Effective oriented direction for enhancement of the piezoelectric properties of crystal-oriented (Li, Na, K) NbO₃ ceramics

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ABSTRACT

Crystal-oriented (Li, Na, K) NbO₃ ceramics (LNKN) were prepared by colloidal processing under a strong magnetic field, sintering, and subsequent electrical poling. The [001] direction of the LNKN particles with a tetragonal phase was oriented parallel to the magnetic field. By changing the direction of the magnetic field and machining, [001]-, [100]- and [110]-, and [101]-oriented LNKN powder compacts were formed. After phase transition during sintering, the crystal reorientation was further enhanced by domain switching under an electric field. The obtained [001]-, [100]- and [110]-, and [101]-oriented LNKN ceramics showed piezoelectric constants $d_{33}$ of 65 and 120 pm/V, 96 and 165 pm/V, 108 and 180 pm/V, respectively. In addition, $d_{33}$ and $d_{31}$ increased in the order of the [001]-, [001]- and [101]-, and [101]-oriented LNKN ceramics, indicating that the [101] orientation caused by domain switching is more effective for enhancing the piezoelectric properties compared to crystal orientation to the c-axis direction.

1. Introduction

(Li, Na, K) NbO₃ (hereafter, LNKN) ceramics are candidate lead-free piezoelectric ceramics that exhibit high performances and high Curie temperatures [1–9]. Their superior properties can be attributed to the composition of the polymorphic phase boundary and the textured microstructure. For example, Saito et al. reported a piezoelectric constant ($d_{33}$) of 300 pC/N for Ta- and Sbsubstituted LNKN ceramics and an enhanced $d_{33}$ of 416 pC/N due to crystal orientation to the c-axis through a texturing process [7].

For polycrystalline ceramics, crystal orientation is an effective strategy to improve the piezoelectric properties of ceramics [10–13]. That is, crystal direction is directly related to the enhancement of piezoelectric properties. For the alkali niobate system, Chen and Zheng [14,15] reported the tensor properties using a tetragonal (K, Na) NbO₃-based single crystal for the [001]-poled crystal with a single domain state. They found that the crystal orientation affects the dielectric constant, electromechanical coupling coefficients, elastic compliance constants, and piezoelectric constant. Their results showed that the piezoelectric property is superior along the [101] direction, but inferior along the [001] direction, indicating that the piezoelectric properties must be considered with respect to crystal orientation. In our previous study [16], the piezoelectric properties of LNKN ceramics were enhanced by texturing the microstructure of the crystal orientation along the [101] direction through the use of monoclinic-phase LNKN particles and magnetic-field-assisted shaping, sintering, and electrical poling. The $d_{33}$ of 236 pm/V was twice that of the one obtained for random LNKN ceramics (i.e. 127 pm/V). The effects of the electromechanical coupling coefficient and specific dielectric coefficient for crystal orientation in the [101] direction enabled the achievement of a higher piezoelectric constant.

For the manufacturing of the crystal-oriented polycrystalline ceramics, the piezoelectric properties must take into account crystal directions, its oriented distribution, and domain switching. X-ray diffraction (XRD) measurements have shown the poling axes of a perovskite crystal with a multi-domain structure such as LNKN ceramics to be along the [001], [100], and [101] directions [16–18]. In the previous study [16], the [101] and [110] directions were mainly oriented from particles with a monoclinic phase in the magnetic field and subsequent sintering. In the XRD patterns, other peaks such as [100] or [001] directions were detected to an extent. However, domain switching from [110] to [101] and from [100] to [001] occurred because of the electrical poling, which contributed to the enhancement of the piezoelectric property. Even in non-oriented ceramics, the [101] and [001] peaks were enhanced by electrical poling, contributing to the enhancement of the piezoelectric property. In this
In this sense, our aim is to examine the effects on the piezoelectric property of the orientation direction and their domain switching to an oriented structure.

The objective of this study is to fabricate crystal-oriented LNKN ceramics with [001] and [101] directions and evaluate the effect of the crystal orientation on the piezoelectric properties of LNKN ceramics. In this study, particles with a tetragonal phase and a composition of \( \text{Li}_{0.07}\text{Na}_{0.52}\text{K}_{0.41}\text{NbO}_3 \) are employed and the crystal-axis-oriented LNKN ceramics are obtained by colloidal processing under a magnetic field. It should be noted here that the crystal-oriented microstructures are developed by particle orientation under various magnetic field and subsequent sintering and electrical poling; that is, if the \( c \)-axis of the particles were oriented in the magnetic field, the crystal axes should change to the \( a \)- and \( c \)-axes orientations above the Curie temperature during sintering. Furthermore, the oriented microstructures are subsequently restored by electrical poling. The contribution of this work is to provide insights into the effect of the crystal direction on the piezoelectric properties of LNKN ceramics.

2. Experimental

\( \text{Li}_{0.07}\text{Na}_{0.52}\text{K}_{0.41}\text{NbO}_3 \) particles with a tetragonal-phase system were synthesized via a solid-state reaction method \([17,18]\). More specifically, reagent-grade \( \text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, \) and \( \text{Nb}_2\text{O}_5 \) (>99.5%) were weighed in accordance with the formula \( \text{Li}_{0.07}\text{Na}_{0.52}\text{K}_{0.41}\text{NbO}_3 \) and mixed by ball-milling using ethanol for 24 h. After drying using an evaporator, the mixture was calcined at 900°C for 3 h and the calcined powder was crushed by ball-milling for 24 h using ethanol. The morphology of particles was observed by scanning electron microscopy (SEM, JEOL JSM5310LV, Tokyo, Japan). The particle size distribution was determined by the sedimentation method (Sedigraph 5100, Micromeritics, USA). The powder was dispersed in deionized water with sodium hexametaphosphate as the dispersing agent. The crystal phase of the powder was confirmed through powder X-ray diffraction, XRD, measurements in the \( 2\theta \) range of 20–70° (Ultima IV, Cu-K\( \alpha \), Rigaku Co. Ltd, Tokyo, Japan). The LNKN powder was dispersed in isopropyl alcohol using polyethyleneimine (MW 10,000, Nacalai tesque, Kyoto, Japan) as a dispersant. The solid content in the slurry was 35 vol %. The obtained slurry was then ground by ball-milling with zirconia balls for 24 h.

Subsequently, the container filled with slurry was placed in the static vertical or horizontal magnetic field (10 T) of a superconducting magnet (TM10VH10, TOSHIBA, Tokyo, Japan) at 20°C until the slurry became dry. An additional portion of the slurry was then dried in the absence of the magnetic field to prepare a reference sample. For the vertical or horizontal static magnetic field, the mold sizes were of 25 mm diameter and 30 mm depth, and each mold contained 3 mL of slurry. The powder compacts were subjected to cold isostatic pressing at 200 MPa for 2 min, after which the samples were heat-treated under air at 450°C for 1 h to burn out the binder. The samples were then sintered in a magnesia container at 1000°C for 1 h under an oxygen atmosphere at a flow rate of 0.5 cm\(^3\)/min. The crystal orientations in the powder compacts and sintered ceramics were characterized by powder XRD analysis in the \( 2\theta \) range of 20–70°. The relative densities of the samples were measured by Archimedes’ method, and the microstructures were observed by SEM. To prepare the SEM samples, the polished samples were thermally etched at 1000°C for 20 min under air.

Figure 1 shows the prepared samples shaped under a strong magnetic field. Three types of samples were machined for measurement. Specifically, the samples were machined to have the correct shape

![Figure 1](image.png)

**Figure 1.** LNKN-oriented \( d_{31} \) and \( d_{33} \) bar cut to (a) \( a \)-axis resonance with \( c \)-axis poling, (b) \( c \)-axis resonance with \( a \)-axis poling, (c) 101-axis resonance with 101-axis poling.
for the $d_{31}$ resonance mode (1 mm × 3 mm × 12 mm) and the $d_{33}$ resonance mode (1.5 mm × 0.5 mm × 0.5 mm) according to the EM-4501 standard ($d_{31}$) [19] and the IEEE-standard ($d_{33}$) [20]. For the XRD analysis and the measurement of the dielectric constant, plate-like samples with dimensions of 1 mm × 4 mm × 4 mm were also prepared. If the c-axis of the LNKN was expected to be oriented along the magnetic field, then [001]-, [100]-, and [101]-oriented powder compacts would be obtained, as shown in Figure 1. After sintering, the oriented structure was changed via phase transition and by the effect of the direct electrical field. The samples were then polished using a polishing machine (MA-200, Musashino Denshi Inc.) equipped with diamond slurries. Gold electrodes were sputtered on both surfaces of the samples using sputtering apparatus (SC-701, SANYU Electron Co. Ltd.) and the resulting samples were heat-treated at 300°C for 20 min.

The poling treatment was conducted at 25°C using commercial apparatus (Type-FCE-1, TOYO Corp., Tokyo, Japan) and application of the resonance–antiresonance method. The samples were poled under an electric field of 4.0 kV/mm in silicone oil at 25°C for 30 min. The poled directions were expected to be the [001], [100], and [101] directions for each sample. For some samples, to characterize domain switching under an electric field, the plate samples were measured by XRD. The gold electrodes on these samples were removed by mechanical polishing.

The electromechanical coupling coefficients ($k_{31}$ and $k_{33}$) and the elastic compliance constants ($s_{33}^E$ and $s_{33}^D$) were measured by the resonance–antiresonance method based on EMAS-4100 standards and IEEE standards using an impedance analyzer (4294a, Agilent Technologies). Mechanical coupling coefficient $k_{31}$ was calculated by the following equation using the rectangular plate with length $l$, width $a$, and thickness $t$ as shown in Figure 1, respectively:

$$k_{31}^2 = \frac{\pi f_p}{\pi f_s} \frac{\rho}{\rho_s} \frac{t}{l} \frac{a}{l}$$

(1)

where $f_s$ and $f_p$ are resonance frequency and antiresonance frequency, respectively. The measured frequencies were 100 Hz to 100 MHz. The elastic compliance $s_{31}^E$ is obtained from resonance frequency $f_c$:

$$f_c = \frac{1}{2} \sqrt{\frac{1}{\rho s_{31}^D}}$$

(3)

where $\rho$ is the density (kg/m³). Here, the permittivity $\varepsilon_{33}^E$ was measured from capacitance $C_t$ at 1 kHz according to the JEITA-EM standard:

$$C_t = \frac{\varepsilon_{33}^E l a}{t}$$

(4)

Therefore, the piezoelectric constant $d_{31}$ was determined from $k_{33}$, $\varepsilon_{33}^E$, and $s_{31}^E$:

$$d_{31} = k_{31} \sqrt{\varepsilon_{33}^E \cdot s_{31}^E}$$

(5)

Similarly, the mechanical coupling coefficient $k_{33}$ was calculated by the following equation using the square prism test pieces with height $h$ as shown in Figure 1:

$$k_{33}^2 = \frac{\pi f_p}{\pi f_s} \frac{\rho}{\rho_s} \frac{t}{h} \frac{a}{h}$$

(6)

The elastic compliance $s_{33}^D$ was obtained from the antiresonance frequency $f_p$:

$$f_p = \frac{1}{2h} \frac{1}{\rho s_{33}^D}$$

(7)

The elastic compliance $s_{33}^E$ was obtained from $s_{33}^D$ and $k_{33}$:

$$s_{33}^E = s_{33}^D - k_{33}^2$$

(8)

The piezoelectric constant $d_{33}$ was determined from $k_{33}$, $\varepsilon_{33}^E$, and $s_{33}^E$ as follows:

$$d_{33} = k_{33} \sqrt{\varepsilon_{33}^E \cdot s_{33}^E}$$

(9)

3. Results and discussion

3.1. Powder characteristics

Figure 2 shows the synthesized LNKN particles, where almost-cubic shape particles can be observed due to their tetragonal crystal form. Figure 3 shows a particle size distribution of the sample measured by the sedimentation method, where the particle size is shown to range from 0.2 to 2.0 μm. The median particle size $D_{50}$ was 0.75 μm. In addition, Figure 4 shows the XRD pattern of the synthesized LNKN powder, where by comparison with the ICDD database (PDF 01-082-3272), the Miller indices were identified as those of a tetragonal phase and a monoclinic crystal phase (PDF 01-082-3273). Figure 5 shows microstructures of
the sintered LNKN ceramics shaped both in the presence and the absence of a magnetic field and subsequent sintering at 1000°C. The relative densities of both samples (oriented and random) were determined to be ~95%. The theoretical density is 4.48 g/cm³, which is calculated by composition ratio and lattice constants. In addition, the grains measured 10–15 μm in size and exhibited an equiaxed shape, with axes of approximately the same length.

3.2. Shaping with a vertical magnetic field and subsequent sintering

Figure 6 shows the XRD patterns of the powder compact shaped with a vertical magnetic field of 10 T, where the measured face is the horizontal plane in the middle of the sample. For comparison purposes, Figure 6 also shows the XRD pattern of the sample shaped in the absence of a magnetic field. For uniaxial crystal systems such as the tetragonal system, either the a- or c-axis is preferentially oriented along the magnetic field due to the anisotropic magnetic susceptibility. Preliminary findings show that the intensity of the c-face is slightly enhanced, demonstrating that the c-axis of the LNKN particles with the tetragonal crystal system is oriented to the magnetic field, and it is different from the [101] direction for the monoclinic phase [16]. However, the intensities of the (001), (101), and (110) planes remain high. This indicates that the crystal phases of these particles contain multi-domain structures. Here, the degree of orientation, \(F\), of the powder compact shaped with the magnetic field to the (00l) plane can be calculated using the following simplified equation [21]:

\[
F = \frac{P - P_0}{1 - P_0}
\]

where \(P = \sum I_{h0l}/\sum I_{hkl}\), \(P_0 = \sum I_{00l}/\sum I_{0kl}\), and \(I\) and \(I_0\) are the intensities of the XRD peaks in the 2θ range of 20–70° for the samples prepared in the presence and absence of a magnetic field, respectively. Thus, the degree of orientation was determined to be 0.22, and although this is a low value, subsequent processes such as sintering and electrical poling should contribute toward enhancing the orientation of the microstructures.

Figure 7 shows the XRD patterns of the sintered LNKN ceramics shaped in the presence and absence of the vertical magnetic field. As shown in Figure 7(a), i.e. the XRD patterns of the horizontal plane and the intensities of the (h00) planes, such as (100) and (200), are twice that of the (001) plane. In comparison, the sample shaped in the absence of a magnetic field (Figure 7(b)) exhibited small (001) peaks. During the phase transition from a tetragonal
to a cubic structure at the sintering temperature (i.e. at temperatures higher than the Curie temperature of ~500°C), the a- and c-planes in the tetragonal phase become the a-plane in the cubic structure. As the crystal structure returns to a tetragonal arrangement during cooling process to the 25°C, the c- and a-planes form in a 1:2 ratio. As a result, the high-intensity diffraction peaks of the (00l) planes in the tetragonal phase of the powder compact become peaks assigned to the (h00) and (00l) planes in the tetragonal phase after sintering. The degree of orientation of the sintered ceramics for the (h00) and (00l) planes was estimated according to Equation (10) with $P_0 = \Sigma l_0(h00) + l_0(00l)/\Sigma l(hkl)$, $P = \Sigma l(h00) + l(00l)/\Sigma l(hkl)$, and $l$ and $l_0$ values in the 2θ range of 20–70°. The degree of orientation of the sintered sample prepared with the vertical magnetic field was 0.30. Notably, an oriented structure was maintained and enhanced after sintering, similar to that reported in previous studies [13,16].

### 3.3. Shaping with a horizontal magnetic field and subsequent sintering

Figure 8 shows the XRD patterns of the powder compacts shaped using a horizontal magnetic field. The polished face is the middle plane in the sample, as shown in Figure 1(b), and the (h00) and (110) peaks are enhanced on the measured plane. This is due to the fact that the c-axis, perpendicular to [h00] and [110], is oriented to the horizontal magnetic field. Other peaks are also retained due to the multi-domain structures of the particles. According to Equation (10), the degree of orientation of the powder compact for the (100), (200), (110), and (220) planes was estimated to be 0.18.

Figure 9 shows the XRD patterns of the sintered samples shaped in the presence and absence of the horizontal magnetic field, where the (h00) and (00l) peaks were found to be concentrated. This observation indicates that the oriented structure is maintained even after the sintering-induced phase transition. The sintering process also renders the peaks of the (101) and (110) planes (2:1 ratio) more clearly defined compared to those observed in the XRD pattern of the powder compact shown in Figure 9. These planes seem to be oriented faces because they are derived from the (110) plane, which is oriented by shaping in the horizontal magnetic field. The calculated degree of orientation based on the intensity of the (h00), (00l), (101), and (110) peaks was approximately 0.23.
3.4. Machining of the sample shaped with the horizontal magnetic field and subsequent sintering

The (101)-oriented sample can be prepared from the sample shaped in the presence of a magnetic field and via subsequent sintering. Thus, Figure 10 shows the XRD patterns of the polished face of the sintered sample, which has a dihedral angle of 45° to the horizontal static magnetic field (Figure 1(c)). As the c-axis was oriented to the horizontal magnetic field, the intensity of the (101) plane of the polished face is clearly identifiable in the XRD patterns. As a result, the intensity of the (101) peak is slightly higher than those of the other peaks. The degree of orientation of the sintered sample prepared using the magnetic field was 0.05. Although this value is low, the XRD patterns of this sample differ from those obtained when evaluating random structures.

3.5. Effect of electrical poling

Figure 11 shows the XRD patterns of all sintered ceramic samples both before and after poling, where a direct electric field was applied normal to the plate samples in silicone oil. In the XRD patterns of the samples shaped by the application of a vertical magnetic field and subsequent sintering (Figure 11(a-c)), the (001) and (002) plane peaks exhibited increased intensities after poling, while the (100) and (200) plane peaks exhibited decreased intensities [25]. The degree of orientation, as calculated using Equation (10) according to the (001) and (002) plane peaks, was found to be 0.33. In addition, the intensity of the (101) peak increased from that prior to poling. In contrast, in the XRD patterns of the sample shaped by the application of the horizontal magnetic field and subsequent sintering, the (001), (002), and (101) planes were considerably enhanced after poling (Figure 11(b-1)) [26]. The degree of orientation obtained using Equation (10) according to the (001), (002), and (101) plane peaks was determined to be 0.26. In particular, the intensity of the (101) peak increased after poling. Furthermore, in the XRD pattern of the sintered [101]-oriented sample shown in Figure 11(c), the (101) plane peak exhibits an increased intensity, while the (110) plane...
peak exhibits a decreased intensity after poling. In addition, the (100) and (001) plane peaks decrease in intensity. The degree of orientation obtained using Equation (10) according to the (101) and (202) plane peaks was calculated as 0.2, which is higher than the value of 0.05 obtained prior to poling. These results indicate that poling treatment leads to reorientation; that is, the electric field induces a domain switch from the [100] domain to the [001] domain, and from the [110] domain to the [101] domain. Thus, mainly [001]-oriented ceramics are obtained from the [001]-axis-oriented powder compact, while the [001]- and [101]-oriented ceramics are obtained from the [001]-axis-oriented powder compact, and the [101]-oriented ceramics are obtained by cutting along the face with a dihedral angle of 45°. In addition, the (001) and (101) peaks increase in intensity upon the application of an electric field to the sample formed in the absence of a magnetic field, and domain switching also occurs.

3.6. Piezoelectric properties

Table 1 shows the material constants of the [001], [001], and [101]-oriented LNKN ceramics, in addition to those of the prepared LNKN ceramics with only poling treatment at 40 kV/cm. For the [001]-oriented LNKN ceramics, the relative permittivity $\varepsilon_{33} / \varepsilon_0$ along [001] is lower than those of the other axes. The results are similar to the one found in previous studies [27,28], thereby indicating that the domain switching to the [001] direction is difficult to occur. In contrast, for the [101]-oriented sample, the high $\varepsilon_{33} / \varepsilon_0$ indicates that the domain switch to the [101] direction does occur easily and that deformation is also facile. This result is considered to be derived from the structure of the perovskite crystal, and these tendencies were found in domain switching in a single crystal [29–31]. Thus, since the piezoelectric constants are calculated from $k$, $\varepsilon_{33} / \varepsilon_0$, and $s$, $d_{31}$, and $d_{33}$ increase in the order of the [001], [001] and [101]-, and [101]-oriented LNKN ceramics. In addition, the $d_{31}$ and $d_{33}$ values for the [001]-oriented LNKN ceramics are comparable to those of ceramics with a random structure, and which are actually oriented along the [001] and [101] directions due to poling. This result indicates that the contribution of the [101] orientation is key to enhancing the piezoelectric properties.

Figure 12 shows that the $d_{31}$ and $d_{33}$ are plotted to the frequency of [101]-oriented grains which are estimated from the ratio of (101) peaks to the sum of (100), (001), (101), (110), and (111) peaks in XRD patterns. The data contains the results in a previous study [16]. The $d_{31}$ and $d_{33}$ show

| Table 1. Oriented direction and electric properties of LNKN ceramics measured by resonance–antiresonance method as shown in Figure 1. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample set as shown in Figure 1 | Forming in mag, fl. | Sintered ceramics | After poling | $k_{31}$ (%) | $s_{11}^T$ (m²/N) | $\varepsilon_{33}$ / $\varepsilon_0$ | $d_{31}$ (pm/V) | $k_{33}$ (%) | $s_{33}^D$ (m²/N) | $s_{33}^E$ (m²/N) | $d_{33}$ (pm/V) |
| (a) [001] | [001],[100] | [001] | 27.6 | 11.6 | 550 | 65.6 | 40.0 | 15.3 | 18.3 | 120 |
| (b) [100],[110] | [001],[100], [001],[101] | [001] | 30.0 | 13.9 | 843 | 96.3 | 44.6 | 14.8 | 18.4 | 165 |
| (c) [101],[110] | [101] | [001] | 31.6 | 14.3 | 918 | 108 | 43.8 | 16.2 | 20.1 | 180 |
| W/O mag, fl. | [001],[101] | [001],[101] | 24.1 | 12.8 | 986 | 80.7 | 35.3 | 11.3 | 12.9 | 120 |

Figure 12. Dependence of the frequency of [101]-oriented grains on $d_{31}$ (circle) and $d_{33}$ (triangle). The frequency of [101]-oriented grains is estimated from the ratio of (101) peaks to the sum of (100), (001), (101), (110), and (111) peaks in XRD patterns. Black circles: this study, open circles: data in reference [16].
the dependency of [101] direction. If the experimental data is roughly extrapolated to 1 of the probability of [101] grains, the $d_{31}$ and $d_{33}$ of perfectly [101]-oriented ceramics can be estimated as 189 pm/V and 318 pm/V, respectively, for this material. This means that the $d_{31}$ and $d_{33}$ can be enhanced by optimizing the process conditions. Considering the results obtained herein and those presented in previous studies, it is apparent that the microstructural design, in which particles are oriented to the [101] direction using monoclinic particles in a magnetic field and subsequent sintering, and polarization in an electric field, is optimal for enhancing their piezoelectric properties.

4. Conclusion
Following the preparation of crystal-oriented (Li, Na, K) NbO$_3$ (LNKN) ceramics by colloidal processing under a strong magnetic field, sintering, and subsequent electrical poling, the properties of the resulting tetragonal-phase Li$_{0.07}$Na$_{0.55}$K$_{0.49}$NbO$_3$ particles were examined in terms of their orientation in shaping under a magnetic field. The [001] direction of the tetragonal-phase particles was oriented parallel to the magnetic field, and by altering the magnetic field and machining, [001]-, [100]-, and [110]-oriented LNKN powder compacts were shaped. The crystal-oriented structures were maintained even after phase transition during sintering, and the [001]-, [001]- and [101]-, and [101]-oriented structures were found to be enhanced by electric field polarization. In addition, high $e$ and $s$ values were obtained for the [001]- and [101]-oriented ceramics, where the [101]-oriented ceramic exhibited the highest values overall. This result is considered to be derived from the structure of the perovskite crystal. Furthermore, the piezoelectric constant increased in the order of the [001]-, [001]- and [101]-, and [101]-oriented structures, thereby indicating that the design of an oriented microstructure via magnetic-field-assisted shaping, sintering, and domain switching by the application of electrical poling is important, and an increase in the [101] orientation is significant for enhancing the piezoelectric properties of LNKN ceramics.

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