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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)NbO\textsubscript{3}-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)K\textsubscript{0.4}Na\textsubscript{0.6}Nb\textsubscript{0.945}Sb\textsubscript{0.055}O\textsubscript{3}-(x)Bi\textsubscript{0.5}Na\textsubscript{0.5}(Hf\textsubscript{1-y}Sn\textsubscript{y})O\textsubscript{3} (0≤x≤0.06 and 0≤y≤0.5) ceramics possessing an ultralow $\Delta U_{TR}$ of 7.4 meV. More importantly, the existence of an intermediate phase, i.e., the electric-induced phase (EIP), bridging the rhombohedral R [P\textsubscript{s}//(111)] and tetragonal T [P\textsubscript{s}//(001)] 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)NbO$_3$ (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 BaTiO$_3$ [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)
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)K_{0.4}Na_{0.6}Nb_{0.945}Sb_{0.055}O_3-xBi_{0.5}Na_{0.5}(Hf_{1-y}Sn_y)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)K_{0.4}Na_{0.6}Nb_{0.945}Sb_{0.055}O_3-xBi_{0.5}Na_{0.5}(Hf_{1-y}Sn_y)O_3 \quad \{(1-x)\text{KNNS}-x\text{BN(Hf}_{1-y}\text{Sn}_y)\},

(\chi=0-0.06, \, \gamma=0.1) \quad \text{and} \quad (\chi=0.03, \, \gamma=0-0.5) \quad \text{ceramics were fabricated via the conventional solid-state method with the raw materials K}_2\text{CO}_3 \quad (99\%), \quad \text{Na}_2\text{CO}_3 \quad (99.8\%), \quad \text{Nb}_2\text{O}_3 \quad (99.5\%), \quad \text{Bi}_2\text{O}_3 \quad (99.999\%), \quad \text{Sb}_2\text{O}_3 \quad (99.99\%), \quad \text{HfO}_2 \quad (99.9\%) \quad \text{and} \quad \text{SnO}_2 \quad (99.5\%). \quad \text{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, CuKα) 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 (λ=1.2348Å), 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 (d33) was tested using a piezo-d33 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 δ) 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 \((\varepsilon-T)\) 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 0.97KNNS-0.03BNHf$_{1-y}$Sn$_y$, the largest $d_{33}$ of 450±5 pC/N was obtained over the wide composition range of $y=0$~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 $\Delta U_{T-R}$ (~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-$x$)KNNS-$x$BNHf$_{1-y}$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 $\nu_1$ and $\nu_5$ modes were used to identify the phase transitions, where $\nu_1$ represented the doubly degenerate symmetric O-Nb-O stretching vibration, and $\nu_5$ 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-$x$)KNNS-$x$BN(Hf$_{0.9}$Sn$_{0.1}$) ceramics. All of the observed vibrations were within the wavelength range 100-1200 cm$^{-1}$. The observations in the wavenumber range 500-700 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 $\nu_1$ [Fig. 2(c)]. Both $\nu_1$ and $\nu_5$ 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 Å to 3.9592 Å, and the parameter $c$ increased from 3.9516 Å to 3.9682 Å, 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 $\nu_1$ and $\nu_5$ remained almost unchanged due to the similar parameters ($a$, $b$, and $c$) of the R and T phases [Table 1].
[18]. Finally, both $\nu_1$ and $\nu_5$ 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 0.97KNNS-0.03BN(Hf$_{1-y}$Sn$_y$) ceramics, as shown in Figs. 2(b) and (c). Both $\nu_1$ and $\nu_5$ 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 $\nu_1$ and $\nu_5$ rapidly increased due to the phase transition from the R-T phase to the pseudo-cubic phase.

![Raman spectra](image)

**Figure 2:** (a)-(b) Raman spectra and (c)-(d) Raman shift of the $\nu_5$ and $\nu_1$ modes of $(1-x)$KNNS-$x$BN(Hf$_{1-y}$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 cm$^{-1}$.

To further identify the phase structure, Rietveld refinement was performed for the $(1-x)$KNNS-$x$BN(Hf$_{0.9}$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 $\text{Sig}$ 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, $\varepsilon_r$-$T$ 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 $(K_{0.4}Na_{0.6})\text{NbO}_3$ 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 $\Delta U_{T-R}$ 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 ($E_{\text{pol}}$) on the piezoelectricity of the ceramics with $x=0.03$. As $E_{\text{pol}}$ 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)$_{\text{PC}}$, (002)/(200)$_{\text{PC}}$, and (202)/(220)$_{\text{PC}}$
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](image.png)

**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 δ) 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 $\varepsilon_r$-$T$ curves, representing the R-T phase boundary [Fig. S4(a)], and the corresponding tan δ-$T$ curves also confirmed one anomaly, at ~ -25 °C [Figs. 5(c) and (f)]. After the poling process, two anomalies were clearly observed in the $\varepsilon_r$-$T$ curves, at ~ -50 °C and ~25 °C, for the two poled samples [Figs. S4(b) and (c)]; furthermore, the tan δ-$T$ 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 δ) 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 [$P_s/(111)$] to the T phase [$P_s/(001)$] 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 $P_s//(111)$ vector to a $P_s//(001)$ 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 $R\rightarrow EIP\rightarrow T$, 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 $\varepsilon_r$-$T$ 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 $R\rightarrow R+EIP\rightarrow R+EIP+T\rightarrow$ decreasing $R$ 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 unpol ed 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.](image)

4. Conclusion

A wide zone where the R and T phases coexist (R-T phase) was constructed in KNN-based ceramics by co-doping $\text{Sb}^{5+}$ 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 $\varepsilon_r$ (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 [$P_s//\{111\}$] to T [$P_s//\{001\}$] phase, and the temperature-dependent Raman spectra showed the possible structural development of the phase transitions in the poled samples to be $R \rightarrow R+EIP \rightarrow R+EIP+T \rightarrow$ 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.

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

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<td>0.01 (O-T) 3.9711 5.5344 5.6617 90</td>
<td>50.61 (Amm2)</td>
<td>9.94</td>
<td>1.20</td>
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<tr>
<td>3.9813 3.9813 3.9516 90</td>
<td>49.39 (P4nm)</td>
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<tr>
<td>0.03 (R-T) 3.9843 3.9843 3.9843 89.64</td>
<td>43.96 (R3m)</td>
<td>10.02</td>
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<tr>
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<td>39.3 (R3m)</td>
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<td>100 (P4nm)</td>
<td>10.12</td>
<td>1.22</td>
<td></td>
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