Textured, lead-free piezoelectric ceramics with high figure of merit for energy harvesting

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Abstract
Piezoelectrics are key materials for energy conversion, for example in ultrasound transducers and energy harvesters. This work presents the synthesis and characterization of the lead-free piezoelectric composition (K0.06(Na0.32Nb0.48)0.94)(Nb0.71Ta0.29)O3 doped with 0.25 mol% Mn (KNNLT′M) as textured ceramics. Templated grain growth from NaNbO3 platelet templates aligned by tape casting was used to introduce texture, and after sintering for 14 h at 1100°C this produced up to 84% (100)pol grain orientation. After high temperature poling, the textured samples exhibit reasonable piezoelectric response with d33 values up to 171 pC N−1, and k3 values of 0.35, which is 71% of the response obtained in a single crystal of the same composition. The low relative dielectric permittivity of the textured and high temperature-poled KNNLT′M (ε33/T/ε0 down to 182) resulted in record-high piezoelectric voltage constants (g33 up to 101 mV m N−1), higher than previously reported for lead-free piezoelectric ceramics, as well as very high figure of merit (d33g33 up to 16 × 10−12 m3 J−1) for non-resonant energy harvesting in compression. These numbers make the textured KNNLT′M materials of this work highly promising for use in thickness mode, non-resonant piezoelectric energy harvesters.

1. Introduction
Piezoelectric materials are, due to their coupling of mechanical and electrical energy, applied in a vast range of technological devices. Important examples are ultrasound transducers for medical diagnostics and treatment, actuators for precise micropositioning, accelerometers and flow sensors [1]. An upcoming application is as energy harvesters, where waste mechanical energy from e.g. ambient vibrations or human motion are converted to electrical charge, such that this charge can power a sensor and transmit information [2]. The required material properties for piezoelectric energy harvesters depend strongly on the mode of operation. This could either be harvesting at the resonant frequency of the piezoelectric material, typically at very high frequencies, where the figure of merit often is given as k2Qm, where k is the electromechanical coupling coefficient and Qm, the mechanical quality factor [3, 4]. While such operation can harvest high amounts of energy, it requires a high frequency energy source and a harvester with a perfectly matched resonance frequency. Non-resonant harvesting on the other hand, is more suitable for low frequency, wide bandwidth harvesters. The figure of merit for such an operation mode is often given as d33g33, where d33 is the longitudinal piezoelectric charge constant and g33 is the piezoelectric voltage constant, also expressed as g33 = d33/(ε33/Tε0), where ε33/T is the relative permittivity of the piezoelectric at constant stress and ε0 is the permittivity of free space [3, 4].

The great majority of the high-performing, ferroelectric ceramics applied as piezoelectrics are based on lead oxides, due to their outstanding performance, low cost and high flexibility for tailored properties through chemical modification [5]. However, the toxicity of lead and the risk of lead exposure to human and
environment during production, use and disposal, has caused bans on the use of lead and an intense research interest in lead-free piezoelectrics [6, 7]. Wide-spread use of piezoelectrics for energy harvesting in consumer devices and remote locations, where the prospects of proper materials recycling are poor, calls for lead-free alternatives. Saito et al. showed in 2004 that a preferential grain orientation (texture) could significantly improve the piezoelectric response of K0.5Na0.5NbO3 (KNN)-based lead-free piezoelectrics, to the level where they compete with the traditional lead zirconate titanate piezoelectric ceramics [8]. Following this breakthrough work, many studies have been published on textured piezoelectrics, and recently texture has been found especially suitable to improve the energy harvesting performance of both lead-free and lead-based piezoelectrics [9–11].

The motivation for this work is to explore the process of introducing texture and the resulting performance of the textured ceramics of a high-performing lead-free piezoelectric composition recently published [12] in the form of a single crystal: (Li0.06(K0.52Na0.48)0.94)(Nb0.71Ta0.29)O3 doped with 0.25 mol% Mn (KNNLTM). We show that the reasonable piezoelectric charge constant, combined with the very low dielectric permittivity results in materials with extremely high voltage constants and a high figure of merit for energy harvesting, and discuss the effects of texture on a wide set of parameters.

2. Method

2.1. Textured ceramic fabrication

Textured KNNLTM was made by tape casting and templated grain growth. The templates were platelet-shaped (100)-oriented NaNbO3 made by molten salt synthesis and conversion according to [13]. In the first step, Bi2.5Na3.5Nb5O18 platelets were prepared by reacting stoichiometric amounts of Bi2O3 (99.8%, Johnson Matthey, London, UK), Nb2O5 (99.9%, Alfa Aesar, Kandel, Germany) and Na2CO3 (99.5%, Sigma Aldrich, St. Louis, Missouri, US). The reactants were mixed with NaCl (99.5%, Sigma Aldrich, St. Louis, Missouri, US) and heated to 1080 °C, hold time 6 h, with heating and cooling rates of 200 °C h⁻¹. The Bi2.5Na3.5Nb5O18 plates were reacted with excess Na2CO3 (twice of the stoichiometric amount required for the reaction) for 6 h at 980 °C to obtain NaNbO3 (100)-oriented plates. In both molten salt steps, the weight of the salt was 1.5 times the weight of the reactants.

Tape casting slurries were made after a previously developed recipe [14]. KNNLTM submicron-sized powder (Cerpotech A/S, Norway) was milled for 72 h with ethanol (solvent) and polyvinylpyrrolidone (Sigma Aldrich, Germany) (dispersant). Then, polyvinyl butyral (Sekisui Chemical Ltd, USA) (binder) and Pycal 94 (Tapecasting Warehouse Inc., USA) (plasticizer) was mixed into the slurry slow rolling for 16–24 h. The slurry was filtered and evacuated immediately before tape casting. When fabricating textured KNNLTM, NaNbO3 templates corresponding to 10 wt% of the KNNLTM was added to the slurry after filtering, but before evacuation. The slurries were mixed in by first 10 min magnetic stirring, followed by 10 min in an ultrasonic bath. The tape caster doctor blade was set to an opening of 200–400 µm and a casting speed of 20 cm min⁻¹ was used. Drying was performed in air for 16–24 h. The dried tapes were laminated at 110 °C, in order to increase the thickness up to ~1 mm. The thermal program for binder burnout and sintering was as follows: ramp up with 15 °C h⁻¹ to 600 °C, isothermal hold for 4 h, ramp up with 60 °C h⁻¹ to 1060 °C–1100 °C, isothermal hold for 2–14 h and ramp down with 200 °C h⁻¹ to 25 °C. A chamber furnace with stagnant air was used, and the samples were placed on top of an alumina substrate.

2.2. Characterization

Scanning electron microscopy (SEM) (Hitachi TM3000, Hitachi High-Technologies Europe GmbH, Germany) was used to study the microstructure of templates and sintered ceramics. The volume of templated grains was found by image analysis with ImageJ (version 1.48v, Wayne Rasband, National Institute of Health, USA). X-ray diffraction (XRD) (Bruker D8, Bruker, USA) was used to investigate crystal structure and phase purity, as well as texture based on Lotgering equation [15] (intensity of the {000} reflections relative to the other reflections). The density of sintered samples was evaluated by Archimedes’ method in isopropanol.

Samples sintered for 1100 °C for 14 h were used for ferro-, piezo- and dielectric characterization. Ag paste (product AGG3790, Agar Scientific, UK) was painted on either side for electrical contact. The ferroelectric response was measured with a TF2000 (aixACCT, Germany) by applying bipolar triangular electric field loops of an amplitude up to 3 kV mm⁻¹ at a frequency of 1 Hz. Three loops were applied at 3 kV mm⁻¹, and the third loop is the one reported here. Since this treatment slightlypoles the samples, they are denoted ‘poled <1 min, RT’. The complex electrical impedance of the piezoelectric samples was measured as a function of frequency with a spectrum analyzer (Agilent 4395A, Palo Alto, CA, USA). The theoretical behavior of the electrical impedance was calculated from the 1D KLM equivalent electrical circuit [16–18]. A fitting process was then used to determine the thickness mode parameters [19, 20]. The samples were then poled at 3 kV mm⁻¹ for 60 min in an oil bath while the temperature decreased from 120 °C at the start to
Figure 1. (a) Bi$_4$Ti$_3$O$_{12}$ platelets made by molten salt synthesis, (b) NaNbO$_3$ platelets made by molten salt conversion of the Bi$_4$Ti$_3$O$_{12}$ platelets.

Figure 2. XRD of NaNbO$_3$ templates and sintered samples of KNNLTM, displaying the development of texture, quantified with the Lotgering factor, $F$, in the textured sample.

40 °C after 60 min. The impedance measurements were repeated after this procedure to see the effect of high-temperature poling. The longitudinal piezoelectric charge constant ($d_{33}$) was measured on high temperature-poled samples with a $d_{33}$-meter (APC International Ltd, Mackeyville, PA, USA).

3. Results

Micrographs of anisometric particles prepared by molten salt synthesis and conversion are shown in figure 1. The Bi$_4$Ti$_3$O$_{12}$ platelets prepared by the first molten salt step are homogeneous in size (~20–30 µm) and shape (platelets with well-defined edges) and a smooth surface, indicating that each particle is a single crystal. After molten salt conversion to NaNbO$_3$, (figure 1(b)) we still have a majority of platelet-shaped particles. But they are smaller and of a wider size distribution (5–30 µm), have a rougher surface and a less defined platelet shape. Many of the particles have one to three sharp corners, and a more curved outline, and they appear to be aggregates of a few crystallites rather than single crystals. XRD (figure 2) of the NaNbO$_3$ templates show that they are phase-pure and have a preferential orientation in the (100) crystallographic plane when dispersed and cast on the XRD sample holder. The Bragg reflections are well indexed with the orthorhombic Pbcm symmetry (ICSD # 247310) [21]. An overall peak shift toward higher 2θ indicates a reduction in the unit-cell volume. The obtained lattice parameters ($a = 5.428$ Å, $b = 5.592$ Å, $c = 15.548$ Å) shows that the orientated growth of the NaNbO$_3$ templates is promoted at the expense of a size reduction along the $a$-axis (~1.37%), whereas the $b$- and $c$-axis does not show significant changes. From figure 3, we can see that the templates have aligned relatively well with their main surfaces parallel to the tape surface after tape casting.

The development of texture at different sintering times was studied in stacked and laminated tapes. The top views of sintered samples in figure 4 shows how increasing sintering time at 1100 °C increases the grain size and promotes templated grain growth. After 2 h of sintering (figure 4(a)), the matrix phase KNNLTM particles are of submicron size, while the templates are of similar size as the as-prepared (figure 1). After 6 h of sintering (figure 4(b)), the matrix phase grains have grown slightly, while the NaNbO$_3$ templates still appear unaltered from the as-prepared state and after 2 h of sintering. However, after 14 h of sintering, the signs of templated grain growth are evident: most grains have a square shape with well-defined edges as
expected for (100)-oriented KNNLTM, and the grain size has increased to 2–30 μm. The pores have also coarsened: the smaller pores disappear while the larger grows, such that the final microstructure contains large, irregular-shaped pores between the larger cuboid grains from the templated grain growth. The materials appeared mainly phase pure from the SEM images, and no other elements than those of KNNLTM were observed by electron dispersive spectroscopy. Some darker areas are visible in figure 4. These were found to be deficient in Na, K and Ta, and enriched in Nb. The XRD patterns (figure 2) of the sintered samples also appear mainly phase-pure, but in some samples, very weak reflections between 20 and 30° 2θ, typical for Nb-rich secondary phases in KNN-based ceramics (e.g. K₂Nb₄O₁₁ or K₄Nb₆O₁₇) [22, 23], were observed. The XRD patterns also show an increase in the relative intensity of the (100)-type reflections (in pseudo-cubic notation) in the textured sample after sintering at 1100 °C for 14 h. This demonstrates that the grain growth seen on the SEM image (figure 4(c)) has occurred from the NaNbO₃ templates and has resulted in (100)-type texture, quantified to a Lotgering factor of 84%.

The development of texture and density with sintering time (for sintering at 1100 °C) is shown in figure 5. Figure 5(a) confirms and quantifies the observations from the micrographs in figure 4: (a) Texture increases with increasing sintering dwell time, and (b) a sintering dwell time of more than 6 h is necessary to get >50% texture. We can also see (figure 5(b)) that the density of the samples does not seem to decay during the prolonged sintering time. The degree of the texture observed by SEM and XRD are correlated in figure 6. The Lotgering factor (calculated from the XRD intensities) and the volume of single crystal (calculated by image analysis of the SEM images) show a good correlation, with a linear regression line with a slope close to 1 (forced intercept at the origin). This means, that the large grains we observe in the SEM images are of the desired (100) orientation, and of minimal disorientation. A deviation between the observed volume and the orientation would indicate templates that are misaligned and therefore not detected as (100)-oriented grains by XRD and contributing to the Lotgering factor.

The results of the electrical characterization of textured and non-textured KNNLTM, all sintered at 1100 °C for 14 h, are summarized in table 1. Figure 7 shows their density and the longitudinal piezoelectric charge constant (d₃₃) after high temperature poling. As expected, the piezoelectric response is higher in the textured samples, and reaches ~170 pC N⁻¹ already at 66% texture, without further increase at higher texture levels. The d₃₃, and other functional properties, are also expected to be affected by density. We can see that the textured samples have relative densities in the range 86%–89%, all lower than the non-textured
Figure 5. Development of (a) texture (Lotgering factor) and (b) density with sintering dwell time at 1100 °C.

Figure 6. Correlation between the volume of templated grains and the Lotgering factor (data + linear regression with forced intercept at x,y = 0,0) in the textured KNNLTM samples sintered at 1060 °C–1100 °C for 2–14 h.

Table 1. Summary of properties of KNNLTM textured and non-textured samples sintered at 1100 °C for 14 h and high-temperature poled.

| Sample     | Non-textured | Textured-1 | Textured-2 | Textured-3 |
|------------|--------------|------------|------------|------------|
| Density (%)| 91           | 86         | 89         | 87         |
| Texture (%)| 0            | 66         | 69         | 84         |
| $P_r$ (µC cm$^{-2}$) | 10.4         | 5.9        | 8.1        | 9.5        |
| $E_c$ (kV mm$^{-1}$) | 1.7          | 1.5        | 1.4        | 1.4        |
| $k_t$ (%)  | 0.23         | 0.35       | 0.35       | 0.33       |
| $e_{33}^T/e_0$ (—) | 188          | 205        | 259        | 182        |
| $c_{15}^D$ (GPa) | 84           | 65         | 63         | 65         |
| $v_L$ (m s$^{-1}$) | 4706         | 4266       | 4124       | 4215       |
| $Z_{ac}$ (MRayl) | 22           | 19         | 19         | 19         |
| $d_{33}$ (pC N$^{-1}$) | 118          | 171        | 168        | 162        |
| $g_{33}$ (mV m N$^{-1}$) | 71           | 94         | 73         | 101        |
| $d_{33}g_{33}$ ($10^{-12}$ m$^3$ J$^{-1}$) | 8            | 16         | 12         | 16         |

(91%). This lower density in the textured ceramics is a consequence of the irregular-shaped templates that do not pack efficiently, and therefore create voids between them that appear as porosity after sintering. Polarization-electric field hysteresis loops and the corresponding current-electric field loops are shown in figure 8. All textured samples show well-developed ferroelectric hysteresis without any signs of pinching or large asymmetries, and clear peaks in the current plots from domain switching at the coercive field. The non-textured sample has more contribution from leakage current (a more rounded hysteresis loop and less sharp switching current peaks). The textured samples have lower remanent polarization ($P_r \sim 6–10 \mu$C cm$^{-2}$) than the non-textured (10.4 µC cm$^{-2}$), as expected based on the KNNLTM (100).
Figure 7. Density and longitudinal piezoelectric charge constant ($d_{33}$) (after high-temperature poling) vs. texture in KNNTLM samples sintered at 1100 °C for 14 h.

Figure 8. (a) Hysteresis loops, and (b) current density (current signal normalized by sample area) loops for textured and non-textured KNNLTM sintered at 1100 °C for 14 h.

The results of the impedance analysis and fit to the KLM equivalent circuit are shown in figure 9 as a function of the degree of texture. The plots show samples both after the short ‘poling’ at room temperature that occurred during the measurement of the hysteresis loops, and after poling at high temperature (120 °C) for 1 h. The dielectric permittivity values (figure 9(a)) decreases both with texture and with poling. This is as expected due to an increase in the thickness mode coupling factor $k_t$ [27] with texture (as seen in figure 9(c)), and is similar to previous observations in textured KNN [25, 28]. The $\varepsilon_{33} T/\varepsilon_0$ range from 369 in unpoled, non-textured KNNLTM to 182 in textured, poled KNNLTM. These values are quite low compared to other KNN-based ceramics [7]. The elastic coefficients $c_{33}^D$ (figure 9(b)) also show similar trends with reduced values for textured and poled samples, here the effect of texture is stronger and the effect of poling lower compared to the trend with $\varepsilon_{33} T/\varepsilon_0$ for most samples. The lower densities of the textured samples probably explains the trends in $c_{33}^D$, since this parameter is the product of the density and the longitudinal wave velocities ($v_L$) (table 1), which also is known to decrease with decreasing density [25]. Acoustic impedances ($Z_{ac}$) (table 1) of all samples were also calculated from the longitudinal wave velocities and the density of the samples. The non-textured sample has an acoustic impedance of 21 MRayl, while for all the textured samples this value is 19 MRayl, similar to values seen in the KNNTLM composition before [25]. The thickness mode coupling factor ($k_t$) (figure 9(c)) increases significantly with both poling and texture. The highest values are 0.35 for poled, textured samples, which is 71% of the single crystal value [12] obtained for the same composition.

The longitudinal voltage constant, $g_{33}$, and the energy harvesting figure of merit, $d_{33} g_{33}$, were calculated based on the $\varepsilon_{33} T/\varepsilon_0$ from the KLM fit and the measured $d_{33}$, and are plotted as a function of texture in figure 10. Both parameters are highest in the textured samples, where they reach a $g_{33}$ of 101 mV m N$^{-1}$ and $d_{33} g_{33}$ of $16 \times 10^{-12}$ m$^3$ J$^{-1}$, respectively, which is very high compared to typical values published for ceramic piezoelectrics [4, 6, 9].
Figure 9. Parameters derived from the KLM analysis of the impedance spectra of textured KNNLTM ceramics sintered at 1100 °C for 14 h: (a) Dielectric permittivity at constant stress, $\varepsilon_{33}^T/\varepsilon_0$, (b) elastic constant at constant electrical displacement, $c_{33}^D$, and (c) thickness mode coupling factor, $k_t$.

Figure 10. Piezoelectric voltage constant ($g_{33}$) and figure of merit for energy harvesting ($d_{33}g_{33}$) for the textured KNNLTM sintered at 1100 °C for 14 h (after poling).

4. Discussion

The results presented here clearly demonstrate that textured KNNLTM can be prepared by templated grain growth from NaNbO$_3$ templates, and that texture improves several key functional parameters. Most interesting are the high voltage constant $g_{33}$ and the energy harvesting figure of merit $d_{33}g_{33}$. The voltage constant obtained in this work (101 mV m N$^{-1}$) is to the best of our knowledge higher than any other reported lead-free ceramics, as shown in figure 11, including the single crystal of the same KNNLTM composition [12]. It is also higher than typical commercial lead-based piezoelectrics (15–55 mV m N$^{-1}$) [29] and almost as high as the best textured lead-based piezoelectrics (115 mV m N$^{-1}$) [9]. The $d_{33}g_{33}$ figure of merit obtain in this work (16 $\times$ 10$^{-12}$ m$^3$ J$^{-1}$) is also higher than the typical range for both lead-free ($\sim$2–14 $\times$ 10$^{-12}$ m$^3$ J$^{-1}$) and lead-based ($\sim$5–14 $\times$ 10$^{-12}$ m$^3$ J$^{-1}$) non-textured ceramics [4]. Since our $d_{33}$ values are not very high, there are, however, some textured ceramics with a higher $d_{33}g_{33}$ than what we obtain: up to 61 $\times$ 10$^{-12}$ m$^3$ J$^{-1}$ was recently reported in a lead-based [30] and 17 $\times$ 10$^{-12}$ m$^3$ J$^{-1}$ in a lead-free [31] textured ceramic. Polymer piezoelectrics also often have higher $g_{33}$ and $d_{33}g_{33}$, due to their very low dielectric permittivity, e.g. polyvinylidene fluoride (PVDF) has a $g_{33}$ of 286.7 mV m N$^{-1}$ [11].

However, the poor temperature stability of these materials (the melting point of PVDF is 166 °C), usually limits their applications to ambient temperature operation. Texture often improves the thermal stability of the piezoelectric response [8, 32], and the KNNLTM composition used in this work is expected to have a $T_C$ of 235 °C [12], but temperature-dependent measurements should of course be performed in a follow-up study to confirm this.

So why are $g_{33}$ and $d_{33}g_{33}$ so high in our textured KNNTLM ceramics? Firstly, the $d_{33}$-values of our materials are of a reasonable magnitude, which contributes positively to both $g_{33}$ and $d_{33}g_{33}$. Secondly, the permittivity of our materials is very low. KNN-based ceramics are typically reported with $\varepsilon_{33}^T/\varepsilon_0$ in the range 230–475 [7], but these values are usually from dense ceramics ($\geq$95% relative density). [001]-oriented and poled KNNLTM single crystal had a $\varepsilon_{33}^T/\varepsilon_0$ of 650 [12]. The permittivity decays rapidly with increasing porosity, and our textured samples are all below 90% dense. A decay in density is usually also followed by a decrease in $d_{33}$, but not as rapidly as the $\varepsilon_{33}^T/\varepsilon_0$ decreases [34, 35], such that $g_{33}$ and $d_{33}g_{33}$ can often be...
increased by introducing porosity or making composites with polymers (with low permittivity compared to the piezoelectric) [36, 37]. Texturing affects both piezoelectric and dielectric response. By considering the directional dependence of these parameters [38], we can see that the $d_{33}$ has a maximum and the $\varepsilon_{33} / \varepsilon_0$ has a minimum (although less pronounced) along the [100]$_{pc}$ crystallographic direction in KNbO$_3$ [28].

Assuming a similar behavior holds for the isostructural KNN and KNN-based compositions (where we lack the complete parameter set for such an analysis), we expect (100) texture to increase $d_{33}$ and decrease $\varepsilon_{33} / \varepsilon_0$. This is observed both in this work and previous studies [25, 28, 39]. As also pointed out by Yan et al [9], texture is therefore a unique method to improve $g_{33}$ and $d_{33}g_{33}$ of piezoelectric ceramics.

The degree of texture (up to 84%) obtained in this work is not among the highest for textured KNN-based ceramics [10, 40, 41]. Even higher performance could therefore potentially be achieved if we managed to increase the degree of texture. Although we observe a decent alignment of the templates during tape casting (figure 3) and after templated grain growth (figure 6), templates with a higher aspect ratio and without irregular edges could improve the texturing. It is also possible that a dwell time during sintering for more than 14 h could further improve the degree of texture, although the longer the sintering time, the higher the risk of compositional changes due to evaporation of alkali elements [26]. Only a template loading of 10 wt% was studied in this work. This amount was chosen based on previous work with texturing of KNN [28]. In general, template loadings between 1 and 10 wt% is common [42]. A lower template loading (of templates of the same size) would be expected to cause larger grains in our final textured ceramic, as the initial templates would have been further separated and would have to grow larger to cover the entire sample volume [42]. A higher template loading could potentially improve the degree of texture at the same templated grain growth time, but would also increase the risk of pores and other defects (e.g. impurities) from the templates.

The low density could also hinder the texture development through the templated grain growth process [42]. While densification of KNN-based ceramics is generally challenging [26, 43], a density below 90% in the textured samples in this work is lower than what is typically possible in bulk KNN-based ceramics [26, 44] and also lower than what can be obtained (sometimes by sintering aids) in textured KNN-based ceramics [39, 45]. However, improving the density might compromise the high $g_{33}$ and $d_{33}g_{33}$ values due to an increase in permittivity as a consequence of higher density.

Low-frequency, off-resonant piezoelectric energy harvesting in compression/expansion mode is a promising application of our textured KNNLTM due to their high $d_{33}g_{33}$ figure of merit. As a lead-free material system, the KNNLTM multilayers especially have an advantage for energy harvesting for consumer electronics, where proper end of life materials recycling and disposal is challenging to implement. A low-profile (2D) structure is applied for many harvesting scenarios [3], and in addition to producing sheets by tape casting and laminating to the desired thickness as in this work, it is interesting to fabricate multilayered structures by tape casting [25] or sol-gel deposition of the KNNLTM on a textured metal support [46].

Ultrasound transducers for medical imaging are also a suitable application for the textured KNNLTM. Differences in the acoustical impedance between the transducer and the biological tissue to be examined, causes loss of ultrasonic energy and affects the ultrasound signal quality. The low acoustic impedance (<20 MRayl) of our materials compared to the traditional lead-based systems (>30 MRayl) [47] is very favorable, since an acoustic impedance value closer to that of biological tissue (1.5 MRayl) [47] limits the
signal loss at the interface. The relatively high $k_t$ values, low dielectric permittivity, and the values of the wave velocity of the textured KNNLTM ceramics (higher than in lead-based composition) are suitable for a single-element transducer operating at high frequency [4].

5. Conclusion

The lead-free piezoelectric composition (Li$_{0.08}$(K$_{0.52}$Na$_{0.48}$)$_{0.94}$)(Nb$_{0.71}$Ta$_{0.29}$)$_3$O$_{15}$ with 0.25 mol% Mn (KNNLTM) was successfully prepared as textured ceramics with (100) grain orientation up to 84% after templated grain growth from NaNbO$_3$ templates. The textured ceramics demonstrated piezoelectric properties of $d_{33}$ up to 171 pC N$^{-1}$ and $k_t$ of 0.35. This value of $k_t$ is 71% of the single crystal values for the same composition, which combined with a low acoustic impedance (19 MRayl) makes the textured KNNLTM samples suitable for medical ultrasound imaging. The low dielectric permittivity ($\varepsilon_r^{1/2}$ down to 182), combined with the reasonably high charge constant ($d_{33}$ up to 171 pC N$^{-1}$) also resulted in very high piezoelectric voltage constants ($g_{33}$ up to 101 mV m N$^{-1}$ for the most textured sample), higher than previously reported for lead-free piezoelectric ceramics. Consequently, the textured materials also have very high values of $d_{33} g_{33}$ (up to $16 \times 10^{-12}$ m$^3$ J$^{-1}$), the figure of merit for non-resonant piezoelectric energy harvesting in compression mode. The textured KNNLTM samples prepared in this work are therefore promising for applications in both ultrasound transducers and energy harvesters.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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