

Local structural changes associated with relaxor behavior in Sn-doped BaTiO₃Dongxiao Fan^{1,*}, Tomoki Kanazawa^{1,2}, Rie Haruki¹, Youngmin Kim¹, and Shunsuke Nozawa^{1,3,†}¹*Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*²*Japan Society for the Promotion of Science, Kojimachi Business Center Building, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan*³*Materials Structure Science Program, SOKENDAI, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*

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Polar nanoregions (PNRs) play an important role in relaxor ferroelectrics. Despite decades of research, structural understanding of their formation is lacking. In this study, we investigate how PNRs form by using Ti *K*-edge x-ray absorption fine structure spectroscopy to observe local structural changes of polar sites when Sn is doped in the order-disorder-type ferroelectric BaTiO₃. Sn doping, which induces local lattice distortion, suppresses the vibronic coupling caused by the pseudo-Jahn-Teller effect. As a result, the displacement of Ti at local polar sites is decreased and the energy barrier of the double-well potential is lowered, thus promoting the ordering of the electric dipole moments of polar domains. Our local structure study suggests that the PNR formation process and emergence of relaxor properties in Sn-doped BaTiO₃ are closely related to the evolution of the local structural symmetry determined by the competition between local lattice distortion and vibronic coupling.

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Ferroelectric materials are characterized by their reversible spontaneous electric polarization at the macroscopic scale [1]. The intrinsic mechanism of such polarization is the microscopic polar regions formed by symmetrically equivalent distortions of the local structure [2]. Atomic understanding of the local structure is essential to interpret the physical behavior of ferroelectrics. However, because ferroelectric crystals possess heterogeneous polarity, it is difficult to examine their local structure using general crystallographic techniques that probe an averaged lattice structure such as x-ray diffraction (XRD) [3].

Relaxor ferroelectrics have local polar regions but no macroscopic spontaneous electric polarization [4,5]. In ordinary ferroelectrics, the local orientation of polar regions in the unit cell correlates with the macroscopic polarization [6,7]. In a relaxor, the long-range correlation of the polar regions is suppressed by structural heterogeneity; polarity is only correlated in localized polar nanoregions (PNRs) [4,5]. These PNRs are oriented randomly, resulting in a macroscopically symmetric phase. The unique characteristics of PNRs underpin the extraordinary dielectric and piezoelectric properties of relaxor ferroelectrics, which have great potential for high-efficiency energy storage and conversion applications. Elucidation of the formation mechanism of PNRs is important for both fundamental re-

search on ferroelectric materials and practical applications. However, a detailed understanding of the microscopic mechanism of PNR formation is lacking because the inhomogeneous nature of relaxor ferroelectrics makes it difficult to observe the local polarity inside PNRs using crystallographic techniques.

In general, structural inhomogeneity in relaxor ferroelectrics is induced by doping with ions with different size and valence [4,5]. In ferroelectrics with the ABO₃ perovskite structure, doping different ions at the *A* and *B* sites leads to inhomogeneous crystal structure, charge distribution, and orientation of the electric dipole moments of the polar domains, disrupting the ordered arrangement of the electric dipole moment of the undoped ferroelectric [8,9]. BaTiO₃ (BTO), a typical ferroelectric material, has been reported to exhibit relaxor properties with excellent dielectric and piezoelectric properties upon Sn doping [10–12]. BTO has four phases when classified as macroscopic average lattice structures: cubic (*C*, >393 K), tetragonal (*T*, 278–393 K), orthorhombic (*O*, 183–278 K), and rhombohedral (*R*, <183 K) [1]. In the order-disorder model, the ferroelectricity of BTO originates from the long-range correlation of the local Ti ⟨111⟩ displacements [7,13,14]. At high temperature (>393), because of the thermal effect, the eight degenerate ⟨111⟩ displacements of the Ti ions are randomly oriented, and the average phase of BTO is *C*. With decreasing temperature, the degeneracy decreases, the macroscopic electrical dipole polarization changes toward the [001], [011], and [111] directions, and the average crystal structure changes accordingly from the *T* phase to the *O* and *R* phases. Upon Sn doping ($0 \leq x < 0.12$), the average lattice structure of BaTi_{1-x}Sn_xO₃ (BTSO) as a function of *x* evolves from *T* to *O* to *R* at room temperature (RT) [10–12] (the corresponding phase diagram is shown in the right inset of Fig. 4). This phase evolution is same as that of BTO with decreasing temperature. However, with further

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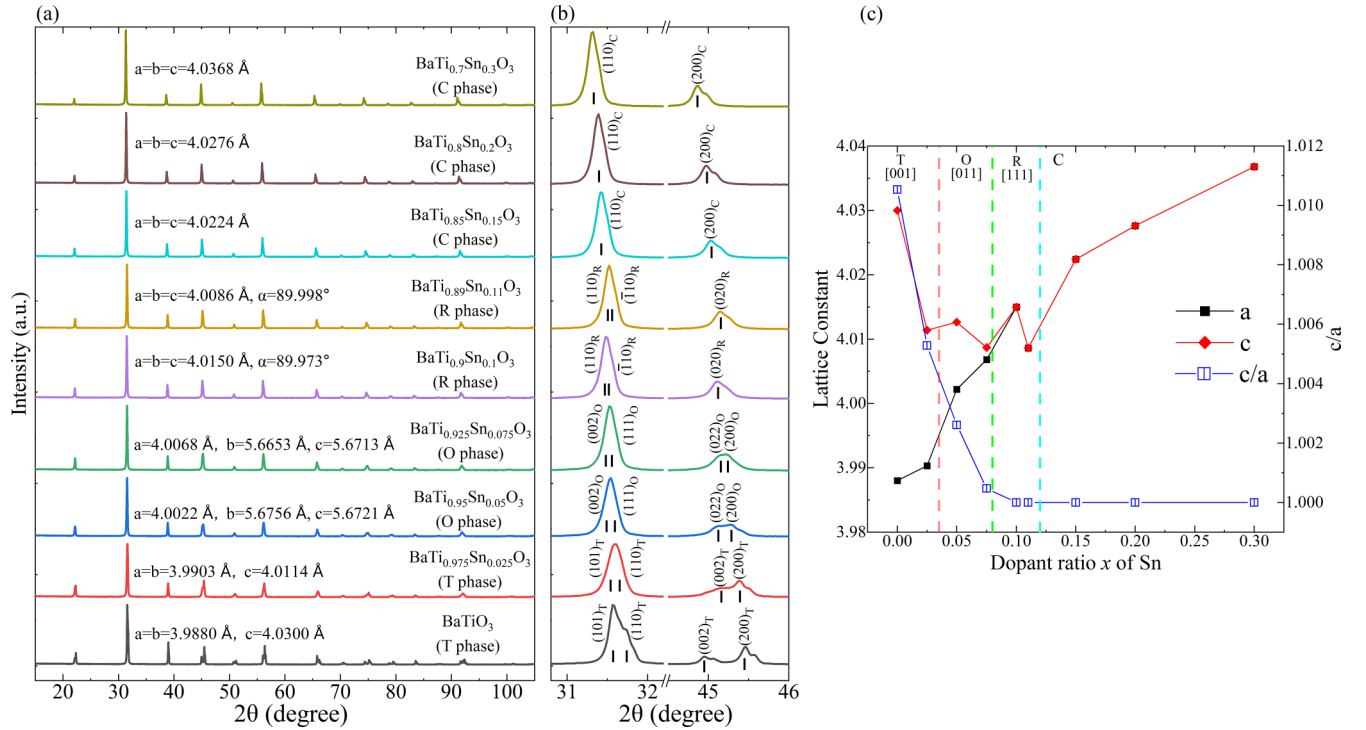


FIG. 1. XRD patterns of BTSO with different Sn doping ratios. (a) Full-range XRD patterns. (b) Enlarged view of XRD patterns in the 2θ range around 31.5° and 45° . (c) Variation of lattice constants and c/a ratio with Sn doping ratio.

Sn doping ($x > 0.12$), the average lattice structure returns to C and relaxor properties appear. Thus, Sn doping of BTO causes a series of phase transitions and plays an important role in the mechanism of relaxor properties. However, the doping effect is closely related to heterogeneity, and it is difficult to probe its properties in detail from the macroscopic average structure. Therefore, in this study, we examine the mechanism of the phase transition from T to O , R , and finally to C symmetry. The lattice constants and angles were determined from the (002) and (200) reflections for the T and C phases; the (200), (111), and (002) reflections for the O phase; and the (110) and (111) reflections for the R phase, based on the appropriate unit cell representations. Figure 1(b) shows changes in diffraction profiles corresponding to each phase near 31.5° and 45° , where peak splitting and shifts associated with structural phase transitions are clearly observed. Figure 1(c) displays variations in lattice constants and the c/a ratio with increasing Sn content. In the O phase, the lattice constant of b is almost the same as that of c . Therefore, the value of c used for the c/a ratio was calculated by averaging the lattice constants of b and c . Vertical dashed lines indicate the compositional boundaries separating the T , O , R , and C phases. This trend of the c/a ratio is consistent

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BTSO ceramics with nominal composition $x = 0.00, 0.025, 0.05, 0.075, 0.100, 0.110, 0.15, 0.20$, and 0.30 were prepared under the same conditions by a conventional solid-state reaction. The starting materials were commercial BaCO_3 (>99.95%, Kojundo, Japan), TiO_2 (rutile, >99.99%, Kojundo, Japan), and SnO_2 (99.99%, Kojundo, Japan). Appropriate quantities of BaCO_3 , TiO_2 , and SnO_2 powders were

ground in an agate mortar with ethyl alcohol for 2 h to achieve a homogeneous mixture. Each mixture was calcined in an electric furnace (Nitto, NHK-170, Japan) at 1200°C for 4 h to decarbonate BaCO_3 . The calcined powders were ground again, and then uniaxially pressed in a stainless-steel die (diameter: 10 mm). The resulting pellets were sintered in an air atmosphere at 1300°C for 2 h. The samples were cooled to room temperature naturally. The sintered pellets were ground to uniform powders for further characterization. The purity and crystallinity of the powders were characterized at room temperature by XRD (Aeris, Malvern Panalytical, Netherlands). The tube settings were 40 KeV and 15 mA with Cu as the target anode material. The scan range was from 5° to 105° with a step of 0.02° . Figure 1(a) shows x-ray diffraction patterns of BTSO samples with various Sn doping concentrations ($x = 0-0.30$), measured at room temperature. As the Sn doping rate increases, a phase transition sequence is observed from T to O , R , and finally to C symmetry. The lattice constants and angles were determined from the (002) and (200) reflections for the T and C phases; the (200), (111), and (002) reflections for the O phase; and the (110) and (111) reflections for the R phase, based on the appropriate unit cell representations. Figure 1(b) shows changes in diffraction profiles corresponding to each phase near 31.5° and 45° , where peak splitting and shifts associated with structural phase transitions are clearly observed. Figure 1(c) displays variations in lattice constants and the c/a ratio with increasing Sn content. In the O phase, the lattice constant of b is almost the same as that of c . Therefore, the value of c used for the c/a ratio was calculated by averaging the lattice constants of b and c . Vertical dashed lines indicate the compositional boundaries separating the T , O , R , and C phases. This trend of the c/a ratio is consistent

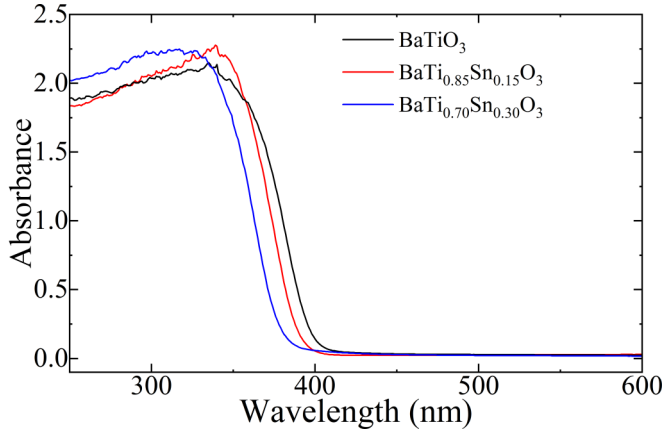


FIG. 2. UV-Vis spectra of BaTiO_3 , $\text{BaTi}_{0.85}\text{Sn}_{0.15}\text{O}_3$, and $\text{BaTi}_{0.70}\text{Sn}_{0.30}\text{O}_3$.

with the sequence of structural phase transitions from T to O , R , and finally C symmetry. In particular, a sharp decrease in the c -axis length is observed in the low doping range ($x = 0$ – 0.035). This behavior is attributed to the collapse of the fourfold degenerate $\langle 111 \rangle$ displacements of the Ti ions, which stabilize the elongated c axis in the room-temperature T phase of pure BaTiO_3 . The fact that such a pronounced change in c -axis length is captured even by XRD, which reflects the average lattice structure, suggests that the local lattice distortion around the dopant sites is extremely large. As discussed below, this interpretation is further supported by the Ti K -edge XANES results shown in Fig. 5, where a clear increase in inversion symmetry breaking around the Ti site is observed in the same doping range ($x = 0$ – 0.035).

To further confirm the quality of the sample powders, ultraviolet-visible (UV-Vis) spectra of BaTiO_3 and $\text{BaTi}_{0.7}\text{Sn}_{0.3}\text{O}_3$ were measured using a UV-vis spectrophotometer (V-670, JASCO, Japan). The light source was a Xenon lamp. As shown in Fig. 2, the band gap of BaTiO_3 increased with Sn doping. This result is consistent with previous experimental and theoretical studies of the optical properties of BTSO [18,19].

To conduct the XANES experiment, each BTSO powder was ground with a suitable amount of BN powder to satisfy the edge jump $\Delta\mu = 1$. The Ti K -edge XANES measurements were conducted at room temperature at beamline BL9C of the Photon Factory (KEK-PF). The energy of the Ti K edge (4966 eV) was calibrated by the first derivative peak of the XANES spectrum of Ti foil. The x-ray energy was varied using an Si (111) double monochromator, and higher-order harmonics were removed by detuning 70% of the x-ray intensity. To obtain reliable information from the data set of the XANES spectra, larch software with a python library was used to conduct a consistent data analysis of all the XANES spectra [20]. As shown in Fig. 3(a), background removal and spectral normalization were performed using first-order fitting functions in the “pre-edge” and “postedge” regions, respectively. In Fig. 4, these processes were performed using the same energy region for all XANES spectra. In Fig. 5, the intensity of peak B was extracted by fitting peak A and peak B with two Gaussian peak functions, as shown in Fig. 3(b).

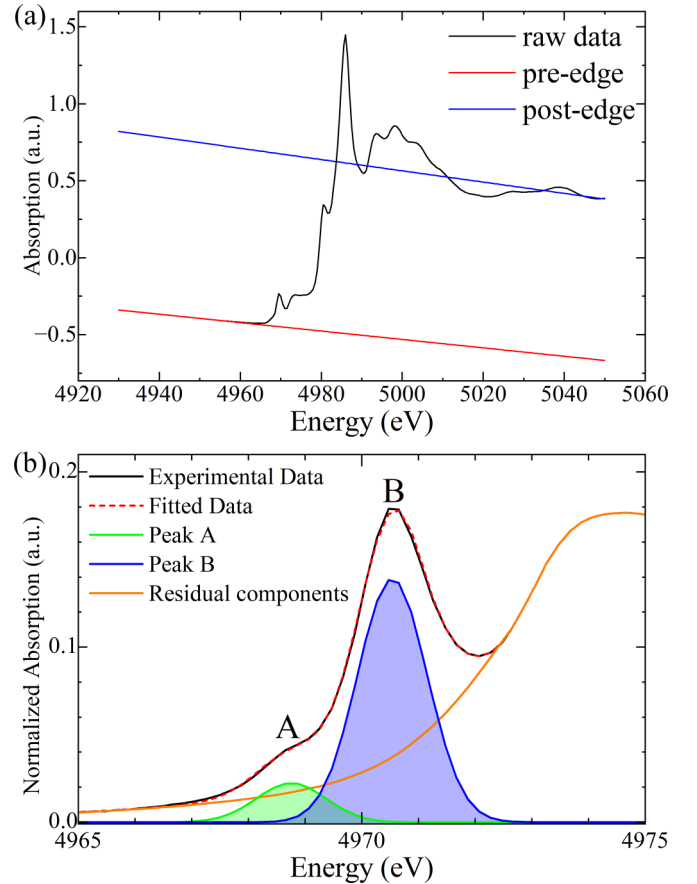


FIG. 3. (a) Raw Ti K -edge XANES data for BaTiO_3 . (b) Fitting of the pre-edge features with Gaussian peak functions.

Figure 4 shows the normalized Ti K -edge XANES spectra of BTSO with different x . Except for peaks A and B , the spectral features were attributed to Ti $1s \rightarrow 4p$ dipole transitions. The intensities of peak A and B are weaker than those

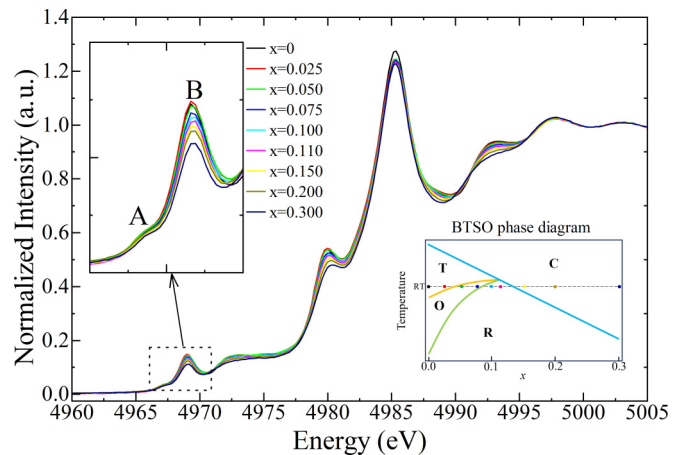


FIG. 4. Ti K -edge XANES spectra of BTSO as a function of Sn doping x . The left inset shows an enlarged view of the A and B peaks. The right inset shows the phase diagram of BTSO with temperature and doping ratio x [10]; colored points in the phase diagram correspond to spectra of the same color.

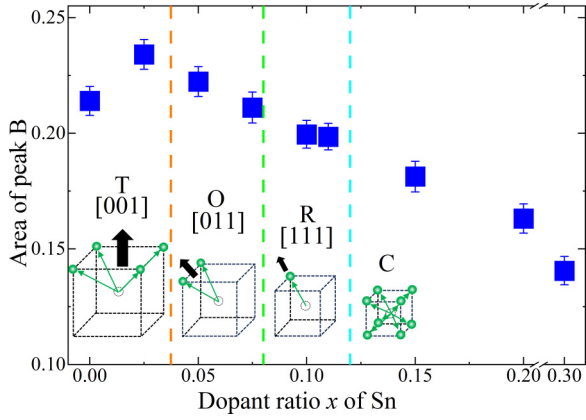


FIG. 5. Area of peak *B* in the Ti *K*-edge XANES spectra of BTSO obtained by Gaussian fitting as a function of *x*. Insets show the BTSO phases, where green arrows indicate the equivalent Ti $\langle 111 \rangle$ displacement and black arrows indicate macroscopic electric polarization.

of the other peaks because they originate from Ti $1s \rightarrow 3d$ quadrupole transitions. The anisotropic Ti $3d$ orbitals localized at Ti sites are closely related to the local structure around Ti, so we focused on the effect of *x* on peak *A* and *B* in this study. An enlarged view of peak *A* and *B* is shown in the inset of Fig. 4. Peak *A* consists of the pure Ti $1s \rightarrow 3d(t_{2g})$ quadrupole transition. In contrast, peak *B* contains two components: the Ti $1s \rightarrow 3d(e_g)$ quadrupole transition and the Ti $1s \rightarrow 4p$ dipole transition [21]. When the inversion symmetry of the TiO_6 octahedron is broken, the $3d$ - $4p$ hybridization of Ti is strengthened, which increases the quadrupole transition component. As a result, the intensity of peak *B* is enhanced as the symmetry of the Ti site decreases [22].

To clearly show the intensity change of peak *B* with the variation of *x*, the area of the Gaussian function for peak *B* is plotted in Fig. 5. The direction of Ti displacement and the macroscopic electric polarization of each phase is illustrated in the bottom of Fig. 5 [11]. With increasing Sn doping, the intensity of peak *B* initially increases up to $x = 0.025$ and then gradually decreases with the progression of $T \rightarrow O \rightarrow R \rightarrow C$ phase transitions. This means that Sn doping breaks the inversion symmetry of the TiO_6 octahedra up to $x = 0.025$, but when $x > 0.025$, the inversion symmetry of the TiO_6 octahedra increases. The dependence of the intensity of peak *B* on the phase transition of BTSO is different from the case of BTO. As mentioned above, the phase transition of BTO is explained by an order-disorder phase transition, and the macroscopic electric polarization of BTO is the average result of equivalent $\langle 111 \rangle$ Ti displacements [7,13,14]. The intensity of peak *B* in the XANES spectrum of BTO has been reported to be almost independent of temperature [23,24], suggesting that the TiO_6 octahedral inversion symmetry in BTO is hardly affected by temperature. This observation implies that the displacement of Ti in the $\langle 111 \rangle$ direction persists regardless of temperature, which is consistent with the order-disorder phase transition mechanism.

In the case of BTSO, because Sn ions are larger than Ti ions, substitution of Ti sites of BTO with Sn causes distortion of the local structure around the substituted sites. With

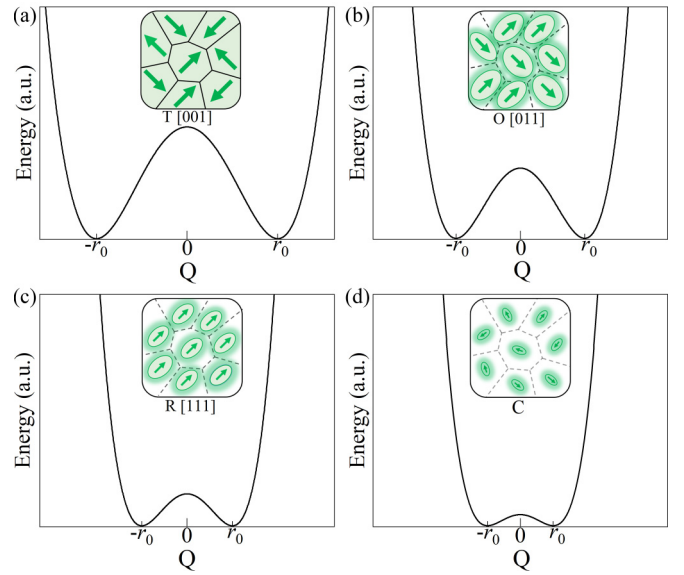


FIG. 6. The local double-well potentials of a Ti ion along the $\langle 111 \rangle$ direction *Q* in BTSO with different Sn doping contents *x*. (a) $0 \leq x < 0.035$. *T* phase with $[001]$ macroscopic electric polarization. The electric dipole moment of the domain is indicated by an arrow. (b) $0.035 \leq x < 0.08$. *O* phase with $[011]$ macroscopic electric polarization. (c) $0.08 \leq x < 0.12$. *R* phase with $[111]$ macroscopic electric polarization. (d) $x \geq 0.12$. *C* phase without macroscopic electric polarization.

increasing Sn doping, the XRD peaks of BTSO shifted to a lower angle as shown Fig. 1(b). However, this shift is not caused by uniform expansion of the lattice, but rather by an increase in local strain at substitution sites, which is observed as an expansion of the average lattice constant. This local distortion also has the effect of suppressing the vibronic coupling, as described later. Figure 5 shows that as Sn doping increases, in the region of $0 \leq x < 0.025$, the local distortion at the Sn doping sites induces a collapse of the inversion symmetry in the surrounding TiO_6 octahedra. However, in the region of $x \geq 0.025$, the suppression of Ti displacement caused by the decrease in vibronic coupling gradually becomes dominant, leading to an increase of the inversion symmetry of the TiO_6 octahedra.

The Ti $\langle 111 \rangle$ displacement in BTO can be explained by the pseudo-Jahn-Teller effect, which is caused by the vibronic coupling between hybridized electrons of Ti $3d$ -O $2p$ and phonons [25,26]. Here, the phase transitions that occur when BTO is doped with Sn at RT are described using changes in vibronic coupling. The energy variation of the system versus the displacement *Q* of Ti caused by vibronic coupling is plotted in Fig. 6 for the (a) *T* ($0 \leq x < 0.035$), (b) *O* ($0.035 \leq x < 0.08$), (c) *R* ($0.08 \leq x < 0.12$), and (d) *C* ($x \geq 0.12$) phases, which appear at different Sn doping contents. BTO with strong vibronic coupling has an energy barrier at $Q = 0$ and a double-well energy potential curve at $Q = -r_0$ and r_0 , where $-r_0$ and r_0 represent the equilibrium positions of the local displacement in the double-well potential [1,27]. Therefore, the r_0 displacement in Ti $\langle 111 \rangle$ is the most stable structure of the unit cell. The inset illustrations in Fig. 6

show the ferroelectric domains in each system, and the green arrows indicate the electric dipole moments in each domain. Because BTO has electric dipole moments in four directions at RT, the T phase is observed as the average structure. With increasing Sn doping, the hybridization between Ti $3d$ and O $2p$ orbitals gradually decreases because of the distortion of the local structure. The associated decrease in vibrational coupling lowers both r_0 and the energy barrier at $Q = 0$. As a result, even under isothermal conditions, the electric dipole moments, which had four directions when $0 \leq x < 0.035$, have two directions when $0.035 \leq x < 0.08$ and one direction when $0.08 \leq x < 0.12$. The electric dipole moments align to minimize the overall electrostatic energy of each system. With the decrease of the electric dipole moment, the average lattice structure changes from T to O to R .

When $x \geq 0.12$, r_0 decreases further. In addition, the ferroelectric domain structure of BTO is also gradually destroyed by Sn doping and independent PNRs begin to form. Here, the electric dipole moments within the PNRs are considered to be unidirectional because the vibronic coupling is weaker than that in the R phase. However, the electrostatic interactions between PNRs disappear, so the moments of PNRs become scattered in eight directions throughout the crystal and phase C is observed as the average structure.

In conclusion, we observed a decrease in Ti $\langle 111 \rangle$ displacement with increasing Sn doping of BTO deduced from the corresponding intensity change of peak B attributed to

the quadrupolar transition observed in the pre-edge region of Ti K -edge XANES spectra. The local structural change was caused by the decrease of vibronic coupling resulting from the weakening of Ti $3d$ -O $2p$ hybridization induced by local structural distortion upon Sn doping. The suppression of vibronic coupling also lowered the energy barrier of the double-well potential, so that phase transitions of BTO were realized at RT with the change of Sn doping. At the same time, Sn doping also disrupted the long-range periodic structure of BTO, leading to the size decrease of polar domains and the formation of PNRs. In the $x \geq 0.12$ region, the electric dipole moments of PNRs were scattered in eight directions throughout the crystal, so the average structure became C , with pronounced relaxor properties. The local structural information for the phase transition of BTO revealed in this study provides unique insight into the PNR formation process in relaxor ferroelectrics.

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The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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