



CHAPTER - 5

SUMMARY AND CONCLUSIONS.

Magnetic ceramics containing ferric oxide as major component are generally known as ferrites. The ferrites are classified as soft, hard microwave and square loop ferrites. The technical importance of the ferrites lies primarily in their high resistivity. They are widely used as transformer cores, inductances, deflection coils, antennas etc. Ferrites with square loop characteristics find extensive use in computer and memory devices. Hard ferrites having low permeability and larger magnetostriction are useful in mechanical filters and ultrasonic generators. The extensive work has been carried out from the point of view of their chemical composition and physical properties to check the suitability of certain applications. Recently in the ICF(3) of 1980, Prof. Takei¹ introduced the need of new power ferrite for future applications.

Widely used ferrites are Mg-Mn, Mn-Zn and Ni-Zn. The substitution of tetravalent ions like Ti, Sn, Ge has been studied by many investigators,^{2,3} to modulate the physical properties. In this dissertation, we have undertaken the tetravalent substitution of magnetic ion Mn^{4+} in the system $Zn_{0.3}Ni_{0.7+x}Mn_xFe_{2-2x}O_4$ and following studies have been carried out.

- (1) Preparation of $Zn_{0.3}Ni_{0.7+x}Mn_xFe_{2-2x}O_4$ ferrite series by ceramic method where x varies from 0 to 0.4.
- (2) X-ray and I.R. studies to confirm the formation of solid solution to determine the lattice parameter, bond length and impurity phases.

- (3) Magnetization and permeability to understand the behaviour of manganese in modulating the cation distribution.
- (4) Scanning electron microscopy to observe the developed microstructure due to substitution and sintering.
- (5) D.C. and A.C. electrical conductivity to understand the conduction phenomenon.

In chapter I, brief review of the ferrite properties such as magnetization, anisotropy, conductivity and permeability is given. The Neel's theory is also discussed in brief. Applications of ferrites are tabulated and orientation of the present work is included at the end of the chapter.

Chapter II, deals with preparation, characterisation and I.R. studies which is divided into two sections. Section-A is devoted to the methods of preparation and x-ray studies, and section-B is devoted to I.R. studies. In section-A, methods of preparation are reviewed and the hot pressing technique is discussed to understand the possibility of obtaining high density ferrites. The details of the ceramic method are included. Pellets and torroids are prepared by applying the pressure of about 5 tonnes for the period of 5 minutes and they are sintered at 1000°C for about 20 hours in air medium. Samples are cooled to room temperature slowly at the rate of 80°C per hour. Chromel-alumel thermocouple was used for the measurement of temperature.

X-ray diffraction technique is used for the confirmation of the structure. Analysis of x-ray diffraction patterns reveals the single phase spinel structure of each sample. The lattice constant increases with increasing Mn content, except for 0.3 Mn concentra-

tion, where a decrease in lattice constant is observed. Ionic radii of Mn^{4+} , Zn^{2+} , Fe^{3+} and Ni^{2+} are 0.60, 0.74, 0.64 and 0.72 Å respectively. Zn content is constant and Mn and Ni replace Fe^{3+} . Hence, increase in the lattice constant is attributed to Ni^{2+} ions. At 1000°C, MnO_2 decomposes as $4MnO_2 \rightarrow 2Mn_2O_3 + O_2$

But x-ray diffraction analysis does not show any phase change in the present system. However this does not preclude that a secondary phase of Mn_2O_3 may possibly be precipitated at higher contents of Mn. Further it is seen that both R_A and R_B increase for almost all the samples, with increase in Mn concentration. Theory of ionic-covalent bonding in ferrites was explained by Levine⁴ on the basis of variation of bond length in the spinel structure. Thus it may be concluded that addition of Mn^{4+} ion has an effect of decreasing the ionic-covalent character of the ferrite.

Necessary theoretical background for I.R. spectra is discussed in section-B. I.R. spectra are recorded in the frequency range of 300cm^{-1} to 800cm^{-1} , with KBr pellet method. Each sample shows the broadening of the absorption bands. The broadening is due to the statistical distribution of cations in the inverse spinel. Waldron⁵ observed two absorption bands around 600cm^{-1} and 400cm^{-1} , due to tetrahedral and octahedral complexes respectively. In present system, two absorption bands are observed in accordance with Waldron's observations. The variations in the positions of absorption bands are not very regular. It may be due to the preparation method and microstructure.

Force constants are found to increase linearly with bond lengths. This type of dependence is attributed to the fact that oxygen

can form under favourable conditions, stronger bonds with metal ions even at larger internuclear separations. Such results are observed in Cu-Ni ferrites.

Magnetization, curie temperature and permeability are dealt with, in section-A and Microstructure studies in section-B of chapter III. Experimental details with necessary formulae are given wherever necessary.

The values of magnetization decrease with increase in content of manganese. A slight increase in the magnetization for $x=0.1$ is observed. The observed magnetization is explained on the basis of cation distribution. Neel's model is considered for calculating theoretical magnetic moment. The cation distribution is given as, $Zn_{0.3}Fe_{0.7}(Ni_{0.7+x}Mn_xFe_{1.3-2x})O_4$. According to many researchers Mn^{4+} , Mn^{3+} and Ni^{2+} prefer B-site, whereas Mn^{2+} and Zn^{2+} prefer A-site. The same is followed in the above cation distribution. Observed and calculated magnetic moments agree well with each other. Slight increase in the magnetic moment for $x=0.1$ is attributed to the super paramagnetic behaviour⁶ of Fe^{3+} ions. Similar results are observed for Ti^{4+} substituted Mg and Li ferrites. Generally microstructure also affects the magnetic behaviour in ferrites.

Curie temperature shows a decreasing trend with increasing Mn content. They show one to one correspondence with magnetization. Variation of curie temperature is due to change in the cation distribution and AB interaction energy. Curie temperatures observed in direct experiment and measured from resistivity experiment agree well and show similar nature in both the experiments. Curie temperature and Magnetization values for undoped sample are

found to be matching with reported values by N.L.Pakhomova et al.⁷

Variations of initial permeability with temperature and with frequency are reported for the present system. In case of undoped sample, initial permeability increases with temperature upto curie temperature from where it drops suddenly. The sharp falls of permeability are not observed near the curie temperature in other samples. Initial permeability varies with content of Mn in analogy with curie temperature and magnetization.

In the range of frequency 1KHz to 10MHz, initial permeability is measured for the series. In the low frequency range upto 10KHz, initial permeability decreases monotonically, from 10KHz to 1MHz it is independent of frequency and above 1MHz to 10MHz it increases significantly. Variation of $\tan\delta_{\mu}$ with frequency shows similar behaviour.

Physical mechanisms contributing to initial permeability are rotations of magnetization and displacement of domain walls. Number of workers⁸ have attributed the variation of initial permeability to the domain wall motion in low frequency region. The increase in permeability is attributed to the complex nature of magnetization and domain wall motion. Also the initial permeability is dependent on preparation method, porosity, grain size and structure of the grain. It is concluded that the addition of Mn^{4+} impedes the domain wall motion in low frequency region, making it almost independent of frequency upto 1MHz region.

Microstructural aspects like grain size and porosity are the important parameters for deciding the permeability behaviour of ferrites. Mechanisms of grain growth, porosity and densification

are discussed in section-B of chapter III. They are mainly dependent on the sintering temperature, atmosphere of sintering, purity of raw materials and their chemical reactivity.

Scanning electron microscope is used to observe the microstructure. The micrographs of the samples are presented. The grain diameter of each sample is determined by intercept method. The general features revealed by the micrographs are:

- (1) The grain size increases upto 0.1 content of Mn and then it decreases for higher contents of Mn.
- (2) Porosity increases with increase of Mn content.
- (3) The segregation of impurities at grain boundaries is observed for Mn concentrations of values 0.2 and 0.3, whereas no intragranular porosity is observed.

For doped samples permeability increases with the grain size upto 0.1 content of Mn and then it decreases with decrease of grain size for higher concentrations of Mn. Microstructural modifications due to Mn are the causes of such variations.

Chapter IV deals with electrical conduction mechanism and dielectric constant behaviour. Electrical measurements are carried out by two probe method from room temperature to 800°K. The resistivity obeys the relation given by Arrhenius. Two distinct breaks are observed in the temperature variation of resistivity⁹. The first break at lower temperature around 100°C remains constant for almost all the samples. Second break at higher temperature changes with Mn concentration. It is found to be coinciding with the curie temperature. These regions¹⁰ of resistivity behaviour with temperature, suggest the different

conduction mechanisms. The conduction in the first region is due to impurity charge carriers and in the second and the third regions, conduction is due to polaron hopping mechanism.

Theory of conductivity in ferrites has been explained with the hopping of polarons due to thermal activation.¹¹ The activation energies are greater than 0.2 eV and it clearly indicates that the hopping process is favoured in the present study. In ferrites, BB distance is smaller than AA and AB distances. However BB distance is much larger than the sum of ionic radii of the cations involved. So the electrons remain fixed at B-site, necessitating a hopping process. In the present system, the conduction is attributed to change of electrons between $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$, $\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+}$ and $\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+}$.

The resistivity increases with Mn^{4+} for the compositions 0.05, 0.1 and 0.15 and then decreases for 0.2 and other higher values of Mn^{4+} . The increase in resistivity is attributed to Mn^{4+} ions which act as electrostatic traps and scattering centres.¹² Addition of Mn^{4+} forms a stable bond with Fe^{2+} . The decrease in resistivity is attributed to the changing valencies of Mn^{4+} , Mn_2O_3 cluster formation and Ni^{3+} . The activation energy increases with increase in resistivity and decreases with decrease in resistivity in the present series. The conduction behaviour is also due to $\text{Mn}^{4+} \rightleftharpoons \text{Mn}^{3+}$ which needs more activation energy, leading to Jahn-Teller Trapping.¹³

The dielectric properties are also presented along with brief discussion of Koops theory.¹⁴ The experimental measurements of dielectric constant and $\tan \delta$ are carried out with variations of frequency in the range of 1KHz to 10MHz. Dielectric constant and

and decrease with Mn content upto 0.1, and then increase for higher values of Mn content.

It is stated that the mechanism of dielectric polarization¹⁵ is similar to that of conduction process. The electron exchange interaction $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ results in a local displacement of electrons in the direction of applied electric field which determines the polarization. The variation of dielectric constant with Mn content is explained with the help of cation distribution,

$\text{Zn}_{0.3}\text{Fe}_{0.7}(\text{Ni}_{0.7+x}\text{Mn}_x\text{Fe}_{1.3-2x})\text{O}_4$. For the sample $x=0$, Fe concentration is maximum at B-site. Hence the number of Fe^{2+} ions for electron exchange on B-site is maximum. Therefore high value of dielectric constant is observed. For other samples, the substitution of ' x ' Mn^{4+} ions, changes the iron concentration from 1.3 to $1.3-2x$ and Ni from 0.7 to $0.7+x$ and thereby decreases the ferrous ions on the octahedral site which are available for polarization, with a consequent decrease in dielectric constant upto $x=0.1$. The increase in dielectric constant at or above $x=0.1$ is attributed to the formation of $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ and multivalent states of Mn and cluster formation at grain boundaries. So it can be concluded that for $x \leq 0.1$ dielectric response is dominated by electron exchange whereas for $x > 0.1$, it is dominated by the complex nature of dielectric. The variation of dielectric constant with frequency reveals dispersion due to Maxwell-Wagner interfacial polarization in agreement with Koop's phenomenological theory. The observed variation in dielectric relaxation intensity can be explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The inhomogeneities in the present system are porosity, impurity phases and their distribution.

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