Temperature dependence of dielectric and electromechanical properties of (K,Na)(Nb,Ta)O₃ single crystal and corresponding domain structure evolution

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Domain structures and their evolution with temperature in the [001]_C oriented (K,Na)(Nb,Ta)O₃ (KNNT) single crystal have been studied before and after poling by polarizing light microscopy. The results indicate that the KNNT crystal is difficult to be completely poled by the room temperature poling process. The domain structure is rather stable in the orthorhombic phase, but exhibits substantial changes near the phase transition temperatures T_{O-T} and T_C . Narrower stripe domains are formed during both the orthorhombic-tetragonal and tetragonal-cubic phase transition processes, no intermediate phases were found during the phase transitions. The temperature dependence of the dielectric and piezoelectric properties were measured, and the influence of domain structures on the dielectric and electromechanical properties were quantified. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891718>]

I. INTRODUCTION

Lead-free piezoelectric materials are attractive from the viewpoint of environmental protection. Among all lead-free piezoelectric materials investigated up to date, the (K,Na)NbO₃ [KNN] based perovskite materials are one of the most promising lead-free alternatives for Pb(Zr,Ti)O₃ (PZT) ceramics due to their high Curie temperature and high piezoelectric properties.¹⁻⁴

Similar to the morphotropic phase boundary (MPB) in Pb-based ferroelectric materials, high piezoelectric and dielectric properties can be obtained near the polymorphic phase transition (PPT) temperature T_{O-T} , where the orthorhombic (O) and tetragonal (T) phases coexist.⁵⁻⁸ However, the origin of the high piezoelectricity near PPT has yet to be understood. It is widely accepted that the intermediate phase (monoclinic phase or orthorhombic phase) formed in the MPB composition plays an important role in the enhancement of the electrical properties in Pb-based ferroelectric materials.⁹⁻¹¹ Whether there is an intermediate phase present between the O and T phases in KNN-based materials is still unclear. For deeper understanding on the mechanism and further improvement of the functional properties of KNN-based materials, it is important to find out the origin of the high piezoelectricity near the PPT.

In general, the dielectric and piezoelectric properties of a ferroelectric material can be divided into intrinsic and extrinsic contributions. The intrinsic one is attributed to the

relative ionic shift that preserves the crystal structure orientation, whereas the extrinsic one is ascribed mainly to the movement of domain walls that causes domain switching, or reorientation of polarization.¹¹⁻¹³ Therefore, domain structure is considered an important factor affecting the piezoelectric properties of ferroelectric materials.¹⁴ However, up to date, investigations on domain structures of KNN-based materials are very limited. The evolution of domain structures with temperature, especially during the polymorphic phase transition is still unclear, which is very important for the understanding of the high piezoelectric properties around the O-T phase transition. For the investigation of domain structures, single crystals are preferred over ceramics for the several reasons. First, different domain structures can be obtained in single crystals by adjusting the poling direction and the poling conditions. Second, it is much easier to observe the evolution of domain structures in single crystals with the variation of temperature using controlled electric field along desired crystallographic directions. The lack of such domain structure studies on the KNN-based single crystals is mainly due to the difficulty of growing high quality KNN-based single crystals.^{15,16}

In our previous work, large-size high quality Ta modified KNN based single crystals, (K,Na)_{1-x}(Nb,Ta)_xO₃ [KNNT], were successfully grown by the top-seeded solution growth (TSSG) method, and the full tensor properties of [001]_C poled crystals with tetragonal 4mm engineered domain structure symmetry were determined.¹⁷ In this work, the evolution of domain configuration with temperature was studied by using polarizing light microscopy (PLM), and the temperature dependence of dielectric and piezoelectric properties were also measured. The variations of the electrical

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properties with temperature were discussed in correlation with the change of domain configurations.

II. EXPERIMENTAL PROCEDURE

The KNNT single crystal was grown by the top-seeded solution growth method, details of the growth procedure can be found in Ref. 17. All samples were oriented along pseudo-cubic direction $[001]_C$ using the Laue X-ray machine with an accuracy of $\pm 0.5^\circ$. The samples used for electrical and elastic measurements were prepared according to the IEEE standards. The dielectric constant was determined using an HP 4284D multi-frequency LCR meter. The longitudinal piezoelectric coefficients d_{33} and electromechanical coupling factor k_{33} were determined by the resonance method. A $[001]_C$ oriented thin plate used for domain configuration observation was cut into the dimensions of $3 \times 3 \times 0.6 \text{ mm}^3$, and the larger surfaces were polished into optical quality. Investigations on domain configurations were performed by using a polarizing light microscope (Axioskop 40) equipped with a hot stage. All samples were poled at room temperature under an electric field of 38 kV/cm.

III. RESULTS AND DISCUSSIONS

A. Basic information of the KNNT single crystal

The KNNT single crystal used in this work is in the O phase with $mm2$ crystallographic symmetry at room temperature. The orthorhombic-tetragonal phase transition temperature T_{O-T} and tetragonal-cubic (C) phase transition temperature T_C are around 120°C and 290°C , respectively. The spontaneous polarizations for the orthorhombic perovskite structure are along the twelve $\langle 011 \rangle_C$ pseudocubic directions, as shown in Fig. 1(a). Four kinds of domains are permissible, i.e., 180° , 90° , 60° , and 120° domains. Here, we use capital letters A, B, and D to distinguish the three groups of polarization configurations. The group A includes the four upward polarizations (the dark red arrows in Fig. 1(a), $[011]_C$, $[101]_C$, $[0\bar{1}1]_C$, and $[\bar{1}01]_C$); group B includes the four polarizations in the $(001)_C$ plane (the green arrows, $[110]_C$, $[\bar{1}\bar{1}0]_C$, $[1\bar{1}0]_C$, $[\bar{1}10]_C$); while group D includes the rest four downward polarizations (blue arrows, $[01\bar{1}]_C$, $[10\bar{1}]_C$, $[\bar{1}0\bar{1}]_C$, and $[0\bar{1}\bar{1}]_C$). After poling along $[001]_C$, it is expected that only group A would be left, as shown in Fig.

FIG. 1. Schematic of spontaneous polarizations in the orthorhombic phase: (a) before poling, polarization are along the 12 $\langle 011 \rangle_C$ families, (b) expected polarization directions after poling along $[001]_C$, only group A polarizations should be left.

1(b), and the effective macroscopic domain pattern symmetry changes to tetragonal 4mm after poling.

The extinction position of the domain pattern is determined by the projective direction of the polarization on the observation plane, i.e., the $(001)_C$ crystallographic plane in this work. When we observe the $[001]_C$ oriented KNNT single crystal between the crossed polarizer/analyzer (P/A) pair, groups A and D show extinction when the polarizer is 0° or 90° to the $[100]_C$ direction, while the extinction angle for group B is 45° . According to the crystallographic analysis, the charged and uncharged 90° domain walls are limited to $\{100\}_C$ plane family, charged 60° and uncharged 120° domain walls are in the $\{110\}_C$ planes, the uncharged 60° and charged 120° domain walls are S_2 domain walls that cannot be written in the Miller indices with integer number.^{18–20} 180° domain walls cannot be identified by the PLM.

B. Domain configurations of KNNT single crystals before and after poling

Fig. 2 shows domain configurations taken by the PLM before [(a) and (b)] and after [(c) and (d)] poling along $[001]_C$. The left column shows images around $\theta = 0^\circ$ and the right column around $\theta = 45^\circ$; here, θ is the angle between the polarizer and $[100]_C$ direction and the polarizer is perpendicular to the analyzer. For the unpoled sample, both extinction and bright areas can be observed in Figs. 2(a) and 2(b). This is due to the different extinction angles between groups A, D and group B, consistent with our analysis above. The image taken at $\theta = 45^\circ$ is much brighter than that taken at $\theta = 0^\circ$, this should be ascribed to the fact that the volume fractions belong to groups A and D together are larger than that belongs to group B. Domain walls along $\{100\}_C$ and $\{110\}_C$ plane families can be observed and S_2 domain walls with the angle around 18.4° to the $[100]_C$ direction can also be observed (marked with arrows in Fig. 2(a)), indicating that all kinds of non- 180° domain patterns (90° , 60° , and 120°) are present in the unpoled sample.

As mentioned above, only polarizations in group A are expected to remain after poling, so that only 60° and 90°

FIG. 2. PLM images for the unpoled [(a) and (b)] and poled [(c) and (d)] KNNT single crystals.

domain walls should exist with complete extinction occurs at $\theta = 0^\circ$. However, in Fig. 2(c), though the image is much darker than the unpoled one, complete extinction was not obtained, dim light filters through the sample. This phenomenon indicates that group B polarizations are not completely switched into the group A after room temperature poling process. The polarizations present in the poled sample should be the vector sum of groups A + B, as shown in Fig. 3, not like that in Fig. 1(b). It can be seen from Figs. 2(c) and 2(d) that all domain walls are in the $\{001\}_c$ and $\{011\}_c$ plane families, S_2 domain walls could not be found in the poled crystal. We can conclude that there are 90° , charged 60° , and uncharged 120° domains in the poled sample.

The extent of polarization rotation during poling greatly affects the material properties. It can be inferred that all group D polarizations can be switched to the group A by 180° reversal and stay stably there since no strain deformation is involved during the 180° polarization reversal. It is important to quantify the percentage of switched group B polarizations during poling. The transmission areas in Figs. 2(a) and 2(c) correspond to domains with group B polarizations, while the dark areas in the two images correspond to domains with groups A and D polarizations and domain walls. Therefore, the percentage of group B polarizations in poled samples can be estimated by the light transmittance of the two images. We have digitized the images of Figs. 2(a) and 2(c) coded the colors from 0 to 1 by using the MATLAB software. Here, 0 represents black, corresponding to totally extinction without the group B polarization, and 1 represents white, corresponding to completely transparent without other polarizations and domain walls. Each digitized element on the picture corresponds to a numerical number between 0 and 1, depending on its color. Adding all numbers together can represent the light transmittance of the whole image. The ratio of light transmittances of Figs. 2(a) and 2(c) is 2.21. Hence, the content of group B polarizations in unpoled sample is 2.21 times higher than that in the poled samples. The percentage of switched group B polarizations during poling process should be $(2.21 - 1)/2.21 = 54.8\%$, which is to say that 45.2% of the B group polarizations stay in their original state after poling.

C. Evolution of domain structures with temperature

Fig. 4 shows the temperature dependence of domain structures for the $[001]_c$ poled KNNT single crystals. The

FIG. 3. Virtual polarization directions after poling along $[001]_c$.

FIG. 4. PLM images for the $[001]_c$ poled KNNT single crystal at various temperature: (a) 25 °C, (b) 115 °C, (c) and (d) 116 °C, (e) and (f) 118 °C. (f) is taken at $\theta = 0^\circ$, while other images are taken at $\theta = 45^\circ$. The inset (g) shows the magnified boundary between orthorhombic and tetragonal phase in the image (d).

images (a)–(e) in Fig. 4 were taken at $\theta = 45^\circ$, while (f) was taken at $\theta = 0^\circ$. Comparing Fig. 4(a) taken at room temperature and Fig. 4(b) taken at 115 °C, we found little change except that the amount of domain walls decreased slightly at higher temperatures, indicating that the domain structure is fairly stable in the orthorhombic temperature range. It should be noted that most of the reduced domain walls are in $\{110\}_c$ plane families, while the amount of 90° domain walls in the $\{001\}_c$ planes keeps almost unchanged in this temperature range. According to the Landau-Devonshire model, 90° domain walls have lower energy than the uncharged 120° and charged 60° domain walls.^{21,22} Therefore, 90° domains are more stable. In other words, the elastic energies of the charged 60° and uncharged 120° domain walls are higher than that of the 90° domain walls. Such high mechanical stresses can be released by the rotation of the polarizations at high temperatures. Therefore, the amount of domain walls in the $\{110\}_c$ planes decreases with increasing temperature.

The domain structures show drastic changes near 116 °C, as can be seen in Figs. 4(c) and 4(d), which correspond to the O-T phase transition, at which the spontaneous polarizations rotate from the 12 orthorhombic $\langle 011 \rangle_c$ directions to the 6 tetragonal $\langle 001 \rangle_c$ directions. The T phase shows extinction at $\theta = 0^\circ$, and the brightest angle is $\theta = 45^\circ$. High strain accumulates at the boundary of the two phases due to the differences in lattice symmetries and lattice parameters. Therefore, phase transition starts at locations where stresses can be easily released, such as edges of the

sample or defect regions. From Fig. 4, we can conclude that the O-T phase transition process is finished in two steps: partial depolarization of the orthorhombic phase and the formation of the tetragonal phase. As shown in Fig. 4(c), a small area of the sample became darker first at 116 °C, then the dark area spreads to the whole sample with further increasing temperature, indicating that more orthorhombic polarizations rotated from group A to group B, which corresponds to the first step. Then, a bright area appeared at the edge of the sample, indicating the formation of the tetragonal phase, which corresponds to the second step. The tetragonal phase spreads to the whole sample gradually with further increasing temperature, as shown in Fig. 4(d). Fine domain structures with the width of several micrometers are formed at the boundary between O and T phase to release the stress originated from the lattice mismatching, as shown in the magnified image in Fig. 4(g). Coexistence of tetragonal 90° domain (domain wall is along $[010]_C$ direction) and orthorhombic charged 60° domain/uncharged 120° domains (domain wall is along $\langle 110 \rangle_C$ family directions) can be observed in Fig. 4(g).

The whole phase transition process is completed in a very narrow temperature range (within 2 °C) around 116 °C. Figs. 4(e) and 4(f) are taken at 118 °C with $\theta = 45^\circ$ and 0° , respectively. The sample shows complete extinction at $\theta = 0^\circ$ but high transmittance at 45° , indicating that the sample is in the T phase at this temperature. Unlike the situation in Pb-based ferroelectric materials, the KNNT crystal changes directly from the O phase to the T phase, and no intermediate phase was observed during the transition process.

Fig. 5 shows the variation of domain structures near the T-C phase transition temperature T_C . At 285 °C, as shown in Fig. 5(a), the sample is translucent at $\theta = 45^\circ$, indicating that the sample is in the T phase. 90° domain walls in $(101)_C/(\bar{1}01)_C$ plane can be observed in the tetragonal temperature range, which is formed between $[001]_C/[00\bar{1}]_C$ and $[100]_C/[\bar{1}00]_C$ polarizations, as shown in Fig. 5(a). As the temperature is increased to 286 °C, extinction area corresponding to

FIG. 5. Variation of the domain structures around the Curie temperature T_C . (a) taken at 285 °C, (b) 286 °C, (c) 287 °C, and (d) 300 °C. The inset (e) shows the magnified domain structures in image (b) during the phase transition.

the cubic (C) phase appears at the edge of the sample [shown in Fig. 5(b)]. At the same time, fine domain structures with domain width of several micrometers are formed to release the stress between the two phases, as shown in the enlarged image (e). Most of domain walls are in the $(110)_C$ plane, with objection along $[\bar{1}10]_C$ direction in the $[001]_C$ surface. According to the direction of the domain walls, we conclude that these domains are tetragonal 90° domains. The C phase spreads quickly to the whole sample with further increasing temperature. Fig. 5(b) shows the coexistence of C phase (extinction areas) and T phase (fine domain structure area). At 287 °C, only small areas at the edge of the sample are in the T phase [Fig. 5(c)]. With further increase of the temperature, this area also changed into the C phase as shown in Fig. 5(d).

D. Temperature dependence of piezoelectric and dielectric properties

The temperature dependence of the longitudinal electro-mechanical coupling factor k_{33} and piezoelectric coefficient d_{33} for the $[001]_C$ poled KNNT crystal are shown in Fig. 6. The inset shows the variation of the dielectric constant ϵ_{33}^T as a function of temperature. In the orthorhombic temperature range, the dielectric constant increases gradually with temperature. At T_{O-T} around 116 °C, a peak of the dielectric constant was observed, corresponding well to the drastic changes of domain structures. The electromechanical coupling factor k_{33} shows nearly temperature independent behavior below T_{O-T} , while d_{33} shows a similar trend to that of the dielectric constant but the change is much gentler as the temperature approaches T_{O-T} . The correlation among the piezoelectric coefficient, dielectric constant, and the electro-mechanical coupling factor is given below

$$d_{33} = k_{33} \sqrt{\epsilon_{33}^T \epsilon_{33}^E}. \quad (1)$$

As can be seen from Fig. 6, ϵ_{33}^T and d_{33} increase as the temperature approaches T_{O-T} . In general, the dielectric and piezoelectric properties can be divided into two parts: the intrinsic contribution from small lattice deformation in single domain regions (polarization extension and rotation in the

FIG. 6. Longitudinal electromechanical coupling factor k_{33} and piezoelectric coefficient d_{33} of the $[001]_C$ poled KNNT crystal as a function of temperature. The inset shows the dielectric constant ϵ_{33}^T for the $[001]_C$ poled KNNT crystal.

vicinity of the equilibrium position) and the extrinsic contribution from the domain wall motions (partial domain switching in the domain wall regions). It is recognized that the extrinsic contributions dominant in polycrystalline systems, such as PZT ceramics. Therefore, in general, the dielectric and piezoelectric properties depend greatly on the domain structures in the sample. As can be seen in Fig. 4, domain structures change very little in the orthorhombic temperature range, so that the increase of the dielectric and piezoelectric constants in the O phase mainly arises from the easier domain wall motions and the softening of lattice structure at higher temperatures.

During the O-T phase transition process, k_{33} , d_{33} , and ϵ_{33}^T show drastic changes. The increased dielectric constant and piezoelectric coefficient near the T_{O-T} should be attributed to the fine domain structures formed during the phase transition, as can be seen in Figs. 4(d) and 4(g).^{20,23–25} It can also be deduced that the increase of the dielectric constant near T_C should be ascribed to the higher domain density formed during the phase transition from the T phase to the C phase. In the O-T phase transition, the spontaneous polarization directions change from $\langle 011 \rangle_C$ to $\langle 001 \rangle_C$ and new domain patterns are formed while the O-phase domain structures disintegrate. The initially $[001]_C$ poled sample becomes largely depoled after the change of domain patterns, which leads to the drastic decrease of the piezoelectric coefficient and the electromechanical coupling factor.

IV. SUMMARY AND CONCLUSIONS

Temperature evolution of domain configurations has been studied for the $[001]_C$ poled KNNT single crystal. Our results can be summarized as follows: (i) Complete poling is difficult to achieve by the room temperature poling process for the KNNT single crystal. (ii) Domain structures are stable in the orthorhombic temperature range, but show drastic changes around the phase transition temperatures T_{O-T} and T_C . Narrow stripe domains were observed near the phase transition temperatures, but no intermediary phase was observed during the phase transitions. (iii) The increase of the dielectric and piezoelectric constants in the O phase temperature range might be ascribed to easier domain wall motions and polar vector rotations in the vicinity of the energy minima at higher temperatures. (iv) The drastic increase of the dielectric and piezoelectric properties near T_{O-T} is caused by finer domains (higher domain wall density) formed during the phase transition process, which enhanced extrinsic contributions.

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