Chapter - VI

SUMMARY AND CONCLUSION

Ferrites are the magnetic oxides. Their applications are growing in the fields like telecommunications, microwave devices, magnetic recording, permanent magnet, sensors etc. The materials pertaining to these applications are synthesized by substituting various constituent oxides and different methods of preparation with precisely maintaining the preparatory conditions. Extensive work is going on worldwide for the study of basic science and technology of these materials. Nickel-Zinc ferrites are technologically important because of their applications in antenna rods, high frequency inductors and transformers. Particularly high density Ni-Zn and Mg-Zn ferrites are suitable for read write heads in high speed digital tapes or discs. It was therefore proposed to prepare and study the electrical and magnetic properties of Ni-Zn ferrites in the following stages

1. Preparation of samples in the $Ni_{1-x}Zn_xFe_2O_4$ (x=0, 0.20, 0.40, 0.60, 0.80 and 1.00) series.
2. Characterization by X-ray and far IR techniques
3. Study of DC electrical resistivity
4. Study of Hysteresis,. Susceptibility and Curie temperature

The usual method of preparing ferrites is the conventional ceramic method, but has several disadvantages. This method requires high sintering temperature, which may cause evaporation of certain elements and thereby changes the desired stiochiomerty. High density Ni-Zn ferrites prepared by ceramic method require high sintering temperature. But at high sintering temperature, zinc in Ni-Zn ferrites evaporates and results in formation of Fe^{2+} ions, thereby increasing the electron hopping and reducing the resistivity [1]. Another disadvantage of ceramic method is that, the particle size gets increased which causes to increase the porosity. This affects the bulk magnetic properties [2].

The chemical method overcomes all these drawbacks in the preparation of ferrites. The electrical and magnetic properties are improved in chemical method.

Therefore, it was decided to prepare Ni-Zn ferrites by oxalate precipitation method using sulphates as the starting materials. This method is simple and commercially cheap because of low cost of sulphates as compared to oxides used in ceramic method. Advantage of this method is to mix the metal ions on a molecular scale giving rise to homogenous mixtures.

The thesis matter is presented in six chapters. The first chapter deals with the brief survey of ferrites. It includes intorduction, spinel structure, theory of ferrimagnetism, survey of literature on electrical and magnetic properties. The applications and orientations of the present work is included at the end of this chapter.

Second chapter is devoted to preparation of ferrites. This chapter includes the various methods of ferrite preparation, a brief discussion on presintering, sintering, hot pressing and mechanism of solid state reaction. The preparation of ferrites under investigation is depicted in flow chart. The ferrite samples in the series $Ni_{1-x}Zn_xFe_2O_4$ (x=0, 0.20, 0.40, 0.60 ,0.80 and 1.00) were prepared by oxalate precipitation method using nickel, zinc and ferrous sulphates as the starting materials. The solid solution of co - precipitated oxalates of nickel, zinc and iron were carried out by using ammonium oxalate. The oxalate precipitates obtained by this method were presintered at 600 °c for 1 h. The presintered powder was milled and sintered at 1000 °C for 4 h in air. For preparation of pellets a small quantity of powder was subjected to the pressure of 7 tons for 5 minutes by keeping it in a die of diameter 1 cm and was finally sintered at 1000 °C for 4 h in air. The physical density of sintered pellets was determined by Archimde's principle. The physical densities of sintered pellets are found to be greater than 5.0 gm/cm^3, which is more than the sample prepared by ceramic method. It was observed that by oxalate precipitation method, high density ferrites can be prepared at relatively low sintering temperature and smaller duration [3].

Third chapter is devoted for characterization of the ferrites and is divided into two parts. The part A of the chapter deals with XRD studies. The diffractograms were recorded on x-ray powder diffractometer. The x-ray diffraction patterns revealed the formation of single phase cubic spinels, showing well defined reflections of allowed planes without any impurity phase. The lattice parameter, interplaner distances, bond lengths and ionic radii on A site and B site were calculated by using usual procedure. The calculated and observed values of interplaner distances are in good agreement with each other. The lattice parameter shows increasing trend with zinc content. This is due to longer ionic radius of zinc (0.83 A^{o}), which on substitution replaces Fe^{3+} (0.67 A^{o}) ion from A site to B site. The values of lattice constants in the present method are smaller than those of ceramic method. Similar conclusion was drawn by Toshio Takada et al [4]. It is observed that radii on A site (R_A) increases with content of zinc. As can be seen from cation distribution, Zn^{2+} is occupying A sites therefore radii on A site will be increasing.

The part B of this chapter deals with IR studies. IR studies carried out on IR spectrophotometer. The IR spectrophotometer studies of the compositions support the formation of the spinel ferrites giving two absorption bands at around 400 cm^{-1} and 600 cm^{-1} for octahedral and tetrahedral sites respectively. It is observed that, the wave number corresponding to tetrahedral vibrations goes on decreasing with increasing zinc content and is minimum for zinc ferrite. Similar variation in wave number corresponding to tetrahedral vibrations for $Ni_{1-x-y}Fe^{2+}Zn_yFe_2^{3+}O_4$ were observed by Potakova et al [5]. The IR spectra of $ZnFe_2O_4$ shows an additional peak at about 330 cm^{-1} where as Srivastava and Srinivasan [6] observed an additional peak at about 338 cm^{-1} for zinc ferrite prepared by conventional ceramic method. The force constants K_t and K_o were calculated by using Waldron analysis [7]. The force constant on tetrahedral site (K_t) shows decreasing trend whereas force constant on octahedral site (K_o) shows increasing trend with zinc concentration. Similar variations in K_o and K_t were observed by Waldron in nickel and nickel -zinc ferrites.

The fourth chapter comprises to dc electrical properties of ferrites. The discussion related to conduction mechanism in oxides and ferrites is presented. The dc resistivity measurement was carried out by using two probe method. The plots of log ρ versus $10^4/T$ gives two distinct regions for the compositions $x \leq 0.80$, separated at magnetic transformation temperature called as Curie temperature (T_c). The resistivity of nickel ferrite at Curie temperature is observed to be 3.2 x 10^4 Ω cm, while Parker [8], Reddy and Rao [9] have reported it to be about 10^4 Ω cm. In zinc substituted ferrites, (x= 0.20, 0.40, 0.60 and 0.80) we observed the maximum resistivity for 0.20, whereas Van Uitert [10] observed minimum conductivity for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ composition in polycrystalline Ni-Zn ferrites. For lower concentration of zinc, conduction mechanism is due to hole transfer from Ni^{3+} to Ni^{2+} ions, whereas in case of higher concentration of zinc, the conduction mechanism is due to hopping of electrons from Fe^{2+} to Fe^{3+}. The activation energy in paramagnetic region is higher than that of the ferrimagnetic region. It is observed that, the resistivity of ferrites prepared by oxalate precipitation method is higher than the reported values of resistivity of ferrites prepared by ceramic methd. The reduction in resistivity of ferrites prepared by ceramic method is attributed to increase in Fe^{2+} concentration caused by the evaporation of zinc during sintering. At room temperature, resistivty of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ is 1.15 x 10^9 Ωcm. However, reported value for same composition prepared by citrate method is 1.5 x $10^8\Omega$ cm [1]. Thus dc resistivity of the ferrites prepared by oxalate precipitation method is improved as compared to ceramic method.

Chapter five briefly reviews the magnetic properties of the ferrites. At the beginning of this chapter most of the magnetic properties are discussed. This chapter is divided into three parts.

The part A of the chapter deals with Hysteresis studies. Hysteresis measurements were carried out on high field loop tracer. The value of saturation magnetization ($4\pi Ms$) is minimum for $NiFe_2O_4$ and $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and maximum for $Ni_{0.6}Zn_{0.4}Fe_2O_4$. It is observed that, saturation magnetization increases with increasing concentration of zinc upto x= 0.40 and then falls off with increasing in zinc concentration. This variation explained interms of cation distribution. The Y-K angles are calculated on the basis of existing formula. The zero values of Y-K angles for the composition $x \leq 0.20$, suggests the existence of Neel's two sublattice model and non-zero Y-K angles for the composition $x \geq 0.40$, suggests the existence of canted spin. The increasing Y-K angles indicates the more favoring of triangular spin arrangement on B site leading to reduction in A-B interaction. For x=0.40, the value of saturation magnetization of the ferrite prepared by oxalate precipitation method is higher than that prepared by ceramic [11] and citrate precursor [1] method. This high value is attributed to very low porosity of this ferrite.

The part B of this chapter deals with Curie temperature measurement . Curie temperature measurement was carried out by using Loria-Sinha technique. It is observed that Curie temperature decreases with increasing zinc content and is attributed to reduction in A-B interaction. The Curie temperature values obtained by Loria- Sinha technique are nearly same as those of observed in dc resistivity and ac susceptibility studies. The Curie temperature values were also calculated by using Upadhaya's model.

The part C of the chapter includes the ac susceptibility studies. The ac susceptibility measurement of samples were carried out in the temperature range 300 to 850 K by using double coil set up. The temperature dependence of normalized ac susceptibility is presented. The composition $x \leq 0.20$, suggests the existence of single domain particle nature and the composition $x \geq 0.40$, suggests the presence of multidomain particle. The addition of zinc forces the sample of go from SD to MD state [12].

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