Synergetic Contributions in Phase Boundary Engineering to the Piezoelectricity of Potassium Sodium Niobate Lead-Free Piezoceramics

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Abstract: Although the pronounced piezoelectricity was obtained in (K, Na)NbO₃ piezoceramics with the phase boundary engineering (PBE), the physical mechanisms remain pending. Here we revealed for the first time how PBE influences the piezoelectric properties through synergetic contributions. Cryogenic experiments confirm that PBE constructs a phase coexistence, consisting of rhombohedral (R), orthorhombic (O), and tetragonal (T) phases, with a structural softening, by which a high piezoelectric coefficient d_{33} of 555 pC/N and the enhanced temperature stability of strain are achieved. The phenomenological theory and transmission electron microscope demonstrate that the superior d_{33} hinges on the flattened Gibbs free energy and the abundant nano-domains (10-80 nm), which respectively induce the enhanced permittivity and the coexisting single-domain and multi-domain zones. In particular, we disclosed a trade-off relationship between ferroelectric domains and polar

nanoregions (PNRs) and found the “double-edged sword” role of PNRs in the piezoelectricity enhancement. Therefore, this work helps understand the physical mechanisms of the piezoelectricity enhancement, benefiting the future research of lead-free piezoceramics.

Keywords: Potassium sodium niobate; Phase boundary engineering; Structural softening; Nano-domains; Physical mechanisms

1. Introduction

Demand for replacing the toxic lead-based piezoceramics has made investigations on lead-free piezoceramics one of the hottest topics in ferro/piezoelectric.¹ Potassium sodium niobate {(K, Na)NbO₃, KNN}-based ceramics attract researchers' attention because of the high Curie temperature ($T_c \sim 410$ °C) and moderate piezoelectricity.² In particular, the newly proposed phase boundary engineering (PBE), simultaneously adjusting two ferroelectric-ferroelectric phase transition temperatures (i.e., rhombohedral-orthorhombic T_{R-O} and orthorhombic-tetragonal T_{O-T}) to room temperature, effectively enhanced the piezoelectric properties and improved the temperature stability,³⁻⁶ endowing KNN-based ceramics with the promising potential in practical application.⁷

Although the PBE brought in the pronounced piezoelectricity, the physical mechanisms remain pending, specifically insufficiently understanding the synergetic contributions from the phase structure, ferroelectric domains, and polar nanoregions (PNRs).⁸ The different phase structures were reported in the similar (or even same) KNN-based ceramics modified by the PBE.⁹⁻¹⁰ The same group even reported different phase structures when proceeding with highly similar compositions.^{5, 11-14}

Ferroelectric domains, the external contribution to the piezoelectricity, were reported to contribute to the piezoelectricity enhancement of KNN-based ceramics.^{4-6, 15} However, most reported ferroelectric domains came from the unpoled samples, which have no net piezoelectricity because of lacking the poling process that causes the domain switching and domain wall motion.^{4-6, 15} In particular, through observing domains of unpoled and poled samples, new physical mechanisms were dug in BT- and BNT-based ceramics.¹⁶⁻¹⁷ However, the related study is rare in KNN-based ceramics but is crucial to further analyze the physical mechanisms.^{16, 18-22}

PNRs were reported to cause distinct dielectric relaxor characteristics and contribute to the enhanced piezoelectric properties.²³⁻²⁴ The PBE inevitably induces PNRs in KNN-based ceramics because of aliovalent substitutions on A- (K/Na) and B- (Nb) sites,²⁵ which was revealed by the frequency dependency of permittivity.^{6, 26} In particular, the relaxor behavior of KNN-based ceramics with PBE differs from that of canonical lead-based relaxors.²⁷ The former occurs near room temperature together with ferroelectric-ferroelectric phase transition, but the latter occurs near T_m (the temperature of the maximum permittivity) or in the low-temperature range, accompanying with no phase transitions.²⁷ Therefore, the different physical mechanisms are predictable. However, the role of PNRs in piezoelectricity was rarely analyzed in KNN-based ceramics. More importantly, the piezoelectric properties of piezoceramics hinge on the synergetic effects of forgoing factors, which have never been reported in KNN-based ceramics.

Here we exemplified $(1-x)(K_{0.48}Na_{0.52})(Nb_{0.955}Sb_{0.045})O_3-x(Bi_{0.5}Ag_{0.5})ZrO_3-0.2wt\%Fe_2O_3$ ceramics to decode the synergetic effects. We first obtained a large $d_{33}=555$ pC/N and the improved temperature

stability at $x=0.04$ where the multi-phase coexistence is. We then demonstrated the composition-dependent phase structure and the structural softening and observed ferroelectric domains of both unpoled and poled samples. Finally, we discussed the synergetic effects of the phase structure, domains, and PNRs on piezoelectric properties by combining experimental results with the phenomenological theory. The analysis shows that the superior d_{33} hinges on the flattened Gibbs free energy profile and the abundant nano-domains (10-80 nm), which respectively induce the enhanced permittivity and the coexisting single-domain and multi-domain zones. In particular, we disclosed a trade-off relationship between ferroelectric domains and polar nanoregions (PNRs) and found the “double-edged sword” role of PNRs in the piezoelectricity enhancement.

2. Methods

The detailed process of preparing $(1-x)(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-x(\text{Bi}_{0.5}\text{Ag}_{0.5})\text{ZrO}_3-0.2\text{wt}\%\text{Fe}_2\text{O}_3$ (abbreviated as KNNS- x BAZ-Fe, $x=0-0.08$) and measuring the phase structure, domain structure, and electrical properties can be found in the Electronic Supporting Information (ESI).

3. Results and Discussion

We first collected d_{33} and T_c (or depolarization temperature, T_d) of representative lead-based and lead-free piezoceramics (Figure 1(a)). Barium titanate $\{\text{BaTiO}_3, \text{BT}\}$ based ceramics exhibit a high d_{33} (620-700 pC/N) but a low T_c (<100 °C);²⁸⁻²⁹ KNN-based ceramics with PBE show a high d_{33} (490-650 pC/N) and a benign T_c (150-250 °C);^{3-4, 27, 30} quenched bismuth ferrite $\{\text{BiFeO}_3, \text{BFO}\}$ based ceramics possess both a high d_{33} (~ 400 pC/N) and a high T_c (~ 450 °C);³¹ and sodium bismuth titanate $\{(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3, \text{BNT})\}$ based ceramics' d_{33} and T_d are seriously limited below 300 pC/N and 200 °C.³²

Therefore, the PBE endows KNN-based ceramics with comparable d_{33} and T_c to those of commercial piezoceramics (e.g., PZT-4 and PZT-5H) and with the promising potential for electronic devices.⁷ Here we obtained a high d_{33} of 555 pC/N and T_c of 220 °C at $x=0.04$, comparable to commercial soft PZT (e.g., PZT-4 and PZT-5H) ceramics and state-of-the-art non-textured KNN-based ceramics (Figure 1(a)).^{4, 27, 30} Besides, the strain is also enhanced in the multi-phase coexistence region, and an electrostriction strain of 0.084% is obtained at $x=0.08$ (Figure S12, ESI), 10 times larger than that of morphotropic relaxor boundary (MRB)-modified KNN-BT ceramics.³³

We then compared the temperature stability of the unipolar strain (S_{uni}) (Figure 1(b)). BNT- and BT-based ceramics exhibit an apparent decrease with temperature.³⁴⁻³⁵ Similarly, KNN-based ceramics with an O-T phase coexistence also show a strongly temperature-dependent S_{uni} .³⁶ Therefore, these ceramics occupy the left bottom area of Figure 1(b), showing the relatively poor temperature stability. The almost vertical morphotropic phase boundary (MPB) endows PZT-4 and PZT-5H ceramics with excellent temperature stability and the increased S_{uni} with temperature.³⁷ Thus, lead-based ceramics take up the top area of Figure 1(b). However, the PBE significantly enhances temperature stability and thus helps KNN-based ceramics fill up the gap between the abovementioned lead-free and lead-based ceramics. In particular, samples with $x=0.04$ show comparable temperature stability to KNN-BLT-BZ-Mn ceramics and highly textured KNN-3T ceramics (Figure 1(b)).⁵⁻⁶ Therefore, the PBE indeed endows KNN-based ceramics with high d_{33} values and improved temperature stability, guaranteeing the reliability of subsequent analysis and discussion.

Figure 1. (a) Relationship between d_{33} and T_c (or T_d for BNT-based ceramics) in state-of-the-art non-textured lead-free piezoceramics; (b) $S_{uni}(T)/S_{uni}(RT)$ varying with temperature in representative lead-based and lead-free piezoceramics. This work means the temperature stability of S_{uni} of KNNS- x BAZ-Fe ($x=0.04$) ceramics (Figure S13, ESI).

To resolve the controversy for the phase structure of KNN-based ceramics with PBE, we first analyzed the composition-dependent phase structure by the combined tools (Figures S1-S9, ESI). In particular, we carried out the systemic temperature-dependent dielectric properties (i.e., real part of permittivity $\epsilon'-T$, imaginary part of permittivity $\epsilon''-T$, and loss factor $\tan \delta-T$) for all compositions for the first time, which were only conducted on the particular a few compositions in most references.^{6, 12, 38} We demonstrated that samples with $x=0.04$ possessed an R-O-T multi-phase coexistence whether before or after poling (Figures 2(a-c) and Figures S1-S9, ESI).

We then studied the structural softening of the R-O-T multi-phase coexistence. Temperature-dependent Raman spectra show that ν_1 mode, doubly degenerated stretching mode of Nb-O octahedron, shows two anomalies at 80 °C and 225 °C, which are respectively ascribed to the R-O-T phase

coexistence to the T phase and the ferroelectric to paraelectric phase transitions (Figures 2(d, e)). In particular, ν_1 mode steadily decreases at $-50\text{ }^{\circ}\text{C} - 75\text{ }^{\circ}\text{C}$ (Figure 2(e)), but the normal R-O and O-T phase transitions cause distinct anomalies in ν_1 mode (Figures S10 (a, b), ESI). Therefore, the R-O-T multi-phase coexistence at $x=0.04$ is the diffused one, indicating the structural softening, which is absent in samples with $x=0$ because of the well-arranged lattice (Figure S10, ESI).

We next studied the origin of structural softening by measuring temperature-dependent dielectric properties at different frequencies. In unpoled samples, $\epsilon'-T$ and $\epsilon''-T$ curves show the distinct relaxor characteristic at $-50\text{ }^{\circ}\text{C} - 75\text{ }^{\circ}\text{C}$ (Figure 2(f, g)), and $\tan \delta-T$ curves exhibit the relaxor characteristic at lower temperatures (Figure 2(h)). The relaxor characteristic here resembles that of relaxor-PbTiO₃ single crystals but is accompanied by the ferroelectric-ferroelectric phase transition (or multi-phase coexistence) (Figure 2(g)). Furthermore, the poling process sharpens $T_{\text{O-T}}$, regains $T_{\text{R-O}}$ (see black arrows), and reduces the relaxor characteristic at $-50\text{ }^{\circ}\text{C} - 75\text{ }^{\circ}\text{C}$ (Figure 2(i-k)). The reappeared $T_{\text{R-O}}$ indicates that unpoled samples possess the diffused R phase that is then reinforced by the poling process, demonstrated by the increased R phase content after poling (Figure 2(c)).³⁹ Therefore, we ascribed the structural softening to the diffused R phase and the relaxor characteristic associated with PNRs that are caused by aliovalent substitutions (e.g., substituting Bi³⁺ on K⁺/Na⁺ and Zr⁴⁺ on Nb⁵⁺). Considering the low R phase content and its high pseudo-cubic characteristic (Table S1, ESI), we speculated that PNRs are the diffused R phase, which needs to be further studied in the future.

Even though the reduced relaxor characteristic in poled samples, $T_{\text{R-O}}$ is still weak, and $T_{\text{O-T}}$ is not as sharp as that of poled samples with $x=0$ (Figure S10, ESI). In particular, the maximum polarization

($P_{\max}$) shows no abrupt decrease at T_{O-T} , and the coercive field (E_c) exhibits the slight increase at 20 °C – 80 °C (Figure 2(l)), differing from samples with $x=0$ whose $P_{\max}$ (E_c) abruptly decreases (increases) near T_{O-T} (Figure S10, ESI). Furthermore, we found the negligible decrease in diffuseness degree (γ) in both unpoled and poled samples by using the modified Curie-Weiss law (Figure 2(m-o) and Figure S10, ESI). Therefore, the structural softening exists at the level of the lattice of the R-O-T multi-phase coexistence and remains in poled samples. Besides, the structural softening is also proved by the temperature-dependent strain properties (Figures S13 and S14, ESI).

Figure 2. Phase structure and structural softening analysis for KNNS-xBAZ-Fe ($x=0.04$) ceramics. Rietveld

refinements for (a) unpoled and (b) poled samples; (c) fraction of R, O, and T phases; (d) Temperature-dependent Raman spectra of the unpoled sample; (e) position of ν_1 mode varying with temperature; (f) $\epsilon'-T$, (g) $\epsilon''-T$, and (h) $\tan \delta-T$ curves of the unpoled sample; (i) $\epsilon'-T$, (j) $\epsilon''-T$, and (k) $\tan \delta-T$ curves of poled sample; (l) variations of $P_{\max}$ and E_c of the poled sample with temperature; (m) ϵ_r-T curves of unpoled and poled samples, measured at 10 kHz; linear fitting between $\ln(T-T_m)$ and $\ln(1/\epsilon_r - 1/\epsilon_m)$ of (n) unpoled and (o) poled samples. FE and RE respectively represent the ferroelectric multi-phase coexistence and relaxor characteristics. The black arrows in (i-k) indicate the R-O phase transition. $P_{\max}$ and E_c are extracted from Figure S13 (ESI).

To unveil the contribution from domains, we then conducted TEM measurements on samples with $x=0$ and $x=0.04$. Unpoled KNNS- x BAZ-Fe ($x=0$) ceramics show the herringbone submicron domains, which resemble those of other pure KNN-based ceramics and are deemed as 90° domains (Figure S15, ESI).⁴⁰⁻⁴¹ Conversely, unpoled KNNS- x BAZ-Fe ($x=0.04$) ceramics exhibit much more complex domains. A rectangular-ambulatory-plane domain configuration is comprised of intensive striped nano-domains with a scale of 20-40 nm (marked as I domain in Figures 3(a, d, g)), which was also reported in other PBE-modified KNN-based ceramics with high performance.^{6, 26} The inset of Figure 3(d) shows its structural illustration. Additionally, the striped nano-domains with a scale of 50-80 nm are also observed in the same area and are labeled as II domain (Figures 3(a, d, j)). More importantly, the intensive root-like nano-domains with a scale of 20-30 nm are observed (Figures 3(b, e, h, k)), which heavily intertwined and formed a labyrinthine domain zone (marked as III and IV domains).⁴²⁻⁴³ The alternative lamellar domains and curved domain walls are also observed (marked as V and VI domains) (Figures 3(c, f)), which were reported in PZT ceramics on the R phase side.⁴⁴ Two sides of these alternative domains show a scale of 10-15 nm and 30-35 nm in width, respectively (Figures 3(i,

l)). Meanwhile, each side of alternative domains is comprised of the hierarchical nano-domains and distinguished by the alternative green and red regions in Figure 3(f). Interestingly, an intermediate domain wall with a scale of 30 nm is also observed within some alternative domains (Figures 3(f, i)). The inset of Figure 3(f) shows the structural illustration of these lamellar domains. The nano-domains are ascribed to the R-O-T multi-phase coexistence and are comparable to those of state-of-the-art lead-free piezoceramics.⁵⁻⁶

Figure 3. Domain structure of unpoled KNNS- x BAZ-Fe ($x=0.04$) ceramics. TEM image and corresponding colored image of (a, d) rectangular-ambulatory-plane domain, (b, e) root-like nano-domain, (c, f) lamellar domain; (g-l)

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4 statistics of domain width of representative domains marked in (d, e, f). The insets of (d, f) show the structural
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6 illustration of rectangular-ambulatory-plane and lamellar domains, respectively.
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11 After poling, the size and morphology of domains are greatly changed. Intensive nano-domains are
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13 found along the direction of the electric field and exhibit a scale of 20-40 nm (Figures 4(a, d, g, h)).
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15 Importantly, the coexistence of single-domain and multi-domain is observed in another grain (Figures
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17 4(b, e)). The multi-domain configuration exhibits a scale of 80-150 nm (Figures 4(e, i)), and the single-
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19 domain configuration shows a flattened morphology (Figures 4(e, j)). The insets of Figures 4(b, e)
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21 show that the single-domain configurations are separated by the straight domain walls. Also, the
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23 coexistence of single-domain and multi-domain is found in other grains (Figures 4(c, f)). The multi-
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25 domain configuration possesses a scale of 15-35 nm (Figures 4(f, k, l)). The simplification of domains
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27 is attributed to the disappearance of 108° domain walls and the re-orientation of non- 180° domains.¹⁰
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29 More importantly, the unique single-domain configuration was also found in (Ba, Ca)TiO₃-Ba(Zr,
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31 Ti)O₃ ceramics during *in situ* TEM observations and believed to be responsible for the piezoelectricity
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33 enhancement.^{16, 19-20} The initial multi-domain was changed into a single-domain after experiencing the
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35 intermediate state of nano-domains.^{16, 19-20} The single-domain was metastable and quickly changed
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37 into the multi-domain after removing or further increasing the electric field.^{16, 19-20} Therefore, the
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39 coexistence of single-domain and nanoscale multi-domain here resembles the situation of (Ba,
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41 Ca)TiO₃-Ba(Zr, Ti)O₃ ceramics and thus contributes to the enhanced piezoelectric properties.^{16, 19-20}
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Figure 4. Domain structure of poled KNNS- x BAZ-Fe ($x=0.04$) ceramics. (a-c) TEM images and (d-f) corresponding colored images of three kinds of representative domains; (g-l) statistics of domain width of representative domains marked in (d, e, f). The black arrow in (a-c) indicates the direction of the applied electric field and “GB” in (a, b) means the grain boundary. The insets of (b, e) show the enlarged view of an alternative single-domain zone.

To unveil the physical mechanisms of high d_{33} , we first discussed the importance of the R-O-T multiphase coexistence. Piezoelectric properties of ferroelectrics can be evaluated by the equation

$$d_{33}=2Q_{33}\varepsilon_{33}P_r \quad (1)$$

where Q_{33} , ε_{33} , and P_r are the electrostriction coefficient, dielectric permittivity, and remanent polarization, respectively.⁴⁵ Q_{33} hinges on the order degree of the cation arrangement and increases with increasing order degree.⁴⁶ The PBE destroys the order degree of K^+/Na^+ and Nb^{5+} to some degree due to aliovalent substitutions (Figures S1-S9, ESI), resulting in a reduction in Q_{33} . Also, P_r decreases with increasing x (Figure S12, ESI). Thus, the increase in d_{33} hinges on the enhanced ε_{33} . Indeed, both unpoled and poled samples show the increased ε_r in the R-O-T multi-phase coexistence region (Figure 5(a)). In particular, the sharp jump is observed when comparing the room-temperature ε_r in the poled samples with $x=0$ and $x=0.04$, being about the quintuple increase (Figure 5(b)). Therefore, this jump is a cornerstone for the piezoelectricity enhancement in KNNS- x BAZ-Fe ($x=0.04$) ceramics. Although poled samples with $x=0.06$ - 0.08 still possess high ε_r because of their relatively low T_c , their P_r values are significantly decreased (Figures S11-S12, ESI). Because of the synergetic effect of ε_r and P_r , d_{33} and $\varepsilon_r P_r$ reach their enhanced values in the R-O-T multi-phase coexistence region (Figures 5(a, d)).

The enhanced ε_{33} originates from the low polarization anisotropy and the flattened Gibbs free energy (Figures 5(f-h)).⁴⁷ On the one hand, the R-O-T multi-phase coexistence has more polarization vectors than the single phase and thus allows more polarization rotation paths (Figures 5(d, e)); on the other hand, its flattened Gibbs free energy significantly reduces the low energy barrier for polarization rotation (Figures 5(f-h)).⁴⁷ Both factors promote the response of polarization to the electric field and thus enhance ε_{33} .⁴⁸⁻⁴⁹

Figure 5. (a) ϵ_r of unpoled and poled KNNS- x BAZ-Fe ceramics; (b) ϵ_r - T curves of poled KNNS- x BAZ-Fe ceramics with $x=0$ and 0.04; (c) d_{33} and $\epsilon_r P_r$ of poled KNNS- x BAZ-Fe ceramics; (d) structural model of spontaneous polarization of R, O, and T phases; (e) possible polarization rotation path in the diffused R-O-T multi-phase coexistence; 3D Gibbs free energy profile of unpoled KNNS- x BAZ-Fe ceramics with (f) $x=0$ and (g) $x=0.04$; (h) two-dimension (2D) Gibbs free energy profile of unpoled KNNS- x BAZ-Fe ceramics ($x=0$ and 0.04). For unpoled KNNS- x BAZ-Fe ($x=0$) ceramics, the strong polarization anisotropy is observed and the O phase exhibits the lowest energy, which coincides with the O phase structure at room temperature. For unpoled KNNS- x BAZ-Fe ($x=0.04$) ceramics, the polarization anisotropy is substantially reduced and the flattened energy profile is observed among R, O, and T phases, indicating an easy polarization rotation at the diffused R-O-T multi-phase coexistence.

We then discussed the contributions from domains and PNRs to high d_{33} . According to the classical

theory, the domain size (d) is proportional to the domain wall energy (F_{DW}), that is, $d \propto \sqrt{F_{DW}}$.⁵⁰ The low polarization anisotropy of the R-O-T multi-phase coexistence significantly decreases F_{DW} and thus reduces the domain size, resulting in the occurrence of nano-domains (Figure 3). Subsequently, these nano-domains are easily re-orientated by the electric field and then form the coexisting single-domain and multi-domain zones, promoting the piezoelectric properties (Figure 4). Furthermore, PNRs act as a seed and further promote the domain switching.²³

Here we emphasized the trade-off relationship between ferroelectric domains and PNRs in the piezoelectricity enhancement. With increasing x , ferroelectric domains reduce in quantity and size, but PNRs show an increasing content (Figures 6(a) and Figure S11, ESI). These factors reduce the barrier energy for domain switching and domain wall motion (Figure 6(b)) and thus decreases E_c monotonously (Figures 6(c) and S12, ESI). However, the increasing (decreasing) content of PNRs (ferroelectric domains) leads to the reduction of polarization vectors along the direction of the electric field, resulting in the dramatic deterioration in P_{max} and P_r (Figures 6(c) and S12, ESI). Therefore, achieving the saturated poling becomes more difficult with increasing x because of the increasing amount of non-collinear PNRs (Figure 6(a)), which is demonstrated by the decreased phase angle (θ) and the lower Raman shifting in poled KNNS- x BAZ-Fe ($x=0.04$) ceramics (Figures 6(d) and Figures S18-S19, ESI). Therefore, PNRs are a “double-edged sword”, that is, although it facilitates the domain switching and domain wall motion, it cannot be re-orientated completely. Hence, the increased d_{33} is the balanced consequence of ferroelectric domains and PNRs at the R-O-T multi-phase coexistence, which explains why d_{33} and $\epsilon_r P_r$ respectively reach their maximum values at $x=0.04$ and $x=0.045-0.05$ (Figure 5(c)).

Inspired by the foregoing analysis, here we proposed a promising concept to further increase d_{33} of lead-free piezoceramics. As expressed in Equation (1), both high ϵ_r and P_r are expected to achieve a high d_{33} . Therefore, an ideal concept is to introduce a small number of PNRs to a ferroelectric matrix with very strong ferroelectricity, which was realized in relaxor-PbTiO₃ single crystals,^{23, 51} but hasn't been reported in lead-free piezoelectric materials so far. Therefore, future work can focus on balancing the ferroelectric domains and PNRs in lead-free piezoceramics.

Figure 6. (a) Structural illustration of the distribution of ferroelectric domains and PNRs in poled KNNS- x BAZ-Fe

ceramics; (b) schematic diagram of barrier energy for domain switching in KNNS-*x*BAZ-Fe (*x*=0 and 0.04) ceramics; (c) *P-E* loops of KNNS-*x*BAZ-Fe (*x*=0, 0.04, and 0.08) ceramics; (d) phase angle (θ) of poled KNNS-*x*BAZ-Fe (*x*=0-0.06) ceramics. The fading color in (a) represents the decrease of ferroelectric domains in amount and size. Phase angle (θ) is extracted from Figure S17, ESI.

4. Conclusion

Here we exemplified KNNS-*x*BAZ-Fe ceramics to reveal physical mechanisms of the enhanced piezoelectricity by PBE. We first obtained a high d_{33} of 555 pC/N and the enhanced temperature stability of S_{uni} at *x*=0.04. We then demonstrated that PBE-modified KNN-based ceramics (e.g., *x*=0.04) possess the R-O-T multi-phase coexistence with a structural softening. The structural softening is ascribed to the diffused R phase and the PNRs induced by aliovalent substitutions. TEM measurements show the abundant nano-domains with a scale of 10-80 nm, which are re-oriented by the electric field and then form the coexisting single-domain and multi-domain zones. The subsequent analysis shows that the increased d_{33} hinges on the low polarization anisotropy, the flattened Gibbs free energy, and nano-domains. The first two enhance ϵ_r and the last one promotes the domain switching and domain wall motion. In particular, we revealed the “double-edged sword” role of PNRs. Although it facilitates the domain switching and domain wall motion, it cannot be re-orientated completely. Therefore, the increased d_{33} is the balanced consequence of ferroelectric domains and PNRs at the R-O-T multi-phase coexistence. Finally, we also proposed a promising concept to further increase the d_{33} of lead-free piezoceramics, that is, introducing a small number of PNRs to a ferroelectric matrix with very strong ferroelectricity.

Conflicts of interest

The authors declare no competing interests.

Acknowledgments

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