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(K, Na, Li)(Nb, Ta)O₃:Mn lead-free single crystal with high piezoelectric properties

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Abstract

Lead-free single crystal, (K, Na, Li)(Nb, Ta)O₃:Mn, was successfully grown using top-seeded solution growth method. Complete matrix of dielectric, piezoelectric and elastic constants for [001]_C poled single crystal was determined. The piezoelectric coefficient d_{33} measured by the resonance method was 545 pC/N, which is almost three times that of its ceramic counterpart. The values measured by the Berlincourt meter ($d_{33}^* = 630$ pC/N) and strain-field curve ($d_{33}^{**} = 870$ pm/V) were even higher. The differences were assumed to relate with the different extrinsic contributions of domain wall vibration and domain wall translation during the measurements by different approaches, where the intrinsic contribution (on the order of 539 pm/V) was supposed to be the same. The crystal has ultrahigh electromechanical coupling factor ($k_{33} \sim 95\%$) and high ultrasound velocity, which make it promising for high frequency medical transducer applications.

Keywords

KNN; single crystal; lead-free; electromechanical coupling factor

1. Introduction

Lead free piezoelectric materials of (K, Na)NbO₃ (KNN) family have been considered as promising candidates to replace lead based piezoelectrics ever since Saito et al. reported high d_{33} in textured (K, Na, Li)(Nb, Ta, Sb)O₃ based ceramics in 2004.^{1–3} During a decade of research, properties of the KNN based ceramics have not been improved significantly by composition modifications or fabrication methods.^{4,5} Piezoelectric responses can be divided into intrinsic and extrinsic contributions. So the improvement of the responses should include changes of the two parts. It has been known that high piezoelectric properties can be

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achieved near the polymorphic phase transition (PPT) in KNN based ceramics due to the instability of polarization state. The reported high piezoelectric properties measured at room temperature are usually improved by shifting the PPT downward from 200°C to room temperature.⁶ The improvement of piezoelectric responses is related to the intrinsic contribution. On the other hand, the piezoelectric coefficients $d_{33}^{**} (S_{\max}/E_{\max})$ calculated by the slope of electric-field-induced strain have been found to be much higher than the d_{33} measured using resonance method, which have been found in many piezoelectric materials.^{1,2,7,8} The difference responses are considered to relate to the extrinsic contributions which can be analyzed by Rayleigh Law.^{9,10,11} Quantifying the amount of intrinsic and extrinsic contributions of piezoelectric responses is necessary to study the underlying nature of piezoelectric responses. Then the piezoelectric properties can be improved by more targeted methods. However, most studies don't differentiate between the two contributions or ignore extrinsic contribution completely.

Recently, large size (K, Na)(Nb, Ta)O₃ (KNNT) and (K, Na, Li)(Nb, Ta)O₃ (KNNTL) single crystals have been successfully grown and full constant sets have been reported.^{7, 12,13} Electromechanical coupling factors k_{33} (above 80%) for the crystals are much larger than that of the ceramic counterparts, making them excellent candidates for electromechanical devices. However, the piezoelectric coefficients have not been enhanced significantly. The constant d_{33} for KNNT single crystal is only 162 pC/N.¹² The coefficient d_{33} is improved to 354 pc/N for KNNTL crystal after the introduction of Li ions, but it is still not as high as expected.¹³ It is interesting that the d_{33}^{**} for KNNTL single crystal is as high as 670 pm/V, almost twice the d_{33} , indicating large extrinsic contribution. However, the effect of extrinsic contribution in the KNN family crystals is not very clear. Furthermore, large leakage current from the hysteresis loop measurement (P - E loop) and high dielectric loss are other problems for KNN based single crystals.¹⁴ For the KNNT and KNNTL single crystals, the dielectric loss increases from 0.4% to 2% after the introduction of Li ions.^{12,13} According to the experience of PIN-PMN-PT:Mn single crystals, dopants such as Mn ions can be used to decrease the dielectric loss.⁹ So it is expected that KNN based single crystals with higher constants d_{33} and lower dielectric loss can be designed by optimizing the composition and the corresponding full constants sets could be provided for further application.

In this work, high piezoelectric properties (K, Na, Li)(Nb, Ta)O₃:Mn (KNNTL:Mn) single crystal ($d_{33} > 540$ pc/N, $k_{33} \sim 95\%$ and dielectric loss $\sim 0.7\%$) was successfully grown by the top-seeded solution growth (TSSG) method. Complete material constant matrix of the crystal was determined using combined resonance and ultrasonic methods. Rayleigh Law was used to analyze the origin of extrinsic contributions to three piezoelectric responses measured by resonance method, Berlincourt meter and piezoelectric strain measurement. In addition, the constants d_{33}^{**} and k_{33} were found as high as 870 pm/V and 95%, comparable with PIN-PMN-PT:Mn single crystals.

2. Experimental

2.1 Crystal growth

KNNTL:Mn single crystal with high properties was grown by TSSG method. Composition of raw materials for the crystal growth was described as $[\text{Li}_x(\text{K}_{1-y}\text{Na}_y)_{1-x}](\text{Nb}_{1-z}\text{Ta}_z)\text{O}_3\text{:Mn}$, where $x=0.06$, $y=0.1-0.3$, $z=0.07-0.17$. The level Mn doping was 0.25 mol%. High purity powders of Na_2CO_3 (99.99%), K_2CO_3 (99.99%), Li_2CO_3 (99.99%), Ta_2O_5 (99.99%), Nb_2O_5 (99.99%) and MnO_2 (99.99%) were prepared as starting materials. After being mixed and calcined to synthesize into perovskite compound at 850 °C, the materials were put into a platinum crucible to grow the crystal. During the growth process, $[001]_C$ oriented KNN based crystal was used as crystal seed. A Pt line was used as seed to grow the first KNN based single crystal. Then a $[001]_C$ oriented bar was cut from the as-grown single crystal to be used as the seed for the next growth. After repeated optimization, a high quality crystal could be successfully grown. The compound were melted at 1200 °C in a furnace and kept a few hours to stabilize the melt. Then the seed was dipped slowly to the melt and pulled up at 0.1–0.6 mm/h. At the same time, the temperature and the rotation rate of the seed rod were controlled carefully. After several days, the single crystal was successfully grown and cooled down to room temperature carefully. The cooling process was as follows: When the single crystal was pulled out from the melt, the platinum crucible was cooled down to 900°C at a rate of 30°C/h. Then it was cooled down from 900°C to 500°C with 50°C/h and from 500°C to room temperature with 20°C/h.

2.2 Characterization procedure

For determining the electrical properties, the KNNTL:Mn single crystal was oriented using the Laue X-Ray orientation system with an accuracy of 0.5°, according to the IEEE standard on piezoelectricity.¹⁵ All samples were cut and sputtered gold as electrodes on the $(001)_C$ faces, and then poled in silicon oil under a DC field of 30 kV/cm at room temperature for 5 minutes. In order to avoid clamping effect during the resonance measurements, silver wires were attached to the end faces of k_{33} mode bar samples (sample dimensions $1 \times 1 \times 2.54 \text{ mm}^3$). The single crystals in orthorhombic phase have twelve spontaneous polarization directions along $\langle 011 \rangle_C$ family, and the intrinsic symmetry for an orthorhombic lattice is $mm2$. After poling along $[001]_C$, only four polarizations which are energetic equivalent to the $[001]_C$ orientation left ($[011]_C$, $[\bar{1}01]_C$, $[0\bar{1}1]_C$, $[101]_C$), as shown in Fig. 1. Considering the contributions from all polarizations (domains), the effective symmetry of $[001]_C$ samples should be tetragonal $4mm$. All the macroscopic properties measured in this work are for the multi-domain crystals with macroscopically tetragonal $4mm$ symmetry. Then there are 11 independent material constants: 6 elastic constants, 3 piezoelectric constants and 2 dielectric permittivities. The complete material constant matrix were determined by using combined resonance and ultrasonic methods. The resonance and antiresonance frequencies were measured by an Agilent 4294A impedance-phase gain analyzer. Electromechanical coupling factor k_t was also checked by the frequency ratio f_2/f_1 . The elastic stiffness constants: c_{11}^E , c_{33}^D , c_{44}^E , c_{44}^D , and c_{66}^E were calculated by phase velocities which were measured using longitudinal and shear wave transducers. Here, $[100]_C$ is defined as the x axis, and $[010]_C$, $[001]_C$ are selected as the y and z axes, respectively. In addition, the piezoelectric coefficient

d_{33}^* was measured using a Berlincourt-type d meter (ZJ-4AN, Institute of Acoustics, Chinese Academy of Science). Temperature dependence of the dielectric constant for the KNNTL:Mn single crystal was measured using k_1 type plate samples by an E4980A LCR meter (Agilent, USA). Polarization hysteresis loops and electric-field-induced strain loops were measured using a Premier II Precision Materials Analyzer (Radiant Tech. USA).

3. Results and discussion

3.1 Composition, structure, dielectric and ferroelectric characterization

The ratios of K/(K+Na) and Ta/(Ta+Nb) of the KNNTL:Mn single crystal with size of $5 \times 5 \times 9 \text{ mm}^3$ were checked by Energy Dispersive Spectrometry (EDS) from 9 points. The ranges of K/(K+Na) and Ta/(Ta+Nb) were determined to be 0.506–0.526 and 0.280–0.294, respectively. The slight compositional variation can be ignored according to the phase transition temperature reported by L. M. Zheng, et al.^{12,13} So the composition of the KNNTL:Mn single crystal in this work was considered as $[\text{Li}_x(\text{K}_{0.516}\text{Na}_{0.484})_{1-x}](\text{Nb}_{0.713}\text{Ta}_{0.287})\text{O}_3\text{:Mn}$. The level of Li and Mn doping were 6% and 0.25 mol%. More than one samples were used in order to mitigate the effect of inhomogeneous composition. Fig. 2 is X-ray diffraction (XRD) pattern of the powder of the KNNTL:Mn single crystal, showing pure perovskite structure without any second phase.

The dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ of [001] poled samples was measured to be 650 at 20°C, and the dielectric loss was on the order of 0.7%. From the temperature dependence of dielectric constant in Fig. 3(a), it was found that orthorhombic (O) to tetragonal (T) phase transition temperature $T_{\text{O-T}}$ is 30°C and the Curie temperature T_{C} is 235 °C. The relationship between ε and T is given by: $\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\text{max}}} = \frac{(T - T_{\text{m}})^\gamma}{C}$, where γ and C are all constants, and the value of γ value is 1 or 2. When $\gamma=1$, the equation is the Curie-Weiss law valid for classical ferroelectrics. When $\gamma=2$, the equation is the quadratic law valid for ideal relaxor ferroelectrics. The curve of $\lg(1/\varepsilon - 1/\varepsilon_{\text{max}})$ as a function of $\lg(T - T_{\text{m}})$ at high temperature for the KNNTL:Mn single crystal is shown in Fig. 3(b). The slope of the curve was found to be 1.09, very close to 1. So the KNNTL:Mn single crystal showed normal ferroelectric property primarily and the curve of ε against T exhibited sharp peak at the Curie temperature T_{C} , as the same as other KNN based crystals grown by the Bridgman method and TSSG method.^{14,16} And the frequency dispersive variations of dielectric constant was not obvious.

Fig. 4 shows the polarization hysteresis loop of the KNNTL:Mn single crystal measured at 5 Hz, and no obvious leakage current was observed, demonstrating a better quality compared to the KNNL crystal grown by the Bridgman method.¹⁴ The P_{r} of the single crystal was found to be $3.45 \mu\text{C}/\text{cm}^2$. The coercive field was found to be 4.86 kV/cm with an internal bias of 0.36 kV/cm. Such bias field was also reported in the Mn modified PMN-PZT and Mn modified PIN-PMN-PT single crystal.^{9,17,18} The low dielectric loss, low leakage current and the existence of internal bias are thought to related to the Mn dopant, which behaves as acceptor dopant and generate oxygen vacancies, resulting in acceptor-oxygen vacancy defect dipoles. These defect dipoles realign themselves during the poling process along the

preferential direction of the spontaneous polarization and give rise to the internal bias, which clamps the domain wall motions and accounts for the low dielectric loss and leakage current.

3.2 Intrinsic and extrinsic contributions of piezoelectric properties

The piezoelectric coefficient d_{33} was measured using the resonance method, Berlincourt meter and electric-field-induced strain measurement, respectively. As shown in Fig. 5, the resonance and antiresonance frequencies were found to be 394 kHz and 1.12 MHz using a longitudinal k_{33} -bar sample. The maximum phase angle was about 89° , indicating a low loss. The piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} were calculated based on IEEE standard on Piezoelectricity. The coefficient d_{33} and coupling factor k_{33} were found to be 545 pC/N and 95%, respectively. Elastic compliances s_{33}^E and s_{33}^D were calculated to be $57.7 \text{ pm}^2/\text{N}$ and $6.04 \text{ pm}^2/\text{N}$, respectively.

The coefficient d_{33}^* measured by Berlincourt meter using d_{33} -meter was found to be about 630 pC/N. The piezoelectric coefficient (d_{33}^{**}) can also be calculated from the slope of the

electric-field-induced strain using the following equation: $d_{33}^{**} = \frac{S_{\max}}{E_{\max}}$. Fig. 6 shows electric-field-induced strain for KNNTL:Mn single crystal along $[001]_C$ direction. The piezoelectric coefficient d_{33}^{**} was calculated to be about 870 pm/V at 10 kV/cm, much higher than the d_{33} and d_{33}^* , illustrating that the piezoelectric coefficients were sensitive to the measurement methods related to the different origin of piezoelectric responses. As shown in Fig. 6, the d_{33}^{**} of KNNTL:Mn single crystal was much higher than that of PZT5 ceramics and KNNTL0.19 ceramics and comparable with PIN-PMN-PT:Mn single crystal.⁹

The piezoelectric response includes two parts: intrinsic contribution and extrinsic contribution. Considering that the intrinsic piezoelectric effect originated from the lattice distortion is at the same level in all three measurements. In order to further investigate extrinsic contributions to the piezoelectric responses for the KNNTL:Mn single crystal, Rayleigh analysis was performed. The Rayleigh Law can be expressed using the following formulas:^{19,20}

$$S(E) = (d_{\text{init}} + \alpha E_0)E \pm \alpha(E_0^2 - E^2)/2, \quad (1)$$

$$d(E_0) = d_{\text{init}} + \alpha E_0, \quad (2)$$

where E_0 is the amplitude of electric field. The d_{init} is the initial reversible piezoelectric responses at zero electric field, representing the intrinsic contribution. The term αE_0 represents the extrinsic contribution to the total piezoelectric response. At small electric field

($E < \frac{1}{2}E_c$), the piezoelectric response is linear with field E .

Strain-field (S - E) loops under small electric field were measured as shown in Fig. 7(a). The corresponding $d_{33}(E)$ was calculated can be expressed as $d_{33}(E) = (539+83E)$ pm/V as shown in Fig. 7(b). The intrinsic contribution was improved to 539 pm/V for KNNTL:Mn crystal from 348 pm/V for KNNTL-1 crystal.¹³ The insert of Fig. 7(b) showed the calculated S - E loop at 2.0 kV/cm by formula (2), which was associated with the corresponding measured loop. Generally, the extrinsic contribution in the Rayleigh analysis is calibrated at 1 kV/cm, which was 13.3% for the KNNTL:Mn single crystal.

The large discrepancy for the three approaches should be ascribed to the different extrinsic contributions in the three methods, which are related to the domain wall motions and domain switching, because the intrinsic contributions are the same (539 pm/V). Domain wall motions can be divided into two types: the domain wall vibration and domain wall translation. As shown in Table I, the test signals were small AC electric field at a high frequency of 10^5 ~ 10^6 Hz for the resonance measurement. While for the Berlincourt method, the test signals were small stress signals at a low frequency of 110 Hz. In these two cases, only domain wall vibration can be excited due to the small signal. At high frequencies, domain walls with small effective mass would vibrate with the test signal, while domain walls with large effective mass failed to keep up with the signal. On the other hand, when the frequency of the driving signals were low enough, all domain walls would vibrate.

Therefore, the coefficient d_{33}^* measured using d_{33} meter was 15.6% higher than the d_{33} due to the inertia effect at high frequencies, which was considered to be 8%–9% in earlier reports.^{8,21} For the case of d_{33}^{**} , it was measured under a high electric field of 10 kV/cm at a very low frequency of 2 Hz. During this measurement, both domain wall vibration and domain wall translation were involved. It is not difficult to understand that d_{33}^{**} was much higher than d_{33}^* and d_{33} , due to the domain wall motions (extrinsic contribution) at high electric field. So enhancing extrinsic contributions, such as activating domain wall motions or improving the density of domain walls, can be used to improving the piezoelectric response. For the second method, improving the density of domain walls (decrease the domain size) have already been proven in the cases of PZN-PT and PIN-PMN-PT single crystals.^{22,23}

As shown in Table II, the properties of several KNN based lead-free materials were compared. It is interesting that the dielectric loss slightly increased after introducing Li ions into the KNNT crystal, but decreased down to about 0.7% with the introduction of Mn ions for the KNNTL:Mn single crystal as a result of the internal bias induced by defect dipoles. The enhanced coefficient d_{33} (~ 545 pC/N) for KNNTL:Mn crystal mostly resulted from the improvement of intrinsic contribution. Both KNN based ceramics and single crystals show higher d_{33}^* and d_{33}^{**} , indicating the effect of extrinsic contributions. As shown in Table II, the extrinsic contribution of KNNTL:Mn single crystal at 1kV/cm was found smaller than that of KNNTL-1 due to reduced domain wall motions, which was effectively clamped by the internal bias. The extrinsic contributions of KNN based single crystal are higher than NBBT95/5, showing more potential to get high piezoelectric properties by domain engineering.

3.3 Complete matrix of dielectric, elastic and piezoelectric constants

High piezoelectric properties were found for the $[001]_C$ poled KNNTL:Mn single crystal. Table III shows the properties, full set of elastic, piezoelectric and dielectric constants, for the KNNTL:Mn single crystal, determined by combined resonance and ultrasonic methods. As shown, the piezoelectric coefficient d_{33} and d_{31} were found to be ~ 545 pC/N and ~ -260 pC/N, three times that of its ceramic counterpart. The coupling factor k_{31} were found to be $\sim 59\%$. Of particular importance is that the factor k_{33} was found to be $\sim 95\%$, which is the highest in lead-free piezoelectrics and comparable with relaxor-PT single crystal.

When the complete constant matrix for KNNTL:Mn single crystal was determined, the elastic stiffness constants c_{33}^E was derived using:

$$c_{33}^E = c_{33}^D (1 - k_t^2). \quad (3)$$

The errors of the measurements of c_{33}^D and k_t will propagate to c_{33}^E by: ²⁴

$$\frac{\Delta c_{33}^E}{c_{33}^E} = \frac{\Delta c_{33}^D}{c_{33}^D} + 2 \left(\frac{\Delta k_t}{k_t} \right) \left(\frac{k_t^2}{1 - k_t^2} \right). \quad (4)$$

The k_t of KNNTL:Mn single crystal was 49%, so the $2k_t^2/(1 - k_t^2) = 0.63$. The relative errors of k_t and c_{33}^D were 2.0% and 2.0%, respectively. So the relative error of c_{33}^E was found to be 3.3%, where the error was 0.5×10^{10} N/m². The relative error of d_{31} can be determined by:

$$\frac{\Delta d_{31}}{d_{31}} = \frac{1}{2} \left[\frac{\Delta \varepsilon_{33}^T}{\varepsilon_{33}^T} + \frac{\Delta s_{11}^E}{s_{11}^E} + 2 \frac{\Delta k_{31}}{k_{31}} \right]. \quad (5)$$

For the KNNTL:Mn single crystal, the relative error of ε_{33}^T was 1.5%. The relative errors of s_{11}^E and k_{31} were 1.8% and 1.7%, respectively. Therefore, the relative error of d_{31} was calculate to be 3.4% with the error of ~ 10 pC/N. Similarly, the errors of s_{33}^E , d_{33} and d_{15} were found to be about 3.7×10^{-12} m²/N, 20 pC/N and 3.0 pC/N, respectively, as shown in Table IV.

Table V compares the properties of KNNTL:Mn single crystal, KNNTL-1 single crystal¹³, KNNT single crystal¹² and KNNTL0.2 ceramics⁸. Compared to KNNTL-1 crystals, the compliance constant s_{33}^E and electromechanical coupling factor k_{33} were enhanced greatly for the KNNTL:Mn single crystal, so that the piezoelectric d_{33} was found to be as high as ~ 545 pC/N. The dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ decreased after the introduction of Mn, similar to the case of PMN-PZT:Mn and PIN-PMN-PT:Mn crystals.^{17,25} The ultrahigh electromechanical coupling factor k_{33} ($\sim 95\%$) makes the crystal a good candidate for ultrasonic transducer applications. After the introduction of Li ions, the piezoelectric d_{33}

was improved, two times that of KNNT crystal. The piezoelectricity of KNNTL:Mn single crystal was significantly enhanced by optimizing the composition, reaching a value about three times that of KNNTL0.2 ceramics. The ultrahigh electromechanical coupling k_{33} and d_{33} make it a promising candidate for replacing lead-based piezoelectric materials.

4. Conclusions

In summary, high property (K, Na, Li) (Nb, Ta)O₃:Mn single crystal was successfully grown by TSSG method. The full matrix of material constants was provided by combined resonance and ultrasonic methods. Furthermore, the coefficients d_{33}^{**} was found as high as ~ 870 pm/V, comparable with PIN-PMN-PT:Mn single crystals and much higher than d_{33}^* (~630 pC/N) and d_{33} (~ 545 pC/N). The intrinsic contribution for the lead-free single crystal analyzed by Rayleigh Law was supposed to be the same, on the order of 539 pm/V and so the large difference arose from the different extrinsic contributions of domain wall motions under the three measurement conditions. The extra high d_{33}^{**} value indicated that extrinsic contribution played an important role for the high piezoelectric responses and it was a non-negligible origin of piezoelectric responses. So enhancing the extrinsic contribution can be considered as an effective way to improve the properties of lead-free materials. The electromechanical coupling factor k_{33} of the KNNTL:Mn single crystal was found to be ultrahigh (~ 95%), much higher than that of other lead-free materials and comparable to that of relaxor-PT single crystals.

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Fig. 1. Spontaneous polarization directions for (a) before and (b) after poled orthorhombic single crystal.

Fig. 2.
KNNTL:Mn single crystal and X-ray diffraction (XRD) pattern of the crushed crystal powder.

Fig. 3.

(a) Temperature dependence of dielectric constant for KNNTL:Mn crystal; (b) $\lg(1/\epsilon - 1/\epsilon_{\max})$ as a function of $\lg(T - T_m)$.

Fig. 4.
Polarization hysteresis loop of the crystal at 5 Hz.

Fig. 5.
Measured impedance amplitude and phase of $[001]_C$ poled k_{33} -bar of KNNTL:Mn single crystal.

Fig. 6. Unipolar electric-field-induced strain for KNNTL:Mn single crystal, PIN-PMN-PT:Mn single crystal, PZT5 ceramics and KNNLT0.19 ceramics.

Fig. 7.

(a) Measured electric-field-induced strain loops for KNNTL:Mn single crystal; (b) electric field dependence of piezoelectric coefficient $d_{33}(E)$ and comparison between the measured and calculated strain-electric field loops.

Table I
Different contributions of domain wall vibration and domain wall translation during the measurements by different approaches.

Methods	Source	Source frequency (Hz)	Lattice distortion (Intrinsic)	Domain wall vibration (Extrinsic)	Domain wall translation (Extrinsic)	Piezoelectric response (pC/N or pm/V)	Extrinsic contribution (%)
Resonance method	Small electric signals	$10^5\text{--}10^6$	Same	Small	Small	$d_{33} \sim 545$	1.10
Berlincourt meter	Small stress signals	110	Same	Large	Small	$d_{33}^* \sim 630$	14.4
Strain	Large electric signals	2	Same	Large	Large	$d_{33}^{**} \sim 870$	38.0

Table II

Comparison of piezoelectric properties achieved from different approaches for several lead-free materials.

Materials	d_{33} (pC/N)	d_{33}^* (meter)(pC/N)	d_{33}^{**} (pm/V)	Loss (%)	Extrinsic contribution%(at 1kV/cm)
KNNTL:Mn single crystal ^a	545±20	630±30	870±30	0.7±0.1	13.3
KNNTL-1 single crystal ^b	354	420	672	2	21.6
KNNTL-2 single crystal ^c	255	280	470	1	-
KNNT single crystal ^d	162	200	305	0.4	-
KNNTL0.2 ceramics ^e	174	195	308	<10	-
NBBT95/5 single crystal ^f	360	420	-	1.1	9.61

^aThis work,

^bRef.13,

^cRef.7,

^dRef.12,

^eRef.8,

^fRef.11

Table III
Measured and derived material properties of KNNTL:Mn single crystal poled along [001]_C.

Elastic stiffness constants: c^E, c^D (10^{10} N/m ²)											
c_{11}^E	c_{12}^E	c_{13}^E	c_{33}^E	c_{44}^E	c_{66}^E	c_{11}^D	c_{12}^D	c_{13}^D	c_{33}^D	c_{44}^D	c_{66}^D
18.2	15.7	15.2	15.3	7.81	7.42	25.3	22.8	9.33	20.1	8.64	7.42
Elastic compliance constants: s^E, s^D (10^{-12} m ² /N)											
s_{11}^E	s_{12}^E	s_{13}^E	s_{33}^E	s_{44}^E	s_{66}^E	s_{11}^D	s_{12}^D	s_{13}^D	s_{33}^D	s_{44}^D	s_{66}^D
33.4	-7.36	-25.8	57.7	12.8	13.5	21.6	-19.1	-1.18	6.07	11.6	13.5
Piezoelectric constants: d (10^{-12} C/N), e (C/m ²), g (10^{-3} Vm/N), h (10^8 V/m)											
d_{15}	d_{31}	d_{33}	e_{15}	e_{31}	e_{33}	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
66	-260	545	5.15	-5.50	4.52	18.6	-45.2	94.7	16.1	-129	106
Dielectric constants: ϵ (ϵ_0), β ($10^{-4}/\epsilon_0$)											
Electromechanical coupling constants: k											
ϵ_{11}^S	ϵ_{33}^S	ϵ_{11}^T	ϵ_{33}^T	β_{11}^S	β_{33}^S	β_{11}^T	β_{33}^T	k_{15}	k_{31}	k_{33}	k_t
362	48.1	400	650	27.7	208	25.0	15.4	31%	59%	95%	49%

Table IV

Reliable errors of some measured and derived piezoelectric coefficients.

coefficient	$e^E, e^D \text{ (} 10^{10} \text{ N/m}^2 \text{)}$				$s^E, s^D \text{ (} 10^{-12} \text{ m}^2/\text{N} \text{)}$				$\epsilon(e_h)$			
	c_{33}^E	c_{44}^E	c_{33}^D	c_{44}^D	s_{11}^E	s_{33}^E	s_{33}^D	s_{33}^T	ϵ_{33}^T	ϵ_{33}^*	ϵ_{11}^T	ϵ_{11}^*
value	15.3	7.81	20.1	8.64	33.4	57.7	6.07	650	400			
$\delta(\%)$	3.3	0.4	2.0	0.5	1.8	6.4	0.8	1.5	1.3			
δ	± 0.5	± 0.03	± 0.4	± 0.04	± 0.6	± 3.7	± 0.05	± 10	± 5.0			
coefficient	$d \text{ (} 10^{-12} \text{ C/N} \text{)}$				k							
	d_{15}	d_{31}	d_{33}	k_{15}	k_{31}^*	k_{33}^*	k_t^*					
value	66	-260	545	0.31	0.59	0.95	0.49					
$\delta(\%)$	4.8	3.4	4.3	4.0	1.7	0.3	2.0					
δ	± 3.0	± 10	± 20	± 0.01	± 0.01	± 0.003	± 0.01					

* Measured properties

Table V
Comparison of properties for KNNTL:Mn crystal, KNNTL-1 crystal, KNNT crystal, and KNNLT0.2 ceramics.

Materials	d_{33} (pC/N)	k_{33} (%)	$\frac{E_{33}}{S_{33}}$	$\frac{D_{33}}{S_{33}}$	$\frac{T_{33}}{\epsilon_0}$
KNNTL:Mn single crystal ^a	545	95	57.7	6.07	650
KNNTL-1 single crystal ^b	354	82	27.0	9.07	790
KNNT single crystal ^c	162	83	15.5	4.40	267
KNNLT0.2 ceramics ^d	174	57	11.0	7.40	956

^aThis work,
^bRef.13,
^cRef.12,
^dRef.8