Correlation between the structure and dielectric constant of \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{Li}_x)_{0.5}\text{TiO}_3 \) (0 ≤ \( x \) ≤ 0.20) solid solutions

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Abstract

Bismuth sodium titanate \( \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 \) (BNT) is a lead-free piezoelectric ceramic material with high Curie temperature. The effect of substitution of the smaller ion \( \text{Li}^+ \) for the larger ion \( \text{Na}^+ \) in \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{Li}_x)_{0.5}\text{TiO}_3 \) (0 ≤ \( x \) ≤ 0.20) on the structure of BNT is studied using powder X-ray diffraction (XRD) and Raman spectroscopy. The Rietveld refinement analysis of the powder XRD patterns showed that all the compositions formed under the monoclinic \( \text{Cc} \) space group, with the lattice parameters showing minor changes above \( x > 0.08 \). Raman spectral parameters such as position and intensity of a peak also showed a similar trend in the same Li concentration range with increasing Li content. A corresponding change in the variation of the dielectric constant with increasing Li content is also observed, suggesting a close correlation between the crystal structure and dielectric properties of the different compositions in the \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{Li}_x)_{0.5}\text{TiO}_3 \) solid solution series.

KEYWORDS
B\( \text{i}_{0.5}\text{Na}_{0.5}\text{TiO}_3 \), bismuth sodium titanate, dielectrics, lead-free ferroelectrics, Li substitution, Raman spectroscopy, structure-property correlation

1 INTRODUCTION

Bismuth sodium titanate, \( \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 \) (BNT), is a piezoelectric ceramic material with strong ferroelectric properties such as large remnant polarization \( (P_r = 38 \mu \text{C/cm}^2) \) and high Curie temperature \( (T_C = 320^\circ\text{C}) \).\(^1\)-\(^4\) The main drawbacks of BNT for practical applications are its large coercive field and high electrical conductivity. Several studies have been reported in the literature on the modifications of the composition of BNT to overcome the drawbacks and to improve its piezoelectric properties.\(^5\)-\(^10\) Most of these studies are centered on the substitution of \( \text{Na}^+ \) by \( \text{K}^+ \) in \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3 \), and these compositions are considered as potential candidates for various piezoelectric applications.\(^11\)-\(^23\) Sasaki et al studied the structural, dielectric, and piezoelectric properties of \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3 \) solid solution series and found the morphotropic phase boundary (MPB) region in the range \( x = 0.16-0.20 \) and the piezoelectric properties are maximum in this compositional range.\(^18\) Many other studies have also reported on the enhanced piezoelectric and dielectric performances of \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3 \) in the MPB region.\(^14\),\(^21\)-\(^23\) Anjali et al reported that the onset of the MPB region is at \( x = 0.16 \) and the MPB region corresponds to \( 0.16 \leq x \leq 0.24 \) where better performance parameters are observed.\(^24\),\(^25\)

There are only few studies reported in the literature on the substitution of \( \text{Na}^+ \) by \( \text{Li}^+ \) in BNT.\(^26\)-\(^31\) Lu et al have reported that \( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{Li}_x)_{0.5}\text{TiO}_3 \) for 0 ≤ \( x \) ≤ 0.20 has the perovskite...
structure with rhombohedral symmetry. The maximum piezoelectric coupling constant, \(d_{33}\), and planar electromechanical coupling factor, \(K_p\), are reported as 110 pC/N and 0.18 at \(x = 0.15\), respectively, compared with 80 pC/N and 0.14, respectively, for BNT. The mechanical quality factor, \(Q_m\), was found to decrease with increasing Li\(^+\) content. Said and Maaoou investigated the dielectric behavior of the Bi\(_{0.5}\)(Na\(_{1-x}\)Li\(_x\))0.5TiO\(_3\) solid solution series and found relaxor-type behavior with a diffuse phase transition for low Li\(^+\) substitution in the range \(0 \leq x \leq 0.20\). The relaxor behavior has been attributed to the cation disorder in the A-site of the perovskite lattice. Lin et al reported that Li\(^+\) substitution effectively lowers the sintering temperature of Bi\(_{0.5}\)(Na\(_{1-x}\)Li\(_x\))0.5TiO\(_3\) solid solutions and significantly contributes to the densification of the ceramics. Optimum ferroelectric and piezoelectric properties are reported for the composition \(x = 0.075\). The depolarization temperature was found to be shifted to lower temperatures with increasing Li\(^+\) substitution, and the compositions exhibited enhanced relaxor characteristics. Thermal energy harvesting potential of Bi\(_{0.5}\)Na\(_{0.425}\)Li\(_{0.075}\)TiO\(_3\) has been investigated, and it was found that the maximum energy density is higher than that obtained for most of the lead-based compounds. Shih et al observed that substitution of Bi by Li improves the ionic conductivity of BNT by one order of magnitude. Comparison with other oxide-ion conductors indicated that Li-substituted BNT compositions are promising candidates for intermediate temperature solid oxide fuel cell applications.

Detailed structural studies on the Bi\(_{0.5}\)(Na\(_{1-x}\)Li\(_x\))0.5TiO\(_3\) solid solution series are not yet reported in the literature. Since the ionic size of Li\(^+\) (0.92 Å) is smaller than that of Na\(^+\) (1.18 Å) (values for eightfold coordination), the substitution of Li\(^+\) for Na\(^+\) in BNT is expected to cause structural changes and/or phase transition. Therefore, a detailed structural characterization of Bi\(_{0.5}\)Na\(_{0.425}\)Li\(_{0.075}\)TiO\(_3\) or (1-x)Bi\(_{0.5}\)Na\(_{0.425}\)Li\(_{0.075}\)TiO\(_3\)-xBi\(_{0.5}\)Li\(_{0.075}\)TiO\(_3\), represented as (1-x)BNT-xBLT, in the range \(0 \leq x \leq 0.20\) has been carried out and correlated with the changes in the dielectric properties. Structural analysis of different close compositions in the (1-x)BNT-xBLT series has been carried out by the Rietveld refinement analysis of the XRD patterns, and local structural changes are studied using Raman spectroscopy.

2 | EXPERIMENTAL

The different compositions in the (1-x)BNT-xBLT (0 \leq x \leq 0.20) series were prepared by a citrate-gel method from the corresponding metal nitrates and titanium isopropanoxide taken in the required stoichiometric ratio. Bismuth nitrate (Bi(NO\(_3\))\(_x\).5H\(_2\)O) was dissolved in dilute nitric acid, and sodium nitrate (NaNO\(_3\)) and lithium nitrate (LiNO\(_3\)) were dissolved in distilled water. A calculated amount of citric acid was dissolved in a solution of titanium isopropanoxide (Ti(OCH\(_2\)CH\(_3\))\(_x\)) in isopropyl alcohol by stirring for 30 minutes. The ratio of citric acid to metal nitrate content was taken as 3:1. The individual metal nitrate solutions were mixed together, and the mixture was added to the titanium solution with constant stirring and evaporated at 60°C until a transparent viscous gel was obtained. The dried gel was heated at 150°C overnight and crushed to a fine powder. The powder samples were initially heated at 400°C, and then at 850°C and 1000°C with intermediate grindings. The resulting powders were uniaxially pressed into circular disks (10 mm diameter \times 3 mm height) at a pressure of 8 MPa and sintered at 1150°C for 2 hours. All the samples were sintered in air under identical conditions with heating and cooling rates of 5°C/min. The samples in the (1-x)BNT-xBLT series were labeled as BNT (x = 0) and xBLT (x > 0).

Structural analysis of the sintered samples was performed by powder X-ray diffraction (XRD) on a PANalytical X’pert PRO powder X-ray diffractometer. Raman spectra were recorded on a Lab RAM HR spectrometer (HORIBA JOBIN YVON, Model No. HR 800) and deconvoluted using the Origin software. Dielectric constants of the sintered pellets were measured at room temperature, using an impedance bridge (Model 1608A, General Radio Company) at 1 kHz. The Rietveld refinement of the powder XRD patterns was carried out using the software “General Structure Analysis System” (GSAS-EXPGUI).

3 | RESULTS AND DISCUSSION

Figure 1 shows the powder XRD patterns of selected compositions (x = 0, 0.04, 0.08, 0.12, 0.16, 0.20) in the solid solution series (1-x)BNT-xBLT. No additional peaks, other than those from the perovskite phase, are detected in the XRD patterns suggesting the single-phase nature of the different compositions. The Rietveld refinement analysis of all the studied compositions of (1-x)BNT-xBLT was carried out using the monoclinic Cc space group. All the compositions gave reasonable good fit with low values for reduced \(\chi^2\) and \(R_p\). Table S1 (Supplemental material) gives the results obtained from the Rietveld analysis for all the studied compositions in (1-x)BNT-xBLT (0 \leq x \leq 0.20).

Figure 2 shows the variation of the monoclinic lattice parameters a, b, and c, as a function of BLT content in (1-x) BNT-xBLT. On increasing the BLT content, the lattice parameters “a” and “c” are decreased, whereas “b” is slightly increased. The ionic radius of Li\(^+\) is 0.92 Å, and that of Na\(^+\) is 1.18 Å, for eightfold coordination. When the larger Na\(^+\) ion is replaced by the smaller Li\(^+\), the unit cell volume is decreased (Figure S1, Supplemental material). The substitution of Li\(^+\) causes contraction of the unit cell, and hence, corresponding changes are seen in the lattice parameters.
The difference between the magnitudes of the lattice parameters “a” and “c” for $x = 0$ and 0.2 is obtained as ~0.02 Å. Although the lattice parameter “b” showed a small increase, the difference is very small (~0.006 Å). The small increase in the value of “b” could be due to the reduced distortion or tilting of the TiO$_6$ octahedra in the unit cell on the substitution of smaller Li$^+$ for larger Na$^+$. It is interesting to note that the rates of decrease in the lattice parameters “a” and “c” are different above and below $x \approx 0.08$, as shown in Figure 2 ($a/\sqrt{3}$ is plotted in the figure). A large reduction in the values of the lattice parameters is observed between $x = 0.08$ and 0.16, and the parameters remain almost constant for $x > 0.16$. Similarly, the lattice parameter “b” remains almost constant up to $x \approx 0.1$, and a small increase is observed up to $x = 0.16$, and “b” becomes almost constant again at higher Li$^+$ concentrations. Similar changes are observed in the variation of the unit cell volume also (Figure S1, Supplemental material). Since the changes in the lattice parameters are very small with increasing Li content, it may be concluded that there is no major structural phase transformation as observed in the case of (1-$x$)BNT–xBKT, where the structure is found to change from monoclinic to tetragonal at higher BKT content. The small change in the variation of the lattice parameters around $x \approx 0.1$ may be due to the local structural changes arising from the inhomogeneous distribution of the substituted Li ions in the lattice for $x < 0.1$. However, the onset of a minor structural phase transition cannot be ruled out in this compositional region, even though good fits are obtained in the Rietveld refinement analysis, using the monoclinic structure in the entire compositional region studied. The fact that the lattice parameters become almost constant for $x > 0.16$ and all three lattice parameters show a major change in the compositional region $0.08 \leq x \leq 0.16$ suggests a probable structural phase transition. If this is true, the compositional region $0.08 \leq x \leq 0.16$ is likely to belong to a morphotropic phase boundary (MPB) region, as observed in the case of (1-$x$)BNT–xBKT.

Raman spectra of all the studied compositions are recorded, and the changes in the Raman spectra as a function of composition in the BNT-BLT series are studied to get more insight into the local structural changes with Li substitution. Raman spectra of different compositions of the (1-$x$)BNT–xBLT series, after baseline correction, are shown in Figure 3. Raman spectra of BNT are similar to those already reported in the literature. As observed in the case of the
BNT–BLT solid solutions consist of three different regions. The band below 200 cm\(^{-1}\) is due to the A-O vibrations in the ABO\(_3\) perovskite lattice, and in the present case, it is likely to be due to Bi-O, Na-O, and Li-O vibrations. The band observed in the 200-400 cm\(^{-1}\) region in the Raman spectra belongs to the Ti-O vibrations, and the band in the 400-800 cm\(^{-1}\) region belongs to the vibration of the TiO\(_6\) octahedra.\(^{25}\)

If the substitution of smaller Li\(^+\) ion for larger Na\(^+\) in the BNT lattice causes contraction of the unit cell volume and local structural distortions, corresponding signatures are expected in the Raman spectra of the BNT–BLT solid solutions. The immediate observation from the Raman spectra, shown in Figure 3, is the decrease in the area and the downward frequency shift of the band centered at \(\sim 135\) cm\(^{-1}\). In the case of BNT–BKT solid solution series, an additional band was observed in the 200-400 cm\(^{-1}\) region, which gave a clear indication about the symmetry changes and phase transition.\(^{25}\) Such prominent changes are not observed in the 200-400 cm\(^{-1}\) and 400-800 cm\(^{-1}\) regions in the Raman spectra of the BNT–BLT solid solutions. Detailed analysis of the Raman spectra is carried out by the deconvolution of each band, and the changes in the parameters are studied.

Raman spectra of the different BNT–BLT compositions are deconvoluted after normalizing with respect to the intensity of the band in the 200-400 cm\(^{-1}\) spectral region. Kreisel et al. earlier reported fitting of the Raman spectra of BNT and BKT using six and seven peaks, respectively.\(^{35}\) However, the best fit to the Raman spectra of all the BNT-BLT compositions was obtained using seven peaks, where an additional peak was required to fit the band in the 200-400 cm\(^{-1}\) region, as reported for BKT. Figure 4 shows the deconvoluted Raman spectra of selected compositions (\(x = 0, 0.04, 0.08, 0.12, 0.16, \) and 0.20) in the (1-x)BNT-xBLT solid solution series. The band below 200 cm\(^{-1}\) is fitted with one peak. The two broad bands in the 200-400 cm\(^{-1}\) and 400-800 cm\(^{-1}\) regions in the spectra of all compositions are deconvoluted into three peaks each, as shown in Figure 4. Variation of the position of the A-O band in the 100-200 cm\(^{-1}\) region of the spectra and the area under the peak as a function of BLT content are shown in Figure S2A (Supplemental material). A small shift in the position of the A–O band of the BNT–BLT solid solutions is observed on Li\(^+\) substitution, with a small

**FIGURE 3** Raman spectra of different compositions in (1-x) BNT-xBLT for 0 \(\leq x \leq 0.20\) (\(\Delta x = 0.02\))

**FIGURE 4** Deconvoluted Raman spectra of selected compositions in (1-x) BNT-xBLT. The black, red, and blue curves correspond to experimental spectra, fitted curve, and the individual components, respectively.
increase in the position of the band up to \(x \approx 0.1\) and a large decrease above this composition. However, the area under the peak is found to decrease almost linearly with increasing Li content (Fig. S2B, Supplemental material). The band below 200 cm\(^{-1}\) belongs to the Na-O/Li-O vibration since the Bi-O band cannot be observed in this frequency region due to the higher mass of the Bi\(^{3+}\) ion.\(^{35}\) The variations in the peak position and area of the band is due to the local structural changes because of Li\(^{+}\) substitution. Also, the low-frequency shift may be due to the diffusion of the smaller Li\(^{+}\) ions in the crystal lattice, which will weaken the Li–O bond strength and results in some local symmetry changes.

As mentioned, the Raman band in the 200-400 cm\(^{-1}\) region is due to the Ti-O vibrations. Figure 5 shows the variation of the position of the individual peaks in the 200-400 cm\(^{-1}\) region with increasing concentration of BLT. On increasing the BLT concentration, the first two components show an upward frequency shift, whereas the third component shows a different trend. For the first two peaks within this band, the positions remain almost the same for \(x < 0.08\) and \(x > 0.12\), with a drastic increase between \(x = 0.08\) and 0.12. Similar changes are observed in the case of the third peak also, except for a large drop for \(0.08 \leq x \leq 0.12\). Figure 6 shows the changes in total area under the band and the area under the individual peaks of the band in the 200-400 cm\(^{-1}\) region with increasing Li content. The area under the individual peaks also shows a major change between \(x = 0.08\) and \(x = 0.12\), as in the case of the changes in the peak positions.

Changes are also observed in the positions of the individual peaks of the Raman band in the 400-800 cm\(^{-1}\) region assigned to the vibration of the TiO\(_6\) octahedra. A linear increase in the position of the individual peaks is observed on increasing the BLT concentration (Figure S3, Supplemental material). The total area and the areas under the first two peaks are increased, whereas the area of the third peak is decreased with increasing BLT concentration (Figure S4, Supplemental material). Even though the total area increased almost linearly with increasing BLT concentration, the changes in the area of the individual peaks showed different trends below and above \(x = 0.08\). The area of peak 1 is independent of \(x\) for \(x < 0.08\) and then increased with \(x\), area of peak 2 increased up to \(x = 0.8\) and then remained almost constant, and the area of peak 3 decreased up to \(x = 0.08\) and then remained almost constant at higher \(x\).

Thus, the changes in the parameters of the Raman spectra for the bands in the 200-400 cm\(^{-1}\) and 400-800 cm\(^{-1}\) regions suggest minor changes in the Ti–O bond length and some associated changes in the distortion of the TiO\(_6\) octahedra with partial substitution of Li\(^{+}\) for Na\(^{+}\) in Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\). Results from the XRD studies also suggested minor structural changes above \(x = 0.08\) in (1-x)BNT-xBKT, and the Raman studies suggest that this is due to the minor changes in the coordination environment at the A and B sites in the perovskite lattice. Hence, a corresponding change in the ferroelectric polarization is expected, which may lead to variations in the dielectric constant.

The dielectric constant of all the studied compositions of (1-x)BNT-xBLT, measured at 1 kHz, as a function of BLT concentration, is shown in Figure 7. The dielectric constant shows a small increase up to \(x = 0.08\), which is shown in the inset of Figure 7, and an abrupt change in the slope is observed above \(x = 0.08\). For \(x \geq 0.12\), the dielectric constant remains almost constant. The maximum dielectric constant observed for the BNT–BLT compositions is ~420. However,
this value is relatively small when compared to the maximum dielectric constant reported for the BNT–BKT series as 1800.24 For the BNT–BKT system, the maximum dielectric constant is observed in the MPB region where the monoclinic and tetragonal phases coexist. Such a phase transition and MPB region are not observed in the case of the BNT–BLT system. Also, the distortion of the monoclinic structure is relatively larger for the BNT–BKT system due to the larger size of the K⁺ ions. The observed dielectric constants of the different compositions of the BNT–BLT ceramics are relatively low when compared to the previous literature reports.26-27 Lu et al reported a dielectric constant of 800 for the \( x = 0.20 \) composition in the BNT–BLT series. This is mainly due to the difference in the synthesis methods, processing conditions, density, sintering temperature, and the pressure used for the compaction of pellets.

Dielectric constant of a ferroelectric material is related to its crystal symmetry and the degree of polarization. The distortion in the crystal structure of a ferroelectric material is expected to change its dipole moment and hence the polarization, which will affect its dielectric constant. Figure 8 shows a comparison of the variations in the lattice parameter \( b \), dielectric constant \( \varepsilon_r \), and area under the first peak of the Raman band in the 200–400 cm⁻¹ region, as a function of \( x \) in the (1-x)BNT–xBLT series.
the crystal structure of BNT leading to local distortion of the TiO$_6$ octahedra and hence the dielectric constant of the material. The dielectric constant shows a small increase up to $x=0.08$ with increasing BLT concentration due to the replacement of larger Na$^+$ by smaller Li$^+$ ions. As shown in Figure 8, both the “b” lattice parameter and the area under the first peak of the Raman band in the 200-400 cm$^{-1}$ region showed relatively large increase in the compositional region $0.08 \leq x \leq 0.12$ suggesting significant structural distortions. A corresponding jump in the dielectric constant is observed up to $x=0.08$. The other hand, as shown in Figure 8, the lattice parameter $a$ remained almost constant in the compositional region $0.12 \leq x \leq 0.20$, and the dielectric constant also do not change much in this region. Since the Raman parameters reflect the changes in the Ti–O bond in Li$^+$ substitution, and a similar trend is followed by the lattice parameter “b” and the dielectric constant, it may be concluded that the minor changes in the structure contributed to the variation in the dielectric constant with the substitution of Li$^+$ for Na$^+$ in Bi$_{0.5}$Na$_{0.5}$TiO$_3$. Thus, as shown in Figure 8, the structural parameters and the dielectric constant show similar variations, where the parameters are not much changed up to $x \approx 0.08$; a large increase is observed for $0.08 \leq x \leq 0.12$, and the parameters remain independent of $x$ in the range $0.12 \leq x \leq 0.20$, showing a direct correlation between the structure and dielectric constant of the Bi$_{1-x}$Na$_x$Li$_{0.5}$TiO$_3$ ($0 \leq x \leq 0.20$) solid solution series.

4 | CONCLUSIONS

Solid solutions in the series (1-x)Bi$_{0.5}$Na$_{0.5}$TiO$_3$—xBi$_{0.5}$Li$_{0.5}$TiO$_3$, represented as (1-x)BNT—aBLT, in the range $0 \leq x \leq 0.20$ are studied to understand the effect of substitution of Na by Li in Bi$_{0.5}$Na$_{0.5}$TiO$_3$. The Rietveld refinement analysis of the XRD patterns suggested small structural distortion and local symmetry changes in the crystal lattice. The Raman spectroscopy analysis supported the results obtained from the XRD studies. The changes in the Raman parameters with substitution followed the same trend as that observed in the case of the unit cell parameters. Variation of the structural, as well as Raman spectral parameters and the dielectric constant, showed similar changes with increasing Li concentration, suggesting a close correlation between the structure and properties of the compositions.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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