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CHAPTER – V

SUMMARY AND CONCLUSIONS

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Magnetic materials viz. ferrites are an integral part of the modern industrial society. They are used in advanced electronics, microwave and computer technology etc. The properties of ferrites have been continuously improved and there seem to be no end to their applications.

Presently, the attention has been focussed on power ferrite materials which require high magnetization and resistivity. For such materials Nickel ferrite is the promising base material. The substitution of Al^{3+} ions increases the resistivity thereby lowering the dielectric losses and decrease saturation magnetization. Besides, aluminium addition inhibits grain growth and improves mechanical strength of microwave ferrites.

The present investigation involved the following steps-

1. Synthesis of $NiAl_xFe_{2-x}O_4$ ferrites by the ceramic method (with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0)
2. X-ray and IR studies to confirm the formation of solid state reaction and to determine the lattice parameter, bond length and site radii and vibrational frequencies.
3. Hysteresis and magnetization studies to understand the effect of Al^{3+} addition.

4. Measurement of DC resistivity and thermoeletric power to understand the conduction mechanism and to determine the type of conductivity.

5. Thermal variation of ac susceptibility to understand the domain structure.

The thesis has been divided into five chapters. The first chapter is devoted to the introduction of ferrites. The spinel structure, classification, theories of ferrimagnetism and properties such as electrical resistivity and magnetization are discussed. Some important applications of ferrites are given along with the orientation of the problem at the end.

The second chapter outlines the preparation and structural characterization of the present ferrites. The chapter has been divided into three sections. These include the preparation of ferrites by the ceramic method, characterization by XRD infrared absorption spectroscopy.

Part A - The said ferrite system was synthesized by the conventional ceramic method using the high purity oxides. The details of the actual sample preparation by using the ceramic method are given. The mechanism of solid state reaction and sintering process are also discussed. The flow chart of ferrite preparation is presented.

Part B - Analysis of x-ray diffraction patterns confirms the formation of spinel structure and all the

samples turn out to be face centre cubic in nature. The lattice parameter and interplaner distances were calculated using the usual procedure. The observed and calculated values of interplaner distances are found to agree well with each other. The value of lattice parameter in the case of Nickel ferrite comes out to be 8.337 A° which agrees well with the earlier reported values. The lattice parameter decreases with the increasing Al content. This is due to the fact that the ionic radius of Al3+ (0.57 A°) is smaller as compared to that of Ni (0.78 A°) and Fe^{3+} (0.67 A°). Similar result is observed when IIIB group metal such as Ga and B are added in Ni ferrites. The bond length and site radii were calculate using x-ray data and these clearly show the decrease in bond length and site radii with increasing Al content since both the terms depend upon lattice parameter and Al^{3+} content. The bond length R_B is always greater than R_A.

X-ray density, actual density and porosity are also calculated. Porosity of all the samples are found to be 30 - 40%.

Part C - IR spectra of $NiAl_xFe_{2-x}O_4$ ferrite samples were recorded at room temperature and reveal two main absorption bands as reported by Waldron earlier and splitting of octahedral band into new band as ν_3. The high frequency band ν_1 is attributed to intrinsic vibrations of tetrahedral ion complexes and

lies in the range 580 cm^{-1} to 600 cm^{-1} while low frequency band is attributed to the intrinsic vibrations of octahedral ion complexes and lies around 410 cm^{-1}. This difference in band positions is expected because of the difference in the Fe^{3+} - O^{2-} distances for octahedral and tetrahedral complexes. The appearance of ν_3 band in ferrite is generally due to the divalent ion - oxygen complexes in the octahedral sites and it is found around 480 cm^{-1}. The peak intensity of ν_3 band goes on decreasing as Al content increases and at higher concentrations of Al i.e. at x = 1 the peak intensity vanishes completely.

The third chapter deals with the electrical properties of the ferrite samples and it is divided into two sections. Section A is devoted to dc conductivity and section B deals with thermoelectric power.

Section A - The discussion related to conduction in metal oxides, ferrites and hopping mechanism in spinel ferrites is presented. The details of the experimental techniques is also included.

The plots of the logarithm of resistivity vs reciprocal of temperature are linear upto Curie temperature and show a ferri to paramagnetic transition at Curie temperature. Such a transition is also observed by many workers in other ferrites. Conduction phenomena at low temperature is due to impurities while

at high temperature, it is due to polaron hopping and magnetic ordering. It is also observed that resistivity of samples in general increases with Al content and decreases with temperature.

From these plots, it is seen that temperature at which spin-spin interaction vanishes due to thermal vibration is known as transition of Curie temperature which separates upper ferromagnetic region from lower paramagnetic region. Transition temperature decreases with increasing Al content. This can be the basis of strength of exchange interaction between the magnetic ions, which in turn depends upon their density & magnetic nature. As no. of Al^{3+} increases in the samples, the no. of Fe^{3+} ions goes on decreasing. This decreases A-B interaction. The thermal energy required to upset the magnetic order decreases and hence Tc decreases.

The activation energy in the paramagnetic region is found to be higher than that of ferrimagnetic region in our samples.

Part B - On the basis of sign of the thermoemf the ferrite samples are found to be n type and p type semiconducting materials except $x = 0.2$. For $x = 0.2$, thermoelectric power is negative indicating that electrons are the majority carriers. For $x = 0.4, 0.6$ and 0.8 initially the thermoelectric power is negative and then it changes its positive sign as temperature

increases and for x = 1.0 at room temperature thermo emf is positive indicating holes are the majority carriers. It decreases with temperature, changes to negative sign at about $385^{o}K$ and increases in the same direction, because activation energy for electron hopping is less than that for holes.

The presence of Ni on B site favours the conduction mechanism as ,

$$Ni^{2+} + Fe^{3+} \leftrightharpoons Ni^{3+} + Fe^{2+}$$

The conduction mechanism for n type is predominantly due to hopping of electrons from Fe^{2+} to Fe^{3+} ions,

$$Fe^{3+} + e^{-1} \Rightarrow Fe^{2+}$$

whereas conduction mechanism is predominantly due to hole transfer from Ni^{3+} to Ni^{2+} ions,

$$Ni^{2+} + h \Rightarrow Ni^{3+}.$$

The fourth comprises of magnetic properties and is divided into two parts.

Part A - The magnetic properties of ferrites like hysteresis behaviour and magnetization are briefly discussed.

In the present system the value of magnetic moment of $NiFe_2O_4$ is slightly lower than the value of magnetic moment that has been report earlier. The saturation magnetization and magnetic moment decreases with increasing Al content. This variation can be explained on the basis of cation distribution and Al^{3+} content. The decrease in saturation magnetization with

increasing Al3+ content can be explained on the basis of magnetization MA and MB of tetrahedral (A) and octahedral (B) sublattices respectively. Al^{3+} besides preferring B site, the partial replacement of Fe^{3+} ions each having a magnetic moment of $5\mu_B$ by diamagnetic Al^{3+} ions results in lowering the value of both MA and MB. The decrease in MA thereby decreases the net magnetization. The magnetic moment nB also decreases with Al content may due to the reduction in Fe content.

Part B - The study of variation of a.c. susceptibility is used for the discussion of the domain structure in the present samples. From the nature of (χ_T/χ_{RT}) against temperature curves, it is clear that for x = 0 and 0.2 sample contain single domain particles which is supported by the observation of large value of coercive force and for x = 0.4 to 1.0 the addition of Ai3+ ions to the system contain multidomain plus single domain particles. Thus as Al content increases, samples contain single domain (SD) + multidomain type of particles.

Curie temperature is measured with the help of a.c. susceptibility. It indicates that Curie temperature goes on decreasing as the Al content increase, may be due to reduction in Fe_A^{3+}-O-Fe_B^{3+} linkage and angle between them.