Preparation and dielectric property of (Li_{0.12}Na_{0.88})NbO_3-based solid solutions

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Three solid solutions [(1–x) Li_{0.12} Na_{0.88} ] x NbO_3 (BT) x BaZrO_3 (BZ) and xK_0.5Ba_{0.5}Ti_0.5Nb_0.5O_3 (KBTN)] based on (Li_{0.12}Na_{0.88})NbO_3 (LNN) with the rhombohedral symmetry were prepared by conventional solid state reaction and their dielectric property was investigated. In the LNN-BT system in x ≤ 0.6 a secondary phase was observed as well as the perovskite-type phase and the pseudo-cubic and tetragonal single phases were observed in 0.7 ≤ x ≤ 0.94 and 0.95 ≤ x ≤ 1.0, respectively. In LNN-BZ and LNN-KBTN systems single phases of the compounds with the rhombohedral symmetry were formed in x ≤ 0.05. The length of the a-axis increased with content of BZ or KBTN and that of the c-axis was almost unchanged except x = 0.1 for LNN-BZ. The secondary phase with the tetragonal tungsten bronze-type (TTB) structure was observed in wide composition range of these solid solutions, and Li_{2}Ba_{2}Na_{2}M_{3}O_{15} (M: Ti, Zr) with the TTB-type structure was prepared and their crystal structure and dielectric property were investigated.

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1. Introduction

Lithium niobate, LiNbO_3, has the LiNbO_3-type structure with the rhombohedral symmetry and applies to the optical device. Sodium niobate, NaNbO_3, has the perovskite-type structure with the orthorhombic cell and exhibits antiferroelectricity. These niobates are important end members for the ternary solid solutions based on LNN and the secondary phase, Li_{2}Ba_{2}Na_{2}M_{3}O_{15} (M: Ti, Zr) with the TTB-type structure were investigated with the scan speed of 1°/min using silicon as an external standard. The structural refinement was carried out with the XRD data collected at intervals of 0.05 from 10.0 to 120.0 2θ at room temperature. The structure parameters were refined by the Rietveld method.

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2 Experimental

Three solid solutions [(1–x) Li_{0.12} Na_{0.88} ] x NbO_3 (LNN), BaZrO_3 (BZ) and K BTN were prepared by high temperature solid state reaction as follows. LNN was synthesized by heating a stoichiometric mixture (ball milling in ethanol with ZrO_2 ball) of Li_2CO_3, Na_2CO_3 and Nb_2O_5 (Kanto Kagaku Co. Ltd.) at 1000°C for 6 h and heating again at 1100°C for 7 h. BZ was synthesized by heating a stoichiometric mixture (in ethanol with a agate mortar) of BaCO_3 and Zr(NO_3)_4·2H_2O (Kanto Kagaku Co. Ltd.) at 1100°C for 3 h. KBTN was prepared by heating a stoichiometric mixture (in ethanol with a agate mortar) of BaCO_3 and KTNBO_3 at 1100°C for 3 h. KTNBO_3 was obtained by heating a stoichiometric mixture (in ethanol with a agate mortar) of BaCO_3 and KTNBO_3 at 1100°C for 3 h. BaCO_3 and KTNBO_3 were prepared by mixing powders with appropriate molar ratio at 950–1200°C for 6 h and by repeating of calcination. Li_{2}Ba_{2}Na_{2}M_{3}O_{15} (M: Ti, Zr) was synthesized by heating a stoichiometric mixture (ball milling in ethanol with ZrO_2 ball) of Li_2CO_3, BaCO_3, Na_2CO_3, TiO_2 [Zr(NO_3)_4·2H_2O] and Nb_2O_5 (Kanto Kagaku Co. Ltd.) at 1100°C for 6 h and heating again at 1200°C for 6 h.

The products were identified by X-ray powder diffraction pattern using monochromated Cu Kα radiation. The lattice constants were determined by the X-ray powder diffraction pattern with the scan speed of 1°/4°/min using silicon as an external standard. The structural refinement was carried out with the XRD data collected at intervals of 0.05 from 10.0 to 120.0 2θ at room temperature. The structure parameters were refined by the Rietveld method.
method using the program RIETAN-2000.\textsuperscript{13,14} Crystal structure was drawn with VESTA.\textsuperscript{15}

The sintering for measurement of dielectric property was carried out as follows. The powder sample was added 1 wt% PVA aqueous solution and pressed under uniaxially at 10 kN and the pellets were sintered at 1000–1200°C for 2 h. The surfaces of the sintered body were polished with emery paper and the electrode was formed using silver paste. Temperature dependence of dielectric constant and tanδ was measured at frequency of 1.0 kHz by using a Hioki-4277A LCZ meter.

3. Results and discussion

3.1 LNN-BZ and KBTN systems

Figures 1 and 2 show X-ray powder diffraction patterns of the products for LNN-BZ and LNN-KBTN solid solutions, respectively. Two end members, LNN and BZ contained a small amount of impurity phase and KBTN was obtained as a single phase and, and their lattice constants were \(a = 5.4744(3)\), \(c = 13.743(1)\) Å (hexagonal cell), \(a = 4.1962(7)\) Å and \(a = 4.0171(6)\) Å, respectively. These values of the former two compounds agreed well with the published values \(a = 5.47398(7), c = 13.7313(1)\) Å (LNN)\textsuperscript{9} and 4.19430(6) Å (BZ)\textsuperscript{11}). The X-ray powder diffraction pattern of KBTN\textsuperscript{12} can be indexed with the cubic cell which implies no ordering of the A and B sites, and the detail of the crystal structure will be reported elsewhere. In the LNN-BZ system the single phases of the rhombohedral and cubic phases were observed in \(x \approx 0.05\) and \(x \approx 0.9\), respectively. In the range of \(0.075 \leq x \leq 0.3\) a secondary phase appeared and in the range of \(0.4 \leq x \leq 0.8\) the cubic and rhombohedral phases coexisted.

The secondary phase found in wide range composition of these solid solution systems was identified with the TTB-type compounds and its crystal structure and dielectric property are described later. In the LNN-KBTN system the rhombohedral and cubic single phases were observed in \(x \leq 0.05\) and \(x \geq 0.8\), respectively and in the range of \(0.075 \leq x \leq 0.7\) the cubic and rhombohedral phases coexisted as well as the secondary phase. In these solid solutions the rhombohedral phases were observed...
Fig. 5. X-ray powder diffraction patterns of \((1-x)\text{LNN-}x\text{BT solid solution.}

Fig. 6. Lattice constants of pseudo-cubic and tetragonal phases and the \(c/a\) ratio of the tetragonal phase in LNN-BT solid solutions. The values of the standard deviation for the lattice constants were less than size of the marks.

Fig. 7. Temperature dependence of dielectric constant (left) and \(P-E\) hysteresis loops (right) for 0.03LNN-0.97BT and BT.

Fig. 8. X-ray powder diffraction patterns of \(\text{Li}_x\text{Ba}_{2-x}\text{NaNb}_{5-x}\text{Ti}_x\text{O}_{15}\) \((x = 0.2, 0.6, 0.1)\) and the simulated X-ray powder diffraction pattern of \(\text{Ba}_2\text{NaNb}_5\text{O}_{15}\) (ICSD \#53267).\(^{16}\)
in a narrow composition range ($x \leq 0.05$) and this is thought to be caused by the size difference of the A site cations. The lattice parameters of the rhombohedral phases are shown in Fig. 3. The lengths of the $a$-axis slightly increased with the value of $x$ though those of the $c$-axis were almost unchanged. Temperature dependence of dielectric constant for LNN and $P-E$ hysteresis loops for LNN and 0.975LNN-0.025KBTN are shown in Fig. 4. The Curie temperature of LNN was observed at about 400°C, however, no apparent peak was observed for LNN-KBTN and -BZ solid solutions. The $P-E$ hysteresis loop for 0.975LNN-0.025KBTN was much deformed than that of LNN, and those of the other LNN-KBTN and -BZ solid solutions indicated similar deformed $P-E$ hysteresis loops. These results suggest that the LNN-KBTN and -BZ solid solutions with the rhombohedral structure ($x \leq 0.05$) do not have ferroelectricity or exhibit high leakage current which may come from formation of deficiency caused by introduction of large A site cation.

### 3.2 LNN-BT system

Figure 5 shows X-ray powder diffraction patterns of the products for LNN-BT solid solution. In this system a secondary phase appeared even in $x = 0.01$ and was observed in $x \leq 0.6$. The pseudo-cubic and tetragonal single phases were observed in $0.7 \leq x \leq 0.94$ and $0.95 \leq x \leq 1.0$, respectively. The X-ray powder diffraction patterns of the products in $0.7 \leq x \leq 0.94$ were indexed with the cubic cell of $a \approx 4.007\text{ Å}$, however, the 200 diffraction peak was broadening when compared with the other peaks and the products in this region exhibited the $P-E$ hysteresis loops. These results suggest that the products in this composition range have the pseudo-cubic cell rather than cubic.
one. The lattice parameters of pseudo-cubic and tetragonal phases and the \(c/a\) ratio of the tetragonal phase in \(0.9 \leq x \leq 1.0\) are shown in Fig. 6. Temperature dependence of dielectric constant and \(P-E\) hysteresis loops for 0.03LNN-0.97BT and BT are shown in Fig. 7. The Curie temperature for 0.03LNN-0.97BT is lowering to 110°C and the value of the remanent polarization is drastically decreased when compared with that of BT. These behaviors correspond to decrease of the \(c/a\) ratio of 0.03LNN-0.97BT. In LNN-BT system a single phase solid solution over wide range composition was observed, however, their ferroelectric property was never superior to that of the end members.

### 3.3 Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (M: Ti, Zr)

In these solid solutions based on LNN an unexpected secondary phase was observed in wide composition ranges and it was found to be identified with the TTB-type compounds, Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (M: Ti, Zr). Figure 8 shows X-ray powder diffraction patterns of Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (\(x = 0.2, 0.6, 0.1\)) and the simulated X-ray powder diffraction pattern of Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (ICSD \#53267).\(^{16}\) The X-ray powder diffraction patterns of Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) were indexed with the tetragonal cell of the space group \(P4\text{bm}\). The single phase of the TTB-type compounds, Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (M: Ti, Zr) was found in \(x \leq 2.0\) for M=Ti and \(x \leq 0.0\) for M=Zr. The lattice constants of Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) (M: Ti, Zr) are shown in Fig. 9. The length of the \(c\)-axis was unchanged for M=Ti and increased for M=Zr, and that of the \(c\)-axis decreased for M=Ti and Zr. The Rietveld crystal structure refinement for Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) using X-ray powder diffraction pattern led to \(R_p = 15.3\) and \(R_f = 11.3\%\) with the assumption of the previous data (ICSD \#53267).\(^{16}\) The Ba and K atoms in Ba\(_2\)K\(_{2}\)Nb\(_5\)O\(_{15}\) with the TTB-type structure were proved to be disordered by single crystal X-ray diffraction analysis.\(^{17}\) The Rietveld crystal structure refinement with the assumption of disordering of Ba and Na atoms decreased to \(R_p = 12.7\) and \(R_f = 9.29\%\). The crystallographic site of Li atom was assumed from that in the Li included TTB-type niobates, Li\(_{4}\)K\(_2\)Na\(_{2}\)Ti\(_3\)O\(_{14}\)\(^{18}\) and K\(_3\)Li\(_2\)Nb\(_5\)O\(_{15}\)\(^{19}\). The atomic parameters of Li atom were not refined because of small values of X-ray scattering factor and occupancy. The observed and calculated X-ray diffraction patterns are shown in Fig. 10. The crystal data and the atomic parameters are summarized in Tables 1 and 2, respectively. The crystal structure of Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) is shown in Fig. 11. For the host compound, Ba\(_2\)Na\(_{0.8}\)Nb\(_5\)O\(_{15}\), the other crystal structure models\(^{20,21}\) based on the TTB-type structure were proposed as well as a simple TTB-type one. The detailed crystal structure of Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\) are shown in Fig. 12. The broad peak around 300-400°C in the temperature dependence of dielectric constant

### Table 1. Chemical data for Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\)

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>(\text{Li}<em>0.2\text{Ba}<em>2\text{Na}</em>{0.8}\text{Nb}</em>{4.8}\text{Ti}<em>{0.2}\text{O}</em>{15})</th>
</tr>
</thead>
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<tr>
<td><strong>Crystal System</strong></td>
<td>Tetragonal</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>(P4\text{bm}) No.100</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Lattice parameters ((\AA))</td>
<td>(a = 12.469(7), c = 3.9939(2))</td>
</tr>
<tr>
<td>Volume ((\AA^3))</td>
<td>620.95(6)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>994.58</td>
</tr>
<tr>
<td>Calculated density (g/cm(^3))</td>
<td>5.32</td>
</tr>
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</table>
| Hysteresis loop for \(L_i\)0.6Ba\(_2\)Na\(_{0.8}\)Ti\(_{0.2}\)O\(_{15}\) (right) and \(P-E\) hysteresis loop for \(L_i\)0.6Ba\(_2\)Na\(_{0.8}\)Ti\(_{0.2}\)O\(_{15}\) (left) for \(L_i\)0.6Ba\(_2\)Na\(_{0.8}\)Nb\(_5\)O\(_{15}\) are shown in Fig. 12. The broad peak around 300-400°C in the temperature dependence of dielectric constant

### Table 2. Structural parameters for Li\(_{0.2}\)Ba\(_2\)Na\(_{0.8}\)Nb\(_4.8\)Ti\(_0.2\)O\(_{15}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupancy</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U(\AA^2))</th>
</tr>
</thead>
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<tr>
<td>Ba(<em>0.87)Na(</em>{0.12})</td>
<td>4c</td>
<td>1.0</td>
<td>0.1719(2)</td>
<td>0.6716(3)</td>
<td>0.1998*</td>
<td>0.90(9)</td>
</tr>
<tr>
<td>Nb(<em>{0.96})Ti(</em>{0.04})</td>
<td>8d</td>
<td>1.0</td>
<td>0.2892(2)</td>
<td>0.4264(2)</td>
<td>0.697(3)</td>
<td>0.74(8)</td>
</tr>
<tr>
<td>Nb(<em>{0.96})Ti(</em>{0.04})</td>
<td>2b</td>
<td>1.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.705(6)</td>
<td>0.6(1)</td>
</tr>
<tr>
<td>Ba(<em>{0.25})Na(</em>{0.75})</td>
<td>2a</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.21(1)</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>Li</td>
<td>4c</td>
<td>0.1</td>
<td>0.62*</td>
<td>0.12*</td>
<td>0.1998*</td>
<td>1.5*</td>
</tr>
<tr>
<td>O1</td>
<td>8d</td>
<td>1.0</td>
<td>0.153(2)</td>
<td>0.506(1)</td>
<td>0.808(7)</td>
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</tr>
<tr>
<td>O2</td>
<td>4c</td>
<td>1.0</td>
<td>0.280(1)</td>
<td>0.780</td>
<td>0.66(1)</td>
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</tr>
<tr>
<td>O3</td>
<td>8d</td>
<td>1.0</td>
<td>0.355(1)</td>
<td>0.571(2)</td>
<td>0.824(7)</td>
<td>1.0*</td>
</tr>
<tr>
<td>O4</td>
<td>8d</td>
<td>1.0</td>
<td>0.207(1)</td>
<td>0.929(1)</td>
<td>0.239(8)</td>
<td>1.0*</td>
</tr>
<tr>
<td>O5</td>
<td>2a</td>
<td>1.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.78(4)</td>
<td>1.0*</td>
</tr>
</tbody>
</table>

*denotes fixed parameters.
is considered to correspond to the Curie temperature. The detail of ferroelectric property for Li$_{x}$Ba$_2$NaNb$_{5-x}$M$_x$O$_{15}$ (M: Ti, Zr) is under investigation.

4. Conclusion

In the LNN-BZ and -KBTN systems the single phases of the rhombohedral phases were observed in $x \leq 0.05$ and ferroelectricity disappeared by solid solution of BZ and KBTN to LNN. In LNN-BT system the pseudo-cubic and tetragonal single phases were observed in $0.7 \leq x \leq 0.9$ and $0.95 \leq x \leq 1.0$, respectively, however, their ferroelectric property was never superior to that of the end members. In three solid solutions, the TTB-type compounds, Li$_{x}$Ba$_2$NaNb$_{5-x}$M$_x$O$_{15}$ (M: Ti, Zr) were observed in wide composition ranges and they exhibited ferroelectricity with $T_c \approx 400^\circ C$.

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References