Full tensor properties of $[111]_C$ poled (Na, K)(Nb,Ta)O₃ lead-free single crystal

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Abstract: Complete sets of elastic, piezoelectric and dielectric constants of $[111]_C$ poled (Na,K)(Nb,Ta)O₃ single crystal have been measured. The results show that the crystal with "3O" domain structure exhibits high shear but low longitudinal **piezoelectric properties** ($d_{15}=140$ pC/N, $k_{15}=0.569$, $d_{33}=64$ pC/N and $k_{33}=0.450$), which is similar to the "1O" single domain state, but different from the "4O" multi-domain state. The orientation-dependent longitudinal properties, *e.g.*, d_{33}^* , ϵ_{33}^* , s_{33}^* and k_{33}^* in the $(0\bar{1}1)_C$ plane have been calculated. The maximum piezoelectricity exists at the position of 38° away from $[011]_C$, which is close to the $[111]_C$ direction. By comparing the measured and calculated parameters, it can be concluded that the piezoelectricity is dominated by the intrinsic contribution while the dielectricity is controlled by the extrinsic contributions.

Keywords: Ferroelectrics; Piezoelectric materials; Dielectric

1. Introduction

Lead-free piezoelectric materials have been paid an increasing attention due to the toxic nature and the environment issues in traditional lead-based piezoelectric materials. Among all lead-free piezoelectric materials, (K, Na)NbO₃ (KNN) family is considered to be an excellent candidate with high piezoelectricity and high Curie temperature [1,2]. With intensive studies in the past decade, great improvements have been achieved in both the preparation technique and material properties of

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KNN-based materials [3,4]. Since it is difficult to grow KNN single crystal, most of the previous studies on KNN-material are focus on ceramics, which complicate the mechanism of piezoelectricity. Recently, high-quality single crystals were obtained, thus both fundamental studies on piezoelectricity and domain-engineered technique can be carried out [5,6].

Properties of ferroelectric materials are highly related with the corresponding domain structures. In our previous work, we have reported full tensor properties of Ta modified KNN based single crystal, (K, Na)(Nb, Ta)O₃, with "4O" domain structure and "1O" single domain structure. The "4O" domain structure refers to the [001]_C poled structure with four existing spontaneous polarization directions after poling, and "O" means the orthorhombic phase. The "1O" single domain structure refers to the [011]_C poled structure[6-9]. In this work, complete sets of elastic, dielectric and piezoelectric constants of (K, Na)(Nb, Ta)O₃ single crystal with "3O" domain structure ([111]_C poled) were determined. The intrinsic properties were calculated, and compared with the experimental results. Extrinsic and intrinsic contributions to dielectric and piezoelectric properties were discussed.

2. Experimental procedure

The (K, Na)(Nb, Ta)O₃ (abbreviated as KNNT-2, the same crystal with that in Ref. 9 crystal is grown by top-seeded solution growth (TSSG) method. Details of the growth process can be referred to Refs. 6-9. The crystal was oriented using the Laue X-ray machine. In this work, [111]_C is the poling direction and noted as *z* axis, while *x* and *y* axes were along $[1\bar{1}0]_C$ and $[11\bar{2}]_C$, respectively. Gold electrodes were sputtered onto the (111)_C and $(\bar{1}\bar{1}\bar{1})_C$ faces. The combination of resonance and ultrasonic methods were employed to determine the material constants to mitigate the effect of inhomogeneous of composition and improve the self-consistency. For the resonance

measurements, at least 4 samples are needed, including samples for length extensional vibration mode (33 mode), thickness extensional mode (k_t mode), thickness shear mode (15 mode) and lateral extensional mode (31 mode). The aspect ratios of the samples were carefully selected according to IEEE standard. Besides, a cube with the dimensions around $3 \times 3 \times 3 \text{ mm}^3$ is used for ultrasonic measurements. All samples were poled at 80°C with an E field of 32 kV/cm . Details of the measuring procedure were discussed in Refs. 10 and 11.

3. Results and discussion

The KNNT-2 single crystal is in the orthorhombic phase at room temperature. There are 12 possible spontaneous polarizations (P_s) orientation along the face diagonal $\langle 011 \rangle_C$ directions as shown in Fig. 1(a). After poling along $[111]_C$, all P_s vectors switch to three directions which are closest to $[111]_C$, *e.g.*, $[110]_C$, $[101]_C$ and $[011]_C$ [Fig. 1(b)]. Therefore, a multi-domain configuration "3O" is formed. Statistically, the remaining three P_s vectors have equal possibility, so that the macroscopic symmetry is rhombohedra $3m$ symmetry with total 12 independent material constants: 6 elastic, 4 piezoelectric, and 2 dielectric constants.

Table I lists the complete sets of elastic, piezoelectric and dielectric constants of the $[111]_C$ poled KNNT-2 crystal. This is the first full tensor properties for KNN system with "3O" domain structure. These data sets are of great importance for theoretical studies and simulation designs of electromechanical devices. As listed in Table I, the "3O" domain structure exhibits high shear piezoelectricity ($d_{15}=140 \text{ pC/N}$, $k_{15}=0.569$) but low longitudinal properties ($d_{33}=64 \text{ pC/N}$, $k_{33}=0.450$). This characteristic is similar to that of "1O" single domain state ($d_{15}=251 \text{ pC/N}$, $k_{15}=0.637$, $d_{33}=56 \text{ pC/N}$, and $k_{33}=0.453$) [9]. We also measured the corresponding properties for "4O" multi-domain structure ($[001]_C$ poled) of this crystal. Dissimilarly, the "4O" domain structure

shows high longitudinal properties ($d_{33}=150$ pC/N, $k_{33}=0.820$) but low shear piezoelectricity ($d_{15}=40$ pC/N, $k_{15}=0.210$).

In order to further understand the electrical properties of $[111]_C$ oriented KNNT-2 crystal, the theoretical intrinsic parameters were calculated based on single domain data sets (in Ref. 9) by coordinate transformation. The intrinsic coordinate system for orthorhombic KNNT-2 crystal is that: x_i along $[0\bar{1}1]_C$, y_i along $[100]_C$, and z_i along $[011]_C$. The coordinate of $[111]_C$ oriented samples can be obtained by rotating the intrinsic coordinate around x_i axis ($[0\bar{1}1]_C$) in a clockwise direction. When rotated an angle of θ , the longitudinal parameters in the $(0\bar{1}1)_C$ plane can be expressed by the following formulas:

$$d_{33}^* = d_{33}^{sd} \cos^3 \theta + (d_{32}^{sd} + d_{24}^{sd}) \cos \theta \sin^2 \theta, \quad (1)$$

$$\varepsilon_{33}^* = \varepsilon_{33}^{sd} \cos^2 \theta + \varepsilon_{22}^{sd} \sin^2 \theta, \quad (2)$$

$$s_{33}^* = s_{33}^{sd} \cos^4 \theta + (2s_{23}^{sd} + s_{44}^{sd}) \sin^2 \theta \cos^2 \theta + s_{22}^{sd} \sin^4 \theta, \quad (3)$$

and the electromechanical coupling factors can be calculated by

$$k_{33}^* = \frac{d_{33}^*}{\sqrt{\varepsilon_{33}^{T*} s_{33}^{E*}}} \quad (4)$$

where the parameters in the right hand side with superscript "sd" are the single domain data, and those on the left hand side with asterisk "*" are the calculated results. The orientation-dependent d_{33}^* , ε_{33}^* , s_{33}^* and k_{33}^* in the $(0\bar{1}1)_C$ plane are shown in Fig. 2. d_{33}^* changes from 0 to 64.1 pC/N with the variation of θ . In our previous work [9], we have calculated that d_{33}^* ranges between 0 and 121.6 pC/N in the $(100)_C$ plane. Generally speaking, the piezoelectric coefficient d_{33}^* in $(0\bar{1}1)_C$ plane is much lower than that in the $(100)_C$ plane, and its dependence on θ is weaker than that in the $(100)_C$ plane [9]. The maximum d_{33}^* value of 64.1 pC/N occurs at $\theta=38^\circ$, near $[111]_C$ direction ($\theta=35.2^\circ$). The dielectric constant ε_{33}^* depends strongly on θ due to the large difference

between ϵ_{33}^{sd} and ϵ_{22}^{sd} .

The $[111]_C$ direction corresponds to the position of $\theta=35.2^\circ$. By using Eq. 1-4, the longitudinal properties of $[111]_C$ orientated sample can be calculated. Table II lists the calculated and measured values for the $[111]_C$ poled KNNT-2 crystal. The measured and calculated d_{33} values coincide well with each other. As is known, the calculated data only represents the intrinsic contributions from lattice anisotropy, while the measured value includes both intrinsic and extrinsic response from domain wall motions. It can be estimated that the extrinsic piezoelectric contributions in the $[111]_C$ poled KNNT-2 crystal are little. Thus the piezoelectric response is dominated by the intrinsic contributions. **The measured dielectric constant (383) is much lower than the calculated one (646).** Large deviation in dielectric constants has also been observed in Pb-based relaxor single crystals. **For the $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{:Mn}$ crystal, the calculated ϵ_{33}^T is 4205 while the measured value is 3315 [11]. For the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-0.07PbTiO}_3$ crystal, the calculated and measured ϵ_{33}^T values are 7567 and 5622, respectively [12].** *Xiang et al* has pointed out that for the rhombohedral $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ system, the calculated dielectric constants ϵ_{11}^T and ϵ_{33}^T are equal along the $[001]_C$ direction. The domain wall contribution will reduce ϵ_{11}^T but enhance ϵ_{33}^T , so that anisotropic dielectric constants were obtained [12]. In this work, the existence of domain walls may clamp the polarization response to the longitudinal external field, and lead to the low dielectric constant. Therefore, it can be concluded that the extrinsic contributions play an important role in dielectric response, while the piezoelectric response is dominated by the intrinsic contributions.

4. Conclusions

In conclusion, full sets of elastic, dielectric and piezoelectric constants for the $[111]_C$ poled

KNNT-2 crystal with "3O" engineered domain structure have been measured. This is the first available complete data sets for the $[111]_C$ orientated KNN system, which is of great significance for both theoretical studies and material applications. The $[111]_C$ poled crystal show high shear but low longitudinal piezoelectricity ($d_{15}=140$ pC/N, $d_{33}=64$ pC/N). The orientation dependence of longitudinal properties, d_{33}^* , ϵ_{33}^* , s_{33}^* and k_{33}^* in the $(0\bar{1}1)_C$ plane has been calculated. The maximum d_{33}^* occurs at $\theta=38^\circ$, near $[111]_C$ direction, which is coincident with the calculated intrinsic value. On the contrary, the dielectric response is away from the calculated results, which may be affected by extrinsic contributions.

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Table I. Measured and derived constants of KNNT-2 single crystal poled along $[111]_c$ (Density: $\rho = 5165 \text{ kg/m}^3$)

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_{14}^E	c_{33}^E	c_{44}^E	c_{66}^E	c_{11}^D	c_{12}^D	c_{13}^D	c_{14}^D	c_{33}^D	c_{44}^D	c_{66}^D		
21.40	7.38	8.28	-0.64	21.80	5.54	7.01	25.37	8.23	6.14	-2.68	23.70	8.20	8.57		
Elastic compliance constants: s_{ij}^E and s_{ij}^D (10^{-12} m ² /N)															
s_{11}^E	s_{12}^E	s_{13}^E	s_{14}^E	s_{33}^E	s_{44}^E	s_{66}^E	s_{11}^D	s_{12}^D	s_{13}^D	s_{14}^D	s_{33}^D	s_{44}^D	s_{66}^D		
5.83	-1.38	-1.69	0.83	5.87	18.24	14.42	4.89	-1.38	-1.69	0.83	5.87	18.24	12.54		
Piezoelectric coefficients: $e_{i\lambda}$ (C/m ²), $d_{i\lambda}$ (10 ⁻¹² C/N), $g_{i\lambda}$ (10 ⁻³ Vm/N), and $h_{i\lambda}$ (10 ⁸ V/m)															
e_{15}	e_{31}	e_{22}	e_{33}	d_{15}	d_{31}	d_{22}	d_{33}	g_{15}	g_{31}	g_{22}	g_{33}	h_{15}	h_{31}	h_{22}	h_{33}
8.27	-7.45	6.33	6.62	140	-44	39	64	33.2	-13.1	9.2	18.9	32.1	-13.1	9.2	28.7
Dielectric constants: ε_{ij} (ε_0) and β_{ij} (10 ⁻⁴ / ε_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				
477	383	291	260	20.9	26.1	34.4	38.4	0.569	0.315	0.450	0.308				

Table. II Calculated and measured material constants for $[111]_C$ poled KNNT-2 single crystal.

	d_{33} (pC/N)	ε_{33}^T (ε_0)	s_{33}^E ($10^{-12} \text{ m}^2/\text{N}$)	k_{33}
Measured	64	383	5.87	0.450
Calculated	63.9	646	5.16	0.378

Figure captions:

Fig. 1 Schematic of P_S vectors in KNNT-2 single crystal: (a) before poling, (b) after poling.

Fig. 2 Orientation dependence of (a) d_{33}^* , (b) ε_{33}^* , (c) s_{33}^* and (d) k_{33}^* for the KNNT-2 single crystal in the $(0\bar{1}1)_C$ plane.

Fig. 1

Fig. 2