**Composition and temperature-induced structural evolution in La, Sm, and Dy substituted BiFeO$_3$ epitaxial thin films at morphotropic phase boundaries**

Daisuke Kan, a) Ching-Jung Cheng, Valanoor Nagarajan, and Ichiro Takeuchi

**Abstract**

Detailed structural investigations on the substitution-induced structural phase transition from the rhombohedral phase to an orthorhombic phase in (Bi,RE)FeO$_3$ epitaxial thin films (RE = La, Sm, and Dy) grown on (100) SrTiO$_3$ substrates are presented. X ray diffraction reveals that the unit cell dimensions of the orthorhombic phase are strongly dependent on the type of the RE dopant. For RE = La$^{3+}$ ion, which has an ionic size comparable to the Bi$^{3+}$ ion, the unit cell is found to be $a_0 \times a_0 \times 2a_0$, where $a_0$ is the pseudo-cubic lattice parameter. This is in contrast with the $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2a_0$ unit cell for the case of smaller ionic radius RE (Sm and Dy) elements. While clear double-hysteresis loops in the polarization versus electric-field curves due to field-induced transitions are observed for smaller ionic radius RE (Sm and Dy), no signature of the double hysteresis loops is observed for the RE = La case across the structural boundary. We have also performed systematic tracking of the structural phases as functions of the RE composition and temperature, based on which we propose a phase diagram. This work reveals that the ionic size of the RE element plays a critical role in the evolution of the structural and functional properties of RE-substituted BiFeO$_3$ thin film materials systems.

**I. INTRODUCTION**

Morphotropic phase boundaries (MPBs) in piezoelectric ferroelectric materials are unique compositions where a giant electric field or mechanical stress. Composition tuning through A or B site substitution in perovskite ferroelectrics is one well-known route to achieving a MPB behavior. BiFeO$_3$ (BFO) is an environmentally friendly (Pb free) ferroelectric, which also offers the added functionality of room-temperature multiferroicity, and chemical substitutions into BFO has been a popular topic of investigation. Recently, we discovered a MPB behavior brought about by substitution of a trivalent rare-earth (RE$^{3+}$) into BFO. TEM analysis shows that the La$^{3+}$ ion, which is comparable to Bi$^{3+}$ ion in the ionic size, is not able to create the local microstructure closely associated with enhanced electromechanical properties. These results suggest that the substitution-induced structure-functional property correlation evolution depends strongly on the ionic size of the RE$^{3+}$ element.

In this paper, we report details of the substitution and temperature-induced changes in the unit cell size for three typical RE-substituted BFO systems (RE = La$^{3+}$, Sm$^{3+}$, and Dy$^{3+}$). The ionic radii of these trivalent ions, with the coordination number of twelve, are Bi$^{3+}$ ($1.36 \text{ Å}$) $\sim$ La$^{3+}$ ($1.36 \text{ Å}$) $>$ Sm$^{3+}$ ($1.28 \text{ Å}$) $>$ Dy$^{3+}$ ($1.24 \text{ Å}$). X ray diffraction reveals that the substitution of the La$^{3+}$ ion results in a structural phase transition from the rhombohedral phase to an orthorhombic phase with the unit cell dimensions of $a_0 \times a_0 \times 2a_0$ ($a_0$ is the pseudo cubic lattice parameter). In contrast, the smaller RE (Sm$^{3+}$ and Dy$^{3+}$) elements result in a phase transition to the orthorhombic phase with unit cell dimensions of $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2a_0$. It is also found that the structural transition to the $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2a_0$ orthorhombic phase is accompanied by a distinct decrease by $\sim$0.06 Å in the out-of-plane pseudo-cubic lattice parameter $d_{001,pc}$ (the subscript $pc$ denotes the pseudo cubic perovskite notation). A systematic tracking of the changes in structural properties as functions of substitution concentration and temperature allows us to construct a phase diagram that is dependent on the ionic size of the A-site RE element.

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**References**

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II. EXPERIMENTAL DETAILS

200 nm-thick epitaxial \((\mathrm{Bi}_{1-x}\mathrm{RE}_x)\mathrm{FeO}_3\) thin films \((\mathrm{RE} = \text{La}, \text{Sm}, \text{and Dy})\) were fabricated on \(\text{SrRuO}_3\) (SRO)-buffered \((001)\) \(\text{SrTiO}_3\) substrates by a pulsed laser deposition (Pascal Inc.). For each RE, a composition spread with gradient from \(x = 0\) to a desired RE concentration (typically, \(x = 0.3\) or larger) was created over a 6 mm length along one direction of the substrate. Sintered ceramic targets of \(\text{Bi}_{1.1}\text{FeO}_3\) and \((\text{RE})\text{FeO}_3\) were ablated with an excimer KrF laser with a wavelength of \(248\) nm (Thin Film Star). During the deposition, temperature and oxygen partial pressure were kept at \(600^\circ\mathrm{C}\) and \(25\) mTorr, respectively. Compositions were determined by an electron probe (JEOL JXA-8900) within accuracy of \(\pm 1\%\). Crystal structures of the fabricated thin-film composition spreads were characterized by a conventional 4-circle x-ray diffractometer and a scanning 2-dimensional x-ray diffraction (XRD) (Bruker D8 with GADSS). For electrical characterization, a 100 nm-thick Pd layer was sputtered at room temperature and patterned by a lift-off process into \(50\ \mu\text{m} \times 50\ \mu\text{m}\) top-electrode pads. Polarization versus electric field \((P-E)\) hysteresis loops were measured at \(25\) kHz with a Radiant Premiere II loop analyzer. The cross-sectional transmission electron microscope (TEM) specimens were prepared by a focused ion beam microscopy (FEI, Nova 200 Nanolab) followed by the “lift-out” technique by a micromanipulator. Selected samples were studied on an \textit{in situ} hot-stage TEM (Philips, CM12) operating at \(120\) kV. All the electron diffraction patterns were captured at the same exposure time.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) display a series of \(2\theta-\theta\) scans around the \((002)\) STO Bragg reflection across the structural phase transition for \((a)\) Sm- and \((b)\) La-substituted BFO thin films. All scans were performed at room temperature. The colored solid arrows denote the \((002)_{\text{pc}}\) reflections from RE-substituted BFO layer. \((c)-(d)\) substitution-induced evolution of the out-of-plane lattice parameter \(d_{001,\text{pc}}\) for \((c)\) Sm- and \((d)\) La-substituted BFO. The lattice parameter is determined from the \((002)_{\text{pc}}\) reflection. The dotted line is drawn as a guide to eyes.

In sharp contrast, the La-substituted films show a gradual shift of the \((002)_{\text{pc}}\) reflections toward the higher \(2\theta\) side (Fig. 1(b)) as we increase the La substitution up to La 40%. Correspondingly, we see a gradual decrease in \(d_{001,\text{pc}}\) from 4.06 Å for 4% to 4.01 Å for 34% in Fig. 1(d), which displays La composition dependence of \(d_{001,\text{pc}}\). The observed difference in behavior of \(d_{001,\text{pc}}\) between \(\text{RE} = \text{La}^{3+}\) and \(\text{Sm}^{3+}\)
already hints at the fact that the substitution-induced evolution from the rhombohedral phase to the orthorhombic one strongly depends on the ionic size of the substitution element and that the orthorhombic phase has a unit cell strongly depending on the ionic size of the RE dopants.

To understand this difference in further detail, x-ray reciprocal space mappings (RSMs) around the STO (203)$_\text{pc}$ Bragg reflection with configurations of $\phi = 0^\circ$, $90^\circ$, $180^\circ$, and $270^\circ$ were carried out for RE = Sm and La (Figs. 2(a) and 2(b)). In Fig. 2(a), it is clear that Sm-BFO shows two reflections at each phi configuration. The position of the Sm-BFO (332) reflection remains constant for all four phi configurations ($\phi = 0^\circ$, $90^\circ$, $180^\circ$, and $270^\circ$). However, another diffraction spot corresponding to the (150)$_\text{Sm-ortho}$ reflection is present at phi configurations of $0^\circ$ and $270^\circ$, while a spot corresponding to the (510)$_\text{Sm-ortho}$ reflection is only present at phi settings of $90^\circ$ and $180^\circ$. The observed multiple reflections from the Sm-BFO layer suggest that a twin structure is formed in the orthorhombic phase and that the unit cell of the film has the dimensions of $a_0 \times a_0 \times 2a_0$ with the (100)$_\text{La-ortho}$ orientation. This finding agrees with the observation of the $1/2(110)_{\text{pc}}$ spots from the previous TEM and electron diffraction (ED) studies for RE-BFO (RE = Sm, Gd, and Dy). In the case of RE = La, the single reflection from the La-BFO layer is observed, and the reflection appears at the same position for each phi configuration. This implies that the orthorhombic phase for La-BFO has the unit cell dimensions of $a_0 \times a_0 \times 2a_0$ with the (100)$_\text{La-ortho}$ orientation. This is also consistent with the fact that no $1/2(110)_{\text{pc}}$ spot was seen for the orthorhombic La-BFO in an ED study.

The observed RSMs in Figs. 2(a) and 2(b) can be understood by considering the epitaxial relationships drawn in Figs. 3(a) and 3(b) for the RE = Sm and La cases, respectively. Figure 3(a) shows that, due to the dimensions of $a_0 \times a_0 \times 2a_0$ in Sm-BFO, the film grows with the (110)$_\text{Sm-ortho}$ orientation on the (001) STO substrate. The epitaxial relationships between the film and the substrate are $[001]_{\text{Sm-ortho}}//[010]_{\text{STO}}$ and $[110]_{\text{Sm-ortho}}//[100]_{\text{STO}}$. Due to the cubic symmetry of the substrate, another relationship, namely $[001]_{\text{Sm-ortho}}//[100]_{\text{STO}}$ and $[-110]_{\text{Sm-ortho}}//[010]_{\text{STO}}$, is also allowed. With these epitaxial relationships,
the reflection that appears at the same position in RSMs with all four phi configurations (Fig. 2(a)) is indexed as (334)$_{\text{Sm-ortho}}$. Another reflection observed at two different positions is (150)$_{\text{Sm-ortho}}$ or (510)$_{\text{Sm-ortho}}$. The appearance of these two reflections in the different reciprocal space indicates that the lattice parameter along (100)$_{\text{Sm-ortho}}$ has a different value from the one along [010]$_{\text{Sm-ortho}}$. With the orthorhombic unit cell, the reflection observed for the 20-0 profiles in Fig. 1(a) is assigned as the (220)$_{\text{Sm-ortho}}$ reflection. The abrupt drop in d$_{001}$pc observed for RE = Sm (Fig. 1(a)) is attributed to the change in the dimensions of the unit cell, associated with the structural phase transition from the rhombohedral to orthorhombic phase. Across the boundary, the unit cell volume (in terms of the pseudo-cubic perovskite unit cell) is decreased by 1.2% due to the abrupt drop in the unit cell volume (in terms of the pseudo-cubic perovskite unit cell). In (d)-(f), the d$_{001}$pc is color-coded by the side bar. The black dotted line in the figure denotes the rhombohedral to orthorhombic structural transition boundary, which is determined by the evolution of the (0, 1/2, 2) XRD spot intensity (Fig. 5).

Thus, the fundamental unit-cell for La-BFO (in terms of pseudo-cubic unit cell) remains unchanged across the structural boundary, although the lattice parameter along the (001)$_{\text{ortho}}$ axis is doubled, as evidenced by 1/2(010)$_{\text{pc}}$ (circles in blue) superstructure reflections of RE-substituted BFO thin films as a function of substitution composition. (d)-(i) display contour plot of x-ray superstructure spot intensities as functions of RE (= Dy, Sm, and La) substitution and temperatures. (d)-(f) and (g)-(i) plots the (0, 1/2, 2) spot intensities, respectively. (a), (d), and (g) are for RE = Dy, (b), (e), and (h) are for RE = Sm, (c), (f), and (i) are for RE = La. The data in (a) and (b) are taken from Ref. 5. For the contour plots in (d)-(i), the same color-scale on the right is used.

Figures 4(a)–4(c) compares the substitution-induced evolution in lattice parameters at room temperature for the cases of RE = Dy, Sm, and La. For both RE = Dy (Fig. 4(a)) and Sm (Fig. 4(b)), we see a similar trend in the substitution-induced evolution. In the rhombohedral phase (circles in red in Figs. 4(a) and 4(b)), the out-of-plane and in-plane lattice parameters gradually decrease as the substitution is increased. With further substitution, a different set of lattice parameters, $a_{\text{ortho}}$, $b_{\text{ortho}}$, and $c_{\text{ortho}}$ (squares, triangles and diamonds in blue in Figs. 4(a) and 4(b)), which correspond to the orthorhombic phase with the unit cell dimensions of $\sqrt{2}a_0 \times 2a_0 \times 2a_0$, are seen. Based on the evolution of the lattice parameters, the composition for the structural transition is determined to be 7% for RE = Dy and 13% for RE = Sm. This is in close agreement with previous analysis performed using changes in the XRD superstructure spots as well as P-E hysteresis loops (see Figs. 5 and 8). 15
sizes of the Sm$^{3+}$ and Dy$^{3+}$ compared to La$^{3+}$, one should expect a larger degree of the FeO$_6$ octahedral rotation around the [001]$_{\text{Sm-ortho}}$ direction, according to tolerance factor arguments. In other words, the role of smaller sized RE elements is analogous to a stronger chemical pressure applied to the unit cell. This leads to the larger unit cell dimensions in the orthorhombic phase for the smaller RE substituted BFO, although the pseudo-cubic unit cell becomes smaller with decreasing ionic radius of the RE element, as confirmed by the discontinuous drop in $d_{001\_pc}$ in Fig. 1(c).

Based on results of first principles calculations, we had proposed that the enhancement in the out-of-plane piezoelectric coefficient at the structural boundary results from the electric-field-induced structural transformation from the orthorhombic phase to the rhombohedral one at the boundary. The discontinuous change in $d_{001\_pc}$ at the structural boundary indicates that there should be a large lattice strain induced by the electric-field-induced structural transformation, and this may be the lattice origin of the enhancement in the piezoelectric coefficient. This model is also supported by the fact that no enhancement is seen for the RE = La case, where there is no obvious discontinuous decrease in $d_{001\_pc}$ at the structural boundary, as shown in Figs. 1(d) and 4(c). The out-of-plane lattice parameter for La-BFO shows a gradual decrease till 50% substitution, while the in-plane lattice parameter remains almost unchanged. The lack of a distinct change in $d_{001\_pc}$ up to La 50% substitution is most likely due to the fact that the primitive unit cell dimensions for La-BFO remain unchanged across the structural boundary.

To further elucidate details in the evolution of the lattice parameters, we investigated temperature dependence of $d_{001\_pc}$. The results are summarized at the lower panel of Fig. 4, where the contour plots of $d_{001\_pc}$ for Dy, Sm, and La-substituted BFO as functions of temperature and substitution compositions are displayed with the color-code shown on the right in Fig. 4. The dotted line drawn in Figs. 4(d)–4(f) correspond to the composition where the rhombohedral to orthorhombic structural transition takes place. This boundary is determined by the evolution of the XRD $1/2\{010\}_\text{pc}$ superstructure spot intensity (Fig. 5), which results from the cell doubling along the [001]$_{\text{Sm-ortho}}$ direction in the orthorhombic phase.

For the cases of RE = Dy (Fig. 4(d)) and Sm (Fig. 4(e)), the drop in $d_{001\_pc}$ is clearly seen in the entire temperature range as one moves toward higher concentration. The composition where the drop in $d_{001\_pc}$ occurs is in very good agreement with the structural boundary (the dotted line in Figs. 4(d)–4(f)), which confirms that this drop results from the structural transition. As temperature is increased, the composition where the drop in $d_{001\_pc}$ takes place shifts toward the lower RE substitution level, which implies that the orthorhombic phase is more stable at higher temperatures.

In order to establish a detailed link between the changes in the lattice parameters and the structural phases, we also examined the substitution- and temperature-induced evolution of the XRD superstructure spot intensities. In our previous report, we demonstrated that the structural evolution from the rhombohedral to orthorhombic phase in the smaller RE-substituted BFO (RE = Dy, Gd, and Sm) can be directly linked to changes in the XRD $1/4\{110\}_\text{pc}$ (referred to as the $1/4$ spot) and $1/2\{010\}_\text{pc}$ (referred to as the $1/2$ spot) superstructure spot intensities. Based on the TEM and electron diffraction (ED) studies, it was determined that the $1/4$ spot arises from the presence of minority phase with a PbZrO$_3$-type structure, with dimensions of $\sqrt{2}a_0 \times 2\sqrt{2}a_0 \times 2a_0$ in local regions and that the $1/2$ spot results from the cell-doubled orthorhombic structural phase. As one increases the RE substitution concentration, at first, the $1/4$ spot begins to appear and is found to have a maximum intensity before the structural boundary. With further substitution, the $1/4$ spot disappears while the $1/2$ spot becomes more prominent. The structural phase boundary corresponds to the composition where the normalized intensities of $1/4$ and $1/2$ spots switch over as the $1/2$ spot arises from the cell doubling along the [010]$_\text{pc}$ direction. In Figs. 5(a) and 5(b), we plot the room-temperature RE composition dependence of the normalized intensities of the $1/4$ and $1/2$ spots for Dy- and Sm-BFO, respectively. For La-BFO in Fig. 5(c), the trend is similar to the Dy and Sm cases, indicating that the occurrence of $1/4$ and $1/2$ spots are indeed universal characteristics for RE-BFO.

Figures 5(d)–5(i) display the contour plots of the $1/2$ (Figs. 5(d)–5(f)) and $1/4$ spot intensities (Figs. 5(g)–5(i)) as functions of temperature and the substitution concentration for the RE = Dy, Sm, and La cases. The intensities in Figs. 5(d)–5(i) are plotted in the same color-code on the right in the figure. Again, we find a universal trend in the temperature-induced variation in $1/4$ and $1/2$ spot intensities. As temperature is increased, the composition space where the $1/4$ spot is stable shrinks and eventually disappears. Concurrently, the $1/2$ spot begins to become more pronounced. By comparing Fig. 5 to Fig. 4 for RE = Dy and Sm cases, it is clear that the composition region where the $1/4$ and $1/2$ spot intensities switch over coincides very well with the composition region in which the discontinuous drop in $d_{001\_pc}$ is seen. More importantly, the stability of the structural phase shows a strong correlation to the strength of the chemical pressure due to the substitution. As the chemical pressure gets stronger, the highest temperature at which the $1/4$ spot appears decreases from 360°C for RE = La to 200°C for RE = Dy, although the overall spot intensity is smaller for the La case. The stronger pressure also moves the $1/4$ spot region into the lower composition side. In the same vein, the composition region where the $1/2$ spot intensity is seen is extended toward lower composition and lower temperature region with decreasing ionic size of the RE elements.

It is interesting to note that, in the contour plots for RE = Dy (Fig. 4(d)) and Sm (Fig. 4(e)), we see another slight decrease of $d_{001\_pc}$ by $\approx 0.03$ Å in the composition region right before the structural transition (on the rhombohedral phase side). This composition region becomes narrower with increasing temperature and disappears above $\sim 200°C$. This behavior strongly resembles the temperature-induced evolution of the XRD $1/4\{011\}_\text{pc}$ superstructure spot intensity in Fig. 5, suggesting a close tie between the slight decrease in $d_{001\_pc}$ and the appearance of the $1/4$ structural phase. However, further examination is necessary to identify an underlying origin of the slight decrease in $d_{001\_pc}$ in this...
composition region. For the RE = La case, this behavior in $d_{001\text{pc}}$ is not obvious. This is probably due to the negligibly weak chemical pressure effect for the La substitution, resulting in the continuous decrease in $d_{001\text{pc}}$.

Figure 6 summarizes the structural evolution in RE-substituted BFO. Figure 6(a) depicts the schematic phase diagram for the case of smaller RE ionic sizes (the strong chemical pressure) that can stabilize the $1/4 = 2$ structural phase with dimensions of $a_0^2 \times a_0^2 \times 2a_0^2$. We define $X$ and $X'$ as a substitution composition at which the $1/4$ and $1/2$ spot intensities begin to appear at room temperature, respectively. (The subscripts 1 and 2 in Figure 6 denote the strong chemical pressure case (RE = Sm and Dy) and the no chemical pressure case (RE = La), respectively.) For lower temperatures, the appearance of the $1/4$ phase (in the composition region between $X$ and $X'$ at room temperature) seemingly “bridges” the rhombohedral structural phase to the orthorhombic phase. The orthorhombic phase emerges in the composition region beyond $X'$ at room temperature. As temperature is increased, the $1/4$ spot disappears, and the orthorhombic phase is located right next to the rhombohedral phase in the diagram.

Based on the observations in Figs. 4 and 5, this phase diagram in Fig. 6(a) can be extended to the case where the chemical pressure effect is negligibly weak (RE = La) by simply shifting the $1/4$ spot region and the structural boundary into the higher substitution composition and higher temperature regions. In this case, the $1/2$ structural phase is the orthorhombic (or tetragonal-like) phase with dimensions of $a_0 \times a_0 \times 2a_0$, although the $1/2$ structural phase is still bridged by the $1/4$ phase to the rhombohedral phase at lower temperatures. In the higher temperature region, where the $1/4$ spot disappears, the $1/2$ phase remains right adjacent to the rhombohedral phase in the diagram.

To confirm microscopically the phase diagram presented in Fig. 6, we have studied temperature dependence of ED spots observed for the $1/4$ phase in a local region at the composition of Bi$_{0.9}$Sm$_{0.1}$FeO$_3$. Previously, we discussed that the regions, which show $1/4\{110\}$ spots are nanoscale (10-20 nm) pockets in the rhombohedral ferroelectric matrix. Fig. 7 displays the ED patterns taken for the local $1/4$ structural phase for Bi$_{0.8}$Sm$_{0.2}$FeO$_3$ as a function of temperature. The $1/4\{110\}$ spot (circled in red), captured for one such pocket at room temperature in Fig. 7(a), disappears as one raises the temperature. Subsequently, the $1/2\{010\}$ spots appear (boxed in blue) and remain with further increase in temperature up to $130^\circ C$ (Fig. 7(d)). Figure 7 thus confirms that the local regions with the $1/4\{110\}$ spots undergo a structural transition to an orthorhombic structural phase that is identical to the majority phase. It should be noted that the orthorhombic phase is a single global phase without any minority phases. The general trend of the $1/4$ to $1/2$ structural phase transition, seen as a function of temperature in Fig. 7, is consistent with the results shown in Figs. 5 and 6.

![FIG. 6](attachment:figure6.png)

![FIG. 7](attachment:figure7.png)
As an important consequence of the substitution-induced structural evolution, ferroelectric properties of the RE-BFO thin films display concomitant changes, which exhibit strong dependence on the degree of the chemical pressure due to the RE elements. Figure 8 displays the evolution of room-temperature P-E hysteresis loops across the structural boundary for Sm- and La-BFO thin films. The compositions for RE = Sm and La cases are chosen such that they capture the representative characteristics of the evolution in sufficient composition ranges. For RE = Sm in Fig. 8(a), the P-E hysteresis loop undergoes a transition from the ferroelectric single loop on the rhombohedral phase side into the double-hysteresis one on the orthorhombic phase. Results from a first principles calculation have been used to propose that the origin of the double hysteresis loops is the electric-field induced structural transformation from the paraelectric orthorhombic phase to a ferroelectric rhombohedral phase. As one approaches the structural phase boundary, a ferroelectric single hysteresis loop with the saturated polarization of 70 \( \mu \text{C/cm}^2 \) first becomes distorted and then fully develops into the double-hysteresis loop. The similar trend is seen for the La case except the orthorhombic phase, as exemplified by the loop for La 27%, where the double hysteresis behavior becomes less pronounced and the P-E loop is likely the one characteristic for the paraelectric phase. This behavior of La-substituted BFO is independently confirmed by the dielectric constant versus electric field curves, which did not show clear quadruple-humped loops observed for the orthorhombic phase adjacent to the boundary in Sm-substituted BFO.

Figure 9 shows the P-E hysteresis loops observed for the Sm 18% and La 34% substituted BFO thin films with the orthorhombic structural phase. Both films show the P-E hysteresis loops characteristic for the paraelectric phase when the applied electric field is below 500 kV/cm. As we increase the applied electric fields further, the Sm-BFO shows the recovery of the well-developed double hysteresis behavior while the paraelectric behavior remains unchanged for the RE = La case. Similar behaviors are observed for the orthorhombic phase with other La substitution composition close to the structural boundary. Based on the fact that the unit cell dimensions of the orthorhombic phase is different for RE = La compared to BFO substituted with smaller RE elements, we conclude that the electric-field induced structural transformation is only favorable for the orthorhombic phase with \( \sqrt{2a_0} \times \sqrt{2a_0} \times 2a_0 \) dimensions.

**IV. SUMMARY**

We have investigated in detail the structural phase transitions in La, Sm, and Dy-substituted BFO thin films as a function temperature and composition space. The common structural transition from the rhombohedral to an orthorhombic phase is observed for all RE elements. However, we find that the orthorhombic phase beyond the structural boundary has the unit cell dimensions that strongly depend on the type of the RE element. In the case of La\(^{3+}\), which has the same ionic radius as the Bi\(^{3+}\) ion, the orthorhombic phase has the dimensions of \( a_0 \times a_0 \times 2a_0 \) as compared to the \( \sqrt{2a_0} \times \sqrt{2a_0} \times 2a_0 \) orthorhombic unit cell for the smaller RE cases, such as Sm and Dy. We attribute this to the greater degree of instability of the perovskite structure and, hence, the rotation of the FeO\(_6\) octahedron for the smaller RE substituted BFO. This leads to larger dimensions in the orthorhombic phase for the smaller RE substituted BFO, which consequently exhibits an abrupt drop in the pseudo-cubic out-of-plane lattice parameter. In contrast, the La-substituted BFO shows a smooth change in the out-of-plane lattice parameter. Based on the substitution- and temperature-induced evolution of the lattice parameters and XRD superstructure spots, we also
established the phase diagrams for cases of the strong (RE = Sm and Dy) and negligibly weak chemical pressure (RE = La) into the BFO lattice.

The phase diagrams reveal the great impact of the chemical pressure effect on the stability of the orthorhombic structural phase of RE-substituted BFO in the composition and temperature space. The RE-BFO displays the concomitant changes in ferroelectric properties across the structural phase transition. For the RE = La case, no signature of the double P-E hysteresis loop is observed across the boundary, while the smaller RE substituted BFO shows fully developed double hysteresis loops. These results underscore the fact that subtle change in the degree of chemical pressure effect provided by substitution of different RE elements has profound influences on structural and ferroelectric properties of RE-substituted BFO.

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