Chapter V
Summary and conclusions

CHAPTER - V

SUMMARY AND CONCLUSIONS

Substituted nickel ferrites are widely used in high frequency and microwave applications. Number of workers have studied electrical and magnetic properties of these ferrites. From the literature survey, it is found that for nickel ferrite with trivalent doping of Cr^{3+} or Mn^{3+}, there is an enhancement of the electrical and magnetic properties. Secondly, Cr^{3+} is a Jahn-Teller ion which gives rise to disorder in the system. Copper ferrites also exhibit interesting features like phase transition and switching behaviour. The phase transition is attributed to the presence of copper ions as they are Jahn-Teller ions. In view of this the study of the physical properties of Cu and Ni mixed system was thought interesting and therefore we had selected the following system for research work,

$$Ni_{0.5}Cu_{0.5}Fe_{2-x}Cr_xO_4$$

where x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0.

The samples were then prepared by standard ceramic method which included mixing of raw materials, presintering, milling and sintering operations.

The dissertation comprises five chapters. First chapter begins with a brief review of properties and applications of ferrites. This is followed by a

discussion on relevant theories and spin structure. 'Orientation of the present work' has been given at the end of the chapter.

Chapter II has been devoted to preparation methods and characterization of the samples by x-ray diffraction and I.R. spectroscopy. Among different methods reviewed here, only the ceramic method has been discussed in detail. Pellets were made from presintered powder and were finally sintered at 1150 °C for 24 hours. Chromel-alumel thermocouple was used to measure the temperature. Analysis of x-ray diffraction patterns revealed that the samples were single phase spinels. The lattice constant was found to decrease gradually with increase in Cr^{3+} content. The decrease can be ascribed to smaller ionic radius of Cr^{3+} ion. The bond lengths R_A and R_B were calculated. Present system exhibits the trend of increasing covalent character with increase of chromium content (Levine [1]). IR spectra were recorded using KBr solvent in the frequency range 300 cm^{-1} to 800 cm^{-1}. Two absorption bands were observed, one at 600 cm^{-1} and the other at 400 cm^{-1}. According to Waldron [2] the absorption band around 600 cm^{-1} is due to tetrahedral complexes of FeO and that around 400 cm^{-1} is due to octahedral complexes of FeO. The difference between these two bands has been

found to be in accordance with corresponding Fe-O distances at A and B sites. Shoulders [3] were observed for higher contents of Cr^{3+}. This has been explained on the basis of Jahn-Teller distortion and the ordering of Cr^{3+} ion clusters.

In chapter III, magnetization, Curie temperature and ac susceptibility studies have been included. Magnetic properties have been briefly reviewed along with the experimental details. The following formula for cation distribution has been used for calculating the theoretical magnetic moments.

$$Cu_y Fe_{1-y} (Ni_{0.5} Cu_{0.5-y} Fe_{1-x+y} Cr_x) O_4$$

It was noted that the observed and calculated magnetic moments agree well with each other. The decrease in magnetic moment has been attributed to the decrease of Fe_A-Fe_B interaction. Curie temperature also showed a decreasing trend with increase in Cr^{3+} content which might be due to the decrease in the strength and angle of Fe^{3+} - O -Fe^{3+} linkages. In order to check the applicability of Neel's model and to understand the magnetization for the present system, the Curie temperatures were calculated with the help of Gilleo's model [4]. It is interesting to note here that Neel's model has been found to be applicable for samples with $x<0.6$, whereas canting behaviour occurred for samples

with x>0.6. This canting effect, presumably due to Cr^{3+} ions, has been discussed in great detail by Goodenough [5]. The a.c. susceptibility of samples was measured with the help of a low field ac susceptibility apparatus of Radhakrishnamurthy et al. [6]. From this study one could get clarifications about the domain structure of ferrites; such as MD- multi domain, SD- single domain and SP - superparamagnetic domain. According to their analysis the ac susceptibility for MD samples does not change appreciably with the temperature and drops sharply at Curie temperature. The samples exhibit similar behaviour up to the Cr^{3+} content of x<0.6, indicating the MD nature. The samples with x>0.6, the ac susceptibility decreased slowly with temperature and showed a tailing effect. This is likely to be due to cluster formation or the canting behaviour. Our results on IR spectra and ac susceptibility study confirm that at higher concentration of Cr^{3+}, canting effect appeared and enhanced.

In chapter IV electrical properties of ferrites have been dealt with. The d.c. resistivity and thermoemf were measured in the temperature range 300 K to 850 K. The variation of $\log\rho$ vs 1/T showed three regions with breaks at two different temperatures. Such

a type of behaviour has been observed in many ferrite systems [7]. The conduction in the first region was assigned to impurity conduction, the second and third regions were due to polaron hopping [7]. The activation energy in the first region has been found to be less than 0.2 eV, while the activation energy in the second and third regions were greater than 0.4 eV.

According to the theory of magnetic ordering a decrease in the activation energy is expected as the sample undergoes a change of state from ferrimagnetic to paramagnetic state. In the present system, the activation energies in ferri-region have also been found to be lower than those in the para-region. However, the samples with $x = 0.8$ and 1.0 showed the reverse behaviour. Therefore, while the change in slope might be linked with magnetic ordering on one hand, the reverse behaviour could be ascribed to the change from n-conduction to p-conduction itself as seen from thermoelectric power studies. The thermoemf measurements showed Seebeck coefficient to be negative for samples $x = 0$, 0.2, 0.4 and positive for $x = 0.8$, 1.0. For samples with $x = 0.6$, n type of behaviour at lower temperature was observed and n to p transition occurred thereafter at 445 °K. Thermoemf or Seebeck coefficient increased slowly with temperature

for all samples, except for x = 1, which exhibited somewhat decreasing trend. In polaron hopping model [8], the variation of conductivity originates from the changes in the mobility rather than the changes in the concentration of charge carriers. Mobilities of the samples have been calculated by using the Seebeck coefficient and resistivity values. A close agreement between the values of activation energies obtained from resistivity measurements in ferri region and those obtained from mobility has been observed. This confirmed the polaron hopping [9] as the conduction process in the present system.

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