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Chemical Substitution-Induced Ferroelectric Polarization Rotation in BiFeO₃

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The direction of the ferroelectric polarization vector is a key factor influencing the properties of ferroelectric/piezoelectric^[1] and multiferroic^[2] materials. For instance, ferroelectric materials at morphotropic phase boundaries (MPB), where multiple structural phases with ferroelectric polarizations pointing in different crystallographic directions coexist, often display large piezoelectric coefficients.^[3–5] It is the ferroelectric distortions, which accompany the polarization rotation that leads to enhancements in the piezoelectric coefficient. In multiferroic BiFeO₃ (BFO), it has been shown^[2] that the coupled antiferromagnetic order can be altered by switching the ferroelectric polarization rotation is recognized as an important precursor to occurrence of an MPB.^[5,6]

Chemical substitution into perovskite BiFeO₃, which displays room-temperature multiferroic properties,^[2,7] has been a subject of much interest since the substitution results in improved ferroelectric properties and enhancement in piezoelectric and dielectric properties.^[8–10] One important consequence of substitution is that a symmetry-lowering structural phase transition from the rhombohedral phase for pure BFO to another structure takes place, displaying the characteristics of an MPB with enhanced dielectric and piezoelectric properties, as observed in Pb-based ferroelectrics.^[3,4]

Recently, we demonstrated^[11] that substitution of rare earth elements (RE = Sm, Gd, and Dy) into the A-sites of BFO thin films results in a ferroelectric rhombohedral to paraelectric orthorhombic structural transition, exhibiting a double hysteresis behavior in the polarization-electric field (PE) hysteresis loop, and that the occurrence of this transition can be universally described by the averaged A-site cation radius regardless of the substituted rare-earth element. The piezoelectric coefficient d_{33} and dielectric constant ε_{33} are enhanced at the boundary, and the maximum d_{33} reaches 110 pm V⁻¹,^[8] which is comparable to the value for epitaxial Pb(Zr_{0.48}Ti_{0.52})O₃ thin films at the MPB.^[12] Based on the results of first-principles calculations, it was proposed^[11] that an electric field-induced structural transformation from the nonpolar orthorhombic to the polar rhombohedral phase is the origin for the double hysteresis behavior and the concomitant enhanced properties at the boundary.

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Here, we demonstrate that the polarization vector in Smsubstituted BiFeO₃ (Sm-BFO) continuously rotates from the [111] direction for pure BFO toward the [001] direction as the Sm concentration is increased. (The pseudo-cubic indices are used in this study.) Although Sm substitution reduces the total amount of polarization from 110 μ C cm⁻² for pure BFO to 60 μ C cm⁻² at Sm 14% where the rhombohedral to orthorhombic structural transition takes place, the piezoelectric coefficient is increased by as much as 50% at the structural boundary.^[8] We show that this polarization rotation is the main reason for occurrence of the enhancement in the piezoelectric coefficient along the [001] direction at the structural boundary. This result indicates that the rare-earth substituted BFO is a unique system in which the ferroelectric polarization vector continuously rotates and, by controlling the substitution composition, we can dial in on a particular direction of the polarization vector with an arbitrary angle between the [111] and [001] directions.

In order to examine the rotation of the ferroelectric polarization vector due to the RE (Sm in the present study) substitution into BFO, we systematically studied polarization versus electric field (PE) hysteresis loops in different orientation directions and at different substitution compositions. Probing the direction and the absolute value of the ferroelectric polarization can reveal how the polarization vector evolves with chemical substitution. We have employed the thin film composition spread technique,^[13] which allows systematic and precise tracking of the evolution in ferroelectric properties as a function of composition. The 400 nm-thick composition spreads of $(Bi_{1-v}Sm_v)$ FeO₃ were epitaxially grown on (001), (110), and (111) SrTiO₃ (STO) substrates (a = 0.3905 nm) with a 50 nm-thick conducting SrRuO₃ buffer layer underneath serving as a bottom electrode for electrical characterization. The composition gradient from x = 0 to x = 0.3 is created over a 7 mm distance along the length of the composition spread samples.

Scanning 2D X-ray diffraction (XRD) of the samples reveals that all the fabricated composition spreads show a common structural evolution^[11] due to the Sm substitution, independent of the substrate orientation. As we increase the Sm composition, 1/4 {011} diffraction spots (referred to as 1/4 spots) begin to appear and show a maximum intensity at Sm \approx 10%. With further Sm substitution, the 1/4 spot disappears while the 1/2{010} spots (1/2 spots) begin to appear and become prominent at Sm \approx 14%, which is the structural boundary. From extensive transmission electron microscopy and electron diffraction studies,^[14,15] it has been determined that the ¼ spots arise from the antiparallel cation displacements in localized regions in clusters, and the 1/2 spots result from an orthorhombic structural phase with the dimensions of $\sqrt{2a_0} \times \sqrt{2a_0} \times 2a_0$, where a_0 is the pseudocubic lattice parameter. We have confirmed that the rhombohedral to orthorhombic structural transition takes





Figure 1. Polarization versus electric field hysteresis loops measured for 400 nm-thick Sm substituted $BiFeO_3$ films grown on a) (001), b) (110), and c) (111) SrTiO₃ substrates as a function of Sm composition.

place independent of the substrate orientation. This is also consistent with the fact that the epitaxial strain created by various substrate orientations has little influence on the structural transition at this film thickness of 400 nm.^[11]

Figure 1a–c show the room-temperature PE hysteresis loops for Sm-BFO thin films grown on (001), (110), and (111) STO substrates as a function of continuously varying composition. For the film grown on the (001) substrate (Figure 1a), the square-shaped ferroelectric hysteresis loop undergoes a clear transition to a double hysteresis loop as we cross the structural phase boundary at Sm 14%. The double hysteresis behavior results from an electric field-induced structural transition from the nonpolar orthorhombic to the polar rhombohedral phase based on first principles calculations results.^[11]

The films grown on the (110) and (111) substrate (Figure 1b,c) undergo different evolutions in PE loops compared to the film on the (001) substrate (Figure 1a). For pure BFO (Sm 0%), square-shaped ferroelectric PE loops with saturated polarization values of 85 and 110 μ C cm⁻² are observed for the (110) and (111) film, respectively. These values are in good agreement with a previous report^[16] and obey the simple projection rule. As we increase the Sm composition, the saturated and remnant polarization values for the (110) film continuously decrease. Beyond the structural transition at Sm \approx 14%, the PE loops display curves characteristic of a paraelectric phase. No double hysteresis behavior is observed at the structural boundary. A similar trend is seen for the film on the (111) substrate shown in Figure 1c. It is important to note that for all orientations, the leakage current was found to decrease with increasing the Sm compositions. For instance, the leakage current for 15% Sm-substituted



Figure 2. a) Remanent polarization as a function of Sm composition for Sm-BFO films grown on (001), (110), and (111) STO substrates. b) Extracted rotation angle θ as a function of Sm composition (red). In (b), the red solid line, which is drawn based on the relationship of $P_{\text{total}} \times \cos\theta = 60 \,\mu\text{C cm}^{-2}$ is a guide to the eye. The rotation angle θ is defined as the angle of the polarization vector with respect to the [001] axis as shown in the inset. The calculation was performed assuming that the total polarization P_{total} decreases linearly with substitution (the black line on the graph).

BFO ($\approx 1 \times 10^{-6}$ A cm⁻² at 100 kV cm⁻¹) is two orders of magnitude smaller than the pure BFO thin film ($\approx 1 \times 10^{-4}$ A cm⁻² at 100 kV cm⁻¹) (not shown here). Based on this result, we conclude that the observed nonferroelectric behavior for Sm compositions larger than 15% is unrelated to the leakage behavior.

In **Figure 2a**, we plot the remnant polarization (P_r) values as a function of the Sm composition for the three orientations. Since the orthorhombic phase is paraelectric,^[11] P_r becomes zero for all orientations beyond Sm 14%. For the (001) film, P_r appears to show a roughly constant value of $\approx 60 \ \mu\text{C cm}^{-2}$ until Sm 14%, while P_r steadily decreases in value to zero for the (110) and (111) films. Since the ferroelectric polarization in BFO mainly arises from Bi 6s lone pair electrons,^[17] Sm substitution for Bi necessarily reduces the absolute value of polarization. Hence, this cannot explain the fact that P_r along the [001] direction appears to remain unchanged in the rhombohedral structural phase.

It is also important to point out that the structural phase associated with the 1/4 spots displaying the antiparallel cation displacements is not an origin of the observed evolution in P_r in Figure 1a, either. Since the structural phase associated with the 1/4 spots appears only in small, spatially localized pockets, [14,15] it is unlikely that this structural phase affects the macroscopic physical properties such as P_r . If this phase were to influence the overall properties, we would expect to see a variation in P_r with pronounced changes at around Sm 10% for all orientations, since the 1/4 diffraction spots show a maximum intensity at this composition as described previously. This is not the case in our observed evolution in Figure 2a. Instead, our observation points to the fact that Sm substitution changes the direction of the polarization from the [111] direction for pure BFO to the [001] direction. The P_r value for the (110) film is always lower than that for the (111) film, which is another evidence of the polarization rotating toward the [001] direction as a function of composition.

To better understand this, we extracted the rotation angle by assuming that the total amount of the polarization P_{total} linearly decreases from 110 μ C cm⁻² (at Sm 0%) to 60 μ C cm⁻² (at Sm

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Figure 3. Piezoresponse force microscopy images of the (001) Smsubstituted BFO thin films scanned along (010) direction. The images were taken for the as-fabricated state for a) pure BFO, b) Sm 2%, c) Sm 6%, d) Sm 10%, and e) Sm 13% films. The out-of-plane (a–e) and in-plane (f–j) images were simultaneously captured. The explanations for the circles are given in the text.

14%) due to the Sm substitution. The polarization projected along the [001] direction $P_{[001]}$ is calculated to be $P_{\text{total}} \times \cos\theta$ where we define θ to be the angle of the polarization vector with respect to the [001] axis as shown in the inset of Figure 2b. Based on our observation in Figure 2a, $P_{[001]} (= P_{\text{total}} \times \cos\theta)$ remains approximately constant at $\approx 60 \ \mu\text{C cm}^{-2}$ until Sm 14%. The calculated angle based on this is plotted in Figure 2b. The angle clearly changes from 54.7° (the [111] direction) for pure BFO to 0° (the [001] direction) at the structural boundary. We also note that with the extracted angle, the calculated value of the polarization projected along the [001], [110] and [111] directions is in good agreement with the evolution in P_r in Figure 2a (see Supporting Information (SI), Figure S1).

To further support the occurrence of rotation in the ferroelectric polarization with visual evidence, we have performed piezoresponse force microscopy (PFM) study in the 400 nm-thick (001) Sm-substituted BFO thin films. Figure 3 shows a series of simultaneously captured out-of-plane (Figure 3a-e) and in-plane (Figure 3f-j) PFM images in the as-fabricated state as a function of the Sm composition, while scanning along the (010) direction of the STO substrate. For pure BFO region (Sm = 0%), we see clear PFM responses (bright and dark contrasts) in both outof-plane (Figure 3a) and in-plane directions (Figure 3f), which is consistent with the fact that pure BFO has the ferroelectric polarization pointing along the {111} direction with four possible polarization variants. For instance, the regions (marked inside the blue circles) that show dark contrast in both out-ofplane and in-plane directions (the polarization points upward), and the regions (marked inside the yellow circle) that show bright contrast in both out-of-plane and in-plane directions (the polarization points downward), the possible domain orientations are either [-111]/[-1-11] or [1-1-1]/[11-1], depending on the right or left domain orientation of the in-plane polarization component. This behavior is in agreement with a previous report.^[18] With increasing Sm composition, the contrast in the in-plane PFM images becomes weaker and appears gray in the contrast, while the out-of-plane images continue to show higher contrast (red circles), as exemplified for Sm 6% (Figure 3c,h), at which composition the polarization vector is pointing at angle $\theta = 45^{\circ}$ (Figure 2b). With further substitution toward the boundary at Sm 14%, the relative strength of the out-of-plane response ((001) component) to the in-plane response clearly increases (Figure 3d and e vs. Figure 3i and j). This qualitative



Figure 4. Structural properties of Sm-substituted BiFeO₃ film grown on (001) STO substrate. a) Evolution in lattice parameters with Sm substitution. b) Changes in tetragonality c/a and rhombohedral distortion angle as a function of Sm composition. The value for c/a is calculated as the ratio of the out-of-plane lattice parameter to the in-plane lattice parameter. c) Schematics describing the rotation of the ferroelectric polarization vector associated with the structural changes induced by the chemical substitution. The black arrow denotes the ferroelectric polarization vector. Note that the unit cells are drawn in terms of the monoclinic lattice with a dimension of $\sqrt{2a_0} \times \sqrt{2a_0} \times a_0$.

observation provides direct evidence for the polarization rotating from the [111] direction to the [001] direction. The overall piezoelectric responses in both out-of-plane and in-plane directions are subsequently decreased as we approach the boundary. This is due to the coexistence of the local ¼ structural phases with the alternating polarization,^[15] which affects the equilibrium ferroelectric domain configurations in the as-fabricated films. It should be noted that the composition region at the boundary still displays robust, ferroelectric domain-switching characteristics when it is subjected to an external DC bias (see SI Figure S2). These results indeed support the fact that the polarization rotates from the [111] direction to the [001] direction as the substitution composition is increased.

We attribute the rotation of the ferroelectric polarization vector to structural modifications caused by the chemical substitution. Figure 4a displays changes in lattice parameters of the 400 nm-thick (001) Sm-BFO thin films on the STO substrate as a function of the Sm composition. This also confirms the structural transition from the rhombohedral to the orthorhomic phase occurring at Sm \approx 14%. It is worthwhile to point out that the films grown on (001) LSAT ((LaAlO₃)_{0.3}-(Sr₂AlTaO₆)_{0.7}) substrates, whose lattice parameters are smaller than those of STO, show a similar structural evolution to the films on STO in Figure 4 (see SI, Figure S3). Films on both substrates have almost identical lattice parameters, especially in the composition region adjacent to the boundary, though these two substrates (STO and LSAT) result in different lattice mismatches between the film and the substrate. This indicates that the fabricated films are fully (or at least partially) relaxed and that it is the chemical pressure effect due to the substitution which has the dominant effect on the observed structural evolution.

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A careful inspection of the dif plane and in-plane lattice parame



A careful inspection of the difference between the out-ofplane and in-plane lattice parameters suggests that the structure before the structural transition (Sm composition slightly less than 14%) can be described as a monoclinic phase with the distortion along the [110] direction. Hereafter we call this as a monoclinic structure. We see that the monoclinic structure is maintained until Sm \approx 14%, which is confirmed by the appearance of the multiple (203) reflections due to the crystallographic twin formation observed in the X-ray reciprocal space mapping. As we substitute Sm for Bi and increase its concentration, the in-plane lattice parameters decrease, while the out-of-plane lattice parameters remain constant. This increases the c/a ratio slightly from 1.005 for pure BFO to 1.013 at Sm \approx 13%, as displayed in Figure 4b.

We note that, as we approach the structural boundary, the monoclinic distortion angle, which is determined from the separation between the {203} reflections,^[9] also continuously increases and reaches 90° at the boundary. This indicates that the monoclinic structure changes to a tetragonal-like one with the c/a ratio of 1.013 at Sm 13%. This evolution is schematically depicted in Figure 4c. For pure BFO, the polarization points to the [111] direction. As we increase the Sm substitution, the lattice becomes compressed and less distorted, resulting in the tetragonal-like structure which allows the polarization to point toward the [001] direction. We also found a similar trend in the structural evolution for the films on (001) LSAT substrates (see SI, Figure S3b). Therefore we conclude that it is the chemical pressure effect induced by the Sm substitution rather than epitaxial strain that results in the observed structural evolution leading to the rotation of the polarization vector from the [111] to [001] direction.

It has been previously reported that a similar change in the ferroelectric polarization vector can be induced by epitaxial strain in BFO thin films.^[19,20] A recent report^[20] has shown that the rhombohedral BFO suffering from a large compressive epitaxial strain undergoes a structural transition to a polymorph tetragonal-like structure with the large c/a ratio of \approx 1.27, where the polarization vector is primarily parallel to the [001] direction. For the chemical-substitution-stabilized tetragonal-like structural phase in our case, the c/a ratio 1.013 (see Figure 4b) is not as large as the one induced by the strain, while the distortion angle is almost 90° in contrast with the angle of ≈88.7° in the strain-driven tetragonal-like phase. The implication is that there are two approaches to stabilizing the ferroelectric polarization along the [001] direction in BFO: one is the application of compressive epitaxial strain, resulting in the very large c/a ratio; the other is chemical substitution, making the distortion angle $\approx 90^{\circ}$. An important consequence of the chemical substitution is that one can dial in on an arbitrary polarization vector angle along any direction between the [111] and [001] directions by tuning the substitution composition.

The impact of the rotation in the polarization vector can be seen from the evolution of out-of-plane piezoelectric constant d_{33} for the Sm substituted BFO films grown on (100), (110), and (111) oriented substrates (see SI, Figure S5). As we showed in a previous report,^[8] the (100) film exhibits enhancement in d_{33} at \approx 14% substitution where the structural transition takes place, and the effective d_{33} value reaches 110 pm V⁻¹. For the (110) and (111) films, d_{33} shows a decrease in value and reaches zero

as the Sm composition is increased up to 14%. It should be noted that the rhombohedral to orthorhombic phase transition takes place at Sm \approx 14% independent of the substrate orientation (see SI, Figure S4). This implies that the structural transition is not playing a direct role in the evolution in d_{33} for the (110) and (111) films. Instead, it is the rotation of the polarization vector acting as a determining factor for the observed d_{33} behavior. As one can see in Figure 2a, the polarization components along the [110] and [111] directions diminish due to the rotation of polarization vector toward the [001] direction. In the composition region adjacent to structural boundary (Sm composition slightly less than 14%), the polarization vector lies along the [001] direction. This dictates the direction along which the dominant piezoelectric coefficient exists and is the main reason why only the (001) film shows the enhancement in d_{33} at the structural boundary.

As mentioned above, based on first-principles calculations.^[11] the origin of the double hysteresis loops at the structural boundary is the electric field-induced transformation from the paraelectric orthorhombic phase to the polar rhombohedral one. Accordingly, the polar phase induced by the applied electric field is energetically favorable due to the non zero polarization *P* through the coupling energy, $-P \cdot E$. Because the polarization vector is pointing along the [001] direction at the boundary, maximum energy stability is achieved by applying the electric field *E* along this direction through $-P \cdot E$. As a result, the double hysteresis behavior is most prominent only when E is applied along the [001] direction, as seen in Figure 1. This is also consistent with the fact that the enhancement in d_{33} is observed for the (001) oriented film.^[8] It is not unreasonable to think that, for the bulk sample of RE-substituted BFO, the double hysteresis behavior appears only the [001] direction. This could be the reason why no double hysteresis loops have been observed for polycrystalline samples of RE-substituted BFO to date.^[21,22]

In summary, we have investigated the rotation of the ferroelectric vector caused by A-site substitution with Sm into BFO. The ferroelectric hysteresis measurements of the Sm-BFO epitaxially grown on (001), (110), and (111) STO substrates reveal that remnant polarization along the [001] direction appears to remain constant for substitution composition up to $Sm \approx 14\%$, while the remnant polarization along [110] and [111] directions continuously decrease with substitution. This is caused by the polarization vector rotating continuously from the [111] direction for pure BFO to the [001] direction as Sm composition is increased. This is consistent with the observed change in lattice parameters with substitution: the distortion angle increases from 89.5° and approaches 90° with increasing substitution composition. The rotation in the polarization vector can explain why the double hysteresis behavior is prominently observed only for the (001) oriented film. These observations indicate that one can continuously tune the angle of the ferroelectric polarization vector arbitrarily between [111] and [001] directions by controlling the composition.

Experimental Section

The 400 nm-thick composition spreads of $(Bi_{1-x}Sm_x)FeO_3$ are epitaxially grown on (001), (110), and (111) SrTiO₃ substrates with a



50 nm-thick conducting SrRuO₃ buffer layer by combinatorial pulsed laser deposition (Pascal Inc.). Composition gradient from x = 0 to 0.3 is created over a 7 mm length along one direction of the sample. The substrate temperature and the oxygen pressure during the deposition of the composition spread layer are kept at 590 °C and 25 mTorr (1 Torr \approx 133 Pa), respectively. Composition variation in the fabricated film was confirmed by an electron probe (JEOL JXA 8900) with an uncertainty of $\pm 1\%$ at each point. The film microstructure is characterized with a scanning 2D XRD system (Bruker D8 with Hi-Star) as well as a conventional 4-circle XRD (Bruker D8) tool. For measuring the composition spread, X-ray beam is focused to a 0.5 mm φ . For electrical characterization, a 100 nm-thick Pd layer was sputtered and patterned by a lift-off process into 50 µm by 50 µm top electrode pads at room temperature. Polarization hysteresis loops were measured at 25 kHz with a Radiant Premiere II loop analyzer. A multimode atomic force microscope (AFM) with Pt/Ir coated cantilever (with typical tip radius 7 nm, force constant 0.2 N m⁻¹, resonant frequency 13 kHz) was employed at a scan rate of 0.8 Hz for the visualization of domain structure. An AC signal $V_{ac} = V_0 \sin(\omega t)$ with amplitude 1.8 V and frequency 7 kHz was applied between the AFM tip (movable top electrode) and the bottom electrode of the sample to acquire the piezoresponse images of the out of plane and in plane components with the aid of two lock-in amplifiers. Then through the same AFM tip, DC bias was applied locally to perform the switching experiment. All the measurements were carried out at the room temperature.

Supporting Information

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

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