1. Introduction

Lead-free piezoelectrics are currently studied and developed as alternatives to lead-based materials, such as Pb(Ti,Zr)O₃ (PZT), due to environmental issues caused by the toxicity of lead. At the present time, Na₀.₃₂Bi₀.₆₂TiO₃-based, BaTiO₃-based, and NaₓK₁₋ₓNbO₃-based (KNN) lead-free piezoelectric materials exhibit the most promising properties, which can compete with those of PZT, as referenced by Saito et al. in 2004. 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. 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⁺, Sb⁵⁺, and Ta⁷⁺ substitutions. For instance, a d₃₃ of about 230 pC N⁻¹, with a planar mode coupling coefficient of kₚ = 0.51, and a relatively high Curie temperature of T_C = 323 °C were reported in a polycrystalline (Li,Na,K)(Nb,Ta)O₃ (KNLSTN) ceramic with 3 mol% Li⁺ and 20 mol% Ta⁵⁺, while even higher properties were reported in textured (Li,Na,K)(Nb,Ta,Sb)O₃ (KNLSTN) polycrystalline ceramics with d₃₃ = 416 pC N⁻¹ and a high planar mode coupling coefficient kₚ = 0.61. 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. Recently, Huo et al. have grown a Mn-doped [Li₀.₄₃(Na₀.₅₆K₀.₄₄)₀.₃₃]₀.₃₃(Nb₀.₇₁₃Ta₀.₂₈₇)O₃ single crystal with a piezoelectric coefficient of d₃₃ = 630 pC N⁻¹ and a very high longitudinal mode coupling coefficient of kₚ = 0.95. Nevertheless, the exact composition was not reported. In general, Li⁺ 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), the Floating Zone Method (FZM), flux-Bridgman and Solid State Crystal Growth (SSCG). As evident, only a few Li⁺ or/and Ta⁺-modified KNN-based single crystals with the orthorhombic–tetragonal phase transition temperature (T₀₋₁) close to the room temperature were reported. The highest measured room temperature dielectric permittivity ε_ᵣ was 1015, while most ε_ᵣ values are lower than 800.

The KNN-based single crystal growth is affected by the difficulty in controlling the stoichiometry of the crystals. On the...
one hand, the compositions of the 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, Prakasham \textit{et al.}\textsuperscript{21} noted that the segregation phenomena for individual elements in KNLTN single crystals were also induced by the preferential volatilization of some elements from the liquid solution during the growth process occurring at high temperature.

In the present work, several growth experiments of KNLTN single crystals were undertaken by the TSSG method and the segregation phenomena of Li\textsuperscript{+} and Ta\textsuperscript{5+} were examined. The influence of Ta\textsuperscript{5+} content on the structural and electrical properties is investigated and electric-field-induced bipolar strain curves of KNLTN single crystals are reported for the first time.

### 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\textsuperscript{-1}. KNLTN single crystals were grown by the TSSG method with [001]_c-oriented KTaO\textsubscript{3} seeds and an excess of Li\textsubscript{2}O and K\textsubscript{2}O acting as a self-flux. Three growth attempts, labeled as KNLTN, KNLTN : Mn, and KNLTN : Ta, were examined. The compositions of the as-grown crystals are given in Table 1. The backscattered diffraction patterns were collected using a CCD-camera device (Photonic Science dual lens coupled X-rays) for orientation of the single crystals. The backscattered diffraction patterns were collected using a CCD-camera device (Photonic Science dual lens coupled X-rays) for orientation of the single crystals.

#### 2.2 Characterization

Chemical compositions were measured by combination of Electron Probe Micro Analysis (EPMA) and ICP-OES. The amount of each element, except Li\textsuperscript{+}, was 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 a crushed crystal in a 40 vol% HF solution at 180 °C with a 5-bar-autogenous pressure. ICP-OES and EPMA analysis results were averaged leading to a per-site-accuracy of 1 mol% for Nb\textsuperscript{3+} and Ta\textsuperscript{5+} and 5 mol% for alkali elements, except Li\textsuperscript{+} 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 K\textsubscript{\alpha2} reflections were removed after the measurement. The Laue backscattering method was used to orient the single crystals. The backscattered diffraction patterns were collected using a CCD-camera device (Photonic Science dual lens coupled X-rays) for orientation of the single crystals. The backscattered diffraction patterns were collected using a CCD-camera device (Photonic Science dual lens coupled X-rays) for orientation of the single crystals. The Laue spectra were carried out on the single crystals by using a LabRAM HR800 Raman spectroscopy with 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 measurement of about 20 °C above the saturation temperature for 24 h and subsequently the [001]_c-oriented KTaO\textsubscript{3} 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\textsuperscript{-1} and 0.5 °C h\textsuperscript{-1}.
electrical measurements. Temperature-dependent permittivity measurements have been carried out by a HP 4284A impedance analyzer with a Nabertherm furnace in the temperature range between 30 °C and 450 °C and a Novocontrol Alpha-A high performance frequency 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 (Philtec, Inc.). Triangular electric field signals with a 10 Hz frequency were used.

3. Results and discussion

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

The chemical compositions of the as-grown crystals are listed in Table 2. The alkali contents of the KNLTN crystals on the A-site are close to each other, making it possible to compare crystal properties as a function of Ta5+ content. The slight concentration difference can be ascribed to the small volatility of the solution during the growth process such as the volatility 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 $k_{\text{eff}}^{20}$

$$k_{\text{eff}} = \frac{1}{1 + \left(\frac{1}{k_0} - 1\right) \exp \left(\frac{-\nu \delta}{D}\right)} \times \frac{1}{k_{\text{volatilization}}}$$  \hspace{1cm} (1)

where $k_0$ is the thermodynamic segregation coefficient, $k_{\text{volatilization}}$ is defined as the volatilization contribution coefficient to the effective segregation coefficient, $\nu$ 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 $\nu$ 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:

$$k_{\text{eff}} = k_0$$  \hspace{1cm} (2)

Moreover, it is assumed that the equilibrium phases were reached during the flux growth process. At the 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 (eqn 3), arising from the well-known Scheil's equation:

$$k_{\text{eff}} = \frac{C_s}{C_s(x)}$$  \hspace{1cm} (3)

where $C_s$ is the concentration of the element in the solid phase, i.e. in the single crystal, and $C_s(x)$ the concentration of the element in the liquid solution at the beginning of crystal growth.

### Table 2 Chemical compositions (EPMA, ICP-OES) and X-ray diffraction (XRD) structure of the as-grown KNLTN single crystals

<table>
<thead>
<tr>
<th>Phase</th>
<th>Li (%)</th>
<th>Na (%)</th>
<th>K (%)</th>
<th>Nb (%)</th>
<th>Ta (%)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNN0</td>
<td>0.0</td>
<td>11.9</td>
<td>88.1</td>
<td>100</td>
<td>0.0</td>
<td>3.963</td>
<td>5.681</td>
<td>5.707</td>
</tr>
<tr>
<td>KNLTN1</td>
<td>2.0</td>
<td>71.2</td>
<td>26.8</td>
<td>86.4</td>
<td>13.6</td>
<td>3.970</td>
<td>5.587</td>
<td>5.704</td>
</tr>
<tr>
<td>KNLTN2</td>
<td>2.0</td>
<td>62.6</td>
<td>33.4</td>
<td>80.8</td>
<td>19.2</td>
<td>3.984</td>
<td>3.984</td>
<td>4.127</td>
</tr>
<tr>
<td>KNLTN3</td>
<td>1.7</td>
<td>63.8</td>
<td>34.5</td>
<td>63.6</td>
<td>34.4</td>
<td>3.997</td>
<td>3.997</td>
<td>4.073</td>
</tr>
</tbody>
</table>

### Table 3 Segregation coefficients with respect to the element concentrations in liquid solution $C_s(x)$

<table>
<thead>
<tr>
<th>Phase</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Nb</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNN0</td>
<td>0.0</td>
<td>5.00</td>
<td>95.00</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>KNLTN1</td>
<td>0.18</td>
<td>3.31</td>
<td>0.40</td>
<td>0.89</td>
<td>4.69</td>
</tr>
<tr>
<td>KNLTN2</td>
<td>0.11</td>
<td>3.98</td>
<td>0.89</td>
<td>0.82</td>
<td>1.72</td>
</tr>
<tr>
<td>KNLTN3</td>
<td>0.13</td>
<td>3.90</td>
<td>0.52</td>
<td>0.85</td>
<td>3.84</td>
</tr>
</tbody>
</table>

Fig. 1 View from (a) the top, (b) the side and (c) the bottom; (d) backscattered Laue diffraction pattern of one of the as-grown (Li,Na,K)(Nb,Ta)O$_3$ single crystals.
Table 3 and Fig. 2(a) display the $k_{\text{eff}}$ of individual elements as a function of $C_L(\infty)$ for the four crystal growth attempts. The effective segregation coefficients $k_{\text{eff}}$(Li$^+$), $k_{\text{eff}}$(K$^+$), and $k_{\text{eff}}$(Nb$^{5+}$) are lower than 1, while $k_{\text{eff}}$(Na$^+$) and $k_{\text{eff}}$(Ta$^{5+}$) are higher than 1. Moreover, the increasing concentration of K$^+$ and Nb$^{5+}$ ions in the initial liquid solutions resulted in increasing $k_{\text{eff}}$ while the opposite trend is observed for Ta$^{5+}$ ions. This trend is directly related to the slope signs of the liquidus and solidus lines, as described by analogy in KNbO$_3$-KTaO$_3$ and NaNbO$_3$-KNbO$_3$ phase diagrams where two ions on the A or B site were considered. From the KNbO$_3$-KTaO$_3$ phase diagram, a positive slope of the liquidus curve induces a $k_{\text{eff}}$(Ta$^{5+}$) $>$ 1. In addition, Fig. 2(b) shows that the calculated $k_{\text{eff}}$(Ta$^{5+}$) in the crystal decreases with increasing Ta$^{5+}$ content in the liquid. The $k_{\text{eff}}$(Ta$^{5+}$) values of the present work are consistent with those calculated from the phase diagram, as presented in Fig. 2(a). In addition, it can be inferred that a $k_{\text{eff}}$(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 leads to a reverse behaviour for K$^+$: $k_{\text{eff}}$(K$^+$) $<$ 1 and increasing K$^+$ content along the growth direction. Changes in Ta$^{5+}$ and K$^+$ concentrations should be detected in principle along the growth directions of all crystals, and they therefore should affect their electrical properties due to compositional inhomogeneity. However, due to the small sample size, the concentration of the elements has been considered as homogeneous for further electrical characterization.

Besides, the $k_{\text{eff}}$ values of Li$^+$ measured in the KNLTN crystals were found to be about 0.13, which is consistent with the previous work of Hofmeister et al., where the $k_{\text{eff}}$(Li$^+$) in (Li$_2$K$_3$)$_2$(Nb$_{0.65}$Ta$_{0.35}$)$_2$O$_7$: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 the KNN matrix, as previously reported in polycrystalline ceramics. Therefore, the Li$^+$ contents in KNLTN single crystals are low and almost constant. Moreover, according to the work of Sadel et al., the $k_{\text{eff}}$(Li$^+$) in (Li$_{0.92}$Na$_{0.08}$)BO$_3$(LNN) crystals grown with NaBO$_2$ 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 Li-based compounds on its effective segregation. Note that substantial evaporation of Li$^+$ from the solution is reported to start at 1197 °C, which is in the working temperature range of the KNLTN crystal growth. In the present work, compared with the work of Sadel et al. where the volatilization contribution of Li$^+$ 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 Li$^+$ solubility in the perovskite matrix and the close Li$^+$ concentrations in the initial solution. Hence, the $k_{\text{volatilization}}$ factor was estimated to be in the range from 1.39 to 2.27 for KNLTN.

Finally, it is worth mentioning that the segregation trends of alkali elements in KNLTN are similar, regardless of whether two or three different ions are present on the A-site: $k_{\text{eff}}$(Li$^+$) $<$ 1, $k_{\text{eff}}$(K$^+$) $<$ 1 and $k_{\text{eff}}$(Na$^+$) $>$ 1. However, we note that $k_{\text{eff}}$(Na$^+$) depends on the presence or the absence of Li$^+$ in the initial composition containing K$^+$. As is evident, $k_{\text{eff}}$(Na$^+$) should decrease monotonically with increasing concentration of Na$^+$ in the liquid solution. In the present work, the initial content of Na$^+$ in KNN0 is 5% and $k_{\text{eff}}$(Na$^+$) = 2.38. Compared with the previous work of Reisman et al., the $k_{\text{eff}}$(Na$^+$) value is higher than 1 as expected. Nevertheless, $k_{\text{eff}}$(Na$^+$) in the KNN0 single crystal should be higher than those of KNLNT2 ($k_{\text{eff}}$(Na$^+$) = 3.90) and KNLNT3 ($k_{\text{eff}}$(5Na$^+$) = 3.98) where the initial content of Na$^+$ is 16.05%. The lower $k_{\text{eff}}$(Na$^+$) in the KNN0 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 the A or B sites. It appears that the presence of Li$^+$ increases $k_{\text{eff}}$(Na$^+$) in the KNLTN crystals, as compared to the systems without Li$^+$.

The 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 the KNLTN single crystals is the variation of the Ta$^{5+}$ content. All samples are in a 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 2θ region around 45° are enlarged in Fig. 3(b). The ratios of intensities $I_{202}$/$I_{200}$ for the KNN0 and KNLTN1 samples are close to 2,
while for KNLTN2 and KNLTN3 the $I_{100}/I_{200}$ values are about 0.5. These ratios confirm that the phase evolves from orthorhombic to tetragonal with increasing Ta$^{5+}$ content. This phenomenon was induced by the substitution of Nb$^{5+}$ with the slightly smaller Ta$^{5+}$ (R = 0.069 nm; CN6) ions by the BO$_6$ octahedra after Li$^+$ substitution. The former changes the ionic radii of the corresponding perovskite sites. The tolerance factor decreases slightly after more B sites are occupied by the smaller Ta$^{5+}$ and therefore the degree of lattice distortion is reduced with increasing Ta$^{5+}$ content. The lower electronegativity of Ta$^{5+}$ also weakens

\[ T_c(\degree C) = -(4.6 \pm 0.23)x(\text{mol}%) + (436 \pm 4.7) \] (4)

\[ T_{O-T}(\degree C) = -(8.6 \pm 1.25)x(\text{mol}%) + (204 \pm 26.19) \] (5)

where x is the Ta$^{5+}$ mol% content. The rates of decrease for $T_c$ and $T_{O-T}$ are 4.6 $\degree$C/mol% Ta and 8.6 $\degree$C/mol% Ta, respectively. The shift of the phase transitions is attributed to the different electronegativity$^3$ of Ta$^{5+}$ and Nb$^{5+}$ and the change in the Goldschmidt tolerance factor $t$. The latter can be expressed as,

\[ t = \frac{(R_A + R_B)}{\sqrt{2(R_A + R_O)}} \] (6)

where $R_A$, $R_B$, and $R_O$ are the ionic radii of the corresponding perovskite sites. The tolerance factor decreases slightly after more B sites are occupied by the smaller Ta$^{5+}$ and therefore the degree of lattice distortion is reduced with increasing Ta$^{5+}$ content. The lower electronegativity of Ta$^{5+}$ also weakens

Fig. 5(a) provides the temperature-dependent dielectric permittivity and losses of the [001]$_{PC}$-oriented KNLTN single crystals at 10 kHz in the temperature range from -100 $\degree$C to 450 $\degree$C. Fig. 5(b) displays the phase transition temperatures of various Ta$^{5+}$ contents, obtained from the dielectric measurements. The increase in Ta$^{5+}$ content shifts both $T_c$ and $T_{O-T}$ to lower temperatures and the decrease could be fitted with linear eqn (4) and (5):

![Fig. 3 XRD patterns of the crushed KNLTN single crystals. (a) Full range and (b) enlarged region of (002)$_I$/(200)$_O$ or (022)$_O$/(200)$_O$ peaks.](Image)

![Fig. 4 Raman spectra of the [001]$_{PC}$-oriented KNLTN single crystals with various Ta$^{5+}$ contents at room temperature.](Image)

![Fig. 5 (a) Temperature-dependent dielectric permittivity and losses of the [001]$_{PC}$-oriented KNLTN single crystals during heating from -100 $\degree$C to 450 $\degree$C (10 kHz), and (b) phase transition temperatures ($T_c$ and $T_{O-T}$) as a function of Ta$^{5+}$ content. The minor discontinuity at 30 $\degree$C is related to the use of different measurement setups for the low and high temperature range.](Image)
the B–O bond and therefore the off-center movement ability of the 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)NbO$_3$ 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 $T_C$ and $T_{O-T}$ 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 $T_C$ and $T_{O-T}$ are predominantly related to the Ta$^{5+}$ content and the influence of the K/Na ratio can be neglected. The relative dielectric permittivities $\varepsilon_r/\varepsilon_0$ of KNN0, KNLTN1, KNLTN2 and KNLTN3 at 30 °C are 107, 371, 964 and 231, respectively (Fig. 5(a)). KNLTN2 with 19.2% Ta$^{5+}$ displays the highest dielectric permittivity at room temperature. Note also that this value is higher than the values from most other literature reports (see Table 1).

Fig. 6(a) depicts the bipolar electric-field-induced strain curves ($S$–$E$) of the [001]$_{PC}$-oriented KNLTN single crystals. All samples exhibit typical butterfly-shaped $S$–$E$ loops with an evident negative strain ($S_{neg}$). The unipolar strain curves are depicted in (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 $T_{O-T}$ to 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 $S_{neg}$ was taken as coercive field $E_C$. The asymmetry in the strain curves in Fig. 6(a) can be explained by the existence of an internal bias field $E_i$. 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 defect dipoles present in the as-grown single crystals. It is expected that the A-site elements K$^+$, Na$^+$, and Li$^+$ evaporate from the crystal during the high-temperature growth process, creating $V_A$ vacancies.$^{46}$ 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.

The coercive field $E_C$ and internal field $E_i$ were calculated by eqn (7) and (8) and are provided in Fig. 7(a).

$$E_C = \frac{|E_C^+| + |E_C^-|}{2}$$

$$E_i = \frac{|E_C^+| - |E_C^-|}{2}$$

where $E_C^+$ and $E_C^-$ represent the positive and negative coercive fields, respectively.

In Fig. 6(a), the maximum positive strain $S_{pos}$ of the [001]$_{PC}$-oriented KNLTN crystals was 0.06% when the Ta$^{5+}$ content reached 19.2%. However, further increase in the Ta$^{5+}$ content up to 34.4% leads to a significant decrease in $S_{pos}$. KNLTN3 with 34.4% Ta$^{5+}$ has a much larger absolute $S_{neg}$ value compared to its $S_{pos}$ value. This phenomenon was
previously observed in 0.62Pb(Mg1/3Nb2/3)O3–0.38PbTiO3 (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.

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-size converse piezoelectric constants $d_{33}^*$ of the [001]$_{pc}$-oriented KNLTN single crystals is depicted in Fig. 7(b). The $d_{33}^*$ values of KNNO, KNLTN1, KNLTN2 and KNLTN3 measured at 2 kHz are 102, 221, 368 and 22 pm V$^{-1}$, respectively. KNLTN2 crystal has the highest $d_{33}^*$ value due to the proximity of the $T_{o-T}$ to room temperature.

Fig. 8 displays the ferroelectric hysteresis loop of the [001]$_{pc}$-oriented KNLTN2 single crystal measured at 2 kHz 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. The piezoelectric, ferroelectric and dielectric parameters of all [001]$_{pc}$-oriented KNLTN single crystals with different Ta$^{5+}$ contents are summarized in Table 4.

### Table 4 Piezoelectric, ferroelectric and dielectric parameters of the [001]$_{pc}$-oriented KNLTN single crystals with different Ta$^{5+}$ contents

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$d_{33}^*$ (pm V$^{-1}$)</th>
<th>$S_{pos}$ (%)</th>
<th>$S_{neg}$ (%)</th>
<th>$S_{max}$ (%)</th>
<th>$E_C$ (kV mm$^{-1}$)</th>
<th>$E_i$ (kV mm$^{-1}$)</th>
<th>$\varepsilon_r$</th>
<th>$\varepsilon_{max}$</th>
<th>$T_{o-T}$ (°C)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNNO (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>
<td>437</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>
<td>367</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>
<td>352</td>
</tr>
<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>
<td>275</td>
</tr>
</tbody>
</table>

$^a$ Obtained from bipolar strain curves. $^b$ Obtained from unipolar strain curves.

Conclusions

Li$^+$ and 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 the literature, the alkali elements (Li$^+$, Na$^+$ and K$^+$) are strongly dependent on each other with regards to 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 in the phase transition temperatures ($T_o$ and $T_{o-T}$) was found with increasing 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 $T_{o-T}$ to room temperature. In addition, the observed internal fields might be related to the presence of $\{V_o^+ - V_o^-\}$ defect dipoles created during the high-temperature crystal growth, and were found to contribute to the asymmetry of bipolar strain curves.

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