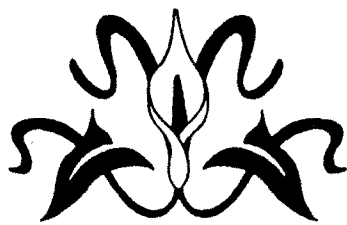


CHAPTER V



CHAPTER V

SUMMARY AND CONCLUSIONS

Villain [1] in 1979 introduced an interesting behaviour of insulating spin-glass where he argued that the spinel structure affords topological frustration. It gives rise to a variety of perturbed magnetic ordering depending on their magnetic dilution of A and B sub-lattices [2]. Recently spin glass behaviour in spinels substituted with chromium have been studied [3,4] to understand the multicritical behaviour they exhibit. In order to understand the role of Cr substitution in cobalt and copper ferrite, on the electrical and magnetic properties, we have undertaken the following work -

- 1) Preparation of $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$ and $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ samples by ceramic method. where x varies from 0 to 1.0 in steps of 0.2,
- 2) X-ray and IR studies to confirm the formation of solid state reaction, to determine the lattice parameters, bond lengths and impurity phases,
- 3) Hysteresis, magnetization and permeability to understand the behaviour of chromium,
- 4) Thermal variation of the AC susceptibility to understand the domain structure and

- 5) DC resistivity, thermoemf and dielectric behaviour to understand the conduction phenomenon.

This dissertation comprises of five chapters. In chapter I, brief review of the ferrite properties and its applications are given. The spinel structure is discussed. The theories of ferrimagnetism like Neel's theory etc. are discussed briefly. The last part of this chapter, deals with orientation of present work.

Section A of chapter II is devoted to methods of preparation, B to x-ray characterization and in section C IR studies are discussed. Samples are prepared by ceramic method. Pellets and toroids are prepared from presintered powder. They are finally sintered at 1100 °C for 24 hours in air atmosphere. Calibrated Chromel Allumel thermocouple is used to measure the temperature of furnace.

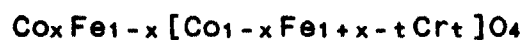
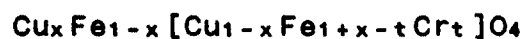
In section B, introduction about x-ray and the relevant Bragg's formula is discussed. X-ray diffractograms are used for the confirmation of single phase formation and for analysis of the crystal structure. The lattice parameter for $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ system remains almost constant upto $x = 0.6$ and then decreases with increase of Cr content. This is explained on the basis of ionic radii of Cr and Fe

ions. In $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$ system the tetragonal structure is observed for the samples with $x = 0.0$ and 0.2 and then it becomes cubic for $x \geq 0.4$. The tetragonal to cubic transition is due to transfer of copper ions from B site to A site [5]. The phase transition in copper ferrite is also discussed.

In section C introduction of IR studies on spinels and the basic theoretical background is given. IR spectra is recorded with KBr pellet method in the frequency range of 200 cm^{-1} to 800 cm^{-1} . IR spectra showed two broad bands around 600 cm^{-1} and 400 cm^{-1} with some shoulders and fine structure for higher content of Cr. According to Waldron [6] the two absorption bands around 600 cm^{-1} and 400 cm^{-1} are due to tetrahedral and octahedral Fe-O complexes respectively. The shoulders and the fine structure observed at lower frequencies around $< 400 \text{ cm}^{-1}$ is discussed on the basis of crystal distortion. This fine structure is related to the cluster formation and ordering of these clusters due to Cr ions.

Chapter III is mainly concentrates on magnetization, hysteresis, Curie temperature and ac susceptibility. Magnetic properties of the ferrites are briefly reviewed. Experimental details with necessary formulae are given. The magnetization and Curie

temperature decrease with increase of chromium content for both series. This behaviour is explained on the basis of cation distribution by applying Neel's two sub-lattice model. The decrease in the magnetic moment is attributed to the decrease of $F_{A} - F_{B}$ interaction energy. Gilleo's model [7] is used to calculate the Curie temperature based on the cation distribution



for copper ferrite and cobalt ferrite systems respectively. The theoretically calculated Curie temperatures and those measured by other methods such as ac susceptibility and permeability are in good agreement. This confirms that, the Neel's two sub-lattice model is applicable to the behaviour of magnetization with chromium in these ferrites.

It is interesting to note that, the Cu ions at A site increases with increase in Cr content, this supports our previous x-ray results on the phase transition of Cu ferrite as the Cu ion decreases for B site, the tetragonality decreases and becomes cubic.

It is well established that from the shapes of the X_{ac} -T curves one can distinguish multidomain (MD), Single domain (SD) and superparamagnetic (SP)

particles. The interesting features of the Xac-T curves in the present study are -

- i) CuFe_2O_4 shows a dramatic peak near T_c
- ii) The peak height decreases to half for $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$
- iii) For remaining samples peak height decreases slowly and becomes broad.

This behaviour is related to formation of SD to SP types of particles due to chromium. Similar results are also observed by many workers in case of chromium substituted spinels [8].

- iv) For $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ system, the CoFe_2O_4 showed SD type of behaviour and then SD to MD type of transition is observed for remaining samples.

The plots of permeability with temperature show similar behaviour.

Chapter IV presents the electrical properties which is in turn divided into three parts. Part A is devoted to dc resistivity, B to thermoemf and ac electrical conductivity is discussed in part C.

The dc resistivity and thermoemf are measured in the temperature range 300 K to 800 K. These samples show semiconducting behaviour and obey Arrhenius relation. The resistivity plots show two regions. The

conductivity in the first region is due to impurities and second due to polaron hopping. The compositional variation of resistivity shows a decreasing trend in $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$ system and $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ system shows an increasing trend. The thermoemf measurements show n-type behaviour for the samples with $x \leq 0.4$ and p type for $x \geq 0.6$ for $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$ system, observing n-type or p-type behaviour throughout the measured temperature range. In case of $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ system all samples show n-type behaviour below 500 K and p-type above 600 K. The temperature of n to p-type transition varies in between 500 K to 600 K.

The conduction mechanism can be explained using following reaction in case of CuFe_2O_4 system



in which first relation gives p-type conduction and second explains n-type conduction.

The conduction mechanism in Cu ferrite is explained with the help of cation distribution and above relation.

From cation distribution, the concentration of Cu ions at A site increases. So possibility of formation of Cu^{1+} ions at A site is more. Secondly Fe^{3+} at B site

decreases due to Cr^{3+} substitution. Hence n to p-type transition occurs.

In $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ system n to p transition with temperature is explained on the basis of oxidation-reduction process.

Polaron hopping model is used to discuss the conduction mechanism in these samples. The mobilities and the activation energies from mobility are calculated. The best agreement is observed between the activation energies calculated from mobility and conductivity.

The dielectric properties are also presented along with brief discussion of Koop's model, in section C. The dielectric constant and $\text{Tan } \delta$ are measured in the frequency range of 100 Hz to 10 MHz. The variation of dielectric constant with frequency reveals the dispersion due to Maxwell - Wagner interfacial polarization which is in good agreement with Koops phenomenological theory [10].

The dielectric constant decreases faster at lower frequency and remains almost constant at higher frequencies. Similar behaviour is observed in number of ferrites. In ferrites there are different mechanisms for polarization like electronic, ionic, space charge etc. The decrease in polarization with increase in

frequency is due to the fact that, beyond certain frequencies of electric field, the electronic exchange $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ can not follow the alternating field.

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