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Research Article

Unraveling phase evolution and polarization anomaly driven by chemical strain in BNT-based energy storage ceramics

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Abstract: Chemical substitution in ferroelectric ceramics is widely used to tune phase stability and electromechanical response; however, the role of substitution-induced chemical strain on polarization and structural stability remains insufficiently understood. Herein, we report an anomalous evolution of phase transition temperature and polarization behavior in Ca-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based (BNT-based) ferroelectric ceramics, and that being distinct from previously reported chemical modification behavior. Those experimental results are closely related to chemical strain-induced oxygen octahedra rotation arising from isovalent substitution with different ion radii at the A-site, and a qualitative composition-strain-polarization response correlation is established. The chemical strain imposes an internal stress for BNT-based ferroelectric ceramics to increase the polarization switching barrier. Notably, a post-annealing treatment effectively relieves this chemical strain, as evidenced by reduced phase transition temperature, dielectric constant, and slimmed polarization curve, and thus energy efficiency for dielectric energy storage is effectively enhanced. This work not only uncovers the critical role of chemical strain in influencing ferroelectric phase evolution and anomalous polarization changes but also provides a strain engineering way for designing high-performance dielectric energy storage materials.

Keywords: Ferroelectric ceramics; Dielectric energy storage; Polarization behavior; Chemical strain; BNT

1. Introduction

Ferroelectric materials have attracted sustained research interest owing to their indispensable roles in modern electronic devices, including non-volatile memories, sensors, actuators, and capacitors [1-3]. Among the various families of ferroelectrics, perovskite-type oxides with ABO_3 structure stand out for their exceptional dielectric, piezoelectric, and ferroelectric properties, which originate from the spontaneous polarization mainly arising from off-centering of the B-site cation within the oxygen octahedron. The electrical performance of ferroelectric materials is governed by the phase transition behavior under external fields, which defines the operational window for device applications [4-9]. To tailor functional properties for specific applications, chemical modification at the A-site, B-site, or both is commonly employed. This approach tunes the phase transition temperature, induces polymorph nanodomain structures, and improves key figures of merit, including polarization, dielectric constant, and breakdown strength [10-14]. The underlying rationale is that substitution of ions with different valences or radii introduces lattice distortion and modifies the balance between long-range dipolar interactions and local random fields, thereby changing phase transition boundaries.

An empirical relationship has been established that isovalent A-site or B-site substitution in ferroelectrics generally produces a predictable and monotonically tunable regularity in phase transition temperature and polarization behavior. For instance, in $Ba_{1-x}Sr_xTiO_3$ and $Bi_{0.5}Na_{0.5}TiO_{3-x}SrTiO_3$ solid solutions, increasing the concentration of the smaller A-site cation lowers the ferroelectric transition temperature and polarization in a nearly linear relationship [15-19]. Those behaviors can be illustrated by the reduced tolerance factor that destabilizes the ferroelectric distortion

[20-25]. Actually, those changes have been rationalized through the classical tolerance factor and Landau thermodynamic model, providing a framework for predicting the effects of chemical substitution. Li *et al.* demonstrated that A-site La^{3+} doping in $\text{BiFeO}_3\text{-BaTiO}_3$ relaxor ferroelectrics introduces local chemical disorder and lattice mismatch, generating chemical strain that enhances octahedral distortions and suppresses long-range ferroelectric order, ultimately yielding a substantial unipolar strain of 0.35% [26]. However, the assumption is challenged by observations in more complex systems and different occupation conditions, where competing effects such as local strain field, oxygen octahedral rotation, and polar-nonpolar coupling, can give rise to non-monotonic composition-property relationships. For example, Ca-doped $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ ceramics exhibit anomalous changes in lattice constant, dielectric constant, Curie temperature, as well as elastic constant with increasing Ca concentration due to different occupation conditions [27,28]. Nevertheless, a comprehensive understanding of how chemical strain couples with oxygen octahedral dynamics to govern phase evolution and ferroelectric polarization response remains elusive.

In this study, we observed an unusual phenomenon upon isovalent Ca^{2+} substitution for Sr^{2+} in the $\text{Bi}_{0.385}\text{Na}_{0.325}\text{Ba}_{0.015}\text{Sr}_{0.245}\text{□}_{0.03}\text{TiO}_3$ (abbreviated as BNBST) ferroelectric system based on our previous work [14]. Being a clear distinct with the well-established relationship on phase transition temperature and polarization behavior, experimental results reveal that phase transition temperature T_{m1} and T_{m2} first shifts toward high temperature at low Ca^{2+} ion concentration, then reduces below room temperature as the Ca^{2+} ion content exceeds a critical threshold. Meanwhile, the polarization behavior also exhibits a similar change, that is, initially broadening with enhanced hysteresis degree, followed by slimming. Those anomalous results cannot be rationalized by the conventional tolerance factor alone, and thus the underlying mechanism needs to be further explored. We hypothesize that

the key lies in chemical strain, that is, the local lattice strain field generated by the ionic radius mismatch between the substituted cation and the host cation. This strain may induce progressive oxygen octahedral distortion, and once the strain exceeds a critical level, it triggers a structural transformation that fundamentally alters the polar ground state. Herein, we investigate this anomalous ferroelectric behavior through a multi-scale experimental approach that integrates structural, spectroscopic, and microscopic characterization techniques. The composition-temperature phase diagram is established across the entire substitution range, and chemical strain is fitted and calculated to develop a composition-strain correlation function that captures the evolution of local lattice distortion. Oxygen octahedral tilting evolves from antiphase to in-phase rotation, as determined by Raman spectroscopy and geometric phase analysis (GPA). Furthermore, we apply an annealing strategy to relieve the chemical strain, as evidenced by reduced dielectric constant and slimmed polarization curve, validating chemical strain as the primary reason behind the observed anomalous electrical properties. This work not only strengthens the understanding of anomalous dielectric and ferroelectric behavior by introducing Ca^{2+} to replace Sr^{2+} but also establishes chemical strain engineering as a powerful paradigm for designing next-generation ferroelectric materials with precisely tailored properties.

2. Experimental section

2.1. Materials fabrication

$\text{Bi}_{0.385}\text{Na}_{0.325}\text{Ba}_{0.015}\text{Sr}_{0.245(1-x)}\text{Ca}_{0.245x}\square_{0.03}\text{TiO}_3$ (abbreviated as BNBSCa_xT , $x = 0, 0.2, 0.4, 0.6, 0.7, 0.8$, and 1.0) ceramics were fabricated by the conventional solid-state reaction. The raw materials of Bi_2O_3 (99.9%), Na_2CO_3 (99.8%), BaCO_3 (99.0%), SrCO_3 (99.9%), CaCO_3 (99.0%), and TiO_2 (99.9%), were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Powders weighed in

stoichiometric proportions were ball-milled in ethanol at 260 revolutions per minute for 24 h. The mixture was calcined at 850 °C and then ball-milled again in ethanol for 24 h. The mixed powder was uniaxially pressed at 60 ± 10 MPa into green pellets with a diameter of 13 mm and a thickness of 0.8 mm, followed by cold isostatic pressing (CIP) at 280 MPa for 20 min to further enhance the green density. The green pellets were sintered in air at 1140 - 1230 °C for 3 h and then cooled in the furnace. The $x = 0.6$ and $x = 1.0$ samples with thickness of 100 ± 5 μm were annealed in air at 700 °C (the heating rate of 3 °C/min) for 2 h, followed by cooling at the same rate.

2.2. Microstructure characterization and electrical properties measurement

Crystal structure was examined by X-ray diffraction (XRD; D8-Advance, Bruker, Germany, Cu $K\alpha$) with Cu $K\alpha$ radiation and Raman spectroscopy (inVia, Renishaw, UK). The XRD slow scanning rate was 2 °C/min to collect data, and Rietveld refinement was used to determine crystal structure and lattice parameter. Surface morphology was observed by scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan). High-resolution TEM (HRTEM) imaging and selected-area electron diffraction (SAED) patterns were obtained using a field-emission transmission electron microscope (Talos F200X, ThermoFisher Scientific, USA) operated at an accelerating voltage of 200 kV. Geometric phase analysis (GPA) is based on the Fourier transform of the HR-TEM lattice image. The phase component of the resulting complex image reflects the local displacement field of the crystal planes, from which the local strain components are subsequently derived by numerical differentiation.

Temperature-dependent dielectric property was measured by using a precision impedance analyzer (HP4294A, Agilent, USA) over the temperature range from -55 °C to 400 °C. For ferroelectric measurements, the samples were further polished to a thickness of approximately 100 ± 5 μm and sputtered with Au electrodes of area 0.01131 cm². Polarization-electric field (P - E) hysteresis

loops and leakage current density were recorded at 10 Hz using a Radiant Technologies Multiferroic II ferroelectric test system equipped with a Trek 609B high-voltage amplifier, based on a Sawyer-Tower circuit.

3. Results and discussion

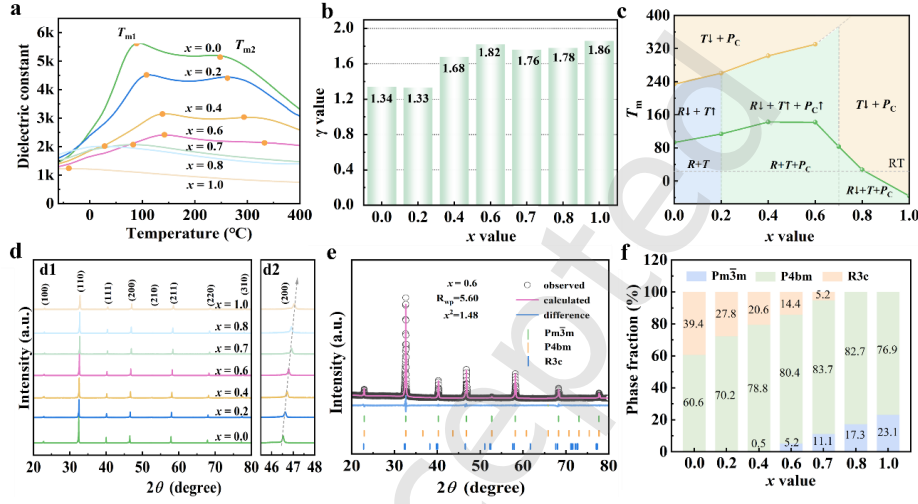


Fig. 1 (a) Temperature-dependent dielectric constant and (b) diffuse factor γ of BNBSCa_xT ceramics with different x values. (c) Phase diagram of composition–transition temperature at T_{m1} and T_{m2} . (d) XRD patterns of BNBSCa_xT ceramics within different 2θ ranges: d1) from 20° to 80° and d2) from 46° to 48° . (e) Rietveld refinement of the $x = 0.6$ composition. (f) Phase fraction changes of BNBSCa_xT ceramics.

Fig. 1(a) exhibits temperature-dependent dielectric constant of BNBSCa_xT ceramics at 10 kHz. For the $x = 0$ composition, two dielectric peaks are observed, and corresponding temperature are labeled as T_{m1} and T_{m2} for the first peak and second one respectively. In this BNBST system, T_{m1} is closed to the reduction of the polar rhombohedral (R) phase accompanied by an increase in the tetragonal (T) phase, while T_{m2} originates from the further decrease of the R phase together with increased content of both T and nonpolar P_c phases. As x value increases up to 0.6, both T_{m1} and T_{m2} initially shift toward high temperatures. This trend contrasts with other reported literature on chemical

doping, where increasing dopant concentration typically lowers the phase transition temperature, and this behavior is generally attributed to enhanced random field that suppress the ordered structure [29-32]. For x value exceeds 0.7, the T_{m1} gradually decreases to room temperature or even below, and T_{m2} disappears together with a reduction in dielectric constant. The decrease of T_{m1} should be attributed to the low Curie temperature of CaTiO_3 -based solid solutions [33-35].

For BNBSCa_xT ferroelectric ceramics, a modified Curie-Weiss law is applied to evaluate the relaxor characteristic, and the equation as follows:

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

where ε_r , T_m , C are relative dielectric constant, temperature at maximum dielectric constant ε_m , and Curie constant, respectively. The diffuseness factor γ usually represents the relaxor degree, and varies between 1 (for normal ferroelectric) and 2 (for ideal relaxor ferroelectric) [36]. Temperature-dependent dielectric spectra of BNBSCa_xT ceramics at frequencies of 1 k, 10 k, 100 k, and 1 MHz is given in Fig. S1. As x value increases, the γ value increases from 1.34 for the $x = 0$ to 1.86 for the $x = 1$ (see Fig. 1(b)), indicating that Ca^{2+} doping enhances the relaxor degree. To clearly illustrate the changes of transition temperature and corresponding phase structure, the phase diagram of composition-transition temperature is plotted in Fig. 1(c). The dielectric peak temperatures (T_{m1} and T_{m2}) for all compositions were extracted from the temperature-dependent dielectric constant measured at 1 kHz, and were then combined with the phase fractions obtained from Rietveld refinement to construct the partial phase diagram [37]. For the region of temperature below T_{m1} , a dominated rhombohedral R phase and tetragonal T phase co-exist for x value below 0.2, a co-existed R, T, and pseudo-cubic P_c phase for $0.2 < x < 0.7$, and a co-existed T and P_c phase for $x > 0.7$ as T_{m1} falls below room temperature. With increasing temperature for x below 0.2, R phase content gradually

decreases, and corresponding weakly polar T phase increases. With further increasing temperature, the P_c phase dominates when temperature over T_{m2} . As x value increases, the relative content of P_c phase increases due to enhanced the phase structure symmetry. For $x > 0.6$, T_{m2} exhibits a slightly increase while T_{m1} reduces to room temperature even below, which leads to the platform between T_{m1} and T_{m2} gets broadens and shifts toward room temperature. Consequently, at room temperature for $x > 0.7$, the P_c phase content increases while the T phase content decreases. This phase diagram summarizes the nonlinear phase evolutions through Ca^{2+} doping, providing a foundation for understanding the abnormal polarization behavior.

A single phase composition with same perovskite structure in macroscopic size can be examined, and without any other secondary phase over the 2θ range from 20° to 80° , as shown in Fig. 1(d1). As the Ca^{2+} concentration increases, the diffraction (200) peak shifts toward high angle, which is due to a low ion radius of Ca^{2+} (1.34 Å for CN=12) compared to Sr^{2+} (1.44 Å for CN=12) at the A-site. Considered to the particularity of Ca^{2+} with different coordinate numbers, it could occupy at A/B-sites of ferroelectric ceramics with $ATiO_3$ structure. Ca^{2+} prefers to substitute Sr^{2+} at A-site not Ti^{4+} at B-site, causing the unit cell volume to shrink [38,39]. Rietveld refinement for the composition of $x = 0.6$ is given in Fig. 1(e). The values of R_{wp} and χ are 5.6% and 1.48 respectively, confirming reliability of the refinement. Furthermore, the changes of specified phase ratio of R, T, and P_c phase is exhibited in Fig. 1(f), and those results align well with the phase diagram. For the $BNBSCa_xT$ ceramics, with increasing Ca^{2+} concentration, the T phase dominates, R phase gradually disappears while P_c phase increases.

Chemical doping is an effective approach for slimming the polarization curve in most ferroelectric materials, however, an abnormal experimental result has been found in Ca-doped

BNBST ceramics, as shown in Fig. 2(a). As Ca^{2+} ion concentration increases, P - E loops initially broaden but subsequently go slim for $x \geq 0.4$. This experimental result differs from other reported literature on chemical doping, which typically serves to reduce hysteresis loss and to obtain a slim polarization curve [40,41]. Herein, the hysteresis degree H is introduced to evaluate the changes of polarization behavior of Ca-doped BNBST ceramics, and the equation is as follows: $H = \Delta P / P_{\max}$, where ΔP is the polarization difference between high polarization and low polarization at $E_{\max}/2$ [42]. Accordingly, the hysteresis degrees H of BNBSTCa $_x$ T ceramics are calculated and plotted in Fig. 2(b). It can be seen that the $x = 0.4$ composition exhibits a high H value of 0.30, indicating that a strong hysteresis loss exists. With further increasing Ca^{2+} ion concentration, the hysteresis degree gradually decreases. Fig. 2(c) shows the change of $P_{\max}$, P_r , and ΔP of BNBSTCa $_x$ T ceramics. As Ca^{2+} ion concentration increases, $P_{\max}$ exhibits a monotonically decreasing tendency, while P_r firstly increases and then decreases. The change of P_r is similar to the hysteresis degree H , and both are attributed to a chemical strain-induced polarization switching [43]. The specified chemical strain will be discussed in the next section.

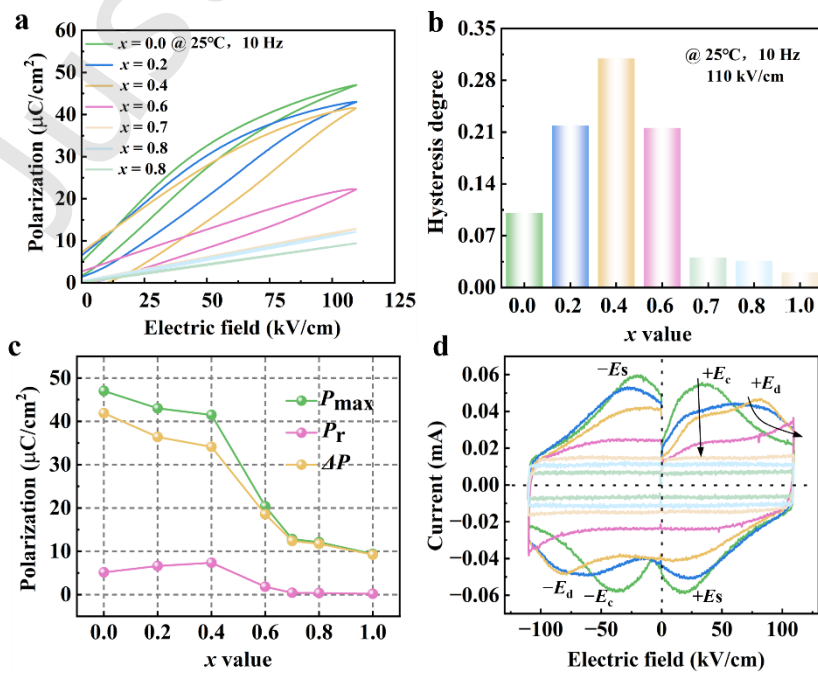


Fig. 2 (a) Unipolar P - E loops, (b) hysteresis degree as functions of x value, (c) $P_{\max}$, P_r , and ΔP , and (d) I - E loops of BNBSCa $_x$ T ceramics with different x values at 10 Hz and 110 kV/cm.

Polarization switching is further investigated via current-electric field curves for BNBSCa $_x$ T ceramics, as exhibited in Fig. 2(d). For pure composition, there are four current peaks in the I - E loops: $\pm E_c$ and $\pm E_s$ correspond to the coercive field and reversible switching field associated with co-existed polar R phase and weakly polar T phase back to the initial state, respectively [44,45]. As Ca $^{2+}$ ion concentration increases, the current peaks at $\pm E_c$ and $\pm E_s$ both gradually disappear, and corresponding $\pm E_d$ values first increase and then decrease. However, a new current peak E_d located at ~ 70 kV/cm occurs and shifts toward a high electric field when introducing Ca $^{2+}$. This behavior is attributed to the increased free-energy barrier for polarization switching caused by the local chemical strain from A-site substitution, requiring a larger external energy to overcome.

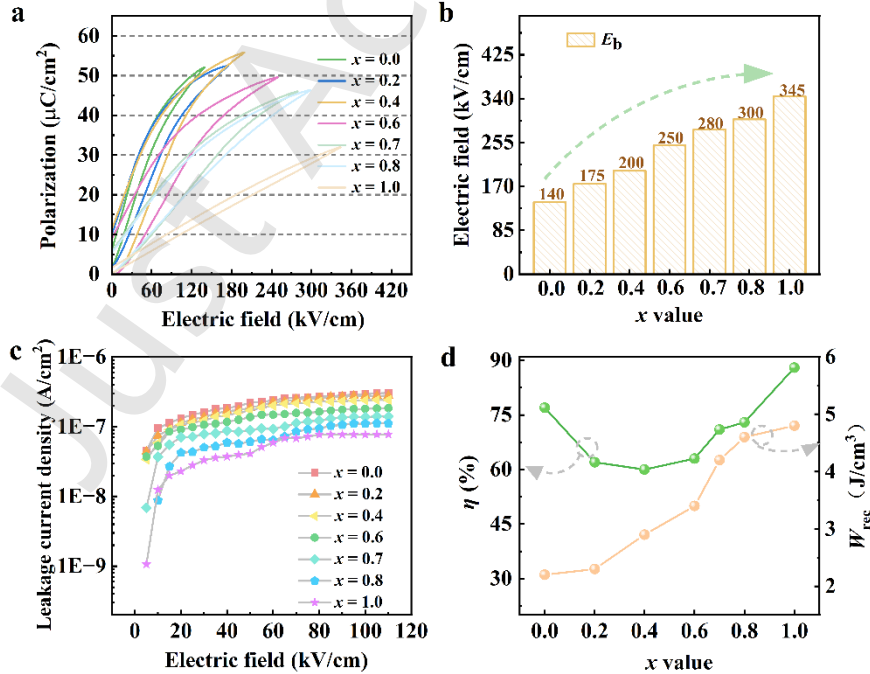


Fig. 3 (a) P - E loops of BNBSCa $_x$ T ceramics at critical electric fields. (b) Electrical breakdown strength and (c) leakage current density of BNBSCa $_x$ T ceramics with different x values. (d) Recoverable energy density W_{rec} and energy efficiency η of BNBSCa $_x$ T ceramics.

To evaluate the influences of Ca doping on energy storage properties of BNBST ferroelectric ceramics, P - E loops of Ca-doped BNBST ceramics at critical electric fields are given in Fig. 3(a). As Ca^{2+} ion concentration increases, the change of polarization and hysteresis degree is similar to Fig. 2(a). Enhanced hysteresis degree occurs at the $x = 0.6$ composition, which is mainly attributed to an enhanced breakdown strength. Actually, the electrical breakdown behavior is a complicated process, which could be influenced by many factors such as defects of vacancy, dislocation, and grain/grain boundary, and so on. For the BNBSCa_xT ceramics, electrical breakdown strength linearly increases from 140 kV/cm for $x = 0$ to 345 for $x = 1$ composition, as shown in Fig. 3(b). The changes in breakdown strength align with leakage current density at different electric fields, as exhibited in Fig. 3(c). As electric field increases, the leakage current density first increases, and then remains basically stable at $10^{-8}\sim 10^{-7}$ A/cm² for all compositions, which demonstrates that BNBSCa_xT ceramics exhibit a good insulation property. Based on above discussion, the energy storage property can be calculated by the equations:

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (2)$$

$$\eta = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \quad (3)$$

where P_{max} , P_r , E and W_{loss} are the maximum polarization, remnant polarization, an applied electric field and dissipated energy, respectively [46,47]. The energy storage performance is determined by both polarization and breakdown strength. Regarding polarization, two aspects are considered: the value (including P_{max} and P_r) and the loop shape (the degree of hysteresis). Fig. 3(d) shows the changes of W_{rec} and η of BNBSCa_xT ceramics. As Ca^{2+} ion concentration increases, the energy efficiency η has an obvious reduced tendency when x value below 0.4, and that gradually enhances,

which should be attributed to increased hysteresis loss. Chemical strain within a certain range increases the free-energy barrier for polarization switching, thereby requiring a higher electric field to drive the switching process. This effect results in a “fatter” hysteresis loop, generating a reduced energy storage efficiency under the same applied electric field. The W_{rec} basically linear increase, and achieves a high value of $\sim 5 \text{ J/cm}^3$ for the $x = 1$ composition, which is mainly due to an enhanced breakdown strength.

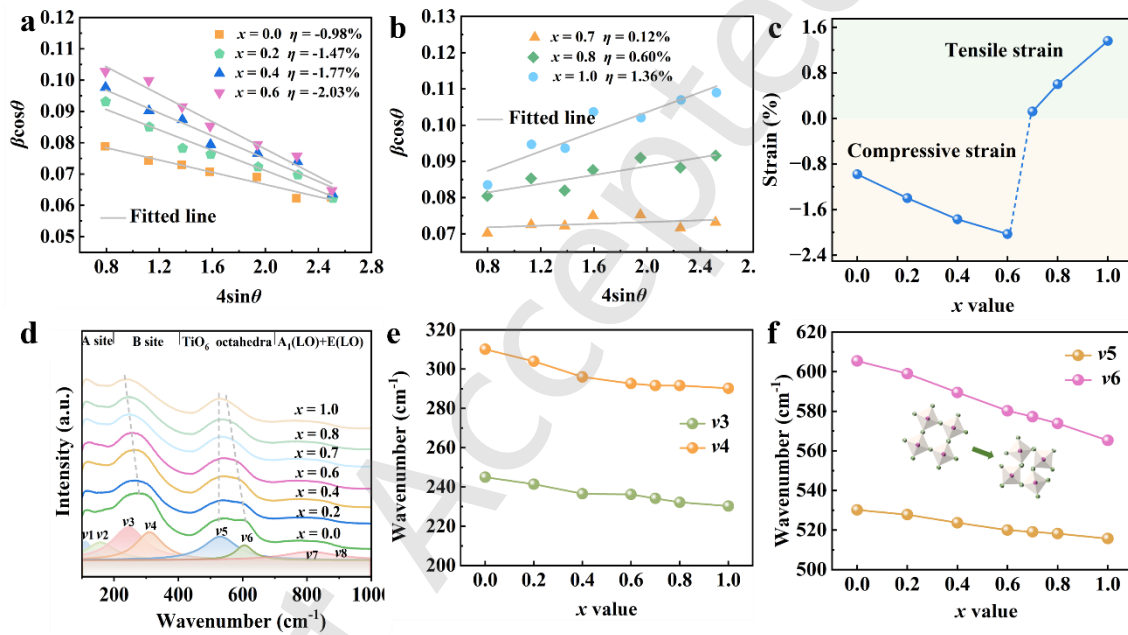


Fig. 4 Williamson-Hall analysis of BNBSCa_xT ceramics with different x values: (a) from 0 to 0.6 and (b) from 0.7 to 1. Changes in chemical strain of BNBSCa_xT ceramics calculated by the Williamson-Hall fitting. (d) Raman spectra and corresponding fitted phonon modes: (e) v_3 and v_4 , (f) v_5 and v_6 as functions of x value for BNBSCa_xT ceramics.

To evaluate the effects of Ca²⁺ doping on chemical strain, the Williamson-Hall equation is employed to qualitatively assess the strain evolution, as given by the equation:

$$\left(\frac{\beta \cos \theta}{\lambda}\right) = \frac{k}{d} + 4\eta \left(\frac{\sin \theta}{\lambda}\right) \quad (4)$$

where β , θ , λ , d , η , and k are the full width at half maximum (FWHM) of the diffraction peaks, Bragg

angle, X-ray wavelength, grain size, lattice strain, and shape factor (0.89), respectively [48,49]. Fig. S2 displays the surface morphology and grain size distribution of BNBSCa_xT ceramics. All samples exhibit clear grains and grain boundaries, and the average grain sizes are similar at ~1 μm, suggesting that the k/d ratio is essentially unchanged. The $\beta\cos\theta$ as functions of $4\sin\theta$ for BNBSCa_xT ceramics with different x values are plotted in Fig. 4(a, b). The slopes η of fitted lines correspond to the strain value of Ca-doped BNBST ceramics. When x value below 0.6, the BNBSCa_xT ceramics exhibit a compressive strain, with its magnitude gradually increasing, which should be related to the smaller Ca²⁺ ion radius than the Sr²⁺ ion at the A-site. However, with further increasing Ca²⁺ ion concentration, a compressive strain transforms into a tensile strain occurs at $x \geq 0.6$, and the magnitude of tensile strain gradually increases, as shown in Fig. 4(b). The change in the type of chemical strain should be attributed to the substitution of Sr²⁺ by the smaller Ca²⁺ ion, which leads to the contraction of the unit cell. The changes in strain of Ca-doped BNBST ceramics with different x values are exhibited in Fig. 4(c). As x value increases, the compressive strain changes from -0.8% for $x = 0$ to -2.4% for $x = 0.6$, and that transforms into tensile strain reaching +1.6% for $x = 1$.

Raman spectra are further used to investigate the influence of Ca-doping on local structure, as shown in Fig. 4(d). Raman spectra can be deconvoluted into eight phonon modes corresponding to four main regions, which is similar to previously reported literature. In the region of wavenumber below 200 cm⁻¹, A-site ion(s) vibration mode dominates; B-O bond mode corresponds to the region of 200~450 cm⁻¹; TiO₆ breathing and stretching vibration modes correspond to the region of 450~700 cm⁻¹; and A₁ and E₁ vibration modes correspond to the regions of >700 cm⁻¹ [50]. As shown in Fig. 4(e-f), the Raman peaks (ν_3 , ν_4 , ν_5 , and ν_6) gradually shift to lower wavenumbers (red shift) with increasing Ca²⁺ concentration, which is a manifestation of phonon softening induced by local lattice

distortion. Specifically, the red shift and merging of the ν_5 and ν_6 modes suggest a structural transition from the low-symmetry rhombohedral phase to the high-symmetry tetragonal or cubic phase [51,52]. Those changes confirm the influence of chemical strain on oxygen octahedra in the local structure.

Fig. 5(a1) exhibits the selected area electron diffraction (SAED) patterns of pure BNBST ceramics along the $[100]$ direction. No superlattice diffraction dots are observed, indicating that a small chemical strain is insufficient to induce ordered oxygen octahedra tilting. The measured average lattice space of $d_{(001)}$ and $d_{(010)}$ are ~ 0.308 nm and ~ 0.309 nm (see Fig. 5(b1)), respectively. The $x = 0.6$ composition exhibits a weak and diffused $1/2(ooo)$ superlattice dot along the $[011]$ direction, where o and e denote odd and even numbers, respectively, as shown in Fig. 5(a2). According to the Glazer notation, the $1/2(ooo)$ diffraction dot comes from antiphase $a^-a^-a^-$ oxygen octahedra tilting [53]. This experimental result reflects that compressive strain through Ca^{2+} ion doping leads to oxygen octahedra tilting. The $d_{(011)}$ space is ~ 0.289 nm, corresponding to the lattice information, as shown in Fig. 5(b2). Moreover, the SAED pattern of $x = 1$ composition exhibits a clear $1/2(ooe)$ superlattice diffraction dot along the $[100]$ direction (see Fig. 5(a3)), which corresponds to in-plane $a^+a^+c^0$ oxygen octahedra tilting. The measured average lattice spaces of $d_{(0-11)}$ and $d_{(011)}$ are ~ 0.284 nm and ~ 0.280 nm (Fig. 5(b3)), respectively, both of which are lower than that for $x = 0.6$ composition. The transformation of oxygen octahedra indicates that chemical doping of Ca^{2+} ion could change the ordered structure via the induced chemical strain.

Geometric phase analysis (GPA) is further used to characterize local chemical strain distribution of Ca-doped BNBST-based ceramics. Fig. 5(c) exhibits the shear strain ϵ_{xy} distribution of BNBSCa_xT ceramics with $x = 0, 0.6$, and 1 . Pure BNBST ceramics exhibit a small compressive strain, as shown in Fig. 5(c1). The $x = 0.6$ samples exhibit a large compressive strain of -2.0% , and a clear periodic

fringe appears in the ϵ_{xy} pattern (see Fig. 5(c2)), indicating a long-range order shear strain modulation structure in the systems. With further increasing the x value to 1.0, a tensile strain of $\sim 1.6\%$ appears, corresponding to a diffused strain region of 1~3 nm, reflecting the disorder characteristic in a short region. It can be clearly seen that chemical strain in ferroelectric ceramics can induce a special change in microstructure characteristics.

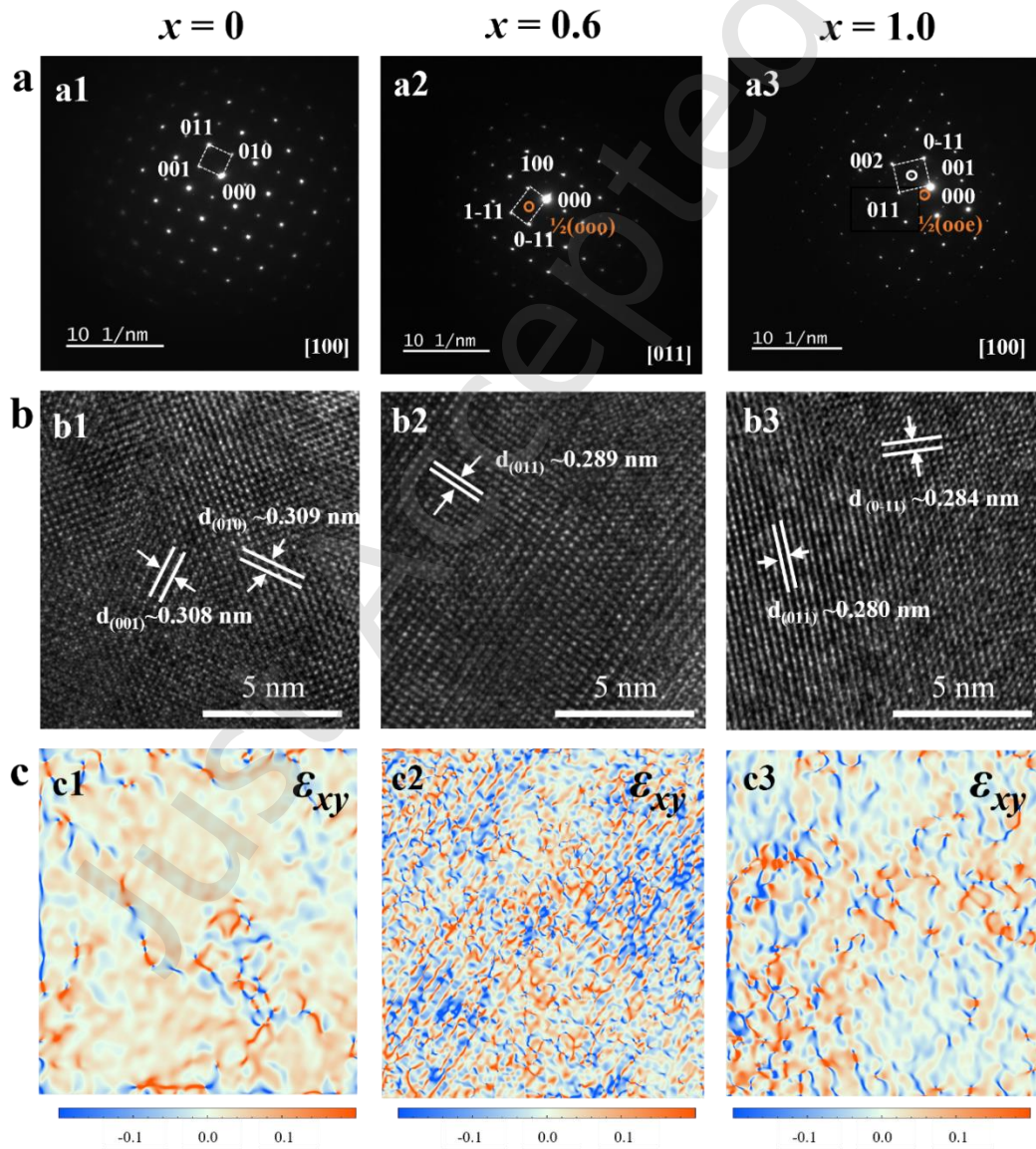


Fig. 5 (a) Selected area electron diffraction patterns (SAED), (b) high resolution transmission electron microscopy (HR-TEM) images, and (c) geometric phase analysis (GPA) of BNBSCa_xT ceramics with different x values: (a1, b1, c1) $x=0$, (a2, b2, c2) $x=0.6$, and (a3, b3, c3) $x=1$.

Based on the above discussion, the substitution of Sr^{2+} by Ca^{2+} at the A-site introduces a no-defected chemical strain that drives crystal structure changes from no obvious octahedral rotation for $x = 0$, to antiphase octahedral rotation for $x = 0.6$, and to in-plane octahedral rotation for $x = 1$, as shown in Fig. 6(a). To understand the influences of chemical strain on electrical properties, the correlation of composition, chemical strain, and polarization is plotted in Fig. 6(b). There is a positive correlation between compressive strain and polarization change, and a negative correlation between tensile strain and polarization change. Certainly, the contribution of specified Ca^{2+} ions to polarization cannot be ignored. After introducing Ca^{2+} at the A-site, phase transition temperatures T_{m1} and T_{m2} shift toward high temperature, and P - E loops get widened together with enhanced P_r . Those experimental results demonstrate that compressive strain inhibits polarization switching. In other words, the energy barrier is high due to the existence of chemical stress. This condition changes when x value exceeds 0.6, which means that large compressive strain exceeds the limit of the crystal structure. Thus, a mixed T and P_c phase coexists, and oxygen octahedra change from antiphase to in-plane phase.

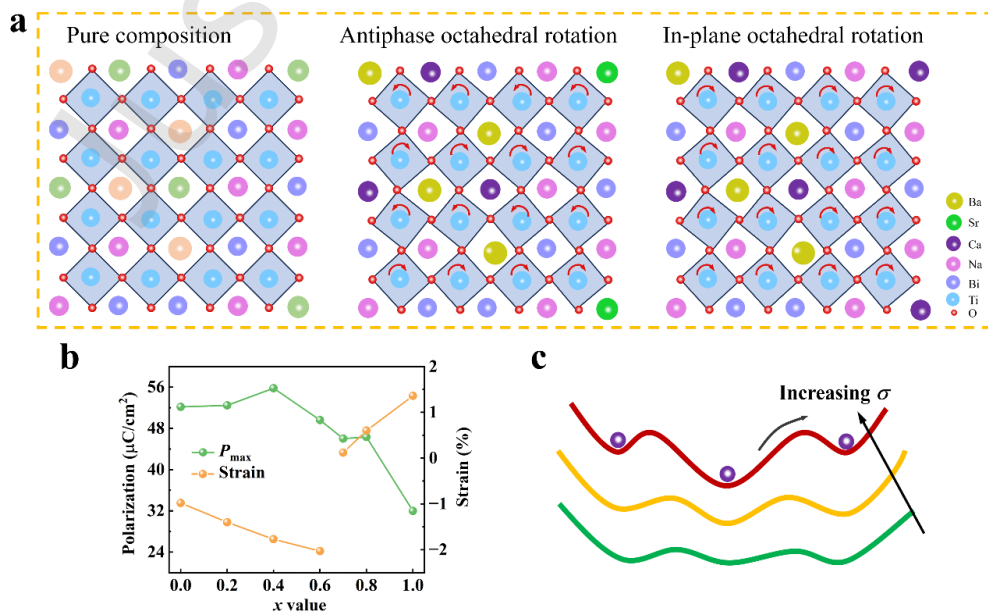


Fig. 6 (a) Schematic of Ca-doped BNBST crystal structure with different octahedral rotation modes.

(b) Polarization and strain as functions of x value for BNBSCa_xT ferroelectric ceramics. (c) Free

energy barrier changes of BNBST-based ferroelectric ceramics after introducing chemical strain.

A modified phenomenological Landau theory, the free energy (G) of ferroelectric BNT-based materials can be described in the following form:

$$G = G_0 + 1/2\alpha P^2 + 1/4\beta P^4 + 1/6\gamma P^6 - EP \quad (5)$$

where α, β, γ are the Landau coefficients, and P is the polarization [54,55]. Herein, chemical strain is viewed as a category of chemical stress σ to modify equation (4):

$$G = G_0 + 1/2\alpha P^2 + 1/4\beta P^4 + 1/6\gamma P^6 - EP - 1/2Q\sigma P^2 \quad (6)$$

where Q is the electrostriction coefficient. It can be seen that the introduction of chemical stress σ could change the free energy barrier. Herein, a compressive stress increases the energy barrier for polarization switching (Fig. 6(c)), while the condition of tensile stress is contradictory to influencing polarization switching. Besides, the low ionic polarizability of Ca^{2+} compared to Sr^{2+} leads to a reduced polarization in BNBSCa_xT ceramics.

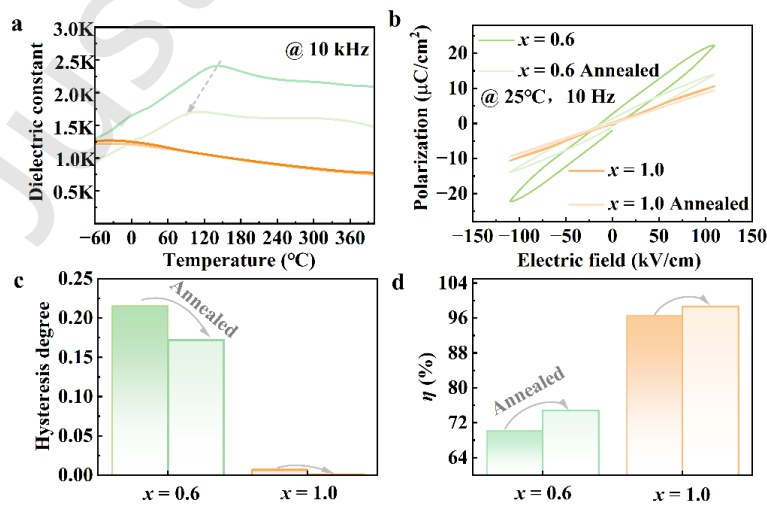


Fig. 7 Comparison of dielectric and ferroelectric properties of BNBSCa_xT ceramics before and after annealing treatments: (a) dielectric constant at 10 kHz, (b) polarization hysteresis loops, (c) hysteresis

degree, and (d) energy storage efficiency.

To further confirm the effects of chemical strain on phase transition temperature and polarization behavior, the samples of $x = 0.6$ and 1.0 are selected to be processed at annealing treatment to relieve part of the chemical stress. Fig. 7(a) presents the temperature-dependent dielectric constant of the annealed samples. After annealing treatment, all compositions exhibit a reduced dielectric constant. Notably, for the $x=0.6$ composition, T_{m1} shifts toward lower temperatures accompanied by a decreased dielectric constant, indicating that chemical stress is effectively released during the annealing process. Fig. 7(b) also compares the polarization hysteresis loops of the $x = 0.6$ and 1.0 samples measured at 110 kV/cm before and after annealing treatment. The annealed samples exhibit slimmer loops with reduced hysteresis degree (Fig. 7(c)), suggesting a relaxation of the strain-induced polar constraint. Consequently, the energy storage efficiency is improved, as shown in Fig. 7(d). These results collectively confirm that annealing effectively modulates chemical stress, thereby enabling the optimization of electrical properties.

4. Conclusions

In this work, we report an anomalous non-monotonic evolution of phase transition temperature and polarization behavior in Ca-substituted BNT-based ferroelectric ceramics. Combined with electrical and structural analyses demonstrate that Ca incorporation induces significant internal chemical strain, which governs both phase stability and polarization. Chemical strain analysis from XRD, Raman spectroscopy, and GPA distribution, confirms that chemical strain leads to pronounced octahedral tilting distortion and a transition from antiphase to in-phase octahedra rotation at high Ca content. The post-annealing strategy effectively relaxes internal chemical stress and partially restores dielectric and ferroelectric performance, further verifying the critical role of chemically induced stress

in controlling functional properties. This study highlights chemical strain as a key driving factor for phase evolution and polarization behavior in perovskite ferroelectrics, providing guidance for stress engineering strategies in other functional oxides.

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Author contributions

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

All authors declare they have no competing interests.

Electronic Supplementary Material (ESM)

Electronic Supplementary Material: Supplementary material is available in the online version of this article.

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