Chapter 2

Experimental techniques

Abstract

In this chapter synthesis and characterization techniques of multiferroic materials studied in this thesis are discussed. Three different techniques were used to synthesize the samples; solid state reaction for polycrystalline, sol-gel, and pulsed laser deposition for thin films. X-ray diffraction, neutron diffraction, SEM, and EDAX were used for structural characterization and their operational principles are discussed briefly. Basic principle of dielectric measurement and its experimental design are also presented.
2.1 Synthesis of bulk materials

2.1-1 Solid state reaction method

The procedure for exchange of ions in the solid state reaction involves heat treatment of a well ground specimen in pellet form under either vacuum, inert gas or ambient atmosphere at high temperatures (often in the range 700 to 1500 °C). The temperature at which the solid state exchange reaction reaches an appreciable rate depends on the type of cation and anion. Solid state processing is a diffusion process in which atoms from one material or phase substitute atoms in another resulting in a solid solution [1]. This technique is simple and versatile allowing for the synthesis of a variety of bulk ceramics.

The first step in the solid state reaction method is to weigh the raw materials in stoichiometry and mix in agate mortar. Fine grained materials should be used in order to maximize the surface area and hence the reaction rate. Agate mortar is preferable for mixing of small quantities since it is hard, unlikely to contaminate the mixture, and with its smooth and non-porous surface, it is easy to clean. In order to make a homogeneous mixture, sufficient amount of volatile organic liquids such as acetone or alcohol are mixed to form a paste. In the grinding and mixing process often organic binder with low evaporation temperature is used. Binder plays a transient role in the overall fabrication route. The binder must provide the desired properties to the seed material so that the powder must be consolidated into the desired shape and then can be removed completely without the disruption of the particle packing or any chemical reaction with the powder. The materials which can be used as a binder in solid state reaction technique are polypropylene, polyethylene, polystyrene, polyvinyl acetate, and polyvinyl alcohol. In order to prepare disc shape pellets, a die made up of stainless steel was designed and fabricated. Using die and hydraulic press, cylindrical pellets of 10 mm diameter and 1 mm thickness were made by applying pressure of 6-8 ton. Pelletization of the compound is helpful in speeding up the chemical reaction during sintering process by increasing the area of contact between the grains. Further, since solid state reaction takes place at high temperatures it is necessary that the container used for sintering process should be chemically inert to the reactants under the desired heating conditions. Metals such as platinum and gold are the most suitable candidates for this purpose but are
expensive so commonly good quality alumina (Al₂O₃) having melting point ~ 1500 °C can be used for sintering purposes. In all our solid state reaction based synthesis we used high purity alumina boats and crucibles.

The pellets were kept in the high temperature furnace and the temperature was raised to ~ 500 °C at the rate of < 5 °C/min and kept for 2-3 hrs. This process is called as preheating stage and is very essential for binder burnout. If the powder contains phases that can undergo significant oxidation at binder burnout temperature, the binder burnout must be accomplished in an inert atmosphere. The major drawback of binder burnout step is that it creates porosity in the sample which make ferroelectric measurements difficult. After preheating, the pellets were heated to a fixed sintering temperature at a fixed rate, and held for fixed time and later cooled down to room temperature. This process (holding the sample at fixed high temperature) is referred to as isothermal sintering and most of the chemical reaction occurs at this step. The heating program to be used depends very much on the form and reactivity of the reactants. Isothermal sintering program varies for different compounds and is mentioned for different multiferroic compounds in their respective chapters of the present thesis. The final product of the reaction usually requires several hours, or even days, depending on the reaction methodology. Reaction is often greatly facilitated by cooling and grinding the sample repeatedly. The effect of grinding is to maintain a high surface area, as well as to bring the fresh surfaces into the contact. Repeated sintering was performed in order to increase the density of the pellets formed during isothermal sintering. The preheating and isothermal sintering were done using high temperature furnace having microprocessor based PID temperature control.

2.1-2 Sol-gel processing

Sol-gel technique is a wet chemical process that is most appropriate for preparing metal oxides. The important advantages of the sol-gel process are lower processing temperatures, good homogeneity, precise composition control of multi-component compounds, and synthesis with simpler and cheaper apparatus. The method is based on the phase transformation of a solution (sol) obtained from metallic alkoxides or organometallic precursors. The solution containing particles in suspension is polymerized at low temperatures to form a wet
gel. This gel is densified through thermal annealing [2]. It is possible to fabricate ceramics, glassy, aerogel materials in a variety of forms, such as ultra-fine powders, fibers, thin films using this method [6]. Our collaborators used citrate sol-gel technique to synthesize target for YMnO$_3$ thin film which is described in chapter 5, section 5.2-1.

2.2 Thin film deposition

2.2-1 Pulsed laser deposition

Pulsed laser deposition (PLD) is a fast and feasible technique for oxide thin film growth. The schematic PLD set up is shown in Fig 2.1. Major advantages of PLD are stoichiometric transfer of elements from target to film, low epitaxial growth temperature, and relatively low number of control parameters [5].

![Figure 2.1: Schematic diagram of a pulsed laser deposition system](image)

Figure 2.1: Schematic diagram of a pulsed laser deposition system
In this technique, a high-energy laser beam is focused on a target to ablate material from it. Our collaborators used a Complex Pro 205 KrF excimer laser with a wavelength of $\lambda = 248$ nm and pulse width of 25 ns for the YMnO$_3$ film reported in this work. In order to prevent the heating of the target, it was rotated at 30 RPM on its axis. The substrate was heated to 700 °C using SiC resistive heaters. Because of enormous power and short interaction period, laser ablation is a non-equilibrium process. A plasma that is generated during this process contains the species removed from the target. This process allows the stoichiometric transfer of the target material to the substrate. With these parameters, multiferroic thin films of YMnO$_3$ on sapphire substrate was deposited as discussed in chapter 5. The deposition rate of 0.3 Å/pulse for both YMnO$_3$ and conducting buffer Zn$_{0.99}$Ga$_{0.01}$O were achieved.

2.3 X-ray diffraction

X-ray diffraction is one of the most fundamental tools for the investigation of crystal structure of matter. X-rays are only a part of the electromagnetic spectrum with wavelengths ($\lambda$) ranging from 0.02 to 100 Å.

![Diagram illustrating crystal planes and Bragg's diffraction condition.](image)

Diffraction of x-ray beam, incident on a crystal can occur when the atomic spacing of the material matches with the wavelength of x-rays. When x-ray beam is incident on the regular, 3-D arrangement of atoms in a crystal, most of the x-rays interfere destructively with each other, but in some specific directions they interfere constructively and reinforce one another. It is these reinforced x-rays that produce the characteristic x-ray diffraction patterns that are used for material identification. W. L. Bragg (1912) showed that diffracted
x-rays act as if they were "reflected" from a family of Bragg's planes within crystal as shown in Fig 2.2.

Bragg's planes are rows of atoms that make up the crystal structure. The path difference introduced between a pair of waves traveled through the neighbouring crystallographic planes are determined by the inter-planer spacing. These "reflections" shown to occur only under certain conditions which satisfy the equation 2.1:

\[ 2d_{hkl} \sin \theta = n \lambda \]  

where n is an integer (1, 2, 3, ...), λ the wavelength, \( d_{hkl} \) the distance between atomic planes with Miller indices \((h, k, l)\), and \( \theta \) the angle of incidence of the x-ray beam and the atomic planes. The path length difference must be equal to an integer value of the incident x-ray beams, for constructive interference to occur, such that a reinforced diffracted beam is produced. For given incident x-rays and interplanar spacing \((d_{hkl})\) in a material, only specific angles will satisfy the Bragg's equation.

The intensity of powder diffraction peaks is in principle determined by the atomic scattering factor or form factor \( f_{hkl} \). Form factor \( (f_{hkl}) \) depends on the crystal structure including relative positions of atoms in the unit cell, types of unit cells and other characteristics such as thermal motion, and population parameters. The expression for \( f_{hkl} \) is given by equation 2.2:

\[ f_{hkl} = \sum_{n=1}^{N} g^{n} t^{n}(s) F(s) e^{2\pi i(hu_n+kv_n+lw_n)} \]  

where \( f^{n}(s) \) is the atomic scattering factor, \( g^{n} \) is the population factor of \( n^{th} \) atom, \( t^{n}(s) \) is the temperature factor, \((h, k, l)\) are the Miller indices, and \((u, v, w)\) are the fractional co-ordinates of \( n^{th} \) atom in the unit cell. In addition to the primary structural factors, the intensity of diffraction is dependent on other factors, which are relevant to sample effects such as its shape and size, grain size and distribution and instrument components such as detector, slit and/or monochromator geometry [3, 4].

For all x-ray diffraction experiments presented in this thesis, a Bruker D8 Advance X-ray diffractometer with Cu Ka (\( \lambda = 1.5418 \text{ Å} \)) radiation was employed and operated at applied voltage of 45 kV, and filament current of 40 mA. The phase identification for all
as-synthesized samples reported here was performed by matching the peak positions and intensities of those patterns that are available in the JCPDS (Joint Committee on Powder Diffraction Standards) database.

2.4 Neutron diffraction

The scattering of slow neutrons is a very powerful technique to investigate the structure and dynamics of condensed matter. The principle of diffraction from x-rays and neutrons are similar, except for some differences such as wavelength, penetration depth, and scattering factors. Neutron diffraction (ND) technique provides significant additional information. The advantage of neutrons over x-rays are summarized as follows:

1. Neutrons does not carry any charge and thus has no electrostatic interaction with the electron charge cloud of an atom. For this reason neutron has higher penetration power comparable to x-ray or electron. An iron plate, 1 cm thick, is opaque to electrons, virtually opaque to 1.5 Å x-rays, but transmits 35 % of 1.5 Å neutrons.

2. The mass of a neutron is 1.0087 amu, leads to a de Broglie wavelength of thermal neutrons of about 1.8 Å which is of the order of the interatomic distances in condensed matter making interference effects possible.

![Figure 2.3: Behaviour of scattering amplitude of x-rays and neutrons as a function of atomic weight [8].](image)

3. Unlike for x-rays, the neutron scattering power of elements varies in a zigzag fashion with respect to the atomic mass, as shown in Fig 2.3. Due to this special property,
neutrons can differentiate neighbouring elements. Neutrons also allow to probe light atoms that are barely visible with x-rays.

4. Neutron has a spin 1/2 and net magnetic moment (1.913 $\mu_B$). Due to this fact neutrons are sensitive to the magnetic fields created by unpaired electrons. The magnetic structures and interactions in a magnetic material can be obtained using neutron scattering, which is not possible by any other method.

5. As the energies of thermal and cold neutrons are in the range of 0.1 - 100 meV, they match very well with the energies of elementary excitations of condensed matter.

ND experiments presented in the thesis were performed at Bhabha atomic research center (BARC) and diffractometer was developed and installed by UGC-DAE Consortium for Scientific Research [6]. It employs a bent perfect crystal monochromator and designed for highly focused neutron beam of about $15 \times 25$ mm$^2$. This arrangement ensures high flux at the sample position. The resolution obtained are up to $\Delta d/d \sim 0.3\%$. Figure 2.4 shows the national facility for ND at BARC, Mumbai, India.

![Figure 2.4: Low temperature (1.4 K) and high magnetic field (8 T) neutron diffraction facility at BARC, Mumbai.](image)

Polycrystalline samples were taken in the form of powders and filled in a Vanadium can. The advantage of using vanadium can is, its transparency to neutrons and it does not
2.5 SEM and EDAX principle

contribute to the diffracted patterns. Only Vanadium can is exposed to impinging neutron beam and the diffracted beam is recorded by four position sensitive detectors (PSD). The diffracted neutrons are collected by PSD, which is filled with helium gas. For every neutron falling on the PSD, the following reaction takes place,

$$3^7He_2 +^1n_0 \rightarrow ^3T_1 +^1H_1 +^1n_0 + 0.765MeV \quad (2.3)$$

One incoming neutron interacts with the molecule of He gas, and breaks it into one tritium and one proton. As protons are charged particles, they ionize the helium gas. These ions are recorded as a pulse by the "cathode-anode setup" kept under high potential. The whole cathode length is distributed or sliced into 1024 channels in the Dhruva reactor setup. The counts (pulses i.e., the number of ions falling on the cathode) at each channel are recorded. The multichannel analyzer (MCA) records the data from each channel. Using appropriate calibration constants, the channels are converted into corresponding angles.

The wavelength of neutrons for ND experiments can vary from 1.1 to 2.3 Å using monochromator. The sample environment consists of a 4 K closed cycle refrigerator (CCR) for standard measurements as a function of temperature, and a cryogen-free 8 T magnet with VTI for in-field measurements down to 1.4 K. All the ND experiments presented in the thesis were performed at neutron wavelength of $\lambda = 1.48 \, \text{Å}$. The software used in order to analyze the ND data is FULLPROF [10]. The crystal structure of various multiferroic compounds were ascertained using Diamond software.

2.5 SEM and EDAX principle

Scanning electron microscopy (SEM) is an important tool for material research. SEM provides topographical and elemental information at magnifications of 10x to 100,000x with virtually unlimited depth of field. It allows the determination of grain size, surface roughness, porosity, particle size distribution, and material homogeneity. In this technique, an electron beam is finely focused by an assembly of magnetic lenses. This focused thin probe beam scans over the selected area of the sample. The interaction of electron beam and the surface of the sample generates a) Secondary Electrons (SE), b) Backscattered Electrons (BSE), and c) Characteristic x-rays. These signals are collected by detectors to form images.
of the sample. SE imaging technique works by detecting secondary electrons emitted by the sample because of the incident electron beam. The energy of the SE produced in this process is very less and these electrons are useful in producing high resolution and high magnification images. SE Imaging shows the topography of surface features to a few nm across. Films as thin as 20 nm can produce adequate image contrasts. The BSE imaging technique uses the electrons backscattered by the sample. The energy of the BSE are higher than the energy of SE. These electrons are useful in determining the surface topography as well as chemical profile within the top micron of the sample. The x-ray radiation emitted by the sample is used for Energy Dispersive Spectrometry (EDS). The emitted radiation is the characteristic of the interaction between the element of the sample and the incident electron. As a result, this technique is ideal for determining the elemental composition of the sample. The major drawback of EDS is its inability to detect elements with atomic number less than 5 i.e., H, He, Li and Be due to absorption of low energy x-rays by detector window. The morphology and the elemental composition of all the samples in the thesis were characterized using a JOEL JFM-840 scanning electron microscope (SEM, 20 kV, JEOL, Japan).

2.6 Dielectric measurement

2.6-1 Basic principle

Establishing magnetoelectric coupling requires measuring the effect of magnetic field on ferroelectric polarization/dielectric constant or conversely, the effect of electric field on magnetic order. The relatively simple and widely accepted method is measuring the dielectric constant (\( \varepsilon \) and \( \tan\delta \)) as a function of temperature and/or magnetic field. Measuring \( \varepsilon(T) \) and looking for deviations around the magnetic transition can be used to detect a multiferroic or magnetoelectric state [11, 12]. Since magnetic field affects magnetic ordering, the field also indirectly alters the dielectric constant of multiferroics. This is known as magnetodielectric (magnetocapacitance) effect, which has been reported for a wide range of materials [13, 14, 15, 16, 17].

Dielectric constant is a complex quantity and is expressed as:

\[
\varepsilon = \varepsilon' + j\varepsilon''
\]
2.6-2 Design of dielectric setup

\[
\text{with } \quad \epsilon' = \frac{C}{C_0}, \quad \text{where,} \quad C_0 = \frac{\epsilon_0 A}{d} \\
\text{and } \quad \tan \delta = \frac{\epsilon''}{\epsilon'}
\]

(2.4)

(2.5)

Here \( \epsilon_0 \) = Permittivity of free space = \( 8.85 \times 10^{-12} \text{ C}^2/\text{N.m}^2 \)

\[ A = \text{Area of the parallel plate capacitor} \]

\[ d = \text{Thickness of the dielectric material} \]

\( \tan \delta \) is also called as dissipation factor and is a measure of the quality of a capacitor. Lower the \( \tan \delta \), the better the capacitor. Since dielectric constant (\( \epsilon \)) is an electrical property, the anomaly in the \( \epsilon' \) and \( \tan \delta \) near the magnetic transition temperature is associated with the magnetoelectric coupling of multiferroic state. The strength of magnetocapacitance (MC) is calculated using the following relation:

\[ \%MC = \frac{\epsilon(T, H) - \epsilon(T, H = 0)}{\epsilon(T, H = 0)} \]

(2.6)

where \( \epsilon(T, H) \) is the dielectric constant in presence of magnetic field at temperature \( T \) and \( \epsilon(T, H=0) \) is the dielectric constant in zero field at temperature \( T \).

2.6-2 Design of dielectric setup

In order to measure the dielectric constant, we have designed a dielectric setup for cryogen free low temperature and high magnetic field system as shown below in Fig 2.5.
In the dielectric setup two circular copper electrodes of diameter 10 mm are separated by using a spring. The copper electrodes are placed in specially designed G-10 plates. The sample is sandwiched between copper electrodes and is screwed to the sample holder with the base of G-10 plates. In order to make electric connections, RG-176 rf coaxial cables were used. The total length of the RF cable used in the dielectric measurement was \( \sim 2 \) meters. In order to compensate the length of the cable, we have calibrated the dielectric experiment by using cable correction compensation. The dielectric constant were measured using QuadTech 1920 Precision LCR meter. The frequency range of the LCR meter is 20 Hz - 1 MHz.

**TABLE 2.1: Comparison of dielectric constant estimated from capacitance and impedance measurement:**

<table>
<thead>
<tr>
<th>frequency (Hz)</th>
<th>( \epsilon )</th>
<th>tan( \delta )</th>
<th>( Z' )</th>
<th>( Z'' )</th>
<th>( \epsilon_{\text{cal}} )</th>
<th>tan( \delta_{\text{cal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>123</td>
<td>59.27</td>
<td>1.002</td>
<td>10.91 M( \Omega )</td>
<td>-10.9 M( \Omega )</td>
<td>42</td>
<td>1</td>
</tr>
<tr>
<td>523</td>
<td>52.77</td>
<td>0.675</td>
<td>3.82 M( \Omega )</td>
<td>-5.66 M( \Omega )</td>
<td>52.8</td>
<td>0.67</td>
</tr>
<tr>
<td>1023</td>
<td>57.6</td>
<td>0.5595</td>
<td>2.16 M( \Omega )</td>
<td>-3.856 M( \Omega )</td>
<td>58</td>
<td>0.56</td>
</tr>
<tr>
<td>5023</td>
<td>30.51</td>
<td>0.2875</td>
<td>393 k( \Omega )</td>
<td>-1.37 M( \Omega )</td>
<td>30.54</td>
<td>0.287</td>
</tr>
<tr>
<td>10003</td>
<td>27.2</td>
<td>0.0935</td>
<td>77.2 k( \Omega )</td>
<td>-827 k( \Omega )</td>
<td>27.2</td>
<td>0.0925</td>
</tr>
</tbody>
</table>

In order to measure the dielectric constant, the surface of the circular pellets were polished and coated with silver paste and sintered at \( \sim 150^\circ C \). The dielectric setup was calibrated at room temperature by calculating the dielectric constant from impedance measurements [18], in the frequency range of 20 Hz - 1 MHz. The impedance \( Z \) is also a complex quantity and its real and imaginary parts are related by the following relation:

\[
Z = Z' + jZ''
\]  
(2.7)

Here \( Z' \) and \( Z'' \) are resistance and reactance respectively. The values of real and imaginary dielectric constants, \( \epsilon' \) and \( \epsilon'' \) were calculated using equations 2.8 and 2.9

\[
\epsilon' = \frac{Z''}{\omega C_0(Z'^2 + Z''^2)}
\]  
(2.8)

and

\[
\epsilon'' = \frac{Z'}{\omega C_0(Z'^2 + Z''^2)}
\]  
(2.9)
In order to compare the value of dielectric constant measured from capacitance and impedance measurements, we conducted measurements on multiferroic $Y_{0.95}Dy_{0.05}MnO_3$ at room temperature at various frequencies. Using equations 2.5 and 2.6, $\epsilon$ and $\tan\delta$ were calculated (from capacitance measurement) and summarized in the table 2.1. 6th and 7th column of the table represent the values of $\epsilon$ and $\tan\delta$ calculated from impedance measurement using equations 2.8 and 2.9. We find that there is slight discrepancy at low frequency but relative variation between the two methods remain unaltered.

### 2.7 Magnetoresistance measurement

The dielectric measurements were performed under the influence of ac electric field. The response to the electric field will contain at least one capacitive (dielectric) and one resistive (leakage) terms. Also it is not possible to have similar work function of dielectric as well as electrode so this causes band bending at the interface of dielectric and electrode. Due to this charge will transfer from one side to the other, and cause artificially high dielectric constants. This dielectric constant may also change due to application of magnetic field due to magnetoresistance. This does not imply the multiferroic nature of the material [19, 20, 21]. Thus, multiferroicity may imply magnetocapacitance, but the converse is not true. To confirm magnetocapacitance appearing in dielectric measurements, magnetoresistance must be ruled out in the whole temperature range.

![Figure 2.6: Circuit diagram for two probe resistivity measurement](image-url)
Resistivity of the insulating multiferroic samples were measured using two probe configuration. The circuit diagram for two probe resistivity measurement is shown in Fig 2.6. In this configuration, the sample resistance is measured by measuring the voltage drop across a known resistance. In the diagram, $V'$ is the voltage applied by voltage source, $V_i$ is the voltage measured by digital multimeter (Keithley 2000 DMM) across the voltage source, $R_1$ is the resistance of the sample, $R_2$ ($\sim 1 \Omega$) is the known resistance, and $V_0$ is the voltage drop across a known resistor, measured by nanovoltmeter (Keithley 2182 NVM). If $I$ is the current passing through sample, then by applying Kirchoff’s law;

\[
V_i = V_o + IR_1
\]
\[
V_i - V_o = R_1 \frac{V_o}{R_2}
\]
\[
R_1 = R_2 \left( \frac{V_o}{V_i} - 1 \right)
\]

By measuring the voltage drop across the known resistor ($R_2$) and using above equation, we have estimated the resistance of the insulating samples.

### 2.8 Cryogen free low temperature and high magnetic field system

A low temperature and high magnetic field facility that can cool down to 1.6 K and can generate 8 T magnetic field is present in our lab at SPS, JNU and is shown in Fig 2.7. Cryogen free system is based on the principle of Gifford-McMahon cycle [23]. It contains a water cooled compressor (SHI compressor CSW71), Nb - Ti superconducting magnet ($T_C \approx 9$ K), variable temperature insert (VTI) and cold head (sumitomo SRDK-408). The compressor is water cooled and requires supply of water ($\sim 15 \degree C$) at the rate of 7 lit/min. The static and dynamic pressures in the compressor are 1.7 and 2.5 MPa respectively. The cooling powers at the first and second stage cold heads are 34 W @ 40 K and 1 W @ 4.2 K respectively. The second stage cooling is shared between sample space and the magnet. The temperature of the magnet always remains $\sim 4$ K during charging and discharging of the magnet. Continuous monitoring of the system throughout the operation is carried out at different points in the cryostat such as first stage, shield, second stage, magnet, condensation.
pot and exchange exhaust by temperature sensors [22]. The resistance of these sensors is scanned by a 10 channel scanner Keithley 2700 multimeter.

![Cryogen free low temperature and high magnetic field system](image)

Figure 2.7: Cryogen free low temperature and high magnetic field system along with 8 T magnet power supply at SPS, JNU.

It takes around 12 hrs for the various components of the cryostat to reach their respective lowest temperatures. The base temperature of VTI is 1.6 K which is acquired after two more hours of reaching base temperatures. The accessible sample space is $\sim 24$ mm in diameter, which is always cooled by helium vapors. The superconducting magnet is attached with the condensation pot which stores the helium and is always maintained below 4 K. The helium pressure in the VTI is always maintained $\sim 8$ mbar. Sample temperature is varied by supplying a regulated DC power supply to the heater from temperature controller and is sensed using a Cernox sensor. The flexibility of system lies in sample changing even at the lowest temperature and to design various attachments based on our requirements.

The system operation and all the experiments are controlled via a software working under LabVIEW. Instruments like Lakeshore 340 temperature controller, SMS120C Cryogenic magnet power supply, QuadTech 1920 Precision LCR meter, Keithley 224 current source, Keithley 2400 source meter, Keithley 2182 dual channel nanovoltmeter, and Keithley 2000 digital multimeter are interfaced to a computer and operated using LabVIEW 6.1 software.
2.9 SQUID magnetometer

Superconducting quantum interference device (SQUID) magnetometry is the standard measurement technique for high sensitive magnetization studies. The functioning of SQUID is based on the principle of Josephson tunneling and flux quantization. A Josephson junction consists of two weakly coupled superconducting electrodes which are separated by a thin insulating barrier. If superconductors separated by a thin insulating layer are brought very close to each other, tunneling of cooper pairs can occur. In SQUID magnetometer the sample is placed in a superconducting pick-up coil as shown in Fig 2.8. The flux associated with the superconducting ring is quantized according to the relation \( f = nf_0 \) with \( f_0 = \frac{h}{2|e|} \), where \( n \) is an integer, \( h \) is Planck’s constant, and \( e \) is the electronic charge. The noise level of this technique can be as low as \( 10^{-8} \) emu, which would make it ideal for studies of weak antiferromagnetic multiferroic samples.

![Schematic illustration of a SQUID magnetometer](image)

Figure 2.8: Schematic illustration of a SQUID magnetometer

There are two types of SQUIDs; DC SQUID and AC SQUID. The first, DC SQUID, consists of two Josephson junctions connected in parallel on a superconducting loop and is operated in the voltage state with a current bias. The second kind, RF SQUID, consists of a single Josephson junction inserted into a superconducting loop. The routine measurements
in SQUID magnetometers can be performed in two ways. The first measurement is the temperature dependence of the magnetic materials under constant magnetic field \( M(T) \) and second is the field dependence of magnetization at constant temperature \( M(H) \). The temperature dependent measurements can be further performed by zero-field-cooled (ZFC) and field-cooled (FC) processes. In ZFC measurement, the sample is cooled from room temperature in the absence of magnetic field to the lowest temperature. On the other hand, in FC measurements, the sample is cooled from room temperature to the lowest temperature in the presence of a magnetic field. Data are collected in the warming cycle in both the cases.

We have used a commercial Quantum Design SQUID magnetometer (MPMS-XL) for all measurements reported in this thesis. A “Reciprocating sample transport option” (RSO) was used in these measurements to achieve better sensitivity.

### 2.10 DSC measurement

Differential scanning calorimetry (DSC) is a technique which measures the heat flow associated with various phase transitions of a materials as a function of temperature and time. This technique is used to study the phase transitions, changes in heat capacity of endothermic and exothermic processes. The change in enthalpy is said be endothermic (\( \Delta H \) positive) when sample absorbs energy, and conversely when the sample releases energy, the process is said to be exothermic (\( \Delta H \) negative).

The DSC has a platform to keep the sample material and the reference material is taken in the appropriate pan. The reference material is chosen in such a way that it does not decompose in the desired temperature range. In DSC, both the sample and reference material are maintained at the same temperature \( i.e. \Delta T = T_s - T_r = 0 \), where \( T_s \) and \( T_r \) are the temperature of sample and reference respectively. In case of endothermic event occurring in the system, \( T_s \) will lag behind \( T_r \). Now an independent heat supplier gives the heat equivalent to energy difference and this energy difference is recorded against the temperature. Different phase transitions in the sample appear as deviations from the base line, either in positive (endothermic) or negative direction (exothermic), depending on more or less energy that needs to be supplied to the sample with respect to the reference material.

For DSC experiments presented in chapter 3, the DSC 10 system with Du Pont thermal
2.11 Ferroelectric measurement

2.11-1 Polarization-electric field measurement

Polarization, which is usually denoted by $P$, is related to electric displacement (or electric flux density) $D$, through the linear expression:

$$D_i = P_i + \varepsilon_0 E_i$$  \hspace{1cm} (2.10)

where the subscript $i$ represents any of the three coordinates $x$, $y$ and $z$, and $\varepsilon_0$ is the permittivity of free space. The amount of polarization is calculated using the relation $P = \frac{Q}{A} = \frac{\int \chi(t)d\mu}{A}$, where $A$ is the area of the capacitor [24].

In order to study ferroelectricity in multiferroic compounds, we performed polarization-electric field (P-E) measurements using a Radiant RT6000, and Marine India Elect. Pvt. Ltd. test systems. The net polarization of an initially unpolarized ferroelectric material is small. When an electric field is applied, there is a linear relationship between switchable polarization and the applied electric field. As the electric field increases, domains in which the direction of spontaneous polarization is opposite to electric field begin to switch to a more energetically favorable direction. The switching process continues until all of the domains are aligned in the electric field direction. When the field returns to zero, the polarization does not return back to the initial value. The amount of switchable polarization after removal of an electric field is called the remnant polarization, $P_r$. The strength of the electric field to switch the opposite polarization domain is called the coercive electric field, $E_c$. Figure 2.9 shows a typical hysteresis loop of BaTiO$_3$ at room temperature.
2.11-2 Capacitance-voltage measurement

Ferroelectric behaviour of multiferroic samples can also be measured by capacitance-voltage (C-V) measurements. C-V measurements were performed using Agilent HP 4285A Precision LCR meter. Figure 2.10 shows a typical room temperature C-V curve of multiferroic Bi$_{0.3}$Co$_{1.7}$MnO$_4$ at 75 kHz frequency [27]. The butterfly nature of C-V curve suggests a weak ferroelectric behavior at room temperature. In the C-V measurement, the bias field is swept slowly over the measuring range at a fixed frequency. It is shown that the sharp capacitance peak/discontinuity which is present in the CV characteristics at different frequencies is directly associated with the polarization reversal [28].

Realization of PE loop in multiferroic materials is extremely difficult due to leakage currents. The origin of leakage current is the presence of impurities, and oxygen vacancies created during sample preparation [25]. The another possible reason which affects the PE measurements is, the injection of electrons and holes from the electrodes into the multiferroic material [26].

Figure 2.9: Typical polarization-electric field hysteresis loop measured in ferroelectric BaTiO$_3$. $P_r$ and $E_c$ are the remnant polarization and the coercive electric fields.


2.12 UV/Visible transmission spectroscopy

UV/Visible transmission spectroscopy was used to measure the band gap and wavelength dependent absorption of multiferroic thin film of YMnO₃. A DU 730 UV/Visible scanning spectrophotometer in scanning wavelength (100 - 900 nm) mode was used. Substrate spectrum was subtracted by scanning a clean substrate. In this technique monochromatic light of intensity I₀ is transmitted through the sample, is measured and compared to the incident source. Transmittance (T) is defined as I/I₀ and can be easily converted to absorbance (α) as α = -log(T). The nature and size of the band gap can be obtained from this technique by fitting α using the following relation:

\[
\alpha = C(h\nu - E_g)^n
\]  (2.11)

where C is a constant, hν is photon energy in eV, and n is 1/2 for direct band gap materials, and 2 for an indirect band gap materials [29].
2.13 Specific heat measurement

Magnetic transition temperature of multiferroic compounds were studied using heat capacity measurement. Phonons and electrons both contribute to specific heat. The contribution of phonon to the heat capacity of a crystal is called as lattice heat capacity and is denoted by \( C_{\text{lat}} \). The magnetic contribution to the heat capacity, denoted by \( C_m \), was obtained by subtracting the lattice contribution from the heat capacity raw data. From \( C_m \) versus temperature plot, one can also calculate the magnetic entropy of the system. Magnetic entropy of a system is the energy needed to fully disorder the magnetic spins. The heat capacity measurement was performed using a Physical Property Measurement System (PPMS) installed at UGC-DAE-CSR, Indore.
References


REFERENCES


