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PII: S1359-6454(17)30652-3

DOI: [10.1016/j.actamat.2017.08.009](https://doi.org/10.1016/j.actamat.2017.08.009)

Reference: AM 13970

To appear in: *Acta Materialia*

Received Date: 5 May 2017

Revised Date: 4 August 2017

Accepted Date: 4 August 2017

Please cite this article as: X. Lv, J. Wu, D. Xiao, J. Zhu, X. Zhang, Electric field-induced phase transitions and composition-driven nanodomains in rhombohedral-tetragonal potassium-sodium niobate-based ceramics, *Acta Materialia* (2017), doi: 10.1016/j.actamat.2017.08.009.

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Electric Field-Induced Phase Transitions and Composition-Driven Nanodomains in Rhombohedral-Tetragonal Potassium-Sodium Niobate-Based Ceramics

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Abstract: The mechanisms behind the high piezoelectricity of (K,Na)NbO₃-based lead-free ceramics were investigated, including electric field-induced phase transitions and composition-driven nanodomains. The construction of a rhombohedral-tetragonal (R-T) phase boundary, confirmed using several advanced techniques, allowed a large piezoelectric constant (d_{33}) of 450 ± 5 pC/N to be obtained in $(1-x)\text{K}_{0.4}\text{Na}_{0.6}\text{Nb}_{0.945}\text{Sb}_{0.055}\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Hf}_{1-y}\text{Sn}_y)\text{O}_3$ ($0 \leq x \leq 0.06$ and $0 \leq y \leq 0.5$) ceramics possessing an ultralow $\Delta U_{\text{T-R}}$ of 7.4 meV. More importantly, the existence of an intermediate phase, i.e., the electric-induced phase (EIP), bridging the rhombohedral R [$P_s//\langle 111 \rangle$] and tetragonal T [$P_s//\langle 001 \rangle$] phases during the polarization rotation was demonstrated. Striped nanodomains (~40 nm) that easily responded to external stimulation were also observed in the ceramics with an R-T phase. Thus, the enhanced piezoelectric properties originated from EIP and the striped nanodomains.

Keywords: Lead-free piezoelectric; Electric-induced phase; Nanodomains

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1. Introduction

Pronounced piezoelectric properties (425~570 pC/N) comparable to those of lead-based ceramics were recently reported in (K,Na)NbO₃ (KNN)-based ceramics with a rhombohedral-tetragonal (R-T) phase boundary [1-5]. These enhanced piezoelectric properties were attributed to the existence of the R-T phase boundary and the nanodomain structures, leading to an easy rotation of the polarization [4-6]. When exploring the relationships between the phase structure and the piezoelectric properties in PZT-based ceramics, an intermediate phase between the rhombohedral (R) and tetragonal (T) phases was thought to play an important role in enhancing the piezoelectricity [7,8]. However, few investigations have looked for an intermediate phase in KNN-based ceramics with an R-T phase boundary [9]. Moreover, the physical mechanisms of high piezoelectricity should be further explored.

Two predominant factors have been intensively considered as the origins of enhanced piezoelectric properties: polarization rotation (and extension) and domain structure [10-16]. For example, Cohen *et al.* theoretically reported that the polarization rotation from the R phase [$P_s//(111)$] to the T phase [$P_s//(001)$] can generate an excellent piezoelectric response in BaTiO₃ [10]. However, there is no group or sub-group relationship between the R and T phases; therefore, an intermediate phase is highly expected to bridge the two phases. An intermediate phase (e.g., orthorhombic or monoclinic phase) has been reported during the poling process in BCTZ and PMN-PT materials, which facilitated the polarization rotation and, thus, enhanced the piezoelectricity [11,12]. Vanderbilt and Cohen theoretically extended the Devonshire theory from a sixth-order to an eighth-order expansion, and successfully explained the occurrence of a monoclinic phase in PZT with a morphotropic phase boundary (MPB)

[16]. Therefore, the existence of an intermediate phase in KNN-based ceramics with an R-T phase is anticipated. In addition to the polarization rotation, the domain structures also affect the properties of a piezoelectric material, and nanodomain structures are especially sensitive to external stimuli (electric field or stress) [15,16].

In this work, the effects of an intermediate phase and nanodomain structures, and the physical mechanisms behind high piezoelectric properties are studied in detail using a typical sample of $(1-x)\text{K}_{0.4}\text{Na}_{0.6}\text{Nb}_{0.945}\text{Sb}_{0.055}\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Hf}_{1-y}\text{Sn}_y)\text{O}_3$ ceramic with an R-T phase boundary. A wide R-T phase boundary was formed in the ceramics with $0 \leq y \leq 0.4$, resulting in a large d_{33} of 450 ± 5 pC/N. More importantly, an electric-induced phase (EIP) bridged the R and T phases, promoting the polarization rotation from R [$P_s // (111)$] to T [$P_s // (001)$]. In addition, the nanodomain structures also enhanced the piezoelectric properties.

2. Experimental

$(1-x)\text{K}_{0.4}\text{Na}_{0.6}\text{Nb}_{0.945}\text{Sb}_{0.055}\text{O}_3-x\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Hf}_{1-y}\text{Sn}_y)\text{O}_3$ $\{(1-x)\text{KNNS}-x\text{BN}(\text{Hf}_{1-y}\text{Sn}_y),$
 $(x=0-0.06, y=0.1)$ and $(x=0.03, y=0-0.5)\}$ ceramics were fabricated via the conventional solid-state method with the raw materials K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), Sb_2O_3 (99.99%), HfO_2 (99.9%) and SnO_2 (99.5%). After being precisely weighted according to the formula, the raw materials were ball-milled for 24 h with zirconia ball media and alcohol in plastic jars. The dried slurry was calcined at 850 °C for 6h, then the calcined powders were pressed into disks of 9 mm diameter and 1 mm thickness under 10 MPa using PVA as a binder. After burning off the PVA, the resulting pellets were sintered at 1060~1120 °C for 3 h under corundum crucible in air. Silver paste was printed and fired onto both sides of

the as-sintered samples at 600 °C for 30 min to form the electrodes for the electrical measurements. Then the samples were poled in a silicone oil bath by applying an electric field of 4kV/mm for 30 min at room temperature.

X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Bruker axs Inc., Madison, WI, CuK_α) characterization was used to collect the crystal information of the ceramics. *In situ* synchrotron XRD was carried out at the Shanghai Synchrotron Radiation Facility using a beam line 14B1 ($\lambda=1.2348\text{\AA}$), and two sides of the ceramics with $x=0.03$ were sputtered with gold electrode for measuring the crystal structure under an electric field. For the Rietveld refinement, the as-sintered samples were ground into powders and then annealed at 600 °C for 30 min to eliminate the internal stress induced by the grinding. Finally, a high-resolution XRD instrument (X' Pert Pro MPD (DY 120 PANalytical, Netherlands)) was used to collect the XRD data from the powder. The Maud software package was used to perform the refinement. The domain structures were observed with FEI Titan 80-300 electron microscopes with an accelerating voltage of 300 kV and vertical piezoresponse force microscopy (VPFM) (MFP-3D, Asylum Research, Goleta, CA). The piezoelectric constant (d_{33}) was tested using a piezo- d_{33} meter (ZJ-3 A, China), and the planar electromechanical coupling factor (k_p) was measured using an impedance analyzer (HP 4299A). The temperature dependencies of the dielectric constant (ϵ_r) and the loss ($\tan \delta$) of the unpoled and poled samples were measured via a broadband dielectric and impedance spectrometer (Novocontrol Technologies, Germany). The Raman spectra were measured using a Horiba Aramis Raman spectrometer (Horiba Scientific) with an excitation source of 473 nm. The temperature was controlled by a connected temperature controller. In order to measure the Raman spectra of the poled samples, the unpoled samples were

painted on both sides with conductive silver adhesives. Then, the unpoled samples were poled in a silicone oil bath by applying an electric field of 4kV/mm for 30 min at room temperature. Finally, the poled samples were immersed in an acetone solution for 1 h to completely wipe off the conductive silver adhesives.

The *ab initio* calculations were performed with the CASTEP program from Dassault Systèmes BIOVIA. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional represented the generalized gradient approximation (GGA) [30,31]. The energy cut off for the plane waves was 598 eV and the Brillouin zone was sampled using a 6×6×6 Monkhorst-Pack grid. For each phase, we fixed the $(K_{0.4}Na_{0.6})NbO_3$ cell with an experimental lattice constant and let the atomic sites become fully relaxed until the force tolerance was 0.01 eV/Å. Additionally, virtual crystal approximation (VCA) was adopted to simulate the real atom distribution in the disordered crystals [32].

3. Results and discussion

The phase structure of the $(1-x)KNNS-xBN(Hf_{1-y}Sn_y)$ ceramics [Figs. S1-3 of *Supporting Information*] was identified by the XRD patterns and the permittivity vs. temperature ($\epsilon-T$) curves. Phase diagrams are plotted in Figs. 1(a) and (b). Both T_{R-O} and T_{O-T} shifted to room temperature as x increased, and converged at $0.03 \leq x \leq 0.05$, resulting in the formation of coexisting R and T phases (R-T phase boundary) at $0.03 \leq x \leq 0.04$ [Fig. 1(a)]. Meanwhile, the R-T phase boundary existed over the wide range at $0 \leq y \leq 0.4$ [Fig. 1(b)]. Figures 1(c) and (d) show the piezoelectric properties of the $(1-x)KNNS-xBN(Hf_{1-y}Sn_y)$ ceramics. The piezoelectric properties of $(1-x)KNNS-xBNHf_{0.9}Sn_{0.1}$ were closely related to the phase structure; that is, a low d_{33}

of 160 pC/N was measured in the ceramics with $x=0$, due to the existence of only the O phase, while d_{33} reached a maximum value of 450 ± 5 pC/N in ceramics with $x=0.03$, due to the involvement of the R-T coexistence phase. For $0.97\text{KNNS}-0.03\text{BNHf}_{1-y}\text{Sn}_y$, the largest d_{33} of 450 ± 5 pC/N was obtained over the wide composition range of $y=0 \sim 0.4$, i.e., in the region of the R-T phase boundary [Fig. 1(d)]. Therefore, the construction of the R-T phase boundary effectively improved the piezoelectric properties of the tested KNN-based ceramics. Here, the enhanced d_{33} is mainly assigned to the easy polarization rotation in the R-T phase, which was supported by the ultralow $\Delta U_{\text{T-R}}$ (~ 7.4 meV) [21]. Therefore, the exact path of the polarization rotation and the related physical mechanisms were investigated, especially to establish the existence of the intermediate phase.

Figure 1: (a)-(b) Phase diagrams; (c)-(d) d_{33} and k_p values of $(1-x)\text{KNNS}-x\text{BNHf}_{1-y}\text{Sn}_y$ ceramics as a function of x and y .

First, we verified the R-T phase boundary in KNN-based ceramics using several advanced techniques. Because of the sensitivity of the crystal to deformation induced by the tilting of the NbO_6 octahedra and cationic displacements [17], the Raman technique was used to analyze the phase progression. Generally, the vibrations of the NbO_6 octahedra consist of six modes, $1A_{1g}(\nu_1)+1E_g(\nu_2)+2F_{1u}(\nu_3,\nu_4)+F_{2g}(\nu_5)+F_{2u}(\nu_6)$, where $1A_{1g}(\nu_1)+1E_g(\nu_2)+1F_{1u}(\nu_3)$ are the stretching modes and the other three are bending modes [18]. Both the ν_1 and ν_5 modes were used to identify the phase transitions, where ν_1 represented the doubly degenerate symmetric O-Nb-O stretching vibration, and ν_5 represented the triply degenerate symmetric O-Nb-O bending vibration [19].

The Raman spectra strongly supported the existence of an R-T phase boundary. Figure 2(a) shows the Raman spectra of the $(1-x)\text{KNNs}-x\text{BN}(\text{Hf}_{0.9}\text{Sn}_{0.1})$ ceramics. All of the observed vibrations were within the wavelength range $100\text{-}1200\text{ cm}^{-1}$. The observations in the wavenumber range $500\text{-}700\text{ cm}^{-1}$, corresponding to the $A_{1g}(\nu_1)$ and $E_g(\nu_2)$ modes, were fitted to the Lorentz function in order to demonstrate the Raman shift of ν_1 [Fig. 2(c)]. Both ν_1 and ν_5 shifted to higher wavenumbers as x increased from 0 to 0.03 [Fig. 2(c)], which suggests an increase in the force constant caused by the decreasing distance between Nb and its coordinated oxygen [19]; more details can be found in Table 1. As x increased from 0.1 to 0.3, the cell parameter a ($=b$) of the T phase reduced from $3.9813\text{ \AA}$ to $3.9592\text{ \AA}$, and the parameter c increased from $3.9516\text{ \AA}$ to $3.9682\text{ \AA}$, resulting in an overall reduction in the distance between Nb and its coordinated oxygen. As x further increased from 0.03 to 0.04, which exactly corresponded to the R-T phase boundary zone, both ν_1 and ν_5 remained almost unchanged due to the similar parameters (a , b , and c) of the R and T phases [Table 1]

[18]. Finally, both ν_1 and ν_5 rapidly decreased as x increased up to 0.06, indicating the phase transition from the T phase to the pseudo-cubic phase. In the same way, we analyzed the Raman spectra of the $0.97\text{KNNS}-0.03\text{BN}(\text{Hf}_{1-y}\text{Sn}_y)$ ceramics, as shown in Figs. 2(b) and (c). Both ν_1 and ν_5 remained almost unchanged in the composition range of $0 \leq y \leq 0.4$, which corresponded to the R-T phase boundary zone [Fig. 2(d)]. As y increased up to 0.5, both ν_1 and ν_5 rapidly increased due to the phase transition from the R-T phase to the pseudo-cubic phase.

Figure 2: (a)-(b) Raman spectra and (c)-(d) Raman shift of the ν_5 and ν_1 modes of $(1-x)\text{KNNS}-x\text{BN}(\text{Hf}_{1-y}\text{Sn}_y)$ ceramics as a function of x and y , respectively. The insets exhibit the Lorentz fitting for the Raman spectrum of the ceramics with $x=0.03$ and $y=0$, in the range $500-700 \text{ cm}^{-1}$.

To further identify the phase structure, Rietveld refinement was performed for the $(1-x)\text{KNNS}-x\text{BN}(\text{Hf}_{0.9}\text{Sn}_{0.1})$ ceramics. Figures 3(a)-(d) show the enlarged Rietveld refinement of the XRD patterns in $2\theta=44-47/48^\circ$. All of the XRD patterns were

well-refined, as indicated by a high match between the fitting data and the original observations [Figs. 3(a)-(d)]. Low R_w (<11%) and Sig values (<1.3) were observed for each composition, confirming the satisfactory selection of the phase structure mode for each composition [Table 1] [20]. Thus, the XRD patterns, ϵ_r - T curves (Figs. S1-3 of *Supporting Information*), Raman spectra, and Rietveld refinement all fully supported the existence of the R-T phase boundary.

Previously, the low polarization anisotropy was recognized at PZT-based ceramics possessing the MPB, which was proved by the flat Gibbs free energy profile between R and T phases [7,8,14]. Therefore, the energy differences between the O and T phases, and between the coexisting R and T phases, were calculated following first-principles methods [plotted in Fig. 3(e)]. The calculations were performed using the simple $(K_{0.4}Na_{0.6})NbO_3$ mode with the cell parameters listed in Table 1. Here, the reference energy ($U=0$) is set to the energy of the O phase of the ceramics with $x=0.01$. The energy of the T phase was much lower than that of the O phase ($\Delta U_{O-T}=9.55$ eV), indicating that the T phase was more stable than the O phase for $x=0.01$. This result matches the corresponding XRD pattern [Fig. S1(b) of *Supporting Information*]. For $x=0.01$, the intensity of the $(200)_{PC}$ peak was slightly higher than the $(002)_{PC}$ peak, suggesting the involvement of the T phase. For the R-T phase boundary, an almost equal energy value between the R and T phases was observed in the samples with $x=0.03$ and 0.04 , possessing $\Delta U_{T-R}=7.4$ meV and 7.3 meV, respectively; this ultralow ΔU_{T-R} allowed the stable coexistence of the R and T phases, with a low rotation barrier either from the T to R phase, or from the R to T phase [21].

Figure 3: Enlarged Rietveld refinement of the XRD patterns with (a) $x=0$, (b) $x=0.01$, (c) $x=0.03$, and (d) $x=0.05$; (e) Energy differences between phases of the ceramics with $x=0.01$, 0.03, and 0.04.

It has been proposed that an electric-induced phase (EIP) acts as an intermediate phase, bridging the R and T phases and facilitating the polarization rotation, thus enhancing the piezoelectric properties [22]. Figure 4(a) displays the effect of the poling electric field (E_{pol}) on the piezoelectricity of the ceramics with $x=0.03$. As E_{pol} increased, d_{33} first increased rapidly, then plateaued. In order to further investigate the mechanisms behind the poling process, we measured the *in situ* XRD patterns under different electric fields, as shown in Fig. 4(b). Six representative diffraction peaks, which respectively correspond to the (001)/(100)_{PC}, (002)/(200)_{PC}, and (202)/(220)_{PC}

peaks, were measured. As the electric fields increased from 0 kV/cm to 2.22 kV/cm, the intensity of the peaks only changed due to the non-180° domain switching [Fig. 4(b)] [22]. As the electric fields increased further to 5.56 kV/cm, the (001)/(100)_{PC} and (202)/(220)_{PC} peaks each merged into a single peak, and the (200)_{PC} peak nearly vanished. As the electric fields continued to increase (11.11~22.22 kV/cm), both splitting peaks, (001)/(100)_{PC} and (002)/(200)_{PC}, merged into a single peak; however, the single (202)/(220)_{PC} peak split into three peaks [see the black arrows in Fig. 4(b)], indicating the occurrence of EIP. After the removal of the electric fields, both the (001)/(100)_{PC} and (002)/(200)_{PC} peaks partially recovered, whereas the (202)/(220)_{PC} peaks merged into a single peak. Some other diffraction peaks appeared in (001)/(100)_{PC} and (002)/(200)_{PC} after the poling process [black arrows in Fig. 4(b)], suggesting that EIP still remained.

Figure 4: (a) d_{33} and (b) *in situ* synchrotron XRD patterns with respect to (001)/(100)_{PC}, (002)/(200)_{PC}, and (202)/(220)_{PC} peaks of the ceramics with $x=0.03$ as a function of electric field.

To find further evidence of EIP, the dielectric properties (e.g., permittivity and $\tan \delta$) of the unpoled and poled ceramics with $x=0.03$ were measured [Figs. S4(a)-(f) and Figs. 5(a)-(f)]. Before the poling process, only one anomaly, at ~ 50 °C, was observed in the ε_r - T curves, representing the R-T phase boundary [Fig. S4(a)], and the corresponding $\tan \delta$ - T curves also confirmed one anomaly, at ~ -25 °C [Figs. 5(c) and (f)]. After the poling process, two anomalies were clearly observed in the ε_r - T curves, at ~ -50 °C and ~ 25 °C, for the two poled samples [Figs. S4(b) and (c)]; furthermore, the $\tan \delta$ - T curves displayed four anomalies, at ~ -110 °C, ~ -10 °C, ~ 50 °C, and ~ 110 °C [Figs. 5(a) and (b)], strongly supporting the occurrence of EIP. Therefore, EIP did exist during the poling process and remained even after the electric fields were removed. Unfortunately, it is nearly impossible to accurately analyze the space group and parameters of EIP in bulk ceramics due to its complexity.

Figure 5: Dielectric loss ($\tan \delta$) of (a) poled sample #1, (b) poled sample #2, and (c) unpoled ceramics with $x=0.03$. (d-f) Corresponding enlarged figures in the

temperature range 50-200 °C. Two poled samples were measured to exclude chance errors.

To follow the path of the polarization rotation and structural progression of EIP, the Raman spectra of the unpoled and poled ceramics with $x=0.03$ were measured, as shown in Figs. 6(a)-(c). Both sides (e.g., 1 and 2) of the poled samples were measured. Figures 6(d)-(f) show the Raman shift of the A_{1g} mode. After the poling process was complete, the decreased strength of the constant force induced by increased distance between Nb and its coordinated oxygen (the Nb-O bond) caused the A_{1g} peak to shift from 609.4 cm^{-1} to either 606.1 cm^{-1} or 604.5 cm^{-1} [23]. A similar phenomenon was shown in KNNLST ceramics with the O-T phase boundary [23]. The polarization rotation from the R phase [$P_s//\langle 111 \rangle$] to the T phase [$P_s//\langle 001 \rangle$] has been extensively reported in PZT-based materials with MPB [8,9,12-14]. Therefore, the stretching of the Nb-O bond observed in this work was probably a result of the polarization rotation from a $P_s//\langle 111 \rangle$ vector to a $P_s//\langle 001 \rangle$ vector causing an elongated tetragonal distortion along the c axis.

A simple schematic in Fig. 6(g) visually represents the effects of EIP on the polarization rotation. We present two possible intermediate phases, either an orthorhombic (O) or a monoclinic (M) phase, due to the lack of exact space group and cell parameters of EIP, which were widely accepted in the BaTiO_3 and PZT-based ceramics [10-14]. Evidently, EIP (either O or M phase), which possesses a crystal symmetry approaching both the R and T phases, appeared and acted as a bridge during the poling process and was partly retained even after removing the external electric fields. Then, the polarization rotated along the route of $R \rightarrow \text{EIP} \rightarrow T$, which

facilitated the polarization rotation and improved the piezoelectric properties. In addition, the tetragonal distortion was elongated along the c axis, resulting in the increase of Nb-O bond length, i.e., the increased distance between Nb and its coordinated oxygen.

Figure 6: Raman spectra of the (a) unpoled ceramics, side #1 (b) and side #2 (c) of the poled ceramics with $x=0.03$; (b-f) Corresponding the fitting of Raman spectra in the wavenumber range 500-700 cm^{-1} ; (g) Schematic of the polarization rotation during the poling process.

To show the development of the phase transitions, we collected the temperature-dependent Raman spectra for the unpoled and poled samples with $x=0.03$, as shown in Figs. S5(a) and (b). Figures 7(a)-(c) show the variation in the A_{1g} mode of the unpoled ceramics with $x=0.03$ as a function of temperature. If there are no phase transitions, then a steady phonon softening and an increase in FWHM are highly expected [24]. In the unpoled ceramics, the A_{1g} mode slightly shifted to a lower wavenumber and FWHM steadily increased before 50 °C. The A_{1g} mode plateaued in the temperature range -25 to 50 °C, which corresponded to the stable region of the

R-T phase boundary. Furthermore, two apparent anomalies were observed around 50 °C and 125 °C, respectively. According to the ε_r - T curves [Fig. S2], a single tetragonal phase should be observed in the ceramics with $x=0.03$ at $T>T_{R-T}$. Therefore, the first anomaly is attributed to the decreasing R phase content and the second is attributed to the phase transition from R-T to T.

In the poled ceramics, four anomalies were visible at around -100 °C, -25 to 0 °C, 50 °C, and 100 °C [Figs. 7(d)-(f)], which were consistent with the four anomalies observed in the $\tan \delta$ - T curves of the poled samples [Figs. 5(a) and (b)]. KNN-based ceramics are known to possess an R phase at low temperatures [25]. In addition, the coexistence of the R, EIP, and T phases was observed in the poled samples at -10 to 50 °C [Figs. 5(a) and (b)]. Therefore, the first anomaly represented the phase transition from the R to R+EIP phase, and the second was the phase transition from the R+EIP to the R+EIP+T phase. Above 50 °C, the phase structure of the poled samples gradually changed into a T phase only. Therefore, the third anomaly should be attributed to the decrease in R and EIP content, and the fourth anomaly is due to the completed transition from a multi-phase coexistence to a single T phase. Thus, we tentatively summarize the structural phase transitions in this work as $R \rightarrow R+EIP \rightarrow R+EIP+T \rightarrow \text{decreasing } R \text{ and/or } EIP \rightarrow T$.

Figure 7: Temperature dependencies of (a) intensity, (b) full width at half maximum (FWHM), and (c) Raman shifts of the A_{1g} mode for the unpoled ceramics with $x=0.03$. (d)-(f) Corresponding counterparts for the poled ceramics with $x=0.03$.

Due to the influence of the domain structure on the piezoelectric properties, we performed TEM and vertical PFM measurement on unpoled ceramics with $x=0.03$. The striped domain structures with widths of ~ 40 nm were clearly observed [Fig. 8(a)], while both striped and irregular domain structures were detected by vertical PFM [Fig. 8(b)]. The striped domain structures were reported previously in the T phase region of KNN-based ceramics [26]. As we know, the occurrence of domain is to reduce the free energy of a material [27,28]; then, the empirical equation $d \propto \sqrt{F_{DW}}$ determines the scale of domain, where d is the scale of the domain and F_{DW} is the domain wall energy [29]. According to the previous reference, a low F_{DW} was observed in the MPB region of PZT-based ceramics with an R-T coexistence phase due to the low polarization anisotropy, leading to the occurrence of

nanodomains [27]. In this work, the polarization anisotropy was greatly diminished due to the stable R-T phase with an ultralow $\Delta U_{T-R}=7.4$ meV, resulting in the occurrence of nanodomains. As a result, these striped and irregular nanodomains easily responded to external stimulation (electric field or stress), enhancing the net piezoelectricity.

Figure 8: Domain structures measured by (a) TEM and (b) vertical PFM.

4. Conclusion

A wide zone where the R and T phases coexist (R-T phase) was constructed in KNN-based ceramics by co-doping Sb^{5+} and $\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Hf}_{1-y}\text{Sn}_y)$ ($0 \leq y \leq 0.4$), which possessed a pronounced d_{33} of 450 ± 5 pC/N. The *in situ* synchrotron radiation patterns and the ϵ_r (and $\tan \delta$)- T curves supported the occurrence of an electric-induced phase (EIP). This EIP acted as an intermediate phase bridging the R and T phases during the poling process, and was even partially retained after the electric fields were removed, facilitating the polarization rotation and, thus, enhancing the piezoelectric properties. The room-temperature Raman spectra of the unpoled and poled samples suggested the polarization rotation moved from the R [$P_s//\langle 111 \rangle$] to T [$P_s//\langle 001 \rangle$] phase, and the temperature-dependent Raman spectra showed the possible structural development of the phase transitions in the poled samples to be $R \rightarrow R + \text{EIP} \rightarrow R + \text{EIP} + T \rightarrow \text{decreasing}$

R and/or EIP→*T*. In addition, striped nanodomain structures with widths of ~40 nm were observed by TEM. Vertical PFM detected both striped and irregular domain structures that easily responded to external stimulation (e.g., electric field or stress), improving the net piezoelectricity. Therefore, we conclude that the piezoelectric properties of KNN-based ceramics are enhanced by the occurrence of EIP and the nanodomain structures.

Acknowledgments

The authors gratefully acknowledge that the research reported in this publication was supported by the National Science Foundation of China (NSFC Nos., 51332003 and 51272164) and the King Abdullah University of Science and Technology (KAUST). The authors thank Mr. Yueliang Gu (*Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Pudong New Area, Shanghai 201204, P. R. China*) for measuring the *in situ* XRD patterns, Mr. Chenhui Zhang for calculating the energy of the O-T and R-T phase coexistence, and Mr. Qiang Zhang for measuring the TEM patterns.

Table 1: Results from the Rietveld refinement for the powder samples with $x=0$, 0.01, 0.03, 0.04, and 0.05.

x (phase)	Cell Parameters				Content (%)	R_w (%)	Sig
	a (Å)	b (Å)	c (Å)	α ($=\gamma=\beta$) (°)			
0 (O)	3.9504	5.6182	5.6425	90	100 (<i>Amm2</i>)	9.94	1.21
0.01 (O-T)	3.9711	5.5344	5.6617	90	50.61 (<i>Amm2</i>)	9.94	1.20
	3.9813	3.9813	3.9516	90	49.39 (<i>P4mm</i>)		
0.03 (R-T)	3.9843	3.9843	3.9843	89.64	43.96 (<i>R3m</i>)	10.02	1.21
	3.9592	3.9592	3.9682	90	56.04 (<i>P4mm</i>)		
0.04 (R-T)	3.9820	3.9820	3.9820	89.68	39.3 (<i>R3m</i>)	10.28	1.22
	3.9612	3.9612	3.9689	90	60.7 (<i>P4mm</i>)		
0.05 (T)	3.9659	3.9659	3.9851	90	100 (<i>P4mm</i>)	10.12	1.22

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