Chapter-2

Experimentation and Characterization Techniques

CHAPTER 2

Experimentation and Characterization Techniques

2.1 Introduction

This chapter outlines the experimental techniques and procedures used for the synthesis and characterization of the samples studied in this thesis. The focus is on synthesis and characterization of Bi-based piezoceramics for high temperature applications. Based on the previous reports, we selected MPB composition, 0.67BF-0.33BT as the base material to tune its microstructure, dielectric, ferroelectric, optical and piezoelectric properties by site engineering. While thermal quenching has been employed in previous studies, as discussed in Chapter 1, to enhance functional properties, there is a notable lack of comprehensive comparative studies in the literature demonstrating that air quenching is superior to conventional closed sintering for the chosen composition. By adopting site engineering we first modified the B site of BF-BT matrix by incorporating Sc, Ga ions. We simultaneously prepared all the samples with different doping concentration using closed sintered and air quenching method utilizing solid state route and high energy ball milling. We also synthesized Sm, Ta codoped BIT based piezoceramics using conventional solid state route and varied the sintering temperature from 950 ℃ to 1150 ℃ within the interval of 100 ℃. The optimization of calcination temperature was done at different temperatures to ensure pure phase formation. Phase determination of the calcined powders was carried out using X-ray diffraction (XRD) measurements. Dense pellets are essential for electrical characterizations such as XPS, SEM, dielectric measurements, and piezoelectric and ferroelectric analysis. The density of these pellets was measured using the Archimedes method and optimized by varying the sintering temperatures. A detailed description of the synthesis and characterization of specific compositions is provided in the respective chapters. In following sections, we will discuss the fundamental methodology used to prepare the bulk piezoceramics and provide details about the instruments used for their characterization.

2.2. Methodology for Synthesis of Samples

2.2.1 Solid State Reaction Methodology

The solid-state route is a highly utilized method for the synthesis of ceramic materials, comprising several critical steps essential for achieving high-quality ceramics with desired properties. The process begins with the careful selection of high-purity raw materials, typically metal oxides, carbonates, or other ceramic precursors. Accurate weighing of the raw materials is followed by thorough mixing to ensure a uniform distribution of the different components. Mixing can be done using various techniques such as ball milling, which not only mixes the powders but also reduces the particle size, enhancing reactivity. The mixed powders are then subjected to calcination, a heat treatment process typically conducted at temperatures between 800°C and 1200°C. Calcination helps to remove volatile substances, decompose carbonates, and initiate solid-state reactions that form intermediate phases. After calcination, the material is ground to achieve a fine powder with a uniform particle size, a crucial step for ensuring the homogeneity of the final ceramic product. Advanced grinding techniques such as planetary ball milling or attrition milling are often employed. The finely ground powder is then shaped into the desired form using methods like uniaxial pressing, isostatic pressing, extrusion, and slip casting, depending on the desired shape and properties of the ceramic. The formed ceramic green bodies are subjected to sintering, a high-temperature process typically conducted between 900 and 1700 °C. Sintering promotes densification through diffusion mechanisms, leading to the formation of strong, cohesive ceramic materials with reduced porosity. Post-sintering, the ceramics may undergo additional machining and finishing processes to achieve the precise dimensions and surface finish required for their intended applications. These processes can include grinding, lapping, polishing, and coating. The final ceramic products are characterized using various techniques to ensure they meet the required specifications, with common methods including XRD, SEM, XPS and mechanical testing for hardness and fracture toughness. Other techniques such as FTIR, XPS, and measurements of ferroelectric, optical, dielectric, and piezoelectric properties may also be used, depending on the application.

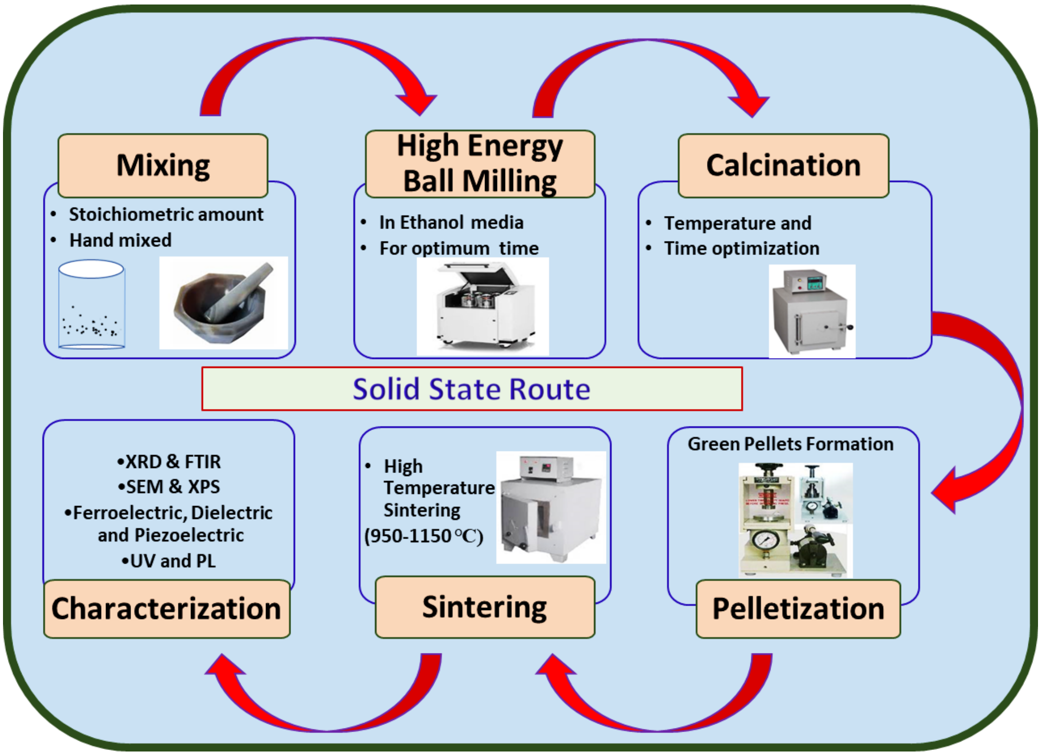

Figure 2.1 Pictorial representation of solid-state route adopted for preparation of samples.

The solid-state route offers several advantages, including simplicity, cost-effectiveness, and suitability for large-scale production, making it possible to achieve high-purity ceramics with proper control of raw materials and processing conditions. However, it also presents challenges such as the need for high temperatures, which can lead to energy-intensive processes, and long processing times due to multiple steps and high-temperature treatments. Additionally, inadequate mixing and calcination can lead to inhomogeneities in the final product. Despite these challenges, the solid-state route remains a cornerstone in ceramic processing due to its versatility, cost-effectiveness, and ability to produce high-quality ceramic materials with a wide range of applications.

2.2.2 Chemicals and Compositions

We utilized high purity oxides and carbonates for the preparation of our samples, the details of which are given below in Table 2.1.

Table 2.1 Precursors used for the synthesis of specific compositions.

Composition	Precursors	Company	Assay (%)
$0.67\{Bi(Fe_{0.97}Ga_{0.03})_{1-x}Sc_xO_3\}$-$0.33(BaTiO_3)$	Bi_2O_3, Fe_2O_3, Ga_2O_3, Sc_2O_3, $BaCO_3$, TiO_2	Sigma Aldrich Hi Media Alfa Aesar Sigma Aldrich Sigma Aldrich Sigma Aldrich	99.9 99 99.9 99.9 99 99
$0.67(Bi_{1-x}La_xFe_{0.97}Ga_{0.03}O_3)$-$0.33(BaTiO_3)$	Bi_2O_3, Fe_2O_3, Ga_2O_3, Sc_2O_3, $BaCO_3$, TiO_2 La_2O_3	Sigma Aldrich Hi Media Alfa Aesar Sigma Aldrich Sigma Aldrich Sigma Aldrich Hi Media	99.9 99 99.9 99.9 99 99 99.9
$(Bi_{4-x}Sm_{0.5})(Ti_{3-0.01}Ta_{0.01})O_{12}$	Bi_2O_3, TiO_2, Sm_2O_3, Ta_2O_3	Sigma Aldrich Sigma Aldrich Alfa Aesar Sigma Aldrich	99.9 99 99.9 99

2.3 Characterization Techniques and Instrumentation

2.3.1 X-ray Diffraction (XRD) Technique

X-ray diffraction (XRD) is a fundamental and powerful analytical technique widely used to characterize the crystallographic structure, phase formation, and various structural parameters of materials. The principle of XRD is based on the interaction of X-rays with the electrons in the crystal lattice. When a crystal is irradiated with X-rays, they are scattered by the electrons, resulting in constructive or destructive interference depending on the crystal lattice geometry and the X-ray wavelength, producing a diffraction pattern that can be recorded and analyzed. In an XRD experiment, a sample is exposed to a monochromatic X-ray beam, and the regularly spaced planes of atoms in the crystal diffract the X-rays at specific angles. By measuring these angles and the intensities of the diffracted beams, a diffraction pattern is obtained, which contains peaks at specific angles corresponding to the distances between the planes of atoms in the crystal. Analyzing the positions and intensities of these peaks reveals the crystal's structure, including atom arrangement and lattice parameters. By comparing the diffraction pattern of the sample with standard reference patterns, the phases present in the material can be identified, making XRD particularly useful for determining the composition of multiphase materials. Furthermore, the broadening of diffraction peaks can be analyzed to estimate the size of crystallites and the level of strain within the material, which is especially important for nanomaterials. XRD can also accurately measure the lattice parameters of a crystalline material, providing insight into its crystal structure. By analyzing the intensities of the diffraction peaks, the relative amounts of different phases in a multiphase material can be quantified. XRD can assess the preferred orientation of crystallites in a polycrystalline sample, which is important for understanding the material's anisotropic properties. X-ray sources are essential in XRD systems, chosen based on the analysis requirements. We use a Copper (Cu) Kα source in our benchtop XRD shown in Figure 2.2 (a), with a wavelength of 1.5406 Å, ideal for metals, alloys, and crystalline materials due to its good resolution and intensity. Some other sources include Cobalt (Co) Kα (1.7889 Å), which reduces fluorescence interference in iron-containing samples; Molybdenum (Mo) Kα (0.7107 Å), offering better penetration for high-resolution studies of thick or dense materials; Silver (Ag) Kα (0.5594 Å), used for very high-resolution studies requiring deep X-ray penetration; and Chromium (Cr) Kα (2.2910 Å), suitable for stress measurements and analyzing thin films and coatings. Selecting the appropriate X-ray source ensures accurate and effective diffraction experiments tailored to the sample's nature and the specific information needed.

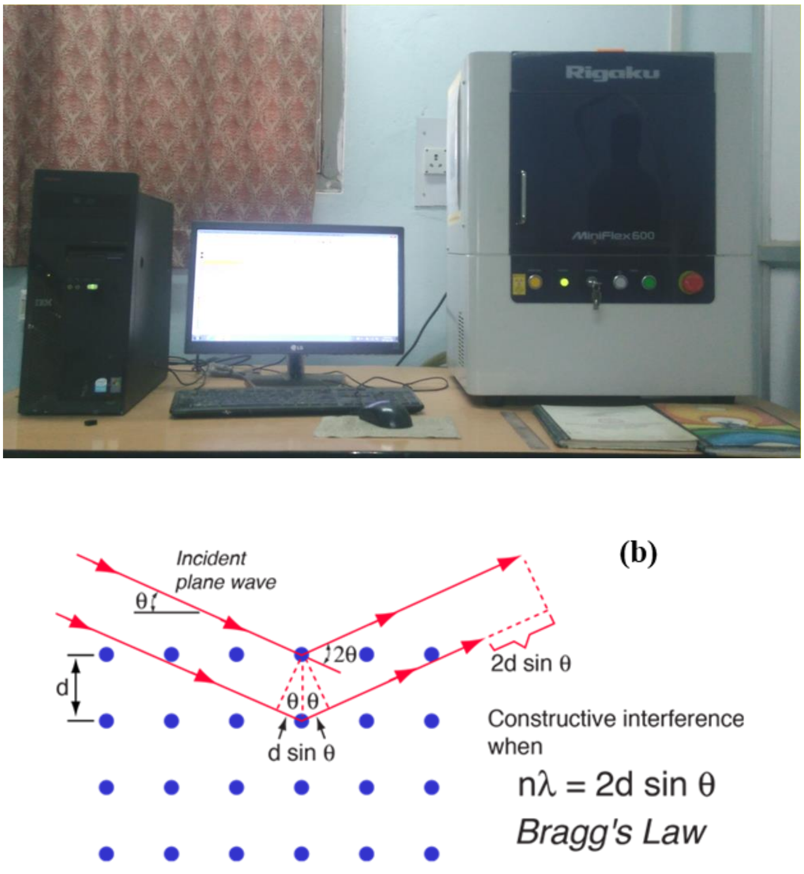

Figure 2.2: (a) Image of the benchtop XRD and (b) the schematic diagram showing the basic principle of Bragg's law.

Overall, XRD is an essential tool in materials science for characterizing the structural properties of crystalline materials. It aids in the development and optimization of new materials and helps understand their behavior, playing a critical role in advancing materials research and technology.

2.3.1.1 Basic Principle of Bragg’s Law

Bragg's Law, named after physicist Sir William Lawrence Bragg, relates the angles at which X-rays are diffracted to the spacing between the planes of atoms in the crystal lattice as depicted in Figure 2.2 (b). It describes the conditions for constructive interference of the diffracted X-rays, leading to observable diffraction peaks. Bragg's Law is given by the equation:

$$n\lambda = 2dsin\theta \qquad (2.1)$$

where n is the order of the reflection, λ is the wavelength of the incident X-rays, d is the interplanar spacing, and θ is the angle between the incident X-ray beam and the crystal plane.

Explanation of Bragg's Law

Bragg's Law explains that for constructive interference to occur, the path difference between X-rays scattered by adjacent planes of atoms must be an integer multiple of the wavelength. This is satisfied when the angle of incidence and the spacing between the planes of atoms cause the X-rays to reinforce each other. Bragg's Law allows us to determine the spacing between planes in a crystal by measuring the angles at which diffraction peaks occur, providing detailed information about the crystal structure, including the unit cell size, shape, and arrangement of atoms.

Application of Bragg's Law in XRD

In XRD analysis, Bragg's Law is used to identify and characterize materials. By comparing the measured diffraction pattern with reference patterns, the phases present in a sample can be identified. The positions of the diffraction peaks provide information about the lattice parameters, while the intensities of the peaks reveal the distribution of atoms within the unit cell. This makes XRD a powerful tool for studying crystalline materials in fields such as materials science, chemistry, geology, and solid-state physics.

2.3.1.2 Crystal Structure Determination Using Rietveld Refinement

Rietveld refinement is a sophisticated technique used for identifying and confirming the crystal structures and phases analysis. This technique, rooted in the pioneering work of H. M. Rietveld, utilizes computational analysis to refine models of crystal structures by fitting calculated diffraction patterns to experimental data [178]. It is especially effective for interpreting X-ray and neutron diffraction data from polycrystalline samples. The process begins with the identification of crystalline phases in the experimental powder XRD pattern. This is typically achieved through search-match techniques using standard databases. Once the phases are identified, if the material is already known, crystallographic information files (CIF) are sourced from databases such as the Inorganic Crystal Structure Database (ICSD) or the Crystallographic Open Database (COD). For unknown materials, a hypothetical structural model is proposed, and Rietveld refinement is employed to verify and refine this model against the experimental data. Key to the refinement process is the need for preliminary information, including instrumental correction factors (such as peak shift, broadening, and asymmetry), initial structural model of the crystal including information about the unit cell dimensions, atomic positions, thermal parameters, and other relevant structural details. Software like FullProf Suite is used to simulate theoretical XRD patterns based on these inputs and CIF files. Using the initial structural model, a theoretical diffraction pattern is calculated based on the crystallographic parameters and principles of diffraction. The calculated pattern is compared to the observed diffraction data, and the Rietveld refinement method iteratively adjusts the structural parameters to minimize the difference between the calculated and observed patterns. This involves refining parameters such as lattice parameters, atomic positions and occupancies, thermal parameters, and background and peak shape parameters. The refinement is typically performed using a least-squares minimization technique, aiming to reduce the residual sum of squares. Evaluation of the quality of fit involves various agreement factors such as the weighted profile R-factor (R_{wp}), expected R parameter (R_{exp}), and goodness of fit (χ^2). A χ^2 value around unity indicates a good fit, though excessively low values may suggest overfitting. The final refined model provides detailed structural information, ensuring that the crystal structure accurately reflects the experimental data. The refinement process continues until the calculated pattern closely matches the observed data, resulting in a final model that provides a detailed and accurate representation of the crystal structure, including precise atomic coordinates and other structural information.

Rietveld refinement software like FullProf Suite facilitates this process with its user-friendly interface, allowing for the precise determination of structural and microstructural parameters. The software supports multiple phase quantitative analysis, automatic parameter adjustments, and the refinement of XRD patterns from various sample types, including powders, pellets, and thin films. The ability to refine both structural and microstructural aspects makes FullProf Suite particularly valuable in material science research.

2.3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a versatile and an advanced analytical technique used to identify various types of materials, including organic, polymeric, and certain inorganic substances. This technique operates by analyzing how infrared radiation interacts with a sample, thus providing comprehensive insights into its molecular composition and structural characteristics. FTIR works on the principle of passing infrared radiation through a sample, where specific wavelengths are absorbed by the material, leading to molecular vibrations. The light that is not absorbed continues through the sample and is measured by a detector, which records the intensity of the transmitted or reflected light across different wavelengths. Figure 2.3 (a) shows the schematic diagram of the working of FTIR. The core component of an FTIR system is the interferometer (typically a Michelson interferometer) which modulates the infrared light's intensity to generate an interferogram. This raw data signal encapsulates all the spectral information, which is then processed using a Fourier Transform to produce an interpretable spectrum. This spectrum displays absorption peaks that correspond to the various molecular vibrations within the sample. Figure 2.3 (b) shows the instrumental setup used for FTIR spectroscopy. FTIR spectroscopy is particularly significant for several reasons. Firstly, it offers precise molecular identification by providing a unique absorption spectrum for different functional groups, thereby enabling the accurate identification of chemical compounds. Secondly, it facilitates qualitative analysis by helping to understand the chemical composition of complex mixtures through the identification of specific functional groups. Additionally, FTIR allows for quantitative analysis by determining the concentration of particular compounds in a mixture based on the absorption peaks' intensity. One of the key advantages of FTIR is that it is a non-destructive technique, allowing for the analysis of samples without causing any alteration or destruction, which is essential for preserving valuable or sensitive materials. Furthermore, FTIR is indispensable tool analyzing solids, liquids, and gases, making it a crucial tool across various fields such as chemistry, biology, environmental science, and materials science. Modern FTIR spectrometers are also noted for their speed and efficiency, rapidly collecting data and producing high-resolution spectra, which makes them suitable for both research and industrial applications.

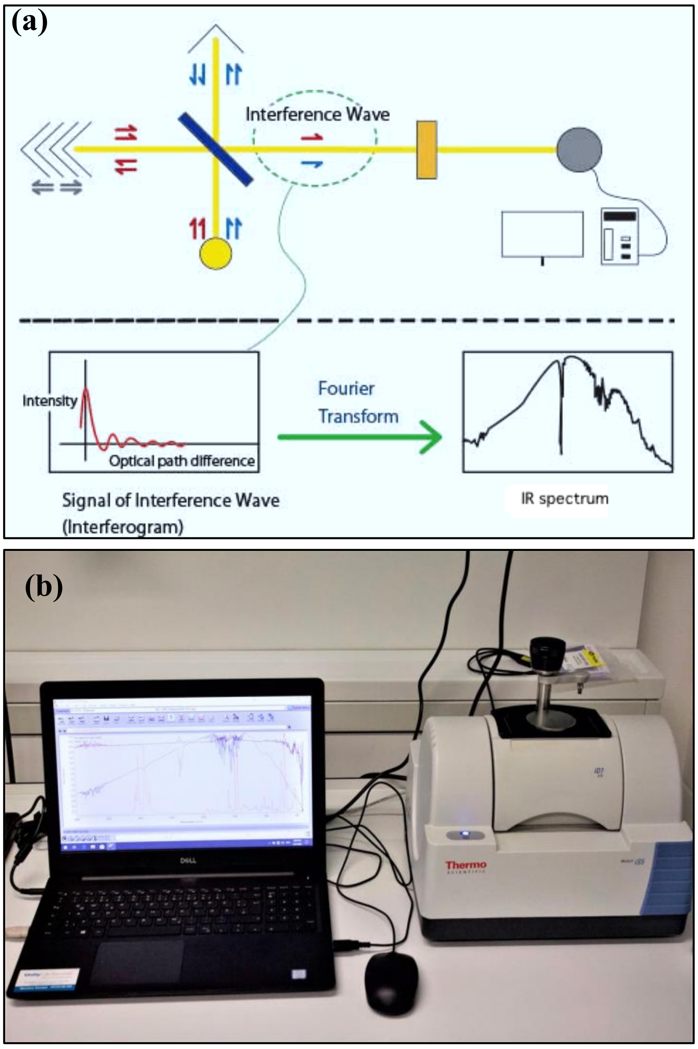

Figure 2.3 (a) Basic principle governing FTIR spectroscopy and (b) a typical FTIR instrument setup.

2.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is an effective imaging technique utilized to capture high-resolution images of surface features of samples, ranging from micro to nanoscale dimensions. Unlike traditional light microscopy, SEM utilizes a focused beam of electrons to achieve magnifications up to 100,000 times, enabling detailed examination of surface morphology and compositional characteristics. This method involves directing a concentrated electron beam onto the sample's surface, generated by an electron gun and accelerated to energies between 100 eV and 40 keV. The beam travels through a high vacuum column, focused by magnetic lenses into a narrow diameter of 0.4 to 5 nm, and scanned across the sample in a raster pattern by scanning coils as depicted in Figure 2.4 (a).

As the electron beam interacts with the sample, it produces various signals, including secondary electrons, backscattered electrons, and characteristic X-rays. These signals are detected by scintillator-photomultiplier detectors and other sensors, which convert them into electrical signals to generate detailed images. The resulting micrographs, which exhibit a large depth of field, provide a three-dimensional perspective crucial for understanding the sample's surface structure. Secondary electrons are low-energy electrons emitted from the sample surface, which provide high-resolution images of the surface morphology. Backscattered electrons are high-energy electrons that offer compositional contrast, with heavier elements appearing brighter in the images. Characteristic X-rays, generated through the interaction of the electron beam with the sample, provide elemental composition information via Energy Dispersive X-ray Spectroscopy (EDS). These signals are captured, amplified, and detected to create detailed images displayed on a computer screen. The resulting micrographs exhibit a large depth of field, offering a three-dimensional perspective crucial for understanding the sample's surface structure. A significant feature of SEM is its capability to perform elemental analysis with EDS. When the electron beam bombards the sample, it induces the emission of characteristic X-rays unique to each element's atomic structure. EDS measures the energy of these X-rays, enabling precise identification and quantification of the elements present. This allows for both qualitative and quantitative analysis, with spatial distribution information provided through elemental mapping. For non-conductive samples, charge buildup can occur, creating a static electric field that interferes with imaging. To prevent this, a thin gold coating is often applied to the sample via sputtering. In this research, SEM imaging of sintered pellets was conducted using ZEISS (Nova Nano SEM 450, Figure 2.4 (b)), ZEISS (MA15 /18), FEI Quanta 200 F instruments.

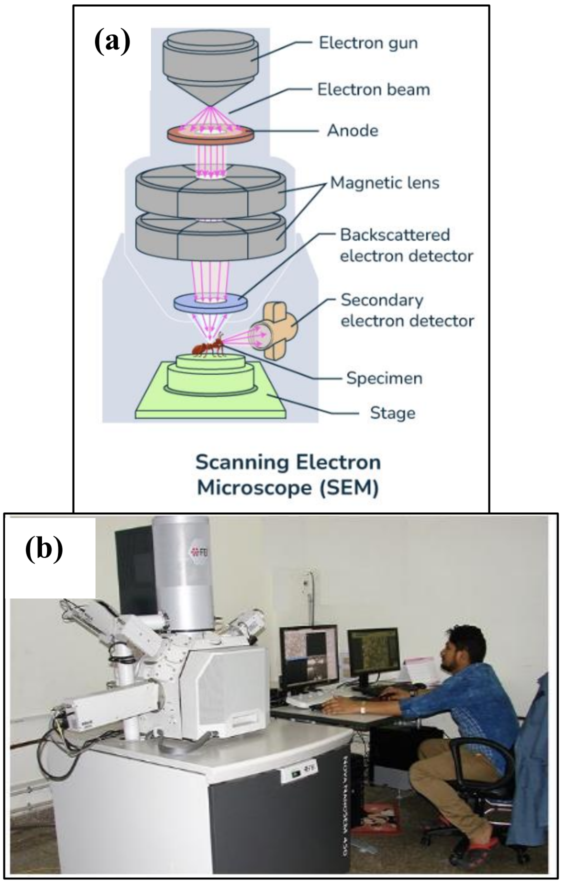

Figure 2.4 (a) Schematic image of different components of SEM instrument and (b) Image of a high resolution SEM.

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive quantitative spectroscopic technique widely used to analyze the elemental composition and chemical state of materials. The basic principle of XPS is depicted in Figure 2.5 (a) which involves irradiating a material with X-rays and measuring the kinetic energy of the emitted photoelectrons. When a sample is exposed to a beam of X-rays, typically generated from an aluminium (Al Kα, 1486.6 eV) or magnesium (Mg Kα, 1253.6 eV) source, the X-rays transfer energy to the core-level electrons in the atoms of the material. This energy transfer causes the electrons to overcome their binding energy and be emitted from the atom as photoelectrons. The kinetic energy of these emitted photoelectrons is measured using an electron energy analyzer. The kinetic energy (E_{kin}) of a photoelectron is related to the energy of the incident X-ray (hν) and the binding energy (E_b) of the electron within the atom by the equation: $E_b = h\nu - E_{kin} - \phi$, where ϕ is the work function. By measuring the kinetic energy of the photoelectrons, the binding energy of the electrons can be determined. The binding energy is characteristic of the specific element and its chemical state, allowing for the creation of an XPS spectrum, which plots the number of electrons detected (intensity) versus their binding energy. The spectrometer operates under ultrahigh vacuum (10^{-8}-10^{-9} mbar) conditions to reduce electron scattering and avoid surface contamination. Figure 2.5 (b) shows the instrument used for characterisation in this thesis. XPS is significant for several reasons. It can detect all elements except hydrogen and helium, providing quantitative information about the elemental composition of the surface layer of a sample, typically within a depth of 1-10 nm. It can distinguish between different oxidation states and chemical environments of the same element, offering detailed chemical state information. Its high surface sensitivity makes it ideal for analyzing thin films, surface coatings, and surface contamination. Additionally, XPS allows for quantitative analysis of the elemental composition, including the detection of trace elements, and is generally a non-destructive technique, preserving the sample for further analysis.

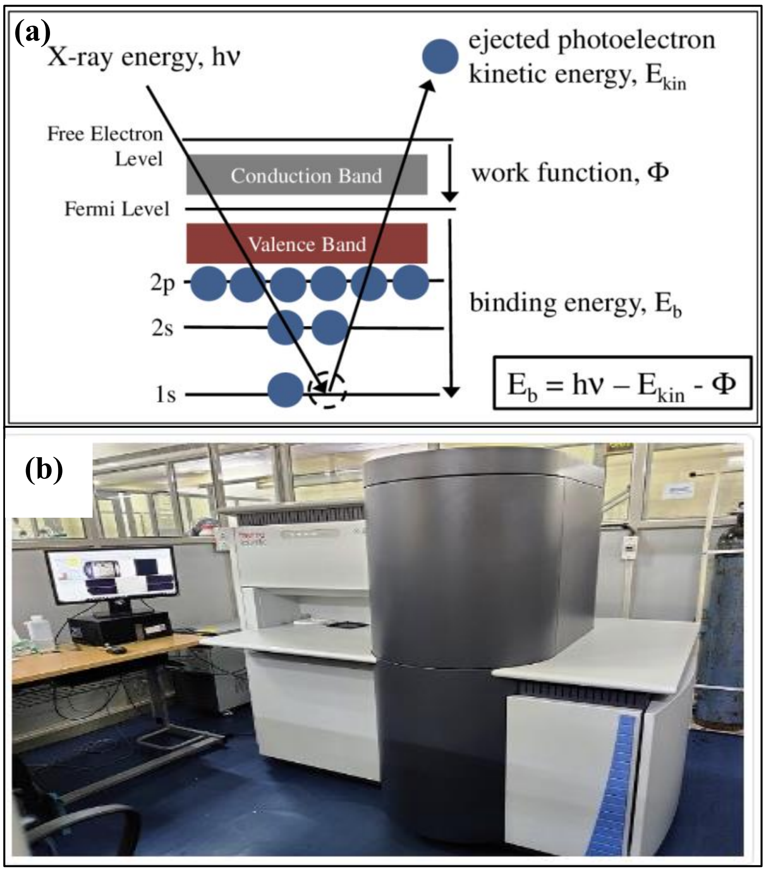

Figure 2.5 (a) Basic principle of XPS and (b) working XPS instrument (Thermo Fisher Scientific (K-alpha)).

In summary, X-ray Photoelectron Spectroscopy (XPS) is a vital tool for surface analysis, providing detailed information about the elemental composition and chemical states of materials. Its ability to offer quantitative, surface-sensitive analysis makes it requisite in numerous scientific and industrial fields.

2.3.5 Dielectric Spectroscopy

Dielectric Spectroscopy, also known as impedance spectroscopy, is an investigative non-destructive technique utilized to measure the dielectric properties of a material across a range of frequencies. Dielectric properties encompass key parameters such as permittivity (dielectric constant), dielectric loss (loss tangent), impedance, admittance, reactance, susceptance, capacitance, and conductivity. The principle of dielectric spectroscopy involves applying an AC electric field to a sample material and measuring its response.

For our research, we used the Keysight E4990A impedance analyzer having a broad operating frequency range of 20 Hz to 10 MHz, allowing for comprehensive analysis (Figure 2.6). Permittivity reflects the capacity of a material to store electrical energy within an electric field and is calculated using the capacitance of the sample, the thickness of the sample (pellet), and its area. The loss tangent, or dissipation factor, indicates the energy dissipation within the material. Additionally, the dielectric constant can vary with temperature, and this temperature-dependent dielectric constant is measured by recording permittivity at different temperatures using a controlled heating system integrated with the impedance analyzer.

The sample preparation for dielectric measurement requires a pellet with good electrical contact, typically achieved by applying a thin layer of silver or platinum paste on the surfaces. The sample is mounted on a holder and placed in a furnace or temperature-controlled chamber connected to the analyzer. Calibration, involving open, short, and load steps, is performed to ensure accurate measurements. The desired frequency and temperature ranges are set, and the analyzer applies an AC signal to the sample, recording the electrical responses. These responses are processed to calculate permittivity, loss tangent, and other dielectric properties.

Figure 2.6 Experimental setup to measure temperature dependent dielectric properties using Keysight impedance analyzer.

2.3.6 Diffuse Reflectance Ultraviolet-Visible (UV-Vis) Spectroscopy

Diffuse reflectance spectroscopy (DRS) is compelling analytical method for examining the optical characteristics of solid materials, especially those that are opaque or strongly scattering. This method extends the principles of traditional UV-Visible spectroscopy to measure the reflectance of light from solid samples, providing valuable insights into the optical properties like bandgap of materials. The basic principle involves directing a beam of UV or visible light onto the surface of a solid sample, where the light interacts with the sample and scatters in various directions as shown in Figure 2.7 (a). Some of this scattered light is absorbed by the material, while the rest is reflected. The reflected light, including both specular and diffuse components, is collected and measured by a detector. The intensity of the reflected light at different wavelengths reveals the sample's optical properties, and this data can be converted into an absorbance spectrum using the Kubelka-Munk function. As shown in Figure 2.7 (b) the instrumentation of a DRS UV-Vis spectrometer typically includes a light source (a deuterium lamp for UV light and a tungsten-halogen lamp for visible light), a sample holder designed for solid samples, an integrating sphere to capture and integrate the diffuse reflected light, a detector (usually a photodiode array or a charge-coupled device), and a data processing unit to convert the raw reflectance data into an absorbance spectrum for further analysis. For our research we used the Shimadzu UV-2600 spectrophotometer (Figure 2.7 (b)) which can be utilized for analyzing both polycrystalline powders and liquid samples.

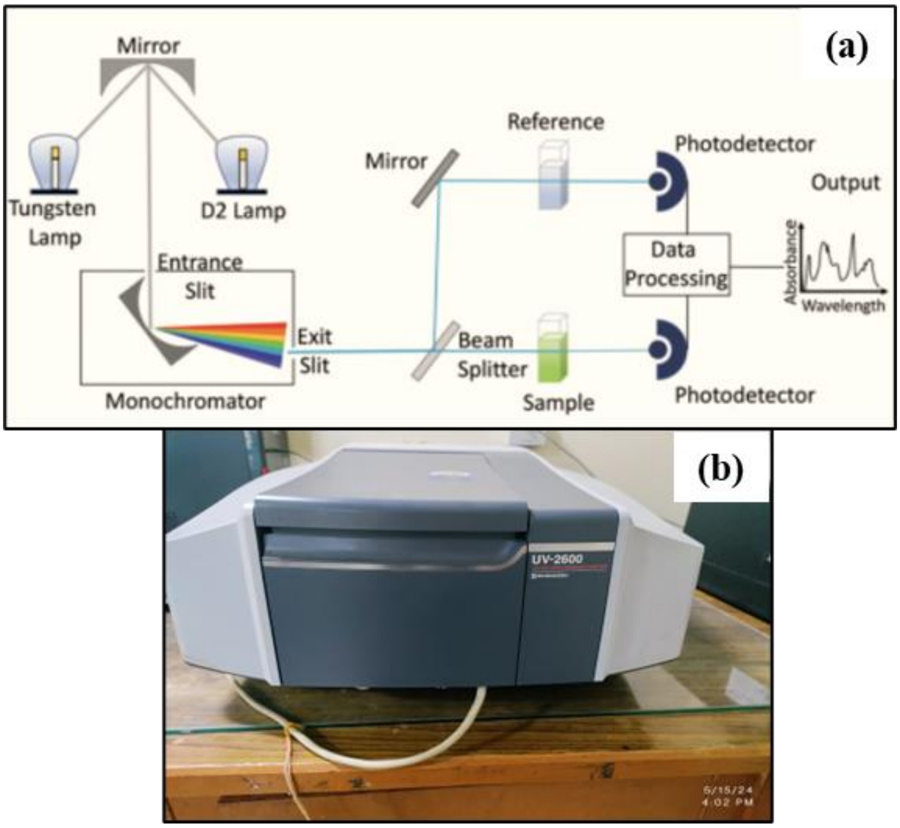

Figure 2.7 (a) Basic principle and schematic picture of operation of UV-vis spectrophotometer and (b) Shimadzu UV-2600 spectrophotometer.

2.3.7 Ferroelectric Characterization

The study of ferroelectric properties of materials consists of Polarization-Electric Field (P-E) hysteresis loop measurement. It provides vital information about the material's polarization behavior in response to an applied electric field, revealing key properties such as remnant polarization, coercive field, and saturation polarization. The principle behind P-E hysteresis loop measurement involves applying an alternating electric field to a ferroelectric material and measuring the resulting polarization (Figure 2.8 (a)). As the electric field varies, the polarization of the material changes, and this relationship is plotted to form a hysteresis loop. The shape and area of the loop provide insights into the ferroelectric characteristics of the material.

The primary instrumentation for P-E hysteresis loop measurements includes a function generator to generate the alternating electric field, a high-voltage amplifier to amplify the electric field to the required levels, a Sawyer-Tower circuit (Figure 2.8 (b)) to measure the polarization, an oscilloscope or data acquisition system to capture and display the P-E loop data, and a sample holder to hold the ferroelectric sample in place during testing. The Sawyer-Tower circuit, central to P-E hysteresis loop measurements, consists of two capacitors arranged in series: the test dielectric sample (ferroelectric material) and a reference capacitor with a known linear value. The reference capacitor is chosen to have a much higher capacitance than the sample to ensure the voltage drop across the sample is maximized.

In the Sawyer-Tower circuit configuration, the sample and reference capacitor are connected in series, and a high-voltage source applies an alternating electric field across the series combination. The drive voltage from the function generator is nearly equal to the voltage across the sample, while the voltage across the reference capacitor is proportional to the polarization of the sample. The voltage across the sample is connected to the horizontal input of the oscilloscope, representing the electric field, and the voltage across the reference capacitor is connected to the vertical input, representing the polarization. As the electric field is cycled, the oscilloscope traces out the P-E hysteresis loop, providing a visual representation of the ferroelectric properties.

In practical implementation, the instantaneous current through the sample is often measured instead of directly measuring the charge. This current is then integrated to calculate the polarization. A prototypical circuit for measuring the P-E loop involves applying an AC voltage to the sample using a high-voltage amplifier, measuring the current with a current sensor or a resistor in series with the sample, integrating the current signal to obtain the polarization, and using a data acquisition system or an oscilloscope to capture the voltage across the sample and the integrated current signal.

P-E hysteresis loop measurements are crucial for characterizing ferroelectric materials used in non-volatile memory devices, sensors, and actuators. They help understand the switching behavior and stability of ferroelectric domains and investigate the effects of temperature, frequency, and material composition on ferroelectric properties. The P-E hysteresis loop measurement is an essential technique in the study of ferroelectric materials, providing comprehensive insights into their polarization behavior under an applied electric field. The Sawyer-Tower circuit plays a critical role in this measurement, enabling precise determination of the material’s ferroelectric properties. This technique is widely used in the research and development of advanced ferroelectric materials and devices. Figure 2.8 (c) displays the instrument used for the data collection in the present research work.

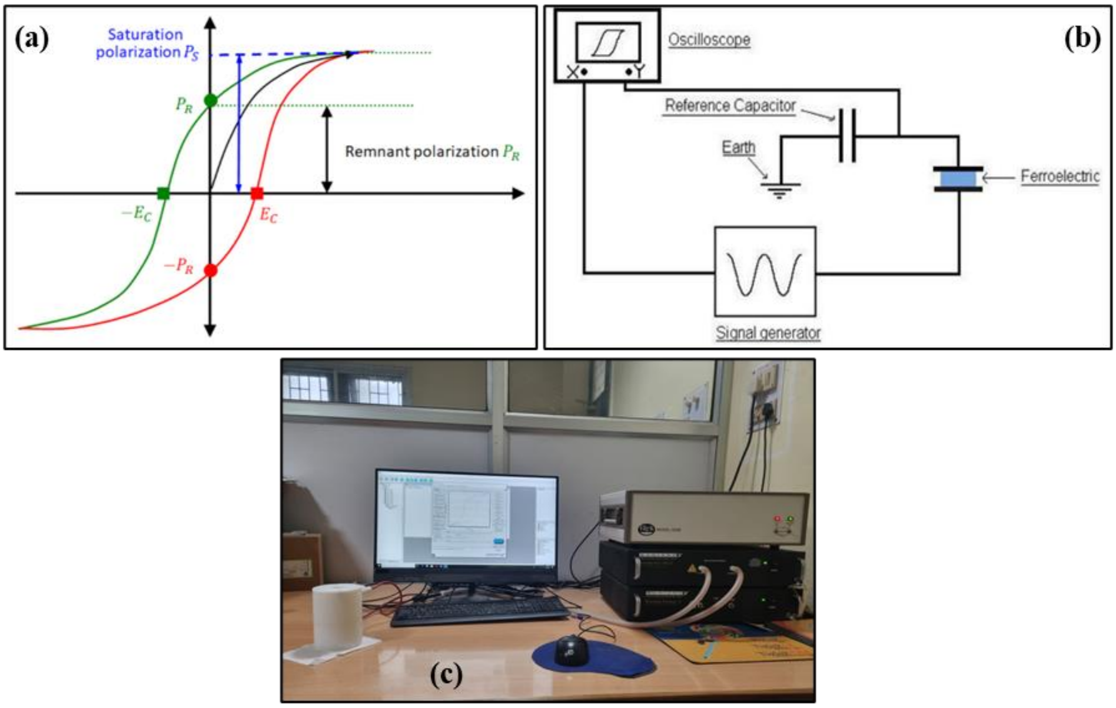

Figure 2.8 (a) A typical P-E Hysteresis loop, (b) Schematic Sawyer Tower Circuit and (c) Ferroelectric property measurement setup by the Radiant Technologies (Precision Premier II).

2.3.8 Piezoelectric Charge Coefficient Measurement

A d_{33} meter is a specialized instrument used to measure the piezoelectric charge coefficient, commonly denoted as d_{33}, which quantifies the piezoelectric response of a material when subjected to mechanical stress. This measurement is crucial for evaluating the performance of piezoelectric materials used in sensors, actuators, and other devices. The basic principle of the d_{33} meter involves applying a mechanical stress to a piezoelectric sample and measuring the generated electric charge. The d_{33} coefficient is defined as the charge generated per unit force applied along a specific axis, typically the polarization axis of the material.

In practice, the piezoelectric sample is clamped securely and prepared with electrodes to ensure good electrical contact. A known and controlled low-frequency force, typically around 110 Hz, is applied to the sample. This frequency is chosen to be below the resonance frequency of the material to avoid resonance effects. The piezoelectric material develops charges on opposite surfaces when the force is applied. These charges are measured using an electrometer or charge amplifier, processed into signals, and compared with a built-in reference to determine the d_{33} coefficient. Modern d_{33} meters often automate this calculation and display the result directly.

The instrumentation of a typical d_{33} meter includes a force generator that provides a controlled mechanical stress to the sample, a sample holder that securely clamps the piezoelectric sample during the measurement, an electrometer or charge amplifier to measure the electric charge generated by the sample, and a control unit that manages the operation of the force generator and charge measurement and computes the d_{33} coefficient. Additionally, the display/interface shows the measurement results and allows for user interaction and parameter adjustments.

Several parameters can be adjusted in a d_{33} meter to optimize and tailor the measurement process, including the magnitude of the applied force, the frequency of the applied force (especially in dynamic measurements), temperature control for studying the temperature dependence of the piezoelectric coefficients, and the sample size and geometry. The most commonly used mode for d33 measurement is the "quasi-static" or "Berlincourt" mode, where both the applied force and the measuring signal are aligned in the same direction as the polarization of the material. This method is especially effective for measuring d_{33} coefficients in poled ferroelectric ceramics and single-crystalline piezoelectric materials.

An example of a d_{33} measuring instrument is the Piezotest d_{33} meter from the UK, which is used in various research and industrial applications to measure the d_{33} coefficient accurately and efficiently. This instrument is shown in Figure 2.9 and represents a typical setup for these measurements. The d_{33} meter is widely used in the development and characterization of piezoelectric materials and devices, including applications such as material research, ensuring the consistency and quality of piezoelectric components in manufacturing, and fine-tuning the properties of piezoelectric sensors, actuators, and transducers for specific applications. Overall, the d_{33} meter is a crucial tool for measuring the piezoelectric strain coefficient d_{33}, providing essential data for the development and optimization of piezoelectric materials and devices. Its ability to vary different parameters makes it a versatile instrument for comprehensive material characterization.

Figure 2.9 A typical d_{33} meter by PIEZOTEST.

2.3.9 Photoluminescence Spectroscopy

Photoluminescence spectroscopy is a powerful, non-destructive optical method used to examine the electronic structure of materials without making contact. In this technique, light is shone onto a sample, which absorbs the light and gains extra energy in a process known as photo-excitation. This additional energy can be released by the material through the emission of light, a phenomenon referred to as luminescence. Specifically, when this luminescence is triggered by photo-excitation, it is termed photoluminescence.

Photoluminescence occurs when electrons in the material absorb light and move to higher energy states. As these electrons return to their original equilibrium states, the excess energy is emitted as light in a radiative process. The energy of this emitted light is determined by the energy difference between the excited state and the equilibrium state. The intensity of the emitted light is proportional to the extent of the radiative process involved.

PL spectroscopy provides insights into the lower energy levels of the material under investigation. In semiconductors, the most common radiative transition happens between the conduction and valence bands, with the energy difference being referred to as the bandgap. During a PL spectroscopy experiment, a laser with energy much greater than the optical band gap is used to excite the sample. The photo-excited carriers, which include electrons and holes, move towards their respective band edges and recombine, emitting light at the band gap energy. These radiative transitions can also involve localized defects or impurity levels, making it possible to identify specific defects or impurities through analysis of the PL spectrum. The strength of the PL signal can also provide information about the concentration of these defects or impurities.

A photoluminescence spectrophotometer is an analytical tool designed to measure and record the fluorescence of a sample. It can scan either the excitation wavelength, the emission wavelength, or both. With additional accessories, it can monitor changes in the signal over time, temperature, concentration, polarization, or other variables. The block diagram of a fluorescence spectrometer, shown in Figure 2.10, includes components such as laser sources, wavelength selectors, sample illumination systems, detectors, and equipment for generating corrected spectra.

Figure 2.10 Fluorescence spectrophotometer (F-4600, Hitachi) for photoluminescence measurement.

2.4 Conclusions

This chapter provides an overview of the synthesis methods and characterization techniques employed in this thesis. We utilized the solid-state synthesis method utilizing high energy ball milling, recognized as one of the most straightforward and effective methods for sample preparation. The chapter also details various characterization techniques and property analysis software used to interpret the resulting data, along with their theoretical foundations. The following chapters will delve into the investigation results on various Bi-based lead free piezoceramic materials, presenting the findings and analyses comprehensively.