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Influence of Ta\textsuperscript{5+} content on the crystallographic structure and electrical properties of [001]\textsubscript{PC}-oriented (Li,Na,K)(Nb,Ta)O\textsubscript{3} single crystals

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A series of centimeter-sized lead-free piezoelectric Li\textsuperscript{+}, Ta\textsuperscript{5+}-modified (Na,K)NbO\textsubscript{3} single crystals with ABO\textsubscript{3} perovskite structure was successfully grown by the top-seeded solution growth method. Effective segregation of the elements was considered in order to further develop the growth of Li\textsuperscript{+}, Ta\textsuperscript{5+}-modified (Na,K)NbO\textsubscript{3} single crystals. Crystallographic structure and electrical behaviour along the [001]\textsubscript{PC} orientation were studied. X-ray diffraction, Raman spectroscopy and dielectric studies reveal that the increase of Ta\textsuperscript{5+} content reduces the orthorhombic-tetragonal phase transition. Bipolar and unipolar strain curves were investigated at 2 kV mm\textsuperscript{-1}. The highest bipolar and unipolar strains associated with a large signal piezoelectric constant of 368 pm V\textsuperscript{-1} were achieved for Li\textsubscript{0.02}Na\textsubscript{0.626}K\textsubscript{0.354}Nb\textsubscript{0.808}Ta\textsubscript{0.192}O\textsubscript{3}. The asymmetric bipolar strain curves were observed and related to the existence of internal bias fields induced by (V\textsubscript{s}−V\textsubscript{j}) defect dipoles, which were created during the crystal growth process.

1 Introduction

Lead-free piezoelectrics are currently studied and developed as alternatives to lead-based materials, such as Pb(Ti,Zr)O\textsubscript{3} (PZT), owing to environmental issues caused by the toxicity of lead.\textsuperscript{1,3} At present time, Na\textsubscript{0.3}B\textsubscript{0.7}TiO\textsubscript{3}-based,\textsuperscript{4,5} BaTiO\textsubscript{3}-based\textsuperscript{6,7} and Na,K\textsubscript{1−x}NbO\textsubscript{3}-based (KNN)\textsuperscript{9,10} lead-free piezoelectric materials exhibit the most promising properties, which could compete with those of PZT, as referenced by Saito et al. in 2004.\textsuperscript{9} Since then, the KNN-based systems have attracted much attention, whereby enhanced dielectric, ferroelectric and piezoelectric properties could be obtained in the vicinity of their Polymorphic Phase Transition (PPT) between the orthorhombic and the tetragonal phases.\textsuperscript{11,14} This phase transition, occurring in pure KNN at 200 °C, can be shifted to room temperature by chemical modifications, which is an effective way to improve electrical performance. Of particular significance are Li\textsuperscript{+}, Sb\textsuperscript{5+} and Ta\textsuperscript{5+} substitutions. For instance, a d\textsubscript{33} of about 230 pC N\textsuperscript{-1} with a planar mode coupling coefficient k\textsubscript{p} = 0.51, and a relatively high Curie temperature T\textsubscript{c} = 323 °C were reported in polycrystalline (Li,Na,K)(Nb,Ta)O\textsubscript{3} (KLNLTN) ceramic with 3 mol % Li\textsuperscript{+} and 20 mol % Ta\textsuperscript{5+}, while even higher properties were reported in textured (Li,Na,K)(Nb,Ta,Sb)O\textsubscript{3} (KLNSTN) polycrystalline ceramics with d\textsubscript{33} = 416 pC N\textsuperscript{-1} and a high planar mode coupling coefficient k\textsubscript{p} = 0.61.\textsuperscript{9,15} At this point it should be noted that Sb is a toxic element and should therefore be avoided.

The research on perovskite lead-based piezoelectric materials revealed that single crystals exhibit much higher piezoelectric properties than polycrystalline ceramics, due to their anisotropic properties and the absence of intergranular interactions.\textsuperscript{16} Recently, Huo et al.\textsuperscript{17} have grown a Mn-doped [Li\textsubscript{0.48}K\textsubscript{0.52}][Na\textsubscript{0.713}Ta\textsubscript{0.287}]O\textsubscript{3} single crystal with a piezoelectric coefficient d\textsubscript{33} = 630 pC N\textsuperscript{-1} and a very high longitudinal mode coupling coefficient k\textsubscript{33} = 0.95. Nevertheless, the exact composition was not reported. In general, lithium content is hardly measured due to the chemical stability of KNN-based crystals which are poorly dissolvable in acid solutions used for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis and due to its low content which is difficult to detect in a precise manner. Table 1 summarizes selected properties of pure and modified-KNN single crystals grown by various techniques such as Top-Seeded Solution Growth (TSSG), floating zone method (FZM), flux-Bridgman and solid state crystal growth (SSCG). As evident, only a few Li\textsuperscript{+} or/and Ta\textsuperscript{5+}-modified KNN-based single crystals with the orthorhombic-tetragonal phase transition temperature (T\textsubscript{O→T}) close to the room temperature were reported. The highest measured room temperature dielectric permittivity \(\varepsilon\) was 1015,\textsuperscript{18} while most \(\varepsilon\) values are lower than 800.

The KNN-based single crystal growth is affected by the difficulty in controlling stoichiometry of the crystals. On the one hand, the compositions of as-grown crystals are different from those of the initial liquid due to the thermodynamic segregation of the elements in KNN-based solid solutions.\textsuperscript{19,20} On the other hand, Prakasam et al.\textsuperscript{21} noted that the segregation phenomena for individual elements...
2 Experimental

2.1 Crystal growth

Crystal growth was carried out in a resistive heating furnace with a longitudinal thermal gradient smaller than 1 °C cm⁻¹. KNLNT single crystals were grown by the TSSG method with [001]-oriented KTaO₃ seeds and an excess of Li₂O and K₂O acting as a self-flux. Three growth attempts, labeled as KNLNT1, KNLNT2 and KNLNT3, with increasing Ta⁵⁺ contents, were performed with a constant initial Li⁻⁺ content. Moreover, a pure (Na,K)NbO₃ (KNN) single crystal has been grown as a reference with the same method. High purity powders of Na₂CO₃ (99.99 %, Aran Isles Chemical Inc.), Li₂CO₃ (99.99 %, Aran Isles Chemical Inc.), K₂CO₃ (99.99 %, Aran Isles Chemical Inc.), Nb₂O₅ (99.99 %, Aran Isles Chemical Inc.) and Ta₂O₅ (99.99 %, Aran Isles Chemical Inc.) were used as the starting materials to synthesize KNLNT by high temperature solid-state reaction. After mixing for 24 h, the powders were kept at 800 °C for 24 h and finally melted at a temperature above 1200 °C. The batch was held at a soaking temperature about 20 °C above the saturation temperature for 24 h and subsequently the [001]-oriented KTaO₃ seed was immersed into the saturated liquid solution with a stirring rate of 40 rpm for 24 h under air atmosphere. The rotation speed was set in the range from 10 rpm to 35 rpm and the cooling rate was fixed between 0.1 °C h⁻¹ and 0.5 °C h⁻¹.

2.2 Characterization

Chemical compositions were measured by combination of Electron Probe Micro Analysis (EPMA) and ICP-OES. Contents of each element, except Li⁺, were first measured locally on polished single crystals by EPMA using a Cameca SX-100 instrument operating at 20 keV and 20 nA. Complementary chemical analyses for all elements were performed by ICP-OES with a Varian 720-ES spectrometer. The solutions were prepared by dissolving 50 mg of crushed crystal in a 40 vol% HF solution at 180 °C with a 5-bar autocatalytic pressure. ICPOES and EPMA analysis results were averaged leading to a per-site-accuracy of 1 mol% for niobium and tantalum and 5 mol% for alkali elements, except lithium for which the accuracy is 0.24 mol%.

Powder X-ray diffraction (XRD) has been performed on crushed crystals using a PANalytical X'pert Pro MPD diffractometer with Cu Kα radiation and Bragg-Brentano geometry, while Kα₂ reflections were removed after the measurement. Laue backscattering method was used to orientate single crystals. Backscattered diffraction patterns were collected using a CCD-camera device (Photonic Science dual lens coupled X-rays Laue system) after a 3–5 min stationary crystal irradiation with polychromatic X-rays supplied by a molybdenum anticathode. Raman spectra were carried out on single crystals by using a LabRAM HR800 Raman spectroscope with the 633 nm radiation from a He-Ne laser at room temperature. Two sides of plate-like samples from all single crystals were covered with silver electrodes for electrical measurements. Temperature-dependent permittivity measurements were carried out on a HP 4284A impedance analyzer with Nabertherm furnace in the temperature range between 30 °C and 450 °C and a Novocontrol Alpha-A high frequency performance analyzer in the temperature range from -100 °C to 30 °C. Electric-field-induced-strain curves and ferroelectric hysteresis loops were measured by a modified Sawyer-Tower setup with a 10 µF reference capacitance and an optical displacement sensor (Pliftec, Inc.). Triangular electric field signals with a 10 Hz frequency were used.

![Fig. 1 View from (a) the top, (b) the side and (c) the bottom; (d) backscattered Laue diffraction pattern of one of as-grown (Li,Na,K)(Nb,Ta)O₃ single crystals.](image-url)
Table 2 Chemical compositions (EPMA, ICP-OES) and X-ray diffraction (XRD) structure of the as-grown KNLTN single crystals

<table>
<thead>
<tr>
<th>Element concentration C_x</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element content</td>
<td>Lattice parameters</td>
</tr>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Li (%)</td>
<td>Na (%)</td>
</tr>
<tr>
<td>KN0</td>
<td>0.0</td>
</tr>
<tr>
<td>KNLTN1</td>
<td>2.0</td>
</tr>
<tr>
<td>KNLTN2</td>
<td>2.0</td>
</tr>
<tr>
<td>KNLTN3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

3 Results and discussion

The KNLTN1 boule is depicted in Fig. 1 and looks overall milky. Fig. 1(d) provides the backscattered Laue diffraction pattern along [001]_LC orientation. Typical size of the as-grown KNLTN crystals was about 20 mm in diameter and about 5 mm in thickness.

Chemical compositions of the as-grown crystals are listed in Table 2. The alkali contents of KNLTN crystals on the A-site are close to each other, making it possible to compare crystal properties as a function of Ta\(^{5+}\) content. The slight concentration difference can be ascribed to the small change of the compositions in the initial solutions and the difficulty in keeping the same crystal growth conditions during every growth process such as the volatilization rate of the liquid solution with respect to the growth time.

The difference between the crystal composition and the concentration of the elements in the initial liquid solution can be described by the classical effective segregation coefficient \( k_{\text{eff}} \):20

\[
k_{\text{eff}} = \frac{1}{1 + \left( \frac{C_x}{C_{\text{eq}}} \right)^{\delta}} \times \frac{\delta}{\text{Volatilization}}
\]

where \( k_0 \) is the thermodynamic segregation coefficient, \( k_{\text{Volatilization}} \) is defined as the volatilization contribution factor to the effective segregation coefficient, \( C_x \) is the growth rate, \( \delta \) is the thickness of the solid-liquid boundary layer and \( D \) is the diffusion coefficient of the element in the liquid solution.

In the case of flux growth, the growth rate is very slow so \( v \) is considered to be close to zero. According to the fact that the volatilization of the solution during the growth process acts as an important factor on the effective segregation coefficients with respect to the growth time, the effective segregation coefficient is assumed as:

\[
k_{\text{eff}} \approx k_0 \times \frac{\delta}{\text{Volatilization}}
\]

Moreover, it is assumed that the equilibrium phases were reached during the flux growth process. At equilibrium state, no composition gradient can be detected in every phase. It is therefore assumed that both solid and liquid phases were uniform. Hence, the effective segregation coefficient \( k_{\text{eff}} \) can also be expressed as equation (3), arising from the well-known Scheil’s equation:20

\[
k_{\text{eff}} = \frac{C_S}{C_x(\infty)}
\]

Table 3 Segregation coefficients with respect to the element concentrations in liquid solution \( C_x(\infty) \)

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Nb</th>
<th>Ta</th>
</tr>
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<tbody>
<tr>
<td>KN0</td>
<td>2.38</td>
<td>0.93</td>
<td>1</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>KNLTN1</td>
<td>0.00</td>
<td>5.00</td>
<td>95.00</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>KNLTN2</td>
<td>0.18</td>
<td>3.31</td>
<td>0.40</td>
<td>0.89</td>
<td>4.69</td>
</tr>
<tr>
<td>KNLTN3</td>
<td>0.11</td>
<td>3.98</td>
<td>0.89</td>
<td>0.82</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Fig. 2 (a) Effective segregation coefficient \( k_{\text{eff}} \) of individual elements as a function of the concentration of the elements in the liquid solution \( C_x(\infty) \), and (b) \( k_{\text{eff}} \) of tantalum as a function of Ta molar concentrations in the liquid solution compared with that deduced from the pseudo-binary KNbO\(_3\)-KTaO\(_3\) phase diagram given by Reisman et al.30.

Please do not adjust margins
be inferred that $k_{\text{eff}}(\text{Ta}^{5+})>1$ leads to a strong depletion of Ta$^{5+}$ in the liquid solution and subsequently to a step by step decrease of its incorporation into the crystal as the growth proceeds. Using the same approach, the negative slope of the liquidus curve in the NaNbO$_3$-KNbO$_3$ system$^{31}$ leads to a reverse behaviour for K$: k_{\text{eff}}(\text{K}^+)1$ and an increasing potassium content along the growth direction. Changes of Ta$^{5+}$ and K$^+$ concentrations should be detected in principle along the growth directions of all crystals, and it therefore should affect their electrical properties due to compositional inhomogeneity. However, due to the small sample size, the concentration of elements has been considered as homogeneous for further electrical characterization.

Besides, the $k_{\text{eff}}$ values of lithium measured in the KNLTN crystals were found to be about 0.13, which is consistent with the previous work of Hofmeister et al.$^{32}$ where $k_{\text{eff}}(\text{Li}^+)$ in (Li$_x$K$_{1-x}$)(Nb$_{0.33}$Ta$_{0.33}$)O$_3$ Cu crystals was calculated to be approximately 0.125. Higher Li$^+$ content could lead to the formation of a secondary tetragonal-tungsten-bronze-type phase because of its limited solubility in KNN matrix, as previously reported in polycrystalline ceramics.$^{33,34}$ Therefore, the Li$^+$ contents in KNLTN single crystals are low and almost constant. Moreover, according to the work of Sadel et al.$^{35}$ the $k_{\text{eff}}(\text{Li}^+)$ in (Li$_{0.33}$Na$_{0.33}$)NbO$_3$ (LNN) crystals grown with NaBO$_3$ flux at 1147°C was calculated to be 0.25. The higher value, as compared to the present work, highlights the influence of volatilization of lithium-based compounds on its effective segregation. Note that substantial evaporation of lithium from the solution is reported to start at 1197 °C, which is in the working temperature range of KNLTN crystal growth. In the present work, compared with Sadel’s et al. work where the volatilization contribution of lithium is not so significant that $k_{\text{eff}} = k_0$ for LNN, we assume that the same thermodynamic segregation coefficient $k_0$ should be obtained for KNLTN due to the low lithium solubility in the perovskite matrix and the close lithium concentrations in the initial solution. Hence, $k_{\text{volatilization}}$ factor was estimated to be in the range from 1.39 to 2.27 for KNLTN.

Finally, it is worth mentioning that segregation trends of alkali elements in KNLTN are similar regardless whether two or three different ions are present on the A-site: $k_{\text{eff}}(\text{Li}^+)<1$, $k_{\text{eff}}(\text{K}^+)<1$ and $k_{\text{eff}}(\text{Na}^+)>1$. However, we note that $k_{\text{eff}}(\text{Na}^+)$ depends on the presence or the absence of lithium in the initial composition containing potassium. As evident, $k_{\text{eff}}(\text{Na}^+)$ should decrease monotonically with increasing concentration of Na$^+$ in the liquid solution.$^{31}$ In the present work, the initial content of sodium in KNNO is 5% and $k_{\text{eff}}(\text{Na}^+)=2.38$. Compared with the previous work of Reisman et al.$^{32}$, the $k_{\text{eff}}(\text{Na}^+)$ value is higher than 1 as expected. Nevertheless, $k_{\text{eff}}(\text{Na}^+)$ in KNNO single crystal should be higher than those of KNLTN2 ($k_{\text{eff}}(\text{Na}^+)=3.90$) and KNLTN3 ($k_{\text{eff}}(\text{Na}^+)=3.98$) where the initial content of sodium is 16.05%. The lower $k_{\text{eff}}(\text{Na}^+)$ in KNNO single crystal suggests a stronger competition between the three alkali elements regarding their incorporation into the A-site, as compared to the previous literature reports where only two ions were introduced into A or B sites.$^{30,31}$ It appears that the presence of lithium increases $k_{\text{eff}}(\text{Na}^+)$ in KNLTN crystals, as compared to systems without lithium.

XRD patterns obtained on crushed single crystals are presented in Fig. 3(a), while the calculated lattice parameters and the crystallographic structure are provided in Table 2. The reason for different room temperature structures of KNLTN single crystals is the variation of the Ta$^{5+}$ content. All samples are single phase with the perovskite structure and no secondary phase is observed. In order to emphasize the details of the crystal structure, the peaks of the 29 region around 45° are enlarged in Fig. 3(b). The ratio of intensities $I_{(022)O}/I_{(200)O}$ for the KNNO and KNLTN1 samples are close to 2, while for KNLTN2 and KNLTN3 the $I_{(022)O}/I_{(200)O}$ values are about 0.5. These ratios confirm that the phase evolves from orthorhombic to tetragonal with increasing the Ta$^{5+}$ content. This phenomenon was induced by the substitution of Nb$^{5+}$ (R=0.069 nm; CN6) ions by the slightly smaller Ta$^{5+}$ (R=0.068 nm; CN6) as previously reported for Ta$^{5+}$-modified KNN-based polycrystalline ceramics.$^{37,38}$

Fig. 4 shows the Raman spectra of [001)$_c$-oriented KNLTN single crystals. The BO$_6$ octahedron of the KNLTN system has six vibrational modes $1A_g(v_1)+1E_g(v_2)+2F_g(v_3, v_4)+2F_u(v_5, v_6)$, where $1A_g(v_1)+1E_g(v_2)$ are stretching modes and others are bending modes.$^{39}$ The Raman peaks between 100 cm$^{-1}$ to 200 cm$^{-1}$ correspond to translational modes of A-site cations and the rotations of the BO$_6$ octahedron. The modes in the range from 200 cm$^{-1}$ to 1000 cm$^{-1}$ come from the stretching and bending vibrations of the BO$_6$ octahedron.$^{39,40}$ With increasing Ta$^{5+}$ content, $v_2$ modes and the shoulders of $v_3$ modes become weaker, indicating a phase transition from the orthorhombic to the tetragonal phase. On the other hand, the pure KNN single crystal possesses a weaker $v_3$ and $v_4$ peaks.
v₄ mode, but a stronger v₁+ v₄ coupling mode and v₆ mode, as compared to KNLTN single crystals. The decoupling effect of v₁ and v₆ modes might result from the weaker interactions among the BO₆ octahedra after Li⁺ and Ta⁵⁺ substitutions.

Fig. 5(a) provides the temperature-dependent dielectric permittivity and losses of [001]₅c-oriented KNLTN single crystals at 10 kHz in the temperature range from -100 °C to 450 °C. Fig. 5(b) displays the phase transition temperatures with various Ta⁵⁺ contents, obtained from the dielectric measurements. The increase of Ta⁵⁺ content shifts both Tc and T₀-T to lower temperatures and the decrease could be fitted with linear equations (4) and (5):

\[
T_c(°C) = -(4.6 \pm 0.23) \cdot x \text{ (mol%)} + (436 \pm 4.7)
\]

\[
T_{0-T}(°C) = -(8.6 \pm 1.25) \cdot x \text{ (mol%)} + (204 \pm 26.19)
\]

where x is the Ta⁵⁺ mol% content. The rates of decrease for Tc and

\[ T_{0-T} \] are 4.6°C/mol%Ta and 8.6°C/mol%Ta, respectively. The shift of the phase transitions is attributed to the different electronegativity between Ta⁵⁺ and Nb⁵⁺ and the change of the Goldschmidt tolerance factor. ⁴¹ The latter can be expressed as,

\[
t = \frac{(R_A + R_D)}{\sqrt{2} (R_B + R_D)}
\]

where Ra, Rb, and Ro are the ionic radii of the corresponding perovskite sites. The tolerance factor decreases slightly after more B sites are occupied by the smaller Ta⁵⁺ and therefore the degree of lattice distortion is reduced with increasing Ta⁵⁺ content. Lower electonegativity of Ta⁵⁺ also weakens the B-O bond and therefore the ability of off-center movements of B-site ions during the cubic-tetragonal phase transition is decreased.

The influence of the K/Na ratio on the phase structure and electrical properties in polycrystalline (K,Na)NbO₃ ceramics was previously discussed by Zhang et al. ⁴² By changing the K/Na ratio from 70/30 to 30/70, both phase transition temperatures Tc and T₀-T decreased by less than 10 °C. Similar results were also obtained by others. ⁴³ ⁴⁴ It can therefore be concluded that the observed changes in Tc and T₀-T are predominantly related to the Ta⁵⁺ content and the influence of the K/Na ratio can be neglected. The relative dielectric permittivities E/E₀ of KNNO, KNLTN1, KNLTN2 and KNLTN3 at 30 °C are 107, 371, 964 and 231, respectively (Fig. 5(a)). KNLTN2 with 19.2% Ta⁵⁺ displays the highest dielectric permittivity at room temperature. Note also that this value is higher than the values from other literature reports (see Table 1).

Fig. 6 (a) depicts the bipolar electric-field-induced strain curves (S-E) of [001]₅c-oriented KNLTN single crystals. All samples exhibit typical butterfly-shaped S-E loops with evident negative strain (Sneg). ⁴⁵ The unipolar strain curves are depicted in Fig. 6(b). KNLTN2 presents the highest bipolar and unipolar strains at the maximum investigated E-field of 2 kV·mm⁻¹. This is due to the proximity of its T₀-T to the room temperature, whereby the energy barrier for polarization rotation decreases, leading to increased strain values.

The electric field corresponding to the largest absolute value in Sneg was taken as coercive field Ec. ⁴⁶ ⁴⁷ The asymmetry in the strain curves in Fig. 6(a) can be explained by the existence of an internal bias field Ei. The measured internal bias fields are approximately 20% of the corresponding coercive fields, as shown in Fig. 7(a). Although the origin of the internal bias fields in these samples is not clear, it might originate from the defects present in the as-grown single crystals. It is expected that A-site elements K⁺, Na⁺, and Li⁺ evaporate from the crystal during the high-temperature growth process, creating V_A’ vacancies. ⁴⁸ As a consequence, oxygen vacancies V_O’ were also created during the perovskite formation due to charge compensation. This could lead to the formation of (V_A’·V_O’) defect dipoles, ⁴⁹ which might be responsible for the observed internal bias field and the asymmetry of the bipolar S-E loops.

Coercive field Ec and internal field Ei were calculated by Equations (7) and (8) and are provided in Fig. 7(a).

\[
E_c = \frac{|E_x|}{2} + \frac{|E_y|}{2}
\]

\[
E_i = \frac{|E_x|}{2} + \frac{|E_y|}{2}
\]
where $E_C$ and $E_i$ represent the positive and negative coercive fields, respectively.

In Fig. 6(a), the maximum positive stain $S_{max}$ of [001]$_{pc}$-oriented KNLTN crystals was 0.06 % when Ta$^{5+}$ content reached 19.2 %. However, further increasing the Ta$^{5+}$ content up to 34.4 % leads to a significant decrease of $S_{max}$. KNLTN3 with 34.4 % Ta$^{5+}$ has a much larger absolute $S_{max}$ value compared to its $S_{max}$ value. This phenomenon was previously observed in 0.62Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-0.38PbTiO$_3$ (PMN-PT) single crystals. It has been explained that the depolarization field and internal stresses are too small to produce significant back switching of polarization in the absence of grain boundaries. However, studies of lead-based single crystals revealed that the shape of the bipolar strain curves depends on the crystallographic orientation and phase structure.50

Fig. 7(a) shows that the $E_C$ of KNLTN3 is more than 2 times higher than those of other crystals with lower Ta$^{5+}$ contents. Increasing the Ta$^{5+}$ content leads to a remarkable increase of $E_C$ due to the presence of the tetragonal phase. The large-signal converse piezoelectric constants $d_{33}^+$ of [001]$_{pc}$-oriented KNLTN single crystals is depicted in Fig. 7(b). The $d_{33}^+$ values of KNN0, KNLTN1, KNLTN2 and KNLTN3 measured at 2 kV-mm$^{-1}$ are 102, 221, 368 and 22 pm-V$^{-1}$, respectively. KNLTN2 crystal has the highest $d_{33}^+$ value due to the proximity of the $T_{0.7}$ to room temperature.

Fig. 8 displays the ferroelectric hysteresis loop of [001]$_{pc}$-oriented KNLTN2 single crystal measured at 2 kV-mm$^{-1}$ and 10 Hz. The remanent polarization is approximately 5 μC-cm$^{-2}$ and the coercive field is 0.80 kV-mm$^{-1}$, which is in agreement with the value 0.76 kV-mm$^{-1}$ obtained from the bipolar strain loop. Unfortunately the ferroelectric loops of other crystals could not be measured due to the high leakage currents. Piezoelectric, ferroelectric and dielectric parameters of all [001]$_{pc}$-oriented KNLTN single crystals with different Ta$^{5+}$ contents are summarized in Table 4.

Conclusions
Li$^+$-Ta$^{5+}$-modified KNN single crystals were grown by the TSSG method and centimeter-sized boules were successfully obtained. The effective segregation coefficients with respect to the initial concentrations of individual elements in the liquid were studied. Whereas Ta$^{5+}$ and Nb$^{5+}$ concentrations measured in the single crystals are consistent with literature, alkali elements (Li$^+$, Na$^+$ and K$^+$) are strongly dependent on each other regarding their incorporation into the lattice as well as the volatilization of the solution during the growth, particularly for Li$^+$. XRD and Raman measurements determine the transition from the orthorhombic to the tetragonal phase with increasing Ta$^{5+}$ content. A linear decrease of the phase transition temperatures ($T_C$ and $T_{0.1}$) was found with increasing the Ta$^{5+}$ content. The highest strain and large-signal piezoelectric coefficient of 368 pm-V$^{-1}$ were observed in the [001]$_{pc}$-oriented single crystal with 19.2 % Ta$^{5+}$, which was ascribed to the proximity of the $T_{0.7}$ to room temperature. In addition, the observed internal fields might be related to the presence of (V$^{4+}$-V$^{2+}$) defect dipoles created during the high-temperature crystal growth, and were found to contribute to the asymmetry of the bipolar strain curves.

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Fig. 7 (a) $E_C$, $E_i$, and (b) piezoelectric constant $d_{33}^+$ at 2 kV-mm$^{-1}$ of the [001]$_{pc}$-oriented KNLTN single crystals with different Ta$^{5+}$ contents.

Fig. 8 Ferroelectric hysteresis loop of [001]$_{pc}$-oriented KNLTN2 single crystal under 2 kV-mm$^{-1}$ and 10 Hz.
Table 4 Piezoelectric, ferroelectric and dielectric parameters of [001]c oriented KNLTN single crystals with different Ta5+ contents

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$d_33$ (pm V$^{-1}$)</th>
<th>$S_{py}$ (%)</th>
<th>$S_{eq}$ (%)</th>
<th>$S_{oa}$ (%)</th>
<th>$E_0$ (kV mm$^{-1}$)</th>
<th>$E_r$ (kV mm$^{-1}$)</th>
<th>$\varepsilon_r$</th>
<th>$T_{ST}$ (°C)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNLN0 (0)</td>
<td>102</td>
<td>0.020</td>
<td>0.002</td>
<td>0.020</td>
<td>0.44</td>
<td>0.040</td>
<td>107</td>
<td>3814</td>
<td>216</td>
</tr>
<tr>
<td>KNLTN1 (13.4)</td>
<td>221</td>
<td>0.024</td>
<td>0.005</td>
<td>0.044</td>
<td>0.52</td>
<td>0.017</td>
<td>371</td>
<td>5765</td>
<td>94</td>
</tr>
<tr>
<td>KNLTN2 (19.2)</td>
<td>368</td>
<td>0.060</td>
<td>0.008</td>
<td>0.074</td>
<td>0.76</td>
<td>0.172</td>
<td>964</td>
<td>5743</td>
<td>1</td>
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<tr>
<td>KNLTN3 (34.4)</td>
<td>22</td>
<td>0.004</td>
<td>0.008</td>
<td>0.004</td>
<td>1.17</td>
<td>0.065</td>
<td>231</td>
<td>7394</td>
<td>-75</td>
</tr>
</tbody>
</table>

* Obtained from bipolar strain curves.
* Obtained from unipolar strain curves.

References

41. V. M. Goldschmidt, Naturwissenschaften, 1926, 14, 477-485.
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