

CHAPTER-V

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Ferrites are the ferrimagnetic oxides having a large number of technological and industrial applications. Their importance in technology and industries arise due to the fact that they are ionic crystals, which put them in insulator or semiconductor class¹. This means that power losses due to eddy current are much reduced and hence they are well suited for high frequency applications in contrast to metals and alloys which suffer from a tremendous eddy current loss. Ferrites are used in audio and video transformers, television scanning yokes, aerial rods, antenna cores, broadcast receivers, flayback transformer, recording heads, chokes etc. High permeability and high resistivity are characteristic features of soft ferrites. Ferrites exhibit typical electric and magnetic properties such as switching, hysteresis loop, Square loop ferrites find their suitability in computer and memory devices. Whereas low permeability and larger magnetostriction make them suitable to use in accelerators, mechanical filters, ultrasonic generators. Hexagonal ferrites are used as permanent magnetic materials. The micro wave application of ferrite which can be exemplified in Faraday rotation, phase shifter, modulator depend upon the nature of gyromagnetic resonance.

A tremendous amount of work have been carried out on various types of ferrites having general formula MeFe_2O_4 or $\text{MeO} \cdot \text{Fe}_2\text{O}_3$, where Me is divalent metal ion such as Ni, Mn, Co, Mg, Cu etc. The divalent metal ion can be partially substituted by other divalent metal ion such as $\text{Me}'_x \text{Me}''_{1-x} \text{Fe}_2\text{O}_4$ where Me' and Me'' are two divalent metal ions. In this way mixed ferrites can be prepared .

The electric and magnetic properties of ferrites depend on physico chemical history, method and conditions of preparation, heat treatment, grain size, porosity etc. By selecting appropriate parameters and controlling them ferrite material with desired properties can be produced for a specific application. The electric and magnetic properties of these can also be altered by doping suitable impurities.

The Co-Zn mixed ferrite system has been studied by many workers^{2,3,4} from view point of understanding the crystal structure electric and magnetic properties etc.. Infrared spectra⁴ of these also have been reported. However data on Co-Zn mixed ferrite system doped with various impurities is scarce . Hence it is felt that it is worthwhile to study how doping of impurities in Co-Zn mixed ferrite system affect their electric, magnetic properties and I.R. spectra.

Therefore, in order to understand the influence of doping of Aluminium (Al) and Gadolinium oxide (Gd_2O_3) in Co-Zn mixed

ferrite system, the following studies have been carried out.

- 1(a) Preparation of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system where $X=0.0, 0.3, 0.5, 0.7, 1.0$ by standard ceramic technique.
- (b) Preparation of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system doped with 0.05 At wt.% Al.
- c) Preparation of $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system doped with 0.05 mol.wt. % Gd_2O_3 .
- 2 X-ray diffraction studies for crystal structure characterisation of ferrite samples and to investigate the structural changes due to doping.
- 3 D.C. and A.C. conductivity measurement to understand conduction mechanism and effect of doping on electrical behaviour.
4. A.C. magnetic susceptibility measurement for determining the existence of multidomain (MD), single domain (SD) and super paramagnetic (SP) particle within the material, for determining Curie temperature and hence to investigate effect of doping on susceptibility.
5. Determination of Curie temperature of samples and to investigate its variation with doping.
6. Hysteresis studies to determine saturation magnetisation, coercive force i.e. magnetic behaviour and to investigate effect of doping on these parameters.

The Chapter I opens with introduction and historical background of ferrites. The crystal structure of ferrites with detailed account of spinel structure and its classification is given. The different types of ferrites are discussed. A short account of electric and magnetic properties together with important applications is given. As well as Neels theory is described in brief limitation of Neels theory are pointed out and a brief account of Yafet-Kittel theory is given. At the end of the chapter the orientation of present work is given.

Chapter II is divided into three sections A, B and C. In section A different methods of preparation of ferrites are described and a detailed account of ceramic technique is given. Mechanism of solid state reaction is discussed. Actual formation of ferrite samples, pellet formation, possible stages in ferrite preparation are explained with the help of flowchart. The section B deals with X-ray diffraction studies. To confirm crystal structure and formation of ferrite samples. X-ray diffraction studies have been carried out. All the samples in system studied either doped or undoped exhibited a cubic spinel structure. The lattice parameter variation obeys Vegards law and is attributed to difference in ionic radii. The slight difference in lattice parameter for doped series is attributed to preparation condition and heat treatment. It is seen that as zinc content increases, the lattice parameter increases and this variation is linear. Also the slight variation of lattice parameter in

case of undoped and doped series may be due to variation in cation distribution and modification of crystal lattice. The lattice parameter calculations using X-ray diffractogram confirm spinel structure. Bond lengths R_A and R_B both increase with increase of zinc concentration. The increase in average bond length R_A is attributed to the increase of lattice parameter with the increase of zinc content⁵. As the content of zinc in system increases, presence of Zn^{2+} ion on A site increase. Zn^{2+} ions selectively occupy A site, since $ZnFe_2O_4$ is a normal spinel and that ionic radius of Zn^{2+} is greater than Fe^{2+} and hence the bond length R_a increases with increase in zinc content. Section C deals with far infrared studies for the undoped and doped ferrite system. The I.R. studies are carried out in the range 300 cm^{-1} to 800 cm^{-1} . The absorption bands observed for these system are found in the expected range and are as reported by earlier workers.⁴ The high frequency band ν_1 is in the range 550 cm^{-1} to 600 cm^{-1} . This band is assigned to tetrahedral group of complexes. The lower frequency band ν_2 is in the range 410 cm^{-1} to 490 cm^{-1} . This band is attributed to octahedral group of complexes. The slight variation of ν_1 and ν_2 from one mixed ferrite to the other is attributed to the changes in Fe-O complexes with increase in cobalt concentration. The increases in bond stretching frequency ν_1 from normal spinel $ZnFe_2O_4$ to inverse spinel $CoFe_2O_4$ is observed. This is due to charge imbalance, in which oxygen ion is likely to shift toward Fe^{3+} ion. Similar variation is

observed for doped series A new bond ν_3 around 350 cm^{-1} is observed in case of aluminium doped sample. This is regarded as splitting of ν_2 band into ν_2 & ν_3 . The intensity of ν_3 band is found to increase with increase in cobalt content. This is attributed to the increase in Co-O complexes. In Gadolinium doped samples splitting of ν_2 into ν_2 and ν_3 is not observed. This is explained on the basis of similarity of electronic configuration of Gd^{3+} and Fe^{3+} and to the fact that Gd^{3+} ions replaces one of Fe^{3+} ion on octahedral site.

Chapter III deals with DC and AC conductivity measurement to understand the conduction mechanism in ferrite system. Section A deals with d.c. resistivity measurement. The electrical resistivity measurement were carried out using two probe method in the temperature range of room temperature to 500°C .

The resistivity obeys Arrhenius relation,

$$\rho = \rho_0 \exp (\Delta E/kT)$$

The $\log \rho$ versus $10^3/T$ plots show two distinct regions with a single break for undoped series. The $\log \rho$ versus $10^3/T$ plots for Al & Gd_2O_3 doped series exhibit three distinct regions with two breaks. The temperature at which break occur agrees well with ferrimagnetic Curie point. The temperature at the break also known as transition temperature increases with increase in cobalt content. This is attributed to increase

in A-B interaction with increase in cobalt content, as higher percentage of cobalt is transferred to B site. Activation energy observed in ferrimagnetic region are less than that in paramagnetic region. This is attributed to the effect of magnetic ordering. Since activation energy are found to be greater than 0.2 eV and thus in conduction mechanism⁶ hopping process is favoured due to polarons. The conductivity is arising due to hopping of electrons from Co^{2+} and Fe^{3+} . The hopping at B-site take place $\text{Co}^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{Fe}^{3+} + \text{Co}^{2+}$. The Aluminium (Al) and Gadolinium oxide (Gd_2O_3) doped samples exhibit three regions with two breaks. The conductivity in first region is attributed to the presence of impurity in second region to phase transition and in third region to magnetic disorder. Section B deals with a.c. conductivity measurement. Experimental measurement of dielectric constant ϵ' , loss tangent $\tan \delta$ with variation of frequency are carried out in the range 100 Hz to 10 MHz. The variation of dielectric constant for various composition reveal dispersion due to Maxwell⁷ and Wagner⁸ polarisation in agreement with Koops phenomenological theory. It is to be noted that increase in dielectric constant ϵ' is more at low content of zinc than at high content of zinc as frequency is lowered. Doping of Al does not significantly change ρ_{ac} , however, there is noticeable drop in ρ_{ac} on doping Gd_2O_3 . This may be because of different electronic configuration of Al^{3+} and Gd^{3+} ions. The decrease may be due to free Fe^{2+} ions on doping of trivalent Gd^{3+} ions. Dielectric loss peaks

were observed for two samples $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 at 2K and 7K respectively. A maximum in dielectric loss is observed when jump frequency is approximately equal to that of external field⁹

Chapter IV is divided into three sections A, B and C. Section A deals with magnetisation studies. Saturation magnetisation and hence magnetic moment varies as expected and attain their respective maximum values when zinc content in mixed Co-Zn system ferrite is 0.5, whereas Guillaud¹⁰ have observed that maximum value of magnetisation and magnetic moment when zinc content in mixed Co-Zn ferrite system is 0.4. The variation is attributed difference in method of preparation, heat treatment etc. For Aluminium doped samples magnetic moment and corresponding magnetisation reduces, whereas for Gadolinium doped sample it increases with in comparison with undoped samples. The trivalent impurity ion Al^{3+} and Gd^{3+} reduces Fe^{3+} ions at octahedral site. Comparing Fe^{3+} and Gd^{3+} ion it is seen that, there are two extra spins associated with Gd^{3+} ion because of which magnetisation values for Gd^{3+} doped samples are greater than those for undoped samples. Section B deals with susceptibility studies.

In the susceptibility studies discussion series A refer to undoped samples and series B and C refer to doped samples doped with Al and Gd_2O_3 . The suffix 1, 2, 3, 4, 5 indicates zinc content 0.7, 3 correspond to Zn content 0.5, 4 correspond to zinc content 0.3, 5 corresponds to Zn content 0. in $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$.

On observing the normalised susceptibility versus temperature curves, it can be stated that, samples A_3, A_4, A_5 and C_4, C_5 contain SD particles, whereas B_3, B_4, C_3 samples contain MD particles.

It is seen that doping affects χ / χ_{RT} characteristically at blocking temperature T_b increasing its value. Similarly comparing curves for samples (A_3, B_3, C_3) , (A_4, B_4, C_4) , it is noted that blocking temperature increases for Gd^{3+} doped samples, whereas it is reduced for Al^{3+} doped samples. This may be regarded as aluminium doping suppresses the magnetic properties, whereas Gadolinium doping enhances the same. This is supported by our magnetisation measurements. Also it is seen that the blocking temperature for these low in comparison with that for the samples A_5 . This may be due to sufficient amount of zinc content in these samples, which favours SD to MD transition as indicated by slow fall of χ / χ_{RT} from the blocking temperature.

- 1 Addition of Aluminium in Co-Zn mixed ferrite system favours (SD+MD) particles.
- 2 Addition of Gd_2O_3 tends to enhance T_b and retains SD behaviour.
- 3 Addition of zinc brings about SD to MD transformation. This is to be expected as pure zinc ferrite is nonmagnetic material.

Section C deals with Curie Temperature determination. It is seen that there is nonlinear decrease in the value of T_c on addition of zinc. The nonlinear variation indicates that, triangular type of spin arrangement is favoured. Similar trend is observed for doped series doped with Al and Gd_2O_3 . The angle $Fe_A^{3+}-O-Fe_B^{3+}$ and distances Fe_A-O , Fe_B-O determined Curie temperature.

It is seen that as zinc content increases Curie temperature drops no matter whether samples are doped or undoped. It appears that T_C values are not significantly affected either by doping of Al or Gd_2O_3 , so it can be concluded that doping does not markedly affect A-B interaction.

R E F E R E N C E S

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