Chapter 2

Experimental and Characterization Techniques

In this chapter we have presented a brief description of materials processing techniques: solid-state reaction route for the polycrystalline bulk and pulsed laser ablation technique for thin films. An overview of swift heavy ion irradiation is also provided. Diverse experimental techniques utilized to characterize structural and electrical properties of bulk as well as and thin films of modified Barium Niobates are discussed here.
2.1 Introduction

This chapter outlines the complex perovskites $A(Mg_{1/3}Nb_{2/3})O_3$ where $A= Ba^{2+}, Sr^{2+}$ and $Ca^{2+}$ and $Sr(B'_{1/3}Nb_{2/3})O_3$ where $B'= [Mg^{2+}, Co^{2+}, Cu^{2+}]$ sample preparation details in bulk as well as in thin film form used in our present study. The working principle of accelerators and various techniques used for bulk measurements, off line analysis of pristine and irradiated thin film are also discussed.

This chapter on the whole describes the experimental techniques used during the course of present research work. It is divided in to two parts (I) synthesis of sample in bulk and thin films forms and (II) characterization techniques employed for evaluating various properties of these samples.

2.1.1 Synthesis of Bulk Materials

There are various methods known for the synthesis of relaxor ferroelectric bulk materials such as solid state reaction [1-6], sol gel [7] and co precipitation [8-9]. In the present thesis, the bulk target materials for thin film deposition of A-site variation in $A(Mg_{1/3}Nb_{2/3})O_3$ (where $A= Ba^{2+}, Sr^{2+}$ and $Ca^{2+}$) and B-site variation in $Sr(B'_{1/3}Nb_{2/3})O_3$ (where $B'= Mg^{2+}, Co^{2+}$ and $Cu^{2+}$) based dielectric/relaxor ferroelectric materials have been synthesized by solid state reaction technique. This route of bulk preparation, which is also acknowledged as ceramic method, has superiority due to easiness of the process involved in the technique. This process involves various steps, for instance (i) mixing the required oxide/carbonate powders in appropriate proportion, (ii) calcinations, (iii) pelletization and (iv) sintering of the polycrystalline bulk.

(i) Mixing of Powders

For the preparation of $A(Mg_{1/3}Nb_{2/3})O_3$ (where $A= Ba^{2+}, Sr^{2+}$ and $Ca^{2+})$ and $B'$- site variation in $Sr(B'_{1/3}Nb_{2/3})O_3$ (where $B'= Mg^{2+}, Co^{2+}$ and $Cu^{2+}$) samples, the high purity fine powders of $BaCO_3, SrCO_3, CaCO_3, MgO, Nb_2O_5CuO, Co_3O_4$, were weighed and mixed in appropriate proportions were thoroughly mixed and ground in highly pure acetone using a mortar and pestle. This process is carried out for several hours in order to accomplish the homogeneity of the mixed powders. The physical uniformity and the chemical homogeneity of the mixtures are of significant importance especially for the doped samples.
(ii) Calcinations

The decomposition of the mixed powder by heating below its melting point is known as calcinations. Mixed powders are kept in crucible/boats and heated in box furnace in ambient environment. The course of calcinations entails heating the homogenously mixed powder to an intermediate high temperature, roughly 600°-800° C lower than the final sintering temperature. The intention of calcinations procedure is to establish the course of nucleation for the grain growth and felicitates the decomposition of the substituent oxides/carbonates. The rationale for this process is the concentration gradient and high temperature. This step crafts a seed for the chemically and crystallographic ally uniform growth of the structure. For A(Mg_{1/3}Nb_{2/3})O_3 and Sr(B_{1/3}Nb_{2/3})O_3 samples, the samples were calcinated at 600°-800° C. Calcination was repeated 2-3 times with intermediate grinding and every time calcinations temperature was kept same as in the previous step.

(iii) Pelletization

In order to make use of these ceramic materials, the calcinated powders must be brought into the required shapes and densities before the final sintering process. This is achieved by using dye-press technique in which a dye of proper shape was filled with calcinated powder and pressed using hydraulic pressure. In our case, pelletization is done in a dye of circular shape of 12mm diameter. The thickness of the pellets was ~1.4mm.

(iv) Sintering

After pelletization of the fine calcinated powder, sintering of the pellet is done at relatively higher temperature and for longer duration used during calcinations. 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 materials. For A(Mg_{1/3}Nb_{2/3})O_3 bulk pellet, the final sintering temperature was kept at 1150° C for 48 hours followed by natural cooling. For Sr(B_{1/3}Nb_{2/3})O_3 bulk pellets, the sintering temperature was maintained at 1250° C for 48 hours followed by natural cooling. Figure 2.1 shows the flow chart used for the preparation of bulk samples.
SYNTHESIS METHOD

Solid-State Reaction Technique

AR GRADE OXIDES IN STOICHIOMETRIC AMOUNTS

BaCO₃  MgO  Co₃O₄  Nb₂O₅  O₂

MIXED THROUGHLY AND GRANDED USING MORTAR AND PESTLE FOR ~ TWO HOURS

ADD BaCO₃ TO THE ABOVE FINAL PRODUCT

CALCINATION AT 900°C FOR 6-8 HOURS

PELLETS OF CIRCULAR SHAPE COMPRESSED FROM DRIED POWDER

FINAL SINTERING AT 1200°C FOR 48 HOURS

FINAL PRODUCT (BULK DIELECTRIC/RELAXOR FERROELECTRIC) SAMPLES OF
A(Mg₀.₃₃Nb₀.₆₇)O₃, Sr(B'₀.₃₃Nb₀.₆₇)O₃
Ba(B'₀.₃₃Nb₀.₆₇)O₃

Figure 2.1   Flow chart for the preparation of bulk samples
2.2 Thin Film Deposition

Pulsed laser Deposition (PLD) Technique

Pulsed laser deposition had several characteristic that made it remarkably competitive in the complex oxide thin-film research arena as compared to other film growth techniques these principle attractive features were stoichiometric transfer, excited oxidizing species, and simplicity in initial setup and in the investigation of arbitrary oxide compounds. One could rapidly investigate thin-film deposition of nearly and oxide compound regardless of the complexity of the crystal chemistry.

The applicability and acceptance of pulsed laser deposition in thin-film research rests largely in its simplicity in implementation. There are many deposition techniques for thin film preparation, such as Pulsed laser deposition (PLD) is a physical vapour deposition process,[1-9], chemical vapour deposition (CVD), metal organic chemical vapour deposition (MOCVD) [10-16], DC and RF sputtering [17-21], molecular beam epitaxy (MBE) [22] thermal evaporation [23] sole gel [24] etc. Among the various techniques as mentioned above for thin film deposition; PLD is one of the most commonly used for thin film growth of multicomponent materials. A pulsed laser is focused onto a target of the material to be deposited, for sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material creating a plasma plume, and the ablated material is ejected from the target in a highly forward-directed plume. The ablation plume provides the material flux for film growth. Matrix has been investigated.

(a) Principles of Excimer PLD

Excimer lasers such as XeF (λ = 352nm); XeCl (λ = 308nm); KrF (λ = 222nm); ArF (λ = 193nm); and F₂ (λ = 157nm) are commercially available and can be used for thin film deposition. It uses a pulsed laser beam, usually but not necessarily, from an ultraviolet excimer laser with pulse energy of about 1J. The typical duration of the laser pulse is a few tens of nanosecond. Because of such a short duration of pulse, tremendous power (∼ 10 – 100 MW/pulse) is delivered to the target. This is because of the non equilibrium nature of PLD, in the sense that the absorption of energy and ablation takes place in a very short time, usually within a nanosecond, before thermodynamic equilibrium is reached. Typical schematic of the pulsed laser deposition technique is shown in Figure 2.2.
The generality of the materials used for PLD research has a very high absorption coefficient in this wavelength region. The shorter the wavelength of the excimer laser, the higher the absorption. The importance of this feature is that it minimizes the interaction time between the laser radiation and the target material, hence making it possible to deposit nanolayers of the target materials during PLD.

The basic components of an excimer PLD system include a vacuum system equipped with a target and substrate holder as well as deposition monitoring systems. The evaporating source is a high-power laser located outside of the vacuum chamber. An optical system (lenses and mirrors) is used to focus the high-power laser beam on the substrate. The mechanism of PLD leading to material transfer to the substrate involves many stages, although it depends mainly on the type of laser, optics, and properties of the target used. First, a target is heated by short, concentrated burst of laser radiation and when the laser radiation is absorbed by the solid surface, electromagnetic energy is converted first into electronic excitation and then into thermal and the material is ablated. Subsequently, the evaporants form a plume which consists of a mixture of high-energy species including atoms, molecules, electrons, ions, clusters, and even micron-sized particulates. The plume that is formed propagates through a background of working gas toward the substrate. The plume is characterized by numerous collisions that may affect the velocities and the mean-free paths of the ablated atoms and ions as well as initiating reactions, the reduction of the mean-free path caused by collision leads to the fast expansion of the plume from the target surface to form narrow forward angular distributions of the evaporants. During this process, some material is redeposited onto the target or chamber walls, but most reaches the substrate where nucleation and growth occur. The eventual formation of the film is not only governed by the ablation and plume propagation but also by the substrate properties such as structure and topography, working gas, and the laser power [25].
In the present work thin films were prepared by pulsed laser deposition (PLD) technique from a single-phase bulk target of basic compositions of Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$[BMN] and Sr(Mg$_{1/3}$Nb$_{2/3}$)O$_3$[SMN] (20-25mm diameter) onto ITO substrate. The target was processed by conventional solid-state reaction technique. For deposition, a KrF excimer laser (model Lambda Physik, $\lambda = 248\text{nm}$) see at 20ns pulse duration, 10hz repetition rate and a home-made stainless steel vacuum chamber were used. The thin film deposition was done at UGC-DAE Consortium for Scientific Research, Indore, India. The target was mounted at an angle of 45° to laser beam inside vacuum chamber, where a base pressure of $2\times10^{-5}\text{mTorr}$ was achieved through a turbomechanical pump. The substrate (10mm $\times$10mm) was attached to a stainless steel holder at a distance of 40 mm from the target and is placed parallel to it inside the heater assembly, which is
capable to heating the substrate up to 650\textdegree{}C. The target material was rotated at about 10rpm and the deposition was carried out in an O\textsubscript{2} partial pressure of 200m1orr by keeping the substrate temperature to 450\textdegree{}C. The deposition was performed for \sim{} 20 min. after the deposition; the thin film was cooled slowly to room temperature by turning down the power to the substrate heater and maintaining the oxygen pressure in the chamber to 200 m Torr. The film thickness was measured by profilometer with 0.5 nm resolution.

2.3 Characterization Techniques

The following characterizing tools are used to study the structural, microstructural, dielectric, impedance and optical study of ceramics.

2.3.1 X-Ray Diffraction Measurement

X-ray powder diffraction is used to determine the atomic structure of crystalline materials without the need for large (~100\textmu{}m) single crystals. “Powder” can be a misnomer; the technique is applicable to polycrystalline phases such as cast solids of films grown on a substrate. X-ray powder diffraction can be useful in a wide variety of situations.

X-ray diffraction (XRD) technique is used for the realization of structural property and can be employed exclusively to categorize the crystalline phase in the sample [26]. This technique is suitable for both form of samples i.e. thin film as well as bulk and can yield the information regarding the crystallinity of the material, nature of the phase present, lattice parameter, grain size, out of plane orientation and relative in plane orientation between the film and substrate. In case of thin film, the change in lattice parameter with respect to the bulk gives the idea of nature of strain present in the film.

The following information is obtained from the X-ray diffractiongram

(i) Quality and confirmation of the prepared samples,
(ii) The interplanar spacing d of the reflections,
(iii) The intensities of the reflections, and
(iv) The unit cell dimensions and lattice type.
The fundamental of XRD is best explained by the Bragg’s equation 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

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

(2.1)

Where \( \lambda \) is the wavelength of the incident X-ray, \( d \) is the interplanar distance, \( \theta \) is the scattering angle and \( n \) is an integer- the order of diffraction.

In thin films, X-rays are diffracted by the oriented crystallites at a particular angle to satisfy the Bragg’s condition. Having known the value of \( \theta \) and \( \lambda \), once can calculate the interplanar spacing which is shown in Figure 2.3.

\[ Figure 2.3 \quad \text{A representation of x-ray diffraction} \]

The XRD can be taken in various modes such as \( \theta - 2\theta \) scan mode, \( \theta - 2\theta \) rocking curve, and \( \phi \) scan. In the \( \theta - 2\theta \) scan mode, a monochromatic beam of X-ray is incident on the sample at an angle of \( \theta \) with the sample surface. 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 (Figure 2.3). The resulting spectrum is a plot between the intensity recorded by the detector versus \( 2\theta \).
Figure 2.4  X-ray diffractometer (UGC-DAE CSR Indore)

The crystalline quality of the oriented samples can be estimated by using it in rocking curve mode wherein a single Bragg peak is measured as the sample is tilted within the diffraction plane. In this arrangement the position of the detector is kept fixed at 2θ value corresponding to a particular d value and sample is rocked around the θ value. The resulting spectrum is a plot between the intensity and θ. The full width at half maximum (FWHM) of the plot estimates the mis orientation of the grains in the film with respect to the sample normal.

In the present work, Bruker D8 Advanced Diffractometer (see Figure 2.4) with Cu-Kα (λ = 1.542 Å) was used for the phase detection of bulk powders and thin films at UGC-DAE Consortium of Scientific Research, Indore. The angle 2θ was varied from 10 to 110 steps of 0.05°. The lattice spacing “d” was calculated using Bragg’s equation (see eqn. 2.1) which is further utilized to calculate lattice constant. The analysis of the XRD pattern was done using Powder-X software [27] at room temperature.

2.3.2 Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) is one of the most widely used instruments in materials research laboratories and is common in various forms in fabrication plants. Scanning electron microscopy is central to microstructural analysis and therefore important to any
investigation relating to the processing, properties, and behaviour of materials that involves their microstructure [28]. The SEM provides information relating to topographical features, morphology, phase distribution, compositional differences, crystal structure, crystal orientation, and the presence and location of electrical defects. The SEM is also capable of determining elemental composition of micro-volumes with the addition of an x-ray or electron spectrometer and phase identification through analysis of electron diffraction patterns. The strength of SEM lies in its inherent versatility due to the multiple signals generated, simple image formation process, wide magnification range, and excellent depth of field.

Lenses in the SEM are not a part of the image formation system but are used to demagnify and focus the electron beam onto the sample surface. This gives rise to two of the major benefits of the SEM: range of magnification and depth of field in the image. Depth of field is that property of SEM images where surfaces at different distances from the lens appear in focus, giving the image three-dimensional information. The SEM has more than 300 times the depth of field of the light microscope. Another important advantage of the SEM over the optical microscope is its high resolution. Resolution of 1 nm is now achievable from an SEM with a field emission (FE) electron gun. As a consequence, TEM sample preparation of bulk materials is tedious and time consuming, compared to the ease of SEM sample preparation, and may damage the microstructure. The SEM is relatively easy to operate and affordable and allows for multiple operation modes, corresponding to the collection of different signals.

The SEM electron beam is a focused probe of electrons accelerated to moderately high energy and positioned onto the sample by electromagnetic fields. A secondary electron (SE) is a low-energy (2- to 5 eV) electron ejected from the outer shell of a sample atom after an inelastic interaction. Backscattered electrons (BSEs) are electrons from the incident probe that undergo elastic interactions with the sample, change trajectory, and escape the sample.
Figure 2.5 Schematic diagram of scanning electron microscope (SEM) (UGC-DAE CSR Indore)

Image construction in a SEM is accomplished by mapping intensity of one of these signals (usually SE and/or BSE) from the specimen onto a viewing screen or film. The region on the specimen from which information is transferred to a single pixel of the image is called a picture element. The size of the picture element is determined by the length of the scan on the specimen divided by the number of pixels in a line of the image. A common digital resolution for the SEM is 1024×1024, and thus the picture element width for the 100× image would be 0.98μm. The picture element width would be 0.098μm at 1000× and 0.0098μm at 10,000×. The SEM image will appear in focus if the sampling volume is smaller in diameter than this picture element size. The SEM image conveys three-dimensional information due to the depth of field in the image. Modern SEM’s with field emission electron guns (FESEMs) are capable of resolutions near 1nm on appropriate samples using the SE signal.

In the present thesis work, Scanning electron microscope measurement has been done using FModel JEOL JSM 5600 with resolution of 3.5 nm shown in (Figure 2.5). Magnification is 18 to 300,000 (in 136 steps) Accelerating Voltage 0.5 to 30 kV (53 steps) Displayed image 640 x 480 pixel Image memory is 1280 x 960 pixels with optional Attachment of Energy Dispersive X-ray spectrometer(EDS)
2.3.3 Atomic Force Microscopy

The atomic force microscope (AFM) is one of the most widely used techniques for studying the surface morphology [28, 29]. It consists of piezoelectric scanner to control the scanning motion, the optical head to vibrate the cantilever and sense the cantilever deflection and a base to support the scanner and head. In this technique, an atomically sharp tip placed at the end of a cantilever is scanned over a surface with feedback mechanisms that facilitate the piezoelectric scanners to sustain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si₃N₄ or Si. The cantilever bends in response to the force between the tip and the sample. A representative view of the function of AFM is shown in Figure 2.6.

The tip approaches the surface of the sample and interacts with it via Van der Waals forces. The interaction translates in a cantilever deflection or a change in the cantilever’s oscillating frequency, depending on the operational mode of the AFM: contact or tapping. The deflection or the frequency changes of the cantilever are detected by an optical system consisting of a laser beam, which is reflected on the cantilever. The vertical and the horizontal deflections are measured using a split photodiode detector that analyses the reflected beam. The displacement of the cantilever on the three directions is done by means of a piezoelectric scanner, combining independently operated piezo-electrodes, for X, Y and Z direction into a single tube. The two operating modes that have been used, contact-AFM and tapping-AFM, are described in more detail in the following text.

2.3.3.1 Contact Mode AFM

As we have mentioned the changes in the cantilever’s deflection are monitored with a split photodiode detector as the tip is scanning the sample surface [30]. A feedback loop maintains a constant deflection between the cantilever and the sample by vertically moving the scanner at each data point to maintain a „set-point” deflection. By maintaining a constant cantilever deflection, the force between the tip and the sample remains constant. The force F is calculated from Hook’s law; \( F = -kx \), where \( k \) is the spring constant and \( x \) is the deflection. Spring constants usually range from 0.01 to 1.0N/m, resulting in forces ranging from nN to \( \mu \)N.
The distance that scanner moves vertically at each point \((x,y)\) is stored by the computer to form the topographic image of the surface.

### 2.3.3.2 Tapping Mode AFM

In tapping mode, the cantilever is oscillated near its resonance frequency with the amplitude ranging typically from 20 to 100 nm. The tip lightly "taps" the surface while scanning, contacting the surface at the bottom of its swing. The feedback loop maintains constant oscillation amplitude by maintaining a constant RMS of the 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 the scanner is stored by the computer, to form the topographic image of the sample surface. In the present work, to study topographic and morphology of the thin films, Atomic Force Microscopy (AFM) measurements have been carried out using Nanoscope III a (Digital Instruments) at UGC-DAE consortium of Scientific Research, Indore.

![Schematic diagram of Atomic Force Microscope (AFM)](image)

*Figure 2.6 Schematic diagram of Atomic Force Microscope (AFM)*
2.3.4 Optical Studies

2.3.4.1 Ultraviolet and Visible Absorption Spectroscopy (UV-Vis)

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Ultraviolet-visible spectroscopy is one of the most ubiquitous analytical and characterization techniques in science. There is a linear relationship between absorbance and absorber concentration, which makes UV-Vis spectroscopy especially attractive for making quantitative measurements. Ultraviolet and visible photons are energetic enough to promoted electrons to higher energy states in molecules and materials. UV-Vis spectroscopy is useful to the exploration of the electronic properties of the materials and materials precursors in basic research and in the development of applied materials. Materials that can be characterized by UV-Vis spectroscopy include semiconductors for electronics, lasers, and detectors; transparent or partially transparent optical components; solid-state laser hosts; optical fibres, waveguides, and amplifiers for communication; fibres, waveguides, and amplifiers for communication; and materials for solar energy conversion. The UV-Vis range also spans the range of human visual acuity of approximately 400 to 750nm, making UV-Vis spectroscopy useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. UV-visible spectroscopy provides direct evidence about electron energy jumps between the two distinct energy levels.

In the present study UV-Vis spectrometer (Perkin Elmer lambda 25) has been used to study the optical properties of bulk as well as polycrystalline thin films. Figure 2.7 shows the schematic diagram of the components of UV-Vis spectrometer. The optical components are coated with silica for durability and a holographic concave grating with 1053 lines/mm in the center is used in the monochromator. Two radiation sources, deuterium lamp and a tungsten halogen lamp cover the working wavelength range from 200-1100nm of the spectrum. During the operation in the visible range, mirror M₁ reflects the radiation from the halogen lamp onto source mirror M₂ and at the same time M₁ blocks the radiation from the deuterium lamp. While in UV range mirror M₁ is raised to permit radiation from the deuterium lamp to strike source
mirror $M_2$. The radiation source and filter change is automatic during monochromator slewing. Radiation from the source lamp is reflected from source mirror $M_2$ through an optical filter on the filter wheel assembly that has been driven by a stepping motor in synchronization with the monochromator. Depending on the wavelength being produced, the appropriate optical filter is located in the beam path to prefilter the radiation before it enters the monochromator. From optical filter the radiation passes through entrance slit ($S_1$) of the monochromator grating. The radiation is dispersed at the grating to produce a spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting the segment through the exit slit ($S_2$) to mirror $M_3$. The exit slit restricts the spectrum segment to a near monochromatic radiation beam. The slit provide spectral band pass of 1 nm. From mirror $M_3$ the radiation is reflected onto a beam splitter which allows

![Schematic View of UV-Vis Spectroscopy](image)

**Figure 2.7  Schematic View of UV-Vis Spectroscopy**

50% of the radiation to pass onto plane mirror $M_4$, and reflects 50% of the radiation onto plane mirror $M_5$. Mirror $M_4$ focus the radiation beam in the sample cell. Mirror $M_5$ focuses the radiation beam in the reference cell and the beam then passes through a convex lens onto the photodiode detector. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. Over a short
period of time, the spectrometer automatically scans all the component wavelengths in the manner described above. If the sample compound does not absorb light of a given wavelength then \( I = I_o \). However, if the sample compound absorbs light then \( I \) is less than \( I_o \) and this difference may be plotted on a graph as a function of wavelength. Absorption may be presented as transmittance \( (T = I/I_o) \) or absorbance \( (A = \log I_o/I) \). If no absorption has occurred then \( T = 1.0 \) and \( A = 0 \). Most spectrometers display absorbance on the vertical axis and the commonly observed range is from 0 (1% transmittance) to 2 (100% transmittance). The wavelength of maximum absorbance is a characteristic value. Different compounds may have very different absorption maxima and absorbance.

### 2.3.5 Dielectric Measurement

#### 2.3.5.1 Electroding

The selection of suitable electrode for the test materials is important. In our case the contacting, conducting thin film electrode method is adopted because (i) it causes minimum error caused by air gap between the electrode and surface of the test material, which is more in case of contacting rigid metal electrode method, and (ii) procedure to measure dielectric constant are simple, which are relatively complex in non-contacting electrode method. In our case, all the ceramic bodies after sintering were polished well and coated on both sides with conducting silver paste. For organic removal printed disks were kept on an alumina plate and fired at 300°C for 60 minutes. This procedure is repeated twice for better electroding.

The main objective behind the development of automated dielectric setup is to study the behaviour of dielectric constant of different type of materials such as magnetic materials, ferroelectric and multiferroic materials etc. Such types of materials require accurate measurements of dielectric constant as a function of temperature and frequency. The dielectric constant as a function of temperature measures the unique property of the materials such as ferroelectric property and the transition temperature etc. The dielectric measurement setup was developed to study the temperature dependence of dielectric constant at various frequencies.

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 was measured using Solatron 1260 LCR meter (for bulk sample) shown in Figure 2.8 and Agilent 4284A precision LCR meter (for thin films). Shielded test leads were used for the electrical connections from the
analysers to the sample in order to avoid any parasitic impedance. The samples were made in the form of circular pellets by applying a pressure of 5 tons. The surface of the disks were polished and coated with silver paste that acts as a good contact for measuring dielectric properties. Before starting the measurement, the samples were heated at 300 deg for 1 hour, so as to homogenize the charge carries and to remove the moisture content, if any.

![Dielectric measurement setup](image)

**Figure 2.8** Dielectric measurement set up Physics department (MSU Baroda)

The measured capacitance was then converted into dielectric constant using the following formula:

\[
C = \varepsilon_0 \varepsilon_r \frac{A}{d}
\]

(2.5)

\[
\varepsilon_r = \frac{C \times d}{\varepsilon_0 \times A}
\]

(2.6)

where, \( C \): Capacitance in farad (\( F \))
\( \varepsilon : \) Permittivity of free space in farad per meter (8.85 \times 10^{-12} F/m)

\( \varepsilon_r: \) Dielectric constant or relative permittivity of the sample.

\( A: \) Area of each plane electrode in square meters (m²)

\( d: \) Separation between the electrodes in meters (m)

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

\[
\varepsilon'' = \varepsilon' \tan \delta
\]

(2.8)

Where \( \tan \delta \) is loss tangent, proportional to the "loss" of energy from the applied field into the sample (in fact this energy is dissipated into heat) and therefore denoted as dielectric loss. The ac conductivity is calculated from the data of dielectric constant and loss tangent (tand) using the relation

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta
\]

(2.9)

Where \( \omega = 2\pi f \)

2.3.6 Impedance spectroscopy Studies

The complex impedance spectroscopy is a powerful tool to investigate the electrical properties of the complex perovskite oxides. The main advantages of the techniques, i) it involves relatively simple electrical measurements that can readily be automated ii) the measurements can be implemented by using arbitrary electrodes iii) the results can be often correlated with the properties such as composition, microstructure, defects, dielectric properties, chemical reaction etc. of the sample iv) the resistance of the grain boundaries and that of grains can be easily separated in most of the polycrystalline samples. AC measurements are often made with a Wheatstone bridge type of apparatus (Impedance analyzer or LCR meter) in which the resistance \( R \) and capacitance \( C \) of the sample are measured and balanced against variable resistors and capacitors. The impedance \( |Z| \) and the phase difference (\( \theta \)) between the voltage and current are measured as a function of frequency for the given sample and the technique is called impedance spectroscopy. Analysis of the data is carried out by plotting the imaginary part of the impedance \( Z'' = |Z| \cos \theta \) against the real part \( Z' = |Z| \sin \theta \) on a complex plane called the impedance plot. An impedance plot with linear scale is used to analyze the equivalent circuit as follows. Impedance plot of a pure resistor is a point on real axis and that of pure capacitor is a straight
line coinciding with the imaginary axis. The impedance of a parallel $RC$ combination is expressed by the following relation,

$$Z^* = Z' - jZ^" = \frac{R}{1 = j\omega RC}$$

(2.10)

After simplification, one gets

$$\left( Z' - \frac{R}{2} \right)^2 + Z^" = \left( \frac{R}{2} \right)^2$$

(2.11)

which represents the equation of a circle with radius $R/2$ and center at $(R/2,0)$. Thus, a plot of $Z'$ vs. $Z^\prime\prime$ (as parametric function of) will result in a semicircle of radius $R/2$ as shown in Figure 2.9 (a) and the equivalent circuit is shown in Figure 2.9 (b). (This plot is often called a Nyquist plot). The time constant of the simple circuit is defined as $t = RC = 1/\omega_m$.

This corresponds to the relaxation time of the sample and the characteristic frequency lies at the peak of the semi-circle. In an ideal polycrystalline sample, the impedance plot exhibits an arc at high frequency corresponds to the bulk property of the sample, an arc at low frequency corresponds to the grain boundary behaviour and a spike at the lowest frequency corresponds to the electrode effect. Figure 2.10 (a) shows a typical impedance plot for a polycrystalline sample and Figure 2.10 (b) represented the equivalent circuit. In the present thesis work, impedance measurements for bulk samples have been performed using Solatron 1260 Impedance Analyser (1Hz-32MHz) in the temperature range (Room Temperature to 450°C). And for the thin films we have used the Agilent 4284A precision LCR meter.
2.4 Swift Heavy Ion Irradiation

To understand the swift heavy ion irradiation induced modifications of thin films, we have used Pelletron accelerator and materials science beam line at IUAC, New Delhi.

2.4.1 Pelletron Accelerator

The 15UD Pelletron, as shown in Figure 2.11, is a versatile tandem type of electrostatic heavy ion accelerator. This is installed in a vertical configurations in an insulating tank of 26.5 meter height an 5.5 meter in diameter, in this machine negative ions are produced and pre-accelerated to 300keV by the cesium sputter ion source known as SNICS( Source of Negative
Ions by Cesium Sputtering) (Now it has been replaced by MCSINCS (Multi Cathode SNICS). The pre-accelerated ions are injected into strong electrical field inside and accelerator tank filled with SF$_6$ insulating gas maintained at a pressure of 6-7 atmospheres. The ion beam is selected by injector magnet, which selects the mass of the ion using mass spectroscopy. The ions are mass analysed by an ion then enter in the strong electrical filed inside the accelerator. A terminal shell of about 1.52 meter in diameter and 3.61 meter in height is located at the centre of the tank, which can be charged to a high voltage (15MV) by a pellet charging system. The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On the reaching the terminal they pass through the stripper (foil or gas), which removes electrons from the negative ions and transforms the negative ions into positive ions with high charge state. For very heavy ions (A>50), the lifetime of the carbon foils used in the stripper are limited to a few hours due to radiation damage. Therefore a gas filled canal or a combination of the gas stripper followed by a foil stripper is used for heavy ions. The transformed positive ions are then repelled away from the positively charged terminal and are accelerated towards ground potential to bottom of the tank. In this way same terminal potential is used twice to accelerate the ion in tandem. Hence, the name given to this accelerator is a Tandem Pelletron Accelerator. The final energy of the emerging ions from the accelerator is given by,

$$ E_i = [ E_{decpot} + (1 + q_i)V ] $$

Where $E_i$ is the energy of the ions having a charge state $q_i$ after stripping, $V$ is the terminal potential in MV and $E_{decpot}$ is the deck potential of the SNICS source. On exciting from the tank, the ions are bent into horizontal plane using analysing magnet. This magnet works as an energy analyser and depending on the dipole magnetic field, ions of particular energy travel in the horizontal direction. The switching magnet diverts the high-energy ion beam into selected beam line of the beam hall. The ion beam kept centered and focused using steering magnets and quadruple triplet magnets. The beam line of the accelerator is in ultra high vacuum (UHV) conditions (10-10 mbar). The beam is monitored by beam profile meter (BPM) and the current is observed using Faraday cups. The entire machine is computer controlled and is operated from the control room. The accelerator can accelerate ions from proton to uranium from a few MeV to hundreds of MeV (200MeV) depending upon the ion.
2.4.2 Material Science Beam Line

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. Materials Science beam line is at 15° to the right w.r.t. the zero degree beam line. This beam line has three chambers-high vacuum chambers, ultra high vacuum chamber and goniometry chamber. The high vacuum chamber is a cylindrical shaped multiport stainless steel chamber. A view of the high vacuum chamber is shown in Figure 2.12 (a). The irradiation experiments were performed in high vacuum chamber (~106 mbar) at room temperature in materials science beam line (see Figure 2.12(b)). The sample to be irradiated was mounted on the four sides of the target ladder (on copper block). The whole body of the ladder is made of stainless steel and a perforated square copper block is brazed at the end of the ladder. The target ladder is mounted through a
Wilson seal from the top flange of the chamber. This top flange is connected to the chamber through a flexible bellow that can be expanding up to 11 cm from its minimum positions. A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. The beam on the ladder can be observed by observing the luminescence of the beam on the quartz crystal mounted on all sides of the ladder. After the observation of the beam on the quartz, the sample to be irradiated is brought to the same position as that of the quartz by moving the ladder in the desirable position. A CCD camera is attached to one of the ports of the chamber for viewing the sample and the quartz position. The positions can be monitored using close circuit television (CTV) in the data acquisition room. The magnetic scanner (that can sweep the beam by 15 mm in y-direction and 15 mm in x-direction) ensures the uniform irradiation of samples. 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. An opening in the suppressor allows the ion beam to fall on the sample. The total number of particles/charges falling on the sample can be estimated by a combination of the current integrator and the pulse counter (Faraday cup) from which the irradiation fluence/dose can be measured.

The counts for the desired fluence for each sample can be calculated using the following relation:

\[
\textit{numberofcounts} = \frac{\textit{fluence} \times q \times 1.6 \times 10^{-19}}{\textit{pulseheight}}
\]  

(2.12)

and

\[
\textit{Time}(T) = \frac{\textit{Dose} \times \textit{ChargeState} \times \textit{Area}}{\textit{Current} \times 6.25 \times 10^9}
\]  

(2.13)
**Figure 2.12** An overview of (a) Experimental chamber and (b) materials science beam line at Inter-University Accelerator Center, New Delhi, India.

### 2.4.3 Ion Solid Interaction

When an energetic ion passes through the matter, it experiences a series of elastic and inelastic collisions with the atoms which lie in its path. These collisions occur because of the electrical forces between the nucleus and electrons of the projectile and those of the atoms which constitute the solid target. During this collision the energetic ions transfer its energy to nuclei (by elastic atomic collision) and electronic (by ionization and excitation) of the target material by two processes:

1. Elastic collision with the target atoms leading to displacement of atoms from their regular lattice sites. This mode of energy transfer is known as nuclear energy loss denoted by \((dE/dX)_n\) or \(S_n\). It is well known mechanism of defect creation in the low energy regime and it has negligible contribution.
2. Inelastic collision with the target electrons causing their excitation/ionization. This mode of energy transfer is referred to as electronic energy loss (dE/dX)e or Se.

It is well known fact that when a material is bombarded by the heavy ion irradiation, it creates damage zones in the material, when swift heavy ion passes through the material then material in the vicinity of the ions trajectory may be transformed into a disordered state, giving rise to the so called latent track (damage zone created along the path of the swift heavy ion). In case of SHI irradiation, electronic energy loss is the most considerable energy loss process. The emergence of these traces is the result of local electronic energy deposition along the ion path. Therefore, a number of experimental results have shown that the higher electronic excitations can induce the structural modifications. This implies that all the \( S_e \) dependent effects induced in different materials are probably related to the basic energy transfer between the incident ions and the target atoms. Two basic models of microscopic energy transfer mechanism, namely thermal spike and the coulomb explosion have been used to establish the relevant parameters governing the basic energy transfer process.

### 2.4.3.1 Thermal Spike Model

Thermal Spike model is based on the transient thermal process. This model was developed to explain the phase transformation after the SHI irradiation. According to this model the heavy ion irradiation may increase the lattice temperature that induces solid to liquid phase transformations into a localized zone of few nanometer (nm), which is followed by the thermal quenching \( (10^{13}\text{K/s}) \) of a cylindrical molten liquid along the ion track. This results in the formation of amorphized latent track. The threshold value for the creation of the latent tracks is associated with the energy needed to induce a liquid phase along the ion path [31, 32].

In this process, the incoming ion gives its energy to the electron gas in \( \sim 10^{17}\text{s} \) which is calculated from the collision time of ion with electron. The local thermalization in electronic system will take \( 10^{-15}\text{s} \) to complete. Heat transfer from the electronic to atomic subsystem becomes substantial between \( 10^{-14} \) to \( 10^{-12}\text{s} \) depending on the magnitude of the coupling (electron-electron coupling and electron-phonon coupling) between the sub systems. The electron-phonon coupling implies the ability of electrons to transfer their energy to the lattice.
2.4.3.2 Coulomb Explosion Model

In the Coulomb Explosion Model [33, 34], it is assumed that the ionizing ions scatter the target electrons and create a column/cylinder of ionized atoms and the excited electrons are ejected by the coulomb repulsion. The electron excitation is rapidly shared with other electrons via electron phonon interaction. The mutual Coulomb repulsion of the ions produces atomic displacements leading to a dense cloud of interstitial atoms and vacancies along the original ion trajectory. This model seems to be well suited for the insulating materials. In metals, which have large electronic mean free path, the free electrons carry away the excitation energy so efficiently that the sample warms up as a whole without considerable atomic motion.

In the present work, the thin films of the BMN or SMN dielectric or ferroelectric samples deposited on ITO substrates have been irradiated with 100 MeV O$^{2+}$ and 200 MeV Ag$^{15+}$ ions. The Ag ions were selected to create the columnar defects. In fact, the defect morphology depends upon threshold value of the particular materials to be irradiated [35]. The electronic energy loss, (dE/dX)$_e$ should be larger than the S$_{th}$. Therefore, there is a possibility of creation of columnar defects/tracks in the materials.

References


[28] *Hand Book of Microscopy for NanoTechnology* by NanYao and Zhong Lin Wang


