CHAPTER I

INTRODUCTION

1.1.a Introduction

Ferrites continue to attract the attention of researth workers because of their applications as electronic and magnatiç ceramics. The technological importance of the ferrites can be gauged from the spectrum of applications mentioned briefly here in the last section.

The ferrites exihibit properties that sensitivity depend on the chemical and thermo-physical history which allows the tailor making of ferrites suitable for various applications. This in itself needs further exploration to be used effectively. Towards the comprehensive understanding of ferrites the interrelationship of properties with crystal structure, cation distribution, magnetic interactions and perparation condition is needed. This being a sort of challenging task, one has to restrict to a limited field of study with a some what modest aim.

1.1.b Historical

The first known magnetic material was made available by nature itself in the form of magnetite which is nothing but ferrous ferrite. There arose a need for the magnetic materials to reduce eddy current losses, which was met by preparing synthetic ferrites. Hilpert[1] synthesized the ferrite first. After some years when the utility of ferrites was proved beyond doubt, the studies on ferrites from the point of view of electrical and magnetic properties and chemical and crystallographic characteristics gathered impetus. In thirties Keto and Takai[2], Forestier[3], Barth and Posjnak[4] have studied ferrites from various points of view. The structure of the ferrite was established to be of spinel type.

The later decade Snoek[5,6] carried out an extensive research on preparation of ferrites and their magnetic properties. This led to various applications of ferrites. Verwey[7] established that the electronic conductivity of ferrite is mainly due to the exchange of electron between divalent and trivalent ions of iron in the ferrites. His study on crystal structure[8] of various ferrites showed ferrites with inverted spinel structure to be ferrimagnetic whereas those with normal structure to be nonmagnetic.

The basic theory of spin-spin interaction in ferrites was announced by Neel[9]. He introduced the concept of magnetic sublattices; appling the same molecular field theory of exchange interaction in ferromagnetic materials except the possibility of spin alignment in the antiparallel sense. A more detailed examination of basic interaction was made by Anderson[10] and Vanvleck[11] who developed the theory of super exchange. Yafet and Kittle[12] extended the theory of magnetic sublattices by postulating a "triangular" arrangement of three sublattices when the antiferromagnetic exchange interactions between sublattices is comparable to that among spin moments within sublattices formed by Fe^{3+} ions on tetrahedral and octahedral sites.

Gorter[13] and Gulliand[14] gave the direct experimental proof of Neel's theory. Gorter measured the magnetization of Mn, Fe, Co, Ni, Cu and Mg ferrites mixed with Zn ferrites as a function of Zn composition. Guilland et al explained the variation of magnetization of a function of temperature for mixed ferrites with varying composition and temperature in ferrimagnetic region. Neel modified the earlier theoritical treatment which could not account for the temperature dependence of Weiss molecular interaction constant as per the experiments[15]. The modified theory was confirmed positively by experimental results[16]. The direct proof of Neel's model of ferrimagnetism came up only with nentron diffraltion studies on magnetite[17] and Zinc ferrite[18].

X-ray diffraction studies on copper ferrite and magnesium ferrite indicated their structure to be inverse spinel. However, Guilland[19] found different values of magnetization for magnesium ferrite samples prepared at different temperatures rather unexpectedly, when he concluded that the specimens were with varying degree of inversion. This was supported by Bertaut's[19] detailed X-ray diffraction studies on Mg-ferrite and cu-ferrite. Thus cation distribution in ferrites assumed importance. Other research workers especially Smart[20] and Gorter[21] also correlated independently the cation distribution found out by microwave resonance and magnetization. Recently the work on ferrites has assumed large proportions during the last two decades and it has proceeded on all the fronts starting from better control of structural parameters as in single crystals and epitaxial films to the use of almost all techniques together lot of information on ferrites towards understanding of ferrites.

1.2 Crystal Structure

The magnetic oxides exhibit the following structures in general

(a) Spinel structure
(b) Garnet structure
(c) Hexagonal structure
(d) Perovskite structure

1.2 (a) Spinel Structure

The general chemical formula for the ferrospinel is M Fe_2O_4, where M is a divalent metal ion and Fe is trivalent ion. All the compounds of this type have a cubic, face centred crystal structure (Fig. 1.1) of the space group $O_h^7 - F_3$ dm with a unit cell containing 8 formula units. In this structure two types of interstitial positions occur with respect to oxygen lattice and these positions are occupied by metal ions. There are 96 interstitial sites per unit cell in all, 64 being tetrahedral and 32 octanedral, out of these

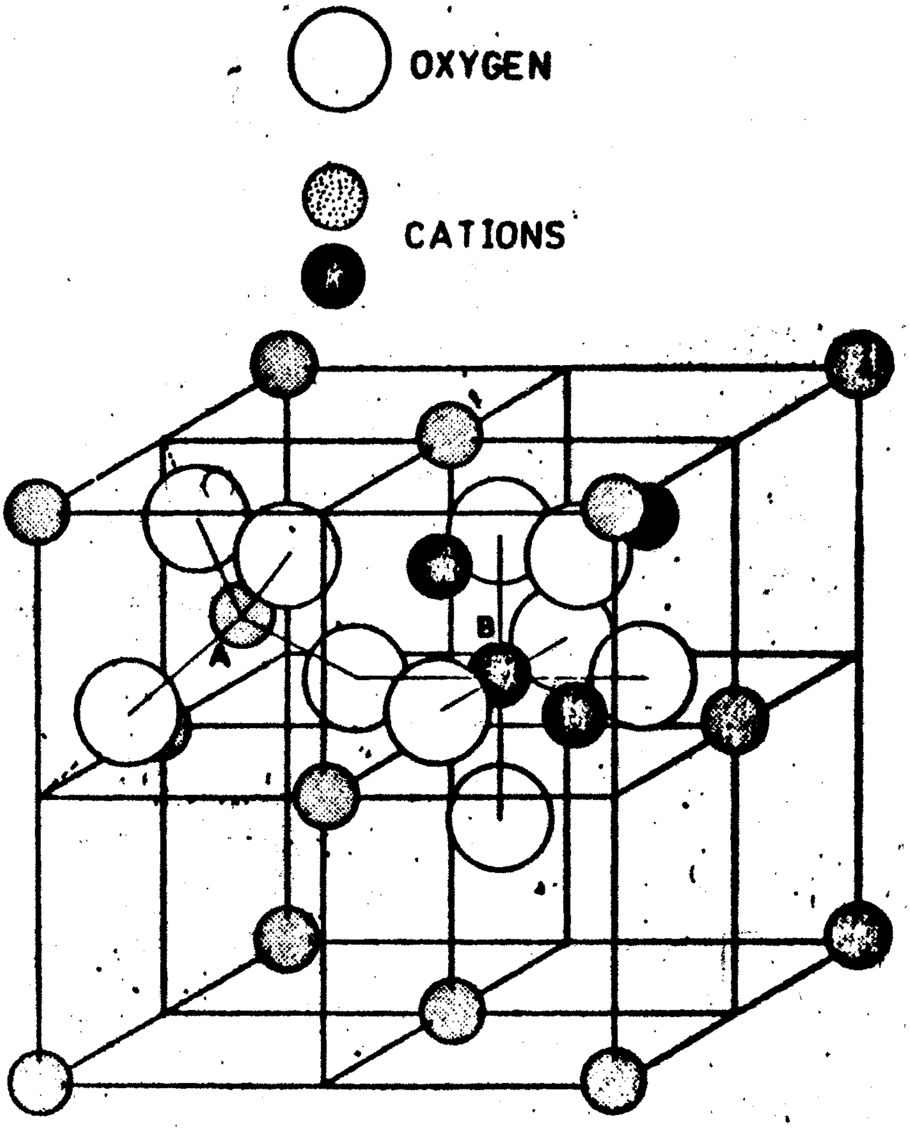

Fig-1·1 – The spinel structure.

8 tetrahedral and 16 octahedral sites are occupied by cations. Tetrahedral sites are usually called A sites and are surrounded by 4 oxygen ions and octahedral sites are called B sites which are surrounded by 6 oxygen ions. When all the 8 divalent ions occupy the tetrahedral sites and all the 16 trivalent ions occupy the octahedral sites then the structure called "normal" spinel. If the tetrahedral sites are occupied by 8 trivalent ions instead of by divalent ions and 8 divalentions occupy the octahedral sites along with the remaining 8 trivalent ions then the structure is called "inverse" spinel.

1.2 (b) Garnet Structure

The natural garnet is grasslarite $Ca_3Al_2(SiO_4)_3$. the most widely studied garnet so far is the Yittrium Iron garnet having chemical formula 5 Fe_2O_3. 3 Y_2O_3. Garnet structure was fully explained by Bertant and Farrat[32] and Geller and Gilleo[23].

The garnet structure is cubic and has space group oh^{10} - Ia 3d. The structure has three types of cation sites designed as a,c,d.The metal ion positions 16a have octahedral,24C have dodecohedral and 24d have tetrahedral oxygen surroundings. The large Y ions are located in dodecohedral sites and small Fe ions are located in tetrahedral and octahedral sites. Each oxygen ion has two Y^{3+} ions, are Fe^{3+} ion from

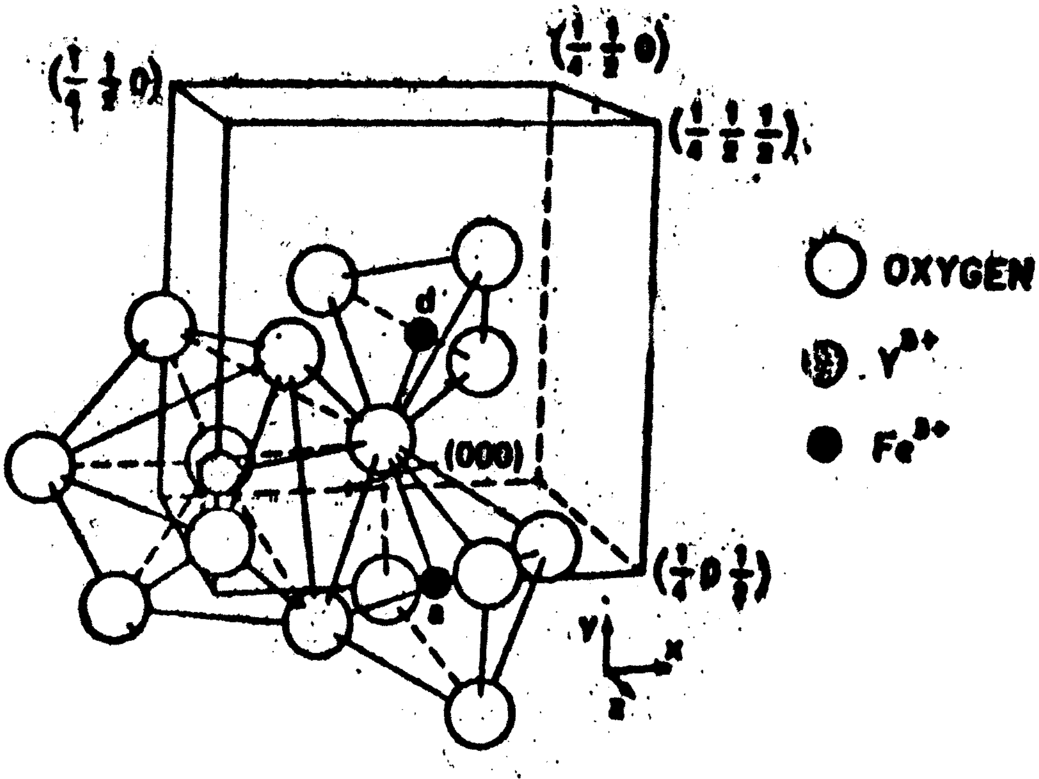

Fig 1·2 : The garnet structure.

'a' sites and one Fe^{3+} ion from 'a' site as nearest neighbours. In Fig. (1·2) the garnet structure is shown with respect of the feature in connection with the interpre--tation of the saturation magnetization data. The Y ion in YIG formula can be replaced wholly or in part by trivalent rare earth ions substitutionally. This changes the magnetic properties. The Fe ion may be replaced by other trivalent ions which may prefer one of the two a,d sublattices depending on size and other unknown considerations e.g. Al and Ga prefer tetrahedral sites whereas In and Sc prefer octahedral sites.

1.2.c Hexagonal Structure

The hexazonal structure has chemical formula $M\,Fe_{12}O_{19}$ where M can be Ba,Sr,Ca and Fe may be substituted by Al or Ga. The magneto plubite compounds also have the Hexagonal structure and other chemical formula is $X\,BaO : Y\,Fe_2O_3 : Z\,M^{+2}O$ where M is transition metal. They are generally known as permanent magnetic materials. This type of compounds were extensively studied by Jonker et al[24] and are discussed in detail in the second chapter.

The crystal structure (Fig.1.3) consists of closely packed oxygen ions; built up of layers of cubic and hexagonal stacking alternatly. The structure consists of cubic blocks which have their triad axis (111) parallel to the C-axis coupled by hexagonal blocks containing oxygen barium layers and iron with unique fivefold co-ordination. The Fe ion

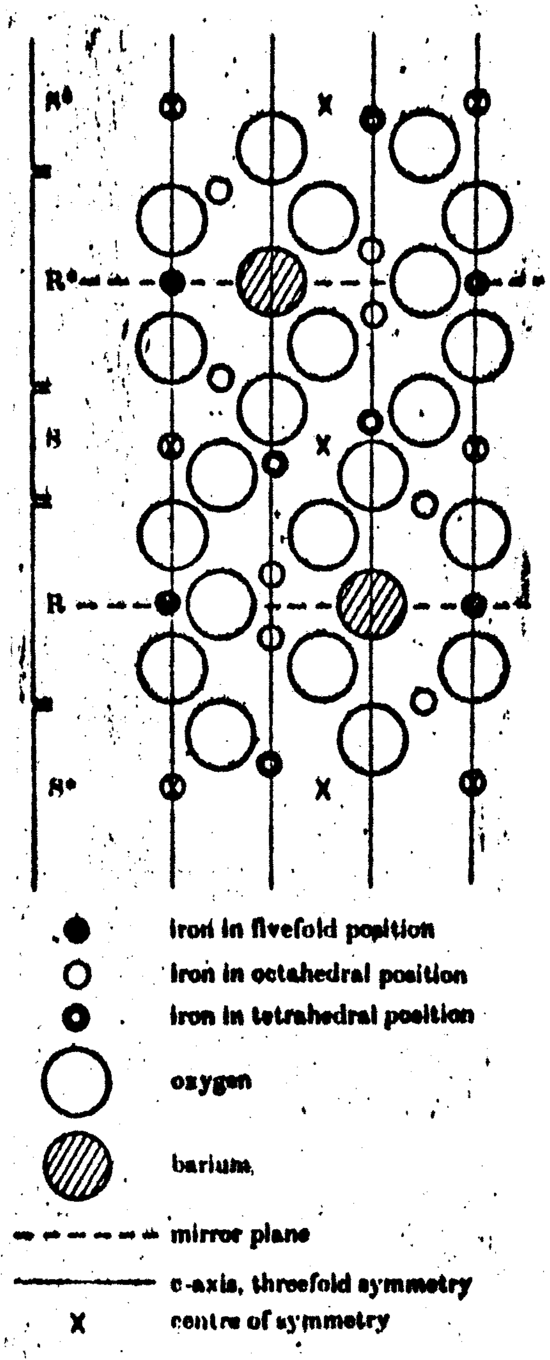

Fig 1·3-: Hexagonal strucure.

may be located in three different interstics octahedral and tetrahedral and sites surrounded by five oxygen atoms forming a single bipyramidal site with triangular base is barium oxygen layer. In this hexagonal structure only one metallic ion is available for two adjucent tetrahedral sites which occupied intermediate position along C-axis.

1.2.d Perovskite Structure

The perovskite structure has chemical formula Ln FeO_3 where Ln may be Y,Ce,Pr,Nd etc. The structure (Fig. 1.4) is orthorombic with space group D_{2h}^{16} - pbnm. The unit cell contains four group of Ln FeO_3. In this, oxygen ions constitute centred cubic blocks with two types of sublattices; one is dodecohedral i.e. rare earth ion is surrounded by 12 oxygen ions and second one is octahedral, i.e. Fe ion is surrounded by 6 oxygen ions. This type of materials have been studied by Geller[25] and Traves[26].

1.3. Electrical behaviour of Ferrites.

1.3.1. The D.C.Condultivity

Ferrites show semiconductor propertins with room temperature resistivity varying from 5×10^{-3} Ωcm in the case of Fe_3O_4 to 10^{11} Ω cm in certain magnesium and Nickel Ferrites. During the course of preperation of polycrystalline are ferrites oxygen dissociation sets up above 1200°C,[27]

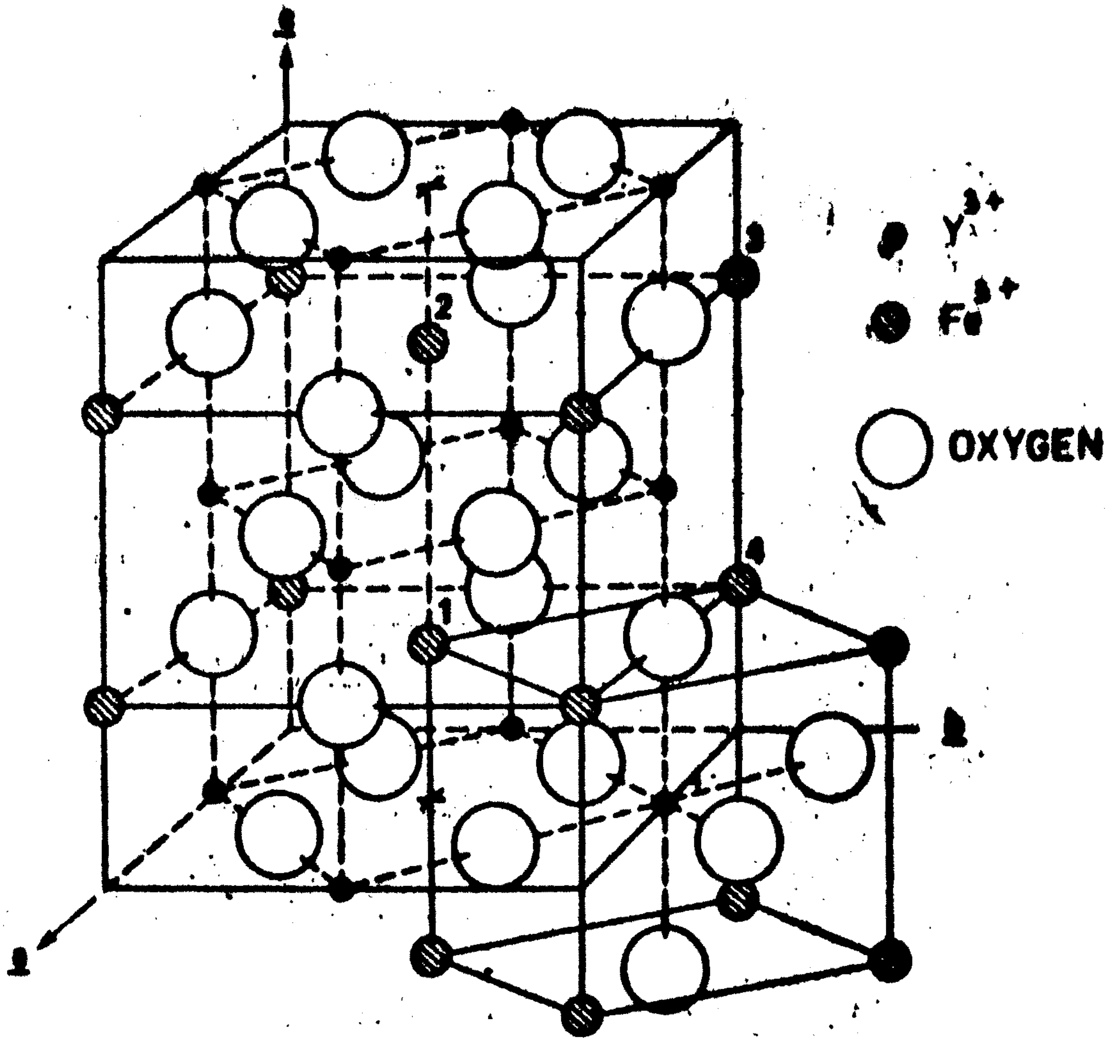

Fig 1·4: Perovskite structure.

giving rise to Fe^{2+} ions if ions having large affinities for oxygen are not present. The Fe^{2+} ions are responsible for the electronic conduction. As the amount of Fe^{2+} ion in a ferrite is sensitively dependent on heat treatment, the electrical conductivity of ferrite is influenced by heat treatment and also the accompanying factors like impunities, prosity and rate of cooling etc. Thus the electronic conduction in ferrites has to be associated as reported by Verwey and de Boer with the presence of a given element in more than one volance state in general[28]. These ions having two valance states get distributed randomly over the - crystallographically equivalent sites. Thus the high conductivity of Fe_3O_4 has been attributed to the presence of both Fe_3O_4 and Fe^{3+} ions[29] on the identical (octahedral) sites. The electrons move from divalent iron ions to the trivalent iron ions within the octahedral positions and the transitions do not cause a change in the energy state of the crystal.

Verwey, Haayman and Romeijn and Van Oosterbout[30] have shown that the conductivity of high resistivity oxides can be increased by addition of small amounts of foreign oxides to the structure whose metal ions have valancies different from that of lost cation. In general, the substitution of a cation of low valance state gives rise to P-type of conduction while the substitution of a cation of high valance state gives rise to n-type of conduction.

The presence of Fe^{2+} is some times desirable[31] as it reduces magnetostriction while it is an hindrance in some cases as it renders the ferrite unsuitable for microwave applications.[32]

1.3.2 Dielectric Dispersion

Ferrites show abnormally high dielectric constants and dispersion of dielectric constant and resistivity in the frequency range from few H_Z upto few MH_z. Investigation of dielectric constant and resistivity have been carried out by Koops[33] on Nickel Zinc ferrite, by Molten on copper zinc ferrite and by Kamiyoshi[34] on Nickel ferrite and cobalt ferrite.

The dispersion in dielectric constants and resistivities have been interpreted by Koops and Moltgen as due to inhomogenous dielectric structure suggested by Maxwell[35] and Wagner[36]. These studies have revealed that the dispersion of dielectric constant in ferrites is unlike that expected for homogenous dielectrics. The origin of the inhormogeneities may be qualitatively understood in terms of the picking up of the oxygen by the ferrite grains from atmosphere while cooling[37]. This results in an insulating layer on the grains while within the grains small amounts of Fe^{2+} ions continue to be present rendering the inner regions as conducting grains.

1.3.3 Electrical Switching and Memory Phenominon

Arousal of further interest in the electrical properties of ferrites results from the recently reported studies on electrical switching and memory phenomenon in ferrites. Yamashiro[38] has studied $CuFe_2O_4$ and reported electrical switching and memory phenomenon in samples quenched from 800°C and 600°C. Histaketal[39] studied lithium ferrite which also showed switching.

1.4 Role of other Factors

The electrical and the magnetic properties of ferrites are influenced by the thermochemical history of the ferrite which affects the cation distribution. The factors that go hand in hand within affecting the properties are, the purity and the activity of the constituent oxides, porosity, grain size, heat treatment, oxygen partial pressure in the environment etc. Besides any variation in the conditions of preparation like applications of external pressure or external magnetic field, quenching also affect the properties of the ferrites.

The effects of firing conditions on the properties of ferrites have been reported by Economos.[41,42] For example squreloop properties of soft ferrites vary with the method of preparation. The require stringent conditions of purity of oxides, homogeneity and controlled, fabrication, firing conditions and the firing atmosphere.

The porosity lowers the conductivity, the saturation magnetization and affects Hc, the coercive force. The values of these parameters can be improved by preparing dense ferrites. Dense ferrites have been prepared by hot pressing[43-45] and also have been manufactured by continuous hot pressing with marked improvement in properties. The relevent control factors during hot pressing are heating temperature, applied pressure, atmosphere, soating time, pressing configuration and particle size. It is also well-known that some non magnetic additives affect micro-structure of ferrite so as to improve the magnetic characteristics.

Electrical switching is shown by some ferrites. If they are quenched from elevated temperatures.[38] The field quenching or water quenching also shows interesting results,for example $MgFe_2O_4$ shows a change in Ms on quenching.

Some ferrites undergo shifts in permeability after a-c magnetisation at high flux levels, or after the materials are heated just through the Curie temperature and cooled again to room temperature. Other ferrites, perticularly extruded rods, have been found to be sensitive to vibrations. This effect may be enhanced after the material has been subjected to a strong ac or dc magnetic field.[46]

1.5 Applications of Ferrites

Ferrites are some of the most important electronic ceramics. Magnetically soft ferrites, having both the permeability and saturation magnetization lower than the metals are widely used in places where the possibility of using metallic care is ruled out due to eddy current losses. In ferrites the high frequency losses are very small. The major applications of soft ferrites are as high frequency transformer, ceres, antenna rods, induction tuners, deflection yokes on TV sets, chokes, recording heads etc.

Rectangular hysteresis loop properties of ferrites are required for their applications in computer memory devices and the flip-flops. The degree of rectangularity and uniformity and stability of characteristics have a direct bearing upon the number of cares which can be used reliably in a memory and hence upon the storage capacity of the memory. The values of the coercive force determine how rapidly the information can be handled. Cores of Mg-Mn ferrite have been produced with a good degree of rectangularity and the expected uniformity is achieved through control of composition and processing.

The alternate selection and control of variables used in the manufacture of ferrites leads to somewhat lowering of permeability but enhance magnetostriction. This is important consideration while using ferrites in accelerometers,mechanical filters and ultrasonic generators.

Ferrites are finding numerous applications in the microwave field due to their unique gyromagnetic resonance properties. The applications in this area include phase shifters, circulators and modulators. The MQ product of ferrites is high over the frequency range from 50 KHz. upto 150 KHz which renders the suitable for filter inductors for band pass fillers in carrier telephone circuits,precise control over inductance and good stability are necessary for the function of the seperating channels. There requirements are met by the conventional coils normally of the pot type construction. The high μQ product also makes the ferrites useful for IF transformers in radio circuits and slug tuned inductors. Because of their high resistivity they can be used as pale pieres for concentrating flux in h - f induction heaters.

Ferrites also occupy and important place in the manufacture of miniature components like inductors and transformers. The power consideration of there circuits are low and ask for the use of ferrites materials. The temperature rise in the transistor circuits is usually low so that use of high permeability materials having low curie temperatures is allowed at this low power.

Magnetically hard ferrites having high uniaxial anisotropy have equally important areas of application, as in loudspeakers, television, telephone generators and also to list a few.

1.6 Orientation of the work

Hexagonal ferrites having the natural magnetoplumbite structure are suitable as permanent magnet materials because of their high uniaxial anisotropy. The barium ferrite and other related ferrites having this structure are extensively used for this purpose. The major applications lie in loud--speakers, motors, generators, sticking devices etc. The high resistivity and the low eddy current losses make the ferrites superior over conventional metal magnets and useful at microwave frequencies.

The properties of the ferrites mainly depend upon their chemical composition, the heat treatment given to them during manufacture and the microstructure under arrest. Therefore, the precise control of properties of ferrites, needs attention to be given towards these physico-chemical factors. The earlier research on the hexagonal ferrites, was used mainly to the development good quality permanent materials through the control of microstructure and comparatively less attention was paid towards their understanding.

The major portion of the research work on hexagonal ferrites is carried out either on the single crystals or the oriented polycrystalline ferrites. Polycrystalline hexagonal ferrites with randomly oriented grains have been rarely studied. In the present work these ferrites have been studied with the following broad orientation.

1. Preparation of hexagonal ferrites with different structures by suitably replacing the conventional metal ions.
2. Detection of the structure by using X-ray diffraction
3. Measurement of D.C. electrical resistivity as a function of temperature.
4. Curie temperature determination from the resistivity studies.

REFERENCES

1. Hilpert S. ; Ber Deut Chem Ges 42 2248 (1909)
2. Kato Y. Takei T. : Trans Am. Electrochem SoC 57 297 (1930)
3. Foresteier H; Vetter M : Compt. rend 209 164 (1939)
4. Barth T.F.W. Posnjak E.; Z. Krist 82 325 (1932)
5. Snock J.L. Physica 3 463 (1936)
6. Snock J.L. "New Development in ferromagnetic material" 2nd Ed. Elsevier Press Inc. New Yark (1949)
7. Verwey E.J.W., F.C. Romeijn and E.L. Heilman,J.Chem.Phys. 15 174, 181 (1947)
8. Verwey E.J.W., F.de Boer, J.H.Van Santen; Jehem Phys. 16 1091 (1948)
9. Neel L. ; Proc. Phys. Soc (London) A 65 869 (1952)
10. Anderson P.W.; Phys. Rev 79 350 (1950)
11. Van Vleck J.H.; Phys. Rev. 78 266 (1950)
12. Yafet Y., Kittle C.; Phys. Rev. 87 290 (1952)
13. Gorter E.W.; phillips Res. Repts. 9 295 (1954)
14. Guilland C.; J. phys. Radium 12 239 (1951)
15. Fallot M., Maroni P.; J. phys. Radium 12 256 (1951)
16. Pauthenet R., Bochirol L.; J. phys. Radium 12 249 (1951)
17. Shull C.G., W.A.Strauser; phys. Rev. 81 483 (1951)
18. Hastings J.M., Corliss L.M.: Rev. Mod. phys 25 114 (1953)
19. Bertaut F.; J. phys. Radium 12 252 (1951)
20. Somart J.S.: phys. Rev. 94 847 (1954)
21. Gorter F.W.; Nature 173 123 (1954)

22. Bertaut F., Forrat F.; Comp Rend Acad Sci. Paris 243 282 (1956)

23. Geller S.; Gilleo M.A.,; Acta Cryst 10 239 (1957)

24. Jonker G.H.; Wi jn HPJ, Braun P.B.: philips Tech. Rev. 18 145 (1956)

25. Geller S; Acta cryst 11 565 (1958)

26. Traves D.; J.Appl. Phys 36 1033 (1965)

27. Hestetter, J.C. and Robberts, H.S. "Notes on dissociation of ferric oxide dissolved in glass and its relation to colour of iron bearing glasses". Jr. Ame Ceram SoC, Vol. 4 (1921) P. 927

28. Verwey, E.J.W. and de Boer, J.H.; Vol. 55,(1936) P. 531.

29. Verwey, E.J.W. and Haayman P.W.; physica Vol. 18 (1941)P.979

30. VerWey, E.J.W., Huyman, P.W., Romeijn, F.C. and Van Oosterbout, G.W.; phil Res. Reports Vol. 5 (1950) P. 173.

31. J.L. Snoek; Elsevier, Amsterdam (1949)

32. Pown, J.H.: Bell System tech Jr., Vol. 68 (1949) P. 1047

33. Koops, C.G.,; phys Rev. Vol. 82, (1951) P. 121

34. Karniyoshi, K; Sci. Repts Res Inst Tohku Univ Vol. A 3(1951) P. 716.

35. Maxwell, J.C.; "Electricity and Magnetism", London Oxford Univ. Press Vol.

36. Wanger, K.W., Ann. dev physik, Vol. 40 (1913) P. 317; Archiv fur Elektrotechnik Vol. 2 (1914) P. 371.

37. Blechscmidt, E, Vol. 39 (1938) P. 212

38. T.Yamashiro; Jap. Jr. Appl. Phys. 12 (1973) P. 148

39. Histake *et al*; Jap Jr. Appl. phys 12 (1973) P.1116

40. A Bergstein, L. Cervinka; Czech Jr. phys. B 11 (1961) P. 584.

41. Economos, G.J.,Bull Am Ceram SoL 38 (1955) P. 335

42. Y. Suemune; Jap Jr. Appl. phys. Vol. 10, No. 4 (1974)

43. P. Coeure; F. Forrat, and J.C. Gray; IEEE Trans. MAG-5 (1969) 698.

44. G.H.Haertling; J. Amer Ceram SoC. 49 (1966) 113.

45. G.J. Oudemans; phil Tech. Rev. 29 (1966) 45.

46. Proceedings of the IRE, Vol. 44, No. 10 (1956).