of both Zn^{2+} ions and sintering conditions.

5. Far-infrared absorption studies to obtain knowledge about internal vibrations and

6. SEM studies to characterize their ceramic microstructure.

In order to see the effect of two sintering durations, above studies have been carried out on two sets of samples sintered at 1100°C for 15 hr. and 30 hr. respectively.

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