Optimized strain performance in <001>-textured Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based ceramics with ergodic relaxor state and core–shell microstructure

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Abstract: Herein, a high strain of ~0.3% with a small hysteresis of 43% is achieved at a low electric field of 4 kV/mm in the highly <001>-textured 0.97(0.76Bi$_{0.5}$Na$_{0.5}$TiO$_3$–0.24SrTiO$_3$)–0.03NaNbO$_3$ (BNT–ST–0.03NN) ceramics with an ergodic relaxor (ER) state, leading to a large normalized strain ($d_{33}^*$) of 720 pm/V. The introduction of NN templates into BNT–ST induces the grain orientation growth and enhances the ergodicity. The highly <001>-textured BNT–ST–0.03NN ceramics display a pure ergodic relaxor state with coexisted ferroelectric $R\bar{3}c$ and antiferroelectric $P4_{b}bm$ polar nanoregions (PNRs) on nanoscale. Moreover, due to the incomplete interdiffusion between the NN template and BNT–ST matrix, the textured ceramics present a core–shell structure with the antiferroelectric NN core, and thus the BNT-based matrix owns more $R\bar{3}c$ PNRs relative to the homogeneous nontextured samples. The high <001> crystallographic texture and more $R\bar{3}c$ PNRs both facilitate the relaxor-to-ferroelectric transition, leading to the low-field-driven high strain, while the ergodic relaxor state ensures a small hysteresis. Furthermore, the $d_{33}^*$ value remains high up to 518 pm/V at 100 ℃ with an ultra-low hysteresis of 6%.

Keywords: Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT)-based ceramics; ergodic relaxor (ER) state; <001> crystallographic texture; core–shell structure; optimized strain performance

1 Introduction

The actuation performance of piezoelectric materials can be reflected in their electric-field-induced strain response ($S$–$E$ curves). Lead-based perovskite ferroelectrics, such as Pb(Zr,Ti)O$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-based ceramics, dominate the market of piezo-actuator due to their excellent electromechanical properties. The strain value of 0.1%–0.2% can be achieved at a low electric field of 2–3 kV/mm with a small hysteresis of ~20%, leading to a high normalized strain ($d_{33}^*$) of > 500 pm/V [1]. However, researchers have been pursuing lead-free alternatives owing to the toxicity of lead. Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT)-based relaxor ferroelectrics are attractive as lead-free actuator materials due to their excellent strain performance [2–6]. High-strain BNT-based material has rapidly become a research hotspot since a large strain value of 0.45% was observed in 0.92BNT–0.06BaTiO$_3$–0.02K$_0.5$Na$_{0.5}$NbO$_3$ (0.92BNT–0.06BT–0.02KNN) ceramics at 8 kV/mm [7], which has been attributed to the reversible relaxor–ferroelectric transition [8–13].

The strain properties of the BNT-based materials are closely related to their relaxor state. The nonergodic
relaxor (NR) state means that the electric field can induce a stable long-range ordered polar state. In this case, the BNT-based material behaves as a normal ferroelectric and exhibits a butterfly-shaped bipolar $S–E$ curve, as shown in Fig. 1(a), in which the poling strain ($S_{pol}$) reflects the difference between high-field polar state and original randomly-oriented state, including all reversible and irreversible contributions. The reversible part is the reusable strain, that is, the positive strain ($S_{rem}$), which arises from the lattice strain, reversible non-180° domain switching, and phase transformation. The irreversible part forms the remnant strain ($S_{rem}$), which results from the irreversible non-180° domain switching and phase transformation. For the BNT-based material in the NR state, an unwished high $S_{rem}$ exists and the $S_{pol}$ is usually at a relatively low level of $\sim 0.1\%$. By composition modulation, the local random fields in the BNT-based materials caused by structural or charge inhomogeneities could be enhanced effectively, and the coherence length of the ferroelectric lattice is reduced, leading to the improvement of ergodic relaxor (ER) phase with randomly scattered polar nanoregions (PNRs) on nanoscale. In general, the ER state displays a reversible relaxor–ferroelectric transition under a cycle of the electric field. During this process, the BNT-based material could undergo a series of reversible dynamic processes including the growth of PNRs, domain switching, and phase transformation. With the increase of ER phase, the butterfly-shaped $S–E$ curve will gradually convert to a sprout-shaped curve, accompanied by the decrease of $S_{rem}$ owing to the disappearance of irreversible contributions and the increase of $S_{pol}$ due to the improvement of reversible contributions. The highest $S_{pol}$ is obtained near the NR/ER phase boundary, where the relaxor and ferroelectric states display competitive free energy, and an easy relaxor–ferroelectric reversible transition can be induced by the electric field, as shown in Fig. 1(b). However, for the BNT-based material lying deep in the ER state, the $S_{pol}$ is unavoidably reduced due to the strong random fields and high energy barrier for achieving relaxor-to-ferroelectric transition, as shown in Fig. 1(c).

Up to now, a lot of work has been conducted to achieve a high strain in the BNT-based ceramics by constructing the NR/ER phase boundary [13–16]. A remarkable study reported a giant strain of $0.70\%$ and $d_{33}$ of $\sim 1400$ pm/V at 5 kV/mm in $[(Bi_{0.5}(Na_{0.72}K_{0.18}Li_{0.1})_{0.5})_{0.95}(Sr_{0.8}La_{0.2})_{0.05}(Ti_{0.985}Ta_{0.015})O_3$ ceramics [13]. However, the applications of high-strain BNT-based ceramics near the NR/ER phase boundary are restricted by their non-negligible $S_{rem}$ from the residual ferroelectricity and high strain hysteresis of $> 60\%$. The hysteresis is intrinsically related to the dynamics of polarization reversal under a cycle of the electric field. The key point of reducing hysteresis is a fast response to the electric field. Compared with the BNT-based materials near the NR/ER phase boundary, the pure ER state shows smaller-sized PNRs with higher mobility and lower domain wall energy, which can provide a more rapid response to the electric field, and the stronger ergodicity ensures a more timely collapse of field-induced ferroelectric order on the removal of the electric field. As a result, the ER state displays a lower strain hysteresis, despite the decreased $\delta_{pol}$ [17,18]. For instance, a strain value of $\sim 0.3\%$ with a low hysteresis of 30% was achieved at 8 kV/mm in the $[Bi_{0.5}(Na_{0.72}K_{0.18}Li_{0.1})_{0.5})_0.995(Ti_{0.985}Ta_{0.015})O_3$ ceramics with the ER state [18]. Obviously, it is hard to obtain high strain and low hysteresis simultaneously in the BNT-based ceramics only by the composition modulation. Moreover, regardless of the relaxor state of the BNT-based materials, a large driving electric field of $> 5$ kV/mm is often required to induce the relaxor–ferroelectric transition, which is not desired in practical applications. The crystallographic texture is an effective strategy to optimize the piezoelectric and strain performance of ferroelectric ceramics by utilization of inherent anisotropy in the material properties and domain engineering [19–21]. The strain output of randomly-oriented ceramics could be suppressed due to the limited polarization reversal caused by grain constraints. The textured ceramics tend to exhibit single crystal-like nature in the direction of grain orientation growth, which provides the opportunity to achieve excellent strain output. It should be noted that the strain response strongly depends on the direction of the electric field with respect to the crystal lattice. In the $0.935\text{BNT–}0.065\text{BT}$ single crystals near the morphotropic phase boundary [22], a giant strain of 0.73% and a low poling field ($E_{pol}$) (the electric field required to trigger the ferroelectric phase out of the existing relaxor phase [23]) of 2.3 kV/mm were achieved in the <001>-oriented sample, superior to the strain performance of <110>-oriented sample ($0.33\%$, 3 kV/mm) and <111>-oriented sample ($0.57\%$, 2.7 kV/mm). This phenomenon is attributed to

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an irreversible phase change from rhombohedral PNRs to tetragonal ferroelectric microdomains under the application of electric field along the <001> direction, which induces the rotation of polarization vector from <111> to <001> with a small angle of ~54°. Similar field-induced polarization rotation and phase transformation were also found in the high-strain <001>-oriented rhombohedral Pb(Mg1/3Nb2/3)O3–PbTiO3 (PMN–PT) single crystal [24]. In the 0.944BNT–0.056BT single crystal at 130 °C (near the NR/ER phase boundary) [25], it was found that the electric field along the <001> direction can induce the transformation from the pseudocubic to the ferroelectric tetragonal structure and generate a high strain of 0.6% at 2 kV/mm, while the electric field along the <111> direction induces a ferroelectric rhombohedral structure with a low strain of 0.13%. In the typical 0.92BNT–0.06BT–0.02KNN system [26], the <001>-oriented single crystal was also found to exhibit a giant strain of 0.83% at 2.8 kV/mm due to the field-induced pseudocubic-to-tetragonal phase transition and strong domain texture. Therefore, the <001> crystallographic texture is often used to enhance the strain output of the BNT-based ceramics [27–30]. For example, a large strain response of ~0.32% at 5 kV/mm was obtained in the <001>-textured 0.97(0.92BNT–0.06BaTiO3)–0.03NaNbO3 ceramics, which was ~2.6 times higher than that of randomly oriented ones [30]. It was demonstrated that the <001> grain orientation results in more homogeneous domain distribution and promotes the domain switching and mobility. An easier relaxor-to-ferroelectric phase transition was achieved in the textured ceramics, contributing to the significantly improved strain response.

In this work, we combine the composition and structure modulation to achieve a highly <001>-textured BNT-based ceramics in the pure ER state to optimize the strain output, driving field, and strain hysteresis simultaneously. 0.76BNT–0.24SrTiO3 (BNT–ST) is chosen as the matrix due to its inherently low driving field. Investigations on the BNT–ST system have shown that a large strain of ~0.2% can be generated at a low electric field of ~3 kV/mm [31–34]. Plate-like NaNbO3 (NN) template is used to induce the grain orientation growth and modulate the relaxor behavior of the BNT–ST–NN textured ceramics. The incorporation of Na+ at the A site and Nb5+ at the B site can effectively increase the chemical disorder and enhance the random fields, leading to the improvement of the ER phase with randomly scattered PNRs. The highest <001> texture degree of 87% is achieved in the BNT–ST–0.03NN ceramics, which lie in the ER phase region with the coexisted ferroelectric $R3c$ and antiferroelectric $P4bm$ PNRs. Intriguingly, a core–shell structure with the antiferroelectric NN core is formed in the textured ceramics, and the BNT-based matrix owns more $R3c$ PNRs compared with the nontextured samples. The high <001> texture and more $R3c$ PNRs both facilitate the relaxor-to-ferroelectric transition of textured ceramics, leading to the low-field-driven high strain, while the pure ER state ensures a low strain hysteresis, as shown in Fig. 1(d).

2 Experimental

2.1 Synthesis of NaNbO3 templates

The NN templates were synthesized by the two-step molten-salt method based on Reactions (1) and (2):

$$5\text{Bi}_2\text{O}_3 + 7\text{Na}_2\text{CO}_3 + 10\text{Nb}_2\text{O}_5 \rightarrow 4\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18} + 7\text{CO}_2 \uparrow \quad (1)$$

Fig. 1 Schematic diagrams of strain performance optimization in BNT-based ceramics by composition and structure modulation.
4Bi_{2.5}Na_{3.5}Nb_{5}O_{18} + 3Na_{2}CO_{3} \rightarrow 20NaNbO_{3} + 5Bi_{2}O_{3} + 3CO_{2}↑ \quad (2)

In the first step, a stoichiometric amount of the Bi$_{2}$O$_{3}$, Na$_{2}$CO$_{3}$, and Nb$_{2}$O$_{5}$ powders were mixed with NaCl by ball-milling in ethanol for 12 h, and then the dried mixture was calcinated at 1140 °C for 5 h. After washing the products several times with hot water to remove NaCl, the Bi$_{2.5}$Na$_{3.5}$Nb$_{5}$O$_{18}$ (BNN5) precursors were acquired. Afterwards, a stoichiometric amount of the BNN5 and Na$_{2}$CO$_{3}$ powders were mixed with NaCl by magnetic stirring for 6 h. The mixture was heated at 1010 °C for 3 h, followed by washing with hot water and HNO$_{3}$ solution, to obtain the NN templates. In both the molten-salt reactions, the mass ratio of oxide to salt is equal to 1 : 1.

2. 2 Fabrication of textured ceramics

Nontextured (1–x)(0.76Bi$_{2.5}$Na$_{3.5}$TiO$_{3}$–0.24SrTiO$_{3}$)–xNaNbO$_{3}$ (BNT–ST–xNN, x = 0.00–0.03) ceramics were prepared by a conventional solid-state reaction route. The detailed processes have been provided in our previous study [35]. The nontextured ceramics were sintered at 1160 °C for 2 h. The textured BNT–ST–xNN (x = 0.01–0.03) ceramics were fabricated by adding the NN templates into the BNT–ST matrix. In a typical process, the solvent of 18 mL xylene and 12 mL ethanol, the dispersant of 0.2 g triethyl phosphate, and 30 g BNT–ST powders were mixed thoroughly by ball-milling for 24 h. Then, the plasticizer of 4.8 mL polyethylene glycol and 1.6 mL dibutyl phthalate, and the binder of 1.6 g polyvinyl butyral were added and ball-milled for another 23.5 h. Afterwards, a stoichiometric amount of the NN templates were added and ball-milled for 0.5 h. The resultant slurry was tape-cast on a glass plate, and the dried green tapes with a thickness of ~60 μm were stacked and laminated by the hot press under a pressure of 1500 N for 20 min at 70 °C. The laminated stack was then cut into individual pellets with a diameter of 1 cm. To obtain the textured ceramics, the pellets were sintered at 1150–1175 °C for 10–30 h after burning out the organic substances at 550 °C for 6 h.

2. 3 Characterization

X-ray diffraction (XRD) measurement was conducted by using a diffractometer with Cu Kα radiation (D/Max 2250, λ = 1.5418 Å, Rigaku Corporation, Japan). The morphology, grain size, and element distribution were observed by a field-emission scanning electron microscope (FESEM, MIRA3, TESCAN, Czech Republic) equipped with an energy dispersive spectroscope (EDS, X-Max 20, Oxford Instruments, UK). The nanostructure observation was performed on a high-resolution transmission electron microscope (HR-TEM, Titan G2 60-300, FEI, USA). The TEM samples were prepared by focused ion beam (FIB) milling. For the electrical characterization, the ceramics were polished to a thickness of ~0.6 mm. Then, a Pt paste was coated on both faces of the ceramics and baked in the air at 800 °C for 10 min to form electrodes. The dielectric temperature spectra of the poled ceramics were measured by using a precision impedance analyzer (Agilent 4294A, Agilent Technologies, USA). The poling treatment was performed under a DC field of 4 kV/mm for 20 min at room temperature. The polarization–electric (P–E) field, current–electric (I–E) field, and strain–electric (S–E) field curves of the unpoled ceramics were measured by using a ferroelectric tester (TF Analyzer 2000, aixACCT systems, Germany) with an electric field of 4 kV/mm and frequency of 1 Hz.

3 Results and Discussion

The synthesis processes of the NN templates comprise the fabrication of plate-like BNN5 precursors with layered perovskite structure and subsequent topochemical conversion from BNN5 to perovskite-structured NN. The detailed mechanisms have been reported elsewhere [35]. Figure 2(a) shows the XRD patterns of the BNN5 precursors and NN templates. The BNN5 precursors display a tetragonal phase structure (PDF Card No. 42-0399), and almost pure NN (orthorhombic phase, PDF Card No. 33-1270) is formed after the two-step molten-salt synthesis. The SEM image given in Fig. 2(b) shows that the BNN5 precursors have a rectangular plate shape and possess a smooth surface, with a side length of 10–40 μm and a thickness of 1–2 μm. The broad faces and strong anisotropy make them suitable for preparing the NN templates through a topochemical reaction. Figures 2(c) and 2(d) show the SEM images of the NN templates, which exhibit a similar plate morphology with a side length of 10–40 μm and a thickness of 1–2 μm.

The plate-like NN templates can be easily aligned by applying the shear stress through tape-casting for the preparation of textured ceramics, as shown in Fig. 3(a).
Fig. 2  (a) XRD patterns of BNN5 precursors and NN templates. SEM images of (b) BNN5 precursors and (c, d) NN templates.

Fig. 3  (a) Schematic diagram of tape-casting process for preparation of textured ceramics. (b) XRD patterns of nontextured BNT–ST ceramics sintered at 1160 °C for 2 h and textured BNT–ST–xNN (x = 0.01–0.03) ceramics sintered at 1175 °C for 20 h. (c) Magnified view of (111) and (002) peaks for all the samples.
Figure 3(b) gives the XRD patterns of nontextured BNT–ST ceramics sintered at 1160 °C for 2 h and textured BNT–ST–xNN (x = 0.01–0.03) ceramics sintered at 1175 °C for 20 h. For comparison, Fig. S1(a) in the Electronic Supplementary Material (ESM) shows the XRD patterns of nontextured BNT–ST–xNN (x = 0.01–0.03) ceramics, and the magnified view of (111) and (002) peaks for all the samples is summarized in Fig. 3(c). All the samples display a pure perovskite structure without any impurity phase. There is no obvious splitting of the (111) and (002) peaks, implying the absence of long-range ordered rhombohedral or tetragonal distortions and the formation of a pseudocubic phase. The addition of NN leads to the slight shift of diffraction peaks towards lower angles due to the substitution of bigger ions (Na+: 1.39 Å, Nb5+: 0.64 Å) for smaller ions (Bi3+: 1.36 Å, Ti4+: 0.605 Å). Importantly, compared to the nontextured samples showing the highest {110} peak, the textured samples exhibit the domination of {00l} peaks, indicating a preferred crystallographic orientation along the <001> direction. Moreover, the intensity of the {110} peak gradually decreases while the {00l} peaks become stronger with increasing NN content. The degree of the <001> orientation can be expressed by Lotgering factor:

\[ F_{(00l)} = \frac{P_{(00l)} - P_0}{1 - P_0} \]  

\[ P_{(00l)} = \frac{\Sigma I_{(00l)}}{\Sigma I_{(hkl)}} \]  

\[ P_0 = \frac{\Sigma I_{(00l)}^{00}}{\Sigma I_{(hkl)}^{00}} \]

where \( I \) and \( I_0 \) represent the intensities of the diffraction peaks of the textured and nontextured samples, respectively. With the addition of the NN templates from \( x = 0.01 \) to 0.03, the \( F \) value monotonically increases from 69% to 87%. The results confirmed the efficacy of the NN templates on the fabrication of highly textured ceramics. Besides, sintering condition optimization is performed in this work. As shown in Fig. S1(b) in the ESM, the \( F \) value of the BNT–ST–0.03NN textured ceramics generally increases with the increase of sintering temperature from 1150 to 1175 °C and dwelling time from 10 to 20 h. However, a longer time (30 h) deteriorates the quality of textured ceramics, which could be ascribed to the increased defects due to the excessive volatilization of Bi and Na.

In addition to the XRD patterns, the texture quality can also be revealed by the grain morphology. The surface SEM images of nontextured BNT–ST and textured BNT–ST–xNN (x = 0.01–0.03) ceramics are shown in Fig. 4(a). Different from the equiaxed grains in the nontextured ceramics with a grain size of 2–8 μm, the textured ceramics show the coexistence of large-sized textured grains (20–60 μm) and small-sized grains (5–10 μm). With the addition of the NN templates, the proportion of the large-sized grains gradually increases, consistent with the enhanced textured degree observed by the XRD measurement. The cross-sectional SEM images are given in Fig. S2(a) in the ESM. It can be seen that the textured ones display higher pore concentrations, which are formed by rearranging the template grains to have a face-to-face contact in the early stage of sintering [36]. Subsequently, the EDS analysis is conducted on the nontextured and textured BNT–ST–0.03NN ceramics to reveal the element content and distribution, as shown in Fig. 4(b) in the ESM and Fig. 4(b), respectively. The elements of Bi3+, Na+, Sr2+, Ti4+, Nb5+, and O2− distributed uniformly in the nontextured ceramic grains, indicating the formation of a homogeneous solid solution. However, for the textured sample, there are obvious Nb-enriched regions inside some textured grains, as marked by the red circles in Fig. 4(b). A core–shell structure with clear interfaces can be found in the corresponding backscattered electron images.

In the BNT-based textured ceramics [27,37–39], it is well accepted that the growth of textured grains is related to an Ostwald ripening process where larger grains (templates) grow at the expense of smaller ones (matrix grains) due to the difference in surface energy, and this process is promoted by the appearance of a liquid phase, which plays an active role in mass transport. In this work, it is proposed that the dissolution of small-sized BNT–ST matrix grains occurs during the high-temperature sintering process to form a metastable liquid phase, followed by the precipitation on the lowest energy sintering process to form a metastable liquid phase, followed by the precipitation on the lowest energy surface (001) of large-sized NN templates. Such a dissolution-precipitation mechanism accounts for the epitaxial orientation growth of textured grains. Besides, it should be noted that the plate-like NN not only acts as a template, but also acts as a reactant component. Owing to the difference in the chemical potential across the BNT–ST matrix and NN templates, there will be an interdiffusion of atoms at...
the crystallization interface/boundary of templates during the epitaxial orientation growth of textured grains. The growth rate is limited by the mass transport occurring as a combination of convection, diffusion, and surface reaction processes [37]. Therefore, high sintering temperature and prolonged sintering time are required to achieve a high texture degree. Herein, after sintering at 1175 °C for 20 h, the incomplete interdiffusion between the BNT–ST matrix and the NN templates leads to an inhomogeneous core–shell structure in the BNT–ST–NN textured ceramics.

The HR-TEM analysis was further performed to directly and deeply probe nanostructure details in the nontextured and textured BNT–ST–0.03NN ceramics. Figure 5(a) shows the low-magnification bright-field TEM image of the nontextured BNT–ST–0.03NN ceramics, demonstrating the formation of a homogeneous microstructure. Randomly scattered PNRs can be observed in the magnification view shown in Fig. 5(b). In our work, the introduction of NN into BNT–ST improves the local random fields, which disrupt the ferroelectric order and lead to the formation of the randomly scattered PNRs. Figures 5(c) and 5(d) exhibit the HR-TEM atomic images viewed from the [110] and [111] zone axes, respectively, and the related selected area electron diffraction (SAED) patterns are given in Figs. 5(e) and 5(f). The $1/2\{00e\}$ and $1/2\{00e\}$ superlattice spots in which the “o” and “e” respectively represent the odd and even values of Miller indices can be detected in the [110]- and [111]-viewed SAED patterns, which result from the anti-phase $a- a- a$ and in-phase $a_0a_0c+c$ oxygen octahedral tilting [40], respectively, and reveal the formation of $R\bar{3}c$ and $P4bm$ phases. Such coexistence of $R\bar{3}c$ and $P4bm$ PNRs is not measurable in the current XRD setup due to its limited analysis accuracy, resulting in an observed pseudocubic phase by XRD. In the BNT-based materials, it has been suggested that the $R\bar{3}c$ symmetry shows a ferroelectric structure with the parallel cation displacements along [111]$c$ in its unit cell, while the $P4bm$ symmetry has an antiferroelectric nature with the unbalanced antiparallel cation displacements along [001]$c$ in its unit cell, leading to a weakly-polar order [41,42].
Fig. 5  (a, b) Low-magnification bright-field TEM images of the nontextured BNT–ST–0.03NN ceramics. HR-TEM atomic images viewed from (c) [110] and (d) [111] zone axes, and (e, f) corresponding SAED patterns, respectively.

Considering the inhomogeneous core–shell structure found in the textured BNT–ST–0.03NN ceramics, we selected some representative large-sized textured grains to prepare the TEM sample by FIB milling. Figure 6(a) shows the low-magnification bright-field TEM image of these textured grains, in which a heterostructure can be observed in Grain 2. Most parts of Grain 2 exhibit a finely dispersed granular contrast, which corresponds to the region of the BNT-based matrix (i.e., shell region). Figure 6(b) shows the higher-magnification view of the area marked by a yellow circle, and clear randomly scattered PNRs can be seen. The corresponding [110]- and [111]-viewed SAED patterns are given in Figs. 6(c) and 6(d), revealing the presence of 1/2{000} and 1/2{001} superlattice spots, respectively. Similar to the nontextured BNT–ST–0.03NN ceramics, the $R\bar{3}c$ and $P4bm$ PNRs coexist in the textured BNT–ST–0.03NN ceramics. However, it is noticed that, the 1/2{001} spots of the textured samples are stronger than that of the nontextured samples while the 1/2{001} spots become weaker. That is to say, the textured BNT–ST–0.03NN ceramics own more ferroelectric $R\bar{3}c$ PNRs, which could be attributed to the incomplete interdiffusion between the NN template and the BNT–ST matrix. The addition of NN leads to disturbance of ferroelectric order. The BNT-based matrix in the textured ceramics owns a relatively lower NN/BNT–ST ratio compared with the homogeneous nontextured ceramics, resulting in the more ferroelectric $R\bar{3}c$ PNRs.

On the other hand, Grain 2 presents a region containing complex and aligned domains of several hundreds of nanometers (i.e., core region), which corresponds to the NN template seed. Figure 6(e) shows the higher-magnification view of the area marked by a yellow box, in which the interface between the BNT-based matrix and the NN template seed is distinct. A typical hierarchy domain configuration of NN can be observed, which is composed of the submicron-sized polydomain blocks, together with well-paralleled translational domains formed inside, as shown in Fig. 6(f). Figures 6(g) and 6(h) show the [110]-viewed HR-TEM atomic images of Area 1 with the matrix/seed interface and Area 2 with the domain wall of NN, respectively. It can be seen directly from Fig. 6(g) that, the area ① related to the BNT-based matrix and the area ② related to the NN template seed share the same lattice preferred orientation, and there is a grain orientation growth along the <001> direction. From Fig. 6(h), we can observe that the <001>-traced translational domain walls and the orientational domain wall are along the \{001\} habit plane, which can be determined as a 90° antiferroelectric domain wall. The SAED patterns for domain areas ②③ and ④ are shown in Figs. 6(i) and 6(j), respectively, which demonstrate the antiferroelectric Pbma symmetry of the NN core, as evidenced by the presence of 1/4\{001\} superlattice spots along the [110] zone axis. The 1/2{001} superlattice spots along the
zone axis imply anti-phase oxygen octahedral tilting and are characteristic for all orthorhombic perovskite cells. Figure 6(k) gives the local-scale high-angle annular dark field (HAADF) image and EDS-mapping images of Grain 2, once again proving the existence of the NN core.

Besides the microstructure, the dielectric, ferroelectric, and strain properties are also affected by the NN content and ceramic texturing. Figures 7(a)–7(d) show the temperature-dependent dielectric constant ($\varepsilon_r$) and loss (tan$\delta$) curves measured at different frequencies for the nontextured BNT–ST and textured BNT–ST–xNN ($x = 0.01–0.03$) ceramics before and after poling treatment. For unpoled BNT–ST ceramics, there are two dielectric anomalies during the heating process. One is the dielectric shoulder with a strong frequency dispersion appeared at the temperature $T_s$. The other is the broad dielectric peak with the maximum dielectric constant appeared at the temperature $T_m$. In BNT-based relaxor ferroelectrics, the dielectric anomalies around $T_s$ and $T_m$ are attributed to a convolution of symmetry change in PNRs from $R3c$ to $P4bm$ and a relaxation of high-temperature $P4bm$ PNRs [43]. For poled BNT–ST ceramics, an additional dielectric anomaly with a sharp change in $\varepsilon_r$ and tan$\delta$ can be detected at $T_{F-R}$ of ~36 °C, where $T_{F-R}$ is defined as the transformation temperature from the ferroelectric to relaxor state. Below $T_{F-R}$, the $\varepsilon_r$ of poled samples is lower than that of unpoled ones, indicating the formation of long-range ferroelectric order after the poling treatment. That means BNT–ST ceramics are in the NR state at room temperature. Besides, the poled BNT–ST ceramics display a higher $T_s$ and a larger $\varepsilon_r$ around $T_s$ compared to their unpoled counterparts, which originates from the enhanced ferroelectric order after the poling treatment.

The introduction of NN can enhance the dielectric relaxation, as evidenced by the suppressed and broadened dielectric peaks. Notably, no sign of $T_{F-R}$ can be found for the poled BNT–ST–xNN ($x = 0.01–$...
Fig. 7  (a–d) ε_r and tanδ curves measured at different frequencies for the nontextured BNT–ST and textured BNT–ST–xNN (x = 0.01–0.03) ceramics before and after the poling treatment. (e) Maximum dielectric constant ε_m and (f) T_m of all unpoled nontextured and textured ceramics measured at 1 MHz.

0.03) ceramics, implying that T_{F→R} has been pushed down to lower temperatures (below room temperature) by the addition of NN. In these cases, the ER phase is dominated at room temperature. Moreover, the difference between the ε_r–T curves of the unpoled and poled samples is getting smaller and smaller with the increase of the NN content, proving that the effect of the poling treatment is gradually weakening. These results imply the enhanced ergodicity by the addition of NN. To quantitatively describe the effects of the NN content and ceramic texturing on the dielectric properties, we summarize the ε_m and related temperature (T_m) for all unpoled samples, as shown in Figs. 7(e) and 7(f), respectively. The ε_m and T_m are obtained based on the ε_r–T curves measured at 1 MHz due to the well-defined dielectric peak, as shown in Fig. S3 in the ESM. We found that no matter whether it is the nontextured or textured sample, the ε_m and T_m both decrease with increasing NN content due to the enhanced ER phase, which restricts the polarization ability of ceramics. However, the textured ceramics exhibit lower ε_m and higher T_m compared to their nontextured counterparts. The suppressed dielectric constant for the textured ceramics is usually ascribed to their higher pore concentrations [44–46], which can be seen in Fig. S2(a) in the ESM. The higher T_m is relative to the enhanced internal compressive stress in the textured ceramics, which has been proven to be beneficial for the stabilization of the ferroelectric phase in the BNT-based ceramics [47,48]. Besides, the TEM results also indicate the more pronounced ferroelectric R̅3c PNRs in the textured ceramics compared to the nontextured ones, which can resist the R̅3c→P4bm transition and lead to a higher T_m.

The transition from the NR to the ER phase can also be reflected in the P–E, I–E, and S–E curves. Figure
8(a) shows the $P$–$E$ and $I$–$E$ curves of the nontextured BNT–ST and textured BNT–ST–$x$NN ($x = 0.01$–$0.03$) ceramics. For comparison, Fig. S4 in the ESM gives the $P$–$E$ and $I$–$E$ curves of the nontextured BNT–ST–$x$NN ($x = 0.01$–$0.03$) ceramics. A well-saturated $P$–$E$ loop can be observed for BNT–ST, suggesting the stable ferroelectric order induced by the electric field. Moreover, the BNT–ST sample exhibits a four-peak $I$–$E$ curve, which is a consequence of the coexistence between the NR and ER phases [49]. Two critical electric fields of $E_{\text{pol}}$ and depoling field ($E_{\text{dep}}$) can be read in the $I$–$E$ curve, representing the establishment and collapse of the ferroelectric order induced by an electric field, respectively. The $E_{\text{pol}}$ and $E_{\text{dep}}$ agree well with the fields related to the abrupt rise and fall in the $P$–$E$ loop. Therefore, it is easy to understand that, the larger the $E_{\text{pol}}$, the more difficult the relaxor-to-ferroelectric transition, and the larger the $E_{\text{dep}}$, the more unstable the induced ferroelectric state. The $E_{\text{dep}}$ is negative for BNT–ST, indicating the NR state. With the addition of NN, the $P$–$E$ loops become more and more pinched, and the intensity of the current peaks gradually decreases. In ferroelectrics, the current peak mainly arises from the domain switching [50]. For the samples with a high NN content, the ER phase is dominated, and the field-induced domain switching related to the relaxor-to-ferroelectric transition is restrained due to the strong random fields, responsible for the decrease of the current density.

For clarifying the effects of the NN content and texturing on polarization reversal behaviors, the remnant polarization ($P_r$), $E_{\text{pol}}$, and $E_{\text{dep}}$ for all kinds of ceramics are summarized in Fig. 8(b). It can be seen that the $P_r$ decreases, and the $E_{\text{pol}}$ and $E_{\text{dep}}$ increase with the increase of NN content. It demonstrates that the hindrance of the field-induced relaxor-to-ferroelectric transition increases gradually, and the induced ferroelectric state becomes more and more unstable, which also reveals the enhancement of the ER phase with the addition of NN. The $E_{\text{dep}}$ changes to be positive in the BNT–ST–$x$NN ($x = 0.01$–$0.03$) samples due to the dominant ER phase. Of particular interest is that the textured ceramics display the lower $E_{\text{pol}}$, lower $E_{\text{dep}}$, and higher $P_r$ compared to their nontextured counterparts. It suggests a significant reduction of the threshold field required to trigger the relaxor-to-ferroelectric transition in the textured ceramics. The difference between the $E_{\text{pol}}$ of the textured and non-textured ceramics becomes more and more pronounced with $x$ increasing from 0.01 to 0.03. Typically, no obvious current peak can be detected for the nontextured BNT–ST–0.03NN ceramics, illustrating that the electric field of 4.0 kV/mm is not enough to induce a long-range ferroelectric order, while the $E_{\text{pol}}$ is 3.0 kV/mm for the textured BNT–ST–0.03NN ceramics. These results indicate that the <001> crystallographic texture facilitates the relaxor-to-ferroelectric transition, and the higher the texture degree, the stronger the enhancement. On the other hand, the more sufficient relaxor-to-ferroelectric transition in the textured ceramics causes a stronger ferroelectric order and makes the backward process lazier, thereby leading to the relatively lower $E_{\text{dep}}$ and higher $P_r$.

Figure 9(a) shows the evolution of $S$–$E$ curves, $S_{\text{pol}}$, and $S_{\text{rem}}$ with the increase of the NN content for both the nontextured and textured samples. The calculated normalized strain ($d_{33}^* = (S_{\text{pol}} - S_{\text{sem}})/E_{\text{max}}$) and

![Fig. 8](image-url)  
Fig. 8  (a) $P$–$E$ and $I$–$E$ curves of nontextured BNT–ST and textured BNT–ST–$x$NN ($x = 0.01$–$0.03$) ceramics. (b) $P_r$, $E_{\text{pol}}$, and $E_{\text{dep}}$ of all nontextured and textured ceramics.

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Fig. 9  (a) Room-temperature $S-E$ curves for all the nontextured and textured BNT–ST–xNN ceramics, as well as the summarized $S_{pol}$ and $S_{rem}$. (b) Calculated $d_{33}^*$ and strain hysteresis.

strain hysteresis ($\Delta S_{hys} / S_{pol} \times 100\%$) are summarized in Fig. 9(b), where $E_{max}$ and $\Delta S_{hys}$ mean the maximum applied electric field and the widest part of the strain loop, respectively. In terms of the nontextured BNT–ST–xNN ($x = 0.00–0.03$) ceramics, it can be found that the strain curve of BNT–ST displays a butterfly shape with a clear $S_{rem}$, which is closely linked to the irreversible phase transition and non-180° domain switching. This phenomenon once again confirms the dominant NR phase in BNT–ST. With the introduction of NN, the $S-E$ curve converts to be sprout-shaped, accompanied by a significant decrease in $S_{rem}$ due to the enhancement of the ER phase. The maximum $S_{pol}$ of 0.241% is achieved at the critical composition of BNT–ST–0.01NN owing to the very competitive free energy between the relaxor and ferroelectric phases near the NR/ER phase boundary, though a high $S_{rem}$ of 0.028% exists. The BNT–ST–0.02NN ceramics exhibit the maximum $d_{33}^*$ of 577 pm/V because of the high-level $S_{pol}$ of 0.237% and negligible $S_{rem}$. For the BNT–ST–0.03NN ceramics, the $S_{pol}$ and $d_{33}^*$ decrease to 0.194% and 480 pm/V, respectively, owing to the restricted relaxor-to-ferroelectric transition caused by the strong random fields. Moreover, the strain hysteresis is found to be reduced from 76% to 47% with $x$ increasing from 0.01 and 0.03. As discussed before, the increase in ergodicity enhances the mobility of dynamically active PNRs, which can respond to electric fields quickly and help to lower the strain hysteresis.

The $S_{pol}$ is promoted to ~0.3% for all the textured BNT–ST–xNN ($x = 0.01–0.03$) ceramics, increased by 23%–50% compared to their nontextured counterparts. Considering the fact that the field-induced strain of BNT-based materials derives from the relaxor-to-ferroelectric transition, the higher strain output of the textured ceramics also indicates that the <001> crystallographic texture effectively promotes this transition. From $x = 0.01$ to 0.03, such a promotion effect on the strain output becomes more and more pronounced due to the improved texture degree. Similar to the strain behaviors in the nontextured samples, the maximum $d_{33}^*$ of 732 pm/V is achieved in the textured BNT–ST–0.02NN ceramics due to the disappearance of $S_{rem}$. More intriguingly, from $x = 0.02$ to 0.03, the $S_{pol}$ and $d_{33}^*$ of the textured ceramics are not significantly reduced as in the nontextured ceramics. A large $d_{33}^*$ of 720 pm/V can be generated in the textured BNT–ST–0.03NN ceramics due to the sufficient relaxor-to-ferroelectric transition under 4 kV/mm. The $P-E$ and $I-E$ measurements have shown a lower $E_{pol}$ of 3 kV/mm for the textured BNT–ST–0.03NN ceramics in contrast to a large $E_{pol}$ of $> 4$ kV/mm for the nontextured ones. Moreover, a low strain hysteresis of 43% is simultaneously achieved in the textured BNT–ST–0.03NN ceramics due to their strong ergodicity. By comparison, all the textured BNT–ST–xNN ($x = 0.01–0.03$) ceramics display a lower hysteresis relative to their nontextured counterparts because of the accelerated relaxor-to-ferroelectric transition. Figure 10 compares the driving electric field, $d_{33}^*$, and strain hysteresis of the textured BNT–ST–0.03NN ceramics with other reported BNT-based ceramics. In most cases, a high threshold electric field of $> 5$ kV/mm is required to induce a high strain, limiting the practical applications. It should be also noted that in some studies, the existence of $S_{rem}$ is ignored, leading to a strain output on the high side. The textured BNT–ST–0.03NN ceramics in this work display a large recoverable
strain of ~0.3% at a low electric field of 4 kV/mm, as well as a relatively small strain hysteresis of 43%. The superior comprehensive strain performance of the textured BNT–ST–0.03NN ceramics makes them promising in solid-state actuator applications.

To better comprehend the underlying microscopic mechanism for facilitated relaxor-to-ferroelectric transition in the textured ceramics, Fig. 11 gives the schematic diagram of the microstructure and polarization reversal process in the non-textured and textured BNT–ST–0.03NN ceramics under a cycle of the electric field. XRD and TEM results indicated that both the ceramics present a pseudocubic structure with the coexistence of the ferroelectric $R\bar{3}c$ and antiferroelectric $P4bm$ PNRs on nanoscale. Compared with the nontextured ceramics with chaotic grains, the textured ceramics display larger <001>-textured grains and more uniformly aligned polarization vectors. Moreover, the TEM results have shown that there are more ferroelectric $R\bar{3}c$ PNRs in the BNT-based matrix of the textured ceramics due to the core–shell structure with the antiferroelectric NN core. For the BNT-based materials showing an original pseudocubic structure with PNRs, many previous studies [22,25,26] have demonstrated that the electric field along the <001> direction tends to induce a long-range ordered ferroelectric tetragonal structure and result in a high strain response. The phase change from rhombohedral PNRs to tetragonal ferroelectric domains can be achieved by the <001>-oriented electric field induced polarization rotation from <111> to <001> with a small angle of ~54°. For our textured ceramics, the direction of the applied electric field is parallel to the texture axis, i.e., the <001> direction. It is proposed that the loading of the external electric field helps the original relaxor state transform to a long-range ordered ferroelectric state with a transition from the coexisted ferroelectric $R\bar{3}c$ and antiferroelectric $P4bm$ PNRs to the tetragonal ferroelectric domains. During this process, the ceramics undergo a series of dynamic processes including the growth of PNRs, domain switching, and phase transformation, which all contribute to the strain output. Compared with the ferroelectric $R\bar{3}c$ PNRs, the antiferroelectric $P4bm$ PNRs is a weakly-polar phase, which needs stronger external excitations to achieve the transition to long-range ordered ferroelectric domains. Therefore, the high <001> crystallographic texture with more uniformly aligned polarization vectors and more $R\bar{3}c$ PNRs in the textured ceramics can effectively accelerate the field-induced relaxor-to-ferroelectric transition compared to the nontextured ceramics, which accounts for their lower $E_{pol}$, higher $S_{pol}$, and smaller strain hysteresis. Moreover, the unloading of the external electric field will lead to a backward ferroelectric-to-relaxor transition process due to the ER nature of the BNT–ST–0.03NN ceramics. The sufficient relaxor-to-ferroelectric transition in the textured ceramics causes a stronger ferroelectric order and makes the backward process lazier, which accounts for their lower $E_{dep}$, higher $P_r$, and the still apparent strain hysteresis of 43%. The NN core in the textured ceramics with the antiferroelectric Pbma phase requires a quite large driving field to achieve the antiferroelectric to the ferroelectric phase transition [51]. Therefore, in our work with a low driving field of 4 kV/mm, the NN core has little effect on the polarization reversal and strain response.
Taking into account the complex operational environment of actuators, the search for the materials with the good thermal stability of the strain response is also significant. Accordingly, the $S$–$E$ curves of the nontextured BNT–ST, nontextured BNT–ST–0.03NN, and textured BNT–ST–$x$NN ($x = 0.01–0.03$) ceramics are measured within the temperature range of 25–100 °C, as shown in Fig. 12. The temperature dependence of $S_{\text{Pol}}$, $S_{\text{Rem}}$, $d_{33}^*$, and strain hysteresis were presented in Fig. S5 in the ESM. Generally, an elevated temperature acts to enhance the random fields and strengthen the degree of ergodicity in the BNT-based materials. For the BNT–ST ceramics, the $S_{\text{pol}}$ and $d_{33}^*$ increase with rising the temperature from 25 to 75 °C while the $S_{\text{rem}}$ gradually converges to zero. Further increase in the temperature leads to the decrease in the $S_{\text{pol}}$ and $d_{33}^*$. 

**Fig. 11** Schematic diagram of microstructure and field-induced relaxor–ferroelectric transition for the nontextured and textured BNT–ST–0.03NN ceramics.

**Fig. 12** $S$–$E$ curves of the nontextured BNT–ST, nontextured BNT–ST–0.03NN, and textured BNT–ST–$x$NN ($x = 0.01–0.03$) ceramics measured within the temperature range of 25–100 °C.
It means that around the critical temperature of 75 °C, the relaxor and ferroelectric phases own competitive free energy, resulting in the maximum strain response. Moreover, the temperature for the maximum strain response is ~50 °C for the textured BNT–ST–0.01NN and further decreases to ~25 °C for the textured BNT–ST–0.02NN and BNT–ST–0.03NN ceramics. The \( S_{\text{pol}} \), \( S_{\text{rem}} \), \( d_{33}^* \), and strain hysteresis all monotonously decrease with the temperature for the textured BNT–ST–0.02NN and BNT–ST–0.03NN ceramics because they are already in the ER state at room temperature and an increase in the temperature is unfavorable for the field-induced relaxor-to-ferroelectric transition due to the increased energy barrier.

In particular, it is found that the textured BNT–ST–0.03NN ceramics show the optimized strain stability over the studied temperature range. Quantitatively, the fluctuations of \( d_{33}^* \) are about 56%, 57%, 39%, 36%, and 28% for the nontextured BNT–ST, nontextured BNT–ST–0.03NN, and textured BNT–ST–\( x \)NN (\( x = 0.01–0.03 \)) ceramics, respectively. There are two main reasons for the favorable strain stability in the textured BNT–ST–0.03NN ceramics. First, the composition BNT–ST–0.03NN deviates from the NR/ER phase boundary (located around the composition BNT–ST–0.01NN), and the variation of the temperature will not lead to an apparent change in the phase structure. Second, despite the ER state, the highly <001> crystallographic texture and more ferroelectric \( R3c \) PNRs can provide an additional driving force for the relaxor-to-ferroelectric transition and resist the effect of the temperature change. It can be found that, the \( d_{33}^* \) still remains high up to 518 pm/V at 100 °C for the textured BNT–ST–0.03NN ceramics with an ultra-low hysteresis of 6%. These results endow the textured BNT–ST–0.03NN ceramics with a potential application in high-temperature actuator technology.

4 Conclusions

In summary, the NN templates are introduced into the BNT–ST matrix to induce the grain orientation growth and tailor the strain performance. With the addition of NN, the ergodicity and texture degree of the BNT–ST–NN ceramics are both gradually improved. The highest <001> texture degree of 87% is achieved in the textured BNT–ST–0.03NN ceramics, which display a pure ER state with coexisted \( R3c \) and \( P4bm \) PNRs on nanoscale. Intriguingly, the interdiffusion between the NN templates and the BNT–ST matrix is incomplete even after sintering at 1175 °C for 20 h, leaving a core–shell structure with the antiferroelectric NN core in the textured ceramics, and thus the BNT-based matrix in the textured ceramics owns more \( R3c \) PNRs relative to the homogeneous nontextured samples. The high \(<001>\) texturing and more \( R3c \) PNRs all facilitate the relaxor-to-ferroelectric transition of textured ceramics, leading to the low-field-driven high strain, while the pure ER state is good for low strain hysteresis. As a consequence, the textured ceramics present a high recoverable strain of 0.3% with relatively small hysteresis of 43% under a low electric field of 4 kV/mm, and the strain response shows favorable temperature stability. This work affords a route to optimize the compressive strain performance of the BNT-based ceramics by the phase structure and grain structure modulation.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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