CHAPTER 4

STUDY OF La/Li AND La/Li/Ba CO-SUBSTITUTED Bi$_{0.50}$Na$_{0.50}$TiO$_3$ CERAMICS

4.1 INTRODUCTION

Materials with high dielectric and ferroelectric properties are extensively used for commercial applications such as memories, multilayer ceramic capacitors, actuators, sensor and transducers [1]. Significant amount of research reports have been published on the effect of dopants on the structure, dielectric, ferroelectric and piezoelectric properties of Bi$_{0.50}$Na$_{0.50}$TiO$_3$ (BNT) based ceramics. Sharma et al. [204] have shown that La$_2$O$_3$ is a typical soft additive and its addition in PZT has effectively enhanced piezoelectric properties and Prabu et al. [205] reported recently that the substitution of La$^{3+}$ (x = 0.05) significantly improves the dielectric and ferroelectric properties of PZT. Similarly, Herabut and Safari [95] proposed that La acts as modifier and enhances the electrical properties of BNT ceramics. Later on, Pengpat et al. [206] have also reported the effect of La$_2$O$_3$ addition on piezoelectric properties and found that the piezoelectric coefficient ($d_{33}$) has been increased for x = 0.06 in (1-x)Bi$_{0.5}$Na$_{0.5}$TiO$_3$-(x) BaTiO$_3$ (BNBT-6) ceramics. In BNT, Li is often used to reduce the sintering temperature in order to avoid the volatilization of Bi$_2$O$_3$ during sintering at high temperature [207]. In recent years, a lot of efforts have been made to improve the densification and electrical properties of BNT based ceramics through substitution as well as different processing by different synthesis routes [158-162]. Recently, few studies have revealed that there were many possibilities to further enhance the piezoelectric properties of KNN-based and Bi-based ceramics even through simple Lithium (Li) doping. Thus, Lithium (Li) has also been found to be useful element to enhance the densification, electrical as well as piezoelectric properties in lead free ceramics [208-210].

Present chapter has been divided into two parts. First part of this chapter gives details about the studies of effect of co-substitution of La/Li on structure, microstructure, dielectric, ferroelectric and piezoelectric properties of BNT ceramics. In the second part, the details about the studies on the effect of co-substitution of La/Li/Ba on structure, microstructure, dielectric, ferroelectric and piezoelectric properties of BNT ceramics has been described thoroughly.
Experimental methods like synthesis of samples and characterization of ceramics with different characterizing equipments and their outcome have been explained systematically.

4.2 SAMPLE PREPARATION AND CHARACTERIZATIONS

4.2.1 SAMPLE PREPARATION OF \((\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3\) (\(x = 0.04\) & \(y \leq 0.10\)) AND 1-z\((\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3\)-z(\(\text{BaTiO}_3\)) (\(x = 0.04, y = 0.025\) & \(z \leq 0.06\)) SYSTEMS

Lead-free ceramic having the chemical formula \((\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3\) (abbreviated as BLNLT-x/y) with \(x = 0.04\) and \(y = 0.025, 0.050, 0.075\) and 0.100 was prepared by semi-wet route. Further, in order to find the morphotropic phase boundary (MPB), a few solid solution compositions in BLNLT-BT system have been prepared with a typical optimised composition for \(x/y = 0.04/0.025\) of BLNLT system. In the present work, all samples were prepared using AR-grade metal oxides or nitrate powders (Sigma Aldrich) with high purity materials like \(\text{Bi}_2\text{O}_3\) (99 %), \(\text{NaNO}_3\) (99 %), \(\text{La}_2\text{O}_3\) (99.9 %), \(\text{LiNO}_3\), \(\text{Ba(NO}_3)_2\) (99.9%), \(\text{TiO}_2\) (99.9 %) and ethylene glycol. All the raw materials were weighed in appropriate amounts according to chemical compositions in BLNLT and BLNLT-BT systems. The precursors for A-site of BLNLT and BLNLT-BT systems were prepared by chemical route using ethylene glycol. It is expected that ethylene glycol distributes the cations homogeneously and forming a polymeric complex network. This was combusted at appropriate temperature (\(T \sim 500 ^\circ\text{C}\)) to form A-site complex oxide in the form of ash powders. The dried powders of mixed oxides of A-site constituents (ash powder, which was fine, homogeneous and highly reactive) were mixed with appropriate amount of \(\text{TiO}_2\) powder thoroughly with the help of mortar pestle in ethanol medium. Dried powder of La doped BNT (BLNT) for composition \(x = 0.04\) and \(y = 0.0\) (i.e. \(x/y = 0.04/0\)) was calcined at 850 \(^\circ\text{C}\) for 2 hrs. In order to get highly dense ceramic, this sample was sintered at 1,200 °C for 2 hrs.

In order to make high dense BNT ceramic at low temperature, Li and La was substituted on A-site in BNT ceramic. Hence, La/Li co-modified system BLNLT (x/y) with compositions \(x = 0.04\) and \(y \leq 0.125\) were synthesized by semi-wet technique. The calcinations process was optimised for La/Li doped BNT system. For this, a typical composition \(x/y = 0.04/0.050\) was calcined at three different temperatures (700, 750 and 800 °C) and X-ray diffraction was recorded for different temperature at room temperature. It was observed that the sample, calcined at 750 °C (2hrs) showed better crystallization. Therefore all Li substituted samples were calcined at 750°C (2hrs). Similarly, all the samples of BLNLT-BT ceramics were calcined at 850°C (2hrs). After
calcinations, powders were reground with binder (Polyvinyl Alcohol) and pressed into pellets in the form of cylindrical disc with 10 mm diameter using co-axial hydraulic press. Density of the sintered samples was measured by Archimedes principle for all the compositions. Silver paste was coated on both of the sides of pellets as electrodes for electrical measurements and cured at 400 ºC for 20 min. The electroded pellets were kept at 400ºC (2hrs) to burn off the binder. All compositions of BLNLT and BLNLT-BT systems were sintered at 1100ºC (2hrs) and 1100-1150ºC (2hrs) respectively.

4.2.2 CHARACTERIZATIONS OF $(\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3$ (x = 0.04 & y ≤ 0.10) AND $1-z((\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3)-z(\text{BaTiO}_3)$ (x = 0.04, y = 0.025 & z ≤ 0.06) SYSTEMS

The identification of phase formation and surface morphological studies has been performed using XRD (XRD-6000, Shimadzu Japan) and field emission scanning electron microscopes (FE-SEM, Quanta 200 FEG, FEI, The Netherlands). The Rietveld refinement method using FullProf program has been employed to confirm the crystal structure and determined the structural parameters for both samples. Investigations of dielectric constant ($\varepsilon_r$) and dielectric loss (tan δ) have been studies as a function of temperature from room temperature to 500ºC at few selected frequencies (1, 10 and 100 kHz) using Impedance analyzer (Nova control α-AT Germany). P-E loop tracer (Marine India) was used to study the polarization vs electric field loops at 50 Hz. For the study of piezoelectric and electromechanical response in BLNLT and BLNLT-BT ceramics, poling was done DC electric field under 6 kV/cm at 70ºC (2hrs) and 3 kV/cm at 50ºC (1hr) respectively. Piezoelectric charge coefficient ($d_{33}$) was directly determined by Piezo-Meter (Take Control, PM- 35, UK). The planar electromechanical coupling coefficient ($k_p$) was analyzed from the resonance-antiresonance frequencies recorded by impedance analyzer (Agilent, 4294A, USA) on the basis of IEEE standards [58] and calculated from the equation (1.11) of Section 1.3.2.2.

4.3 RESULTS AND DISCUSSION OF La/Li CO-SUBSTITUTED BNT CERAMICS; BLNLT (x/y)

4.3.1 STRUCTURAL ANALYSIS

Figure 4.1 shows the XRD patterns of BLNLT ceramic system for the compositions with x/y = 0.04/0-0.10. The XRD patterns have been recorded at room temperature in 2θ range from 20–70º. It is clearly pointed out from XRD patterns that the samples of La/Li co-doped BNT for
various x/y values appear to have single phase and no reflections belonging to other phases are seen, suggesting the diffusion of La$^{3+}$/Li$^+$ into the crystal lattice of BNT ceramics.

Figure 4.1: XRD patterns of (Bi$_{1-x}$La$_x$)$_{0.5}$(Na$_{1-y}$Li$_y$)$_{0.5}$TiO$_3$ (x/y) ceramics with compositions x/y = 0.04/0.0-0.10.

To determine the crystal structure and lattice parameters, XRD data of BLNT ceramic have been analysed by Rietveld refinement using FullProf Program [171]. Rietveld fitted XRD patterns are shown in Figure 4.2(a)–4.2(e). It is observed that Rietveld refined data (dotted line) fits well with the experimental diffraction data (solid line), which confirms single phase formation with rhombohedral (R3c) structural symmetry. The good fit with R3c model for two representative peaks (110) and (200) is shown in the inset of Figures 4.2.
Figure 4.2: Rietveld refined XRD patterns of \((\text{Bi}_{1.4-0.04}\text{La}_{0.04})0.5(\text{Na}_{1.4-0.04}\text{Li}_{0.04})0.5\text{TiO}_3\) ceramics with compositions \(x/y\) (a) 0.04/0.0, (b) 0.04/0.025, (c) 0.04/0.050, (d) 0.04/0.075 and (e) 0.04/0.10. Inset shows best fit with R3c model for two representative peaks (110) and (200) in all the samples.

The lattice parameters and agreement factors, obtained from Rietveld refinement, are given in Table 4.1. It is found that lattice parameters and volume of the unit cell decrease with increasing \(y\) (as \(x = 0.04\) for all the samples), which may be due to the smaller size of \(\text{Li}^+\) (1.25 Å) as compared to the \(\text{Na}^+\) (1.39 Å).
Table 4.1: Rietveld refined Lattice parameters, volume and agreement factors of all compositions in (Bi₁₋ₓLaₓ)₀.₅(Na₁₋ₓLiₓ)₀.₅TiO₃ (x/y) ceramics.

<table>
<thead>
<tr>
<th>Compositions x = 0.04 (fix) &amp; y = 0-0.10</th>
<th>Lattice parameters (Å)</th>
<th>V (10⁻³⁰ m³)</th>
<th>Rietveld fitted parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a_H</td>
<td>c_H</td>
<td></td>
</tr>
<tr>
<td>y = 0</td>
<td>5.4996</td>
<td>13.4650</td>
<td>352.69</td>
</tr>
<tr>
<td>y = 0.025</td>
<td>5.4960</td>
<td>13.4608</td>
<td>352.10</td>
</tr>
<tr>
<td>y = 0.050</td>
<td>5.4950</td>
<td>13.4600</td>
<td>351.97</td>
</tr>
<tr>
<td>y = 0.075</td>
<td>5.4943</td>
<td>13.4595</td>
<td>351.87</td>
</tr>
<tr>
<td>y = 0.10</td>
<td>5.4883</td>
<td>13.4556</td>
<td>351.00</td>
</tr>
</tbody>
</table>

The average crystallite size of the calcined powders for each composition in this system has been calculated using Debye–Scherer equation, as illustrated in chapter 3 according to equation (3.2). The crystallite size was found to be decreased from 38.97 nm for x/y = 0.04/0 to 22.59 nm for x/y = 0.04/0.125. The Williamson Hall (WH) approach was also used for de-convoluting crystallite size and strain contribution to the X ray line broadening. The Williamson Hall plots of βCosθ vs Sinθ are shown in Figure 4.3. The crystallite size was calculated from the intercept of the line at sin Θ = 0 (on the x – axis) and the slope value estimates the strain whose values are given in Table 4.2. In the present work, tolerance factor (T.F.) was calculated for all the compositions using the following equation:

\[ T.F. = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}} \]  \hspace{1cm} (4.1)

Where, t is the tolerance factor, r_A is the ionic radius of A-site cations, r_B is the ionic radius of B-site cations and r_O is the ionic radius of oxygen anions. Tolerance factor play a key role in the stability of perovskite structure. The tolerance factor for all the compositions has been calculated and given in Table 4.2. In case of BLNT (0.04/0), value of t is 0.972 and it decreases from 0.972 to 0.968 with increasing the fraction of Li (from 0.0 to 0.125), indicating a negligibly small
distortion present in the lattice. So, this small distortion does not affect the crystal structure which remains rhombohedral throughout the composition range studied.

Figure 4.3: Variation of $\beta \cos \theta$ vs $\sin \theta$ for BLNLT $(x/y)$ ceramics with compositions $x/y$ (a) 0.04/0.0, (b) 0.04/0.025, (c) 0.04/0.050, (d) 0.04/0.075 and (e) 0.04/0.100.

Table 4.2: Physical parameters of all the compositions in $(\text{Bi}_{1-x}\text{La}_x)_{0.5}(\text{Na}_{1-y}\text{Li}_y)_{0.5}\text{TiO}_3$ $(x/y)$ ceramics.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Tolerance factor (T.F.)</th>
<th>Average crystallite size $(t)$</th>
<th>Strain $(\varepsilon)$ %</th>
<th>Average grain size $D$ $(\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.04$ (fix) $y = 0-0.10$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$y = 0$</td>
<td>0.972</td>
<td>38.97</td>
<td>68.73</td>
<td>0.60</td>
</tr>
<tr>
<td>$y = 0.025$</td>
<td>0.971</td>
<td>38.49</td>
<td>68.55</td>
<td>0.58</td>
</tr>
<tr>
<td>$y = 0.050$</td>
<td>0.970</td>
<td>38.25</td>
<td>58.10</td>
<td>0.45</td>
</tr>
<tr>
<td>$y = 0.075$</td>
<td>0.970</td>
<td>27.70</td>
<td>42.35</td>
<td>0.38</td>
</tr>
<tr>
<td>$y = 0.10$</td>
<td>0.968</td>
<td>25.95</td>
<td>39.31</td>
<td>0.32</td>
</tr>
</tbody>
</table>

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4.3.2 DENSITY AND SURFACE MORPHOLOGY

Bulk density ($\rho_{\text{bulk}}$), relative density ($\rho_{\text{rel}}$) and average grain size ($D_{\text{av.}}$) of BLNLT samples are shown in Figure 4.4(a) and 4.4(b), as a function of co-doping of La/Li (x/y). It is found that both bulk density and relative density increases up to (x/y) = 0.04/0.050, thereafter decreases for (x/y) $\geq$0.04/0.075. The specimen with x/y = 0.04/0.050 has been found to have the maximum relative density. All the specimens show better density, which is greater than 95 % of the theoretical density. Average grain size decreases with Li up to y = 0.075 and increases for y = 0.10 as shown in Figure 4.4(b). It may be attributed to the addition of Li promotes densification during sintering and hence may assist in lowering the sintering temperature of these ceramics [211-212].

![Figure 4.4](image)

**Figure 4.4:** (a) Variation of bulk density ($\rho_{\text{bulk}}$) and relative density ($\rho_{\text{rel}}$), (b) variation of average grain size ($D_{\text{av.}}$) of all the compositions in (Bi$_{1-x}$La$_x$)$_{0.5}$(Na$_{1-y}$Li$_y$)$_{0.5}$TiO$_3$ ($x/y$) ceramics.
Microstructures of all the sintered specimens with compositions x/y = 0.04/0.0–0.10 are shown in Figure 4.5. It is observed that average grain size decreases with Li up to y = 0.075 and thereafter increases for y = 0.10 as shown in Figure 4.5(b). It appears that densification for low concentration of Li occurs due to capillary action of liquid phase formation [213-214], which is supported from the variation of relative density upto y = 0.050. With higher concentration of Li, localized molten grains are seen in Figure 4.5(e), as indicated by white circle in the micrographs for y = 0.10, leading to the anomalous grain growth [215]. Thus, co-substitution of La/Li causes a significant change in the microstructure. Average grain size (D_{av}) of these specimen samples has been determined by line intercept method and given in Table 4.2.

Figure 4.5: Microstructures of the compositions with x/y (a) 0.04/0.0, (b) 0.04/0.025, (c) 0.04/0.050, (d) 0.04/0.075, and (e) 0.04/0.10 in (Bi_{1-x}La_{x})_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3 (x/y) ceramics.
4.3.3 DIELECTRIC STUDY

Temperature dependence of dielectric plots of all unpoled specimen samples of BLNLT (x/y) = 0.04/0-0.10 at few selected frequencies 1 kHz, 10 kHz and 100 kHz are shown in Figure 4.6(a) – 4.6(e). It has been observed from these plots that dielectric constant ($\varepsilon_r$) for the compositions x/y = 0.04/0 increases up to certain temperature and shows a broad dielectric maxima around the temperature, this temperature referred as $T_m$, and thereafter it decreases with temperature. Here, ‘$T_m$’ is the temperature that corresponds to anti-ferroelectric to paraelectric phase transition. In addition to this, careful observation shows one more dielectric anomaly in the $\varepsilon_r$ vs T plots of pure BLNT, which is termed as $T_d$ where, ‘$T_d$’ refers to depolarization temperature and corresponds to the transition from ferroelectric to anti-ferroelectric transition at temperature below $T_m$. It can also be identified from the peak in dielectric loss ($\tan \delta$) vs temperature plots [197]. It is further observed from dielectric plots of Figure 4.6(a) – 4.6(c) that dielectric maxima with specimens (x/y) = (0.04/0.025-0.075) exhibit a strong frequency dependence near $T_m$. The dielectric constant decreases with increasing frequency while corresponding $T_m$ increases, suggesting that a few compositions with (x/y) ≤ 0.04/0.075 exhibit relaxor behavior. It is earlier reported in the literature that frequency dependent phase transition has been observed in several ABO$_3$ type perovskite compounds e.g. PMN-PT in general [216] and BNT based ceramic in particular [217], of which either A-sites or B-sites are occupied at least by two cations. In these ceramics, Bi$^{3+}$, La$^{3+}$, Na$^+$, Li$^+$ elements are randomly distributed on A-sites. Compositional fluctuation and disordering of A-site cations may be attributed to the broad transition and dielectric dispersion around $T_m$ leading to the relaxor behavior for x/y ≤ 0.04/0.075 [218]. With further increasing Li concentration for x/y = 0.04/0.10, dielectric plots exhibit a broad frequency independent transition at temperature around $T_m$ as shown in Figure 4.6(d). From these observations, it is clear that a switching from relaxor type to normal phase occurs with increasing Li concentration in these ceramics. Further, it is clearly observed from Figure 4.6(c) that at 1 kHz, dielectric constant for x/y = 0.04/0.050 initially decreases above $T_m$ followed by an increase in high temperature region above 400 ºC, which may not be observed for 10 and 100 kHz. It may be noted that rapid rise in dielectric loss ($\tan \delta$) is also associated with the rise in dielectric constant above 400 ºC. Whereas for x/y = 0.04/0.075, dielectric constant at 1 kHz increases continuously without observing any dielectric hump whereas at high frequencies a trend of
increase in $\varepsilon_r$ with a broad hump appears. Almost similar broad transition but frequency independent $T_m$ is observed for composition with $y = 0.10$. Furthermore, a sharp increase in dielectric loss at temperature $\geq 400^\circ$C has been observed for specimens with $y \geq 0.050$. In addition to the above features, the transition temperature ($T_m$) shifts towards lower temperature side continuously with increasing the concentration of $y$ upto 0.075 except for $y = 0.10$.

![Figure 4.6: The temperature dependence of $\varepsilon_r$ and $\tan \delta$ of all the specimens x/y (a) 0.04/0.0, (b) 0.04/0.025, (c) 0.04/0.050, (d) 0.04/0.075, and (e) 0.04/0.10 in $(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3$ (x/y) ceramics at 1 kHz, 10 kHz and 100 kHz, Inset of Fig. 4.6 (a) shows dielectric plots for pure BNT.](image)

Physical mechanism underlying for this behavior is discussed below. It is obvious that $La^{3+}$ (1.36 Å) may occupy either $Bi^{3+}$ (1.32 Å) or $Na^+$ (1.39 Å) sites. As discussed above, A-sites of $La$
substituted BNT (i.e. BLNT) is prepared by semi-wet method using ethylene glycol. A-site (Bi$^{3+}$ and Na$^+$) substitution by La$^{3+}$ in BNT ceramics can be formulated in the following way,

$$La_2O_3 + BNT \rightarrow 2La_{Bi} + 3O_o$$  \hspace{1cm} (4.2)

$$La_2O_3 + 2BNT \rightarrow 2La^{*}_{Na} + 4V_{Na} + 3O_o$$  \hspace{1cm} (4.3)

If the substitution occurs according to Eq. (4.2), then only change in size is expected systematically. If the substitution follows Eq. (4.3), then defect formation is expected to be enhanced in sample. Inset of Figure 4.6(a) shows dielectric plots for pure BNT. On comparing dielectric behavior of La modified BNT as shown in Figure 4.6(a) with pure BNT, it is seen that dielectric loss is nearly same (< 0.5). It may, therefore, be suggested that La occupies only Bi-sites and no defects are created, however, dielectric constant is significantly modified with La substitution.

On the other hand, when Li ion is substituted along with La$^{3+}$, there are two possibilities for Li ion to occupy A-sites in these ceramics. Thus, Li - ions (1.25 Å) may either occupy A-sites of Bi$^{3+}$ (1.32 Å) or Na$^+$ (1.39 Å). The defect reaction due to Li$^+$ substitution at Bi$^{3+}$ and Na$^+$ sites can be expressed according to Kröger–Vink notation of defects [219]:

$$Li_2O + BNT \rightarrow 2Li^+_{Na} + O_o$$  \hspace{1cm} (4.4)

$$3Li_2O + BNT \rightarrow 6(Li^{+}_{Bi}) + 4(V_{Bi}^+) + 3O_o$$  \hspace{1cm} (4.5)

According to Eq. (4.4), it may occupy Na site without creating defects or vacancies while the occupancy of Li at Bi$^{3+}$ positions increases the possibility of defect formation according to Eq. (4.5). It may be expected that for low concentration of Li$^+$ ions, charge compensation takes place in the materials internally via iso-valent substitutions [2] and no additional charges are created which also supported by tan δ values with y. Further, if charge compensation occurs via vacancy creation according to Eq. (4.5) or off valent substitutions for higher concentration of Li$^+$ ions [220], then defect concentration increases which in turn leads to increase in dielectric loss as well as distortion in the lattice, but this is not the case, as loss remains small and less than 0.5 for all the samples up to certain temperature. Crystal structure also does not change with increasing Li concentration. It may, therefore, be concluded that Li only substitutes Na$^+$-sites.
The relaxor behavior in these materials can be analysed by determining degree of diffuseness of the peak in dielectric plots according to the following relation [45]:

\[
\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r\text{max}}} = C^{-\gamma} (T - T_m)^{-\gamma}
\]

where, \( C \) is Curie coefficient, \( \gamma \) is degree of diffuseness and \( \varepsilon_{r\text{max}} \) is maximum value of dielectric constant at \( T_m \). The exponent ‘\( \gamma \)’ can have a value ranging from 1 (for normal ferroelectric) to 2 (for an ideal relaxor ferroelectric). All the samples above \( T_m \) show a linear relationship, which is shown in Figure 4.7. For present system, value of ‘\( \gamma \)’ is in the range of 1.5 - 1.8, indicating relaxor ferroelectrics with diffused phase transition. The diffused type phase transition behavior of these samples may be explained on the basis of presence of micro-heterogeneities present in these materials due to thermo-chemical diffusion controlled solid state reactions.

![Figure 4.7: The log (1/\( \varepsilon_r \) - 1/\( \varepsilon_{r\text{max}} \)) versus log (T - \( T_m \)) plots of all compositions in (Bi\(_{1.5}\)-La\(_x\))\(_{0.5}\)(Na\(_{1.5}\)-Li\(_y\))\(_{0.5}\)TiO\(_3\) (x/y) ceramics at 100 kHz.](image)
Micro-heterogeneities arise due to random occupation of A-sites by different ions. Such a heterogeneous distribution of cations leads to different state of polarization and hence different relaxation time in different regions. This causes dielectric relaxation up to $y \leq 0.075$. The dielectric maxima gets diffused [141] for higher concentration of Li and dielectric relaxation is completely washed out for $y = 0.10$. Frequency independent dielectric maxima position is observed that may be due to the enhanced liquid phase formation during sintering in the localised regions producing melting of grains which is further evidenced by microstructure for this sample where anomalous grain growth has taken place.

4.3.4 FERROELECTRIC STUDY

Hysteresis (P–E) loops at room temperature for all specimens are shown in Figure 4.8(a)–4.8(e). It has been observed that all specimens exhibit nearly saturation polarization under an applied electric field at 50 Hz.
Figure 4.8: P–E hysteresis loops of all compositions (a) x/y = 0.04/0.0, (b) x = 0.04/0.025, (c) x/y = 0.04/0.050, (d) x/y = 0.04/0.075, and (e) x/y = 0.04/0.10 in (Bi$_{1-x}$La$_x$)$_{0.5}$(Na$_{1-y}$Li$_y$)$_{0.5}$TiO$_3$ (x/y) ceramics at RT (50 Hz).

Pure BLNT specimen (x/y = 0.04/0.0) has been found to have low value of $P_r$ (20.96 $\mu$C/cm$^2$) and high value of $E_c$ (35.53 kV/cm) whereas composition with x/y = 0.04/0.025 has shown highest value of $P_r$ (29.26 $\mu$C/cm$^2$) and relatively low $E_c$ (28.81 kV/cm) as compared to pure BLNT. However, as y is further increased from 0.025 to 0.10, the magnitude of $P_r$ and $E_c$ decrease significantly from 29.26 to 25.83 $\mu$C/cm$^2$ and from 28.81 kV/cm to 21.44 kV/cm respectively. Thus, electric field induced switching of domains becomes more easy by the substitution of Li ion. This may be due to small ionic radius of Li$^+$ (1.25 Å) as compared to Bi$^{3+}$ (1.32 Å) and Na$^+$ (1.39 Å), which is in agreement with the previous report of Wang et al. [221]. The values of $P_r$ and $E_c$ of these samples with compositions (y) are given in Table 4.3.

Table 4.3: Dielectric, ferroelectric and piezoelectric properties of all compositions in (Bi$_{1-x}$La$_x$)$_{0.5}$(Na$_{1-y}$Li$_y$)$_{0.5}$TiO$_3$ (x/y) ceramics.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>at RT (100 kHz)</th>
<th>at RT (50 Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_r$</td>
<td>$T_m$ ($^\circ$C)</td>
</tr>
<tr>
<td>$x = 0.04$ (fix)</td>
<td>$y = 0$</td>
<td>3410</td>
</tr>
<tr>
<td>$y = 0.025$</td>
<td>3989</td>
<td>0.28</td>
</tr>
<tr>
<td>$y = 0.050$</td>
<td>2740</td>
<td>0.17</td>
</tr>
<tr>
<td>$y = 0.075$</td>
<td>2715</td>
<td>0.06</td>
</tr>
<tr>
<td>$y = 0.100$</td>
<td>1842</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4.3.5 PIEZOELECTRIC STUDY

Figure 4.9 displays the variation of piezoelectric charge coefficient ($d_{33}$) and planer electro-mechanical coupling factor ($k_p$) of the poled specimens. The piezoelectric charge coefficient ($d_{33}$) was increased from 40 pC/N to 70 pC/N with x/y substitution from x = 0.04/0.0 to 0.04/0.025. Thereafter, it decreased and attain minimum for x/y = 0.04/0.100. Similar trend has
been obtained with the magnitude of \( k_p \). Therefore, \( d_{33} \) and \( k_p \) attains enhanced values (70 pC/N and 0.25 respectively) for a typical specimen with \( x/y = 0.04/0.025 \). Generally, piezoelectric response can be explained by a convectional Landau – Devonshire relation, in which it is directly proportional to dielectric permittivity (\( \varepsilon_r \)) and remnant polarization (\( P_r \)), as per the following relation:

\[
d_{33} = 2\varepsilon_r \varepsilon_0 Q_{11} P_r
\]  

(4.7)

Where, \( \varepsilon_0 \), and \( Q_{11} \), are vacuum permittivity and electro-strictive coefficient respectively. Hence, it is clear from the above equation that values of \( \varepsilon_r \) and \( P_r \) are the main factors that influence \( d_{33} \) in piezoelectric systems.

![Figure 4.9: Piezoelectric charge coefficient (\( d_{33} \)) and the planer electromechanical coupling factor (\( k_p \)) of (\( Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3 \) (x/y) ceramics.](image)

**4.4 RESULTS AND DISCUSSION OF La/Li /Ba CO-SUBSTITUTED BNT CERAMICS; BLNLT-BT (x/y/z)**

**4.4.1 STRUCTURAL ANALYSIS**

Figure 4.10 shows X-ray diffraction pattern of lead free compositions with \( x/y/z = 0.04/0.025/0-0.06 \) in 1-z(BLNLT)-z(BT) system. It is observed from the x-ray diffraction
patterns that all specimen exhibit single phase with rhombohedral structure and no secondary phase as well as MPB has been observed within detection limit of XRD. It implied that La$^{3+}$, Li$^+$ and Ba$^{2+}$, have diffused into BNT lattice to form a solid solution.

![XRD patterns of [1 - z(BLNL)-z(BT), x/y/z = 0.04/0.025/0, 0.02, 0.04, 0.06] system.](image)

**Figure 4.10:** XRD patterns of [1 − z(BLNL)-z(BT), x/y/z = 0.04/0.025/0, 0.02, 0.04, 0.06] system.

In the present system, we found that the symmetry of the solid solution became more complex for BLNL-BT solid solution. In order to determine the crystal structure and symmetry of BLNL-BT ceramics, we have analysed XRD data of BLNL-BT ceramics with the help of Rietveld refinement using FullProf Program [171]. Rietveld fitted XRD patterns are shown in **Figure 4.11(a) – 4.11(d).** It is observed that Rietveld refined data (dotted line) fits well with the experimental diffraction data (solid line), which confirms single phase with rhombohedral (R3c) structural symmetry without any signature of MPB. The good fit with R3c model for two representative peaks (110) and (200) is shown in inset of **Figure 4.11.**
Figure 4.11: Rietveld refined XRD patterns of (1-z)BLNLT-(z)BT ceramics with compositions (a) z = 0, (b) z = 0.02, (c) z = 0.04 and (d) x/y = 0.06. Inset shows best fit with R3c model for two representative peaks (110) and (200) in all the samples.
Table 4.4: Rietveld refined Lattice parameters, volume and agreement factors of all compositions in 1-z BLNT-zBT (x/y/z) ceramics.

<table>
<thead>
<tr>
<th>Compositions x=0.04, y = 0.025 (fix) z = 0-0.06</th>
<th>Lattice parameters (Å)</th>
<th>V $(10^{-30} m^3)$</th>
<th>Rietveld fitted parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_H$</td>
<td>$c_H$</td>
<td>$V$</td>
</tr>
<tr>
<td>$z = 0$</td>
<td>5.4996</td>
<td>13.4650</td>
<td>352.6900</td>
</tr>
<tr>
<td>$z = 0.02$</td>
<td>5.4965</td>
<td>13.4632</td>
<td>352.2441</td>
</tr>
<tr>
<td>$z = 0.04$</td>
<td>5.4901</td>
<td>13.4601</td>
<td>351.3520</td>
</tr>
<tr>
<td>$z = 0.06$</td>
<td>5.4882</td>
<td>13.4587</td>
<td>351.0703</td>
</tr>
</tbody>
</table>

4.4.2 DENSITY AND SURFACE MORPHOLOGY

The bulk density of the sintered specimens was measured by the Archimedes method. The relative density was determined using bulk density and theoretical density. The bulk density observed in [1-z(BLNLT)-z(BT), x/y/z = 0.04/0.025/0] system was 5.8 gm/cm$^2$ which is 97% of theoretical density and the bulk density in the case of [1-z(BLNLT)-z(BT), x/y/z = 0.04/0.025/0.06] system was 5.7 gm/cm$^2$ which is 95% of theoretical density.

Figure 4.12 showed microstructure of all the sintered samples of BLNLT-BT [1-z(BLNLT)-z(BT), x/y/z = 0.04/0.025/0, 0.04/0.025/0.02 & 0.04/0.025/0.06] ceramics. The microstructures of all the sintered samples were found homogeneous and dense. The linear intercept method was used to determine the average grain size ($D_{av}$) of these samples [See Table – 4.5]. From the micrographs, it was evident that average grain size was found to decrease with Ba substitution in BLNLT system, which was consistent with the reported results [222]. In the present system, grain growth was slightly inhibited with the substitution of Ba$^{2+}$ and small grains were formed, which may be due to the reduction in the mobility of the grain boundary. Thus, the mass transportation was weekend after the addition of Ba$^{2+}$ [223].
Figure 4.12: Microphotographs of [1 − z(BLNLT)-z(BT)] system for z = 0, 0.02, and 0.06.

4.4.3 DIELECTRIC STUDY

Figure 4.13 illustrated the temperature dependence of dielectric constant and dielectric loss of these compositions in BLNLT-BT ceramics at different frequencies (1, 10 & 100 kHz). The temperature dependence of $\varepsilon_r$ shows that $\varepsilon_r$ increases upto certain temperature followed by a broad dielectric maxima around $T_m$, thereafter $\varepsilon_r$ decreases with further increasing temperature above $T_m$. In addition to this, one more dielectric anomaly is observed at lower temperature ‘$T_d$’ referred as depolarization temperature, corresponding the transition from ferroelectric to anti-
ferroelectric phase transition and it can also be derived from the peak in the temperature dependence plot of tan δ [197] and ‘Tm’ referred as the temperature of maximum dielectric constant which corresponds to the anti ferroelectric to para-electric phase transition. It has been observed that dielectric plots of specimen (x/y/z) = (0.04/0.025/0) exhibit slight frequency dependence behavior above Td (near Tm) for specimens (x/y/z) = (0.04/0.025/0.02-0.06), the dielectric constant has been found to be frequency and temperature dependent especially at higher temperature. The phase transitions Td (blue circle) and Tm (red circle) shifted towards low temperature with increasing Ba content in BLNLT system (see Figure 4.13), which was expected owing to low Curie temperature (Tc ~ 130 °C as compared with that of BLNT ~ 355 °C) of Barium titanate. The maximum dielectric constant and low value of dielectric loss were observed for the specimen x/y/z = 0.04/0.025/0.06 at room temperature.

Figure 4.13 (a–c): The temperature dependence of εr and tan δ of [1-z(BLNLT)-z(BT)] system for samples z = 0, 0.02 and 0.06 at 1 kHz, 10 kHz and 100 kHz.
The value of dielectric constant ($\varepsilon_r$), dielectric loss ($\tan \delta$), and phase transitions temperature ($T_d$ and $T_m$) with other ferroelectric and piezoelectric parameters for all the specimens are shown in Table 4.5.

Table 4.5: Electrical Properties of [1-z(BLNLT)-z(BT) ceramics, x/y/z = 0.04/0.025/0-0.06] system.

<table>
<thead>
<tr>
<th>Compositions x/y/z</th>
<th>at RT (100 kHz)</th>
<th>$T_d$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\gamma$</th>
<th>$d_{33}$ (pC/N)</th>
<th>$D_{av}$ (µm)</th>
<th>at RT (50 Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z = 0$</td>
<td>1365</td>
<td>0.08</td>
<td>170</td>
<td>375</td>
<td>1.69</td>
<td>70</td>
<td>2.67</td>
</tr>
<tr>
<td>$z = 0.02$</td>
<td>1386</td>
<td>0.27</td>
<td>130</td>
<td>305</td>
<td>1.58</td>
<td>65</td>
<td>2.34</td>
</tr>
<tr>
<td>$z = 0.04$</td>
<td>1423</td>
<td>0.08</td>
<td>120</td>
<td>290</td>
<td>1.66</td>
<td>47</td>
<td>-</td>
</tr>
<tr>
<td>$y = 0.06$</td>
<td>1494</td>
<td>0.06</td>
<td>80</td>
<td>225</td>
<td>1.79</td>
<td>20</td>
<td>1.78</td>
</tr>
</tbody>
</table>

### 4.4.4 FERROELECTRIC STUDY

The hysteresis (P-E) loops for the sample x/y/z = 0.04/0.025/0.06 has been shown in Figure 4.14 (at room temperature) at different frequencies and inset of Figure 4.14 shows the room temperature P-E loop for all the samples of BLNT-BT ceramics. It was found that the sample with x/y/z = 0.04/0.025/0 exhibit nearly saturated polarization under an applied electric field of 50-60 kV/cm at 50 Hz. The shape of P-E loop for specimen $z = 0.06$ has been found to change with increasing frequency. This may be due to the fact that the contributions of all type of polarization are present at low frequency region. As the frequency is increased, this type of contribution is decreased. The variation of $P_r$ and $E_c$ for all the samples was listed in Table-4.5.
4.4.5 PIEZOELECTRIC STUDY

The piezoelectric measurements of the poled samples in BLNT-BT system, sintered at 1150 °C (2hrs) have been carried out at room temperature (Table-4.5). With Ba$^{2+}$ substitution, the piezoelectricity was reduced. According to thermodynamic theory of ferroelectricity, piezoelectric charge constant ($d_{33}$) is greatly dependent on the relative permittivity and polarization, which is directly proportional to dielectric permittivity ($\varepsilon_r$) and remnant polarization ($P_r$), as per the equation [4.7]. Thus, value of $d_{33}$ has been found to decrease with increasing Ba concentration which may be due to weak ferroelectricity in these materials.

4.5 CONCLUSIONS

The compositions with $x = 0.04$ and $y \leq 0.10$ in $(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3$ (BLNLT) system have been synthesized by semi wet technique. All the compositions have shown single phase formation with rhombohedral structure (R3c symmetry). Co-substitution of La/Li ($x/y$) has shown a significant effect on the microstructure, phase transition temperatures and dielectric properties of BNT system. FE-SEM micrographs show decrease in grain size upto $y = 0.075$.
thereafter anomalous grain growth for $y \geq 0.100$, which may be attributed to liquid phase sintering. The temperature and frequency dependent dielectric behavior upto $y = 0.075$ reveals relaxor type characteristic which may be ascribed to the micro-heterogeneities due to atomic disorder at A-sites in these materials. A broad, however non-relaxer type transition is observed for compositions $y = 0.100$, may be caused by localized liquid phase formation due to higher concentration of lithium leading to anomalous grain growth. All the samples exhibit low dielectric loss. The specimen with composition $x/y = 0.04/0.025$ has shown excellent dielectric, ferroelectric and piezoelectric properties at room temperature, which makes it promising for high temperature dielectric application.

In view of this, taking this composition into consideration in BLNLT system, a solid solution of few compositions with barium titanate in BLNT-BT system has been synthesized to investigate the MPB region. Structural analysis has shown rhombohedral structure with absence of MPB region up to $z = 0.06$. However, a significant effect on the microstructure, phase transition temperatures ($T_d$ & $T_m$), dielectric, ferroelectric and piezoelectric properties have been obtained. Microstructure of all the specimens exhibit homogeneous grain growth and the grain size has been found to decrease with substitution of Ba in $(1-z)$BLNLT-$(z)$BT system. Dielectric constant has been found to increase with increasing Ba concentration, which may be due to significant influence of the reduced grain size with Ba doping.