

Chapter-V

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SUMMARY AND CONCLUSIONS

Ferrites are magnetic oxides containing iron as a major metallic component. Magnetic performance of ferrites leads to their classification as soft, hard, square loop and microwave ferrites. The applications of ferrites in telecommunication and other microwave devices are widely known and a number of review articles, technical reports and proceedings of international conference are available.^{1,2} The properties of ferrites for technical application depend on the combination of intrinsic properties and the microstructure of ferrites. Commercially important ferrites require high purity materials, chemical homogeneity, fine grain size and high density. High density with minimum uniform grain size is desired for low loss ferrites.

Most widely used ferrites are Ni-Zn, Mg-Zn, Mn-Zn. Recently to increase the resistivity of the materials the substitution like Ti, Zr, Sn in these ferrites were under taken as many workers.³ The studies of Ni-Cd ferrites by other workers indicate that their magnetic properties are comparable to those of Ni-Zn ferrites, whereas these have low resistivity resulting in the higher losses. It is also observed that the addition of CoO and V_2O_5 changes the magnetic properties of Mn-Zn and Ni-Zn ferrites.⁴ These additives act as a flux on sintering. The electrical and magnetic properties of Sn substituted Ni-Cd ferrites were studied by Puri et al.⁵ They have observed that the addition of Sn, increases resistivity where as decreases the

saturation magnetisation. Therefore, in order to unravel the role of magnetic ion substitution such as Mn^{4+} on the cation distribution and other physical properties, on Cd-Ni ferrites. The following studies on $Cd_{0.3}Ni_{0.7+t}Mn_tFe_{2-2t}O_4$ ferrites have been undertaken.

1. Preparation of the series with the formula $Cd_{0.3}Ni_{0.7+t}Mn_tFe_{2-2t}O_4$ where $t = 0$ to 0.4 by ceramic method
2. X-ray diffraction studies : Confirmation of single phase formation and spinel structure. Calculation of lattice constant and bond lengths.
3. Microstructure : Study of microstructure; by using S.E.M. technique; to observe the developed microstructure, grain size, grain growth etc.
4. Magnetisation and Permeability : To understand the magnetic behaviour of the substituted element, cation distribution and Curie temperature.
5. D.C. and A.C. conductivity : To understand the conduction phenomenon.

In chapter I the brief review of the ferrite properties such as magnetisation anisotropy, conductivity, dielectric constant and structure of ferrite is given. The Neel's theory for ferrites is also discussed. The orientation of the problem is given at the end of this chapter.

In chapter II, Part A is devoted to the method of preparation and part B deals with the X-ray diffraction and scanning electron microscopy studies. In Part A, method of preparation of ferrites are reviewed and microstructure development during the sintering process

is discussed. The possibility of obtaining high density ferrites by hot pressing technique is also discussed. The procedural details of ceramic method followed in this work have been included in this section. The oxides were mixed thoroughly and presintered at 700°C for 7 hours in air atmosphere. Pellets were prepared by applying 6 to 7 ton pressure and sintered at 950°C for 20 hours. They were then furnace cooled. The rate of cooling of the furnace was 100°C per hour. The toroids were prepared with special die and the same sintering procedure was followed.

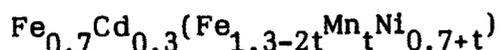
In part B of chapter II the details of experimental techniques, indexing of powder patterns are presented. From X-ray diffraction analysis it is observed that all the samples form complete solid solution and no extra phases have been observed. They show pure cubic spinel structure. No definite trend is observed due to compositional variations of Mn on lattice parameter. However, the undoped sample shows maximum lattice constant than the doped samples. In our system Mn^{4+} ions are substituted by an amount t , the Fe^{3+} ion concentration decreases by $2-2t$ while the Ni ion concentration increases by $0.7 + t$. Since the ionic volume of Ni is greater than that of Fe^{3+} , the lattice parameter is expected to be found to increase. The change in the lattice parameter can be explained on the basis of charge on A-site and modelung constant, where it is proportional to $(b/M)^{1/9}$ of the system.⁶ Since Mn has multivalence state and addition of Mn does not change the lattice parameter may cause such variations in the present system.

In the same section B, the scanning electron micrographs of the samples are presented. The grain size of the sample is calculated by intercept method. The important features of the micrographs are:

1. The sample Cd₁ reveals large size grains. The sample Cd₁ which is undoped, having higher permeability and higher porosity.
2. for the samples Cd₂ and Cd₃ the grain size decreases where as Cd₄, Cd₅ and Cd₆ the grain size increases. The samples Cd₂, Cd₃ and Cd₄ show fine grain structure with less porosity.
3. The Cd₅ and Cd₆ samples show more porosity. The segregation of impurity phases have not been observed clearly in all the samples. In the present system the normal grain growth is observed except for undoped samples. The properties such as permeability and losses are dependent on the microstructural conditions, grain size and porosity. The observed grain size and increase of porosity is related with the permeability values of the present ferrite system.

Magnetisation and permeability measurements are reported in chapter III. The properties like hysteresis, losses and permeability are discussed briefly. The experimental procedure and mathematical relations are also given. Magnetisation measurements are carried out at room temperature. It is seen that except for $t = 0.1$ the values of n_B decreases almost linearly on addition of Mn⁴⁺ in the system. In the sample corresponding to $t = 0.1$, there is sudden increase in

the value of n_B . For our system the cation distribution is of the form



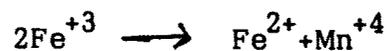
$\text{Fe}_{0.7}\text{Cd}_{0.3}(\text{Fe}_{1.3-2t}\text{Mn}_t\text{Ni}_{0.7+t})$ Addition of Mn^{4+} in the system reduces Fe^{3+} ion concentration. Whatever amount Mn^{4+} and Ni^{3+} ions are added to the system, they occupy B sites has an effect to force the Fe^{3+} ions from B to A site. Thus addition of Mn ions reduces A-B interaction and hence n_B . The sudden increase of n_B for the case $t = 0.1$, may be due to superparamagnetic behaviour of Fe^{3+} ions in the system. Similar results are observed for Ti doped Li ferrite by Mossbauer study⁷ and Ti in Mg ferrites.⁸

In Curie temperature measurement it is seen that Curie temperature decreases on addition of Mn. There is close agreement between the experimentally measured Curie temperature and that obtained from resistivity and permeability measurements. The fact that Curie temperature decreases linearly on addition of Mn^{4+} suggests that the total number of A.B interactions and its energy reduces in the system. In our system triangular spin arrangement may not be favourable. The Curie temperature is roughly proportional to the product of concentration of Fe^{3+} ions on A site and B site. Accordingly Curie Temperature T_c varies with X and t as,

$$(1-x)(1+x-2t) = (1-x^2) - 2t(1-x).$$

permeability measurements are carried out on toroid samples with temperature. It is seen that room temperature permeability decreases with increase of Mn^{4+} content. For the sample with $t=0$, the μ_i , slowly

increases up to the temperature 500⁰K and then decreases slowly. Sharp fall down of μ_i at temperature 778⁰K is observed, which is equal to the Curie temperature of the sample. It is also observed that effect of Mn⁴⁺ suppresses the peaking behaviour and remains almost invariant with temperature. The observed decrease of permeability with Mn⁴⁺ content is attributed to decrease of density and increase of porosity in the present system. Similar results have been observed in Ti substituted Mn-Zn ferrites.⁹ This behaviour is also attributed to the compensation of anisotropy constant due to replacement of ferric ions by Mn according to relation.



The experimental measurements of initial permeability, $\tan\delta$ with the frequency range from 1K to 10MHz are carried out on LCR Bridge HP 4219 at ETDC Bangalore. It is found that the initial permeability decreases with frequency upto 10KHz remains constant upto 1MHz and then suddenly increases at and above frequencies. All the samples show similar behaviour. The observed results are explained on the mechanism of rotation of magnetisation and displacement of domain walls. Both these contributions are related to anisotropy constant K_1 and saturation magnetisation. Globus¹⁰ has given the following relation.

$$\mu_i = M_s^2 d_m / K_1$$

The low frequency dispersion in the present system is attributed to domain wall displacement. The initial permeability, also depends on microstructure, grain size and porosity. The decreased permeability

is attributed to the pores and overfiring effect and to increased demagnetising effects due to higher porosity. It is observed that permeability increases with increase of grain diameter upto $d=2\mu\text{m}$ and then decreases with increase of grain size, similar results are observed by many workers.¹¹ This is attributed to an increased bulging volume of domain walls and decreased domain wall pinning by grain boundaries with increasing grain size and these diminishing demagnetising effects. The lower value permeability in Mn doped samples compared with that of undoped sample is attributed to the formation of secondary phases, porosity, which may hinder domain wall motions. Even though the X-ray and SEM micrographs fail to identify any impurity phases in the samples, this does not preclude that secondary phase may possibly be precipitated.

Chapter IV deals with D.C. conduction phenomenon and dielectric measurements. The conduction phenomenon and the Koop's theory for ferrites are briefly discussed. The electrical resistivity measurements are carried out by two probe method from room temperature to 800°K .

The resistivity with temperature obeys Arrhenius relation $\rho = \rho_0 \exp(\Delta E/kT)$

where ΔE = is activation energy.

k = is Boltzman constant.

T = is absolute temperature.

The $\log \rho$ versus $10^4/T$ plots show three distinct regions with two breaks. The transition temperature T_1 is at lower temperature side, whereas T_2 is at higher temperature side which corresponds to Curie temperature of the sample. The Curie temperature decreases with increase of Mn content, whereas the first transition temperature T_1 increases with Mn. The variation of D.C. resistivity with temperature can be attributed to ionic drift current, current due to electron hopping and current due to electrons in the conduction band. The observed variation of resistivity with temperature in the present system for the first region may be due to ionic drift current and current due to electron hopping. The II and III regions are characterised due to polaron hopping. The theory of conductivity in ferrites has been explained on the hopping of polarons due to thermal activation. In ferrites the conductivity is associated with the presence of ions of given element in more than one valence state and these ions get distributed over the crystallographically equivalent sites. The activation energy to cause normal electron hopping are of the order of 0.2 eV and less. In the present system the calculated activation energies are in the range 0.5 to 0.9 which clearly indicates the conduction mechanism is due to polaron hopping.

Ferrites having the spinel structure, the B-B distances are smaller than A-A and A-B distances, even then the B-B distance is much larger than the sum of ionic radii of cations. This gives rise to a situation in which electrons are not free to move through the crystal, but remain fixed on B-site necessitating a hopping process.

For the present system the cation distribution is given as $\text{Cd}_{0.3}\text{Fe}_{0.7}(\text{Fe}_{1.3-2t}\text{Ni}_{0.7+t}\text{Mn}_t\text{O}_4)$. The A-A hopping may not exist as there are only Fe^{3+} ions and any Fe^{2+} formed occupies the B-site. Therefore B-B hopping is more predominant.

It is observed that the resistivity increases upto $t = 0.15$ and then decreases for high concentrations. The increase in resistivity is due to Mn^{4+} which acts as electrostatic traps for exchange of electron between Fe^{2+} and Fe^{3+} ions at B-site. They can also act as scattering centers. The Mn ion gives a Jahn-Teller trapping when exchange of $\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+}$ transition takes place.¹² The decrease in resistivity at and above $t \cong 0.15$ is attributed to the formation of more number of Fe^{2+} , Ni^{3+} ions, so conduction can easily be possible for exchange of electrons between them. However, the resistivity also depends on sintering condition, chemical inhomogeneity, grain size, porosity and impurity phases.

Experimental measurements of dielectric constant, $\tan \delta$ with variation of frequency are carried out in the frequency range 5KHz to 10MHz. It is found that the dielectric constant decreases upto $t = 0.15$ and again increases, where as the D.C. resistivity increases for the same content of Mn and again decreases. The polarisation process in these materials take place through mechanism similar to conduction process.¹³ The electric conduction in our system is explained by Verwey mechanism. According to cation distribution the Fe concentration is maximum at B-site for the sample with $t=0$, hence

the number of Fe^{2+} ions on B-site are more which take part in the electron exchange and hence are responsible for polarisation. Therefore, a comparatively high value of dielectric constant is observed. Addition of Mn^{4+} ion decreases the ferrous ions at B-site and localizes Fe^{2+} ion by forming stable electrical bonds with Fe^{2+} ions. This localization effect obstructs electron exchange with a consequent decrease in dielectric constant. For the samples $t > 0.15$, the formation of more number of Fe^{2+} ion and the cluster of Mn_2O_3 is possible which consequently increase the dielectric constant.

The variation of dielectric constant with frequency for various compositions reveal dispersion due Maxwell and Wagner interfacial polarisation in agreement with Koop's phenomenological theory. The observed variation in dielectric relaxation intensity is explained on the basis of space charge polarisation due to inhomogeneous dielectric structure. It is concluded that for $t < 0.15$, the response of dielectric is dominated by Mn^{4+} ions and Ni^{2+} ions in usual manner such as electron exchange takes place between $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$, where as for $t > 0.15$, the dielectric response is dominated by the complex nature of dielectric. The complex nature of dielectric may be due to presence of Mn in multivalence state, the cluster formation of impurity phases and the unexplod nature of ferrite grains.

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