CHAPTER IV
CHAPTER - IV
SYNTHESIS, CHARACTERIZATION & MEASUREMENTS

Introduction

The Spinel ferrite systems

1) \( \text{Ni}_{0.7} \text{Cd}_{0.3} \text{Al}_x \text{Fe}_{2-x} \text{O}_4 \) (\( x=0, 0.1, 0.2, 0.3, 0.4 \& 0.5 \))

and 2) \( \text{Ni}_{0.7} \text{Cd}_{0.3} \text{Cr}_x \text{Fe}_{2-x} \text{O}_4 \) (\( x=0, 0.1, 0.2, 0.3, 0.4 \& 0.5 \))

were prepared by the standard ceramic method. These systems were studied using the following experimental techniques.

1) X-ray diffraction

2) High field Magnetization

3) Low field a.c. susceptibility

4) D.C. resistivity

5) Dielectric properties

6) Thermoelectric power

4.1 Preparation of ferrites

The spinel ferrite systems \( \text{Ni}_{0.7}\text{Cd}_{0.3}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) and \( \text{Ni}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4 \) with \( x=0.0 \) to \( 0.5 \) in the steps of \( 0.1 \) were
prepared by the ceramic technique. The chemicals for ferrite systems were of analytical grade high purity oxides. For the first system NiO, CdO, Al₂O₃ & Fe₂O₃ (Merck) were used as starting chemicals and NiO, CdO, Cr₂O₃ & Fe₂O₃ were used for the second system. These oxides were mixed in proper proportion so as to yield the desired stoichiometry composition. Each of these compositions was ground for half an hour in an agate mortar. This mixture was then presintered at 850°C for 24 hours using a programmable furnace. The samples were then slowly cooled to room temperature. The presintered samples were again milled to fine powder. The powder was then pressed at around 5 tones/square inch of pressure to form pellets of about 1 cm in diameter. Pellets of good quality were obtained by using poly vinyl alcohol as binder & maintaining the pressure for about ten minutes each time. The pellets were finally sintered at 900°C for 24 hours and naturally cooled to room temperature. In all eleven samples were prepared, five for each of the two systems and one that of the base system.
4.2 X-Ray diffraction

To study the structural aspects of the prepared ferrite samples the X-Ray powder diffraction method was employed. The X-Ray diffraction patterns for all the samples of both the systems were recorded at the Department of Physics, Pune University, Pune on X-ray diffractometer. The X-Ray diffraction was taken with following considerations.

1) X-ray wavelength used Cu $K\alpha$ ($\lambda = 1.542$ Å)

2) Scanning rate 1° per minute

3) Range of $2\theta$ between 20° to 80°

4) Count rate of 4 x $10^3$ counts/sec

The schematic diagram of X-Ray diffractometer is shown in figure (4.1). The recorded XRD were used to determine lattice parameter, x-ray density and particle size of all the samples. Intensity calculations were carried out and cation distribution was determined using structure sensitive intensity ratios.
4.3 Magnetization Measurements

The magnetization measurements of each sample in the pellet form were carried out at room temperature using high field hysteresis loop trace technique. The values of saturation magnetization ($\sigma_s$) & magneton number ($n_B$) i.e. the magnetic moment per formula unit in Bohr magneton of all the samples were determined. The schematic diagram and experimental setup of the hysteresis loop tracer are shown in figure 4.2(a) and figure 4.2(b) respectively. The set up consists of electromagnet, pick up coil, phase correcting network, integration network, amplifier & C.R.O.

1) Electromagnet:-

The electromagnet consists of a copper wire wound on a U shape yoke made of high permeability iron. The U shape yoke produces high magnetic field between the pole pieces of the electromagnet. The intensity of magnetic field can be varied up to 5 KOe by variation of the alternating current supplied to the winding. The intensity of magnetic field is calibrated as 100 mA of current for 1 KOe of magnetic field.
2) **Pick up coil**

The pick up coil consist of two coils of equal area and equal turns of copper wire. The pick up coil can be inserted between the two poles of electromagnet. There is a gap in the middle of the coil where the sample in the pellet form was inserted in one of the coils. The terminals of the pick up coils are connected to the cathode ray oscilloscope. As alternating current was supplied to the electromagnet the field between the pole pieces was changing continuously. This changed the magnetic flux of the magnetic sample. As a result of the changing magnetic flux of the sample a voltage is developed in the pick up coils. This leads to the magnetizing cycle of the sample inserted in the coil. The hysteresis loop is obtained with the help of phase correcting network, integrated network & amplifier on the monitor of C.R.O. Hysteresis loop is then traced from the monitor of C.R.O.

First the instrument was calibrated by using the standard sample of pure nickel. The magnetization values of other sample were then determined with the help of calibration done with pure nickel sample. Pure nickel pellet has saturation magnetization of
54.39 emu/gm. Magnetization is noted on the Y-axis of C.R.O. Saturation magnetization was determined with the help of loop that appeared on C.R.O.

The calibration factor for Nickel sample is given by

\[ C.F = \frac{\text{Standard magnetization for Ni} \times \text{Mass of Ni sample}}{\text{Vertical displacement} \times \text{volt per div on C.R.O.}} \quad -- (4.1) \]

The vertical displacement ‘h’ in terms of mV is taken for all the samples & saturation magnetization is calculated using the relation.

\[ \sigma = \frac{h \times \text{volt per div on C.R.O.} \times \text{C.F}}{\text{Mass of the pellet}} \quad --(4.2) \]

The magnetic moment per formula unit is Bohr magneton \( (n_B) \) is given by

\[ n_B = \frac{\sigma \times \text{Molecular weight of the sample}}{5585} \quad --(4.3) \]

Thus the magnetization measurements are carried out using the above formula.
4.4 Low field a.c susceptibility measurement:

The measurements of the low field a.c susceptibility of the samples were made with respect to temperature within the range of 300 K to 850 K. A double coil set up as shown in the schematic diagram (figure 4.3(a)) was used for the measurements. The set up consists of Helmoltz coil, pick up coil, furnace and sample holder.

The Helmoltz coil consists of two coils made up of enameled copper wire wound on wooden stool. The two coils are fixed in such a way that a distance equal to their radius separates them.

The pick up coil also consists of two coils connected in series and wound in opposite directions. The pick up coil is located at the centre of Helmoltz coil. The turns of the pick up coil are in such a way that emf induced in them, nullifies each other.

The magnetic field was produced using double coil set up operating at the frequency of 260 Hz & r.m.s. field varied between 0 to 10 orested. Uniform magnetic field along the axis perpendicular to the coil is produced.

The temperature variation is achieved with the help of furnace made up of platinum wire wound on a silica tube so as to
eliminate inductance effect. This coil is kept inside a tube which is properly insulated from outside by asbestos sheets. A glass jacket with a provision of water circulation was used to avoid over heating of the coils. The temperature of the furnace is measured with the help of Pt-Rh thermocouple.

The sample holder was a quartz tube of about 30 cm long & 1.5 cm in diameter. The sample was placed inside the sample holder tube. The thermocouple was inserted in such a way that it touched the sample. At various temperature the signal corresponding to magnetic moment were recorded. The measurements were carried out from room temperature to well beyond the curie temperature (Tc).

Figure 4.3(b) shows the experimental set up for a.c susceptibility.

4.5 Electrical resistivity measurements with temperature:

The d.c electrical resistivity of the prepared sample was measured by two probe method. The experimental set up consists of sample holder, furnace, temperature controller & d.c power
supply. For good electrical contact the pellets were polished and silver paste was applied on the end surfaces.

A typical sample holder for resistivity measurement is shown in figure 4.4. It consists of two ceramic beads with supporting stainless steel rods. One of the stainless steel rods introduced into the ceramic beads is spring-loaded so as to press the surfaces of the pellets. The other rod is fixed at the other end. The sample in the pellet form was placed in the sample holder between the two rods. This sample holder assembly with pellet was placed in the electric furnace. The experimental setup is shown in figures 4.5(a) and 4.5(b).

The temperature of the furnace was controlled by adjusting current passing through the heater coil by means of dimmer stat. The temperature of the sample was measured by Cr-Al thermocouple. The measurements were carried out for all the samples from room temperature to well beyond Curie temperature. During the measurement sufficient time was allowed for every sample to attain equilibrium temperature.
The d.c resistivity measurements were carried out adopting the simple principle of voltage current characteristic (V=IR)

The resistivity (ρ) was calculated by using relation

\[ \rho = \frac{\pi r^2}{t} R \text{ Ohm. cm.} \quad ----(4.4) \]

where, \( r \) is radius of the pellet

t the thickness of the pellet and

R the resistance of the pellet

A graph of \( \log \rho \) verses \( l/T \) was plotted & activation energies were determined from the slope of the plot.

4.6 Thermoelectric Power Measurements:-

The thermoelectric power measurements were carried out in the temperature range from 300 K to 500 K by differential method. The experimental set up consists of a sample holder with two non-magnetic copper electrodes between which the sample is firmly fixed. An auxiliary heating coil is fixed to the upper electrode for additional heating & to maintain a temperature gradient of about 10 K between the two sides of the sample. The temperature of the two
faces of the sample was measured by two Cromel-Alumel thermocouples, which are kept very close to the sample. Thermo e.m.f was measured between the two electrodes with the help of digital voltmeter. Seebeck coefficient, charge concentration & drift mobility were determined. The experimental setup for thermoelectric power measurement is shown in figure 4.6.

4.7 Dielectric Properties Measurements:-

The dielectric measurements were carried out as a function of temperature for all the samples using two probe method with L-C-Q-R meter (figure 4.7(a)). The experimental set up is shown in figure 4.7(b). Measurements of ac resistance, capacitance & quality factor were taken at 1 KHz frequency for various temperatures.

The dielectric constant was calculated using the following relation.

\[
\varepsilon' = \frac{Cd}{\varepsilon_0 A}
\]

\[\text{--( 4.5)}\]

where, \(C\) is the capacitance,

\(d\) is the thickness of pellet,
A is cross sectional area of the flat surface of the pellet &

\( \varepsilon_0 \) is the permittivity of free space.

The value of dielectric loss tangent (\( \tan \delta \)) was calculated using the relation.

\[
\tan \delta = \frac{1}{2\pi \varepsilon_0 f} \times \frac{1}{\rho_{AC} \varepsilon'}
\]  
\[(4.6)\]

where, \( \rho_{AC} \) is the ac resistivity and

\( f \) is the frequency of applied signal.

The dielectric loss (\( \varepsilon'' \)) was calculated using the relation

\[
\varepsilon'' = \varepsilon' \tan \delta
\]  
\[(4.7)\]
Figure 4.1 Schematic diagram of X-ray Diffractometer.
Figure 4.2(a) Schematic diagram of Hysteresis loop tracer
Figure 4.2(b) Experimental setup of hysteresis loop technique.
Figure 4.3(a) Schematic diagram of the a.c. susceptibility apparatus.
Figure 4.3(b) Experimental setup of a.c. susceptibility.
Figure 4.4 Sample holder for resistivity measurements.
Figure 4.5(a) Experimental setup for d.c resistivity.
Figure 4.5(b) Experimental setup of d.c. resistivity.
Figure 4.6 Experimental setup of thermoelectric power.
Figure 4.7(a) Block diagram for dielectric constant measurement.
Figure 4.7(b) Experimental setup of dielectric constant.