Modifying Temperature Stability of (K,Na)NbO₃ Ceramics through Phase Boundary

Xiang Lv, Jiagang Wu,* Dingquan Xiao, Jianguo Zhu, Junwei Zhang, and Xi-xiang Zhang*

(0.99–*x*)(K_{0.5}Na_{0.5})(Nb_{0.965}Sb_{0.035})O₃–0.01SrZrO₃–*x*(Bi_{0.5}Na_{0.5})ZrO₃ ceramics are chosen as an example to illustrate the effects of phase boundaries on strain. Temperature-dependent dielectric permittivity and convergent beam electron diffraction patterns confirm the multiphase coexistence of rhombohedral, orthorhombic, and tetragonal phases in the ceramics with *x* = 0.03–0.04. Intriguingly, the ceramics with *x* = 0.03 display improved temperature stability in strain, e.g., a high retention (≈95%) of unipolar strain at 180 °C and low variation of 24% at 20–180 °C. A mode is proposed to show how to effectively tailor the strain and consolidate its temperature stability in potassium sodium niobate-based ceramics.

1. Introduction

Piezoelectric materials are indispensable parts in all electronic devices due to the exceptional ability of interconverting electrical energy and mechanical energy.^[1] Wook et al. predicted a piezoelectric market of 38.4 billion US dollars, of which the piezoelectric actuators governed the share percentage as high as 32–37%.^[2] At present, the driving elements of piezoelectric actuators are dominated by lead zirconate titanate {Pb(Zr,Ti)O₃, PZT}-based ceramics due to their high piezoelectric properties and favorable temperature stability.^[3] However, from the viewpoint of sustainable development, the lead-free piezoceramics are highly desired to replace the toxic lead-based ones.^[4] Motivated by the abovementioned circumstances, lead-free piezoceramics have been widely investigated to partly replace the lead-based ones in actuator applications.^[5]

For actuator applications, both large strain and favorable temperature stability are basically desired.^[3] As one of the promising lead-free candidates, potassium sodium niobate-based {(K,Na)NbO₃, KNN} ceramics have attracted the researchers' interest because of relatively high piezoelectricity and Curie temperature (*T_c*).^[4]

Particularly, unipolar strain and its temperature stability comparable to those of soft PZT-4 ceramics were reported in textured (K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O₃ (LF4T) ceramics synthesized by the reactive template grain growth (RTGG) method.^[6] Subsequent investigations focused on the improvement of both unipolar strain and its temperature stability using conventional sintering method due to high cost of RTGG. Vast studies strongly proved that phase boundary is an effective way to improve strain properties of KNN-based ceramics.^[1]

Particularly, the construction of new phase boundary by simultaneously shifting the rhombohedral–orthorhombic and orthorhombic–tetragonal phase transition temperature (e.g., *T_{R-O}* and *T_{O-T}*) toward room temperature proved to enhance the piezoelectric properties of KNN-based ceramics.^[1,7] Although the improved piezoelectricity can be guaranteed by means of phase boundaries, the related electrical properties still exhibited the strong temperature dependence due to the nature of polymorphic phase boundary that is different from the morphotropic phase boundary in PZT-based ceramics.^[1,2,4,5] More importantly, the systematical investigations on how the phase boundaries affected the strain and its temperature stability is still missing, which could further promote the understanding of KNN-based ceramics.

Recently, the temperature-insensitive dielectric properties were reported in SrZrO₃-modified KNN-based ceramics, accompanying with small permittivity variation of ±15% (–65 to 201 °C).^[8] Here, (0.99–*x*)(K_{0.5}Na_{0.5})(Nb_{0.965}Sb_{0.035})O₃–0.01SrZrO₃–*x*(Bi_{0.5}Na_{0.5})ZrO₃ (*x* = 0–0.05) ceramics were chosen as an example to illustrate the effects of phase boundaries on the strain and its temperature stability. Through the study of temperature-dependent unipolar strain at different phase boundaries and similar phase boundary with different locations, effects of phase boundaries on strain and its temperature stability were illustrated. More importantly, the improved temperature stability of unipolar strain (*S_{uni}*) was observed in the ceramics (*x* = 0.03), e.g., high retention (≈95%) of *S_{uni}* at *T* = 180 °C and low variation of 24% at *T* = 20–180 °C. The related physical mechanisms were discussed in detail.

2. Results and Discussion

A typical perovskite structure without any other secondary phases was found in all samples (Figure S1, Supporting Information).

X. Lv, Prof. J. Wu, Prof. D. Xiao, Prof. J. Zhu
 Department of Materials Science
 Sichuan University
 610064, Chengdu, P. R. China
 E-mail: wujiagang0208@163.com, msewujg@scu.edu.cn
 Dr. J. Zhang, Prof. X. Zhang
 King Abdullah University of Science and Technology (KAUST)
 Physical Science and Engineering Division (PSE)
 Thuwal 23955–6900, Saudi Arabia
 E-mail: xixiang.zhang@kaust.edu.sa

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aelm.201800205>.

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Figure 1. a) XRD patterns of (0.99- x)KNNS-0.01SZ- x BNZ ceramics with $2\theta = 45^\circ$ – 46° . b) Temperature-dependent dielectric permittivity (ϵ_r - T) curves of (0.99- x)KNNS-0.01SZ- x BNZ ceramics as a function of x .

To further analyze the phase structures of (0.99- x)KNNS-0.01SZ- x BNZ ceramics, both XRD patterns with $2\theta = 45^\circ$ – 46° and temperature-dependent permittivity (ϵ_r - T) curves were simultaneously considered (Figure 1a,b). For the ceramics with $x = 0$ and 0.01, an intensity ratio of 2:1 was found in $(002)_{PC}$ and $(200)_{PC}$ peaks, which was a fingerprint of orthorhombic (O) phase.^[9] The corresponding ϵ_r - T curves respectively showed a rhombohedral–orthorhombic phase transition temperature (T_{R-O}) of -75°C and an orthorhombic–tetragonal phase transition temperature (T_{O-T}) of 125°C for $x = 0$ and a T_{R-O} of -50°C and a T_{O-T} of 94°C for $x = 0.01$ (Figure 1b), further testifying a pure O phase in the ceramics $x = 0$ and 0.01 at room temperature.^[10] With increasing x , the intensity of $(002)_{PC}$ peak reduced while the one of $(200)_{PC}$ peak increased. As x increased up to 0.02, the intensity of $(200)_{PC}$ peak was higher than that of $(002)_{PC}$ peak (Figure 1a), signifying the involvement of T phase.^[11] ϵ_r - T curve of the ceramics with $x = 0.02$ displayed a board T_{R-O} of $-40 \pm 20^\circ\text{C}$ and a T_{O-T} of 72°C (Figure 1b), suggesting the existence of O phase. Thus, an O–T phase coexistence was deduced in the ceramics with $x = 0.02$ at room temperature, which was also observed in other KNN-based ceramics.^[10] When x increased up to 0.03, an intensity ratio of 2:1 was observed between $(200)_{PC}$ and $(002)_{PC}$ peaks, indicating a dominating T phase structure. Meanwhile, the corresponding ϵ_r - T curve showed a suppressed T_{R-O} and a T_{O-T} of 52°C (Figure 1b). The suppressed T_{R-O} indicated the diffusion of R–O phase boundary toward room temperature and T_{O-T} of 52°C was close to room temperature. Therefore, the ceramics with $x = 0.03$ should possess a mixed phase boundary comprising R–O and O–T phase boundaries.^[12] This phenomenon further extended to the ceramics with $x = 0.04$ that exhibited the similar XRD patterns to that of the ceramics with $x = 0.03$ (Figure 1a). More importantly, due to the further reduction of T_{O-T} and suppressed T_{R-O} , both

of them merged near the room temperature, resulting in a board $T_{R-O\&O-T}$ of $25 \pm 25^\circ\text{C}$ in the ceramics with $x = 0.04$ (Figure 1b). Therefore, both the ceramics with $x = 0.03$ and 0.04 reasonably possessed a mixed multiphase coexistence consisting of R, O, and T phases, at room temperature. Finally, a single $\{200\}_{PC}$ peak occurred at $x = 0.05$ (Figure 1a), which was assigned as a pseudo-cubic or cubic phase.^[13] ϵ_r - T curve of the ceramics with $x = 0.05$ exhibited a vanishing $T_{R-O\&O-T}$ with increasing frequency and a board T_C peak was also observed (Figure 1b), which was due to the reduced grain size (Figure S2a–d, Supporting Information). Considering the disappearance of d_{33} (Figure 3a), a cubic phase should exist in the ceramics with $x = 0.05$.

To further testify the multiphase coexistence, both Rietveld refinement and CBED were employed on the ceramics ($x = 0.03$), which can reflect the crystal symmetry of a piezoceramic.^[14] As shown in Figure 2a, b, the calculated data well matched the original one, accompanying with low Sig and R_{wp} values of 1.35 and 4.35%, respectively. The refined parameters were listed in the inset of Figure 2a. Therefore, the Rietveld refinement results supported the three-phase coexistence (involving rhombohedral, orthorhombic, and tetragonal) in the ceramics with $x = 0.03$.

One can see that a mirror parallel to $[11-2]$ suggests a 4 mm point symmetry (e.g., tetragonal), two mirrors perpendicular to each other point an $mm2$ point symmetry (e.g., orthorhombic), and a mirror parallel to $[110]$ indicates a $3m$ point symmetry (e.g., rhombohedral) (Figure 2c).^[15] Therefore, CBED patterns clearly proved the mixed multiphase coexistence consisting of R, O, and T. Based on variations of T_{R-O} , T_{O-T} , and T_C values (Figure 1b; Figure S3a–f, Supporting Information), the corresponding phase diagram was established in Figure 2d. At first, an O phase was observed at $x = 0$ and 0.01. As x increased

Figure 2. a) Rietveld refinement of the ceramics with $x = 0.03$ with $2\theta = 20^{\circ}$ – 90° and b) enlarged refinement with $2\theta = 45^{\circ}$ – 46° . The inset of (a) showed the refinement results. c) CBED patterns of the ceramics with $x = 0.03$ from $[111]_{PC}$ and $[001]_{PC}$ incidences. The CBED patterns were obtained in different areas. d) Phase diagram of $(0.99-x)\text{KNNS}-0.01\text{SZ}-x\text{BNZ}$ ceramics.

up to 0.02, the phase structure changed into O–T phase coexistence. With further increasing x , T_{R-O} gradually diffused into room temperature and T_{O-T} shifted toward room temperature, resulting in the multiphase coexistence consisting of R, O, and T phases at $x = 0.03$ and 0.04. Finally, both T_{R-O} and T_{O-T} vanished at $x = 0.05$, leading to a cubic phase.

Effects of phase structure on piezoelectric and dielectric properties were investigated (Figure 3). With the increase of x , d_{33} first increased and then reduced, reaching the maximum value of 450 pC/N at $x = 0.03$ as well as a large value of 410 pC/N at $x = 0.04$ (Figure 3a). In addition, k_p slightly increased, and then sharply reduced for $x > 0.04$. For dielectric properties of $(0.99-x)\text{KNNS}-0.01\text{SZ}-x\text{BNZ}$ ceramics, ϵ_r first increased and then reduced, reaching the maximum at $x = 0.04$, while $\tan \delta$ gradually increased as x increased (Figure 3b). Thus, both piezoelectric and dielectric properties were boosted in the ceramics with $x = 0.03$ or 0.04 that possessed a mixed multiphase coexistence. According to the previous publications, the multiphase coexistence can promote the polarization rotation and intensify the density of domain structures, which benefits macroscopic piezoelectric and dielectric properties.^[16,17]

Considering the important contributions of domain structures to piezoelectric properties, the domain structures of the ceramics with $x = 0.03$ were characterized by PFM and TEM (Figure 3c,d). Through PFM image, the substantially irregular

nanodomains were clearly observed and the large domains with scale of $\approx 1 \mu\text{m}$ were also observed (Figure 3c), which were mainly due to the multiphase coexistence.^[18] The further TEM analysis demonstrated the existence of lamellar domain configuration that comprised nanodomains with average size of 30 nm and hierarchy distribution (Figure 3d). Such a lamellar domain configuration was observed in Pb-based and textured KNN-based ceramics, which was prone to switching under the stimulation of external electric field and benefited the piezoelectric properties.^[14,19,20]

For the practical applications, the benign temperature stability is highly desired, which is a tough issue for KNN-based ceramics.^[5] Figure 4a–c showed the temperature-dependent unipolar strain (S_{uni}) curves of the ceramics ($x = 0, 0.03$, and 0.04). For the ceramics ($x = 0$ and 0.03), S_{uni} first increased and then reduced, reaching the maximum values at $T = 120$ and 60°C , respectively (Figure 4a,b), while a continuous reduction of S_{uni} was observed in the ceramics with $x = 0.04$ (Figure 4c). The observed variations were attributed to the locations of phase boundaries. T_{O-T} of 125 and 52°C were observed in the ceramics with $x = 0$ and 0.03 (Figure 1b). Thus, the abrupt increase of S_{uni} at $x = 0$ and 0.03 was mainly due to phase transition that could give rise to the larger lattice distortion.^[21,22] The ceramics with $x = 0.04$ exhibited a broad $T_{R-O\&O-T}$ of $25 \pm 25^{\circ}\text{C}$, which was responsible for the reduced S_{uni} .

Figure 3. a) d_{33} & k_p and b) ϵ_r & $\tan \delta$ of (0.99-x)KNNs-0.01SZ-xBNZ ceramics varying with x . c) Vertical PFM amplitude and d) TEM images ($x = 0.03$).

Considering the important role of S_{uni} in piezoelectric actuators, the variation of S_{uni} was further analyzed. Generally, the electrostrictive behavior concerning the relationship between field-induced strain (S) and polarization (P) can be presented by the equation of $S = QP^2$, where Q is the electrostrictive constant and is normally temperature independent.^[23,24] It was previously reported that $S_{\text{uni}} \approx QP_{\text{max}}^2 - QP_r^2 = Q(P_{\text{max}}^2 - P_r^2)$, where P_{max} and P_r are the maximum and remanent polarization, respectively.^[23,24] Thus, the similar variation traces are predicted in S_{uni} and $P_{\text{max}}^2 - P_r^2$. The variations of P_{max} and P_r can be found in Figure S4 (Supporting Information). The temperature dependence of S_{uni} and $P_{\text{max}}^2 - P_r^2$ of the ceramics ($x = 0, 0.03$, and 0.04) was contrasted in Figure 4d–f. For these

ceramics ($x = 0, 0.03$, and 0.04), both S_{uni} and $P_{\text{max}}^2 - P_r^2$ exhibited the similar variations. Thus, the enhanced temperature-dependent unipolar strain in the ceramics ($x = 0.03$ and 0.04) was mainly attributed to the constant values of the difference of P_{max}^2 and P_r^2 at $T = 20$ – 180 °C (below T_C values).^[23,24] In other word, a reduced P_{max} with temperatures can be compensated by a stronger reduction in P_r with temperature, improving the temperature stability of unipolar strain.^[23,24]

Based on the effects of phase boundaries on unipolar strain, the method how to obtain the adequate S_{uni} and temperature stability was concluded in Figure 5a,b. Firstly, to obtain the highly initial S_{uni} in KNN-based ceramics, the constructing of phase boundary (particularly R–T or R–O–T phase boundary)

Figure 4. Temperature-dependent unipolar strain curves of the ceramics with a) $x = 0$, b) $x = 0.03$, and c) $x = 0.04$. d–f) Corresponding variations of ($P_{\text{max}}^2 - P_r^2$) and S_{uni} in (a)–(c).

Figure 5. a) Variation of normalized unipolar strain of the ceramics ($x = 0.03$ and 0.04) under $E = 4 \text{ kV mm}^{-1}$. b) Effects of phase boundaries' locations on temperature stability. c) Comparison of temperature stability of several representative lead-free piezoceramics and our results. d) Comparison concerning d_{33} , T_c , and initial S_{uni} values of our results and others.

is necessary, as proved before and in this work.^[1,3,5] Subsequently, the location of phase boundary is another important factor to tailor the temperature stability. As shown in Figure 5a, when the locations of phase boundaries shifted from 52 to 25 °C, the maximum S_{uni} also shifted toward low temperature, resulting in a continuous reduction of S_{uni} at $x = 0.04$. While S_{uni} of the ceramics with $x = 0.03$ first increased and then reduced, resulting a high retention of 95% at $T = 180$ °C. Although shifting phase boundaries away from room temperature will inevitably reduce the initial S_{uni} value measured at room temperature, a relatively high S_{uni} value of 0.148% was still obtained in the ceramics with $x = 0.03$ at $T = 20$ °C, which was comparable to those of other KNN-based ceramics at the same electric field.^[25] Thus, a simple mode was proposed to show how the locations of phase boundaries affected the temperature stability (Figure 5b). Shifting the locations of phase boundaries from room temperature to higher temperature will generate an arch-shaped variation of S_{uni} , resulting in the relatively high normalized S_{uni} values at high temperature, as shown in the variations of black, red, and blue lines (Figure 5b). Furthermore, if one can broaden the temperature range of the phase boundaries, such as by applying high electric field and optimizing composition design,^[25,26] not only the highly initial S_{uni} but also the smooth variation can be obtained, producing an ideal temperature stability for piezoelectric actuator applications, as shown in the variation of green line (Figure 5b).

We compared the temperature stability of $(0.99-x)\text{KNNs-}0.01\text{SZ-}x\text{BNZ}$ ($x = 0-0.05$) ceramics and other representative lead-free piezoceramics (Figure 5c). Previously, both MnO_2 -modified KNN-BLT-BZ and KNN-BKH ceramics were endowed with good piezoelectric properties and temperature stability due to R-T

phase coexistence (Figure 5c).^[15,27] A temperature-insensitive behavior was reported in KNNLT-CZ5 ceramics at $T = 22-175$ °C, accompanying with an initial S_{uni} of <0.13%.^[23] Recently, Zhai et al. improved the temperature stability of strain in textured KNN-CZ-BKH ceramics using the RTGG method.^[20] Here, a high normalized S_{uni} of 95% at $T = 180$ °C and low variation of 24% at $T = 20-180$ °C were observed in the ceramics with $x = 0.03$, which possessed the initial S_{uni} of 0.148% (Figure 4b,e). For the ceramics with $x = 0.04$, a highly initial S_{uni} of 0.16% and relatively high normalized S_{uni} of 74% at $T = 180$ °C were observed (Figure 4c,f). Thus, our results were visibly comparable to those of abovementioned lead-free ceramics in both S_{uni} and its temperature stability,^[6,15,20,27,28] which was promising for the lead-free piezoelectric actuator applications. In addition, the obtained d_{33} and T_c values in this work were also superior to those of other KNN-based ceramics (Figure 5d).

3. Conclusions

In this study, $(0.99-x)\text{KNNs-}0.01\text{SZ-}x\text{BNZ}$ ($x = 0-0.05$) ceramics were synthesized by the solid-state reaction method. The mixed multiphase coexistence of R, O, and T phases was constructed at $x = 0.03$ and 0.04 , as confirmed by ϵ_r - T curves and CBED patterns. In the multiphase coexistence zone, the improved d_{33} of 410–450 pC/N and S_{uni} of 0.148–0.16% were observed due to both the adequate extrinsic and intrinsic contributions. More importantly, the ceramics with $x = 0.03$ exhibited the high retention ($\approx 95\%$) of S_{uni} at $T = 180$ °C and low variation of 24% at $T = 20-180$ °C. The temperature dependence of unipolar

strain was phenomenologically explained by considering the constant values of the difference of $P_{\max}^2$ and P_r^2 . Furthermore, according to the effects of phase boundaries' locations on the temperature stability in KNN-based ceramics, a mode was proposed to show how to tailor the initial S_{uni} and its temperature stability.

4. Experimental Section

In this work, $(0.99-x)(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{0.965}\text{Sb}_{0.035})\text{O}_3-0.01\text{SrZrO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{ZrO}_3$ $\{(0.99-x)\text{KNNs}-0.01\text{SZ}-x\text{BNZ}, x = 0-0.05\}$ ceramics were fabricated by the solid-state method. Raw materials were K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Bi_2O_3 (99.999%), Sb_2O_3 (99.99%), SrCO_3 (99.9%), and ZrO_2 (99.5%) (Sinopharm Chemical Reagent Co., Ltd., China). All raw materials were dried at 180 °C for 3 h due to the hygroscopicity. Mixtures of the raw materials with the designed compositions were ball-milled for 24 h with zirconia ball media and alcohol in plastic jars. Then, the dried slurry was calcined at 850 °C for 6 h. The calcined powder was pressed into disks of 10 mm diameter and 1 mm thickness under 10 MPa using PVA as a binder. After burning off the PVA at 500 °C, the disks were sintered at 1060–1120 °C for 3 h under a corundum crucible in air.

The phase structures of the ceramics were detected using X-ray diffraction (XRD) characterization (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuK α , USA). The as-sintered samples with $x = 0.03$ were ground into powder and then annealed at 600 °C for 30 min to eliminate internal stress. The powder XRD data was collected using a high-resolution XRD apparatus (X'Pert Pro MPD, DY 120 PANalytical, Netherlands). Maud software package was used to conduct the Rietveld refinement. The samples for transmission electron microscopy (TEM) were prepared by focused ion beam processing techniques. Then, domain structure and convergent beam electron diffraction (CBED) patterns were obtained via a FEI Titan 80–300 electron microscope with the accelerating voltage of 300 kV. To perform the piezoelectric force microscopy (PFM), the as-sintered disks were mechanically polished to a thickness of about 20 μm . The PFM observations were conducted on a commercial atomic force microscope (MFP-3D, Asylum Research, Goleta, CA, USA) with a conductive Pt-Ir-coated cantilever PPP-NCHPt (Nanosensors, Switzerland). FE-SEM images were measured using a field emission-scanning electron microscopy (FE-SEM) (JSM-7500, JEOL Ltd., Tokyo, Japan). To characterize the electric properties of the materials, silver paste was printed on both sides of the as-sintered disks, which were then baked at 600 °C for 30 min to form electrodes. Then, the disks were poled at room temperature in a silicone oil bath by applying an electric field of 4 kV mm^{-1} for 30 min. After aging for 24 h, the d_{33} values of the poled disks were measured using a quasi-static piezo- d_{33} meter (Z)-3 A, China), and the k_p values were measured using an impedance analyzer (HP 4299A, Palo Alto, CA, USA). The polarization–electric field (P – E) loops and strain–electric field (S – E) curves were measured using a ferroelectric analyzer (aixACCT TF Analyzer 2000, Germany) with a laser interferometer vibrometer (SP-S120/500, sios Mebtechnik GmbH, Germany), at a frequency of 1 Hz. Room-temperature permittivity (ϵ_r) and loss factor ($\tan \delta$) were measured using an LCR meter (Agilent 4294, USA). Temperature-dependent ϵ_r was measured using a broadband dielectric spectrometer (Novocontrol Technologies GmbH, Germany).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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