Chapter 2
Sample Preparation
AND
Experimental Techniques
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Sample Preparation and Experimental Techniques

2.1 Sample Preparation:

2.1.1 Introduction:
Sample preparation plays the most important role for scientific research. Sample preparation and physical parameters optimization are the vital part to study material properties. Now-a-days, there are many improved methods available for the preparation of ultra-fine, high purity and homogeneous ceramic powders. Though multiferroic materials can be prepared in the form of single crystals or thin films or polycrystalline form, the polycrystalline form, the polycrystalline ceramics have some added advenges over single crystal or thin films [186]. There are some positive aspects of polycrystalline ceramic processing over single crystal as:

- Ceramics are usually easier to fabricate into different shape and size.
- Ceramics have their additional structural and microstructural (i.e. grain shape, size and porosity, etc.) features. These microstructural features can be exploited in designing the electro-ceramic materials for proper device requirements. The presence of grain boundaries (which is not present in single crystals) give rise to additional effect and play an important role in practice.
- Ceramics have the added advantages of thermal, chemical and mathematical stability.

The above features may justify the use of ceramics in spite of their brittle and non-ductile characteristics. Ceramic processing is a sequence of operation like mixing, calcinations, sintering etc., that internationally and systematically changes the chemical and physical properties of the material [187]. The aim of the science of ceramic processing is to identify the important characteristics of the system and to understand the effect of processing variables on the evolution of these characteristics. However, reliability and economy is the prime factors that control the successful processing of the ceramic products. These factors contributed to the derivation of a variety of methods of synthesis.

2.1.2 General methods for ceramics preparation:
A suitable method for preparation of ceramics depends largely on the production cost and the capability to achieved desired characteristics required for potential application. The nature of the new materials has a major effect on the final properties of a ceramic component. Purity, particle size distribution, reactivity, polymorphic form and availability must all be considered and carefully controlled during sample preparation. The growing applications of ceramics have
received increasing interest in the multidisciplinary approach to their synthesis [188, 189]. Different techniques developed for power preparation sizing are divided mainly into three categories:

(i) Mechanical methods:
Different mechanical methods include the mixed oxide process (MOP) or solid-state reaction process, high energy ball milling, vibratory milling, turbo milling, fluid energy milling, hammer milling, roll crushing etc.

(ii) Chemical methods:
The chemical methods are co-precipitation method, sol-gel process, decomposition, plasma, laser, hydrothermal, cryochemical processing, molten salts, hydrothermal techniques, liquid-phase and gas-phase reactions, polymer pyrolysis, pechini and citrate gel methods, aerosols and emulsions.

(iii) Miscellaneous:
Some other techniques for power preparation are calcining, rotary kiln, and fluidized bed and combustion synthesis techniques.

Now-a-days both the processes are used, for example, mixed oxide method for the cost conscious applications, and chemical methods for the more stringent applications. The MOP method, although successful for a large scale production of bulk ceramic powers at its low cost and easy adaptability, has several limitations in the production of fine ceramics. In conventional solid – state reaction method, high temperature and heating for prolonged time make the particles coarse, and as a result high energy destruction (break down) force is required to get fine powders. Several authors studied the fabrication and properties of the ceramics prepared by a solid-state reaction technique. Using this method ceramics are produced at high temperatures. The completeness of the reaction and uniformity of the product depend on particle size, homogeneity of the mixture, thermal schedule, and even on the atmosphere during calcinations.

2.1.3 Mixed Oxide/ Solid State Reaction Technique:
This is the conventional method in which mostly oxides and carbonates are used. The general method of processing of the materials is explained below.
• **Raw Materials**

Raw materials are selected on the basis of purity and particle size, which are required for attainment of chemical equilibrium, particularly for the formation of solid solution. Impurities can affect the reactivity as well as electrical properties of the mixed ceramics. When raw materials have volatile ingredients or impurities, the ignition losses must be taken into account.

• **Weighing and mixing**

The weighing exact amount of the constituent materials of the sample with due allowance for impurity and moisture content is the first step in preparation of ceramic sample. Often to reduce the moisture content the raw material are kept in oven at 150°C for several hours before they are weighed. The constituents must be taken in a desired stoichiometry. The required amount of different chemicals (i.e., metallic oxides/ carbonets) needs for the synthesis of a given amount of ceramics is calculated as follows:

Let \( M \) be the molecular weight of the desired ceramics and \( m \) be the amount (in gram) of prepared material. \( M_a \)is the molecular weight of \( a^{th} \) metallic oxides/carbonets used in the fabrication of ceramics in which \( Z \) fraction of the ‘a’ metallic ion is present. Then the weight required for \( a^{th} \) metallic oxides/carbonets is given by \( m_a \) where

\[
m_a = \frac{M_a mZ}{M}
\]

The next step is mixing, eliminating aggregates and / or reducing the particle size. The constituents of a ceramic body need to be intimately mixed so that the neighboring particles can inter-diffuse, which is essential for compound formation during calcinations. So the mixing process makes homogeneous mixture of the precursors. The physical properties of the ceramics (i.e., dielectrics, ferroelectrics, etc) are greatly suffered, if there is lack of homogeneity in the ceramics. For better homogeneity proper mixing is necessary in dry medium followed by wet mixing (i.e., in solvent like methanol, acetone) for sufficient time. Then the weight mixture is kept in air foe sometime to dry by slow evaporation. The air-dried power is normally kept just above 100°C and ground by an agate mortar for a few hours.

• **Calcination**

Calcinations process is an endothermic decomposition reaction in which an oxy-salt, such as carbonate or hydroxide, decomposes leaving an oxide as a solid product and also liberating the gaseous products. During this decomposition reaction the particle size, its distribution, extent of
agglomeration, porosity and morphology are usually established. Calcination causes the constituents to interact by inter diffusion of their ions and so reduces the extent of the diffusion that must occur during sintering in order to obtain a homogeneous body. Calcination is often the final step in the production of high purity ceramic powders. During calcination surface absorbed water vapours, any volatile impurities and carbon dioxide from carbonates are removed and thermochemical reaction among the constituent oxides takes place to form the desired compound. The calcination temperature is optimized for both the completion of reaction as well as the prevention of volatile oxides. Double calcination step is often useful to get a homogeneous and single phase compound.

- **Grinding and Pelletization**
  The calcined powers are ground to very fine powder. Grinding is generally accomplished by any suitable means e.g., agate mortar and pestle, ball milling etc. it helps to mix the constituent materials for ceramic preparation and also homogenize the compositional variation, which may arise during calcination. If the grinding is coarser, then the ceramics can have large intergranular voids and lower density. If grinding is too fine, then the colloidal properties may interfere with subsequent forming operations. The ground material is mixed with a binder solution (polyvinyl alcohol (PVA)) to reduce brittleness and for better compactness among the granules of the materials. After adding binder the powder sample is pressed to give it a final shape. Mostly the conventional method of cold pressing is followed, where the samples are used to be pressed die-punch in a hydraulic press. The samples are usually circular, rectangular or cylindrical in shape.

- **Sintering**
  In addition to composition and powder preparation, densification of the powder into a pore-free, fully dense ceramic element is extremely critical to achieve a high quality product. This is achieved by a process called sintering. Prior to the densification the ceramic powers are compared to specific form by different methods. Sintering is the process in which fine grains/powders are transform to dense polycrystalline product after heating to an appropriate temperature below the melting point of the materials. Sintering converts a compacted powder into a denser structures of crystallites joined to one another by grain boundaries. Grain boundaries vary in thickness from about 100µm to over 1µm. they may consists of crystalline vitreous second phase, or may be simply a disorder form of major phase because of the differing lattice orientations in neighboring grains. Sintering is accompanied by the elimination of
intergranular voids (pores) and by shrinkage of the whole system. Initially in the volume fraction of pores takes place due to the process of crystalline growth and rearrangement of grains in the power. The whole sintering process is a very complicated phenomenon. The binder present in the sample burnt out during the sintering process.

2.2 Preparation of the Compounds:
Polycrystalline sample of (Bi$_{1-x}$, A$_x$) (Fe$_{1-x}$,Ta$_x$) O$_3$ Where A= Li, Na and K x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5 were prepared from pure oxides/carbonates. Bi$_2$O$_3$, Fe$_2$O$_3$, Ta$_2$O$_5$,Li$_2$CO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$ (M/S LOBA Chem. Co India) using a standard solid-state reaction (mixed oxide) technique. The above ingredients were thoroughly mixed and ground in dry condition for 1h, and thereby wet atmosphere (methanol) for 2h in agate mortar and pestle to get homogenous mixture of the materials. Then the mixed powders of the compounds were calcined at different temperature in alumina crucibles for different time interval in air atmosphere given in the table. The process of grinding and calcination was repeated to ensure the formation of the compounds. The quality and formation of the compounds were verified by an X-ray diffraction (XRD) technique. The fine and homogeneous powder of the above compounds were pressed into cylindrical pellets of 10 mm diameter and 1-2 mm thickness under a uniaxial pressure of 5x10$^6$ N/m$^2$ using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The pellets were then sintered for time interval at different temperature in air atmosphere. The binder was burnt out during the high temperature sintering. Crystal structure and microstructure of the prepared compounds were studied by an X-ray diffraction technique (XRD) and scanning electron microscopy (SEM) respectively. The sintered pellets were polished with fine emery paper and then coated with high-purity conducting silver paste. The pellets were dried at 150$^\circ$C for about 4h.
Figure 2.1 Flow chart for the preparation of ceramics samples by a solid-state reaction technique

(1-x) BiFeO₃ + xATaO₃
(Bi₁₋ₓAₓ)(Fe₁₋ₓTaₓ)O₃
A=Li,Na& K x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5

Dry Mixing

Wet Mixing

Calcination

Grinding

Recalcination

Cold Pressing

Sintering

Polishing

Electroding

Formation checked by XRD

Characterization
Table 2.1: Calcination and sintering temperature with respective duration of time of different samples

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Concentration (x)</th>
<th>Calcination temperature and Time</th>
<th>Sintering temperature and time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi$_{1-x}$ Li$<em>x$) (Fe$</em>{1-x}$,Ta$_x$)O$_3$</td>
<td>0.1</td>
<td>750°C, 4h</td>
<td>780°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>750°C, 4h</td>
<td>780°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>750°C, 4h</td>
<td>780°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>750°C, 4h</td>
<td>800°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>750°C, 4h</td>
<td>820°C, 4h</td>
</tr>
<tr>
<td>(Bi$_{1-x}$ Na$<em>x$) (Fe$</em>{1-x}$,Ta$_x$)O$_3$</td>
<td>0.1</td>
<td>850°C, 4h</td>
<td>860°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>850°C, 4h</td>
<td>860°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>850°C, 4h</td>
<td>880°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>850°C, 4h</td>
<td>890°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>850°C, 4h</td>
<td>910°C, 4h</td>
</tr>
<tr>
<td>(Bi$_{1-x}$ K$<em>x$) (Fe$</em>{1-x}$,Ta$_x$)O$_3$</td>
<td>0.1</td>
<td>880°C, 4h</td>
<td>950°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>900°C, 4h</td>
<td>950°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>950°C, 4h</td>
<td>980°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>980°C, 4h</td>
<td>1000°C, 4h</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>980°C, 4h</td>
<td>1050°C, 4h</td>
</tr>
</tbody>
</table>
2.3. Electroding:

To study electrical properties of the sintered samples, one needs to electrode the samples using a suitable conducting material. Silver, Gold, Graphite, Platinum etc. are normally used as electrode materials after taking care of the following factors.

- The material should adhere the sample
- It should have almost zero contact resistance and
- It can be pasted in the form of a thin layer / film.

Electrode adherence is critical on the smooth ceramic pellet. There should not be any gap between electrode and the flat faces of the pellet otherwise these gaps will affect the electrical properties of the sample. In the present study the sintered pellets of all the compounds where polished with fine emery paper to make the both the faces flat, parallel and smooth. Then the parallel faces where electroded with high purity silver paste so that each become parallel plate capacitor and ready for the electrical characterization.

2.4. Experimental Techniques:

Scientific disciplines have been identified and differentiated by the experiment and the measurement techniques they employ. The same is true for ceramic technology. A single experiment is not sufficient to characterize the material. Different aspects of the materials like structure, surface morphology, thermal, electrical, mechanical, optical etc should be studied in details in order to understand the chemistry and physics of the materials in order to get a better understanding of the structure – property relationship of solids, various experimental techniques are used. The basic principles, preliminary descriptions and uses of important experimental methods along with the scope of the present investigation are furnished in the following sections.

2.4.1 Structural properties:

The properties of the materials are very sensitive to the structures. Structure is dependent on composition, heat treatment & processing. Thus it is necessary to characterize both composition and micro structure at the highest level of resolution possible in order to understand material behavior. Such characterization requires advanced and sophisticated equipment based on diffraction, microscopic & spectrographic phenomenon.

2.4.1.1. X-ray Diffraction (XRD):

Physical properties of solids (i.e., electrical, optical, magnetic, ferroelectric, etc.) depend on the atomic arrangements in the atomic arrangements in them. Therefore, crystal structure is an
indispensable part of the characterization of the materials. The radiation of X-ray, electron and neutron are usually employed for crustal diffraction studies by analogy with the diffraction of light by an optical grating. The X-ray diffraction is one of the powerful technique for the figure print characterization crystalline material and determination of their structure. In fact after every calcination the ceramic material was ground to fine powder, which was subsequently subjected to X-ray diffraction to confirm whether the material was formed in the desired phase or not. In 1912, Bragg recognized that X-ray diffractions in crystal obey particular geometric restrictions related to inter-planner crystal spacing. Later, this relation was designated was Bragg’s law that states $2d \sin \theta = n \lambda$; where $\lambda$ is the X-ray wavelength, $d$ is the crystal inter-planner spacing, and $\theta$ is the X-ray incident angle. This forms for the basis for the interpretation of XRD data. When a monochromatic beam of X-ray falls on a powder sample of poly crystalline material, the randomness of the crystallite orientation always allows a fraction of the sample to be suitably oriented with respect to the incident beam, which in turn enables an arbitrary diffraction line to be observed. In such a sample, the various lattice plane also present in every possible orientation. Therefore, at least some crystals must be oriented at the Bragg angle, thus diffraction occurs for this crystals and planes. The most important use of the powder method is in the qualitative identification of the crystalline phase or compound because is each crystalline phase has a characteristic powder pattern that can be used as finger print for identification purposes. The accurate determination of inter-planner spacing of a plane (hkl) and lattice parameters (a, b, c, $\alpha$, $\beta$ and $\gamma$) provide an important basis in understanding various properties of a material. The calculation of $T$ using peak position can be carried out using a general formula:

$$\frac{1}{d^2_{hkl}} = \frac{1}{V^2} \left[ h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2abc \{kla (\cos \beta \cos \gamma - \cos \alpha) + hlb (\cos \alpha \cos \gamma - \cos \beta) + hkc (\cos \alpha \cos \beta - \cos \gamma)\} \right]$$

Where, $V = \text{volume of the unit cell} = abc \left(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma\right)^{1/2}$

Where, a, b, c are cell dimensions, $\alpha$, $\beta$, $\gamma$ are interfacial angles and h, k, l are the Miller indices. The above equation for 'd' spacing reduces to

$$\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

for orthorhombic system
\[ \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \] for tetragonal systems.

The powder profile is the characteristic of a material, and it can be used for identification of materials without any need of further interpretation. From the measured position of a given powder diffraction line, Bragg angle \( \theta \) can be determined. By knowing the wavelength of x-ray beam used and the Bragg angle, interplanar spacing of the corresponding reflecting lattice planes can be calculated. The interpretation of powder diffraction pattern/profile can be a simple or difficult task depending upon the number of atoms present in the unit cell and the complexity of the phase composing the specimen. The simplest way to interpret the experimental data is by comparing it with the standard pattern of reference material. The X-ray diffraction experiment apparatus consists of an X-ray source, the sample to be investigated and a detector to collect the diffraction of X-ray. The general features of a powder diffractometer are shown in the Figure 2.3.

![Figure 2.3 General feature of powder diffractometer](image)
A monochromatic beam of X-ray strikes a finely powdered sample in which crystals are randomly arranged in every possible orientation. The diffracted beam can be detected either by surrounding the sample with a strip of photographic film or by using a movable detector. The most commonly and widely used powder diffraction technique of X-ray diffraction studies are the photographic and counter techniques [190]. For a polycrystalline material consisting of sufficiently large and strain free crystallites, the lines of powder pattern should be extremely sharp. But actually it is difficult to expect such sharp diffraction profile due to the combined effects of instrumental errors and other physical factors, which broadens the diffraction line profile [191, 192]. There are many theoretical and experimental studies on powder samples to obtain crystallite size and lattice strain. Among the theories Scherrer’s [193], Warren-Averbach’s [194] and Wilson [195] theories are considered to be most important. If broadening of the line profile of the diffraction pattern is solely due to small crystallite size, the Scherrer’s equation is used to calculate the effective or apparent crystallite size. The Scherrer’s equation used to calculate the crystallite size from a particular reflection (hkl) is given by

\[ P_{hkl} = \frac{k\lambda}{\beta_{1/2} \cos \theta} \]

Where \( \beta_{1/2} \) full width at half maximum (FWHM) in radians on the 2\( \theta \) scale and \( k \) is a constant approximately equal to unity and related to the crystallite shape. The best possible value of \( k \) was obtained as 0.89. Using Scherrer’s equation, the particle/crystallite size of all the samples of the present study was calculated. In order to eliminate the instrumental error, the value of FWHM (\( \beta_{1/2} \)) of the standard sample is subtracted from the \( \beta_{1/2} \) value of the sample (i.e., \( \beta_{1/2}^{\text{effective}} = \beta_{1/2}^{\text{sample}} - \beta_{1/2}^{\text{silicon}} \)). Certain factors such as temperature, polarization of x-rays, scanning rate, structure factor, sensitiveness and limitations of the instrument, etc. influence the intensities of x-ray diffraction lines. The intensity of the beam diffracted from an actual crystal depends on the number, type and distribution of atoms in the unit cell. The different factors affecting the diffraction intensities can be grouped into single expression for use in calculating the relative intensity of reflections. For powder method, the intensity is given by [196]:

\[ I = |F|^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M}, \text{ where } \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} = \text{Lorentz- polarization factor}, \]

\[ e^{-2M} = \text{Temperature factor, } F = \text{structure factor and } J = \text{scale factor.} \]
In the present study, the X-ray diffraction (XRD) patterns of all compounds have been recorded at room temperature using X-ray powder diffractometer (Rigaku Miniflex, Japan) with wavelength $\lambda = 1.5405$ Å (CuK$\alpha$ radiation) in a wide range of Bragg angles, $2\theta$ ($20^\circ \leq 2\theta \leq 80^\circ$) at a scanning rate of $3^\circ$/min. The operating voltage and current of the X-ray tube are 30 kV and 15 mA respectively. The proportional counter (Ar-filled) is attached to an arm rotating around an axis by an angle $2\theta$. The divergence of X-ray tube is limited to $3-5^\circ$ along the vertical direction. Soller slits were used to make the radiation effectively monochromatic. A $1^\circ$ slit was used to limit the divergence of X-ray beam in horizontal direction. Before recording the intensity distribution (profiles), the calibration and accuracy of the diffractometer were checked with the help of standard silicon powder sample provided with the instrument. The powder for X-ray analysis of our samples was prepared by reducing the particle size by grinding it in agate mortar. Klug and Alexander illustrated that the size of the crystallites composing the powder must fall within the acceptable limits for the diffraction lines to remain smooth. It is found that the mean deviation in intensity remains within 1–2%, when the coarsest grain size is of 5 µm. However, the mean deviation rises to as large as 18% when the coarsest grain size is in the order of 10 to 50 µm. If the crystallite sizes are not allowed to exceed 5 µm, then the effects of micro-absorption and particle orientation statistics can be neglected. The powder of the calcined sample was packed uniformly into a slotted-glass slide in order to avoid preferred orientation and induced packing. The glass slide having the powder specimen was placed at the center of the instrument. Ideally, the powder was mounted in such a way that no foreign material was exposed to the X-ray beam. Initially, with a continuous chart recording, the diffraction pattern was made in a wide range of $2\theta$ ($+20 \rightarrow +80^\circ$). After the initial run, the line profiles were obtained by point counting of the small interval in $2\theta$. At the background and tail of the intensity distribution (where the counting rate was slow), counts were made high enough at each setting so as to keep statistical fluctuation less than 1% throughout the experiment. The average crystallite size (P) of the studied compounds was calculated from the broadening of the XRD peaks of different Bragg’s angles using Scherrer’s equation.
2.4.2. Microstructure and Surface Morphology:

2.4.2.1. Scanning Electron Microscopy (SEM):

Scanning Electron Microscope is very useful technique to analyse the topography, morphology, crystallographic structure of the materials. It provides topographical and elemental information at magnification of 10X to 100,000X with virtually unlimited depth of field.

The contrast is due to topographical variation and differences in atomic number in the specimen. The high magnification along with a large depth of field makes the SEM and outstanding technological system for micro fabrication. SEM is powerful tool that uses a beam of highly energetic electron to examine objects on a very fine scale. This device is able to scan very small region such as grain and grain boundaries in the microstructure of the materials. SEM gives us information regarding (i) the surface feature of the materials (textature) and its direct relation with material properties (i.e. hardness, reflectivity (topography)). II) the shape and size of the particles and their direct relation between structure and material properties (i.e.) ductility, strength, reactivity etc (morphology). III) direct relation between composition and material properties (i.e. melting point, hardness etc. (composition)). IV) arrangement of the atoms in their crystal structure and also their relation with material properties (i.e. conductivity, strength, electrical properties etc.). The density, porosity (apparent/ open, closed, true/ total), grain size
and shape, grain boundaries, crystal defects internal stress are some of the important microstructural variables.

Figure 2.4 Schematic diagram of Scanning electron microscope.

SEM produces micrographs by scanning the surface of the specimen with a small electron probe (a beam of electron). Synchronous with an electron beam from a source. The basic units of SEM are: a) electron / optical column b) the vacuum system which include the specimen chamber and stage c) the signal detection and display system. The interaction of high energy electrons with specimens leads to the excitation of a variety of signals which can be used for characterization of microstructure. Figure 2.3 shows the schematic diagram of SEM. In scanning electron microscope electrons emerging from the gun (i.e. the electron source are alternated by a potential of 1-30kV, and focused on the specimen. The main advantage of SEM is that the signals are generated from a relatively small volume of material (typically $10^{-18}$ m$^3$) and therefore it provides analysis with spatial resolution. For microscopic study a small piece of sintered pellet has been taken and then gold was coated (thickness~ 40Å) using a vacuum coating unit of SEM. The micrographs at different magnifications were taken using JEOL JSM – 5800.
2.5. Dielectric Properties:
The most useful properties of ferroelectric and multi ferroics depend on their overall response to applied electric field. Study of dielectric characteristic of ceramic materials is most important among its all the electrical properties. The relative permittivity ($\varepsilon_r$) (the ratio of permittivity of dielectric material ($\varepsilon$) to the permittivity of free space ($\varepsilon_0$)) is a way to characterize the reduction in effective field between the plates of a capacitor because $\varepsilon$ of the polarization of the dielectric [197]. Ferroelectric behavior depends on external stress by temperature, electric field, frequency of applied field and ion substitution etc. and also on the intrinsic modifications like defects and domain configuration etc.. When an alternating field is applied to a sample the dipoles responsible for the polarization are no longer able to follow the oscillation of the electric field at certain frequencies. The field reversal and dipole orientation become out – of – phase, giving rise to energy dissipation. The loss factor ($\tan\delta$) is expressed as the ratio of imaginary part ($\varepsilon''$) to the real part ($\varepsilon'$) of the permittivity. Thus relative permittivity ($\varepsilon_r$), loss tangent ($\tan\delta$) and dielectric strength are some of the important characteristics of ferroelectric materials relevant to their suitability for different electronic applications. On application of alternating electric fields the polarization $P$ (the dipole moment per unit volume) varies periodically with time as well as electric displacement $D$.

In general, $P$ and $D$ may lag behind in phase relative to electric field $E$, so that;

$$D = D_0 \cos (\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t$$

Where $\delta$ is the phase angle and slightly less than 90°. $D_1 = D_0 \cos \delta$ and $D_2 = D_0 \sin \delta$.

The ratio of displacement vector to electric field ($D_0/E_0$) is generally frequency dependent. To describe the situation one may thus introduce two-frequency dependent dielectric constant: $\varepsilon'(\omega) = (D_0/E_0) \cos \delta$ and $\varepsilon''(\omega) = (D_0/E_0) \sin \delta$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are real and imaginary components of complex dielectric constant respectively.

These two constant can be expressed in term of single complex dielectric constants,$$
\varepsilon = \varepsilon' - j \varepsilon''$. The applied voltage (V) varies periodically with time as follows:
\[ V = V_0 e^{j\omega t}. \] The total current, \[ I = \frac{dQ}{dt} = \frac{d(CV)}{dt} = jC \omega V = jC_0 \omega V \]

where \( C \) and \( C_0 \) are the capacitance in the dielectric medium and vacuum, respectively. Therefore, \[ I = j \omega C_0 V (\varepsilon' - j \varepsilon'') = \omega \varepsilon'' C_0 V + j \omega \varepsilon' C_0 V = I_l + I_C \]

The dielectric or tangent loss is given by \( \tan \delta = \frac{\varepsilon''}{\varepsilon'} \). Here the total current \( I \) through the capacitor can be resolved into two components, a charging current \( (I_C) \) in quadrature with voltage and conduction current \( (I_c) \), in phase with the voltage. The vector resolution of current is shown in Figure 2.4. For a parallel plate capacitor with sinusoidal applied voltage, the charging current is given by \( I_C = \omega C_0 \varepsilon V \) and loss current \( I_l = \sigma V \), where \( \sigma = \omega \varepsilon_0 \varepsilon \tan \delta \) is the dielectric conductivity. The dielectric and impedance parameters are usually obtained as a function of temperature and frequency using the following experimental methods.

- RF method-lumped circuit method
- Microwave method (distributed circuit method)
- Impedance method
Generally bridge methods (impedance method), where impedance bridges like Schering bridge, transformer bridge, etc. are used in the frequency range of $10^{-2}$Hz to $10^7$Hz. In this method the impedance of the capacitor contacting the dielectric is balanced against a known combination of discrete resistances or inductances. PSM-1735, LCR 4NL impedance analyser having a touch panel and user friendly interface has been employed in the present investigation to find the dielectric and impedance parameters. The frequency can be freely adjusted with four digit precision in a white range (42Hz to 5 MHz). The instrument measures maximum of 14 test parameters such as L, C, R, Z, $\theta$ etc., out of which four parameters can be simultaneously displayed on the screen. In the present study C, Z (impedance), $\theta$ (phase) and tan$\delta$ were measured. However the rest of the parameters derived from these four quantities. This LCR meter can be set, not only in a floating voltage setting but also in a constant voltage setting or a constant current setting mode. A laboratory made sample holder (Figure 2.5(b)) was used in consumption with the impedance analyzer. The sample was heated above the room temperature with the help of a laboratory made furnace connected with a bariace. The temperature was controlled by a thermo-couple (chromel- alumel) connected with a dc micro voltmeter with accuracy of 0.01 mV (equivalent to accuracy in temp $\pm$ 0.25 kV). The readings were taken when the sample attend the steady temperature. The temperature interval of the measurement was

Figure 2.6 PSM-1735, LCR 4NL

Figure 2.7 Laboratory fabricated Sample holder
about 2-3 °C. The measurements were carried out in the frequency range of 1 kHz – 1MHz at different temperature. All the samples after electroding kept at 150°C for few hours before taking any electrical measurement to remove moisture from the sample, if any. During experiment silica gel was also used inside the sample holder to get rid of the moisture. The relative permittivity ($\varepsilon_r$) was calculated using the formula: $\varepsilon_r = C/C_0$ where C is the sample capacitance, $C_0 = \frac{\varepsilon_0 A}{l}$ is the geometrical capacitance of the sample ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, A is the flat faces of the sample and l is the thickness of the pellet).

2.6. Electrical Properties:
The electrical behavior of a multiferroic material needs to be properly analyzed to decide its suitability for multifunctional applications. Also the change in magnetic order in multiferroics with temperature considerably influences their overall dielectric response. Hence for proper assessment of the dielectric behavior of these materials, a distinction between the lattice and carrier response is very necessary. In order to study the polarizibility and / or structural phase transitions, two types of experimental techniques are needed; one sensitive to long range cooperative phenomena, the other sensitive to changes in the local order. Technique in the first category tends to have large interaction volume and highly sensitive to cemetery changes of crystal. One such technique is dielectric and impedance spectroscopy. The AC impedance measurement is widely used to characterize ferroelectric materials. The method mainly involves analyzing data in terms of different complex formalisms like complex impedance (Z), complex admittance (Y), complex electric modulus (M) etc...

They are interrelated to one another as follows

$$\varepsilon = \varepsilon' - j\varepsilon'', \ Z = Z' - jZ''', \ M = M' - jM''', \ Y = Y' - jY'''$$

$$M = j\omega C_0 Z, \ Z = \frac{1}{j\omega C_0 \varepsilon'}, \ M = \frac{1}{\varepsilon'} \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z''}{Z'} = \frac{Y''}{Y'}$$
Where $\epsilon'$, $Z'$, $M'$ and $Y'$ are the real parts and $\epsilon''$, $Z''$, $M''$ and $Y''$ are the imaginary parts of $\epsilon$, $Z$, $M$ and $Y$ respectively. $C_0$ is the geometrical capacitance of the cell, $\omega$ is the angular frequency and $j = \sqrt{-1}$. For proper data analysis both complex plane plots (real vs. imaginary part) & the spectroscopic plots (variation of both real & imaginary part with frequency) of these quantities are required. The graph between $Z'$ and $Z''$ is called Nyquist plot or impedance spectroscopy plot and the graph between $M'$ and $M''$ is called modulus spectroscopy plot. Complex impedance spectroscopy (CIS) is an experimental tool for the characterization of electrical properties of materials [198]. The technique is based on analyzing the ac response to a sinusoidal perturbation and subsequent calculation of the impedance as a function of the frequency of the perturbation. The technique enables us to evaluate and separate the contribution of the different electro active regions such as grain, grain boundary and electrode / material interface to the overall electrical response of a material. The impedance data can be represented in terms of a better diagram or in the form of real & imaginary components of a complex number in the complex plane as shown in Figure 2.6. The diagonal distance represents the magnitude of the impedance from center (origin) of the plane whereas the angel subtended with the abscissa (real axis) corresponds to the phase angle between the input voltage applied across the sample and the output current measure.
So, the impedance of the sample is known as the “Complex Impedance”. The display of impedance data in the complex plane plot appears in the form of a succession of semi circles attributed to relaxation phenomena with different time constants due to the contribution of grain (bulk, grain boundary and interface – polarization in poly crystalline material (Figure 2.7). Ideally the above electro active regions can be represented in terms of equivalent circuits’ representations by a series combination of parallel RC units (Figure 2.8).

![Diagram showing relationship between microstructure and electrical properties in complex impedance plane.](image)

**Figure 2.9** Relationship between microstructure and electrical properties in complex impedance plane

![Diagram showing an electrical equivalent circuit in complex impedance plane.](image)

**Figure 2.10** An electrical equivalent circuit in complex impedance plane.

The complex plane plots result in different semicircles, intercepting along X-axis (Z-axis) at different region as shown in Figure 2.7. The intercept of the first semicircle in the high frequency region is due to grains; the second one at intermediate frequency is due to grain boundaries and the third one in the low frequency region is due to that of electroding effect [199]. The resistance
of the material, obeying Arrhenious behavior is evaluated in terms of bulk resistance ($R_b$) and expressed as $\sigma = \sigma_0 \exp \left( \frac{-E_a}{RT} \right)$ where $\sigma_0 =$ Pre exponential factor, $E_a =$ Activation Energy, $K =$ Boltzmann Constant and $T =$ absolute temperature.

The peaks of the semicircles in the complex plane plot enable us to evaluate the relaxation frequency ($f_{\text{max}}$) of the bulk material in accordance with the relation $\omega_{\text{max}} \tau = \omega_{\text{max}} R_b C_b = 2\pi f_{\text{max}} R_b C_b = 1$

$$f_{\text{max}} = \frac{1}{2\pi R_b C_b} \text{ and } \tau = \frac{1}{2\pi f_{\text{max}}}$$

Where $R_b =$ Bulk resistance, $C_b =$ Bulk capacitance and $\tau =$ relaxation time. The impedance data also enable us to obtain the information on relaxation dipoles in the material (dielectric relaxation spectroscopy) in terms of the real and the imaginary parts of the complex dielectric constant $\varepsilon^* = \varepsilon' - j \varepsilon''$ through the relation

$$\varepsilon' = -\frac{Z''}{\omega C_0 (Z'' + Z''')} \text{ and } \varepsilon'' = -\frac{Z'}{\omega C_0 (Z'' + Z''')}$$

The real and imaginary parts of complex electric modulus represented as $M' = \omega C_0 Z''$ and $M'' = \omega C_0 Z'$. The impedance spectroscopy combined with modulus spectroscopy gives more information about the electrical behaviour of the better picture of electrical micro structure [200]. The plots of impedance spectroscopy and the corresponding equivalent circuit shown in Figures 2.7 and 2.8 respectively represent the ideal Debye – type behaviour. However in practice appreciable distortion of the semi-circular shape of Nyquist plots are observed. So the equivalent circuits need to be modified for better fitting for experimental data.

Also the study of variation of both dc and ac conductivity with respect to frequency & temperature helps in investigating the detail conductivity phenomena (both localised & non localised), types of conducting species and their influence on ferroelectric properties of these multiferroic materials. When a sinusoidal voltage is applied to a parallel plate capacitor the charging current is given by $I_C = j \omega C_0 \varepsilon V$ and loss current $I_l = \omega C_0 \varepsilon V = \sigma_{ac} V$, where $\sigma_{ac} = \omega \varepsilon_0 \tan \delta = \sigma_0 \exp \left( \frac{-E_a}{KT} \right)$ is the ac conductivity of the dielectric material in the capacitor. The effective conductivity defined in this manner depends upon frequency and is always greater than DC conductivity. In the present study the ac conductivity was calculated using the formula $\sigma_{ac} = \omega \varepsilon_0 \tan \delta$ and the dc conductivity was calculated using the formula $\sigma_{dc} = \frac{l}{R_b A}$ where $R_b =$ the
bulk resistance obtained from complex impedance plot, \( l = \) the sample thickness and \( A = \) area of electrode on the sample surface [201].

2.7 Polarization Study:

![High-Voltage Test Fixture (HVTF)](image)

**Figure 2.11 (a):** High voltage test fixture

**Figure 2.11 (b):** High Temperature Test Fixture (Sample Holder)

**Figure 2.11 (c):** High voltage
The polarization (the electric dipole moment per unit volume) can be obtained from hysteresis loop parameters [10]. All the samples in the present study were poled at an optimized electric field for 24h using a dc electric field of 5kV/cm in a silicon oil bath at room temperature using APLAB high voltage dc power supply (model 7342P). Poling is a process wherein a large electric field is applied to a randomly oriented virgin ceramic to endow it with a remnant polarization through domain switching. The hysteresis loops were obtained on the poled samples using precision workstation (M/S. Radiant Technologies Inc., USA). This workstation has two test fixtures.

(a) Radiant high voltage test fixture (HVTF) and (b) Radiant high temperature text fixtures (HTTF). The Radiant high voltage test fixture (HVTF) provides a stable and convenient platform for measurements of hysteresis loop parameters ceramic capacitors. Both HVTF and HTTF fixtures are shown in Figure 2.13 (a) and (b) respectively.

The HVTF is constructed of thick teflon to provide excellent safety protection for the researcher even up to voltages as high as 10KV. High temperature test fixture (HTTF) is used for testing of bulk ceramic capacitors at temperatures up to 520°C and 3000 Volts in a muffle furnace or tube furnace. The fixture is constructed to allow easy loading of the sample but to also prevent stress cracking in the fixture at high temperatures. The test fixture is constructed of MACOR, a dow-corning machinable glass ceramic. The bottom electrode plate and the top electrode gravity contact are constructed from Nickel 200, a high temperature electrical conductor. Nickel 200 has a melting point of 1435°C. The electrical attachment hardware is constructed of 14-4 stainless steel. The high temperature test fixture is constructed of a glass ceramic. The fixture consists of five parts: (i) The base, (ii) The bottom electrode plate, (iii) The top electrode probe, (iv) the bridge, (v) Cable attachment points. The top electrode contact bridge is designed to sit in slots in the fixture base with no mechanical attachment points. This prevents stress build-up due to expansion of the bridge and base during changes in temperature. The bottom electrode plate sits in a well in the fixture base. The sample rests on the plate. The bridge guides the top electrode probe so that it rests directly on the top contact of the sample during testing. The top and bottom electrode contacts are connected to the cable attach points using ring terminals. The cables also end with ring terminals. The cables (Figure 2.13(c)) consist of 20KV spark igniter cable from thermal wire and Cable Corporation.