In this chapter, the detailed description of the methodology adopted for the sample preparation and various experimental techniques used for the characterization of the samples are presented. The experimental techniques utilized for the study of structural, electrical, magnetic and magneto-electric properties of bulk and thin films have been discussed. An outline of swift heavy ion irradiation is also provided.
2. 1 Samples preparation: Solid state reaction

The solid state reaction method of sample preparation is also known as ceramic method. It has advantage over other methods such as sol gel or co-precipitation technique [1-3] due to easiness of the process involved in this method. This process involves various steps like:

(i) Mixing of oxide powders
(ii) Calcination
(iii) Pelletization
(iv) Sintering

(i) Mixing of oxide powders

The starting materials for the preparation of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (LBFMO, 0.0 $\leq$ x $\leq$ 0.4) multiferroic bulk samples were high purity (> 99.99 % pure) powders of lanthanum oxide (La$_2$O$_3$), bismuth oxide (Bi$_2$O$_3$), iron oxide (Fe$_2$O$_3$) and manganese oxide (MnO). Powders weighed in the right stoichiometry were mixed thoroughly and ground using a mortar and pestle. This process is carried out rigorously for several hours in order to accomplish the homogeneity of the mixed powder. The uniformity and the chemical homogeneity of the mixture are of significant importance.

(ii) Calcination

The purpose of calcination procedure is to establish the initiation of nucleation for grain growth and to felicitate the decomposition of substituent oxides/carbonates. The basis for this process is concentration gradient and high temperature. It is for chemical and crystallographically uniform growth of the structure. Mixed powders were kept in an alumina crucible with proper labeling of sample’s name and kept in furnace. The course of calcination leads to heating of homogeneously mixed powder to an intermediate high temperature ~100 - 300 °C lower than final sintering temperature. LBFMO (0.0 $\leq$ x $\leq$ 0.4) samples were calcined at 750 °C for 12 hours and repeated at 800 °C for same duration with intermediate grinding.

(iii) Pelletization

It is achieved with a die-press technique in which a die of proper shape was partially filled with calcinated powder and pressed at 8 tone using hydraulic press. This is done to increases the solid state reaction among oxides and to bring the calcined powder into the required shapes and densities for characterization purpose. In our case, pelletization is done in a circular dye of 15 mm diameter and thickness of the pellets was ~3 mm.

(iv) Sintering

After the pelletization, the pellets were kept for final heating, relatively at higher temperature
**SOLID STATE REACTION METHOD**

Stoichiometric quantities

La$_2$O$_3$  Bi$_2$O  Fe$_2$O$_3$  MnO

All Powder were 99.99% Pure Aldrich

Dry mixed in Powder form in Agate Mortar

First and second calcination

750 °C / 12 hrs
800 °C / 12hrs

Grinded thoroughly followed by pelletization

Sintering of precalcined pellets

950 °C / 24 hrs

Grinding with polvinyl alcohol & then palletized.

Final sinteirng

1000 °C / 24 hrs

No  Yes

Single Phase La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4)

**Fig 2.1** Flow chart for solid-state reaction method used for synthesis of bulk La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4) samples.
and for longer duration compared to that used during calcination. This is followed by slow cooling with a suitable predefined rate, which is an essential and important process as it favors the required oxygen content in the material. LBFMO \((0.0 \leq x \leq 0.4)\) sample’s pellets were kept at 950 °C for 24 hours and the final sintering temperature was given to be 1000 °C for 24 hours followed by slow cooling at the rate of 2 °C /min. The flowchart shown in Fig 2.1 (previous page), depicts the method of solid state reaction route adopted for preparing the bulk samples of \(\text{La}_{0.8}\text{Bi}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3\) \((0.0 \leq x \leq 0.4)\).

### 2.1.2 Thin film deposition

**Mechanism of RF magnetron sputtering**

Sputtering is a widely used technique for the deposition of films. It is the phenomena of ejection of surface atoms that takes place by momentum transfer from bombarding ions to surface atoms as shown in Fig 2.2. It is usually done by means of plasma, which generates charged particles that can be accelerated towards a surface applying high voltage producing attrition of surface atom [4]. Properties of thin films are dependent on various deposition parameters like deposition technique, substrate temperature, total pressure and composition of the operating gas [5]. For the purpose of thin film deposition either RF or dc voltage is applied to system for accelerating charged particles. In dc system, electrons and ions are accelerated by a constant electric field applied between an anode and the cathode. In dc sputtering, the target is kept at a negative potential (cathode) and the substrate on which film is to be deposited is kept at a positive potential (anode), as shown in Fig 2.3. Any type of conducting material can be deposited by this technique but for insulating target it is not possible because of the formation of positive charge on the target surface that resists any further ion bombardment on the target.

RF-sputtering system is used for deposition of insulators. RF potential is applied to target electrode and substrate electrode is kept at ground as shown in Fig 2.4. Electrons oscillating in alternating field have sufficient energies to cause ionizing collisions and the discharge will be self sustained. Generally, argon (Ar) gas is used for sputtering and argon ions are formed by oscillating electrons. RF sputtering essentially works because the target self biases to a negative potential. Negative target bias is due to the fact that electrons are considerably more mobile than the ions. During positive half cycle, electrons are attracted towards target and being an insulator, the target acts as capacitor and electrons are stored there. However, during negative half cycle due to less mobility positive ions are not able to follow field as fast as electrons could. As a result, target self biases to a negative potential
**Fig 2.2** Schematic diagram showing the sputtering due to impact of energetic ions on surface.

For RF sputtering, frequency ($f$) at which system is operated must be greater than 10 MHz because at $f$ less than this there will be space charge accumulation. Also, $f$ should not be higher because the ions will be unable to respond to the $f$. Generally, 13.56 MHz frequency is used \[6\]. The most important aspect in this technique is the impedance matching network between power supply and discharge chamber that consists of an LC circuit with variable impedance. The impedance is matched, by varying the impedance of this network to transfer maximum power to the load. Grounding of the substrate is done to avoid the undesirable RF voltages which can be developed on the surface. Capacitive coupling is essential for sputtering metals and alloys to sustain the self biased negative potential. However, if an insulator is to be sputtered, it is not required as the insulator itself serves the purpose of the capacitor \[6\]. In RF-magnetron sputtering system, to increase the ionization rate by emitted secondary electrons even further, a permanent magnet is placed behind the target. Due to this arrangement, there is an increase in the path length of electrons and hence extremely dense plasma is formed \[4\]. Schematic of RF-magnetron sputtering system used for present thesis work at Inter-University Accelerator Centre (IUAC) is shown in Fig 2.4. The system consist of three parts: sputtering chamber along with vacuum system, the gas flow system and the RF system with matching network. The system contains a target holder acting as cathode and a substrate holder acting as anode. Substrates are kept on anode at a distance of 3 cm from the cathode. The selection of the distance is based on the fact that enough number of collisions should take place in gaseous medium for an operating pressure (~5x10$^{-2}$ torr). The cathode is connected to RF power supply while anode and rest of the system are properly grounded with metallic strips. The substrate holder is kept on an electrically insulated height adjustable table. It is attached to a heating coil, which acts as
Chapter 2

Experimental techniques

Fig 2.3 Schematic diagram of dc sputtering unit.

Fig 2.4 A schematic view of RF sputtering unit used for deposition of thin films at IUAC, New Delhi.
a substrate heater. Variac is connected to this heater to change the current in the heater and thereby the temperature. A thermocouple based temperature sensor is used to read the temperature. Target holder is made up of metal, which is provided with water connections to cool it. A proper RF shielding in the sides of the cathode is done to check the spread of plasma within the cathode and the anode. The gas flow system of the set up is used to flow the gases required. Ar ions are formed by the impact of electrons under the applied voltage and the required operating pressure is adjusted using the pumping system. Thin films of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ multiferroic were prepared by RF sputtering. Detailed parameters for thin film growth are described in Chapter 6 of present thesis.

2.2 X-ray diffraction (XRD)

XRD is a versatile, non-destructive technique to identify the crystalline phases present in solid materials and analyze the structural properties. This is an appropriate technique for both forms of samples i.e. thin film as well as bulk. XRD was first demonstrated by Von Laue in 1912. These days XRD [7] is a routine technique for the characterization of the materials. X-rays are electromagnetic radiation and are produced when any electrically charged particle of sufficient kinetic energy is rapidly de-accelerated. The wavelength ($\lambda$) of X-rays is of order of $\sim 10^{-8}$ cm. For diffraction purposes X-rays of wavelength $\lambda \sim 0.5 - 2.5$ Å are taken because for diffraction to occur wavelength of incident waves must be of the order of interatomic separation. When a beam of X-rays interacts with an arbitrary material, its atoms may scatter the rays into all possible directions. In a crystalline solid, however, the atoms are arranged in a periodic array and this imposes strong constraints on the resulting diffraction pattern. As a result, constructive and destructive interference takes place in certain directions only as shown in Fig 2.5 (a, b). For the study of present multiferroic system, X-ray emitted by copper is taken. The characteristic wavelength for the copper K$_\alpha$ radiation is 1.542 Å, which is about

![Fig 2.5](image)
the same size as an atom. Diffracted lines in XRD are Gaussian shaped instead of straight lines due to following factors, (1) Non-monochromaticity of incident beam, (2) Instrumental resolution, (3) Finite grain size, (4) Absence of perfect parallel beam. The fundamental of XRD is best explained by the Bragg’s eq. 2.1, which places the condition for the constructive interference for the scattered X-ray from the successive atomic planes formed by the crystal lattice of the material. The Bragg’s condition is formulated by the equation,

\[ 2dsin\theta = n\lambda \]  

where, \( \theta \) is the angle between the incident rays and crystal surface, \( d \) is the spacing between layers of atoms and \( n \) is the order of diffraction. The constructive interference occurs when \( n \) is an integer. The detector motion is coupled with the X-ray source in such a way that it always makes an angle 2\( \theta \) with the incident direction of the X-ray beam (Fig 2.6). Using this technique, we get information regarding the crystallinity of the material, epitaxial quality of the nanostructures, nature of the phase present, lattice parameter and grain size [8]. In the case of the thin films, the change in the lattice parameter with respect to the bulk indicates the nature of the strain present in the films. In thin films, X-rays are diffracted by the oriented crystallites at a particular angle to satisfy the Bragg’s condition. By knowing the value of \( \theta \) and \( \lambda \), one can calculate the inter-planar spacing. The XRD pattern can be taken in various modes such as 0 - 20 scan mode, 0 - 20 rocking curve and \( \phi \) scan. Diffractometer shown in Fig 2.7, was used for the phase detection of bulk powders and thin film at IUAC, New Delhi. Room temperature powder XRD studies of the samples were performed within the 20 range of 20º to 80º for bulk samples and 20º to 60º for the thin films. The lattice spacing \( d \) was
calculated using Bragg’s law (eq 2.1), which is further utilized to compute lattice constants. The analysis of the XRD pattern was done using powderX software [9] and FULLPROF code [details in Chapter 3].

2.3 Transport measurement

2.3.1 Dielectric setup

Basically it is a four probe setup, with two left probes (current probe) and two right probes (voltage probe) shorted with the help of thin copper wires. This four probe setup has been converted into two probe setup as shown in Fig 2.8. The dielectric constant as a function of temperature reveals FE property of material. On this setup we had performed the following type of measurements:

(i) Frequency dependent dielectric properties (10 kHz - 30 MHz).

(ii) Temperature dependent dielectric properties (80 – 450 K).

(iii) Temperature dependent capacitance versus voltage (C vs V) measurement for knowing the FE nature of samples in the range of 80 – 450 K.

The LBFMO (0.0 ≤ x ≤ 0.4) multiferroic samples were cut into rectangular shape using diamond cutter. Samples were mounted on the base of ladder as shown in Fig 2.9 and electrically connected using the thin copper wire by applying the silver paste on both sides of
it with the help of brush carefully. No part of silver paste should touch the cylindrical part of the pallet. The temperature of the sample is controlled using the Lakeshore temperature controller (Model 340) and stabilized within ± 50 mK (see Fig 2.9). This setup is fully automated and program had been written using Lab-View software. The dielectric constant for the bulk sample was calculated by measuring the capacitance of the material. The capacitance as a function of frequency and temperature has been measured using Agilent 4285A precision LCR meter (Fig 2.9). Shielded leads were used for electrical connections from the analyzer to the sample in order to avoid any scrounging impedance. Before starting the measurement, samples were heated at 500 °C for 1 hour to remove the moisture content, if any. C vs V measurement was also performed using the same setup. A different program has been written in Lab-view software for this. We have to give the range of voltage. For this

**Fig 2.8** Block diagram showing the dielectric measurement setup.
Fig 2.9 Diagram showing the setup used for Dielectric measurement at transport lab IUAC, New Delhi.
measurement the temperature has been stabilized prior of starting the program for C vs V and dc bias voltage was kept ‘ON’ during whole duration.

### 2.4 Magnetic measurement setups

The study of magnetic properties of materials is a basic requirement for understanding magnetism in condensed matter physics. There are various techniques for knowing magnetic properties of the material under study. Vibrating Sample Magnetometer (VSM) and Superconducting Quantum Interference Device (SQUID) magnetometer are used for magnetization measurements of the samples in bulk and thin film form respectively.

#### 2.4.1 Vibrating sample magnetometer (VSM)

VSM is based upon Faraday’s law according to which an e.m.f. is induced in a conductor by time-varying magnetic flux. In VSM setup (Fig 2.10) a sample magnetized is vibrated sinusoidally at small fixed amplitude with respect to stationary pick-up. When a magnetic material is placed in a homogenous magnetic field, a dipole moment is induced in the sample which is proportional to the product of sample susceptibility and the applied magnetic field. This sample is made to vibrate perpendicular to the uniform magnetic field by a transducer assembly and an electrical signal induced in suitably located pick-up coils around the sample. This induced voltage, which is vibrating at frequency \( f \), is proportional to magnetic moment induced in the sample. Since the signal at vibrating \( f \) is proportional not only to the magnitude of the magnetic moment of sample but also to the vibration amplitude and frequency. Therefore, to get the magnetic moment of the sample, a comparison voltage is induced in the same set of reference coils by a vibrating capacitor, which is being vibrated by same transducer. This comparison signal varies with vibration amplitude and \( f \) of vibration in the same manner, as that of the signal from the pickup coils placed near the sample. These two signals are applied to two inputs of a differential amplifier to cancel the effects of vibration amplitude and frequency. Thus the signal at the output of the differential amplifier is now a function of only the magnetic moment of the sample. This signal is then applied to a synchronous detector (lock-in amplifier), where it is compared with a reference signal and is also applied to transducer which oscillates the sample. Therefore, at the output a signal is proportional to amplitude of the magnetic moment. This signal is then amplified and used in two different ways. One part is fed back to the movable plate assembly of the vibrating capacitor and second part is applied to the output display circuits, where the amplitude of the moment is recorded. The effect of the feedback is to automatically adjust the signal to required level to maintain the capacitor output signal at the same level as the pickup coil.
signal. In the present study, we have used the VSM for the magnetization measurement of LBFO (0.0 ≤ x ≤ 0.4) multiferroic samples. The magnetization measurements were carried out using the VSM option of Quantum Design PPMS set up within a temperature range of 5 - 320 K in field cooled (FC) mode under a constant magnetic field (H = 500 Oe). Field dependent magnetization measurements (M vs H) were performed at various fixed temperatures (20, 100, 200 and 300K). All the measurements were carried out in warming up cycles.

**Fig 2.10 Schematic block diagram for the VSM setup used in present work.**

### 2.4.2 Superconducting quantum interference device (SQUID)

In a SQUID based magnetometer a magnetic sample passes through a set of sensing coils. The sensing coils are comprised of superconducting coils separated by thin insulating layers (Fig 2.11) that are less than 30 Å thick. These layers are called Josephson junctions because Brian Josephson in 1962, showed that Cooper pairs (electron pairs) in superconductors could tunnel through an insulating layer between the superconductors [10]. If superconductors separated by a thin insulating layer are brought very close to each other, tunneling of electrons occur. If the distance is reduced even more, tunneling of Cooper-pairs will also
occur. For currents below a critical value, the pair tunneling constitutes a super current and no voltage is developed across the junction. However, a voltage appears for currents greater than the critical value. The presence of the insulating layer typically restricts the value of the super current flowing in the coil to less than $10^{-5}$ A. Most of the low $T_c$ SQUIDs are made from Niobium thin films which have a transition temperature around 9.25 K, well above the boiling temperature of liquid helium and are also mechanically very stable. Tunnel junctions are patterned from Nb/AlO$_x$/Nb trilayers in which a AlO$_x$ barrier is formed by oxidization of a few nanometers of aluminum [11]. Figure 2.11 shows a schematic of a Josephson junction. There are two types of SQUIDs. 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. Second RF SQUID consists of a single Josephson junction inserted into a superconducting loop. The sample is placed in a superconducting pick-up coil that is connected to the actual SQUID. Since the magnetic flux through a superconducting ring is quantized, the sample will induce a super current in the pick-up coils that will keep the flux at a constant value. In the present study, magnetic properties of unirradiated and irradiated La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ thin films (details Chapter 6) were characterized using Quantum Design MPMS XL SQUID Magnetometer (Fig 2.12).

![Schematic of a Josephson junction](image)

**Fig 2.11** Schematic of a Josephson junction consisting of two superconductors separated by thin insulating layers.

### 2.5 Magneto-capacitance (MC) setup

The low temperature high magnetic field facility [12] used for MC measurement can cool down to 1.6 K and can generate magnetic field up to 8 tesla without any use of liquid cryogen. With separate attachments, the sample space can be cooled to 1.6 K and heated up to 1000 K (encapsulated oven). It is a single compressor open-ended system purchased from
cryogenics of UK. The compressor is water cooled and requires continuous supply of chilled water (15°C) at the rate 7 lit/min. The cooling powers at the first and second stage cold heads are 34 W at 40 K and 1 W at 4.2 K, respectively. The second stage cooling is shared between the sample space and the Nb-Ti superconducting magnet ($T_c = 9$ K). The first stage is connected to an ultra pure aluminium radiation shield. The magnet is latched to the second stage of the compressor. A condensation pot is attached to the magnet. When low pressure helium gas from a separate close cycle reservoir is brought in contact with condensation pot, the gas liquifies and with suitable pumping, the base temperature of 1.6 K can be achieved. It is to be emphasized that the process is entirely liquid cryogen free. Further the sample space is always cooled by the helium vapor, the vibrations due to mechanical movement of displacer do not interfere with the measurements. The block diagram of the cryogen-free system is shown in Fig 2.13. The cryostat also includes a vertical column where the sample is inserted using a dip-stick (variable temperature insert or VTI), a superconducting magnet and a condensation pot. The temperature of the superconducting magnet always remains 4 K.
except for small variation (~ 0.5 K) during charging and discharging of the magnet. The condensation pot is connected to a separate helium gas recycle consisting of a reservoir (50 liter helium gas), an air filter and a dry pump. The helium gas gets liquefied locally at the pot and its vapour flow (and therefore the temperature) in VTI chamber is controlled by a needle valve. To reach 1.6 K, a pressure of 8 mbar is maintained in the VTI chamber. Controlled heating using 25 W heater near VTI base dictates the temperature of the helium vapour at the sample space. Resistive temperature sensors are placed at various points in the cryostat such as shield, magnet, condensation pot and exchanger exhaust to continuously monitor the system parameters. Resistance (temperature) at these points is measured using a Keithley 2700 multimeter with a 10 channel scanner. The temperature in the VTI and on the sample holder is measured and controlled by Cernox sensors using a Lakeshore 340 temperature controller. The magnet power supply is cryogenic Model SMS 120 C. Maximum field of 8 tesla requires current flow of 108 A. The magnet is fitted with a persistent switch that enables very stable homogeneous field. The interfacing software and automation have been developed using Labview software. The sample can be taken out of the system without warming the system to room temperature.

**Fig 2.13** Block diagram of low temperature high magnetic field facility used for magneto-capacitance measurement at JNU, New Delhi.
In the present work, MC studies has been performed at Jawaharlal Nehru University (JNU), New Delhi as a function of temperature with applied magnetic field ranging from 0 to 3 tesla on the $\text{La}_{0.8}\text{Bi}_{0.2}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($0.0 \leq x \leq 0.4$) bulk samples.

### 2.6 X-ray absorption spectroscopy (XAS)

The schematic of arrangement used to collect XAS spectra in the transmission as well as fluorescence mode is shown in Fig 2.14. Advantage of measurements in transmission mode is that it probes the entire sample. However, measurements in transmission mode are severely restricted by the fact that most of the materials are not transparent to X-rays. Thus in most of the experiments, secondary effects are exploited to measure the absorption coefficient. The electron excited by the incident photon leaves behind a core hole which relaxes mainly via emission of Auger electron or X-ray fluorescence. In both cases, probability of emission of electron or photon is directly proportional to absorption probability under certain conditions. Thus, detecting fluorescence photons or the Auger electron yields the absorption coefficient. Correspondingly, there are two other methods of collecting XAS, one is total electron yield (TEY) and the other is total fluorescence yield (TFY) mode. In TEY mode, spectra are collected by measuring the drain current from sample. As the probing depth of secondary electrons is few nm, TEY is surface sensitive. Disadvantage with TEY measurements is that it cannot be used for insulating samples. These shortcomings can be overcome by employing TFY measurements. In this, emitted photons are used for measurements. As the escape length of photons is much larger than the Auger electrons, TFY spectra provide information which is bulk sensitive. These spectra are best suited for diluted samples. For concentrated samples, there are large nonlinear effects as then the fluorescence yield is not directly proportional to the absorption coefficient. These self-absorption effects result from the attenuation of the penetrating and escaping radiation while propagating through the sample. Typical XAS spectra consist of three main features when the absorption coefficient is plotted as a function of incident photon energy $E$ [13]:

1. There is an overall decrease in absorption coefficient with increasing photon energy.
2. There is sharp rise at certain energies called edges.
3. Above the edges, a series of wiggles or oscillatory structures are present.

When the transition is from the first, second, third... to the empty states above the Fermi level, the edges are named as K, L, M... edges respectively. Further, the edges are named as L1, L2 and L3 when the transitions to the empty states are from $2s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ respectively. Similar rules are followed for naming other edges. In the first approximation,
X-ray absorption can be described by the dipole transition and hence are governed by the electric dipolar selection rules as enumerated in eq 2.2 for the various polarizations of the incident photon. These selection rules endow XAS with great advantage, giving them orbital selectivity along with the ability to probe electronic structure.

In the present work, NEXAFS measurement has been performed at O-K, Mn-L\textsubscript{3,2}, Fe-L\textsubscript{3,2} and La-M\textsubscript{4,5} edges of LBFMO (0.0 ≤ x ≤ 0.4) bulk samples along with other reference compounds at the soft X-ray beam line 7B1 KIST of the Pohang Accelerator Laboratory (PAL), Korea, operating at 2.5 GeV with a maximum storage current of 200 mA and for hard X-ray range, Mn-K edge, 10B XRS KIST-PAL beamline of the Pohang Light Source (PLS) was utilized. For unirradiated as well as irradiated thin films of La\textsubscript{0.8}Bi\textsubscript{0.2}Fe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3}, NEXAFS measurements have been performed at the (European Synchrotron Radiation Facility) ESRF ID08 beamline, which uses an APPLE II type undulator giving ~ 100 % linear/circular polarization.

**2.6.1 X-ray magnetic circular dichroism (XMCD)**

In optics, the term "dichroism" refers to changes in the absorption of polarized light on passing through a material in two different directions. The dichroic signal is proportional to the projection of the magnetic moment along the incident X-ray direction and can be used to separate out the orbital and the spin contributions to the magnetic moment [14]. Apart from these, XMCD can be used for measuring the anisotropy of charge, spin and orbital moment [15] which can be very critical for magnetic multilayer being used in the data storage industry. When XAS spectra are collected for the left and right circularly polarized X-rays, the difference between these spectra is what we called as the “XMCD signal”. For a non-
magnetic material, there is no XMCD signal. For a magnetic material, XMCD signal arises due to the dependence of the absorption cross-section on the magnetic state. First verification of XMCD was done in 1987 and thereafter this technique has become a widely useful tool as a probe for the element-specific characterization of magnetic materials [16]. The concepts of XMCD are illustrated in Fig 2.15. Simple sum rules can be used to separate out the spin and orbital contributions to the magnetism. The first X-ray absorption sum rule links the total intensity of the L$_3$ and L$_2$ resonances with the N number of empty d states (holes) [17, 18]. The d valence shell can hold up to 10 electrons which are filled into band states up to the Fermi level and the number of filled states is therefore 10-N. For a magnetic material the d shell has a spin moment which is given by the imbalance of spin-up and spin-down electrons or equivalently (except for the sign) by the imbalance of spin-up and spin-down holes. Electronic transitions in conventional L-edge X-ray absorption and X-ray magnetic circular X-ray dichroism are shown in Fig 2.15 (a, c) respectively. Figure 2.15 (b, c) illustrates, in a one-electron model the total transition intensity of the two peaks is proportional to the number of d holes (first sum rule). By use of circularly polarized X-rays, the spin moment and orbital moment can be determined from linear combinations of the dichroic difference in intensities of A and B in Fig. 2.15 (a, b).

![Fig 2.15 Schematic showing the X-ray circular dichroism (XMCD) concept.](image)

2.7 Surface Studies

2.7.1 Field emission scanning electron microscopy (FESEM)

FESEM is widely used techniques to get information about the topographical features, morphology, phase distribution, crystal structure, crystal orientation and the presence and location of defects [19]. In this technique, an accelerated beam of mono-energetic electrons...
with energies from a few hundred of eV to tens of KeV is focused in a vacuum of 10^{-4} to 10^{-10} torr with the help of electromagnetic lens on the surface of the sample and is scanned over it on a small area. The signal obtained from these types of electrons conveys information on the topology of the sample. Some of these electrons get scattered elastically (i.e. change of direction without change of energy) from the coulomb field of the nucleus whereas some other undergo inelastic scattering (with change in energy) from the electrons of the host atoms giving secondary electrons. The secondary electrons are collected by a detector for every position of the incident electron beam and are used to form an image. The signal is amplified and made to form synchronous image on a cathode ray tube. A camera is used to photograph the image or it may be digitized and processed on a computer. A line diagram of typical scanning electron microscope is given in Fig 2.16. Essential requirement is that the sample should be conductive. Surface of non-conductive samples are rendered conductive usually by coating a thin layer of gold. The resolution and depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the probe forming objective lenses. The electrons interact with the sample from few nanometers to several microns of the surface depending on the beam parameters and the sample type. Electrons are emitted from the sample primarily as either backscattered or secondary electrons and detected by scintillation photomultiplier detector.

In the present work, morphological and microstructural features of LBFMO (0.0 ≤ x ≤ 0.4) multiferroic samples were investigated with a FEI Quanta 200F FESEM shown in Fig 2.17 at Indian Institute of technology (IIT), Roorkee.

![Field Emission Scanning Electron Microscope (FESEM)](image)

**Fig.2.16** Schematic diagram of field emission scanning electron microscope (FESEM).
2.7.2 Atomic force microscopy (AFM)

Binnig, Quate and Gerber invented the first AFM in 1986. It is a powerful technique for probing the surface of the thin film and deducing valuable information of its topological features [20]. It consists of piezoelectric scanner to control the scanning motion, the optical head to vibrate the cantilever, sense its deflection and a base to support the scanned surface with feedback mechanism that facilitates the piezoelectric scanners to sustain the tip at a constant force (to obtain height ), or height (to obtain force ) above the sample surface. Tips are typically made from Si₃N₄ or Si. Cantilever bends in response to the Force (F) between tip and the sample. A representative view of the function of AFM is shown in Fig 2.18. Displacement of the cantilever in three (X, Y, and Z) directions is done by means of a piezoelectric scanner into a single tube. Two operating modes of AFM, that may be used are, contact and tapping mode.

(a) Contact mode AFM

As we had mentioned, changes in the cantilever’s deflection are monitored with a split photodiode detector as the tip is scanning the sample surface [21]. A feedback loop maintains a constant deflection between the cantilever and sample by vertically moving scanner at each data point to maintain a ‘set-point’. By maintaining a constant cantilever deflection, the force between the tip and sample remains constant. F is calculated from Hook’s law: \( F = -k x \),
where $k$ is the spring constant and $x$ is the deflection. $k$ usually range from 0.01 to 1.0 N/m, resulting in forces ranging from $nN$ to $\mu N$.

(b) Tapping mode AFM

The cantilever is oscillated near its resonance $f$ with amplitude ranging typically from 20 to 100 nm. Tip lightly ‘taps’ the surface while scanning, contacting the surface at bottom of its swing. The feedback loop maintains constant oscillation amplitude by maintaining a constant RMS of oscillation signal acquired by the split photodiode detector. In order to maintain constant oscillation amplitude, the scanner has to move vertically at each point $(x, y)$. The vertical position of scanner is stored by computer to form the topographic image of sample surface. In the present work, AFM measurements have been carried out using the Nanoscope III a (Digital Instruments) at IUAC, New Delhi (Fig 2.19).

Fig 2.18 Schematic diagram of Atomic Force Microscope (AFM)

Fig 2.19 Atomic force microscopy setup at IUAC, New Delhi.
2.8 Swift Heavy Ion (SHI) Irradiation

Pelletron Accelerator

It is a well-established reality that the irradiation of solids with energetic particle ions crafts a wide range of defect states in the system. SHI irradiation is known to create controlled defect states in the material and offers the possibility of tailoring the properties of materials [22-24]. Fig 2.20 (a) presents here the versatile, heavy ion tandem type electrostatic accelerator. The accelerated beam from the Pelletron accelerator is brought to the beam hall and can be switched to any of the seven beam lines by using the switching magnet. In this negative ions are produced and pre-accelerated to ~300 keV in ion source. The ion beam is selected by injecting magnet, which selects the mass of the ion using mass spectroscopy. The pre-accelerated ions are injected into strong electrical field inside an accelerator tank filled with SF$_6$ insulating gas. At the centre of the tank is a terminal shell, which is maintained at a high voltage (~15 Mega Volt). Negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On reaching the terminal they pass through a stripper, which removes some electrons from the negative ions, thus transforming the negative ions into positive ions. These positive ions are then repelled away from the positively charged terminal and are accelerated to the ground potential to the bottom of the tank. In this manner, same terminal potential is used twice to accelerate the ions. On exiting from the tank, the ions are bent into horizontal plane by analyzing magnet. The switching magnet diverts high energy ion beams into various beam lines into the different experimental areas of the beam hall. The irradiation was done at IUAC New Delhi, in materials science beam line of the 15 UD pelletron accelerator as shown in Fig 2.20 (b, c) which is at 15° to the right with respect to the zero degree beam line. The irradiation experiments were performed in high vacuum chamber (~ 10^-6 mbar) at 300 K. The samples to be irradiated were mounted on the four sides of the target ladder (copper block). The whole body of ladder is made of stainless steel and a perforated square copper block is brazed at the end of the ladder. Target ladder is mounted through a Wilson seal mechanism from the top flange of chamber that is connected to the chamber through a flexible bellow that can be expanded up to 11 cm from its minimum position. Beam on the ladder is observed by examining luminescence of it on the quartz crystal. Once the beam is tuned on quartz area, the sample to be irradiated is brought to the same position as that of quartz. Positions of sample are monitored using close circuit television (CCTV) in the data acquisition room. Magnetic scanner (to sweep the beam by 15 mm in y-direction and 15 mm in x-direction)
ensures the uniformity of irradiation. A cylindrical enclosure of stainless steel surrounds the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of the sample during the irradiation. Entire experimental setup is interfaced with computer in data room to control all the functioning.

Fig 2.20 (a) Schematic diagram of 15 UD pelletron accelerator at IUAC, New Delhi. (b) materials science beam line. (c) Experimental chamber used for irradiation.
References