Piezoelectric Properties of Li-Doped (K_{0.48}Na_{0.52})NbO_3 Ceramics Synthesized Using Hydrothermally-Derived KNbO_3 and NaNbO_3 Fine Powders

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Using Hydrothermally-Derived KNbO_3 potassium niobate ceramic, which has been considered to gated intensively.1–18) It is well known that Li, Ta, and Sb doped ceramics (KNbO_3–NaNbO_3 (KNN) systems). 7–12) Saito et al. succeeded in realizing high-piezoelectric-constant ceramics whose piezoelectric constant were investigated, and their properties are referred to as their piezoelectric and ferroelectric properties.

2. Experimental Procedure

2.1 Hydrothermal synthesis of KNbO_3 and NaNbO_3 powders

As the raw materials for the alkaline niobate powders, NaOH pellets (97.0%, Kanto-Kagaku), KOH pellets (85.0%, Wako), and Nb_2O_5 powders (99.95%, Kanto-Kagaku) were used for the hydrothermal method. For the NaNbO_3 powders, 37.2 g of Nb_2O_5 and 70 mL of 9 N NaOH were mixed in a pressure vessel (Parr 4748). The pressure vessel was placed in a preheated oven at 210 °C and the reaction time was 6 h. To prepare the KNbO_3 powders, 140 mL of 8.8 N KOH and 9.18 g of Nb_2O_5 were mixed together in the pressure vessel (Taiatsu Techno TAF-SR Type). The hydrothermal process was carried out for 12 h at 210 °C in the preheated oven. After hydrothermal processing, each powder was filtered with Teflon filter paper (hole size: 0.45 μm) and washed thoroughly with 1 L of distilled water. After drying these powders for 1 h at 130 °C, these powders were weighted to be 45.0 g for NaNbO_3 and 11.2 g for KNbO_3. A neutralization process is important for the high-resistivity performance of the sintered ceramics(22) and involves the removal of ions, such as K^+ and Na^+, from the surface of the obtained powders. For the neutralization process, each powder was put into 300 mL of distilled water, and 0.01 mol/L HCl (high-grade Kanto-Kagaku) solution was added until the solution reached a pH of 7. The obtained powders were filtered again with filter paper of similar size and washed with 1 L of distilled water. The neutralized powders were then dried for 1 h at 130 °C. The crystal characteristics of the powders were analyzed using an X-ray diffraction (XRD) meter (Rigaku Miniflex II), and to observe their microstructures, scanning electron microscopy (SEM; JEOL JSM 5330LV) was performed. The particle size distributions were measured with a diffraction particle
analyzer (Shimadzu SLD-2100). To break the aggregates, the powders were treated ultrasonically for 40 min before measurement.

2.2 Sintering process
To synthesize \( [\text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3 \) ceramics, 4.000 g of K\( \text{NbO}_3 \), 3.946 g of Na\( \text{NbO}_3 \), and appropriate amounts of Li\( \text{NbO}_3 \) powders were weighed and placed in a 500 mL polyethylene jar. The Li\( \text{NbO}_3 \) powder was prepared by crushing the commercial Li\( \text{NbO}_3 \) (Yamaju-Ceramics Li\( \text{NbO}_3 \) wafer) single crystal using alumina mortar and pestle. The mixed powders were ball-milled for 12 h with 200 mL of ethanol using one hundred zirconia balls (diameter: 10 mm) and 100 g of zirconia balls (diameter: 2 mm). After ball milling, the mixed powder was filtered with Teflon filter paper (hole size: 0.45 \( \mu \)m) and dried. The powders were uniaxially pressed into disks that were 10 mm in diameter and 2 mm in thickness, which were then pressed by cold isostatic pressing (CIP) at 200 MPa. The obtained disks were sintered at temperatures between 1075 and 1125 \( ^\circ \)C for 2 h using a tubular furnace (Yamada Denki TSR-430). Before reaching the sintering temperature, the samples were soaked at 600 \( ^\circ \)C for 4 h. The heating and cooling rates were 150 and 100 \( ^\circ \)C/h, respectively. The density was measured by the Archimedes technique using a density meter (Alfamirage SD-200). The optimal sintering temperature for each composition was determined in order to realize the maximum density from various sintering temperatures.

2.3 Piezoelectric properties
In order to measure the longitudinal piezoelectric properties, the disk-shaped samples were cut using a diamond cutter (Musashino Denshi MPC-130) and their surfaces were polished with sandpaper (#2000) into appropriate shapes whose dimensions were 5.0 \( \times \) 1.3 \( \times \) 1.3 mm\(^3\). Poling treatments were carried out using a high-voltage supply device (Matsusada HARb-10P10) at 3.0 kV/mm in 100 \( ^\circ \)C silicone oil for 20 min. The electromechanical coupling factor \( k_{33} \) was calculated by the resonant–antiresonant method. The relative free permittivity \( \varepsilon_{33}/\varepsilon_0 \) was determined from the capacitance value at 1 kHz of the poled specimen. The stiffness \( c_{33} \) was calculated from the resonant frequency. With these parameters, the piezoelectric factor \( d_{33} \) was calculated according to the IEEE standard.\(^{19}\) To measure the dielectric properties, the sintered ceramic disks (diameter: around 8.5 mm; thickness: 1.3 mm) were polished with abrasive paper (#2000) and the gold electrodes were deposited on each side using a sputtering coater (Sanyu Electron Quick Coater SG-701). The dielectric permittivity and dielectric loss tan\( \delta \) were measured at 1 kHz from room temperature to 550 \( ^\circ \)C in a muffle furnace (Yamada Denki Y-1218-P) using an inductance–capacitance–resistance (LCR) meter (NF ZM2353) controlled by a personal computer.

3. Results and Discussion
Figures 1(a) and 1(b) show the SEM micrographs of the obtained powders. Figure 1(c) shows the particle size distributions of K\( \text{NbO}_3 \) and Na\( \text{NbO}_3 \). The average particle sizes were 1 \( \mu \)m for the K\( \text{NbO}_3 \) powder and 2 \( \mu \)m for the Na\( \text{NbO}_3 \) powder. Figure 2 shows the XRD patterns of the powders. From the results, it was confirmed that the powders had no impurities or secondary phases.

Figure 3(a) shows the XRD patterns of the \( [\text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3 \) ceramics with various \( x \) chemical components. The strong peaks are labeled with the Miller components. The strong peaks are labeled with the Miller indices of the KNN phase with the perovskite structure. Figure 3(b) shows the lattice parameters \( a \) and \( c \), which were calculated using the (001), (100), (002), and (200) peaks. When the chemical component \( x \) reached 0.06, the crystal phase changed from orthorhombic to tetragonal as the \( c/a \) ratio increased from 1.016 to 1.024.\(^{10}\) From this result, we considered that this chemical component corresponded to the MPB. Figure 4 shows the comparison between the SEM images of the \( [\text{Li}_{0.065}(\text{Na}_{0.52}\text{K}_{0.48})_{0.935}]\text{NbO}_3 \) and \( (\text{Na}_{0.52}\text{K}_{0.48})\text{NbO}_3 \)
ceramic surface. The optimum sintering temperatures of \([\text{Li}_i(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3\) and \((\text{Na}_{0.52}\text{K}_{0.48})\text{NbO}_3\) ceramics were 1085 and 1125 °C, respectively. According to Fig. 4(a), large grain appeared between small grains. In this study, we obtained highly dense \([\text{Li}_i(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3\) ceramics of 97.8% at a theoretical density of 4.51 g/cm³ using hydrothermal powder.

Figure 5 shows the admittance results for the longitudinal vibration mode of the \([\text{Li}_i(\text{Na}_{0.48}\text{K}_{0.52})_{0.935}]\text{NbO}_3\) ceramics. The minimum phase reached −60.5° and \(k_{33}\) of 0.51 was obtained. Figure 6 shows the piezoelectric properties of \([\text{Li}_i(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3\) ceramics. The piezoelectric constant \(d_{33}\) value reached a maximum at \(x = 0.065\), whose chemical component is close to the MPB found in XRD measurements.

The permittivity and \(\tan \delta\) changes for \([\text{Li}_i(\text{Na}_{0.48}\text{K}_{0.52})_{0.935}]\text{NbO}_3\) are shown in Fig. 7(a). There were two phase transitions, from orthorhombic to tetragonal and from tetragonal to cubic in the case of \([\text{Li}_i(\text{Na}_{0.48}\text{K}_{0.52})_{0.935}]\text{NbO}_3\). Figure 7(b) indicates the phase diagram of \([\text{Li}_i(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3\). The Curie temperature \(T_c\) of \([\text{Li}_i(\text{Na}_{0.48}\text{K}_{0.52})_{0.935}]\text{NbO}_3\) was 480 °C, which was 60°C higher than that of non doped \((\text{K}_{0.48}\text{Na}_{0.52})\text{NbO}_3\).16

Table 1 shows the properties of the obtained ceramics. By comparing the results with those of non doped \((\text{K}_{0.48}\text{Na}_{0.52})\text{NbO}_3\), the piezoelectric constant \(d_{33}\) and \(\varepsilon_{33}/\varepsilon_0\) were found to improve. However, the dielectric loss tangent \(\tan \delta\) was worse with \(\text{LiNbO}_3\) doping. To overcome this problem, other doping materials, such as Mn,12 are being examined.

4. Conclusions

In this study, \([\text{Li}_i(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}]\text{NbO}_3\) ceramics were synthesized by the hydrothermal method with NaNbO₃ and KNbO₃. Lithium doping was effective in obtaining excellent piezoelectric properties. The results were as follows: (1) The hydrothermal method enabled the synthesis of high-quality
powders; (2) Highly dense \(\text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}\text{NbO}_3\) ceramics were obtained using hydrothermal powder; (3) A phase transition from orthorhombic to tetragonal at around \(x = 0.06\) was found and the piezoelectric properties of the ceramics were improved. However, the \(\tan \delta\) of \(\text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}\text{NbO}_3\) was worse; (4) A high Curie temperature of 482 °C was realized by Li doping.

The measured piezoelectric properties of the \(\text{Li}_{0.065}(\text{K}_{0.48}\text{Na}_{0.52})_{0.935}\text{NbO}_3\) ceramics were as follows: the electromechanical coupling factors \(k_{31}\) and \(k_{33}\), the relative free permittivity \(\varepsilon_{33}'/\varepsilon_0\), the piezoelectric qualities factor \(d_{33}\), the mechanical quality factor \(Q_m\) (longitudinal), and the Curie temperature \(T_c\), were 0.51, 836 and 203 pC/N, 29, and 482 °C, respectively.

Acknowledgements

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\[\text{Fig. 7.} \quad (\text{Color online}) \ (a) \text{ Temperature dependence of the dielectric constant for the } \text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}\text{NbO}_3 \text{ ceramic. (b) Curie temperature (}T_c\text{) and ortho tetra transition temperature for } \text{Li}_x(\text{Na}_{0.52}\text{K}_{0.48})_{1-x}\text{NbO}_3.\]

\[\text{Table I. Piezoelectric and ferroelectric properties of the } \text{(K}_{0.48}\text{Na}_{0.52})\text{NbO}_3 \text{ and } \text{[Li}_{0.065}\text{(K}_{0.48}\text{Na}_{0.52})_{0.935}\text{]NbO}_3 \text{ ceramics.}\]

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{31})</th>
<th>(\varepsilon_{33}'/\varepsilon_0)</th>
<th>(\tan \delta) (%)</th>
<th>(\varepsilon_{33}) (GPa)</th>
<th>(Q_m) (longitudinal)</th>
<th>(d_{33}) (pC/N)</th>
<th>(T_c) (°C)</th>
<th>(\rho) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{(K}<em>{0.48}\text{Na}</em>{0.52})\text{NbO}_3)(^{17})</td>
<td>0.55</td>
<td>446</td>
<td>2.7</td>
<td>73</td>
<td>53</td>
<td>130</td>
<td>420</td>
<td>4.43</td>
</tr>
<tr>
<td>([\text{Li}<em>{0.065}\text{(K}</em>{0.48}\text{Na}<em>{0.52})</em>{0.935}]\text{NbO}_3)</td>
<td>0.51</td>
<td>837</td>
<td>7.8</td>
<td>46</td>
<td>29</td>
<td>203</td>
<td>482</td>
<td>4.41</td>
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