Chapter V
Summary and conclusions

Ferrites are the technologically important materials. They possess interesting magnetic as well as electrical properties. The simultaneous requirement of the properties of ferrites in advanced electronics and microwave and computer technology has focussed the attention of many research workers on ferrites. Now-a-days the attention has been focussed on power ferrite materials which require high magnetization and resistivity. For such applications the nickel ferrite is the promising base material. Nickel ferrite has been found to be an inverse spinel ferrite having n type conductivity.

Non stoichiometry plays an important role in the properties of ferrites. A few workers have studied the electrical and magnetic properties of non-stoichiometric nickel ferrites. When the stoichiometric nickel ferrite is quenched from high temperatures, it shows significant changes in the magnetic properties. So in the present we have selected non-stoichiometric nickel ferrite samples to see the effect of quenching in air, water and magnetic field on their electrical and magnetic properties.

The present investigation involved the following steps -

1. Synthesis of $Ni_xFe_{3-x}O_4$ ferrites by the ceramic method (with x = 0.2, 0.4, 0.6, 0.8, 1.0)

2. X-ray and I.R.studies to confirm the formation of solid state reaction, to determine the lattice constants, bond lengths, site radii and vibrational frequencies.

3. Hysteresis and magnetization studies to understand the effect of quenching and non-stoichiometry.

4. Curie temperature measurement to investigate ferri to paramagnetic transition and the effect of quenching.

5. D.C. resistivity and thermo emf studies to understand the conduction mechanism, determination of activation energies in the ferri and para-region and to determine the type of conductivity.

6. Thermal variation of A.C. susceptibility to understand the domain structure.

7. A.C. conductivity to study the dielectric behaviour.

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 and magnetic are discussed. After discussing the properties, the applications and orientation of present work have been given at the end of the chapter.

The second chapter outlines the preparation and structural studies of $NiFe_2O_4$ ferrites. The chapter has been divided into three sections. These include preparation of the ferrites by ceramic method, characterizations by XRD and IR absorption studies.

Part A - The ferrite system $Ni_xFe_{3-x}O_4$ (with x = 0.2, 0.4, 0.6, 0.8, 1.0) was synthesized by the conventional ceramic method using the high purity oxides. The details of the actual sample preparation by using ceramic methods are given. The mechanism of solid state reaction and sintering process are also discussed. Other methods of preparation of ferrites are discussed and flowchart of preparation of ferrite is presented.

Part B - Analysis of x-ray diffractograms confirms the formation of spinel ferrites. The lattice parameter and interplaner distances were determined using usual procedure. The calculated interplaner distances are found to be in close agreement with the observed values. From the x-ray diffraction patterns, it can be seen that there is no impurity phase present. The value of lattice parameter for $NiFe_2O_4$ comes out to be 8.39 Å which is slightly larger than the reported value 8.34 Å . This is attributed to the cation distribution and Madulung constant. The bond length and site radii are calculated using X-ray data. There are no remarkable changes in these parameters as the composition is changed. X-ray density, actual density and porosity are also calculated.

Part C - IR spectra of $Ni_xFe_{3-x}O_4$ ferrite samples were recorded at room temperature and reveal two main absorption bonds as reported by Waldron earlier. The high frequency band ν_1 is attributed to intrinsic vibrations of tetrahedral ion complexes and lies in the range 570 cm^{-1} to 590 cm^{-1} while the lower frequency band ν_2 is attributed to the intrinsic vibrations of octahedral ion complexes and lies around 480 cm^{-1}. This difference in the band positions is expected because of the difference in the Fe^{3+}--O^{2-} distances for octahedral and tetrahedral complexes.

The third chapter deals with the electrical properties of the ferrite samples and it is divided into three sections. Part A' is devoted to d.c. conductivity, part B deals with thermo electric power and part C is devoted to a.c. conductivity.

Part A - The discussion related to conduction mechanism in metal oxides, ferrites and hopping mechanism in spinel ferrites is presented. The details of experimental techniques is also included. The plots of the logarithm of resistivity versus reciprocal temperature are linear upto Curie temperature and show a ferri and paramagnetic transition at Curie temperature. Such a transition is also observed by many workers in other ferrites. Conduction phenomena at low temperatures is due to the impurities while at high temperature, it is due to polaron hopping and magnetic ordering. Generally conduction in ferrites is explained on the basis of small polaron hopping model. The activation energies in the para region is generally found to be higher than that of the ferri region. The change in the activation energy at Curie point can be attributed to the effect of magnetic ordering in conduction process. The conduction by hopping process is due to large effective mass and low mobility of current carriers.

Part B – On the basis of sign of the thermo emf, the ferrite samples are found to be n-type semiconducting materials. The behaviour clearly indicates that the charge carriers are electrons. The small polaron model suggests that the thermo emf is independent of temperature. By using mobility relations we have calculated the activation energies and are nearly same as those obtained from resistivity. This confirms that the conduction in these ferrites is due to polaron hopping.

Part C – The dielectric behaviour is also presented here along with the brief discussion on Koops theory. The dielectric loss (tan δ) decreases rapidly with increasing frequency and then reaches a constant value. The resistivity with frequency plots also show a similar behaviour. The variation of dielectric constant with frequency reveals the dispersion due to Maxwell-Wagner interfacial polarization in agreement with Koops phenomenological theory. The dielectric constant decreases with increasing frequency and reaches a constant value for all samples.

The fourth chapter comprises of magnetic properties and is divided into three parts. Part A deals with hysteresis loop characteristics, part B includes the Curie temperature and part C gives a.c. susceptibility.

Part A - The properties of ferrites like anisotropy, magnetization, hysteresis behaviour are briefly discussed. The saturation magnetization (Ms) and magnetic moment (nb) increase with increasing nickel content. This variation can be explained in terms of cation distribution and nickel content. The observations were made both at room temperature and liquid nitrogen temperature. The Ms and nb values are higher at liquid nitrogen temperature than at room temperature. Also the values of Ms and nb are found to be higher for differently quenched samples than the slow cooled samples. If Nickel ferrite is cooled rapidly from higher temperatures a certain amount of Ni^{2+} ions are frozen on the A sites which cause a small change in magnetic moment. It has been shown that magnetic moment increases upon quenching.

Part B - For the direct determination of Curie temperatures of the samples the method based on the attraction between an electromagnet and the sample was used. Curie temperatures are nearly the same for all slow cooled samples of each compositions. For air quenched samples, Curie temperatures come out to be nearly the same as those for slow cooled samples. For water quenched and field quenched samples Curie temperatures are slightly lower in comparison with slow cooled samples. The Curie temperatures depend on the magnetic ordering and consequently the cation distribution.

Part C - 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 Xac - T curves it is clear that the samples contain multidomain particles.