Tuning the Covalency of A-O Bonds to Improve the Performance of KNN-Based Ceramics with Multiphase Coexistence

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ABSTRACT: Although a room-temperature multiphase coexistence (MPC) strategy improves the piezoelectric coefficient (d_{33}) of potassium sodium niobate ((K, Na)NbO₃, KNN) ceramics, it still suffers from the dependencies on composition and temperature, making it remain challenging to further improve d_{33} and temperature stability of strain for an already-built MPC. Here we proposed a new route to resolve this issue, that is, tuning the covalency of A-O bonds in an already-built MPC. We chose 0.96(Na_{0.60}K_{0.40})(Nb_{0.955}Sb_{0.045})O₃-0.04(Bi_{0.5}Na_{0.5})ZrO₃ ceramics as an already-built MPC and replaced (Bi_{0.5}Na_{0.5})²⁺ with Ba²⁺ to tune the covalency of A-O bonds. Thus, we synthesized 0.96(Na_{0.60}K_{0.40})(Nb_{0.955}Sb_{0.045})O₃-0.04(Bi_{0.5}Na_{0.5})_{1-x}Ba_xZrO₃ ceramics. We not only improved d_{33} values from 450 pC/N (at $x=0$) to 500-505 pC/N (at $x=0.05$ -0.10) but also obtained the enhanced temperature stability for strain at $x=0.10$, outperforming that of samples with $x=0$ and other KNN-based ceramics. The increased d_{33} is attributed to the well-preserved MPC and the repaired long-range ordering (LRO), and the improved temperature stability of strain is due to shifting the MPC to a slightly higher temperature than room temperature. Therefore, the new route is useful to further improve the

performance of an already-built MPC, benefitting to the future design of MPC and the practical application of KNN-based ceramics.

KEYWORDS: *KNN, new route, piezoelectricity, temperature stability, covalency of A-O bonds*

INTRODUCTION

KNN-based lead-free piezoceramics have received more and more concern to hopefully replace the widely utilized lead-containing ones.¹⁻² In particular, constructing an MPC near room temperature via moving the rhombohedral-orthorhombic and/or orthorhombic-tetragonal phase transition temperatures (T_{R-O} and/or T_{O-T}) has significantly enhanced its piezoelectricity (e.g., d_{33}), making it promising as a lead-free candidate.³⁻⁴

To construct an MPC near room temperature, $(\text{Bi}_{0.5}\text{M}_{0.5})\text{ZrO}_3$ (BMZ, $\text{M} = \text{Na, K, Ag, and } (\text{Na}_{0.82}\text{K}_{0.18})$) has been utilized to shift T_{O-T} to room temperature (Figure 1(a)),³ which brings in two outcomes. First, the room-temperature ϵ_r first increases because of approaching to the MPC but then decreases because of the significantly destroyed LRO at high contents of BMZ (e.g., $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$, BNZ in Figure 1).⁵⁻⁶ Second, both A- and B-sites are heterovalent-substituted, which gradually breaks the KNN matrix's LRO and increases the volume fraction of polar nanoregions (PNRs).⁶⁻⁷ For ferroelectric ceramics, their d_{33} values are determined by equation (1):

$$d_{33}=2Q\epsilon_rP_r \quad (1)$$

where Q , ϵ_r , and P_r are the electrostriction coefficient, relative dielectric permittivity, and remanent polarization, respectively.⁸ Q hinges on the B-site cation arrangement and thus decreases with

increasing BNZ content because of substituting on B-site with Zr^{4+} (Figure 1(c)).⁹ The destroyed LRO worsens the ferroelectricity, and the increased PNRs enhance the backs-switching of domain switching, both of which reduce P_r (Figure 1(c)).¹⁰ Thus, d_{33} reaches the maximum value at a very particular content of BNZ and shows a highly similar variation to $\epsilon_r P_r$ (Figure 1(a)).⁵ Therefore, two serious issues have come out. First, the highest d_{33} is highly sensitive to the BNZ content and rapidly reduces when deviating from the optimal BNZ content within even a 0.5% molar ratio (Figure 1(a)), making it difficult to further improve d_{33} .⁵ Second, the strain significantly reduces with increasing temperature because the MPC is at room temperature (Figure 1(c)).^{4, 11}

We recently found that the high electronegativity of Bi (1.9) in $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ results in the high covalency in A-O bonds and reduces $T_{\text{O-T}}$ due to the high hybridization between Bi 6s and O 2p orbitals.¹² The hybridization between Pb 6s and O 2p orbitals has been reported to lead to a large strain that stabilizes the tetragonal phase in PbTiO_3 .¹³ Therefore, the stronger hybridization between Bi 6s and O 2p orbitals could further stabilize the tetragonal phase, which has been validated by the larger tetragonality (c/a) and higher Curie temperature (T_c) in $\text{PbTiO}_3\text{-BiFeO}_3$ compared to PbTiO_3 .¹⁴ However, the large valence difference between Bi^{3+} and A-site causes the rapidly destroyed LRO and increased PNRs.^{6-7, 12} Besides, a smaller ionic radius of Bi^{3+} (0.145 nm) than K^+ (0.164 nm) worsens the perovskite structural stability of KNN-based ceramics when replacing A-site with $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$.¹² Thus, higher d_{33} values are expected if simultaneously remaining the MPC near room temperature and repairing its LRO and perovskite structural stability. Herein, we proposed a new route to achieve this, that is, tuning the covalency of A-O bonds in an already-built MPC by replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with other ions. These ions must meet the followings: i) the smaller valence state than Bi^{3+} ; ii) lower

electronegativity than Bi; iii) and larger ionic radius than Bi^{3+} . Encouragingly, barium (Ba) ion is an ideal candidate because it has a valence state of +2, a lower electronegativity of 0.89, and an ionic radius of 0.161 nm close to that of K^+ .¹⁵ By appropriately replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} , we hope to remain the MPC close to room temperature (Figure 1(b)) and expect that Q remains unchanged because of not affecting B-site, ϵ_r almost keeps unchanged because of the still preserved MPC, and P_r increases because of the repaired LRO. In particular, the modified MPC guarantees high room-temperature strain and higher retention with increasing temperature because it locates at a temperature slightly higher than room temperature ((Figure 1(c)).¹⁶ The increased temperature of the modified MPC is attributed to the Ba-O ionic bonds that weaken the covalency of A-O bonds and favor a ground-state phase (i.e., a rhombohedral phase in KNN-based ceramics).¹³ Therefore, we can expect not only higher d_{33} values but also the improved temperature stability of strain (e.g., achieving large retention of strain at high temperatures) (Figures 1(a, c)).

Since $0.96(\text{Na}_{0.60}\text{K}_{0.40})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-0.04(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ ceramics have an already-built MPC (Figure 1(a)),⁵ we thus prepared $0.96(\text{Na}_{0.60}\text{K}_{0.40})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-0.04(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{ZrO}_3$ (abbreviated as KNNS-BNBZ, $x=0-1.0$) ceramics. We systematically studied the effects of replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} on the structure (i.e., phase and domains) and performance (i.e., electrical properties and temperature stability). Our results demonstrate the validity of the new route. We not only improved d_{33} values from 450 pC/N (at $x=0$) to 500-505 pC/N (at $x=0.05-0.10$) but also the temperature stability of strain at $x=0.10$, outperforming that of samples with $x=0$ and other KNN-based ceramics. Finally, we discussed related physical mechanisms from intrinsic and extrinsic contributions.

Figure 1. The core idea of this work. (a) Issue of $(1-x)(\text{Na}_{0.60}\text{K}_{0.40})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ ceramics; (b) our new route to further modify an already-built MPC; (c) expectation from further modifying an already-built MPC. RT in (b) represents the room temperature. S and T in (c) represent the strain and temperature, respectively. (a) Reproduced from Ref. 5 with permission from the Royal Society of Chemistry, Copyright 2014.

EXPERIMENTAL PROCEDURE

Preparation of Materials

We prepared the $0.96(\text{Na}_{0.60}\text{K}_{0.40})(\text{Nb}_{0.955}\text{Sb}_{0.045})\text{O}_3-0.04(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{ZrO}_3$ (abbreviated as KNNS-BNBZ, and $x=0, 0.05, 0.10, 0.20, 0.40, 0.60, 0.80$, and 1.0) ceramics via the conventional solid-state sintering method. Here we chose Na_2CO_3 (99.8 %), K_2CO_3 (99 %), Nb_2O_5 (99.5 %), Sb_2O_3 (99.99 %), Bi_2O_3 (99.999 %), ZrO_2 (99.5 %), and BaCO_3 (99.9%) as raw materials, which were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Before weighing, all raw materials were dried at 120 °C for 2 h because of the hygroscopicity. All raw materials were weighed and mixed in a plastic jar that was then ball-milled for 20 h using zirconia balls and absolute ethyl alcohol (99.5 %) as media. After ball-milling, the well-mixed raw materials were dried in an oven to get rid of the

alcohol and then calcined at 850 °C for 6 h. After calcining, the unripe powder was moulded into disks (i.e., a thickness of 1 mm and a diameter of 10 mm) under a pressure of 10 MPa by utilizing a binder that synthesized by dissolving the polyvinyl alcohol (PVA) into pure water (8wt%). Then, the PVA was burnt off at 550 °C for 6 h. The green disks were sintered at 1070-1090 °C for 3 h in air, under a corundum crucible. To collect the electrical properties, both sides of as-sintered samples were printed with the silver paste, and then electrodes were formed after baking at 550 °C for 60 min. Eventually, the samples with electrodes were polarized under a direct current (DC) electric field of 3.5 kV/mm for 40 min at ambient temperature, and the silicone oil was used as the high voltage protection.

Characterization

We collected the crystal structure by using an XRD instrument (Bruker D8 Advance XRD, BrukerAXS Inc., Madison, WI, Cu- $K\alpha$). To conduct the Rietveld structural refinement, we manually ground as-sintered samples into fine powder and heated them at 650 °C for 2 h to remove the internal stress. We then collected the powder XRD patterns by an XRD instrument (X' Pert Pro MPD, DY 120 PANalytical, Netherlands) with high-resolution. We next used the Materials Analysis Using Diffraction (MAUD) to perform the Rietveld structural refinement.¹⁷ To observe ferroelectric domains, we first polished as-sintered ceramics' surface with diamond polishing suspension and heated them at 650 °C for 2 h to remove the internal stress due to the grinding. We collected the ferroelectric domains using an atomic force microscope (MFP-3D, Asylum Research, Goleta, CA) equipped with a conductive Pt-Ir coated cantilever (Econo-SCM-PIT, Oxford Instruments, CA). We chose the dual AC resonance (DART) mode to perform the out-of-plane piezoresponse force microscope (OP-PFM) characterizations. The driving voltage for detecting the ferroelectric domains was set to be 2 V.

After aging for 24 h, we measured the direct piezoelectric coefficient (d_{33}) for the poled samples with

a quasi-static d_{33} meter (ZJ-3 A, China). We measured the planar electromechanical coupling factor (k_p) and phase angle (θ) with an impedance analyzer (HP 4299A). We collected dielectric properties varying with temperature and frequency (i.e., the real part of permittivity ϵ' , the imaginary part of permittivity ϵ'' , and the dielectric loss factor $\tan \delta$) by using a commercial dielectric spectrometer instrument (Novocontrol Concept 80, Novocontrol, Germany). The temperature-temperature dependent dielectric properties were measured from -150 °C to 300 °C, with a temperature interval of 1 °C. We measured room-temperature relative dielectric permittivity (ϵ_r) by an LCR meter (HP 4980, Agilent, USA). To measure ferroelectric hysteresis (P - E) loops, strain properties (S - E curves), and d_{33} - E loops, we utilized a commercial ferroelectric workstation (aixACCT TF Analyzer 2000, Germany) equipped with a laser system (SP-S120/500, SIOS Meßtechnik GmbH, Germany), and the measurement frequency was fixed at 1 Hz.

RESULTS

Phase Structure

We first checked the phase structure of KNNS-BNBZ ceramics by using composition-dependent XRD patterns. We found a pure perovskite structure in all samples and evidence for the O phase at $x \geq 0.40$ (Figure S1). To further determine the phase structure, we measured dielectric properties varying with temperature and frequency (Figures S2-S3). We extracted ϵ' - T , ϵ'' - T , $\tan \delta$ - T curves, measured at 9997 Hz, to see the variations of T_{R-O} and T_{O-T} (Figure 2). Both unpoled and poled samples show two anomalies in their ϵ' - T curves (Figure 2(a)). The one at lower temperature has been regarded as the character of an R-O-T or an R-T coexistence phase and is caused by the coalesced T_{R-O} and T_{O-T} , and the other one represents T_c .^{4, 18} Besides, increasing x monotonously shifts the first anomaly to higher

temperatures (even higher than 100 °C at $x=1.0$) but slightly reduces T_c . As we know, it is impossible to shift T_{R-O} to such a high temperature, $\epsilon'-T$ curves, thus, cannot accurately reflect the variations of T_{R-O} and T_{O-T} for samples with an MPC due to the weak anomaly of T_{R-O} .¹⁹

By contrast, $\epsilon''-T$ curves show relatively more distinct T_{R-O} and T_{O-T} than $\epsilon'-T$ curves (Figure 2(b)).²⁰ Thereafter we only discussed the anomalies below T_c . Unpoled samples with $x=0-0.10$ still show the one anomaly, indicating the coalesced T_{R-O} and T_{O-T} . The anomaly becomes broadened and shifts from -7 °C (at $x=0$) to 10 °C (at $x=0.10$). Therefore, three compositions possess an R-O-T coexistence phase. Interestingly, unpoled samples with $x=0.20$ show a slightly splitting anomaly with a weak shoulder on the left, suggesting the separated T_{R-O} and T_{O-T} . Since its T_{R-O} and T_{O-T} are close to room temperature, we assigned it to have an R-O-T coexistence phase. As x further increases up to 0.40, the more distinct separation between T_{R-O} and T_{O-T} is observed. In particular, neither T_{R-O} (~ -14 °C) nor T_{O-T} (~ 59 °C) is very near room temperature, which causes the occurrence of a characteristic peak of an O phase in $\{220\}_{pc}$ diffraction (Figure S1). The latter Rietveld structural refinements demonstrate an R-O-T coexistence phase dominated by an O phase for this composition. As for unpoled samples with $x=0.60-1.00$, T_{R-O} gets closer to room temperature, and T_{O-T} becomes far higher than room temperature. Therefore, we assigned them to have an R-O coexistence phase.

Generally, the poling process makes the phase transitions more distinct due to the aligned ferroelectric domains.²¹⁻²² Indeed, poled samples with $x=0.40-1.0$ show more sharpened anomalies of T_{R-O} and T_{O-T} than unpoled counterparts, accompanying with almost unchanged T_{R-O} and T_{O-T} values (Figures 2(b, c)). Interestingly, the poling process splits the single anomaly of samples with $x=0-0.20$ into two. The

left one represents T_{R-O} , and the right one represents T_{O-T} . T_{R-O} almost remains unchanged, but T_{O-T} shifts to a higher temperature, resulting in the enhanced separation between two anomalies. The reappeared T_{R-O} after the poling process was reported to be associated with the electric-induced phase transition that enhances the R phase content.^{21, 23} Therefore, as we expected, replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} does simultaneously shift T_{R-O} and T_{O-T} to higher temperatures.

$\tan \delta$ - T curves have been reported to reflect the relaxor characteristics induced by the locally heterogeneous PNRs.²⁴⁻²⁵ Here, $\tan \delta$ - T curves of all compositions exhibit an anomaly near -100 °C, at which no phase transitions occur (Figure 2(c)). The phase-transition-unrelated anomaly is due to the energy dissipation induced by the switching of PNRs.²⁴⁻²⁶ Increasing x reduces the maximum $\tan \delta$ of the anomaly, indicating the decreased volume fraction of PNRs (Figure S4).²⁴⁻²⁵ Note that the decrease in the volume fraction of PNRs shall be at all temperatures because of the smaller valence state mismatch between Ba^{2+} and A-site than that between Bi^{3+} and A-site, as validated by the reduction in $\tan \delta$ in the phase-transition-unrelated regions (e.g., from -150 °C to -50 °C in Figure S4(c)). For classical ferroelectrics, the poling process well re-aligns the major domains and then decreases the loss in the phase-transition-unrelated regions (Figure S6). However, although the poling process can re-orientate some PNRs, it also intensifies the Gibbs energy difference between the PNRs and the ferroelectric matrix, leading to the easier back-switching of the PNRs under stimuli. Thus, for samples with $x=0$, the volume fraction of PNRs is high, and the poling cannot fully re-orientate the PNRs, resulting in an increase in the maximum $\tan \delta$ near -100 °C in poled samples. Increasing x gradually reduces the volume fraction of PNRs and thus weakens the increase, leading to the classical ferroelectric characteristics at $x=0.40$ -1.00 (Figure 2(c)). Besides, the anomalously increased $\tan \delta$ at

T_{R-O} of poled samples with $x=0.80$ is due to the interference by the ice during liquid nitrogen cooling, which is elaborated in Figure S5.²⁷

Figure 2. (a) ϵ' - T , (b) ϵ'' - T , and (c) $\tan \delta$ - T curves of KNNS-BNBZ ceramics before poling (colored solid lines) and after poling (black dashed lines), measured at 9997 Hz. The blue arrows in (a) indicate the location of T_C , and the blue numbers are T_C values. The white area in (b) indicates the room temperature. The red and purple arrows indicate the anomalies of R-O and O-T phase transitions, respectively. Similarly, the red numbers and the purple numbers present T_{R-O} and T_{O-T} values of poled samples, respectively.

To further validate the analysis for the phase structure, the Rietveld structural refinements were performed for unpoled powder samples ($x=0, 0.10, 0.40$, and 0.80) by using different models (Figures S7-S10). The results show that the best match is an R+O+T model for $x=0-0.40$ and an R+O model for $x=0.80$ (Figures 3(a-d)), which is supported by the lowest reliability factor ($R_{wp}<4.7\%$) and goodness-of-fit indicator ($sig<1.6$) (Table S1).²⁸ With increasing x , the content of R and O phases increases, and the T phase content reduces and becomes zero at $x=0.80$ (Figure 3(e)). Besides, the tetragonality (c/a) also decreases with increasing x (Table S1). T_{R-O} and T_{O-T} increase with increasing x (Figure 2(b)), thus leading to the forgoing variations of phase content and c/a . Therefore, the Rietveld structural refinements coincide with the foregoing analysis in Figure 2.

Figure 3. Rietveld structural refinements for unpoled powder samples with (a) $x=0$, (b) $x=0.10$, (c) $x=0.40$, and (d) $x=0.80$;

(e) variations of phase content.

Here we depicted the phase diagram of unpoled and poled KNNS-BNBZ ceramics (Figure 4). The phase diagram is divided into three regions with increasing x . In the region I (i.e., $0 \leq x \leq 0.10$), samples

possess an R-O-T coexistence phase with the major fraction of O and T phases since T_{O-T} is close to room temperature. In the region II (i.e., $0.20 \leq x \leq 0.40$), samples still own an R-O-T coexistence phase but have a dominating O phase, which is due to the expanded O phase zone induced by the faster increase of T_{O-T} than T_{R-O} . In the region III (i.e., $0.60 \leq x \leq 1.00$), samples possess an R-O coexistence phase because T_{O-T} is much higher than room temperature and T_{R-O} is near room temperature. Furthermore, T_{R-O} moves nearer room temperature as x increases from 0.60 to 1.00, suggesting the increased R phase content. However, the O phase still dominates the R-O coexistence phase (Table S1). Therefore, replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} does remain an R-O-T coexistence phase in samples with $x=0-0.10$, repair LRO, and reduce the volume fraction of PNRs, consistent with our expectation.

Figure 4. Phase diagram of (a) poled and (b) unpoled KNNS-BNBZ ceramics.

Domain Structure

We then collected the domain structure by utilizing a piezoresponse force microscopy with out-of-plane mode (OP-PFM). All samples exhibit the typical ferroelectric domains with distinct response and phase contrast (Figure 5). Specifically, samples with $x=0$ show the irregular domain configuration containing the submicron domains (0.5-1 μm) and isolated nano-domains (100-300 nm) (Figures 5(a1, a2)). Samples with $x=0.10$ exhibit the dominating submicron domains (0.5-1 μm), but they are still isolated (Figures 5(b1, b2)). The larger submicron domains are observed at $x=0.40$ (Figures 5(c1, c2)), well connecting with each other. Finally, the major domains of samples with $x=0.80$ are a micron size (Figures 5(d1, d2)), much larger than those of the first three compositions. The related physical mechanisms will be discussed soon.

Figure 5. OP-PFM amplitude and phase images of samples with $x=0$ (a1, a2), $x=0.10$ (b1, b2), $x=0.40$ (c1, c2), and $x=0.80$ (d1, d2). All images have the same scale bar.

Electrical and Strain Properties

We next measured the electrical properties varying with x . With increasing x , d_{33} , maximum

polarization (P_m), and ε_r first increases and then decreases, reaching the maximum values at $x=0.05-0.10$ (Figures 6(a-c)). In particular, d_{33} is elevated from 450 pC/N (at $x=0$) to 500-505 pC/N (at $x=0.05-0.10$) with an increase of 11%, and the increased d_{33} has a front-rank position among the largest d_{33} values documented in KNN-based ceramics without texturing.^{4, 29} The planar electromechanical coupling factor (k_p) and P_r first increase (at $x=0-0.20$) and then reduce (at $x=0.40-1.00$) (Figures 6(e, f)). The increase in P_m and P_r at $x=0-0.20$ is due to the remained R-O-T multiphase coexistence and the slightly repaired LRO, yet the decrease in P_m and P_r at $x=0.40-1.00$ is due to the reduced degree of MPC.¹⁰ However, increasing x divides the variation of the coercive field (E_c) into three regions (Figure 6(g)). In the region I (i.e., $0 \leq x \leq 0.20$), the domains remain to be isolated nano-domains (100-300 nm) or submicron domains (0.5-1 μm), indicating the relatively easy domain wall motion.³⁰ Thus, the decreased E_c is mainly ascribed to the reduced T phase content and degraded c/a of the R-O-T coexistence phase.³¹ In the region II (i.e., $0.20 \leq x \leq 0.60$), the domains change into larger submicron domains, making the domain wall motion difficult. Moreover, the faster increase of T_{O-T} than T_{R-O} results in higher T_{O-T} but lower T_{R-O} than room temperature, gradually weakening the degree of the R-O-T coexistence phase. Thus, both factors lead to increased E_c in this region. In the region III (i.e., $0.60 \leq x \leq 1.00$), all compositions show the major micron domains, but T_{R-O} gets closer to room temperature with increasing x , resulting in the reduction in E_c . Therefore, the increase in d_{33} , P_m , P_r , and ε_r at $x=0.05-0.10$ coincides well with our expectation.

Figure 6. Electrical properties of poled KNNS-BNBZ ceramics, (a) d_{33} , (b) P_m , (c) ϵ_r , (d) k_p , (e) P_r , and (f) E_c . P_m , P_r , and E_c are extracted from Figure S11.

Figure 7 shows the strain properties of poled samples. The poling strain ($S_{pol}=S_{neg}+S_{pos}$) and negative strain (S_{neg}) first increase and then decrease (Figures 7(a, b)), but the positive strain (S_{pos}) and unipolar strain (S_{uni}) gradually decrease (Figures 7(c, d)). Despite the reduced S_{uni} , samples with $x=0.05-0.10$ still show relatively high S_{uni} values ($\sim 0.155\%$) at $E=40$ kV/cm, comparable to that of other high-performance KNN-based ceramics (Figure 7(e)).³²⁻⁴³ Therefore, as we expected, appropriately replacing $(Bi_{0.5}Na_{0.5})^{2+}$ with Ba^{2+} does remain high strain properties. In particular, both relatively high S_{uni} and d_{33} values make samples with $x=0.10$ comparable to other notable KNN-based ceramics with MPC (Figure 7(e)), indicating the promising potential for practical applications. For poled KNN-based ceramics, S_{uni} and S_{pos} stem from the dominating converse piezoelectric response and negligible non-180° domain switching and electrostriction effect, and S_{neg} is attributed to the switching of non-180° domains.^{4, 44} Therefore, the reduction in S_{uni} and S_{pos} is due to the decreased converse piezoelectric

response, and the increased S_{neg} at $x=0-0.20$ indicates the enhanced non-180° domain switching. Based on the variations of S_{pos} and S_{neg} , S_{pol} thus increases at $x=0-0.10$ but decreases at $x=0.10-1.00$.

Figure 7. Strain properties of poled KNNS-BNBZ ceramics, (a) S_{pol} , (b) S_{neg} , (c) S_{pos} , and (d) S_{uni} ; (e) room-temperature S_{uni} and d_{33} values of non-textured KNN-based ceramics with MPC. Strain properties come from Figure S11. The solid symbols in (e) represent the S_{uni} measured at 40 kV/cm, and the (half-) hollow symbols represent the S_{uni} measured at 30 kV/cm.

Since the performance of KNN-based ceramics strongly relates to the phase structure, we thus measured their variations with temperature. Normalized E_c of samples with $x=0$ and $x=0.10$ has a similar variation with temperature, but that of samples with $x=0.80$ shows a different one (Figures 8(a1-c1)). The increase in normalized E_c of samples with $x=0$ and 0.10 at $T=20-80$ °C is ascribed to

the transition from an R-O-T coexistence phase to a single T phase, and the abnormal increase in normalized E_c of samples with $x=0.80$ at $T=80-110$ °C is attributed to the transition from an O phase to a T phase.^{16, 22, 45} Besides, samples with $x=0.10$ have a larger increase in normalized E_c than samples with $x=0$, indicating the more distinct phase transition due to the repaired LRO. For the same composition, normalized S_{pos} and normalized d_{33} show the highly similar variation with temperature (Figures 8(a2-c2, a3-c3)). Specifically, normalized S_{pos} and normalized d_{33} of samples with $x=0$ gradually decrease with increasing temperature, and both values of samples with $x=0.10$ and 0.80 show an increase near $T_{\text{O-T}}$. The difference is that samples with $x=0.10$ exhibit a slight increase, whereas a sharp one in samples with $x=0.80$, which is due to the more distinct $T_{\text{O-T}}$ in samples with $x=0.80$. Therefore, the variations of electrical properties coincide well with the phase structure, further revealing the increased $T_{\text{O-T}}$ and the repaired LRO.

Figure 8. Normalized E_c , S_{pos} , and d_{33} of samples with (a1-a3) $x=0$, (b1-b3) $x=0.10$, and (c1-c3) $x=0.80$. “Normalized” means the ratio between values measured at increasing temperatures and room temperature, that is, $X_{\text{T}}/X_{\text{RT}} \times 100\%$, where X represents one property. All values are extracted from Figure S12.

We next measured temperature-dependent S_{uni} under different electric fields. S_{uni} depends on both the phase structure and electric fields. For the same electric field, the normalized S_{uni} of samples with $x=0$ gradually reduces with increasing temperature, but that of samples with $x=0.10$ and 0.80 first increases at $20\text{ }^{\circ}\text{C} \leq T \leq T_{\text{O-T}}$ and then decreases at $T_{\text{O-T}} \leq T \leq 180\text{ }^{\circ}\text{C}$ (Figures 9(a-c)). Similarly, samples with $x=0.80$ show a more sharpened increase than samples with $x=0.10$ because of its more distinct $T_{\text{O-T}}$. For the same composition, the higher electric fields endow S_{uni} with the weaker temperature dependency, which is due to the dominating contribution from the converse piezoelectric response and decreased contribution from domain switching at high electric fields.¹⁶

Further analysis shows that although samples with $x=0$ have a high room-temperature S_{uni} , a distinct reduction is observed with increasing temperature, resulting in the relatively low retention (or normalized S_{uni}) of 60.9-70.5% at $T=180\text{ }^{\circ}\text{C}$. Even though the high retention of 97.5-100.8% at $T=180\text{ }^{\circ}\text{C}$, S_{uni} of samples with $x=0.80$ has a low value at room temperature and a more sharpened increase compared to samples with $x=0.10$. Encouragingly, samples with $x=0.10$ show the comprehensive improvement in S_{uni} and its temperature stability. Specifically, its room-temperature S_{uni} remains relatively high (Figures 7(d, e)), and it also shows high retention of 69.2-78.5% at $T=180\text{ }^{\circ}\text{C}$, leading to the weaker temperature dependency of S_{uni} than that of samples with $x=0$ and 0.80 , irrespective of electric fields (Figures S13(g-i)). Then, we collected the temperature stability of the strain of MPC-featured KNN-based ceramics (Figures 9(d-g)).^{38, 42, 46-51} Samples with $x=0.10$ exhibit higher retention at the same electric field and temperature, indicating the superior temperature stability (Figures 9(d-f)). Besides, the retention of S_{uni} at $T=180\text{ }^{\circ}\text{C}$ of samples with $x=0.10$ also outperforms those of samples

with $x=0$ and others, such as KNNS-0.0475BNMZ ceramics (Figure 9(g)).⁴⁸

Figure 9. Normalized S_{uni} of samples with (a) $x=0$, (b) $x=0.10$, and (c) $x=0.80$; (d-f) normalized S_{uni} of MPC-feathered KNN-based ceramics under different electric fields; (g) retention of S_{uni} at $T=180$ °C of KNNS-0.0475BNMZ ceramics and samples with $x=0$ and 0.10. Normalized S_{uni} in (a-c) is extracted from Figures S13(a-f). One-color area in the scale bar represents an amplitude of 5%.

DISCUSSION

As we expected, replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} increases (decreases) the ionicity (covalency) of A-O bonds due to the higher electronegativity of Bi than Ba (Figure 10(a)).^{12, 52} The high covalency of

A-O bonds, induced by the hybridization between the Bi 6s orbits and O 2p orbits, induces a large strain that favors a T phase, while the high ionicity of A-O bonds, induced by the completely ionic interaction between the Ba and O, favors the ground state (i.e., the R phase for KNN-based ceramics).^{12-14, 52-54} Therefore, replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} causes a simultaneous increase in $T_{\text{R-O}}$ and $T_{\text{O-T}}$, leading to the observed variations of the phase structure (Figure 4).

The variations of the phase structure then affect ferroelectric domains (Figure 5). $T_{\text{O-T}}$ increases faster than $T_{\text{R-O}}$, which reduces the degree of the MPC at room temperature. Therefore, even though an R-O-T or an R-O coexistence phase is observed at $x=0.20-1.00$, the volume fraction of the O phase is dominating (Table S1). The reduced degree of the MPC increases the anisotropy energy and the domain wall energy (F_{dw}), which increases the domain size (d) via $d \propto \sqrt{F_{\text{dw}}}$.⁵⁵ Besides, the increase in the O phase content and the repaired LRO make the domains more regular.⁵⁶

d_{33} and strain hinge on the intrinsic lattice distortion and extrinsic domain switching.⁵⁷ As shown in the equation (1), Q remains unchanged because replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with Ba^{2+} has little influence on B-site. In the region of $0 \leq x \leq 0.10$, $T_{\text{O-T}}$ is still close to room temperature, and the R-O-T coexistence phase is thus dominated by the O and T phases (Table S1), which guarantees high ε_r values due to the easy polarization rotation (Figure 6(c)).⁵⁸ Furthermore, the domain size remains hundreds of nanometers (Figures 5(a1, b1)). Thus, the repaired LRO and domains enhance the ferroelectricity, and the decreased volume fraction of PNRs reduces the back-switching of domains (P_{bs} , $P_{\text{bs}}=P_{\text{m}}-P_{\text{r}}$) (Figure 10(b)), both of which lead to the increased P_{r} and the enhanced degree of poling (i.e., the higher phase angle (θ)) (Figure 10(b)).^{10, 59} Consequently, d_{33} increases in this region because of the

remained high ε_r and the increase in P_r and θ (Figure 10(b)). By contrast, in the region of $0.20 \leq x \leq 1.00$, T_{O-T} moves far away from room temperature with increasing x , yet T_{R-O} is not very close to room temperature, weakening the degree of MPC at room temperature, which leads to a monotonous reduction in ε_r . Furthermore, the domain size has increased up to the micron scale, which significantly reduces the degree of the effective domain switching and domain wall motion (as supported by the decreased P_r and phase angle (θ) and the increased P_{bs}) (Figure 10(b)). Thus, d_{33} monotonously decreases in this region because of the simultaneous decrease in P_r and ε_r , resulting in a similar variation of d_{33} and $\varepsilon_r P_r$ against x (Figures 6(a) and 10(c)).

Because of the monotonously increased T_{O-T} and reduced degree of MPC, the room-temperature lattice distortion under electric fields gradually decreases, leading to the reduced converse piezoelectric response.¹¹ Thus, S_{pos} and S_{uni} monotonously decrease with x (Figures 7(c, d)). The reduced P_{bs} and the increased θ at $x=0-0.20$ indicate the enhanced domain switching (including non-180° domain switching), which explains why S_{neg} increases at $x=0-0.20$ (Figure 7(b)). Therefore, the synergistic effects of the lattice distortion and the domain switching lead to similar variations in S_{pol} and d_{33} against x (Figures 6(a) and 7(a)). Furthermore, to achieve high d_{33} values and S_{uni} , the lattice distortion associated with T_{O-T} seems more important than the domain switching, which explains why researchers have achieved high performance by moving T_{O-T} near/to room temperature.^{3-4, 44}

Finally, we depicted the schematic diagrams of the temperature dependency of S_{uni} for three compositions. Samples with $x=0$ have a high S_{uni} but an obvious temperature dependency (Figure 10(d)); samples with $x=0.10$ show a high S_{uni} and a weak temperature dependency (Figure 10(e)); and

samples with $x=0.80$ exhibit a low S_{uni} and a strong temperature dependency (Figure 10(f)). Therefore, as we expected, tuning the covalency/ionicity of the A-O bonds in an already-built MPC simultaneously improves d_{33} values and weakens the temperature stability of S_{uni} , which provides a new route to regulate the MPC and benefits to the practical application.

Figure 10. (a) Schematic diagram showing the effects of the inter-replacement between $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ and Ba^{2+} on the ionicity and covalency of the A-O bond; (b) variations of P_{bs} , $\varepsilon_r P_r$, and θ with x ; schematic diagrams of temperature-dependent S_{uni} for (c) $x=0$, (d) $x=0.10$, and (e) $x=0.80$. θ is extracted from Figure S14. Ideal poling results in a θ of 90° , and a higher θ indicates a higher degree of poling.⁵⁹ RT, S, and TD represent the room-temperature, the initial S_{uni} , and the temperature dependency, respectively.

CONCLUSIONS

In this work, we presented a new route, tuning the covalency of A-O bonds in an already-built MPC, to further improve its d_{33} and temperature stability of strain. We exemplified

0.96(Na_{0.60}K_{0.40})(Nb_{0.955}Sb_{0.045})O₃-0.04(Bi_{0.5}Na_{0.5})_{1-x}Ba_xZrO₃ ceramics, in which 0.96(Na_{0.60}K_{0.40})(Nb_{0.955}Sb_{0.045})O₃-0.04(Bi_{0.5}Na_{0.5})ZrO₃ ceramics has an already-built MPC and replacing (Bi_{0.5}Na_{0.5})²⁺ with Ba²⁺ tunes the covalency of A-O bonds. We investigated the variations of the structure (i.e., the phase structure and ferroelectric domains) and performance (i.e., electrical properties and temperature stability of strain) with increasing x . Both T_{R-O} and T_{O-T} shift to higher temperatures, LRO is repaired, and the volume fraction of PNRs is reduced, coinciding well with our expectations. Due to the faster increase of T_{O-T} than T_{R-O} , the room-temperature phase structure changes from an R-O-T coexistence phase to an R-O coexistence phase, and the domains change from the isolated nanodomains and submicron-domains to the connected micron-domains. Despite this, an R-O-T coexistence phase dominated by the O and T phases remains at $x=0-0.10$, which guarantees high ϵ_r . The repaired LRO and domains and the reduced volume fraction of PNRs enhance the ferroelectricity and the degree of poling, leading to an increase in P_r and phase angle (θ). Therefore, d_{33} increases from 450 pC/N (at $x=0$) to 500-505 pC/N (at $x=0.05-0.10$), with an increase of 11%. More importantly, samples with $x=0.10$ remain a high room-temperature S_{uni} and show enhanced temperature stability, outperforming samples with $x=0$ and comparable to other notable KNN-based ceramics, which is due to shifting the MPC to a temperature slightly higher than room temperature. Therefore, the new route not only helps further improve the performance of an already-built MPC but also benefits to the future design of MPC and the practical application of KNN-based ceramics.

ASSOCIATED CONTENT

Supporting Information

Composition-dependent XRD patterns (Figure S1); dielectric properties varying with temperature and

frequency (Figures S2-S6); Rietveld structural refinements (Figures S7-S10); ferroelectric and strain properties (Figures S11 and S12); unipolar S - E curves and S_{uni} with increasing temperature (Figure S13); poled samples' impedance ($|Z|$) and phase angle (θ) (Figure S14); Rietveld structural refinements (Table S1)

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Notes

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