

Large size lead-free (Na,K)(Nb,Ta)O₃ piezoelectric single crystal: growth and full tensor properties

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Environmental friendly piezoelectric single crystal, Ta-modified (K,Na)NbO₃ with the size of 12 × 11 × 11 mm³, has been successfully grown using the top seeded solution growth technique. This orthorhombic phase (K,Na)(Nb,Ta)O₃ single crystal is the largest size to date in KNN-based crystals with homogeneous composition. The large size allowed us to apply the domain engineering technique to further enhance its piezoelectric properties. In addition, a self-consistent complete set of elastic, dielectric and piezoelectric constants for the [001]_c poled domain engineered crystal has been measured, which is urgently needed for theoretical studies and simulation designs of electromechanical devices using this lead-free piezoelectric material. The electromechanical coupling factors are very high ($k_{33} = 0.827$, $k_t = 0.646$) and the dielectric loss tangent is as low as 0.004 for this lead-free piezoelectric crystal. Such excellent properties make this crystal an excellent candidate to replace lead-containing piezoelectric materials in electromechanical devices.

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1 Introduction

Lead-based piezoelectric materials with high piezoelectric and electromechanical coupling properties, such as PbZrO₃–PbTiO₃ (PZT) and Pb(Nb,Mg)–PbTiO₃ (PMN–PT) solid solution systems, are the primary piezoelectric materials used today.^{1–3} Due to the toxic nature of Pb and PbO, people have been intensively searching for lead-free piezoelectric materials. Through the effort of many researchers in the past two decades, it was recognized that the (K_{0.5}Na_{0.5})NbO₃ (KNN) family and their derivatives are the most promising candidates, which have high piezoelectric coefficient and high Curie temperature.^{4–6} Substantial improvements in KNN-based materials have been achieved in recent years, both in preparation techniques and in piezoelectric performance.^{7–9} However, most reported studies were limited to ceramic form of materials due to the difficulty in growing large size crystals.

Single crystals are preferred over ceramics because they can be poled along different crystallographic directions to further enhance their piezoelectric performance through domain engineering. Domain engineering enhancement of piezoelectric properties has been successfully applied to relaxor-based single crystals, such as (1 – x)Pb(Mg_{1/3}Nb_{2/3})–xPbTiO₃ and (1 – x)Pb(Zn_{1/3}Nb_{2/3})–xPbTiO₃.^{10–14} In fact, the domain

engineering method was also used to enhance the piezoelectric properties of lead-free BaTiO₃ single crystal.¹⁵ Therefore, large size KNN-based single crystals are urgently needed to carry out fundamental investigations and to improve properties using the domain engineering method. In addition, a sufficient number of samples could be cut from one large size homogeneous crystal to allow the determination of full set of materials coefficient matrices with high self-consistency.

It has been a real challenge to grow high quality KNN-based single crystals with large dimensions because of the volatility of K and Na, and the incongruent melting nature. Many methods have been adopted to grow KNN-based single crystals. Solid state crystal growth (SSCG) process was employed to grow crystals of 1–4 mm in size,^{16,17} but the crystals were porous. Modified KNN single crystal grown by the Bridgman method showed excellent piezoelectric properties, yet the size of the crystal was limited and the oxygen vacancies in the crystal led to leakage current as shown in the polarization hysteresis loop.¹⁸ Relatively large-sized (with the dimension of about 6 mm) Mn-doped KNN single crystals were obtained by the flux method¹⁹ and floating zone method was also adopted to grow Mn-doped KNN single crystals,²⁰ however, inhomogeneity could be observed from the color variation in the photographs of their crystal. In fact, in the past decade, the lack of large-size high quality single crystals has been the biggest obstacle for the advancement of KNN-based lead-free piezoelectric materials.

Restricted by the size and quality of the available crystals, only limited material properties have been reported in the

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literature. Researchers mainly focused on the study of ferroelectric properties, domain structures, dielectric and longitudinal and transverse piezoelectric properties.^{21,22} In most reports, only ϵ_{33}^T , d_{33} , k_{33} and k_t were provided. Up to date, no single complete set of dielectric, piezoelectric and elastic constants for KNN-based crystals has been reported in the literature. For practical applications and fundamental studies, a self-consistent complete set of material properties is necessary and urgently needed.

Here, we report the successful growth of a large size high quality Ta-modified KNN-based crystal using the top-seeded solution growth (TSSG) method. The obtained crystal with the dimensions of $12 \times 11 \times 11 \text{ mm}^3$ possesses homogeneous composition and high quality. Ta is commonly used to improve the piezoelectric and dielectric properties in KNN-based ceramic materials.^{23,24} We found that Ta also helps the growth of large size single crystals. The obtained homogeneous crystal allowed us to perform domain engineering by poling along $[001]_c$ of the pseudo-cubic direction and the large size makes it possible to cut a high enough number of samples to determine the complete set of piezoelectric, dielectric and elastic properties with self-consistency. The very high electromechanical coupling factor ($k_{33} = 0.827$, $k_t = 0.646$) and low dielectric loss tangent (0.004) obtained through domain engineering showed the competitive potential of this lead-free material to replace $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) piezoelectric ceramics, whose electromechanical coupling factors are $k_{33} = 0.68$ and $k_t = 0.507$.²⁵

2 Experiments

2.1 Crystal growth

High purity (99.99%) Na_2CO_3 , K_2CO_3 , Ta_2O_5 and Nb_2O_5 were chosen as raw materials. Proportional raw materials²⁵ were ball-milled in alcohol for 12 h and then pressed into pellets and calcined at $860 \text{ }^\circ\text{C}$ for 6 h to synthesize perovskite structure powders. Then, the synthesized $(\text{K,Na})(\text{Nb,Ta})\text{O}_3$ [KNNT] compounds were put into a Pt crucible, heated to melt ($\sim 1140 \text{ }^\circ\text{C}$) and kept there for 2 h to ensure that the melted solution became stable. A $[001]_c$ oriented seed was used to pull the crystal out of the melted solution at the rate of $0.2\text{--}0.5 \text{ mm h}^{-1}$, and the pulling rod was rotated with the angular velocity of $6\text{--}10 \text{ rpm}$. After the growth was completed in 2–3 days, the crystals were cooled down to $500 \text{ }^\circ\text{C}$ at the rate of $40 \text{ }^\circ\text{C h}^{-1}$, and then further down to room temperature at the rate of $25 \text{ }^\circ\text{C h}^{-1}$.

2.2 Characterization procedure

The crystal structure was confirmed by powder X-ray diffraction (XRD) using a diffractometer with $\text{Cu K}\alpha$ radiation after crushing a piece of the crystal into powder, and the density of the crystal was measured by the Archimedes method. The composition of the crystal was estimated by Energy Dispersive Spectrometry (EDS). All samples were oriented using the Laue X-ray machine with an accuracy of $\pm 0.5^\circ$. Each sample was cut and polished into a parallelepiped with three pairs of parallel

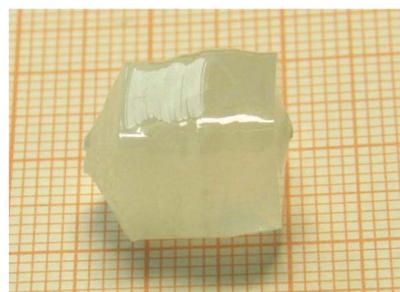


Fig. 1 Photograph of the as-grown KNNT single crystal.

surfaces along $[100]_c$, $[010]_c$, $[001]_c$ in the pseudo-cubic coordinates. Then, samples were sputtered with gold electrodes on both sides of $[001]_c$ surface, and then poled using a field of 38 kV cm^{-1} at room temperature for 10 min. The dielectric constant was determined using an HP 4284A multi-frequency LCR meter. The resonance and antiresonance frequencies were measured using an HP 4294A impedance-phase analyzer. Piezoelectric coefficients and electromechanical coupling factors were determined by resonance and antiresonance frequencies following the method given in the IEEE standards. A piezo- d_{33} meter (ZJ-2) was also used to estimate the d_{33} value for comparison.

After being poled along $[001]_c$, the effective symmetry of the multidomain KNNT samples became tetragonal with $4mm$ macroscopic symmetry, which has a total of 11 independent material constants: 6 elastic, 3 piezoelectric, and 2 dielectric constants. Combined resonance and ultrasonic methods were used to determine the complete sets of the elastic, dielectric and piezoelectric constants. Details of the measurement procedure were previously published in the literature.^{26,27}

3 Results and discussion

3.1 Dimensions, structure and composition characterization

A photograph of the as-grown $(\text{K,Na})(\text{Nb,Ta})\text{O}_3$ (KNNT) crystal is shown in Fig. 1. The crack-free crystal is semi-transparent due to the presence of many domain walls inside. The dimensions of the crystal are $12 \times 11 \times 11 \text{ mm}^3$. For comparison, the dimensions of the KNN-based crystals grown by different methods are listed in Table 1. One can see that our single crystal is the largest achieved so far. The uniformity and large size of our crystal make it possible to perform the measurements of the complete set of material constants.

Fig. 2 shows the X-ray diffraction (XRD) pattern of the powder obtained by crushing a small piece of the KNNT crystal. It can be seen that the KNNT crystal has pure perovskite structure without any second phase. Fig. 3 shows the temperature dependence of the dielectric properties of the two unpoled $[001]_c$ samples cut from the same KNNT crystal. For each sample, there are two dielectric anomalies in the measured temperature range. For this system, the dielectric anomaly at around $300 \text{ }^\circ\text{C}$ corresponds to the tetragonal–cubic phase transition and the one around $120 \text{ }^\circ\text{C}$ corresponds to the

Table 1 Dimensions of KNN-based single crystals grown by several methods

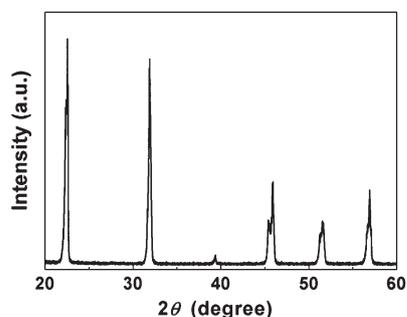
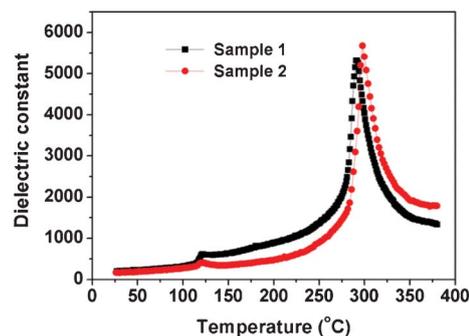
Compounds	Growth method	Dimensions
KNNT (this work)	TSSG	$12 \times 11 \times 11 \text{ mm}^3$
$(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (ref. 21)	Solid state	Diameter: 4 mm ^a
Mn-doped KNN ¹⁹	Flux	6×6^a
$0.95\text{KNN}-0.05\text{LiNbO}_3$ (ref. 18)	Bridgman	9.5×3.6^a
Mn-doped KNN ²⁰	Floating zone	Diameter: 4.5 mm Length: 13 mm
$(\text{Na}, \text{K}, \text{Li})(\text{Nb}, \text{Ta})\text{O}_3$ (ref. 28)	Solid state	Thickness: 50 nm ^b

^a The thickness of the crystal was not provided in the literature but is generally very thin. ^b Other dimensions were not provided in the literature.

orthorhombic–tetragonal phase transition. At room temperature, the KNNT crystal is in the orthorhombic phase with $mm2$ symmetry. The spontaneous polarization for the orthorhombic phase is along one of the twelve $\langle 011 \rangle_c$ pseudo-cubic directions. Fig. 4 shows the schematic diagram of perovskite ABO_3 structure and the orthorhombic unit cell with $mm2$ symmetry, in which the spontaneous polarization is along the $[011]_c$ direction.

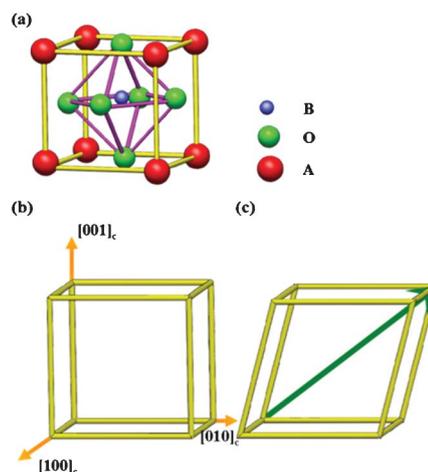
Because of segregation during the growth process, local compositional gradient along the growth direction is a common problem. In order to verify the compositional homogeneity, local compositions were checked by EDS from 3 different representative locations (top, middle and bottom) on the crystal. The compositions were determined to be $(\text{Na}_{0.451}\text{K}_{0.549})(\text{Nb}_{0.760}\text{Ta}_{0.240})\text{O}_3$, $(\text{Na}_{0.439}\text{K}_{0.561})(\text{Nb}_{0.768}\text{Ta}_{0.232})\text{O}_3$, and $(\text{Na}_{0.425}\text{K}_{0.575})(\text{Nb}_{0.775}\text{Ta}_{0.225})\text{O}_3$ for the upper, the middle, and the lower parts, respectively. The contents of Na and Ta decreased slightly along the growth direction, because the concentration of Ta and Na in the solution decreased gradually during the growth process. But the change is not significant.

In order to verify the influence of the slight compositional variation on phase transition temperatures and piezoelectric properties, some measurements were carried out. Two samples were cut from the upper (sample 1) and bottom (sample 2) parts of the KNNT crystal, respectively. From the results in Fig. 3, the tetragonal–cubic phase transition temperature (T_C) and orthorhombic–tetragonal phase transition temperature (T_{O-T}) for sample 1 are 291 °C and 121 °C, respectively, and for sample 2 are 298° and 120 °C,

**Fig. 2** X-ray diffraction (XRD) pattern of crushed KNNT single crystal powder.**Fig. 3** Temperature dependence of dielectric constant for KNNT crystals. Samples 1 and 2 were cut from the top and bottom parts of the as grown crystal.

respectively. Hence, in our case, the influence of the slight compositional variation on T_{O-T} and T_C is negligible. The longitudinal piezoelectric coefficient d_{33} determined by the d_{33} -meter for samples cut from the top and bottom parts are all around $195 \pm 5 \text{ pC N}^{-1}$. Although there is a slight composition variation along the growth direction based on the EDS results, it is small enough not to cause noticeable changes in phase transition temperatures and electrical properties. Therefore, the full sets of self-consistent material constants can be measured using these samples cut from the same crystal.

Taking advantage of the large size, homogeneous composition and high quality of our KNNT crystal, a series of comprehensive measurements have been carried out, and more importantly, a complete set of self-consistent material constants has been determined. The measured properties are of great significance for fundamental studies as well as device designs using finite element packages.

**Fig. 4** (a) Schematic diagram of perovskite ABO_3 structure, (b) illustration of perovskite primitive unit cell in the cubic phase without spontaneous polarization, and (c) in the orthorhombic phase with spontaneous polarization along the $[011]_c$ direction.

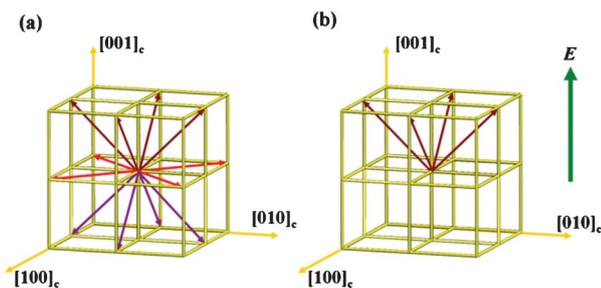


Fig. 5 Schematic of spontaneous polarization of perovskite orthorhombic phase: (a) before poling, the polarizations are along 12 $\langle 011 \rangle_c$ families, (b) after poling along $[001]_c$, only 4 polarization directions are left.

3.2 Elastic, dielectric and piezoelectric properties

As mentioned above, the spontaneous polarization for the as-grown KNNT single crystal is along the twelve $\langle 011 \rangle_c$ pseudocubic directions. After poling along $[001]_c$, there are only four of the twelve spontaneous polarizations left ($[011]_c$, $[0-11]_c$, $[101]_c$, and $[-101]_c$), so the effective macroscopic symmetry becomes tetragonal $4mm$. Fig. 5 illustrates the polarization changes before and after poling. The measured and derived elastic, piezoelectric and dielectric constants of the KNNT crystals poled along $[001]_c$ are given in Table 2. The density determined by Archimedes' method is 5101 kg m^{-3} . Material constants marked with a star (*) were determined directly by the resonance or ultrasonic or dielectric measurements, while others were derived values. The elastic properties and the piezoelectric and electromechanical factors for the lateral and shear modes for the KNN-based single crystals have not been reported up to date. In other words, our data here is the first full set of material constants for a KNN-based system.

It should be noted that the d_{33} value determined by the resonance method listed in Table 2 is 162 pC N^{-1} , which is lower than that measured directly by the piezo- d_{33} meter (195 pC N^{-1}). Based on our experience, the directly measured values using the piezo- d_{33} meter are not reliable because the sample geometry does not meet the requirements of the standard sample. In addition, for samples containing charge

defects, the piezo- d_{33} meter reading often produces much larger false values.

Some important electrical properties for KNN-based crystals grown by different methods are listed in Table 3 for comparison. It can be seen that the longitudinal and thickness electromechanical coupling factors, k_{33} and k_t , of our KNNT crystal are much higher than that of other crystals. The longitudinal piezoelectric coefficient d_{33} is comparable to or higher than that of pure KNN or Mn-modified KNN single crystals, but lower than that of the 0.95KNN-0.05LiNbO₃ crystal grown by the Bridgman method. The dielectric loss tangent of our KNNT crystal is only 0.004, which is one order of magnitude lower than previously reported values. The dielectric constants of those listed crystals vary greatly from 165 to 1015. Even crystals with similar composition grown by the same method showed great difference in dielectric constants, for example: 240 for KNN,²⁴ 600 for $\text{K}_{0.53}\text{Na}_{0.47}\text{NbO}_3$,²⁵ 740 for $\text{K}_{0.53}\text{Na}_{0.47}\text{Mn}_{0.004}\text{Nb}_{0.996}\text{O}_3$,²⁵ and 424 for Mn-doped KNN grown by the flux method.¹⁵ We believe that such large variations may be due to the difference in crystal quality. In general, crystals will become conductive if they contain substantial amounts of charged defects, which will also cause drastic increase of the dielectric loss.

4 Conclusions

In summary, large size ($12 \times 11 \times 11 \text{ mm}^3$) and high quality Ta-modified KNN-based single crystal was successfully grown by the TSSG method with homogeneous composition. The obtained KNNT single crystal has perovskite structure with orthorhombic $mm2$ symmetry at room temperature. A full set of elastic, dielectric, and piezoelectric constants for the $[001]_c$ poled KNNT single crystal was measured by using the combination of resonance and ultrasonic methods, which is the first self-consistent complete set of material constants for a KNN-based lead-free piezoelectric single crystal to date. The longitudinal and thickness electromechanical coupling factors reach $k_{33} = 0.827$ and $k_t = 0.646$ for the $[001]_c$ poled domain engineered KNNT single crystals, which are much higher than those previously reported values for KNN systems and even

Table 2 Measured and derived constants of KNNT single crystal poled along $[001]_c$ (density = 5101 kg m^{-3})

Elastic stiffness constants: c_{ij}^E and c_{ij}^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
17.2	11.0	10.2	13.8	8.3	9.3	22.9	16.8	2.8	23.2	8.9	9.3
Elastic compliance constants: s_{ij}^E and s_{ij}^D ($10^{-12} \text{ m}^2 \text{ N}^{-1}$)											
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
11.9	-4.3	-5.6	15.5	12.0	10.7	9.4	-6.8	-0.3	4.4	11.2	10.7
Piezoelectric coefficients: $e_{i\lambda}$ (C m^{-2}), $d_{i\lambda}$ ($10^{-12} \text{ C N}^{-1}$), $g_{i\lambda}$ ($10^{-3} \text{ Vm N}^{-1}$) and $h_{i\lambda}$ (10^8 V m^{-1})											
e_{15}	e_{31}	e_{33}	d_{15}^*	d_{31}^*	d_{33}^*	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
3.7	-5.2	6.7	45	-77	162	17.4	-32.6	68.5	15.5	-110	140
Dielectric constants: $\epsilon_{ij}(\epsilon_0)$ and $\beta_{ij}(10^{-4}/\epsilon_0)$						Electromechanical coupling factors					
ϵ_{11}^T *	ϵ_{33}^T *	ϵ_{11}^S *	ϵ_{33}^S *	β_{11}^T	β_{33}^T	β_{11}^S	β_{33}^S	k_{15}^*	k_{31}^*	k_{33}^*	k_t^*
291	267	272	54	34.4	37.5	36.8	186	0.234	0.46	0.827	0.646

Table 3 Comparison of dimensions and some important material constants for several KNN-based single crystals grown by different methods

Compound [001] _c poled	Growth method	d_{33} pC N ⁻¹	k_{33}	k_t	ϵ_{33}^T (1 kHz)	tan δ
KNNT (in this study)	TSSG	162 ^a 200 ^b	0.827	0.646	267	0.004
(K _{0.5} Na _{0.5})NbO ₃ [1–31] poled (ref. 21)	Solid state	80 ^c	—	—	1015	0.01
Mn-doped KNN (ref. 19)	Flux	161 ^a	0.64	—	424 (10 kHz)	—
KNN (ref. 29)	Flux	160 ^b	—	0.45	240	0.02
0.95KNN–0.05LiNbO ₃ (ref. 18)	Bridgman	405 ^b	—	0.61	185	—
Li _{0.02} (Na _{0.5} K _{0.5}) _{0.98} NbO ₃ (ref. 22)	TSSG	—	—	0.70	164	0.025
K _{0.53} Na _{0.47} NbO ₃ (ref. 30)	Flux	110 ^d	—	—	600	<0.1
K _{0.53} Na _{0.47} Mn _{0.004} Nb _{0.996} O ₃ (ref. 30)	Flux	103 ^d	—	—	740	<0.1

^a Determined by resonance method. ^b Measured by d_{33} meter. ^c Measured by atomic force microscopy at 2 Hz. ^d Calculated from the slope of high field strain curve.

larger than the best values for PZT piezoelectric ceramics ($k_{33} = 0.68$, $k_t = 0.507$).

The large dimensions, high electromechanical coupling factors and low dielectric loss make our crystal the best KNN-based single crystal to date. From its properties, one can conclude that it is a very promising candidate to replace lead-based piezoelectric materials, such as PZT ceramics, for many electromechanical applications.

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