
CHAPTER - III



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CHAPTER -III

Experimental Techniques

3.4 General Introduction

The various methods have been used in the synthesis of magnetoelectric composites. Among these, the solid state reaction method (ceramic method) has been widely employed and the properties of resulting materials studied extensively [1, 2]. The ceramic method for the preparation of composites was preferred over the other methods because ceramic method is easier and cheaper than other methods. Further, the preparation of composites by ceramic method offer certain advantages such as choice of mole ratio of constituent phases, free choice of sintering temperature etc [3].

The properties of composites depend on the purity of the starting material, mixing, sintering temperature and the time of sintering. Also it depends upon the micro structural factors like grain size, dopant concentration, porosity etc. which considerably affect the properties of composites. Hence, during the preparation, various factors are controlled to have a good quality of the composites. The prepared material; was

characterized by standard technique like X- ray diffractometer, Infrared spectroscopy etc.

3.5 Preparation of composite materials

Ceramic method of preparation

This is the most widely used and accepted commercial method for the preparation of ferrite, ferroelectric and their composites. In this method, metal oxides are thoroughly and uniformly mixed with special techniques. This mixture of ferrite and ferroelectric is sintered for a prolonged time at a specified temperature in order to attain solid-state reaction among the oxides and the formation of the compound.

The ceramic method consists of the following stages.

- (1) Intimate mixing of correct molar proportions of oxides as required for the final product.
- (2) The process of “pre-sintering” involves heating the intimate mixture of raw materials. The purpose of this method is to decompose carbonates and higher oxides there by reducing the evolution of the gas in the final sintering process [4]. It helps in homogenizing the material and control the shrinkage of the material which otherwise occurs during the final sintering. In solid-state reaction the raw material partly reacts to produce the final product. The rate of reaction depends upon the reactivity of the components as well as the pre-sintering temperature.

(3) The pre-sintered powder is ground to a fine powder so as to reduce the particle size and to promote the mixing of any un-reacted oxides. The resulted powder is then pressed to the required shape using the binder polyvinyl alcohol by using a conventional die applying pressure of several tons from a hydraulic press. Thus, the pellets of required shape are formed.

(4) For a good quality of ferrite, ferroelectric and their composites the grain size should be uniform. This can be achieved in the final sintering.

(5) The final sintering involves heating the pressed material to a high temperature. The sintering is done to increase the density and hence to reduce porosity. The final microstructure together with correct oxygen content and cation distribution depends upon the time and temperature of sintering. In the final sintering it is not always possible to obtain desired microstructure. The ability to apply pressure to a material in addition to firing temperature increases the possibility of obtaining required microstructure and improved physical properties. Such a technique is known as hot pressing. The hot pressing technique gives fully dense material with small grain size. The ferrite, ferroelectric and their composites prepared by this method have high density and are

useful in high frequency applications. The flowchart for preparation of ferrite, ferroelectric and their composites are shown in Fig. 3.1

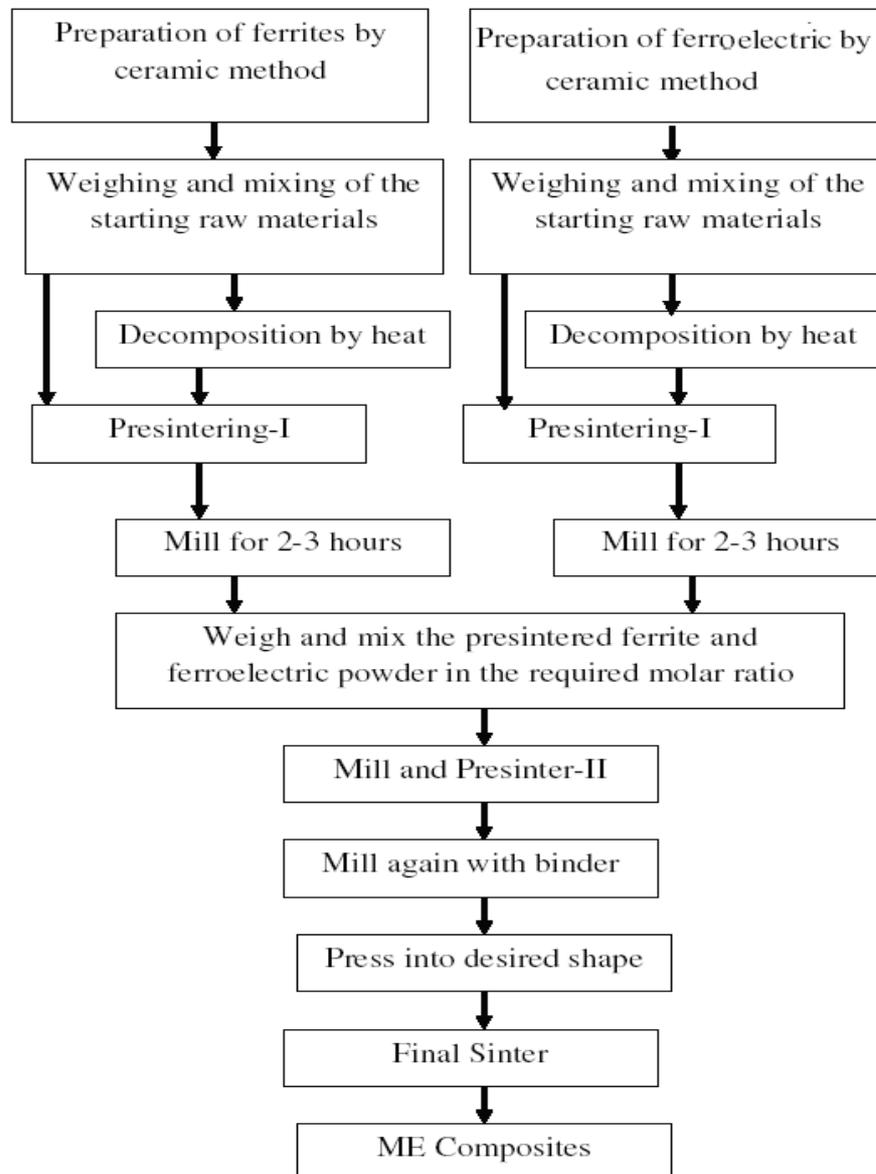


Fig. 3.1 Flow chart of preparation of ferrites, ferroelectrics and their composites.

3.6 Structural analysis by X-ray diffraction.

a) Introduction

X-ray diffraction method is widely used for characterization of composite materials. It also provides the information about amorphous content of the sample, crystallite size, crystallinity, solid solutions, stress and texture. Bragg discovered the study of crystal structure by x-ray diffraction in 1912. X - ray diffraction technique is a well-established tool to study crystal structure and confirm to the formation of solid state reaction.

b) Condition for X-ray diffraction

According to Bragg, the diffraction is possible when the wavelength of X-ray is comparable to interplaner distance (d)

The Bragg's condition is given by-

$$2d \sin\theta = n\lambda \quad \dots\dots\dots(3.1)$$

where,

d = interplaner distance.

θ = angle of diffraction.

n = order of diffraction.

λ = wavelength of monochromatic X-rays.

c) X-ray diffractometer

The schematic diagram of the X - ray diffractometer is shown in Fig. 3.2. The specimen 'c' is in the form of a fine powder that is mounted on table 'H' which is capable of rotating about an axis passing through 'O'. The incident beam of X-rays is allowed to pass through the slit 'A' of the collimator. As the crystallites are randomly oriented, a reflection of particular position is due to a set of atomic planes, which satisfy Bragg's condition. The diffracted beam gets converted and focused at slit 'F', which further enters the counter 'G', connected to a count rate meter. The output of the circuit is fed to an automatic recorder which registers count per sec (2θ). The location of the centroid of the recorded peak gives $2\theta_{hkl}$ for corresponding Bragg's reflection.

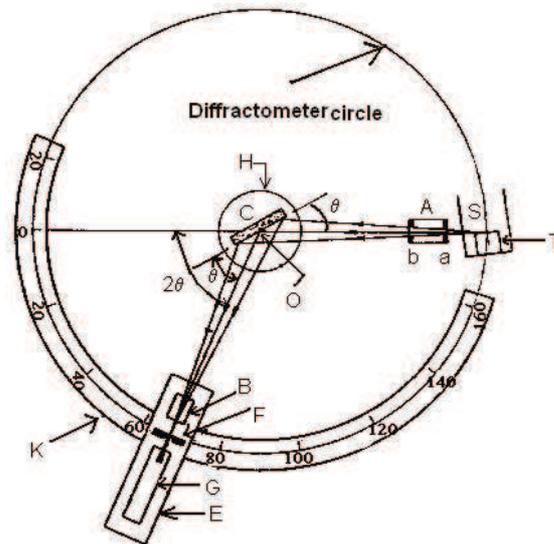


Fig 3.2 Schematic diagram for the X-ray diffractometer.

However, in modern X-ray diffractometer a proportional or scintillation counter is mounted which records automatically a graph of intensity 2θ angle. The main advantage of the diffractometer over the Debye Scherrer camera is that it gives a quantitative measure of intensity of diffracted beam. X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayer and atomic arrangements in amorphous materials (including polymers) and at interfaces.

3.4 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the micro structural characteristics of materials. The reason for using the SEM is the high resolution and appropriate magnification. With the help of SEM photograph we can study grain size, grain boundaries etc.

a) Grain size calculation:

Calculation of grain diameter or grain size is done using Cottrell's method [5]. This method gives the relation between the number of

intercepts of the grain boundary per unit length (PL) and total number of intercept (n) as

$$P_L = \frac{n}{2\pi r} M \quad \dots\dots\dots(3.2)$$

where, M is the magnification, r is the radius of circle and n is the number of intercepts. Using P_L , grain diameter (L) can be calculated as

$$L = \frac{1}{P_{L-1}} \quad \dots\dots\dots(3.3)$$

b) Bulk density

The bulk density of samples was determined by liquid immersion technique, The actual density of the samples can be measured by Hendricks and Adams methods [6]. The method depends upon the weight of sample in air and weight in a liquid of known density in which the sample is insoluble. For these samples xylene was used. The actual density (d_B) was calculated using the formula.

$$d_B = \frac{\text{weight of sample in air}}{\text{weight of sample in air} - \text{weight in xylene}} \times 100 \quad \dots\dots\dots(3.4)$$

c) X-ray density

The X-ray density of the samples was calculated using the following relation,

$$d_x = \frac{BM}{N_{abc}} \quad \dots\dots\dots(3.5)$$

where M is a molecular weight

N is a Avogadro's number (6.023×10^{23})

a, b and c are the lattice constant,

for ferrite phase x-ray density is calculated by

$$d_{x_{\text{ferrite}}} = \frac{zM}{Na^3} \dots\dots\dots(3.6)$$

For ferroelectric phase having tetragonal Perovskite structure the X-ray density is calculated by

$$d_{x_{\text{ferroelectric}}} = \frac{zM}{Na^2c} \dots\dots\dots(3.7)$$

And for composite X-ray density is calculated by

$$d_{x_{\text{composite}}} = (M_1+M_2) / (V_1+V_2) \dots\dots\dots(3.8)$$

where M_1 is (1-x) times molecular weight of ferrites and M_2 is x times molecular weight of ferroelectric

$$V_1 = (M1)/d_{x_{\text{ferrites}}} \text{ and } V_2 = (M2)/d_{x_{\text{Ferroelectric}}}$$

d) Porosity

The percentage porosity (P) of the samples was determined using the values of bulk density and X-ray density. The relation used to determine porosity is given by,

$$\text{Percentage porosity} = \frac{d_x - d_B}{d_x} \times 100 \dots\dots\dots(3.9)$$

Where d_x is x-ray density and d_B is the actual density.

3.7 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) is a standard procedure for identifying and quantifying elemental composition of sample areas as small as a few cubic micrometers. Characteristic x-ray are produced when a material is bombarded with electrons in an electro beam instrument, such as a SEM. Detections of the X-ray can be accomplished by an energy dispersive spectrometer, which is a solid state device that discriminates amount of X-ray energies. EDS provides the analytical information including qualitative analysis, quantitative analysis, line profile analysis and elemental mapping.

3.8 Infra-red (I.R.) spectra

When a molecule interacts with a radiation of a proper frequency, it absorbs energy and the molecule is set into vibration. By measuring transmission energy as a function of radiation frequency, one can determine which frequency has been absorbed by the sample. The resulting plot of energy versus frequency is the infrared spectra of the sample. Electronic radiation, in which wavelength lies in the range 1 micron to 1 mm is known as infrared radiation, it has a wavelength just little longer than that of the visible light range. The comprehensive study of I.R. spectra of the ferrites in the wave number 200 cm^{-1} to 800 cm^{-1} is useful in understanding the structural properties. The infrared spectroscopy studies are useful to determine local symmetry in crystalline

and non-crystalline solids and also to study the ordering phenomenon in ferrites. Studies of the relation between structure and electromagnetic response of ferromagnetic semiconductors are useful in understanding their properties. Since the electrical and magnetic properties of these materials are destructively dependent on the prescribed configuration of the atoms or ions the structure, method of non-destructive analysis are specially suited to such investigation. In particular, vibrational, electronic and magnetic dipole spectra can give information about the position and valence of the ions in the crystal lattice. In the infrared region the molecular vibrations gives rise to absorption bands in the ferrites, which help to compute the vibrational energy of the molecules.

3.7 Magnetic studies

a) Magnetization

The saturation magnetization, coercivity, remanence magnetization etc. magnetic properties are measured using pulse field magnetic hysteresis loop tracer supplied by Magneta Company. The measurements were carried out at room temperature. The experimental setup for hysteresis loop technique is shown in Fig. 3.3.



Fig 3.3 Experimental setup for Hysteresis loop technique

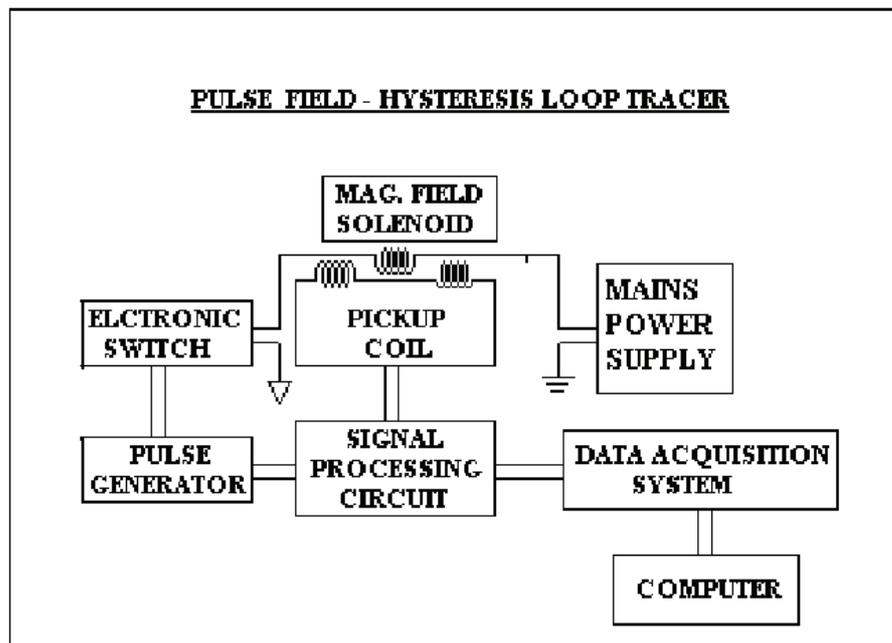


Fig 3.4 Schematic of pulse field hysteresis loop tracer system

The system consists of pulse power supply, solenoid and pick up coil assembly, signal processor and data acquisition system.

1. Solenoid and Pick-up Coil Assembly

The solenoid is wound on a high quality Bakelite former with an enameled copper wire. A pickup coil system is wound with a fine copper wire on a former concentric with the solenoid. It consists of two main windings whose resultant voltage is very nearly balanced. An additional winding is used for perfect balance. The output of this winding is connected to a balancing network consisting of a magnitude and phase balance. The assembly containing the solenoid and pickup coil is housed in an acrylic box.

2. Signal Processor

The signals produced in the pickup coil are proportional to the rate of change of magnetization of the sample as well as to the applied field. These are processed using integrating, amplifying and phase correcting circuits to produce signals representatives of magnetization of the sample and the applied magnetic field.

3. Data Acquisition System (DAS)

The Data Acquisition System consists of a micro-controller with fast digitizing and high resolution circuit. The digitized data is sent to a PC through RS-232 port. Special software is designed to plot the hysteresis

loop and display the hysteresis parameters. Measurement was taken after applying magnetic field of 5 KOe having the magnetization sensitivity 10 emu with accuracy 1 to 5 %. High magnetic field is generated in a solenoid by passing a pulse current of sinusoidal shape. A pickup coil system is kept in solenoid to detect field and magnetization signal of a sample placed in the pickup coil. The signals produced are then processed by an electronic system. These transitory signals are digitized by a micro-controller and then sent to computer for plotting a hysteresis loop, which is observed on the monitor with calculated values of hysteresis parameters. The hysteresis loop gives the values of coercivity (H_c), remnant magnetization (M_r) and saturation magnetization (M_s).

3.9 A.C. susceptibility

The Curie temperature of each sample was determined from the low field a.c. susceptibility data. The measurements of a.c. susceptibility were carried out in the temperature range 300K – 800 K. From the plots of χ_T / χ_{RT} versus temperature, Curie temperature of the sample is obtained.

The experimental setup for the thermal variation of a.c. susceptibility is as shown in Fig. 3.5 the setup consists of

- a) A.C. susceptibility unit,
- b) Solenoid and pickup coil assembly,
- c) Platinum furnace,

- d) Furnace power supply,
- e) Thermocouple and temperature indicator.

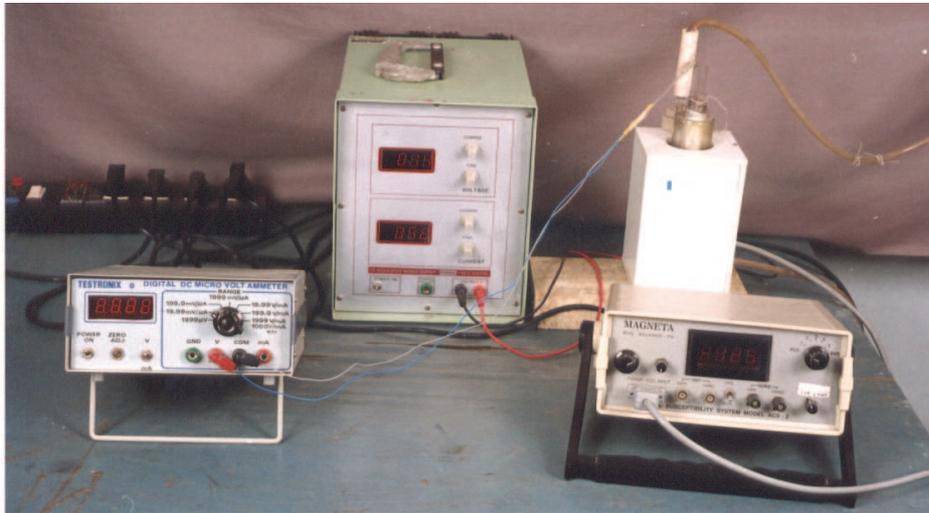


Fig. 3.5 Experimental setup for thermal variation of a. c.

Susceptibility.

a) A.C. susceptibility unit: Model ACS 2A

The schematic diagram of a.c. susceptibility unit is shown in Fig. 3.6. It consists of function generator, balancing circuit and signal processing circuit based on lock-in amplifier principle.

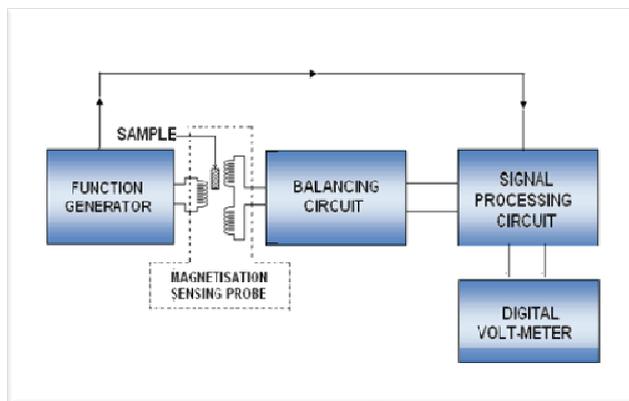


Fig. 3.6 Schematic diagram of a.c. susceptibility system.

b) Solenoid and pickup-coil assembly

The pickup coil is wound in two sections comprising three windings. The main two windings are identical and wound in opposition direction. The sample under test is placed in the vicinity of one of the windings producing a differential voltage proportional to the magnetization of the sample.

c) Platinum furnace

The sketch of the furnace is shown in Fig. 3.7. The platinum wire is wound on a quartz tube of diameter 18 mm and wrapped with a fiber glass ribbon and pushed tightly in another quartz tube. The furnace is introduced in a double wall jacket which can take water for cooling the outer region of the furnace. This whole assembly is put into the solenoid and then held in a container.

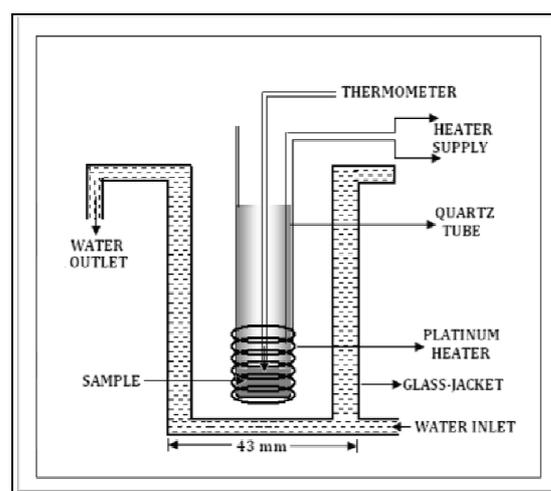


Fig.3.7 Schematic diagram furnace assembly.

d) Furnace power supply

It is a regulated d. c. power supply whose voltage and current can be varied continuously in the range 0-30 volts, 0-5 amperes respectively.

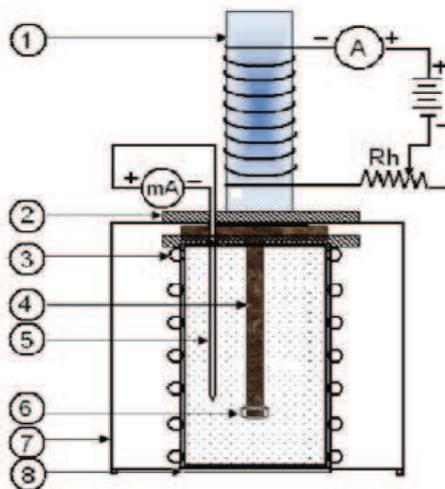
e) Thermocouple and temperature indicator:

The thermocouple is Platinum-Platinum-Rhodium (13%) junction which is terminated into a linear temperature indicator and also into one channel of Data Acquisition Unit. When the thermocouple is in good contact with the samples, the temperature indicator directly reads the temperature of the sample.

3.9 Curie temperature measurement by Loria technique

The Loria technique is the most simple and versatile technique to measure Curie temperature of magnetic materials. A schematic diagram of the experimental setup is shown in Fig. 3.8 and Fig.3.9. The electromagnet and the soft iron piece well insulated from each other by using a porcelain sheet. The soft iron piece, which is kept at the center of the furnace, gets magnetized due to the electromagnet [7]. The temperature of the sample is measured using a calibrated chromel - alumel thermocouple. A ferrite sample in the form of pellet is fixed to the soft iron piece and introduced into the furnace. The position of pellet is confirmed with the help of the mirror. The temperature of the sample is

increased slowly by gradually increasing the current in the heating coil with the help of a dimmer stat. The temperature at which the ferrite sample loses its magnetization and drops is measured with the help of thermocouple. The procedure is repeated for other pellets of the same sample an average value of Curie temperature is determined.



3.8 The experimental setup of Loria technique used to measure Curie temperature.



3.9 Experimental set up for Loria method

3.10 D. C. electrical resistivity

D.C. resistivity of all the samples of the system $\text{CoMn Fe}_2\text{O}_4 + \text{BaTiO}_3$ was studied by using two probe methods in the temperature range 300K to 800K. The experimental set up for measurement of d.c/a.c resistivity is shown in Fig 3.10.



Fig.3.10 Experimental setup for d.c. electrical resistivity

measurements

The sample pellets were polished gently to have smooth parallel surfaces and then they were coated with silver paste for good electrical contact this polished and coated pellets were held in a sample holder and whole assembly was place in electrical furnace. The temperature of which can be controlled by temperature controller. Calibrated chromium – aluminum thermocouple was placed in contact with the sample to know the gradual heating of it. The resistance of each pellet was measured for decreasing temperature the resistivity ‘ ρ ’ of each sample was calculated with the help of following formula.

$$\rho_{dc} = \frac{R(\pi r^2)}{t} \dots\dots\dots(3.10)$$

where, ‘r’ is radius of the pellet ‘t’ is thickness of the pellet ‘R’ is resistance of the pellet. The graph of $\log \rho$ Vs $1000/T$ are plotted to study the resistivity behaviour of sample. These graphs are the straight lines with change in their slopes at particular point, showing clearly the two straight lines with different slopes. This indicates that there is change in behaviour of samples from ferromagnetic to paramagnetic at a certain temperature.

The temperature at which the slope changes corresponding to the Curie temperature. Above which ferrimagnetic sample is converted into paramagnetic sample.

3.11 Dielectric Properties

The measurement of dielectric constant (ϵ'), dielectric loss (ϵ'') and dielectric loss tangent ($\tan\delta$) were carried out as a function of frequency ranges from 100 Hz to 1MHz.

The dielectric constant ϵ' was determined by using relation.

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \dots\dots\dots(3.11)$$

where, C is capacitance, d is thickness of the pellet,

ϵ_0 is permittivity of the free space,

A is area cross-section of the pellet.

The dielectric loss (ϵ'') was calculated by using relation

$$\epsilon'' = \frac{1}{(2\pi \times 1000 \epsilon_0)} \times \sigma \dots\dots\dots(3.12)$$

where σ is a.c. conductivity,

The dielectric loss tangent ($\tan \delta$) was calculated using the relation

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \dots\dots\dots(3.13)$$

3.12 Magnetoelectric effect

3.12.1 Measurement Techniques of ME effect

There are three methods for the measurement of ME output.

a) Static method

In this method, the ME output (voltage) is measured as a function of increasing magnetic field using electrometer having high input impedance. The experimental set up for static method is simple and one can get rid of the magnetic loss produced by recurring cycles of magnetization due to the superimposed ac magnetic field.

b) Quasi static method

It involves a time varying dc magnetic field, the output is measured as a function of time. This method is useful for single crystal, while in polycrystalline materials, the charge built up at the grain boundaries affects the ME output.

c) Dynamic method

In this method, the ME output voltage is measured with a basic AC magnetic field i.e. the measurement is carried out with a D. C. magnetic field in the presence of AC field. The bias AC magnetic field will not allow the charges to move towards the electrodes; hence a suitable signal with an appropriate frequency is used where the polarity of the signal changes with time. The static measurements have been carried out in the present work. Thus, the static ME voltage coefficient $(dE/dH)H$ is a measure of the change of output ME voltage with increasing dc magnetic field, measured with respect to a constant flux of magnetic field [8].

3.13 Experimental Procedure

ME voltage coefficient i.e. (dE/dH) was measured by static method. In order to measure this ME output, the composite samples has to be poled both electrically and magnetically. Since in the ME composites the electric polarization is a function of the applied electric and magnetic fields, one can apply them simultaneously and measure polarization. They have measured the polarization by keeping the electric field constant and varying the magnetic field. Thus, the ratio of the increase in polarization per unit increase in magnetic field gives the ME coefficient.

a) Electric poling

For electric poling, the samples were heated up to 30 - 40⁰C above the ferroelectric Curie temperature (T_c) and cooled under the influence of an external electric field of 3 KV/cm to room temperature. The transistorized regulated power supply was used for the poling of palletized samples. The pellets were heated above the ferroelectric Curie temperature to switch the ferroelectric domains in the direction of an external electric field. [9].

b) Magnetic poling

The samples were poled magnetically by applying an external d.c. magnetic field of about 5KOe at room temperature, for the magnetic poling, laboratory made sample holder was fitted between the poles of a

d.c. electromagnet. Two silver electrodes were drawn from either sides of the pellet. The stray charges developed during poling were removed by grounding the plates of sample holder. The ME signals were registered by measuring the developed electric potential across the sample as a function of applied increasing d.c. magnetic field. The output ME voltage generated in the sample was measured using Keithley's electrometer (Model 2000). The static ME voltage coefficient $(dE/dH)H$ is calculated by change in ME output voltage with respect to d.c. bias magnetic field at a constant applied flux of magnetic field [10, 11].

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