Structural and Dielectric Properties of Ba-Doped BNT Ceramics

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Abstract:
In this study, lead-free Ba-doped ((Bi₁₀₃)Na₀₅)TiO₃ ceramics were synthesized by the conventional solid-state reaction method and characterized by X-ray diffraction technique, which indicates the pure crystalline nature of ceramics with ABO₃ symmetry. The splitting in the peaks reveals that the ceramics with x = 0.10 and 0.30 are well in Morphotropic Phase Boundary where rhombohedral and tetragonal phases co-exist. The scanning electron microscope images show that the average grain size of the ceramics increases with an increase in the Ba concentration. Dielectric properties of pure and Ba-doped ((Bi₁₀₃)Na₀₅)TiO₃ ceramics measured by LCR meter in the frequency range of 1 k Hz – 1 M Hz shows the decrease in the value of dielectric constant with an increase in frequency. ε_max = 5563 was obtained at x = 0.30 with T_C = 300 °C at the frequency of 1 k Hz, whereas σ (f) curves were found to be merging at a high value of frequency and temperature regions.

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1. INTRODUCTION

In the 20th century, Pb-based ceramics have ruled the industries in the field of piezoelectric actuators, sensors, and transducers owing to their excellent piezoelectric, and ferroelectric properties. But up to the end of the 20th century, Pb imposes strong threats to the environment and human life. Therefore, there is a need to develop lead-free ceramics having high piezoelectric properties as those responses lead-based possess significant economic and social values. So, over the numerous experiments, scientists able to find several alternatives (i.e. lead-free piezoelectric ceramics) to Pb like (Bi_{0.5}Na_{0.5})TiO_{3} (BNT), (Bi_{0.5}K_{0.5})TiO_{3} (BKT), (K_{0.5}Na_{0.5})NbO_{3} (KNN), etc [1, 2].

Ferroelectric Bismuth sodium titanate (BNT) was discovered by Smolenski et al. [3] in 1959 and has been most extensively studied. Ferroelectric materials of the perovskite family (i.e. ABO_{3}-type) have received great attention from the last few decades due to their promising potential for various device applications like piezoelectric transducers, pyroelectric sensors/detectors, electrostrictive actuators, multilayer capacitors (MLCCs), etc [4-6]. BNT ceramics have unique superiority because Bi^{3+} has a similar electronic structure (long pairs 6s^{2} electrons) with Pb^{2+}. This 6s^{2} pair of electrons leads to the high polarizable nature of BNT, which makes it potential application in actuators [7, 8].

BNT is also an A-site complex perovskite ferroelectric relaxor material and is recognized due to its high Curie temperature T_{C} = 320 °C. Pure BNT ceramics has a large coercive field E_{C} = 73 kV cm^{-1} at room temperature as well as a phase transition from rhombohedral to tetragonal below Curie temperature [9]. A lot of BNT based ceramics have been reported for their high-temperature dielectric behavior [10-12]. As BNT contains Bi, Na ions, these are highly volatile at higher temperatures and most difficult to pole due to their high ion conductivity. High conductivity is due small loss of Bi_{2}O_{3} amount during the ceramics synthesis and processing of BNT ceramics at high temperatures [13-15]. This problem was later overcome by using 10-15% excess amount of Bi_{2}O_{3} and Na_{2}CO_{3} during its processing. But an extremely small amount of oxygen vacancy (i.e. about 0.005~0.0025) were resulting in high oxide conductivity which implies that the mobility of oxygen ions in BNT is very high [16]. The structural, dielectric, and electrical properties of BNT ceramics have been improved and enhanced by the substitution of dopants on A and B-site cations, such as Li, Al, La, Ta, Nb, Mg, Zr, Hf, etc [17-20]. In 1993, Takenaka et al. [21] reported that BNBNT6 ceramics with MPB (Morphotrophic Phase Boundary), have relatively good piezoelectric properties [22]. Ba doped BNT also shows MPB with x = 0.10 as reported by Yadav [23] with relaxor-like behavior.

Pure BNT ceramics are restricted to various applications due to some of their shortcomings in properties like low dielectric constant, exhibiting weak piezoelectricity high conductivity at room temperature, and having a narrow sintering temperature range. These ceramics are also difficult to pole and sinter [23-25]. Therefore, to overcome these problems, Ba is doped on A-site in BNT and a modified solid-state method is used to synthesize BNT ceramics (i.e. used hot distilled water in place of ethanol) with the existence of MPB. In this report, we have synthesized pure and Ba-doped BNT ceramics using the conventional solid-state reaction method. Investigated their structure via X-ray diffraction (XRD), scanning electron microscope, and dielectric properties by an LCR meter.

2. MATERIALS AND METHODS

2.1. Raw Materials

The metal oxide and carbonates (high purity > 99%, Sigma Aldrich, India) Bismuth Oxide (Bi_{2}O_{3}), Sodium Carbonate (Na_{2}CO_{3}), Titanium Dioxide (TiO_{2}), Barium Carbonate (BaCO_{3}) were used as raw materials.

2.2. Experimental Procedure

The pure and Ba-doped (Bi_{0.5}Na_{0.5})TiO_{3} ceramics were prepared by conventional solid-state reaction. These raw materials were weighed according to their stoichiometric ratio (as given in Table 1) and milled continuously using an agate mortar and pestle in the hot distilled water medium for 10-12 h. Then calcined at 900 °C for 5hrs. The calcined powder was ground and converted into green pellets (having 10 mm diameter and 2 mm thickness) by a hydraulic press under a pressure of 70 MPa (using 10% PVA solution as the binder). These green pellets were finally sintered in an alumina crucible containing Na_{2}CO_{3}, Bi_{2}O_{3} powders to suppress the volatility of Na, Bi at 1100 °C for 3 hrs.

2.3. Measurements

The X-ray diffraction (XRD) pattern of these ceramic composites was done using an X-ray diffractometer (Rigaku Miniflex II Desktop, Japan) in the 2θ range 20°...
to 60° (with step size $\Delta \theta = 0.02^\circ$). Surface morphology was measured by Scanning electron microscopy (SEM) JEOL (JAPAN) JSM 6100. The polished surfaces of the sintered samples were electrodes with air-drying silver paste. Dielectric properties were done by using an LCR meter from 1 kHz to 1 MHz at different temperatures (RT-400°C).

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD)

Figure 1 shows the X-ray diffraction (XRD) patterns of ((Bi(0.5-x)Ba_x)Na_0.5)TiO_3 (abbreviated as BBNT) with an increase in Ba content at room temperature. However, the spectrum of BBNT ceramics exhibits well-defined diffraction peaks at $2\theta$ of 22.90, 32.62, 40.20, 46.75, 52.70 and 58.21 corresponding to (100), (110), (111), (200), (210) and (211) planes [26, 27]. It also confirmed that BNT at $x = 0.00$ has a rhombohedral structure with the space group R3c. With an increase of Ba$^{2+}$ content, the diffraction peak shifts towards the lower angle $2\theta$. This peak shift indicates the increase in the volume of the unit cell because of the replacement of smaller ionic radii of Bi$^{3+}$ (~1.17 Å) with larger ionic radii Ba$^{2+}$ (1.39 Å). Also, the Ba$^{2+}$ substituted BNT $x = 0.30$ shows the peaks (002) and (200) are merging into a single peak as shown in Figure 1b. This may be due to the equal contribution of phases at this composition.

Rietveld refinement of the XRD pattern was done to further confirm the crystal structure and the lattice parameters (as shown in Figure 2). Rietveld refinement also confirms that BBNT with $x = 0.00$ has rhombohedral, whereas BBNT for $x \geq 0.10$ exhibits the morphotropic phase boundary (MPB) where the rhombohedral and tetragonal structure co-exists [28]. The various Rietveld refined parameters are listed in Table 2. The single-phase nature of BBNT ceramics is evident without a trace of any impurity phase. Thus, the sharp and clear peaks strongly confirm the pure crystalline nature of ceramics.

Figure 3 shows the fitting of the XRD peaks for (200), (210), and (211) planes of ((Bi(0.4)Ba0.10)Na_0.5)TiO_3 ceramic fitted to the Gauss function. The coefficient $R^2$, interpreted as the best fit of a regression, determines the fitting of the peaks to the Gaussian function, which is closer to unity than other functions. But when $R^2$, is close to unity then the regression line fits the data well but if, close to zero then it is called a poor fit [29]. The

![Table 1: Mass Percentage of Raw Materials Used for ((Bi(0.5-x)Ba_x)Na_0.5)TiO_3 Ceramics](image)

| Composition (x) | Bi$_2$O$_3$ | BaCO$_3$ | Na$_2$CO$_3$ | TiO$_2$ | Total |
|-----------------|------------|----------|--------------|--------|-------|
| 0.00            | 52.274 %   | -------- | 11.890 %     | 35.836 % | 100   |
| 0.10            | 42.888 %   | 08.162 % | 12.195 %     | 36.755 % | 100   |
| 0.30            | 21.962 %   | 27.904 % | 12.490 %     | 37.644 % | 100   |

![Figure 1: (a) XRD pattern of ((Bi(0.5-x)Ba_x)Na_0.5)TiO_3 (where 0.00 ≤ x ≤ 0.30) ceramics and (b) the enlarged view of (200) peak.](image)
Figure 2: (a-c) Rietveld refinement of \((\text{Bi}_{0.5-x}\text{Ba}_x\text{Na}_0.5)\text{TiO}_3\) for \(x = 0.00, 0.10,\) and 0.30 ceramics.

Table 2: FullPROF Based Rietveld Refined Lattice Parameters and Atomic Positions of \((\text{Bi}_{0.5-x}\text{Ba}_x\text{Na}_0.5)\text{TiO}_3\) Ceramics

| \(x\)   | \(\text{Space group}\) | \(\text{R3c}\) | \(\text{P4bm}\) | \(\text{R3c}\) | \(\text{P4bm}\) |
|--------|------------------------|----------------|----------------|----------------|----------------|
|        | \(a = b\) (Å) | 5.48870 | 5.49830 | 5.52660 | 5.49830 | 5.52660 |
|        | \(c\) (Å)     | 13.50480 | 13.43430 | 3.98200 | 13.43430 | 3.98200 |
| \(x = 0.00\) | \(\text{Bi}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{Ba}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{Na}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{Ti}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{O}\) | 0.12600 | 0.14283 | 0.27375 | 0.14283 | 0.27375 |
| \(x = 0.10\) | \(\text{Bi}\) | 0.00000 | 0.00000 | 0.50000 | 0.00000 | 0.50000 |
|        | \(\text{Ba}\) | 0.00000 | 0.00000 | 0.50000 | 0.00000 | 0.50000 |
|        | \(\text{Na}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{Ti}\) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
|        | \(\text{O}\) | 0.33600 | 0.33691 | 0.22625 | 0.33691 | 0.22625 |
| \(x = 0.30\) | \(\text{Bi}\) | 0.26270 | 0.26227 | 0.52106 | 0.26227 | 0.52106 |
|        | \(\text{Ba}\) | 0.26270 | 0.26227 | 0.52106 | 0.26227 | 0.52106 |
|        | \(\text{Na}\) | 0.26270 | 0.26227 | 0.52106 | 0.26227 | 0.52106 |
|        | \(\text{Ti}\) | 0.00630 | 0.01411 | 0.03091 | 0.01411 | 0.03091 |
|        | \(\text{O}\) | 0.83300 | 0.08401 | 0.03179 | 0.08401 | 0.03179 |
| GOF (\(\chi^2\)) | 1.954 (3) | 1.585 (5) | 1.694 (1) |
Figure 3: Shows the XRD peaks for 110, 111 and 200 peaks fitted to Gaussian function for (Bi_{0.5}Na_{0.5})TiO_{3} ceramic.

Table 3: Details of the Parameters Used to Calculate the Strain of ((Bi_{0.4}Ba_{0.1})Na_{0.5})TiO_{3} Ceramic

| Plane | 2θ  | Sinθ   | Cosθ   | FWHM_{obs.} (degree) | FWHM_{inst.} (degree) | FWHM_{tot.} (degree) | FWHM_{tot.} (radian) | FWHM_{tot. cosθ} |
|-------|-----|--------|--------|----------------------|----------------------|----------------------|----------------------|-------------------|
| 110   | 32.59541 | 0.28063 | 0.95982 | 0.27868 | 0.23669 | 0.14711 | 0.00257 | 0.00246 |
| 111   | 40.1755  | 0.34346 | 0.93917 | 0.36652 | 0.3113  | 0.19347 | 0.00337 | 0.00317 |
| 200   | 46.7396  | 0.39666 | 0.91796 | 0.35219 | 0.29913 | 0.1859  | 0.00324 | 0.00298 |

FWHM_{obs} values of the peaks measured from the fitted peaks are given in Table 3.

The reflection of the 2θ value of the XRD data is used to compute the average crystalline size of all samples from the Debye Scherrer equation which is as follows [30]

$$ t = \frac{k\lambda}{\beta \cos \theta} $$

Where, $t$ is the average crystallite size, $k = 0.89$ is the Scherrer constant, $\lambda = 1.5406$ Å is the wavelength of the X-ray beam and $\beta$ is the full-width half. However, the Scherrer formula does not give an accurate size because it does not account for the lattice strain.

Thus, to calculate the accurate crystallite size Williamson’s-Hall plots was constructed as shown in Figure 4a-c for ((Bi_{0.5-x}Ba_{x})Na_{0.5})TiO_{3} (where 0.00 ≤ x ≤ 0.30) ceramics. The Williamson’s hall is used for deconvoluting shapes (crystalline shapes) and strain that contributes to X-ray line broadening because Scherrer’s formula does not take the strain contribution into the account.

The small crystallite size ($\beta_{siz}$) and the broadening caused by the lattice strain ($\beta_{strain}$) together gives the X-ray line broadening ($\beta$) in the sample i.e. [30-32]

Total broadening = Broadening due to crystallite size + Broadening due to strain

$$ \beta = \beta_{siz} + \beta_{strain} $$

Where, $\beta_{siz}$ again the Debye Scherrer equation:

$$ \beta_{siz} = \frac{k\lambda}{t \cos \theta} $$

And also,

$$ \beta_{strain} = 4 \eta \tan \theta $$

Here, $\eta = \Delta l/ l$ is the strain and $\theta$ is the peak position in radians.
So, putting the values of \( \beta_{\text{size}} \) and \( \beta_{\text{strain}} \) in equation 1, we get,

\[
\beta = \frac{k\lambda}{t \cos \theta} + 4\eta \tan \theta
\]

As we know,

\[
\tan \theta = \frac{\sin \theta}{\cos \theta}
\]

Therefore, equation (5) can be written as,

\[
\beta = \frac{k\lambda}{t \cos \theta} + 4\eta \frac{\sin \theta}{\cos \theta}
\]

Multiplying both sides by \( \cos \theta \) we get:

\[
\beta \cos \theta = \frac{k\lambda}{t} + 4\eta \sin \theta
\]

Or

\[
\beta \cos \theta = \eta(4 \sin \theta) + \frac{k\lambda}{t}
\]  

The equation represents a straight line, in which \( \eta \) is the gradient (slope) of the line and \( \frac{k\lambda}{t} \) is the y-intercept.

Consider the standard equation of a straight line,

\[
y = mx + c
\]

Now, we will plot \( 4 \sin \theta \) on the x-axis and \( \beta \cos \theta \) on the y-axis.

The value of the strain (\( \eta \)) will be given by the value of “m” which represents the gradient (slope) of the line and the crystallite size can be calculated from the y-intercept \( \frac{k\lambda}{t} \).

The average crystallite size of ceramics decreases (i.e. 63.59 to 30.11 nm) and strain increases from \( 5.25 \times 10^{-3} \) to \( 7.74 \times 10^{-3} \) as the \( \text{Ba}^{2+} \) content increases in the BBNT ceramics, respectively (as given in Table 4). The substitution of \( \text{Ba}^{2+} (1.39 \text{ Å}) \) for the smaller ionic radii of \( \text{Bi}^{3+} (~1.17 \text{ Å}) \), causes the lattice distortion. Thus, the increase in \( \text{Ba}^{2+} \) content results in an increase in the
lattice strain, which further results in the reduction of crystallite size of these ceramics.

3.2. Scanning Electron Microscope (SEM)

Figure 5a and b for $x = 0.00$, (c and d) for $x = 0.10$, and (e and f) for $x = 0.30$ represents the SEM images of $((\text{Bi}_{0.5-x}\text{Ba}_x\text{Na}_{0.5})\text{TiO}_3$ ceramics. It was observed that the average grain size increases with an increase in Ba concentration [33]. Small crystallites are leading information of larger size grains (as results of small crystallites obtained in XRD section) may be another reason for larger size grains. The BNT with $x = 0.00$ and 0.10 samples are more compact and exhibited

![Figure 5: SEM images of $((\text{Bi}_{0.5-x}\text{Ba}_x\text{Na}_{0.5})\text{TiO}_3$ ceramics.](image)

| Composition               | $x = 0.00$ | $x = 0.10$ | $x = 0.30$ |
|---------------------------|------------|------------|------------|
| Crystallite Size (nm)     |            |            |            |
| W-H Plots                 | 65.83      | 50.68      | 32.05      |
| Scherrer Formula          | 63.59      | 49.73      | 30.11      |
| Crystallite strain        |            |            |            |
| $5.25 \times 10^{-3}$     |            | $7.05 \times 10^{-3}$ | $7.74 \times 10^{-3}$ |
| Transition temperature    |            |            |            |
| $T_1$ (°C)                | 80         | 90         | ---        |
| $T_C$ (°C)                | 250        | 280        | 300        |
| Dielectric constant ($\varepsilon$) | 2917      | 2698       | 5563       |
uniform microstructure with smaller grains, due to the formation of MPB [34].

3.3. Dielectric Studies

Figure 6a-c shows the variation of Dielectric constant ($\varepsilon$) as a function of frequency of ($\text{Bi}(0.5-x)\text{Ba}_x\text{Na}_{0.5})\text{TiO}_3$ (where $0.00 \leq x \leq 0.30$) ceramics at higher temperature (i.e. 300 to 400 °C). It is observed from these figures that there is a decrease in the value of the dielectric constant with an increase in frequency, which is a typical characteristic of normal dielectric [35].

A high dielectric constant at low frequencies is characteristic of all-dielectric materials, which means overall polarization contributes to the dielectric constant. With an increase in frequency the dielectric constant decrease due to the frequency-dependent nature of polarization. The order of different polarization is ionic $<$ dipolar $<$ atomic $<$ electronic shows dominance up to frequency $10^7$, $10^{11}$, $10^{15}$ Hz, and electronic polarization shows its dominance even in $G$ Hz or above range [36]. This means different polarization vanishes with the increase in the frequency and thus leading to a decrease in the value of the dielectric constant. Thus, the value of the dielectric constant decreases at high frequency.

Temperature dependence of Dielectric constant ($\varepsilon$) for ($\text{Bi}(0.5-x)\text{Ba}_x\text{Na}_{0.5})\text{TiO}_3$ (where $0.00 \leq x \leq 0.30$) Ceramics (at frequencies 1, 10, 100 k Hz and 1 M Hz) is shown in Figure 7a-c, respectively. From these figures, two phenomena were observed. They were; (i) In ceramics $x = 0.00$ and 0.10 two peaks were observed, the first peak corresponds to ferroelectric-ferroelectric ($\varepsilon_1$) and the second peak corresponds to ferroelectric-paraelectric phase transitions ($\varepsilon_2$). The first phase transition shows a structural change from rhombohedral to tetragonal and the second phase transition from tetragonal to the cubic structure. The first phase transition is well supported by XRD as getting rhombohedral structure at room temperature. With a further increase in Ba content (i.e. at $x = 0.30$), the value of the dielectric constant gradually increased to (5563) at 1 k Hz, and $T_C$ shifted to 300 °C. (ii) The decrease in the value dielectric constant with increase in frequency because of frequency-dependent nature. The various values of dielectric constant and phase transition temperatures are shown in Table 4.
The ac conductivity in ceramics is mainly controlled by the migration of space charges under the action of the electric field and by the defect-ion complexes, the polarization field, the relaxation, etc. The ac conductivity of ceramics was calculated using the formula:

\[ \sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon \tan(\delta) \]  

(8)

Where \( f \) is the applied frequency in Hz,

\( \varepsilon_0 = \frac{8.85 \times 10^{-12}}{\text{Fm}^{-1}} \) is the permittivity of the free space, \( \varepsilon = \frac{\text{permittivity of ceramics}}{\text{permittivity of ceramics}} \) and \( \tan(\delta) \) is the loss tangent.

Figure 8a-c represents the ac conductivity of \(((\text{Bi}_{0.5-}x\text{Ba}_x)\text{Na}_{0.5})\text{TiO}_3\) for \( x = 0.00, 0.10 \) and 0.30 ceramics as a function of frequency in the high temperature range (i.e. 300 to 400 °C). The \( \sigma(f) \) curves are found to be merging at high frequency due to the presence of more defect mobility and high conductivity in the materials [37]. The magnitude of ac conductivity increases with an increase in temperature. Because the band-gap decreases with an increase in temperature and ions in the valance band get thermal energy (in form of heat) easily jump to conduction and resulting in high conductivity. The increase in conductivity on doping is due to an increase in the specific surface area in \( x = 0.30 \) ceramic.

4. CONCLUSION

Ba-doped BNT lead-free ceramics were synthesized successfully by the conventional solid-state reaction method. Rietveld’s refinement of the XRD pattern confirms the structural change from rhombohedral to tetragonal with MPB. W-H plots show that crystallite size increases with a decrease in lattice strain. SEM shows that an increase in grain size was recorded with the increase in Ba-doping. The dielectric constant of BBNT ceramics is increased with the addition of Ba-content. An increase in the ac conductivity was observed on doping which is due to an increase in the specific surface area.

5. FUTURE DEVELOPMENT AND RESEARCH PROPOSED

- Extension of this work is suggested towards HRTEM for confirming the particle size and structure.
• XPS/EDAX for confirming the presence of different elements within the ceramics.

• FESEM of sintered ceramics to check the grain, grain boundary formation and can be able to an established relationship between structural and electrical properties of materials.

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