Supporting information

Enhanced thermal stability by short-range ordered ferroelectricity in K_{0.5}NbO₃based piezoelectric oxides

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Note 1. Phase-field calculations and first-principles calculations

As shown in Fig. S1a, in the coarse grained KNN (considering 6 grain in 100 nm \times 100 nm), normal strains (ε_{xx} and ε_{yy}) are significant than shear strains (ε_{xy}). In Fig. S1b, for the fine grained KNN (considering 50 grain in 100 nm \times 100 nm), normal strains are significant than shear strains, which is the same with coarse grains.

Fig. S1c and Fig. S1d shows atomic models used for the first-principles calculations. We evaluated the domain wall (DW) energy (γ_{DW}) for the 180° domain wall within a single grain by using Fig. S1c. When simulating polar configuration at grain boundaries, we used atomic models such as Fig. S1d illustrating Σ 3(112) grain boundaries.



Fig. S1. The total strain and elastic strain maps illustrating normal strain, ε_{xx} and ε_{yy} , and shear strain, ε_{xy} , in (a) coarse-KNN and (b) fine-KNN, respectively. Schematics of KNN for (c) 180° domain walls with $\gamma_{DW} = 9.77$ mJ m⁻² (d) $\Sigma 3(112)$ grain boundaries with $\gamma_{GB} = 905.04$ mJ m⁻². The blue arrows indicate the direction of polarization.

Note 2. Grain morphology

Fig. S2 shows FE-SEM images of the KNN-0.03BNKLZ-xBS ceramics (x = 0.0075 - 0.015). With the addition of BS, the grain morphology changes significantly at a certain point, exhibiting a bimodal grain size distribution. The large grains are dominant from x = 0.0075 to x = 0.01125 with grain sizes averaging tens of micrometers, while the fine grains start to appear at x = 0.01125. At x = 0.0125, the average grain size dramatically decreased to ~2.76 µm, still having a few large grains with a number of small grains. The large grains finally disappear completely from x = 0.01375, with an average grain size below ~0.3 µm. Accordingly, the perimeter also greatly increased from x = 0.01375. The perimeter was measured in the same area (0.534369 mm²) considering the area ratio of large grains. This bimodal behavior is similar to that of the BNT-BS doped KNN system, suggesting that the addition of a small amount of BS suppresses the grain growth by aggregating at the grain boundary. ¹



Fig. S2. Grain-size distributions obtained from FE-SEM images for ring-shaped KNN-0.03BNKLZ-xBS ceramics (x = 0.0075 - 0.015). Because of the bimodal grain size distribution characteristic, quantitative measurements were carried out for small and large grains using an automatic image analysis software (Matrox imaging library 10) for FE-SEM images taken from each sample (total number of grains ~1000). The scale bar is 50 µm.

Note 3. Measurement of electrical characteristics

The grain-size dependency of the relaxor ferroelectric nature of KNN is shown in Fig. S3. In temperature-dependent dielectric permittivity, the diffused dielectric peak is a signal indicating the transition to relaxor ferroelectrics. In Fig. S3a, a transition from the normal ferroelectric phase to the diffuse ferroelectric phase is observed at x = 0.01375, where the grain morphology becomes completely fine. The Curie temperature, T_c , can be determined from the dielectric permittivity peak. T_c declines as the grain size decreases, but does not show a strong dependency on grain size (Fig. S3b). The average grain size undergoes a drastic decrease between coarse- and fine-KNN; however, regardless of this change, the T_c keeps quite constant.

The representative constant expressing the relaxor behavior is γ , a constant from the modified Curie-Weiss law, as follows:

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = C^{-1} (T - T_m)^{\gamma}$$

where ε_r is the dielectric permittivity, ε_m is the dielectric permittivity when the peak reaches the maximum, *C* is the Curie-Weiss constant, and T_m is the temperature at which the dielectric peak is maximum. In addition, γ is the degree of dielectric relaxation and is equal to the

proportional constant for the linear-like relationship between $\log \left(\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m}\right)$ and $\log (T - T_m)$. Its value varies from 1 to 2; conventional ferroelectrics have $\gamma = 1$ theoretically, which approaches 2 as for relaxor ferroelectrics. As mentioned in the main manuscript, the relaxor ferroelectric nature usually arises when the grain size decreases. This relationship is illustrated in Fig. S3c. The relaxor nature, γ , sharply increases when the BS content is x = 0.01375, where the grain size starts becoming fine uniformly without any large grains. The slope of the linearlike relations, γ , for coarse- and fine-KNN is shown in Fig. S3d, indicating that fine-KNN is closer to relaxor ferroelectrics. Consistent with the value of γ , the fine-KNN displays a more frequency-dependent behavior than the coarse-KNN in dielectric permittivity and its loss tangent as a function of temperature (Fig. S3e and f).

The intimate relationship between the grain size and piezoelectric characteristics of KNN is shown in Fig. S4. Considering that the average grain size drastically declines at x = 0.0125, but the bimodality of the grain size vanishes at x = 0.01375, it is worth noting that the piezoelectric properties strongly depend on the absence of grain size bimodality. As shown in Fig. S4a and b, the bipolar and unipolar strains are suppressed in uniformly fine grains ($x \ge 0.01375$), unlike the KNN grains possessing large grains ($x \le 0.0125$). This tendency is also observed in the piezoelectric constant, d_{33} , and the converse piezoelectric constant, d_{33}^* (Fig. S4c and d). With the extinction of large grains, d_{33} and d_{33}^* also sharply decline, which is a typical trend during the transition from normal ferroelectrics to relaxor ferroelectrics.

Interestingly, the thermal stability of d_{33}^* is noteworthy (Fig. S4e). If the KNN ceramics have a large average grain size (x ≤ 0.01125), the normalized d_{33}^* rapidly deteriorates below 0.6 over the temperature range of 300°C. At x = 0.0125, where the average grain size drops to a few micrometers but large grains remain, the normalized d_{33}^* also rapidly deteriorates to ~0.7, with a slight improvement. With the meticulous addition of BS (x \geq 0.01375), the thermal stability of d_{33}^* is greatly enhanced, resulting in little fluctuation and loss as soon as the grain size bimodality is eliminated. Otherwise, the *P-E* curves gradually flattens as the BS content increases, indicating that the grain-size bimodality dependency is especially correlated with the strain (Fig. S4f).



Fig. S3. Electrical characteristics of KNN-0.03BNKLZ-xBS with varying BS compositions (a) Temperature dependence of dielectric permittivity at frequency of 100 kHz. (b) Curie temperature and average grain size. (c) γ , a constant expressing the degree of relaxor nature and average grain size. (d) The linear-like relations between $\text{Log}(1/\varepsilon_r - 1/\varepsilon_m)$ and $\text{Log}(T - T_m)$ for the coarse- and fine-grained samples, respectively. The slopes represent the value of γ . (e-f)

Temperature dependence of dielectric permittivity and its loss at frequency values of 1, 10, and 100 kHz.



Fig. S4. Characteristics of KNN-0.03BNKLZ-xBS with varying BS compositions. (a) Bipolar *S-E* curves at 10 Hz. (b) Unipolar *S-E* curves at 10 Hz. (c) d_{33} and average grain size. (d) d_{33}^* and average grain size. (e) Normalized d_{33}^* with wide range of temperature from RT to 300°C. (f) *P-E* curves at 10 Hz.

Note 4. Local crystallographic analysis using TEM and dark-field imaging

Prior to TEM observation, we narrowed down the phase candidates into three possible perovskite structures for the following reasons. ² First, the XRD data (Fig. S9 and Table S1) showed that both coarse and fine grains are composed of a polar phase (tetragonal P4mm and rhombohedral R3m). The results revealed that grains of both sizes mainly comprised the polar phase. Second, in the case of fine-grained samples showing relaxor behavior, we deduced that nonpolar phases may exist in a local part that is difficult to detect via XRD because the XRD data uses averaged crystallographic information. Even in this case, the tetragonal and rhombohedral frames did not deviate significantly from the XRD results. ^{3,4} Third, the KNN composites have a low doping concentration of 0.03BNKLZ and ~0.01BS; thus, largely distorted phases passing through two or more steps of oxygen octahedral tilting are eliminated. ⁵ Finally, three candidates, polar, nonpolar tetragonal (nonpolar-T, P4/mbm), and nonpolar rhombohedral (nonpolar-R, R3c) are selected because nonpolar phases are commonly found in multiphase relaxor ferroelectrics. ^{6,7}

Fig. S5a shows three phase candidates incorporated in the KNN compound: polar, nonpolar-T, and nonpolar-R phases. The three phases are distinguished by the oxygen octahedral tilting mode: the polar phase without oxygen octahedral tilting, nonpolar-T with inphase oxygen octahedral tilting, and nonpolar-R with out-of-phase oxygen octahedral tilting. TEM diffraction analysis distinguishes these three phases based on the presence and location of superlattice reflections, that is, weak diffraction spots between strong spots. However, superlattice reflections do not appear in every plane. Furthermore, in addition to the limitation in which planes can have distinguishable diffracted spots, the sample tilt angle is also limited to 35.0° or less along both the X- and Y-directions in TEM, and we can browse planes only within a certain angle between the transmission electron beams. Owing to these limitations, establishing experimental flows is essential for classifying all the three phases in TEM.

Fig. S5b-d presents the TEM experimental flows, which start from the low-index planes of <001>, <101>, and <111>, respectively. All Miller indices in this study were indexed based on the pseudocubic system. The red spots indicate superlattice reflections. Fig. S5b covers the low-index plane <001> to the high-index plane <103> by tilting the sample by 18.43°. In <001>, polar and nonpolar-R phases are undistinguishable, while nonpolar-T phase is distinguishable by superlattice reflection at $\frac{1}{2}(ooe)$; 'o' and 'e' stand for odd and even in Miller indices, respectively. Tilting to <103>, nonpolar-T is still distinct by $\frac{1}{2}(oeo)$, and polar and nonpolar-R are now determined by superlattice reflection $\frac{1}{2}(000)$ in the nonpolar-R phase. Fig. S5c covers the low-index plane <101> to the high-index planes <312> and <201> by tilting the sample 18.43° and 19.12°, respectively. In <101>, the polar and nonpolar-T phases are indistinguishable, whereas the nonpolar-R phase is distinguishable by superlattice reflection at $\frac{1}{2}(000)$. Tilting to <312>, nonpolar-R is still distinct by $\frac{1}{2}(000)$, and polar and nonpolar-T are now determined by superlattice reflection $\frac{1}{2}(ooe)$ in the nonpolar-T phase. Returning to <101> and tilting to <201>, polar and nonpolar-T are determined by superlattice reflection $\frac{1}{2}(ooe)$ in the nonpolar-T phase. Fig. S4d covers the low-index plane <111> to the high-index planes <112> and <132> by tilting the sample by 19.47° and 22.21°, respectively. In <111>, the polar and nonpolar-R phases are indistinguishable, whereas the nonpolar-T phase is distinguishable by superlattice reflection at $\frac{1}{2}(ooe)$. Tilting to <112>, nonpolar-T is still distinct by $\frac{1}{2}(ooe)$, and polar and nonpolar-R are now determined by superlattice reflection 1/2(000) in the nonpolar-R phase. Returning to <111> and tilting to <132>, nonpolar-T is still distinct by $\frac{1}{2}(ooe)$, and polar and nonpolar-R are now determined by superlattice reflection $\frac{1}{2}(ooo)$ in the nonpolar-R phase.

Following the flow, we obtained TEM images and analyzed the local phase distribution

in the coarse- and fine-grained samples. Fig. S6a-b shows the bright-field and dark-field images of one grain in a coarse-sized sample. Seeing the two SAEDs in Fig. S6b, the diffraction patterns along [111] and [112] have spots corresponding only to polar and nonpolar-T phases, excluding the existence of a nonpolar-R phase. The dark-field image (Fig. S6b) was extracted from the superlattice reflection spot $\frac{1}{2}(110)$ of the nonpolar-T phase along the zone axis [111]. The bright region indicated by the yellow arrow consists of a nonpolar-T phase, and the other dark region indicated by the green arrow consists of a polar phase. Fig. S6c-d shows the brightfield and dark-field images of one grain in a fine-sized sample. Seeing the two SAEDs in Fig. S6c-d, diffraction patterns along the [101] and [201] have spots corresponding only to polar and nonpolar-T phases, excluding the existence of the nonpolar-R phase. The dark-field image (Fig. S6d) was extracted from the superlattice reflection spot $\frac{1}{2}(112)$ of the nonpolar-T phase along the zone axis [201]. The bright region indicated by the yellow arrow consists of a nonpolar-T phase, and the other dark region indicated by the green arrow consists of a polar phase.

Both coarse and fine grains were mainly composed of a polar phase, and the amount of nonpolar-T phase was minute in both samples. This is reasonable in the coarse-grained samples because the ferroelectric characteristics are dominant in the coarse grains. However, relaxor ferroelectric fine grains also involve a large amount of the polar phase. The ferroelectric coarse grains and relaxor ferroelectric fine grains are crystallographically identical, but electrically far from identical.

In addition, not every grain in the coarse and fine grains consisted of polar and nonpolar mixed phases. As shown in Fig. S7a and b, the two grains in coarse-KNN reveal different superlattice reflections, even along the same zone axis of [001]. Fig. S6a shows the bright-field and dark-field images of one grain with superlattice reflection spots corresponding to polar and nonpolar-T phases. The dark-field image was extracted from the superlattice reflection spot $\frac{1}{2}(110)$ of the nonpolar-T phase along the zone axis [001]. The bright region indicated by the yellow arrow consists of a nonpolar-T phase, and the other dark region indicated by the green arrow consists of a polar phase. However, in the same zone axis, the other grain does not show the superlattice reflection spot $\frac{1}{2}(110)$ of the nonpolar-T phase (Fig. S7b). This is also observed in fine-KNN. As shown in Fig. S6c and d, the two grains in fine-KNN reveal the different superlattice reflections, even along the same zone axis of [111]. Fig. S7c shows the bright-field and dark-field images of one grain with a superlattice reflection spot corresponding to polar and nonpolar-T phases. The dark-field image was extracted from the superlattice reflection spot $\frac{1}{2}(112)$ of the nonpolar-T phase, and the other dark region indicated by the green arrow consists of a polar phase. However, in the same zone axis [111]. The bright region indicated by the yellow arrow consists of a nonpolar-T phase, and the other dark region indicated by the green arrow consists of a polar phase. However, in the same zone axis [111]. The bright region indicated by the green arrow consists of a polar phase. However, in the same zone axis, the other grain does not show the superlattice reflection spot $\frac{1}{2}(112)$ of the nonpolar-T phase along the zone axis [111]. The bright region indicated by the green arrow consists of a polar phase. However, in the same zone axis, the other grain does not show the superlattice reflection spot $\frac{1}{2}(112)$ of the nonpolar-T phase (Fig. S7d).

Thus, the nonpolar phase is not only less distributed in a single grain but the number of grains with such a nonpolar phase is small as well. Accordingly, we concluded that the coexistence of polar and nonpolar phases and their quantitative distribution does not regulate thermal stability.



Fig. S5. (a) Three phase candidates for KNN-BNKLZ-xBS. (b-d) TEM experimental flows defining local phases, which start from low-index planes (violet-colored planes) of <001>, <101>, and <111>, respectively. Superlattice reflection spots are colored red.



Fig. S6. (a) Bright-field image of one grain in coarse-KNN and its (b) dark-field image corresponding to the superlattice reflection with Z. A. = [111] and the SAED insets exclude nonpolar-R phase. See the flow of Fig. S5d. (c) Bright-field images of a fine-KNN along Z. A. = [101] and its (d) dark-field image corresponding to the superlattice reflection with Z. A. = [201]. The SAED insets exclude nonpolar-R phase. See the flow of Fig. S5c. Yellow and green arrows in dark-field images indicate the area with nonpolar-T and polar phases, respectively. All the scales in this Fig. are 200 nm.



Fig. S7. (a) Bright-field image of coarse-KNN and its dark-field image corresponding to the superlattice reflection with Z. A. = [001]. (b) Another coarse grain that only possesses polar phases without superlattice reflections at the same Z. A. = [001]. See the flow of Fig. S5b. (c) Bright-field image of fine-KNN and its dark-field image corresponding to the superlattice reflection with Z. A. = [111]. (d) Another fine grain that only possesses polar phases without superlattice reflections at the same Z. A. = [111]. See the flow of Fig. S5d. Minor nonpolar-T phases exist regardless of grain sizes. Yellow and green arrows in dark-field images indicate the area with nonpolar-T and polar phases, respectively.

Note 5. Tetragonality and phase analysis in atomic scale by STEM

The local tetragonality (c/a ratio) and phase distribution can be observed at the atomic scale using STEM. Unit cell scale analysis was conducted by extracting the atomic positions in the inversed ABF-STEM images of the coarse- and fine-KNN (Fig. S8b and c). As shown in Fig. S8d and e, the tetragonality (c/a ratio) was mapped by unit cells, and both KNN ceramics possess cubic-like structures with an average tetragonality of ~1.00, indicating that both coarse- and fine-KNN are in the vicinity of the diffuse phase transition. The difference between the two KNN systems at the atomic scale was revealed in the phase analysis. The phase was determined by the direction of atomic off-centering for each unit cell, as illustrated in Fig. S8a. The ions move toward the faces of the cubic-like unit cells in the tetragonal (T) phase and toward the corners in the rhombohedral (R) phase. In this way, the local phase distribution was mapped at the atomic scale for coarse- and fine-KNN (Fig. S8f and g). The coarse-grained KNN dominantly consists of the T phase with a smaller R phase, whereas the fine-grained KNN consists of a larger amount of R phase.



Fig. S8. (a) Schematics showing the ion off-centering in one unit cell as T and R phases. The phase can be determined by the off-centered direction of ions in unit cells. (b, c) Inversed ABF-STEM images, and in the corresponding area, unit cell mapping for (d, e) tetragonality (c/a ratio) (f, g) R/T phase distributions in the coarse-grained and fine-grained KNN, respectively.

Note 6. Phase distribution changes by in-situ heating XRD

We conducted in-situ heating XRD under varying temperatures from room temperature to 400°C and analyzed the phase distribution via Rietveld refinement. Fig. S9a and b show the full range of in-situ heating XRD data from 2θ of $20 - 140^{\circ}$ over the temperature range from room temperature to 400°C. The characteristic peaks at 2 θ values of 44 – 47° are shown in Fig.s S9c and d. As shown by the peak shapes in Fig. S9c-d and the inset of Fig. S9b, the fine grains present a broad shape, indicating a larger content of R phase. When approaching the Curie temperature (~300°C), the separated peaks tend to merge into one peak, indicating a transition to the cubic phase. More precisely, we performed Rietveld refinement to quantify the distribution of the T, R, and cubic phases. Both composites are mixtures of the T and R phases, and it is notable that the proportion of the R phase is much larger in the fine grains (Fig. S9d) than in the coarse grains (Fig. S9c) over the complete temperature range. The ratio of the R phase loss from room temperature to 300°C was also lower in the fine grains. The in-situ heating XRD results show that the fine grains are prone to preserve the multidirectional polarization states to the Curie temperature (above 300°C) better than the coarse grains. The multiphase state in fine grains implies that the materials can embrace variable polar configurations, and the ability to maintain multiphase during heating can be a demonstration of how much the polarization can endure high temperatures. The phase distribution, R_p, and R_{wp} are summarized in Table S1.



Fig. S9. In-situ heating XRD results from room temperature to 400°C of (a) coarse-grained and (b) fine-grained KNN, respectively. The inset is an example depicting the overlap of the two tetragonal peaks and one rhombohedral peak in the range of 2θ of $45 - 46^{\circ}$ (c) and (d) illustrate enlarged diffractions in the 2θ of $44 - 47^{\circ}$ under temperature range from room temperature to 400°C for coarse- and fine-KNN, respectively. The color bars represent phase distribution of tetragonal, rhombohedral, and cubic phases calculated by Rietveld refinements.

Coarse	Tetragonal	Rhombohedral	Rp	Rwp
RT	92.4(2)	7.6(4)	8.12	11.5
50°C	93.7(3)	6.3(9)	7.54	10.9
100°C	94.2(1)	5.8(3)	7	10.7
150°C	94.8(1)	5.2(4)	7.2	11.1
200°C	96.1(1)	3.9(3)	7.63	12.1
250°C	97.9(1)	2.1(3)	8.04	12.7
300°C	100	-	10.4	16.1
-	Tetragonal	Cubic	R _p	Rwp
350°C	5.4(7)	94.6(7)	8.15	11.25
400°C	0.1(5)	99.9(5)	9.9	14.0

Fine	Tetragonal	Rhombohedral	Rp	Rwp
RT	63.2(4)	36.8(9)	5.61	7.99
50°C	67.0(3)	33.0(7)	5.44	7.84
100°C	68.1(3)	31.9(6)	5.32	7.52
150°C	73.2(3)	26.8(7)	5.09	7.1
200°C	76.0(4)	24.0(10)	5.42	7.44
250°C	80.3(3)	19.7(6)	5.99	8.35
300°C	86.5(4)	13.5(7)	9.19	12.5
-		Cubic	R _p	Rwp
350°C		100	13.5	19.8
400°C		100	13.5	20.1

Table S1. Phase distribution (wt.%) in the coarse and fine grains calculated by Rietveld refinement based on Fig. S9.

Note 7. Piezoelectric performance over the high-temperature range

The experimental setup for piezoelectric performance at high temperatures is illustrated in Fig. S10a. The cantilever-type actuator sample was clamped to one side of a customized high-temperature chamber on the hot stage. Voltage was applied to a sample, and the infrared light from the infrared source was detected to measure the deflection of the cantilever. A part of actual setup is in Fig. S10b. The deflection amplitude is presented in terms of displacement as a function of temperature for three samples: PZT, coarse-grained KNN, and fine-grained KNN in Fig. S10c. The piezoelectric performance of PZT was the best at room

temperature, showing the largest displacement; however, the deflection deteriorated sharply at temperatures above 75°C. The actuating performance of the coarse-grained KNN slightly degraded as the temperature increased. The fine-grained KNN, particularly throughout the temperature range, maintained its piezoelectric performance. This tendency was clearer when the displacement was normalized to the value at room temperature (Fig. S10d). At 150°C, the normalized displacement of PZT harshly degraded to 0.2, and the coarse-KNN decreased to less than half, whereas the fine-KNN remained above 0.87.



Fig. S10. (a) Schematic for high-temperature piezoelectric deflection experiment setup (b) Photographs of the experimental setup. (c, d) In-situ heating measurements of the displacement

and normalized displacement of deflection amplitude for PZT, coarse-grained KNN, and finegrained KNN actuators, respectively.

Note 8. Synthesis procedure of KNN based piezoceramic samples

The piezoceramic samples with (1-x-y)KNN-xBNKLZ-yBS compositions (x = 0.03, y = 0.0075 - 0.015) were prepared using the conventional solid-state reaction method. The synthesis procedure is as shown in Fig. S11.



Fig. S11. Schematic diagram of synthetic procedure of KNN-BNKLZ-BS piezoceramic samples.

References

- 1. L. Fu, L. Lin and Y. Chen, *Mater. Res. Bull.*, 2017, 94, 506-512.
- 2. A. M. Glazer, Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 1972, 28, 3384-3392.
- H. Yamada, T. Matsuoka, H. Kozuka, M. Yamazaki, K. Ohbayashi and T. Ida, J. Appl. Phys., 2015, 117, 214102.
- 4. X. Liu, J. Shi, F. Zhu, H. Du, T. Li, X. Liu and H. Lu, *J. Materiomics*, 2018, 4, 202-207.
- C. J. Howard and H. T. Stokes, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2005, 61, 93-111.
- T. W. Surta, A. Manjón-Sanz, E. Qian, T. T. Tran and M. R. Dolgos, *Inorg. Chem. Front.*, 2018, 5, 1033-1044.
- 7. K. Li, X. Li Zhu, X. Qiang Liu and X. Ming Chen, *Appl. Phys. Lett.*, 2012, **100**, 012902.