Dielectric and piezoelectric properties of lead-free K$_{0.5}$Na$_{0.5}$NbO$_3$–LiSbO$_3$–Bi$_{0.5}$Li$_{0.5}$TiO$_3$ system

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The effects of Bi, Li and Ti substitutions for K, Na, Li, Nb and Sb on the piezoelectric properties of (1 – x)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–xBi$_{0.5}$Li$_{0.5}$TiO$_3$ [KNN–BLT] ceramics were investigated. X-ray powder diffraction profiles indicate the formation of a morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases in the (1 – x)KNN–xBLT ceramics. The ratio of tetragonal to orthorhombic phase increased with x, which suggests a decrease in the orthorhombic–tetragonal phase transition temperature ($T_{o-t}$). The dielectric constant at room temperature was increased by the substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb. In addition, the temperature dependence of the dielectric constant indicated a $T_{o-t}$ shift from approximately 90°C to room temperature, and resulted in a piezoelectric constant of 272 pC/N for the 0.98KNN–0.02BLT (x = 0.02) ceramic.

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Key-words: Lead-free, MPB, K$_{0.5}$Na$_{0.5}$NbO$_3$. Piezoelectric properties, Ferroelectric properties

1. Introduction

Recently, lead-free piezoelectric ceramics have been widely studied as alternatives to Pb(Zr,Ti)O$_3$ (PZT).1–6 Among the various potential candidates, (K,Na)NbO$_3$ (KNN)-based materials have received considerable attention due to their excellent piezoelectric properties (d$_{33}$ = 80 pC/N) and high Curie temperature ($T_C$ = 425°C).7 The existence of a morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases in KNN-based ceramics has been reported to be effective in enhancing the piezoelectric properties as well as PZT.8–10 A site substitutions of elements such as Li, Ag, Ba, Sr, Ca, and Bi for K and Na have been reported, while Ta, Sb, Ti, and Sc have been substituted for Nb. The co-substitution of A site and B site elements has been conducted in an attempt to enhance the piezoelectric properties of KNN ceramics, in which Li, Ta, and Sb substitutions for K, Na and Nb have been reported as the most effective,6–12 and the mechanism has also been clarified on the basis of the relationship between the crystal structure and the MPB. On the other hand, the addition of Bi$_2$O$_3$/Li$_2$O/TiO$_3$ can improve the piezoelectric properties of other lead-free ceramics,13 although the influence of such addition on the piezoelectric properties of KNN-based ceramics has not been reported.

Therefore, to improve the piezoelectric properties of the Li- and Sb- substituted (K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$ ceramic, (1 – x)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–xBi$_{0.5}$Li$_{0.5}$TiO$_3$ [KNN–xBLT] ceramics were synthesized and piezoelectric properties were investigated.

2. Experimental methods

(1 – x)KNN–xBLT was prepared by the conventional solid-state reaction method. High purity K$_2$CO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$, Nb$_2$O$_5$, Sb$_2$O$_5$, TiO$_2$ and Bi$_2$O$_3$ powders were used as starting materials. Stoichiometric amounts of these materials were weighed and mixed with ethanol. After drying, the powders were calcined at 700°C for 6 h in air. The calcined powders were reground with 5 wt% polyvinyl alcohol (PVA) as a binder. The powders were uniaxially pressed into disks at 60 MPa and then sintered at 1095 to 1200°C for 3 h in air. The crystalline phases of (1 – x)KNN–xBLT ceramics were identified using X-ray powder diffraction (XRPD) with CuKα radiation; crystal structure analysis was performed using the Rietveld method.14,15 The microstructure of the (1 – x)KNN–xBLT ceramics were observed using scanning electron microscopy (SEM) (JEOL JSM-6330F). The bulk densities of the samples were estimated using the Archimedes method. The temperature dependence of the dielectric constant for the ceramics was measured using precision LCR meter (Agilent 4284A). Poling treatment was conducted using a DC power supply at 4 kV/mm in silicon oil at 120°C for 30 min. The piezoelectric constant was measured using a d$_{33}$ meter (Institute of Acoustic, Chinese Academy of Sciences ZJ-4B).

3. Results and discussion

Figure 1 shows the XPRD profiles of the (1 – x)KNN–xBLT ceramics. Single phase (1 – x)KNN–xBLT ceramics were obtained in the compositional range of x = 0 to x = 0.06. A secondary phase K$_3$Li$_2$Nb$_5$O$_{15}$ compound with a tetragonal tungsten bronze structure was detected at x = 0.08; such secondary phase was also recognized in the KNN-LiNbO$_3$ system.16 A similar XRPD profile, which implies the formation of an MPB between the orthorhombic and tetragonal phases in the KNN-LiSbO$_3$ system was reported by Wu et al.16 therefore, it is considered that a MPB region may also be formed in the (1 – x)KNN–xBLT ceramics. Moreover, the dielectric peaks of the ceramics shift to the higher angles of 2θ from 21 to 23.5° and from 44 to 48°, respectively. The intensities of the (010) and (200) peaks

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increased with increasing \( x \) whereas the intensities of the (100) and (002) peaks were decreased by the substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb, which implies a decrease in ratios of the orthorhombic to tetragonal phases. Thus, a small amount of Bi, Li and Ti for K, Na, Li, Nb and Sb, which implies a decrease in ratios of orthorhombic to tetragonal phases. The reliability factors and the-goodness-of-fit indicators for the refined (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were recognized in Table 2. The ratios of orthorhombic to tetragonal phases are shown as a function of \( x \) in Fig. 2. The weight fraction of each phase in the mixture, which was identified in the XRPD patterns, was also estimated according to the following equation:

\[
W_p = \frac{\sum_i s_i(ZMV)_i}{\sum_i s_i(ZMV)_i}
\]

where \( W_p \) and \( i \) represent the weight fraction of phase \( p \) and the number of phases identified in the XRPD patterns, respectively. Moreover, \( s \), \( Z \), \( M \) and \( V \) are the refined scale factor from the Rietveld analysis, the formula number of the compound, the formula unit volume and the unit cell volume, respectively. The ratios of the orthorhombic to tetragonal phases decrease with increasing \( x \), which is also supported by the variation in the XRPD peak intensities. The variation in the orthorhombic to tetragonal phase ratios may have an influence on the orthorhombic-tetragonal phase transition temperature (\( T_{O-T} \)).

The details on ferroelectric and piezoelectric properties and bulk density of (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were summarized in Table 3 and the temperature dependence of the dielectric constant for the (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics is shown in Fig. 3(a). Two dielectric peaks of the (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were recognized.

### Table 1. Refined atomic coordinates of (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics at \( x = 0 \)

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<th>Atom</th>
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<th>( y )</th>
<th>( z )</th>
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<td>( \text{K}^+ / \text{Na}^+ / \text{Li}^+ )</td>
<td>1a</td>
<td>0.562</td>
<td>0.562</td>
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<td>0.0</td>
</tr>
<tr>
<td>( \text{Nb}^{5+} / \text{Sb}^{5+} )</td>
<td>2b</td>
<td>0.948</td>
<td>0.562</td>
<td>0.0</td>
<td>0.562</td>
</tr>
<tr>
<td>( \text{O}^{2-} )</td>
<td>4c</td>
<td>1.000</td>
<td>0.562</td>
<td>0.0</td>
<td>0.25</td>
</tr>
<tr>
<td>( \text{O}^{2-} )</td>
<td>1a</td>
<td>0.474</td>
<td>0.052</td>
<td>0.0</td>
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### Table 2. Details on the crystal structure refinement results of (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Composition</th>
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<th>( x = 0.02 )</th>
<th>( x = 0.04 )</th>
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<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
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<tr>
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<td>8.01</td>
<td>8.55</td>
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<td>( R_{wp} )</td>
<td>9.25</td>
<td>7.32</td>
<td>8.73</td>
<td>8.23</td>
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<td>9.64</td>
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<td>( R_{wp} )</td>
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<td>5.42</td>
<td>5.05</td>
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<tr>
<td>( S )</td>
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<td>1.73</td>
<td>1.61</td>
<td>1.63</td>
<td>1.66</td>
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<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
<td>( \text{Amn}2 )</td>
</tr>
</tbody>
</table>

The reliability factors and the-goodness-of-fit indicators for the refined (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were also listed in Table 2. The ratios of orthorhombic to tetragonal phases are shown as a function of \( x \) in Fig. 2. The weight fraction of each phase in the mixture, which was identified in the XRPD patterns, was also estimated according to the following equation:

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The details on ferroelectric and piezoelectric properties and bulk density of (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were summarized in Table 3 and the temperature dependence of the dielectric constant for the (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics is shown in Fig. 3(a). Two dielectric peaks of the (1–\( x \))-\( \text{K}_0.474\text{Na}_{0.474}\text{Li}_{0.052}\text{Ti}_0.052 \text{Sb}_{0.052} \text{O}_3 \text{O}_2 \text{BLT} \) ceramics were recognized.
in the approximate temperature ranges of 40 to 90°C and 300 to 400°C, and the dielectric peaks at higher temperatures were shifted to the lower temperature with increasing $x$. The $T_{O-T}$ and tetragonal–cubic phase transition temperature ($T_{T-C}$) were reported to be 225 and 435°C for the KNN ceramic, whereas those of the (1-$x$)KNLNS–$x$BLT ceramic with $x=0.02$ were approximately 40 and 330°C, respectively. The temperature dependence of the dielectric constants near room temperature are shown in Fig. 3(b), where the dielectric peaks shift toward room temperature; the dielectric constant of the (1-$x$)KNLNS–$x$BLT ceramics increased with $x$ up to 0.02. However, the dielectric peak at lower temperature for $x=0.06$ was not observed in the measurement range, which suggests the formation of a tetragonal phase at room temperature. The dielectric peaks were shifted toward the room temperature by the substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb. The dielectric constant is related with the piezoelectric constant ($d_{33}$); therefore, the $d_{33}$ value of (1-$x$)KNLNS–$x$BLT ceramics may be enhanced by variations in the ratio of orthorhombic to tetragonal phases, which results in an increase of the dielectric constant at room temperature.

**Table 3.** Details on ferroelectric and piezoelectric properties and bulk density of (1-$x$)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–$x$Bi$_{0.5}$Li$_{0.5}$TiO$_3$ ceramics

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$E_c$ (kV/cm)</th>
<th>$d_{33}$ (pC/N)</th>
<th>Dielectric constant (1 kHz)</th>
<th>Bulk density (g/cm$^3$)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>18.8</td>
<td>14.2</td>
<td>187</td>
<td>1159</td>
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<td>0.01</td>
<td>18.9</td>
<td>15.0</td>
<td>256</td>
<td>1332</td>
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<tr>
<td>0.02</td>
<td>29.5</td>
<td>16.7</td>
<td>272</td>
<td>1556</td>
<td>4.38</td>
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<td>0.04</td>
<td>25.8</td>
<td>16.8</td>
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<td>1248</td>
<td>4.29</td>
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<tr>
<td>0.06</td>
<td>34.7</td>
<td>16.7</td>
<td>156</td>
<td>1203</td>
<td>4.26</td>
</tr>
</tbody>
</table>

in Fig. 2. Compositional dependencies of orthorhombic to tetragonal phase ratios and the tetragonal to orthorhombic phase ratios for (1-$x$)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–$x$Bi$_{0.5}$Li$_{0.5}$TiO$_3$ ceramics.

**Fig. 3.** (a) Temperature dependencies of dielectric constants for (1-$x$)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–$x$Bi$_{0.5}$Li$_{0.5}$TiO$_3$ ceramics and (b) enlarged temperature dependency of dielectric constant in temperature range of 20–120°C.

**Fig. 4.** $P$-$E$ hysteresis loops of (1-$x$)(K$_{0.474}$Na$_{0.474}$Li$_{0.052}$)(Nb$_{0.948}$Sb$_{0.052}$)O$_3$–$x$Bi$_{0.5}$Li$_{0.5}$TiO$_3$ ceramics.

**Figure 5** shows the relationship...
between the $d_{33}$ values and dielectric constants of the $(1-x)$-KLNLS–xBLT ceramic as a function of composition $x$. The $d_{33}$ values were increased with $x$ up to 0.02, with 187 pC/N for $x = 0$ and 272 pC/N for $x = 0.02$, whereas further substitution led to a decrease in the $d_{33}$ values. $d_{33}$ is related to the dielectric constant as follows:

$$d_{33} = 2Q_{11}e_0\varepsilon_1P_t,$$

where $Q_{11}$ is the electrostrictive coefficient, $e_0$ is the electric constant, and $P_t$ is the remanent polarization; however, $Q_{11}$ should not change significantly by doping. The $P_t$ values for the $(1-x)$KLNLS–xBLT ceramics increased with $x$ as shown in Fig. 4, although the dielectric constant and $d_{33}$ value decreased above $x = 0.04$; therefore, the increase in the $d_{33}$ value is due to enhancement of the dielectric constant.

Figure 6 shows SEM micrographs of the surface morphologies of the as-sintered $(1-x)(K_{0.474}Na_{0.474}Li_{0.052})_2\text{O}_3$–xBi$_2$O$_3$–xLi$_2$O–xTiO$_3$ ceramics. All of the ceramics have dense microstructures; the bulk density of the $(1-x)$KLNLS–xBLT ceramics improved from 4.27 g/cm$^3$ at $x = 0$ to 4.38 g/cm$^3$ at $x = 0.02$ by the Bi, Li and Ti substitutions for K, Na, Li, Nb and Sb as shown in Table 3, indicating that the compositional modifications are effective in promoting the densification of KNN-based ceramics. Cube-like or rectangular particle morphologies are especially evident in the ceramics with $x > 0.02$. The morphological changes support the results of the crystal structure analysis and temperature dependence of the dielectric constant because the ratio of tetragonal to orthorhombic phases is increased by the substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb.

4. Conclusions

$(1-x)$KLNLS–xBLT ceramics were prepared using the conventional solid-state reaction method and the influences of Bi, Li and Ti substitution for K, Na, Li, Nb and Sb on the piezoelectric constant were investigated. XRPD patterns of the $(1-x)$KLNLS–xBLT ceramics indicate single phase materials until $x = 0.06$. The ratio of tetragonal to orthorhombic phase was increased by the substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb. The dielectric constants of $(1-x)$KLNLS–xBLT ceramics increased with $x$, while $T_{0.5}$ decreased. The $d_{33}$ values of the $(1-x)$KLNLS–xBLT ceramics increased from 187 pC/N for $x = 0$ to 272 pC/N for $x = 0.02$; the variation in the $d_{33}$ values may be related to the increase in the dielectric constant of the ceramics.

References