Chapter 2

Experimental Techniques for Materials

Characterization

Chapter II describes, in brief, various techniques used for synthesizing bulk and thin films of manganites and multiferroics. This chapter include details about experimental characterization techniques such as XRD ($\theta$ - 2$\theta$, $\phi$-scan and RSM), SEM, AFM, MFM, \( \rho \)-T, dielectric, I - V, P - E, M - H and spectroscopic techniques (RBS and XPS) used during the course of present studies. Also, simulation methods used during present work have been discussed.
**Chapter 2: Experimental Techniques for Materials Characterization**

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2.1 Introduction

Synthesis and characterization are the most important initial steps in materials science for tailoring functional materials which are useful in technological applications. Important aspect of achieving desired properties in oxide materials in the form of good quality films and novel devices is the synthesis and characterization of the sample. Various properties of materials, such as structural, microstructural, transport, electrical and magnetic, can be tuned by varying synthesis parameters used during the sample preparation. Different material forms such as, polycrystalline powders and pellets, amorphous, single crystals, thin films (bi-layer and multilayer) are used in various applications. Material scientists have developed large number of synthesis techniques depending on their requirements, such as, Solid State Reaction (SSR), Co-precipitation, Sol - Gel, Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD), Chemical Solution Deposition (CSD), Metal-Organic Chemical Vapor Deposition (MOCVD), RF/DC Sputtering, Thermal evaporation, Flux Growth Technique, Electrochemical Methods etc.

During the course of this work, polycrystalline bulk manganites and multiferroics were synthesized using solid - state reaction method and sol-gel method respectively for the preparation of targets. These targets were used in Pulsed Laser Deposition (PLD) technique for making thin films and devices. An important aspect of this study is the study of effect of Swift Heavy Ion (SHI) irradiation on the properties of manganite and multiferroic based thin films and devices. Polycrystalline bulk and thin film samples (pristine and irradiated) were characterized using various techniques, such as,

1. Structural characterization: X-ray Diffraction (XRD), φ-scan and Reciprocal Space Mapping (RSM)
2. Spectroscopic Characterization: Rutherford Backscattering (RBS) and X-ray Photoelectron Spectroscopy (XPS)
4. Transport Characterizations: D.C. four probe resistivity (R - T) and Current-Voltage measurements (I - V)

5. Electrical Characterizations: Dielectric and Polarization vs. Electric field (P - E loop) measurements

6. Magnetic Characterizations: M - H hysteresis loop measurements

A brief description about various synthesis and characterization tools used during the course of present work is given in the following pages –

2.2 Synthesis Techniques

2.2.1 Solid State Reaction (SSR)

Polycrystalline bulk manganites used in the present study were synthesized using SSR method. Solids do not react with each other at room temperature (RT), hence, it is necessary to heat oxides, carbonates, etc at high temperatures (1000 - 1500°C) for the proper reaction to occur. Therefore, thermodynamic and kinetic factors are important in SSR. Mixing of the required oxide or carbonate powders in stoichiometric proportion, calcinations, pelletization and sintering of pellet of bulk are main steps of the SSR method. Flow chart of SSR method is given in fig. 2.1. The final solid pellet obtained possesses all the required properties of manganites. The final temperature and duration of sintering may vary depending on the nature and properties of the sample under preparation [1, 2].

The advantages of SSR method are (i) the solid reactants react chemically without the presence of any solvent at high temperatures yielding a stable product (ii) the final product, in solid form is structurally pure with the desired properties depending on the final sintering temperatures (iii) it is environment friendly and no toxic or unwanted waste is produced after getting final product.
2.2.2 Sol – Gel

Sol-Gel process is a method for synthesizing solid materials from small molecules. The method is widely used for the fabrication of metal oxide particles. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (gel) of either discrete particles or network polymers.

Out of several methods for synthesizing polycrystalline BiFeO$_3$ multiferroic, Sol-Gel is the cost-effective method, easy to handle and yields stoichiometrically predefined compounds. It offers a variety of starting materials as precursors to choose. The different processing stages of Sol-Gel technique are given below:
In this method, the solution gradually evolves towards the formation of a gel-like biphasic system containing both, a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the particle density may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties.

Removal of the remaining liquid phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural pattern during this phase of processing.

Afterwards, a thermal treatment is necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via
final sintering, densification and grain growth. One of the distinct advantages of using this technique is, much lower temperature required for densification.

During the course of present work, BiFeO$_3$ multiferroic samples were synthesized using Sol-Gel technique. The flow chart of Sol-Gel method is given in fig. 2.2. Bismuth nitrate pentahydrate [Bi(NO$_3$)$_3$ × 5H$_2$O] and iron nitrate nonahydrate [Fe(NO$_3$)$_3$ × 9H$_2$O] used as a starting materials and were dissolved in acetic acid and double distilled water with 1:1 ratio resulting in blackish red solution. The solution was stirred constantly for 6 hrs between 70˚C to 150˚C and then heated on hot plate for 24 hrs. Heating of the solution, at elevated temperature, results in dark brownish BFO powder. The pellets made under 4 Ton pressure were sintered initially at 600˚C for 12 hrs and finally at 800˚C for 12 hrs.

### 2.2.3 Pulsed Laser Deposition (PLD)

PLD is a powerful and efficient method for the fabrication of good quality and reliable thin films of mixed oxides suitable for device applications. Laser used in PLD is suitable for vaporizing oxide materials such as manganites, ferroelectric and ferrites [3, 4]. The main purpose of using PLD is to maintain stoichiometry and homogeneity of the film as compared with other deposition techniques such as RF Sputtering, Metal Oxide Chemical Vapor Deposition (MOCVD) or spray pyrolysis, etc.

Various manganite and multiferroic based thin films studied during the course of present work, were synthesized using PLD facility at UGC-DAE CSR, Indore and National Institute of Technology, Hamirpur.

Main steps of film growth using PLD techniques are (i) interaction of laser beam with target material (ii) dynamics of plasma plume (iii) deposition of plasma plume on heated substrate and (iv) nucleation and growth of the film on the substrate surface. During the process of film deposition, high power excimer laser beam enters into the vacuum chamber via the quartz window which is sufficient to melt and evaporate the target molecules. Because of high energy, material is ejected out in the form of plasma plume from the target surface which move towards the heated substrate and get deposited.
homogenously on it. Also, the composition of the deposited films is stoichiometrically identical to that of the target materials. Fig. 2.3 shows the schematic diagram of PLD set up and plasma plume produced at the time of deposition.

![Schematic diagram of PLD setup and plasma plume during deposition](image)

**Figure 2.3:** PLD set up and Plasma plume during deposition

**Advantages of PLD technique**

- Easy to handle and less time required (10-15 Min) for Deposition
- One Laser can be used for more than one chamber
- Use Different Substrate Temperature
- Wide Range of materials can be Deposited
- Precise control over thickness
- Use Different gas pressure
- Using Multi target chamber one can easily fabricate multilayers
- Maintain Stoichiometry
Disadvantages of PLD technique

(a) Formation of large particulates during the deposition
(b) It is difficult to grow larger films
(c) Proper energy selection is required for maintaining film stoichiometry

2.3 Structural characterization

2.3.1 X-ray Diffraction (XRD)

X-ray diffraction is a powerful non-destructive testing method for the determination of crystal structure of the materials [5, 6]. It is widely used in all fields of science and technology. Fig. 2.4 shows the schematic representation of X-ray diffractometer. In this technique, the monochromatic beam of X-rays is applied onto crystalline material, interact with the structural planes of the lattice and produce diffraction in which lattice point of each plane act as a slit. Bragg’s condition to be satisfied for constructive interference of reflected X-rays from lattice plane is,

\[ n \lambda = 2d \sin \theta , \]

where, \( d \) is interplaner spacing, \( \theta \) is the angle between incident beam and lattice planes, \( \lambda \) is the wave length of X-ray and \( n \) is the integer (1, 2, ….). According to this law, for a given set of parallel planes the diffraction will give maxima only in that direction for which the angle will satisfy the Bragg’s law (fig. 2.5).

Applications of XRD

- XRD is nondestructive technique
- To identify crystalline phase and orientation
- To determine structural properties: Lattice parameters, strain, grain size, epitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion
- To measure thickness of thin films and multi-layers
- To determine atomic arrangement
Experimental Techniques of Materials Characterizations

Figure 2.4: Schematic representation of X-ray diffractometer

Figure 2.5: Schematic representation of diffraction of x-rays by crystallographic plane (Bragg’s Law)
2.3.2 $\phi$ - Scan measurements

Texture measurements are used to determine the orientation distribution of crystalline grains in the polycrystalline sample. One can see textured state of a material (generally in the form of thin films). A material is called as textured, if the grains are aligned in a preferred orientation along certain lattice planes. The texture measurements have been performed on thin films at a fixed scattering angle and consists of a series of $\phi$ - scans (in-plane rotation around the center of the sample) at different chi-angles ($\psi$), as illustrated in the fig. 2.6.

![Schematic diagram depicting $\theta$, $\psi$, and $\phi$ angles during XRD measurements of films](image)

Figure 2.6: Schematic diagram depicting $\theta$, $\psi$, and $\phi$ angles during XRD measurements of films

2.3.3 Reciprocal Space Mapping (RSM)

Reciprocal Space Maps are useful to define crystal structure, epitaxial nature and stress on thin film [7]. For, RSM measurement, Philips X’pert high-resolution system with high resolution PIXcel$^{3D}$ detector was used to record the diffracted intensity from films. During measurements, the sample can be tilted ($\Psi$) by $\pm 90^\circ$ or rotated ($\phi$) by $360^\circ$ to find the corresponding crystal faces. Usually the angle of the sample ($\omega$) and the angle of the detector (20) have the relationship of $2 \times (\omega + \text{offset}) = 20$, as shown in fig. 2.7.
RSM of BFO multiferroic films were acquired by rotating the film to vary the incident angle of the x-ray beam, while the CCD detector was held at a fixed position. The angular position of each pixel in the CCD was calibrated by measuring the position of the direct beam on the CCD at several positions of the detector arm. The detector arm was then moved to $2\theta$ of the Bragg condition and the incident angle was scanned in discrete steps. A CCD image was captured at each incident angle. $2\theta$ and $\chi$ were determined by the pixel position, $\theta$ by the incident angle. Two-dimensional maps were created by summing the intensity of all pixels at the same $2\theta$.

2.4 Spectroscopic Characterization

2.4.1 Rutherford Backscattering (RBS)

Rutherford Backscattering Spectrometry (RBS) is a widely used nuclear method for the near surface layer analysis of solids [8]. A target is bombarded with ions at an energy in the MeV-range (typically 0.5 - 4 MeV), and the energy of the backscattered
projectiles is recorded with an energy sensitive solid state detector. RBS allows the quantitative determination of the composition of a material and depth profiling of individual elements. RBS is a nondestructive having good depth resolution of the order of several nm and very good sensitivity for heavy elements of the order of parts-per-million (ppm). The analyzed depth is typically about 2 µm for incident He-ions and about 20 µm for incident protons. The drawback of RBS is the low sensitivity for light elements, which often requires the combination of other nuclear based methods like nuclear reaction analysis (NRA) or elastic recoil detection analysis (ERDA). RBS includes all types of elastic ion scattering with incident ion energies in the range 500 keV - several MeV [9]. Usually protons, 4He, and sometimes lithium ions are used as projectiles at backscattering angles of typically 150–170°. Different angles or different projectiles are used in special cases.

**Advantages of RBS**

- **Depth Information:** RBS provides composition and depth information. Routine depth resolution is on the order of 150 Å but with very careful sample and detector alignment, 50 Å at the sample surface may be resolved.

- **Thin Film Analysis:** RBS technique is very useful in the analysis of film thicknesses.

- **Rapid Analysis:** Typical analysis times are 10 minutes or less.

- **High Sensitivity:** RBS is very sensitive to heavy elements so accurate determinations of coverage of a fraction of a monolayer are possible.

- **Simple Calculations:** RBS spectrum is easy to interpret. Unlike X-ray based spectroscopies, RBS offers a simple and direct conversion of a spectrum into useful data. Simulation and analysis software is available to optimize measurement parameters or to analyze spectra.
Figure 2.8: Schematic view of experimental arrangement of RBS

Figure 2.9: Rutherford Backscattering facility at Inter University Accelerator Centre, New Delhi

Experimental Techniques of Materials Characterizations
2.4.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative spectroscopic technique that measures the elemental composition, chemical state and electronic state of the elements present in a material. The basic principle of XPS is shown diagrammatically in fig. 2.10. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons escaped from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.

XPS can be performed using either a commercially built XPS system, a privately built XPS system or a synchrotron-based light source combined with a custom designed electron analyzer. Commercial XPS instruments uses either a highly focused 20 to 200µm beam of monochromatic Al Kα X-rays or a broad 10 - 30mm beam of non-monochromatic (polychromatic) magnesium X-rays. Because the energy of an X-ray with particular wavelength is known, the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \]

where, \( E_{\text{binding}} \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument and \( \phi \) is the work function of the spectrometer.

Figure 2.10: Schematic diagram of basic principle of XPS –“Photoelectric effect”
2.5  Microstructural Characterization

2.5.1  Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected which contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image [10]. SEM can achieve resolution > 1 nm. Specimens can be observed in high and low vacuum. In environmental SEM, specimens can be observed in wet conditions. Schematic diagram of SEM is shown in fig. 2.11.

Figure 2.11:  Schematic block diagram of SEM
The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodo-luminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details < 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 5,000,000 times, about 250 times the magnification limit of the best light microscopes.

2.5.2 Atomic Force Microscopy (AFM)

AFM, first invented by Binning, Quate and Gerber in 1986 [11] is one of the powerful tools for probing the surface of the thin film at the nanoscale. The most important features of AFM technique are, high resolution (~2 Å) and magnification (~ × 10^7) which gives the better idea of topography of the film surface as well as biological substance such as bacteria and viruses etc. Now a day, AFM is also useful for measuring magnetic and electric response of the surface along with the topographical image.

AFM is operated by scanning a very sharp and tiny tip attached to the end of a cantilever across the sample (fig. 2.12). The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law. Depending on the situation, forces which are measured in AFM include mechanical contact force, van der waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, etc. Typically, the deflection is measured using a laser spot reflected from the top surface of the
cantilever into an array of photodiodes. We can choose different mode for its operation, depending our requirements, such as tapping mode, contact mode and non-contact mode.

![AFM Working Principle](image)

Figure 2.12: Working principle of AFM (schematic)

1) Contact mode:

One method of AFM is the use of contact mode where the cantilever remains in contact with the surface during scanning. When it encounters variations in the surface it responds by deflecting to follow the contours. This process produces accurate topographical maps of the surface for many different samples, but there are some unwanted drawbacks. With the cantilever in continuous contact of the sample, damage to the surface can occur which can then alter both the resulting image and properties of the material.

2) Non-contact mode:

In this method, the tip is few nanometer above the surface of the material vibrating with frequency little higher than the resonance frequency of tip. The amplitude of such vibrations are generally very small (< 10nm). It scans the sample by measuring
the interaction of long range forces with cantilever tip. It is mostly used to scan liquid layers on the solid surface without damaging the sample surface.

3) Tapping mode:

In the tapping mode, the cantilever arm is oscillating at a resonant frequency as it scans the surface. When the tip begins to lightly touch the surface, a sensor reverses the motion of the cantilever to continue the oscillation. The tip then intermittently touches the surface, instead of being dragged avoiding damages. But since the cantilever is not in continuous contact with the surface, a method of measuring the differences in the surface height must be determined. This results from changes in the amplitude of oscillation of the cantilever. When it encounters bumps on the surface, the amplitude of oscillation is reduced. Conversely, valleys or depressions cause the amplitude to increase. By recording these changes, an accurate topographical map can be produced without damaging the surface of the material. To ensure that the oscillation and amplitude remain fairly constant, a digital feedback loop is also implemented.

2.5.3 Magnetic Force Microscopy (MFM)

Magnetic force microscope (MFM) is a variant of atomic force microscope, where a sharp magnetized tip scans a magnetic sample. The tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface. Many types of magnetic interactions are measured by MFM, including magnetic dipole - dipole interaction. MFM scanning often uses non-contact AFM mode shown in figure. The scanning method used in MFM is called the "lift height" method [12]. When the tip scans the surface of a sample at close distances (< 10 nm), not only magnetic forces is sensed, but also atomic and electrostatic forces. The lift height method helps to enhance the magnetic contrast through the following:

- First, the topographic profile of each scan line is measured. That is, the tip is brought into a close proximity of the sample to take AFM measurements.
The magnetized tip is then lifted further away from the sample. MFM image is compared with the AFM (shown in figure). Magnetic response of the sample can clearly identified.

In the second step, the magnetic signal is extracted.

Figure 2.13: Working principal of MFM (schematic)

Figure 2.14: Identical images of AFM and MFM
2.6 Transport and Magnetotransport Characterizations

Manganite and multiferroic samples studied during the cause of present work were characterized for their transport and magnetotransport behaviour using the D.C. four probe method, without and with applied magnetic field. The details are given below:

2.6.1 D.C. Four Probe Resistivity (without and with field)

The measurement of electrical resistance as a function of temperature gives information about the various temperature dependent electronic phase transitions. A low contact resistance is desirable due to the small resistance of the samples, such as manganite, HTSC, etc. To accomplish this requirement, standard four-probe method was used for measuring resistance of the samples [13]. To measure the resistivity using this technique, the samples were cut in a rectangular bar shape using a diamond saw. For the electrical contacts on the sample surface, conductive silver paste or Indium contacts were made. Due to very less resistance, thin copper wires were connected with silver paste as shown in fig. 2.15 and the whole assembly was put onto a sample holder, where the wires were connected with leads to the measurement instruments. This type of sample holder is known as resistivity puck for measuring resistivity using Quantum Design a Physical Property Measurement System (PPMS).

![Figure 2.15: Four probe contacts, used in the D.C. for probe method for resistivity measurements.](image-url)
As shown in the fig. 2.15, current was passed through the outer probes (+I & -I) and resultant potential difference developed between two inner probe was measured (+V & -V). Resistance of sample was determined using the ohm’s law “\( V = IR \)”, where I is the current passed and V is the voltage developed. Using dimensions, shown in figure, the exact resistivity (\( \rho \)) of the sample can be calculated using the relation,

\[
\rho = R \frac{A}{l}
\]

where R is the resistance, \( A \) (\( A = b \times t \)) is the cross-sectional area of the sample. Here, it is mentioned that, thermo emf is automatically compensated during the measurements.

Figure 2.16: PPMS probe and sample chamber geometry (courtesy, Quantum Design)

To study magnetoresistance (MR) behaviour of the samples, resistance was measured by using the standard four probe method, in the presence of an external magnetic field using Quantum Design physical property measurement system (PPMS). At a constant applied field, resistance was measured as a function of temperature
(magneto R-T) in the temperature range of 5-300K. All the mixed valent oxide samples studied in the present work were characterized for magnetoresistance using this method. Fig. 2.16 shows the PPMS probe and sample chamber geometry. During, the course of this work, PPMS facility at UGC-DAE CSR, Indore was used for measuring resistivity of all the samples.

2.7 Electrical Characterizations

2.7.1 Dielectric Measurements

Dielectric is an electrical insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric field which reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, these molecules not only become polarized, but also reorient so that their symmetry axis aligns to the field.

While the term insulator implies low electrical conduction, ‘dielectric’ is typically used to describe materials with a high polarizability. The latter is expressed by a number called the dielectric constant. The term insulator is generally used to indicate electrical obstruction while the term dielectric is used to indicate the energy storing capacity of the material (by means of polarization). A common, yet notable, example of a dielectric is the electrically insulating material between the metallic plates of a capacitor (fig. 2.17).

Dielectric constant for the bulk sample can be calculated by measuring the capacitance of the material. The temperature and frequency dependent capacitance was measured using Agilent 4281A precision LCR meter. In order to avoid any parasitic impedance, shielded test leads were used for electrical connection from the analyzer to sample. First, polycrystalline bulk sample pellet and films were heated at 100C for 1 hour for homogenization of charge carrier and remove the moisture content. For making a
capacitor type arrangement, sample surfaces were coated using silver paste, which act as a good contact for measuring dielectric properties.

![Schematic diagram of a parallel plate capacitor with dielectric spacer](image)

Figure 2.17: Schematic diagram of a parallel plate capacitor with dielectric spacer

The value of the dielectric constant ($\varepsilon'$) was calculated using formula;

$$\varepsilon' = \frac{C}{C_0} \tag{2.1}$$

where, $\varepsilon'$ is the real part of dielectric constant, $C$ is the capacitance of the material inserted between the electrodes and $C_0$ is the capacitance of the medium as air or no medium between the electrodes. The $C_0$ for the parallel plate capacitor can be calculated using the following relation

$$C_0 = \frac{\varepsilon_0 A}{t} \tag{2.2}$$

where, $\varepsilon_0$ is permittivity in vacuum ~ $8.85 \times 10^{-12}$ C$^2$/N. m$^2$, $t$ is the thickness of the sample and $A$ is the area of the specimen in sq.m.

Now, using eq. (1) & (2), the dielectric constant can be calculated as

$$\varepsilon' = \frac{C \times t}{\varepsilon_0 A} \tag{2.3}$$

The imaginary component of dielectric constant ($\varepsilon''$) is calculated using the formula

$$\varepsilon'' = \varepsilon' \tan\delta \tag{2.4}$$
where, \( \tan\delta \) is loss tangent, proportional to the ‘loss’ of energy from the applied field into the sample, in which energy is dissipated into heat and therefore known as a dielectric loss.

### 2.7.2 Polarization vs. Electric Field (P - E hysteresis loop) Measurements

Ferroelectricity is usually defined as irreversibility of the spontaneous polarization by an applied electric field. P - E hysteresis loop is the essential characteristic of ferroelectric materials. From, the P - E loop, one can get the information about the saturation polarization (\( P_s \)), remnant polarization (\( P_r \)) and coercive field (\( E_c \)) which help us to understand the effect of applied electric field with frequency. Fig. 2.18 shows the schematic diagram of typical P - E hysteresis loops observed in ferroelectric materials. Depending on types of samples, shape of the P - E loop changes according to their ferroelectric behaviour. There are four types of shape (i) linear P - E loop (ii) resistive capacitor loop (iii) lossy hysteresis and (iv) non-linear hysteresis loop (fig.2.18).

![Figure 2.18: Typical types of ferroelectric loops](image)

- (a) linear P - E loop
- (b) resistive P - E loop
- (c) lossy P - E loop
- (d) non-linear P - E loop

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The most often quoted method of hysteresis loop measurement is based on a Sawyer and Tower circuit, in which, the field applied across the sample is attenuated by a resistive divider, and the current is integrated into charge by virtue of a large capacitor in series with the sample. Both these voltages are then fed into the X and Y axes of an oscilloscope to generate the P - E loop. The applied voltage is usually a sinusoidal at mains frequency. Also, there are commercially available high voltage amplifiers which allow frequencies other than those tied to the mains frequency and also enable waveforms other than sine waves to be used. Sine waves are most often used since these can be easily produced, however a triangle wave drive is more attractive for frequency dependent measurements since dE/dt is constant.

2.8 Magnetization Measurements - SQUID

Superconducting Quantum Interference Device (SQUID) magnetometer is the most powerful, sensitive and widely used instrument for magnetic characterization of thin films. SQUIDs are very sensitive detector of magnetic flux which combines the physical phenomena of flux quantization and Josephson tunneling. This Josephson junction (sensor) mainly consists of the superconducting ring interpreted by a thin insulting film called weak link. The schematic diagram of the Josephson junction consisting of two superconducting coils is shown in the fig. 2.19. The sensor and its pick up system is sensitive to change in the magnetic fluxes and thus to the change of the magnetization of magnetic material as a function of temperature, magnetic field and time. The SQUID has one or more Josephson junctions as its active element.

In most practical systems in use today, the SQUID is located inside a small cylindrical, superconducting magnetic shield in the middle of a liquid helium Dewar. Superconducting pickup coils, typically configured as gradiometers that detects the difference in one component of the field between two points, are located at the bottom of the Dewar, and are placed beneath the magnetometer. The rest of the hardware is designed to minimize helium boil off, eliminate rf interference, and avoid Johnson noise or any external distortion a. c. fields. If a constant biasing current is maintained in the
SQUID device, the measured voltage oscillates according to the changes in phase at the two junctions, which depends upon the change in the magnetic flux. The flux change can be evaluated by counting the oscillations. It may be noted that the sensitivity of SQUID is $10^{-14}$ Tesla, which is incredibly large to measure any magnetic signal.

During the course of present work, SQUID - VSM facility at UGC-DAE CSR, Indore was used to study M - H behaviour of multiferroic films.

![Schematic diagram of the SQUID sample measurement probe](image)

**Figure 2.19:** A schematic diagram of the SQUID sample measurement probe

### 2.9 Swift Heavy Ion (SHI) Irradiation Experiment at IUAC, New Delhi

During the course of present work, 200MeV Ag$^{+15}$ ion irradiation on multiferroic and manganite samples was performed using Material Science Beam Line of pelletron facility at Inter University Accelerator Centre, New Delhi. For the measurement of reported in this work, high vacuum chamber was used for irradiation experiment (fig. 2.20). Samples were mounted on the four side of target ladder made up of copper block and mounted through a Wilson seal mechanism from the top flange of chamber. The stepper motor is used to provide up and down motion to the ladder. A CCD camera is attached to the chamber to observe the sample on closed circuit television (CCTV) in data room. Also, for suppression of secondary electrons coming out of the sample during irradiation, cylindrical stainless steel surrounds the samples and ladder kept at a negative potential of 120V.
After, successfully installing the irradiation set up, following steps were used for irradiating samples.

1. Chamber vacuum maintained \( \sim 10^{-6} \) mbar using turbo pump

2. Check the beam falling on the quartz crystal mounted at end of the ladder

3. Fix the beam scanning area using magnetic scanner (\( \sim 10 \times 10 \text{mm} \)) for uniform irradiation and marked scanning area on CCTV

4. Calculate the total numbers of ions falling on the sample using current integrator and pulse counter using the equation

\[
\text{No. of counts} = \text{Ion fluence} \times \text{charge} \times 1.6 \times 10^9 / \text{pulse height}
\]

\[
\text{Time (second)} = \text{Ion fluence} \times \text{area} / \text{current (pnA)} \times 1.6 \times 10^9
\]

5. Using stepper motor, fix the sample position according to scanning area on CCTV camera and start the beam for irradiation of sample films

Figure 2.20: Photograph of high vacuum chamber at Material Science Beam Line, IUAC, New Delhi
2.10 Simulation Methods

The act of simulating something first requires that a model be developed; this model represents the key characteristics or behaviors/functions of the selected physical or abstract system or process. The model represents the system itself, whereas the simulation represents the operation of the system over time. Simulation is used in many contexts, such as simulation of technology for performance optimization, safety engineering, testing, training, and education. Simulation is also used with scientific modeling of natural systems to gain insight into their functioning. Simulation can be used to show the eventual real effects made alternative conditions and courses of action.

During the course of present study, electronic ($S_e$) and Nuclear energy loss ($S_n$) during ion interaction with material was calculate using Stopping and Range of Ion in Matter (SRIM) simulation software and chemical composition and thickness of films were calculated from the Rutherford Backscattering (RBS) data analysis using SIMNRA simulation program.

2.10.1 Stopping and Range of Ion in Matter (SRIM)

SRIM is a group of programs which calculate the stopping and range of ions (up to 2 GeV/amu) into matter using a quantum mechanical treatment of ion-atom collisions (assuming a moving atom as an "ion", and all target atoms as "atoms"). This calculation is made very efficient by the use of statistical algorithms which allow the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap.

SRIM was developed by James F. Ziegler [14] to understand the (i) electronic ($S_e$) and nuclear energy loss ($S_n$) of ion into the material, (ii) ion range in the material, (iii) ion path in the material, (iv) intermixing and sputtering during irradiation and (v) defects and vacancies formation, etc. In the present work, PLD grown BiFeO$_3$ (BFO) multiferroic and La$_{0.6}$Pr$_{0.2}$Sr$_{0.2}$MnO$_3$ (LPSMO) manganite films were irradiated using 200MeV Ag$^{+15}$ ions for creating structural defects. Using SRIM simulation program, the calculated values of electronic energy loss ($S_e$) and nuclear energy loss ($S_n$) were
~14.05 keV/nm and ~42.76 eV/nm for BFO films and ~13.61 keV/nm and ~37.78 eV/nm for LPSMO films, respectively. Variation in energy loss with Ag-ion energy in BFO and LPSMO films has been plotted in fig.2.21.

Figure 2.21: Variation in electronic and nuclear energy loss of Ag ion in (a) BFO and (b) LPSMO films
2.10.2 Simulation Program for analysis of RBS, NRA and ERDA (SIMNRA)

SIMRNA is a Microsoft windows program for the simulation of backscattering spectra for ion beam analysis with MeV ions. SIMNRA is mainly intended for the simulation of non-Rutherford backscattering, nuclear reactions and elastic recoil detection analysis (ERDA). More than 300 different non-Rutherford and nuclear reactions cross-sections for incident protons, deuterons, $^3$He, $^4$He and Li - ions are included in this program. SIMNRA can calculate spectra for any ion – target combination including incident heavy ions and any geometry including arbitrary foils in front the detector. In addition data fitting (layer thickness, compositions etc.) is possible by means of simplex algorithm [15].

SIMNRA has many tabs allowing the user with considerable flexibility for analysis of different forms of ion-solid interactions (including nuclear reactions). The key operations are contained in the tabs TARGET, CALCULATE, TOOLS, and PLOT. In TARGET we should enter our best guess for the sample (e.g., film on a substrate, elemental composition, and description of target either in terms of atomic concentration or areal density). Using CALCULATE, we can create a simulated spectrum to match the experimental data and determine elemental composition, thickness, and (if relevant) depth profile. From TOOLS, we use the INTEGRATE SPECTRUM option to find the total counts under the elemental peaks in both the experimental and simulated spectra and use this info to refine our description of the target. PLOT allows us to change in the way the data is displayed. Now, using the intuition you have to form a the qualitative way in which if the simulation misses the data, change the assumptions for the film and target and try to get the best possible fit [16].

Following steps gives the method to obtain good fit by changing the film thickness and then adjusting the composition.

a) Keeping the target window in the “Concentration” mode, adjust the thickness in an attempt to improve the fit

b) After you choose a new thickness, go to the CALCULATE tab and select “calculate spectrum”
c) Repeat this process until you believe you have the correct film thickness

d) Now, use the “integrate spectrum” function from the TOOLS tab to compare the integrated counts in the right peak in the experimental and simulated spectra. Get the ratio

e) Now, using this ratio, go to the target window in the “areal density” mode, update the areal density

f) Recalculate the spectrum and see how it works

g) Now, return to the “concentration” mode, change the thickness to best fit the material peak

h) Repeat the spectrum integration and repeat the process until you get a fit that agrees both in peak widths and integrated intensity
References


