3.1 SYNTHESIS OF BNBT AND Zr, Sn, Nb,(Mg & Nb)MODIFIED BNBT CERAMICS

3.1.1 Powder Preparation

The various steps involved in solid-state synthesis process are shown in the flow chart (Figure 3.1). Required quantities as per stoichiometry were weighed and dry mixed followed by wet mixing with organic solvent as medium. The mixing is accomplished using an agate mortar and pestle. The amount of organic solvent used is just enough to form slurry to prevent the selective sedimentation of the reagents. After proper mixing, with ground mixtures are calcined at the required temperature range for certain period of time using a programmable furnace. During the process of calcination, solid state reaction takes place between the constituents of the mixture giving the required phase. The calcination temperature should be carefully chosen as it affects the density and hence the electromechanical properties of the final product. The higher the calcining temperature, the better the homogeneity and density of the final ceramic product. Proper calcination at the right temperature gives the best electrical and mechanical properties [101]. For the present study samples of four systems (1-4) given below have been prepared by solid state method.

1. \((\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06} (\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3 \) (BNBTZx) with \(x = 0\%, 4\%, 8\%, 10\% \text{ & } 20\%

2. \((\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06} (\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3 \) (BNBTSx) with \(x = 0\%, 0.5\%, 1.5\%, 3\%, 15\%

3. \((\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06} (\text{Ti}_{1.5x/4}\text{Nb}_x)\text{O}_3 \) (BNBNTNx) with \(x = 0\%, 0.3\%, 1.2\%, 5\%, 10\%

4. \((\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}(\text{Ti}_{1-x}((\text{Mg}_{1/3}\text{Nb}_{2/3})_x)\text{O}_3 \) (BNBT(MN)x) with \(x = 0\%, 1\%, 5\%, 15\%, 20\%, \) Where \(x\) refers to the mol\% of the additive added to BNBT.
Figure 3.1 Flow chart describing various steps involved in solid in synthesis and characterization of pure and modified BNBT.
The reagents used for the preparation of the materials are listed in Table 3.1. Weighed powders as per stoichiometry were mixed well in ethanol medium in an agate mortar and ground for more than six hours to get homogenized powders. An extra amount of 3 wt% Bi₂O₃ and Na₂CO₃ were added to the initial mixture to compensate for the respective losses of bismuth and sodium at high temperature. The resultant well ground mixture was calcined in the temperature range of 850°C-900°C for 2-3hrs in programmable furnace with 10°C per minute heating and cooling rate. Typical heating and cooling profile used is shown in the figure 3.2.

Table 3.1: Reagents used for synthesis of BNBT and modified BNBT-based materials.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth (III)Oxide</td>
<td>Bi₂O₃</td>
<td>99.9%</td>
<td>High Media</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Na₂CO₃</td>
<td>99.5%</td>
<td>Wako</td>
</tr>
<tr>
<td>Barium Carbonate</td>
<td>BaCO₃</td>
<td>99.9%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Titanium (IV)Oxide</td>
<td>TiO₂</td>
<td>99.5%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>MgO</td>
<td>99.9%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Niobium (V)Oxide</td>
<td>Nb₂O₅</td>
<td>99.9%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Zirconium(IV)Oxide</td>
<td>ZrO₂</td>
<td>99.9%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Tin(IV)Oxide</td>
<td>SnO₂</td>
<td>99.9%</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
3.1.2 Sintering

Sintering is a processing technique used to produce dense materials and components from metal or and ceramic powders by applying thermal energy [102]. For the systems under investigation after the phase formation, the calcined powders were again mixed and ground with 1 wt% aqueous poly vinyl alcohol (PVA) solution which acts as a binder amongst the granules of the powders. The green compacts with a diameter of about 12 mm and thickness of 1mm were pressed using uniaxial stress of 6MPa with the help of tungsten carbide dye. The pellets were taken on a platinum foil and covered by platinum crucible to minimize evaporation of materials and sintered at 1150°C for 2hrs in a programmable furnace at 5°C per minute heating and cooling rate with an intermediate
soak time 1hr at 500°C for organic binder removal in the initial heat treatment as illustrated on Fig.3.3.

Figure 3.3. Typical heating profile used for sintering the pellets.

3.1.3 Electroding

Electroding is the process of formation of a layer of metallic conductor i.e. silver paste on the surface of the sintered pellets. The conductor adheres very strongly to the ceramic. The coated pellets are then heated at 600°C for 1hr to form a continuous conducting layer intimately bonded to the ceramic surface. The elecroding heating profile for the present work is indicated in the figure 3.4. Figure 3.5 Shows the pictre of pellets at different process stages.
Figure 3.4 firing profile used to electrode the pellets.
Figure 3.5 Picture of pellets at different processing stages: (a) green body (b and c) polished sintered pellets of different dopant (d) metal coated pellet.
3.2 CHARACTERIZATION METHODS

3.2.1 Powder X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) technique is a powerful tool for material characterization as well as for detailed structural elucidation. For the present work XRD data have been taken on the calcined powders with x-ray diffractometer (PANalytical- X’ Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K\textsubscript{α} radiation (\(\lambda = 1.54059 \, \text{Å}\)), over the range of Bragg angles (10° \(\leq 2\theta \leq 80°\)) with a scanning speed of 2° min\(^{-1}\). The instrument was run at power settings of 40 KV and 40 mA and the powder samples were mounted into a top loaded circular sample holder to be rotated in the instrument at 50 rpm.

3.2.2 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) is a useful technique to study the topography, morphology and composition of the materials with much higher resolution. In this work the microstructural investigations of the sintered ceramic samples were made on the fractured surface of the sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan) after a thin layer of gold was coated by using Auto Fine Coater (JFC-1600) for 90 second. Energy Dispersive X-ray Spectroscopy (EDS) with conjunction of SEM was used to characterize the elemental composition of the analyzed volume.
3.2.3 Differential Scanning Calorimetry (DSC)

Measurement of physical and chemical properties of the materials as a function of temperature is called the thermal analysis. Measurements have been performed using METTLER TOLEDO, DSC 823e instrument. The instrument was calibrated by using pure indium for low temperature and pure zinc for higher temperature. 10mg of calcined powder samples were taken in the 40µl aluminum crucible. The crucible was capped and sealed after making a hole on the cap for the removal of evolved gas before it was placed in DSC furnace. A similar 40µl sealed empty crucible was used as a reference. The experiment was conducted in air atmosphere at a flow rate of 40ml/min with a heating rate of 10°C within the temperature range of 30-600°C.

![DSC Profile](image)

Figure 3.6 Heating Profile used for Differential Scanning Calorimeter Measurements.
3.2.4 Dielectric Measurements

The dielectric properties of ferroelectrics depend on the field strength at which it is measured. It is a consequence of non-linear relation between polarization and electric field. For ferroelectric materials, the dielectric constant increases up to the transition temperature and after that it obeys the Curie-Weiss law. For the present work to study the electrical properties of the materials Phase Sensitive LCR Multimeter was used. Phase sensitive multi meter is a new generation of versatile measurement instruments that can be used to measure different electrical properties. It is interfaced with programmable furnace to supply heat on the material at different temperatures and equipped with a computer for data acquisition. A sample holder has been specially designed for electrical measurement with an attachment of thermocouple for temperature measurement. The silver electroded samples were kept in a sample holder so that it works as a capacitor. For temperature variable electrical measurement the sample holder containing sample was then kept inside furnace and a variac voltage regulator was used to control the current to the heating coil for uniform and the slow heating environment. The temperature inside the sample holder was measured by measuring the current of the thermocouple using a milli-voltmeter and converting that current to temperature. Measurement of capacitance (C), loss tangent (tanδ), complex impedance (z*), resistance (R), phase angle (ϕ), quality factor (Q) and inductance (L) at variable temperature up to 400°C in the frequency range of 100 Hz - 1 MHz were taken in parallel and series with phase sensitive multi meter (N4L PSM 1700) Japan, with
heating rate of 3°C/min as depicted on Fig.3.7. The dielectric constant is calculated using an empirical formula: $\varepsilon' = \frac{C_p}{C_o}$ where $C_p$ is the parallel and $C_o$ is air capacitance.

![Dielectric Measurement Profile](image)

Figure 3.7: Heating profile used for dielectric measurements.

3.2.5 Impedance Studies

The complex impedance spectroscopy (CIS) is a non-destructive method, used to analyze the electrical response of polycrystalline sample in a wide range of frequencies and temperatures [8]. Complex impedance formalism offers wide scope for a graphical analysis of the various parameters under different conditions of temperature and frequency. The CIS technique easily separates bulk (grain), grain boundary, and material electrode contributions in the electrical properties of the materials. In CIS a constant current signal ($I$) of variable frequency is applied to the object under test (OUT) and the
potentials (V) developed across the OUT are measured at each frequency. The complex impedance is estimated by dividing the voltage measured with the applied current. The complex impedance ($Z^*$) is a function of material properties which create a phase difference ($\Phi$) between I and V [9]. AC measurements were often made with LCR meter (N4L PSM 1700, Japan) in which the complex impedance $Z^*$ and the phase difference ($\Phi$) 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.

$$Z^* = Z' - jZ'' = R / 1+j\omega RC$$

After simplification, one gets which represents the equation of a circle with radius R/2 and center at (R/2, 0). Thus, a plot of $Z'$ vs. $Z''$ (as parametric function of) will result in a semicircle of radius R/2 as shown in Figure 3.8 (a) and the equivalent circuit is shown in Figure 3.8 (b). (This plot is often called a Cole – Cole (or 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 behavior and a spike at the lowest frequency corresponds to the electrode effect. Figure 3.9 (a) shows a typical impedance plot for a polycrystalline sample and Figure 3.9(b) represented the equivalent circuit [103].

**Figure 3.8(a)** The impedance plot for a circuit of a resistor and a capacitor in parallel and (b) the corresponding equivalent circuit.

**Figure 3.9 (a)** The impedance plot for an ideal polycrystalline sample and (b) the corresponding equivalent circuit.
3.2.6 Piezoelectric coefficient (\(d_{33}\))

For this work sintered samples were pollied to align the domains of a piezoelectric material by applying a dc electric field of 30-40kV/mm for 20-30 minutes in silicone oil bath at different temperature and then aged for 24hr. The piezoelectric constant \(d_{33}\) measurements were taken with \(d_{33}\) meter (KCF d33 Meter PM3001) Japan at the frequency of 100Hz.

3.2.7 Conductivity

Many dielectrics possess conductivity due to motion of charges and such conductivity is usually expressed by volume conductivity. The motion of charges in the dielectric gives rise to the conduction current and additionally polarizes the dielectric [104]. The conductivity may therefore be contributes to the dielectric loss.

AC conductivity was determined from dielectric constant and dielectric loss measurements for pure & modified BNBT pellets carried out using LCR Multimeter as point out in section 3.2.4. The dielectric constant \((\varepsilon)\) was calculated from measured capacitance \((C)\) using the relation:

\[
\varepsilon = \frac{Cd}{\varepsilon_A}
\]

where \(d\) is the thickness, \(\varepsilon_\infty\) is the permittivity in the vacuum and \(A\) is the area of cross-section of the sample. Then the ac conductivity \((\sigma_{\omega\omega})\) was calculated using the relation by (Kingery, 1976)[105]:

\[
\sigma_{\omega\omega} = \varepsilon_\infty \varepsilon_i \omega \tan \delta
\]
Josher has suggested the conductivity as a function of frequency in a large number of materials follows a relation as:

\[ \sigma = \sigma_0 + A \omega^n \]

The value of “n” varies between 0 - 1. The variation in “n” is associated with displacement of carriers which move within the sample by discrete hops between randomly distributed localized sites. The term \(A \omega^n\) can often be explained on the basis of two distinct mechanisms for carrier conduction:

(i) Quantum mechanical tunneling (QMT) through the barrier separating the localized sites.

(ii) Correlated barrier hopping (CBH) over the same barrier.

D.C. conductivity is a thermally activated quantity and it obeys the Arrhenius behavior.

\[ \sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \]

where, \(\sigma_0\) is a preexponential factor, \(E_a\) is the activation energy, \(R\) is the Boltzmann constant, and \(T\) is the absolute temperature. At low frequency conductivity is dominated by dc conductivity. The electrical conductivity transforms from frequency independent dc conductivity to frequency dependent ac conductivity upon increasing the frequency. The frequency at which this transition occurs is called as hopping frequency \(\omega_p\) which follows the relation:

\[ \sigma(\omega) = k \omega_p \left[ 1 + \left(\frac{\omega}{\omega_p}\right)^2 \right]^{\frac{1}{2}} \]
For DC conductivity the resistance of the pellets was measured by two probe technique using a Keithley 617 electrometer in the V/I mode, over a temperature range from 30°C to 400°C. To measure the resistance, 25V DC is applied (for a short interval to avoid possible polarization effects) from the constant voltage source provided in the electrometer and the resistance is read from the electrometer. The observations were repeated for different pellets. The dc conductivity of the pellets of pure and modified BNBT were calculated knowing the dimensions of the pellet and their respective resistances.
4.1 EFFECT OF ZIRCONIUM SUBSTITUTION ON THE ELECTRICAL PROPERTIES OF FERROELECTRIC (Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$Ba$_{0.06}$TiO$_3$ CERAMICS

4.1.1 Phase Identification and lattice Parameters

XRD patterns of pure and zirconium substituted BNBTZ$_x$ powders for $x = 0.0, 0.04, 0.08, 0.10$ and $0.20$ calcined at $850^\circ$C for 2hrs are shown in Fig.4.1. From the XRD pattern it is evident that the rhombohedral phase (indicated by the peaks at $22.7, 32.4, 46.4, 57.7$ and $67.67^\circ$) has been already formed. All the observed peaks could be indexed as shown in the figure4.1. All the XRD patterns of BNBTZ$_x$ compositions for $0 \leq x < 0.1$ are in good agreement with that of rhombohedral Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (JCPDS file number 36-0340). There is a small extra peak near to $2\theta \sim 28^\circ$ for BNBTZ$_{10}$ and one more extra peak around $2\theta \sim 32^\circ$ for the higher Zr dopant BNBTZ$_{20}$. Even at slightly higher calcination temperature of about $950^\circ$C, these extra peaks still remained in the XRD pattern. The presence of extra peaks at $2\theta = 28^\circ$ and $32^\circ$ in the composition range of $0.1 \leq x \leq 0.2$ are due to the presence of monoclinic ZrO$_2$ (JCPDS file number: 89-9066), which means the maximum limits for Zr$^{4+}$ to enter the crystal lattice of BNBT is between 0.08 and 0.10. The unit cell parameters, $a$, $\alpha$, volume, density and others were calculated for the new compositions characterized with the PANalytical’sX’Pert PRO XRD scans and equation 4.1 from (B.D. Cullity 2001)[106] are given in table 4.1.
Figure 4.1 X-Ray Diffraction patterns of BNBTZx ceramic samples sintered at 1150°C for 2 hrs with x = 0.0, 0.04, 0.08, 0.1 and 0.20.

\[
\frac{1}{d^2} = \frac{(h^2+k^2+l^2) \sin^2 \alpha + 2(hk+kl+hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1-3\cos^2 \alpha + 2\cos^3 \alpha)} \quad \ldots \quad 4.1
\]

where \(d\) is the lattice plane spacing, \(h, k,\) and \(l\) represent the Miller indices of the plane, \(a\) is the edge of the unit cell, and \(\alpha\) is the angle. The volume of the unit cell was calculated using Equation 4.2 from B.D. Cullity (2001):
X-ray densities were calculated using the relation

\[ \rho = \frac{\sum A}{N} \]

\[ = \frac{1.66042 \sum A}{V} \]

Where \( \rho \) is x-ray density (g/cc), \( \sum A \) : sum of all the atomic weights of the atoms in the unit cell, \( N \); Avogadro’s number, \( V \); volume of the unit cell.

Table 4.1. Lattice parameters and related properties of BNBTZx (\( x = 0.0, 0.04, 0.08 \) & 0.10).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>( a(\text{Å}) )</th>
<th>( \alpha (^\circ) )</th>
<th>Crystallite size (nm)</th>
<th>Micro-strain ( \epsilon(\times10^{-3}) )</th>
<th>Experimental ( \rho(\text{g/cc}) )</th>
<th>%( (\rho) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNBT</td>
<td>3.899</td>
<td>89.79</td>
<td>44</td>
<td>1.6</td>
<td>5.67</td>
<td>94%</td>
</tr>
<tr>
<td>BNBTZ4</td>
<td>3.893</td>
<td>90.03</td>
<td>49</td>
<td>2.2</td>
<td>5.73</td>
<td>95%</td>
</tr>
<tr>
<td>BNBTZ8</td>
<td>3.901</td>
<td>90.01</td>
<td>54</td>
<td>2.6</td>
<td>5.63</td>
<td>93%</td>
</tr>
<tr>
<td>BNBTZ10</td>
<td>3.933</td>
<td>89.96</td>
<td>78</td>
<td>2.9</td>
<td>5.71</td>
<td>96%</td>
</tr>
</tbody>
</table>

The crystallite size and micro-strain of BNBTZx ceramics were estimated by analyzing the x-ray diffraction peak broadening, using the Williamson–Hall approach. Figure 4.2
Shows the plot of $\beta \cos \theta$ on the y-axis in radians and $4 \sin \theta$ on the x axis for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$ composition, where $\beta$ is the difference in integral breadth between a standard ($\beta_{\text{std}}$) and experimental ($\beta_{\text{obs}}$) and $\theta$ is the Bragg angle. The slope of this straight line will be the strain ($\eta$), and the intercept is $k\lambda/L$, from which the crystallite size (L) can be estimated where $\lambda = 1.54059\text{Å}$ and Scherer constant ($k$) = 0.94. The crystallite size increased with increased zirconium doping level, from 44.2 nm for pure BNBT sample to 78.1 nm for BNBT doped with 10% Zr. Simultaneously, the micro-strain increased from 0.16% for pure sample to 0.23% for 10% Zr. The increase of lattice cell constant, crystallite size and lattice strain of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramic samples in the studied range of $0 < x \leq 0.1$ may be due to the replacement of small ionic radii Ti$^{4+}$ (0.62Å) by large ionic radii of Zr (0.72Å) as reported by (Suchanicz et al., 2010)[107].

Figure 4.2 Williamson-Hall plot of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}(\text{Ti}_{0.92}\text{Zr}_{0.08})\text{O}_3$. 

$$\eta = 2.6 \times 10^{-3}$$

**linear fit**