Dielectric and piezoelectric properties of lead-free K0.5Na0.5NbO3–LiSbO3–Bi0.5Li0.5TiO3 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)(K0.474Na0.474Li0.052)–(Nb0.948Sb0.052)O3–xBi4Li4.5Ti5O15 (K0.474Na0.474Li0.052)(1–x)KNLNS–xBLT 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)KNLNS–xBLT ceramics. The ratio of tetragonal to orthorhombic phase increased with x, which suggests a decrease in the orthorhombite-tetragonal phase transition temperature (T0,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 T0,T shift from approximately 90°C to room temperature, and resulted in a piezoelectric constant of 272 pC/N for the 0.98KNLNS-0.02BLT (x = 0.02) ceramic.

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Key-words : Lead-free, MPB, K0.5Na0.5NbO3. Piezoelectric properties, Ferroelectric properties

1. Introduction

Recently, lead-free piezoelectric ceramics have been widely studied as alternatives to Pb(Zr,Ti)O3 (PZT). Among the various potential candidates, (K,Na)NbO3 (KNN)-based materials have received considerable attention due to their excellent piezoelectric properties (d33 = 80 pC/N) and high Curie temperature (Tc = 425°C). The existence of a morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases in KNN-based systems has been reported to be effective in enhancing the piezoelectric properties as well as PZT. A site substitutions of elements such as Li, Ag, Ba, Sr, Ca, and Bi for K and Na have been conducted, while Ta, Sb, Ti, and Sc have been substituted for Nb. The co-substitution of A site and B site elements has been attempted in an attempt to enhance the piezoelectric properties of KNN, in which Li, Ta, and Sb substitutions for K, Na and Nb have been reported as the most effective, 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 Bi2O3 to Bi0.5Li0.5TiO3 can improve the piezoelectric properties of other lead-free ceramics, although the influence of such addition on the piezoelectric properties of KNN-based ceramics has not been reported.

To improve the piezoelectric properties of the Li- and Sb-substituted (K0.474Na0.474Li0.052)(Nb0.948Sb0.052)O3 (1–x)KNLNS–xBLT ceramics, a primary phase boundary (P-E) hysteresis curves of the ceramics with Au electrodes were measured using the Sawyer-Tower circuit (aixACCT TF-analyzer 2000). 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 d33 meter (Institute of Acoustic, Chinese Academy of Sciences ZJ-4B).

3. Results and discussion

Figure 1 shows the XPRD profiles of the (1–x)KNLNS–xBLT ceramics. Single phase (1–x)KNLNS–xBLT ceramics were obtained in the compositional range of x = 0 to x = 0.06. A secondary phase K3Li2Nb5O15 compound with a tetragonal tungsten bronze structure was detected at x = 0.08; such second-phase formation was also recognized in the KNN-Li NbO3 system. A similar XRPD profile, which implies the formation of an MPB between the orthorhombic and tetragonal phases in the KNN-LiSbO3 system was reported by Wu et al., therefore, it is considered that a MPB region may also be formed in the (1–x)KNLNS–xBLT ceramics. Moreover, the diffraction peaks of the ceramics shift to the higher angles of 2θ with increasing x.

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2 Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.122.P6-1

DOI http://dx.doi.org/10.2109/jcersj2.122.398
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, Nb and Sb, which implies a decrease in ratios of the orthorhombic to tetragonal phases. The ratios of the orthorhombic to tetragonal phases decrease with increasing \( x \), and the weight fraction of each phase in the mixture, which was identified in the XRPD patterns, was also estimated according to the following equation:

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

where \( W_p \) and \( i \) represent the weight fraction of phase \( p \) and the number of phases identified in the XRPD patterns, respectively. Moreover, \( s_i \), \( Z \), \( M \) 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.29) 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 \((1-x)\)KNLNS-\(x\)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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### Table 1. Refined atomic coordinates of (1-x)(K0.474Na0.474Li0.052)(Nb0.948Sb0.052)O3-xBi0.5Li0.5TiO3 ceramics at x = 0

| Phase          | Site | Site occupancy | x   | y   | z   |
|----------------|------|----------------|-----|-----|-----|
| Orthorhombic   | K+/Na+/Li+ | 2a | 0.474/0.474/0.052 | 0   | 0   | 0   |
|                | Nb3+/Sb3+  | 2b | 0.948/0.052      | 0.5 | 0   | 0.590(9) |
|                | O2−        | 4c | 1.000             | 0.25| 0   | 0.31(4) |
|                | O2−        | 2a | 1.000             | 0   | 0   | 0.565(9) |
| Tetragonal     | K+/Na+/Li+ | 1a | 0.474/0.052      | 0   | 0   | 0   |
|                | Nb3+/Sb3+  | 1a | 0.948/0.052      | 0   | 0   | 0   |
|                | O2−        | 2c | 1.000             | 0.5 | 0   | 0.589(9) |
|                | O2−        | 1a | 1.000             | 0.5 | 0.036(8) |

### Table 2. Details on the crystal structure refinement results of (1-x)(K0.474Na0.474Li0.052)(Nb0.948Sb0.052)O3-xBi0.5Li0.5TiO3 ceramics

| Crystal data          | Composition | x   | x     | x     | x     |
|-----------------------|-------------|-----|-------|-------|-------|
|                       | P4mm        | P4mm| P4mm  | P4mm  | P4mm  |
| Space group            | Amm2        | Amm2| Amm2  | Amm2  | Amm2  |
| Pattern matching       |             |     |       |       |       |
| R-value                |             |     |       |       |       |
| Rwp (%)                | 7.19        | 7.65| 8.01  | 8.55  | 7.84  |
| Rexp (%)               | 9.25        | 7.32| 8.73  | 8.23  | 9.64  |
| Reexp (%)              | 5.54        | 4.21| 5.42  | 5.05  | 5.80  |
| S                      | 1.67        | 1.73| 1.61  | 1.63  | 1.66  |

Fig. 1. (a) XRPD profiles of (1-x)(K0.474Na0.474Li0.052)(Nb0.948Sb0.052)O3-xBi0.5Li0.5TiO3 ceramics and enlarged XRPD profiles in the 20 ranges of (b) 21–23.5° and (c) 44–48°.
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 tetragonal–orthorhombic and tetragonal–cubic phase transition temperature (\( T_{\text{T}} \)) were reported to be 225 and 435°C for the KNN ceramic,\(^8\) whereas those of the \((1-x)\)KNLNS–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–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–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.

**Figure 4** shows \( P-E \) hysteresis loops for the \((1-x)\)KNLNS–BLT ceramics measured at room temperature. The remanent polarization (\( P_r \)) was enhanced from 18.8 \( \mu \)C/cm\(^2\) for \( x = 0 \) to 24.3 \( \mu \)C/cm\(^2\) for \( x = 0.02 \), although the coercive field (\( E_c \)) also increased. Wu et al.\(^{16}\) reported that the increase in \( E_c \) is related with enhancement of the domain pinning effect, which leads to an increase in the dielectric constant; therefore, substitution of Bi, Li and Ti for K, Na, Li, Nb and Sb may also have an influence on the domain pinning effect. **Figure 5** shows the relationship

![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\(_3\)–xBi\(_{0.5}\)Li\(_{0.5}\)TiO\(_3\) ceramics.](image1)

![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\(_3\)–xBi\(_{0.5}\)Li\(_{0.5}\)TiO\(_3\) ceramics and (b) enlarged temperature dependency of dielectric constant in temperature range of 20–120°C.](image2)

| Composition \( x \) | \( P_r \) (\( \mu \)C/cm\(^2\)) | \( E_c \) (kV/cm) | \( d_{33} \) (\( \text{pC/N} \)) | Dielectric constant (1 kHz) | Bulk density (g/cm\(^3\)) |
|---------------------|---------------------|------------------|---------------------|--------------------------|--------------------------|
| 0                   | 18.8                | 14.2             | 187                 | 1159                     | 4.27                     |
| 0.01                | 18.8                | 15.0             | 256                 | 1332                     | 4.31                     |
| 0.02                | 29.5                | 16.7             | 272                 | 1556                     | 4.38                     |
| 0.04                | 25.8                | 16.8             | 188                 | 1248                     | 4.29                     |
| 0.06                | 34.7                | 16.7             | 156                 | 1203                     | 4.26                     |

**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\(_3\)–xBi\(_{0.5}\)Li\(_{0.5}\)TiO\(_3\) ceramics**

**Figure 4.** \( P-E \) hysteresis loops of \((1-x)\)K\(_{0.474}\)Na\(_{0.474}\)Li\(_{0.052}\)Nb\(_{0.948}\)-Sb\(_{0.052}\)O\(_3\)–xBi\(_{0.5}\)Li\(_{0.5}\)TiO\(_3\) ceramics.
between the $d_{33}$ values and dielectric constants of the $(1-x)$-KLNNS–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:

$$d_{33} = 2Q_{11}e_0e_rP_r,$$

where $Q_{11}$ is the electrostrictive coefficient, $e_0$ is the electric constant, and $P_r$ is the remanent polarization; however, $Q_{11}$ should not change significantly by doping. The $P_r$ values for the $(1-x)$-KLNNS–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 $(1-x)$KLNNS–xBLT ceramics. All of the ceramics have dense microstructures; the bulk density of the $(1-x)$KLNNS–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. Cubic-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**

$(1-x)$KLNNS–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 $(1-x)$-KLNNS–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 $(1-x)$KLNNS–xBLT ceramics increased with $x$, while $T_{0,T}$ decreased. The $d_{33}$ values of $(1-x)$KLNNS–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.

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