3.1. Chapter Introduction

As mentioned earlier, a multiferroic is a material that possesses ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase. This implies that they possess spontaneous magnetization which can be reoriented by an applied magnetic field, spontaneous polarization which can be reoriented by an applied electric field and spontaneous deformation which can be reoriented by an applied stress. It is, however, customary to exclude ferroelasticity and only consider magnetic and ferroelectric characteristics.

Multiferroic behavior in Rare earth manganites especially with orthorhombic structure is very interesting because they are expected to exhibit incommensurate antiferromagnetic (ICAFM) order below 40 K. Apart from this, these materials also exhibit spin frustration, lock-in transitions and ferroelectricity in the low temperature regime. In order to understand all these complexities in these materials, a systematic investigation of their magnetic and ferroelectric behavior is essential. For this purpose, measurement of magnetic and dielectric properties was undertaken. Similarly, in order to see both the magnetic and ferroelectric properties in a single measurement, a common property viz., specific heat studies have also been undertaken. Experimental procedures adopted in these three measurements are given in detail in this chapter.

3.2 Magnetization measurements

Magnetization studies over a wide temperature range explain various phenomena exhibited by these materials. From the magnetization data, susceptibility ($\chi$) values can be computed. In fact, based on these studies one may find the type of magnetism present in the material under investigation. For example, if the extrapolated $1/\chi$ vs $T$ plot cuts the positive X-axis, the material is ferromagnetic. On the other hand, when it passes through the origin the material is paramagnetic while the negative intercept on X–axis indicates the antiferromagnetic behavior of the material. In view of this, a systematic investigation of magnetization studies was undertaken in two fixed magnetic fields (0.05 T and 0.5 T) over a temperature range of 4–300 K (M Vs T).
3.2.1 Principle of the measurement

In the present investigation, the magnetization of the samples was measured using the well-known principle based on Faraday’s Law of induction. According to this law, whenever relative motion exists between a conductor and a magnetic field a voltage is induced in the circuit and that the magnitude of this voltage is proportional to the rate of change of the flux. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidally with the help of a piezoelectric oscillator. The induced voltage in the pickup coil as shown in Figure.3.1, is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material. The vibrating sample magnetometer measures the magnetization of a small sample of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an ac electrical signal.

Figure 3.1 Schematic representation of a VSM
In the present investigation PPMS-VSM (PPMS-16) with Quantum make has been used (Figure 3.2) by applying a maximum field of ±140 kOe. The description of the experimental set up is given here.

3.2.2 Description and working of VSM

Heart of the instrument is NbTi/Nb$_3$Sn hybrid 16-Tesla (@4.2K) longitudinal magnet. The PPMS probe is inserted into Dewar/magnet assembly. This design optimizes for cryogenic efficiency leading to an expected He boil off rate of ~ 6 liters/day. A pair of specially designed High-T$_C$ magnet leads is used mainly to reduce the helium boil-off during high field magnet field sweeps. The basic measurement is accomplished by oscillating the sample near a detection (pickup) coil and synchronously detecting the induced voltage. By using a compact gradiometer pickup coil configuration, relatively large oscillation amplitude (1-3 mm peak) and a frequency of 40 Hz, the system is able to resolve magnetization changes of less than 10$^{-6}$ emu at a data rate of 1 Hz. The VSM option for the PPMS consists primarily of a VSM linear motor transport (head) for vibrating the sample, a coil set puck for detection, electronics for driving the linear motor transport and detecting the response from the pickup coils, and a copy of the MultiVu software application for automation and control.

The sample is attached to the end of a sample rod that is driven sinusoidally. The centre of oscillation is positioned at the vertical center of a gradiometer pickup coil. The precise position and amplitude of oscillation is controlled from the VSM motor module using an optical linear encoder signal read back from the VSM linear motor transport. The voltage induced in the pickup coil is amplitude and lock-in detected in the VSM detection module. The VSM detection module uses the position encoder signal as a reference for the synchronous detection. This encoder signal is obtained from the VSM motor module, which interprets the raw encoder signals from the VSM linear motor transport. The VSM detection module detects the in-phase and quadrature-phase signals from the encoder and from the amplified voltage from the pickup coil. These signals are averaged and sent over the CAN bus to the VSM application running on the PC.
Figure 3.2 Magnetization measurement system.
3.3. Dielectric constant measurements

Multiferroic materials have been the subject of intensive research due to their interesting magnetic and electric properties and the mutual correlation between magnetic and ferroelectric orderings in the same phase. In fact, magnetism and ferroelectricity (FE) in perovskites seem to exclude one another. All conventional FE perovskites containing transition metal (TM) ions have such ions with the formal configuration $d^0$, i.e. they have an empty d-shell (of course not all such systems are ferroelectric, the well-known example being the ‘‘virtual’’ ferroelectric SrTiO$_3$); thus this ‘‘$d^0$-ness’’ seems to be the necessary, but not sufficient condition for FE in this class of materials. All the known FE perovskites contain TM ions with empty d-shells: Ti$^{4+}$, Ta$^{5+}$, W$^{6+}$ etc. However, as soon as we have at least one or more real d-electrons on the d-shell, such systems may be magnetic, but they are never FE.

When considering the microscopic conditions for the coexistence of magnetism and ferroelectricity, one has to note that, whereas the microscopic nature of magnetic ordering is, in principle, the same in most strong magnets (it is an exchange interaction of predominantly localized magnetic moments), this is not the case with ferroelectricity. There exist many different mechanisms of FE ordering and different types of FE. In contrast to magnetism, real microscopic mechanisms of FE are, in many cases, not well understood. In fact, FE in rare earth manganites (RMnO$_3$ and RMn$_2$O$_5$) systems appears only in certain magnetically ordered states, it is probably not surprising that the coupling between magnetic and electric subsystems in them is especially strong, and one can expect giant effects. In fact, materials with electric dipoles induced by magnetic ordering are the best candidates for useful multiferroics, because such dipoles are highly tunable by applied magnetic fields. Therefore, when discussing multiferroic systems, the main problem lies in the FE part of the story. To understand the nature and origin of the ferroelectricity in these materials a systematic investigation of dielectric constant measurements were carried out. The principle involved in the measurement of the dielectric constant and details of the apparatus are given in the following sections.
3.3.1. Principle involved in the measurements

The definition of dielectric constant ($\varepsilon$) of a given material is given by a well-known relation,

$$\varepsilon = \frac{C}{C_0}$$

where $C$ and $C_0$ are the capacitances of the given material and free space respectively. Here the capacitance of the free space is given by,

$$C_0 = \varepsilon_0 \frac{A}{d},$$

where $\varepsilon_0$ is the permittivity of the free space, ‘A’ the area of the plate and ‘d’ the distance between the plates. Care is also taken to consider the capacitances of both the electrode and connecting wires while calculating the dielectric constant. Proper grounding and guarding are also to be provided.

The dielectric constant of the materials of present investigation was measured by the parallel plate capacitor technique. The salient features of the technique used in the present investigation are explained briefly here. The test sample, with the complex dielectric function $\varepsilon'(f)$ is placed between the plates of a parallel plate capacitor experimental set up as shown in skeleton diagram (Fig.3.3). The ac voltage $U_S$ with the frequency of $f$, is applied to the sample from a signal generator. The resistor $R$ converts the sample current $I$ into a voltage. The amplitudes and the phases of ac voltage $U_S$ and the sample current $I$ are measured with the help of two phase sensitive voltage meters. If

$$Z = \frac{U_S}{I}$$

(1)

denotes the impedance of the sample capacitor, its complex capacity is calculated from

$$C = -i/2\pi fZ$$

(2)

Neglecting the border effects, the dielectric function is obtained from the standard equation of parallel capacitor

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$

(3),

where $d$ is the distance between the plates, $A$ is the area of either plate, and $\varepsilon_0$ is the permittivity of the vacuum.
3.3.2 Working of experimental set up: -

In the present studies, dielectric constant measurements were performed using Novo control Alpha-A high frequency analyzer. The description of the experimental set up is given here.

To measure the dielectric constant of the sample, commercially available equipment provided by the NOVO Control Dielectric Spectrometer was used. It works over a wide frequency band of $10^6$ to $10^7$ Hz. It provides fast accurate measurement of the dielectric/electrical properties of the solid materials over a wide range temperature and frequencies was used, where the measurements are made automatically and the data are processed on-line into any convenient form like permittivity, capacitance, tan δ, impedance etc. vs. frequency or temperature, or dc bias. This equipment is named as Alpha –A High Performance Frequency Analyzer. Alpha–A has an accessory which boosts the power of characterization of materials; HVB-1000 High Voltage Impedance Interface, which is described in detail in the next sections.

Dielectric constant was measured by using the configuration of parallel plate capacitor method. The sample holder has a sprig-loaded arrangement, the upper and lower electrodes are made of copper (diameter approx. 5 mm), and insulated by Hylam
from the other conducting part of the probe. A heater is wound at the lower electrode-extension to achieve the desired temperatures. A calibrated platinum resistance thermometer (PRT) (PT100, Lake Shore) is mounted in a slot in the lower electrode. For the purpose of the vacuum sealing grease-cone & cup method (both machined from brass and the cone brazed on a steel pipe) was used. The lower and upper parts of the sample holder are shown in Figure 3.4.

The sensor has four wire configurations to read its resistance and the heater has two wire configuration, these connections of heater and sensor are connected to the temperature controller (Lake Shore) through the Lake Shore feed through 19-pin vacuum–compatible connector. To take the signal from the sample electrodes, a high voltage rating (750V) RF Cryo Coaxial cable (Lake Shore) was used.

The center parts of the two coaxial cables which carry the signal are connected one each to the electrodes. Special save high voltage (SHV) connectors are necessary to connect the coaxial cables to the meter because they have high insulation quality. The
total probe length is approximately 130 cm, to minimize the thermal leaks all feed through wiring is anchored wound down over a hollow thin rod of steel which contains 9 baffles over its vertical length. These connections were given to Alpha-A High Performance Frequency Analyzer (Figure 3.5) and a High Field Booster (HVB-1000) (Figure 3.6). The nature of charge motion, and its associated relaxation, inorganic and organic materials may be investigated using broadband Alpha-A High Performance Frequency Analyzer by NOVO Control. With the HVB-1000 connected, the system can create up to $\pm 500V_{pp}$ ac and/or dc bias voltage at the sample. The frequency range is $3\mu Hz$-$10$ kHz. The system can measure samples both with high impedance up to $10^{15}$ and low impedance down to 1.

Dielectric constant measurements over a wide temperature range will give the ferroelectric transitions of the materials. In the present study the dielectric constant studies were undertaken at a fixed frequency (1kHz) over a temperature range of 4 - 300 K ($\epsilon$ vs $T$).

Figure 3.5 Alpha-A High Performance Frequency Analyzer by NOVO Control.
Specific heat is a thermodynamic quantity and is complementary to magnetization and resistivity data for a given material. It is indeed a bulk property, and is not having the vectorial character of magnetization (the average projection of magnetic moments along one direction is measured). The specific heat measurements are also useful in studying various types of transitions especially the magnetic and ferroelectric. In some cases, the specific heat technique is the only way of determining whether the transitions observed by other measurements is characteristic of the bulk of the material or to the presence of minority second phase. Heat capacity measurements play an important role in the investigation of phase transitions in magnetic materials. While these measurements are commonly carried out in zero external fields, heat capacities in a finite field can provide additional information. Certain thermodynamic quantities can be
determined more accurately by heat capacity measurements than by magnetization measurements. In fact, the low temperature specific heat measurements reveal a great deal of information about the lattice and electronic properties of material. As mentioned earlier, the multiferroic materials are expected to exhibit a series of transitions originated from various mechanisms, In order to understand the complexities of all these transitions, a systematic investigation of specific heat was carried out.

Heat capacity of a material can be measured by various methods such as the semi adiabatic calorimeter [Lakshmikumar et al. (1981), Gmelin et al. (1987) and Pecharsky et al. (1997)], relaxation calorimeter [Bachmann et al. (1972)], AC calorimeter [Sullivan et al. (1968)], differential scanning calorimeter [Lakshmikumar et al. (1981)] etc. Each method has its advantage and disadvantage. In the present investigation Semi adiabatic heat pulse method was used.

3.4.1 Principle of the measurement

Although this method takes longer time, the method gives absolute values of heat capacity with very good accuracy. In this method a small amount of heat pulse (Q) is provided to the material, which is kept under adiabatic conditions, and the change in temperature (T), before and after the heat pulse is measured. Then the ratio Q/T gives the heat capacity of the sample. The method is called semi-adiabatic, as it is impossible to attain the perfect adiabatic conditions in practice.

3.4.2 Working of experimental set up

In the present investigation, the specific heat (C_p) measurements were performed by the semi adiabatic heat pulse method using indigenous set up along with 8-Tesla Oxford superconducting magnet system. The measurements were carried out in the temperature range of 4-300 K under different magnetic fields.

The schematic diagram of the sample holder arrangement is shown in Figure 3.7. The sample holder is made up of OFHC (Oxygen free High Conductivity Copper). For temperature measurements a calibrated Cernox temperature sensors (model CX-1050-SD) was used. The diagram clearly shows the positions of test sample, sensor, heater and input/ output connections.
Salient features of the set up:

(i) The absolute accuracy of ~0.5% even with small amount of sample (few hundred mille grams).

(ii) Measurement of four samples can be performed in a single run, which reduces the experimental time effectively.

(iii) Heat capacity versus temperature plot can be monitored online on a computer monitor, which helps to adjust various parameters for good quality data acquisition.

Figure 3.7. Schematic diagram of the sample holder arrangement
Chapter 3. Experimental methods

A block diagram of the heat capacity set-up is shown in Figure 3.8. A PC, which interacts with the instrument through the IEEE-488 interface, is used for data collection. The automation program is written in Quick Basic language. Lakeshore (model DRC 93CA) temperature controller is used to monitor and control the temperature of the sample. Keithley digital voltmeter (model 182) and Current source meter (model 2400) are used for measuring the voltage and input current respectively. Few hundred milligrams of sample is required for reliable heat capacity measurements.

According to the definition of heat capacity, an amount of heat required to raise the temperature of a substance to one degree temperature. Initially, the temperature of the sample before applying heat was noted as $t_i$, and then an amount of heat $Q = i^2 R t$, where $R$ is the resistance of the heater used and $t$ is the time) was supplied to the sample by sending a constant current for a second. The $Q$ is selected in such a way that the temperature rise of the sample is within 1-4% of the temperature at which the heat capacity is measured. After that, the temperature of the sample was again measured as $t_f$. The difference between final and initial temperatures will give the $T$. Therefore, the ratio of $Q$ to $T$ gives the heat capacity of the sample.

![Figure 3.8 Block diagram of Heat capacity set up](image)
Chapter 3. Experimental methods

References


