Piezoelectric Properties and Local Structure of (Na$_{0.50}$K$_{0.45}$Li$_{0.05}$)NbO$_3$–Ca(Zr$_{0.50}$Ti$_{0.50}$)O$_3$ Solid Solutions Produced by Malic Acid Complex Solution Method

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(1-x)(Na$_{0.50}$K$_{0.45}$Li$_{0.05}$)NbO$_3$–xCa(Zr$_{0.50}$Ti$_{0.50}$)O$_3$ (NKLN–CZT, x = 0–0.08) powders were synthesized by a malic acid complex solution method, and NKLN–CZT solid solutions were then fabricated using a conventional solid-state reaction technique. The piezoelectric properties of the resulting materials were measured, and the sample with x = 0.02 was found to exhibit a maximum longitudinal piezoelectric coefficient and radial electromechanical coupling factor of 238 pC/N and 35%, respectively. Based on both its piezoelectric properties and the results of a local structural analysis using high-energy X-ray diffraction, this sample has potential for use as a high-temperature, high-performance, lead-free piezoelectric material.

Key words: lead-free piezoelectric, alkali niobate, NKLN–CZT, local structure analysis

1. INTRODUCTION
Piezoelectric ceramics are widely used as functional elements in sensors and actuators in medical devices, communications devices, home electrical appliances, and automobile and aerospace applications. Due to its excellent piezoelectric properties (longitudinal piezoelectric coefficient d$_{33}$ of 300–421 pC/N, and radial electromechanical coupling factor k$_p$ of 58–65%), and its comparatively high Curie temperature T$_{c}$ of 260–365°C [1–4], lead zirconium titanate, Pb(Zr,Ti)O$_3$ (PZT), is a commonly used piezoelectric material. However, it contains a high fraction (60–70%) of lead, which is an environmentally harmful substance whose use is regulated by the RoHS and ELV directives. Therefore, the development of high-performance, lead-free piezoelectric materials has become an urgent issue, and research on such materials is being actively pursued.

One highly promising lead-free material is sodium potassium niobate, (Na,K)NbO$_3$ (NKN), which also exhibits a high T$_{c}$ of 410°C [5,6] and a comparatively large d$_{33}$ value of 100-160 pC/N. In 2004, Guo et al. reported that (Na,K,Li)NbO$_3$, which is produced by isovalent replacement of Li ions at the A-sites in the NKN perovskite structure, exhibited excellent piezoelectric properties and a high T$_{c}$ of $\geq$ 450°C [7]. Moreover, Nakai et al. revealed that (Na$_{0.50}$K$_{0.45}$Li$_{0.05}$)NbO$_3$ (NKLN) solid solutions produced by a malic acid complex solution method (MACSM) involving sintering at 950°C, which is somewhat lower than the temperature used in conventional processes, exhibited a d$_{33}$ of 151 pC/N, a k$_p$ of 32%, and a T$_{c}$ of 462°C [8]. Furthermore, Takada et al. reported that 0.99(Na$_{0.50}$K$_{0.45}$Li$_{0.05}$)NbO$_3$–0.01(Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.10}$Ti$_{0.90}$)O$_3$ (0.99NKLN–0.01BCZT) solid solutions produced by MACSM had excellent piezoelectric properties, with a d$_{33}$ of 177 pC/N and a k$_p$ of 33%. They proposed that measuring the degree of distortion of NbO$_6$ octahedra using high-energy X-ray diffraction (HEXRD) was an effective approach to developing high-performance piezoelectric materials with an ABO$_3$ perovskite structure [9].

In the present study, the fabrication of (1-x)(Na$_{0.50}$K$_{0.45}$Li$_{0.05}$)NbO$_3$–xCa(Zr$_{0.50}$Ti$_{0.50}$)O$_3$ (1-x)NKLN–xCZT, x = 0–0.08) solid solutions was attempted using CZT as an end member. This composition is also taken account of temperature stability including polymorphic phase boundary in addition to further improvement of piezoelectric properties. Piezoelectric measurements and local structural analysis of the fabricated NKLN–CZT solid solutions were performed using a piezoelectric evaluation system and HEXRD in order to investigate the relation between the piezoelectric and structural properties (average and local structures).

2. EXPERIMENTAL
NKLN–CZT powder was synthesized by the MACSM [10–12] using the following procedure. Reagent-grade niobium metal (Nb, $\geq$ 99.9%), sodium carbonate (Na$_2$CO$_3$, $\geq$ 99.9%), calcium carbonate (CaCO$_3$, $\geq$ 99.95%), calcium nitrate tetrahydrate
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[C(Na(NO3)2)·4H2O ≥ 99.9%], zirconium nitrate oxide dehydrate (ZrO(NO3)2·2H2O ≥ 99.0%) and TASFINE ((NH4)2[Zr(C2H5O2)2]·2H2O, Ti ≥ 18.9 mass%) were used as starting materials. Nb metal and DL-malic acid (C4H6O5) were dissolved in ammonia (1.9 mol/L) and hydrogen peroxide (4.4 mol/L) aqueous solutions at a molar ratio of [Nb] : [malic acid] = 1 : 5. The solution was water cooled without stirring for 48 – 72 h to dissolve the Nb completely. Na2CO3, K2CO3, Li2CO3, Ca(NO3)2·4H2O, ZrO(NO3)2·2H2O and TASFINE were also dissolved in distilled water with DL-malic acid, at a molar ratio of [Na, K, Li, Ca, Zr, Ti] : [malic acid] = 1 : 1 and subsequently heated at 70°C for 18 h with stirring to promote dehydration and polymerization between the complexes. After pyrolyzing the resulting gel at 400°C for 1 h, the materials were calcined at 850°C for 3 h in oxygen to remove the residual carbon. The calcined powders were dry milled using zirconia balls at 400 rpm for 5 min. After a given amount of acrylic binder was added to the ground powders, the resulting powders were pressed uniaxially under a pressure of 15 MPa to prepare disks with a diameter of 12.0 mm and a thickness of 1.2 mm, followed by cold isostatic pressing under a pressure of 200 MPAs. These green compacts were then fired at 1000 – 1060°C for 2 h in air by the powder-bed method [13] using calcined powders with the same composition as the compacts.

Phase identification was carried out by powder X-ray diffraction (XRD) with a diffractometer (Rigaku Ultima IV) using Cu-Kα radiation. Local structural analysis was performed at beamline BL14B1 of the Spring-8 facility, which is a bending-magnet beamline equipped with a double-crystal monochromator. After grinding the samples using an alumina mortar, the powders were encapsulated in a Kapton capillary. Powder HEXRD data were collected at 300 K with an incident X-ray energy of 60 keV. Both short- and long-range structural parameters were refined by the PDFFIT program using the atomic pair-distribution function (PDF) technique and by Rietveld refinement with the RIETAN-FP program. The cross-sectional microstructure of the NKLN – CZT samples was observed using field-emission scanning electron microscopy (FE-SEM; JEOL JSM7001F). The average grain size was determined by the linear intercept method from the FE-SEM images. The bulk density was measured using the Archimedean method. The disk-shaped samples with a diameter of approximately 10.0 mm were polished to a thickness of approximately 0.6 mm. Polished samples with silver electrodes were poled under a DC field of 30 – 50 kV/cm for 30 min at 130°C in a silicone oil bath. The room-temperature d33 values were measured using a PIEZO d33 meter (Chinese Academy of Sciences ZJ-4B). The Curie temperature Tc was determined based on the temperature dependence of the relative permittivity (εr) at RT – 500°C using an LCR meter (Agilent 4284A). Another piezoelectric parameter, kh, was measured at room temperature by the resonance-antiresonance frequency method on the basis of the JEITA standard (EM-4501), using an impedance analyzer (Hewlett-Packard 4194A).

3. RESULTS AND DISCUSSION

Figure 1 shows room-temperature XRD profiles for NKLN – CZT solid solutions with x = 0 – 0.08 (denoted by NKLN – CZT0, NKLN – CZT1, NKLN – CZT2, NKLN – CZT3, NKLN – CZT4, NKLN – CZT5, NKLN – CZT6 and NKLN – CZT8) produced by the MACSM. All solid solutions had a single-phase perovskite structure. This result suggests that NKLN – CZT0 and NKLN – CZT1 are orthorhombic, NKLN – CZT2 has a mixture of orthorhombic and tetragonal phases, and NKLN – CZT3-8 are tetragonal, and the phase transition of the crystal structure occurs from orthorhombic to tetragonal as the CZT content increases, as seen from the enlarged view in the vicinity of 2θ = 45–46° of Fig. 1(B).

Figure 2 shows measured and calculated XRD profiles for (a) NKLN – CZT0, (b) NKLN – CZT2 and (c) NKLN – CZT6 solid solutions determined by room-temperature HEXRD experiments. The Rf value represents the misfit between the calculated and observed XRD profiles, and is used to evaluate

![Fig. 1.](image1.png)

![Fig. 2.](image2.png)
dehydration and polymerization between the then fired at 1000 °C for 1 h, the materials were calcined at 850 °C for 18 h with stirring to promote the reliability of the model. The degree of reliability for the structure becomes higher as \( R_f \) approaches 0. The observed Bragg peaks for NKLN-CZT0 and NKLN-CZT2 were indexed by assuming a monoclinic structure with a space group \( Pm \), while that for NKLN-CZT6 was indexed by assuming a tetragonal structure with a space group \( P4mm \). The average structures for NKLN-CZT0 and NKLN-CZT2, and for NKLN-CZT6 are concluded to be monoclinic and tetragonal, respectively, based on the small \( R_f \) values of 1.06-1.12%. The relative densities of NKLN – CZT0, NKLN – CZT2 and NKLN – CZT6 calculated using the bulk densities and the above crystal structures were 89.8, 92.3 and 87.5%, respectively.

Figure 3 shows 200 diffraction peaks for NKLN-CZT0 measured by assuming a tetragonal structure using (a) HEXRD and (b) XRD. The peaks appear at different angles in each pattern because of the different X-ray wavelengths for HEXRD and XRD. The X-ray energy also affects the penetration depth. With HEXRD, it is possible to evaluate entire grains, whereas XRD can obtain information from at most a 0.2 μm depth from the surface. The HEXRD profile in Fig. 3(a) exhibits a relatively broad low-angle peak and a sharp high-angle peak. The broadness of the former peak suggests that the crystal structure is monoclinic, since this would produce a pattern consisting of two overlapping peaks at low angle, and a single peak at higher angle [14]. On the other hand, as seen in Fig. 3(b), the pattern obtained by normal XRD exhibits two diffraction peaks with the same width, indicating an orthorhombic crystal structure.

Figure 4(a) shows observed and calculated PDFs in the range \( 1.5 \leq r \leq 4.5 \) Å for NKLN-CZT2 at 300 K. Since the Rietveld and PDF analyses were carried out with the same dataset, the difference between the average and local structures can be extracted. The PDF calculated by assuming a rhombohedral structure is consistent with the observed PDF. Therefore, it can be concluded that the local structure of NKLN-CZT2 is rhombohedral. Similarly, based on PDF refinements for NKLN-CZT0 and NKLN-CZT6, the local structure is rhombohedral, as is clear from Fig. 4(b) [15], which shows observed PDFs in the range \( 1.2 \leq r \leq 4.2 \) Å for NKLN – CZT0, NKLN – CZT2 and NKLN – CZT6 at 300 K. It can be seen from the figure that the PDF peaks at approximately 4.0 and 3.4 Å correspond to the unit cell size in the perovskite structure and (Na,K,Li) – Nb bonds, respectively, and they appear at almost the same position for the three samples. Moreover, the first and second nearest-neighbor bond lengths correspond to the bonds between Nb and O at approximately 2.0 Å and (Na,K,Li) and O at approximately 2.8 Å, respectively. Especially, in the case of NKLN-CZT0, the Nb – O bonding state in NbO6 octahedral units of the \( AB_0_3 \) perovskite structure is expected to have a significant influence on the ferroelectric and piezoelectric properties because it is closely related to the lattice distortion. In general, when Nb is in an off-center position in the NbO6 octahedral unit, the first nearest-neighbor Nb – O bonds are known to give rise to a doublet peak reflecting shorter and longer bonds with lengths of about 2.0 Å [16-18]. For all samples, the Nb – O bonds produced split peaks as was previously reported for NKLN and 0.99NKLN-0.01BCZT. Since with increasing CZT content, the peak associated with Nb – O bonds gradually changes from a doublet to a broad singlet, a higher CZT

![Fig. 3. 200 diffraction peaks for NKLN measured by (a) HEXRD and (b) XRD.](image)

![Fig. 4. (a) Observed and calculated pair distribution function \( G(r) \) of NKLN – CZT2 and (b) \( G(r) \) for NKLN – CZT0, NKLN – CZT2 and NKLN – CZT6.](image)

![Fig. 5. Variations in \( d_0 \) and \( k_0 \) at room temperature for NKLN – CZT0-8 solid solutions as a function of CZT content.](image)

![Fig. 6. Cross-sectional FE-SEM images of (a) NKLN – CZT0, (b) NKLN – CZT2 and (c) NKLN – CZT6 solid solutions.](image)
content leads to a decrease in the lattice distortion within NbO₆ octahedral units.

Figure 5 shows the compositional dependence of $d_{33}$ and $k_p$ measured at room temperature for NKLN – CZT–0.8 solid solutions produced by the MACSM. Maximum values of 238 pC/N and 35%, respectively, were obtained for NKLN – CZT2, and these are approximately 1.8 and 1.3 times higher than those for NKLN – CZT0. Thus, we succeeded in improving the piezoelectric properties by the addition of CZT. From the results of Figs. 4(b) and 5, NKLN – CZT2 was found to have the largest distortion of the NbO₆ octahedra and to exhibit maximum $d_{33}$ and $k_p$ values. These results suggest that $d_{33}$ has a proportional relation with the distortion of NbO₆ octahedral unit.

Figure 6 shows cross-sectional FE-SEM images of NKLN – CZT0, NKLN – CZT2 and NKLN – CZT6 solid solutions. The average grain sizes estimated by the linear intercept method are 1.8, 1.2 and 1.1 μm, respectively. With increasing CZT content, the samples become more dense, and the grain size decreases and becomes more uniform. This can be attributed to the increase in the amount of Zr, which has low sinterability, in the NKLN – CZT solid solutions. The grains in NKLN – CZT0 are rounded in appearance, while those in NKLN – CZT2 and NKLN – CZT6 exhibit a cuboid shape with well-developed automorphic crystal faces. This suggests that volatilization of alkali metals (Na, K, and Li) at the $A$-sites in the perovskite structure was effectively restrained by partially substituting CZT for NKLN.

Table I lists the firing temperature, piezoelectric properties and Curie temperature for NKLN – CZT2, 0.99NKLN – 0.01BCZT and NKLN produced by the MACSM, and for 0.95K₀.₅Na₀.₅NbO₃·0.05CaTi₀.₉Zr₀.₁O₃ (0.95KNN·0.05CTZ) produced by the oxide mixing method (OMM) for comparison. The $d_{33}$ value for NKLN – CZT2 is approximately 1.3 and 1.6 times higher than those for 0.99NKLN·0.01BCZT [9] and NKLN [8], respectively. In addition, the MACSM allows a reduction of 50 – 130 °C in the firing temperature and yields an increase of 74 °C in $T_c$ compared with those for 0.95KNN·0.05CTZ [20] produced by the OMM. The reduction in firing temperature can be expected to lead to more green processing techniques. Also, the higher $T_c$ value than that for 0.95KNN·0.05CTZ makes NKLN – CZT2 suitable for automotive com-bustion pressure sensors operating at temperatures of ≥ 400 °C. Therefore, it can be concluded that NKLN – CZT2 solid solutions have potential for use as high-performance, lead-free piezoelectric materials for piezoelectric actuators and sensors.

Table 1. Comparison of firing temperature and physical properties of NKLN – CZT solid solutions with similar compositions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Firing temperature (°C)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKLN-CZT2</td>
<td>1000</td>
<td>238</td>
<td>416</td>
</tr>
<tr>
<td>0.99NKLN·0.01BCZT [9]</td>
<td>1000</td>
<td>177</td>
<td>426</td>
</tr>
<tr>
<td>NKLN [8]</td>
<td>950</td>
<td>151</td>
<td>462</td>
</tr>
<tr>
<td>0.95KNN·0.05CTZ [20]</td>
<td>1110–1190</td>
<td>203</td>
<td>342</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

$(1-x)(\text{Na}_{0.50}\text{K}_{0.45}\text{Li}_{0.05})\text{NbO}_{3}$ – $x\text{Ca(Zr}_{0.50}\text{Ti}_{0.50})\text{O}_{3}$ (NKLN – CZT, $x = 0–0.08$) powders were synthesized by a malic acid complex solution method, and NKLN – CZT solid solutions were then fabricated using a conventional solid-state reaction technique. Maximum $d_{33}$ and $k_p$ values of 238 pC/N and 35%, respectively, were obtained for NKLN – CZT2. Based on these piezoelectric properties and the results of a local structural analysis, it can be concluded that measuring the degree of distortion of NbO₆ octahedra using HXRD can be an effective approach to developing high-performance piezoelectric materials with an $ABO₃$ perovskite structure.

REFERENCES


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