

# Universal Behavior and Electric-Field-Induced Structural Transition in Rare-Earth-Substituted BiFeO<sub>3</sub>

By Daisuke Kan, Lucia Pálová, Varatharajan Anbusathaiah, Ching Jung Cheng, Shigehiro Fujino, Valanoor Nagarajan,\* Karin M. Rabe, and Ichiro Takeuchi\*

The discovery of a universal behavior in rare-earth (RE)-substituted perovskite  $BiFeO_3$  is reported. The structural transition from the ferroelectric rhombohedral phase to an orthorhombic phase exhibiting a double-polarization hysteresis loop and substantially enhanced electromechanical properties is found to occur independent of the RE dopant species. The structural transition can be universally achieved by controlling the average ionic radius of the A-site cation. Using calculations based on first principles, the energy landscape of  $BiFeO_3$  is explored, and it is proposed that the origin of the double hysteresis loop and the concomitant enhancement in the piezoelectric coefficient is an electric-field-induced transformation from a paraelectric orthorhombic phase to the polar rhombohedral phase.

### 1. Introduction

A material compositionally tuned to be at a phase boundary with a first-order transition could be viewed as being "on the brink," and it can often display a colossal response in reaction to weak external stimuli such as temperature, electric field, or magnetic field. For instance, giant piezoelectric responses are achieved in some Pb-based ferroelectrics by tuning their compositions to their morphotropic phase boundaries (MPBs),<sup>[1–5]</sup> where two different structural phases that are close by in the energy level coexist. Multiferroic BiFeO<sub>3</sub> (BFO)<sup>[6–8]</sup> has a perovskite structure with a

Multiferroic BiFeO<sub>3</sub> (BFO)<sup>[6–8]</sup> has a perovskite structure with a rhombohedral distortion along the [111] direction (space group R3c). Since its ferroelectricity mainly arises from the Bi 6s lone pair electrons,<sup>[9]</sup> chemical modification of the A-site of the perovskite structure (ABO<sub>3</sub>, A = Bi and B = Fe) is expected to affect the

[\*] Prof. I. Takeuchi, Dr. D. Kan, Dr. S. Fujino Department of Materials Science and Engineering University of Maryland College Park, Maryland 20742 (USA) E-mail: takeuchi@umd.edu Prof. V. Nagarajan, Dr. V. Anbusathaiah, C. J. Cheng School of Materials Science University of New South Wales Sydney New South Wales 2052 (Australia) E-mail: nagarajan@unsw.edu.au
L. Pálová, Prof. K. M. Rabe Department of Physics and Astronomy Rutgers University Piscataway, New Jersey, 08854 (USA) ferroelectric (FE) properties. In fact, chemical modification of BFO has been a popular topic of investigation and there continue to be new reports of attempts at improving its FE properties, for example, reduction of leakage currents or lowering of the coercive field by substitution.<sup>[10–17]</sup> Despite the collection of literature that now exists on such studies, a comprehensive picture on the substitutional effect of rare-earth (RE) ions in BFO is still missing.

An important consequence of the chemical substitution is a phase transition from the rhombohedral FE phase of the parent compound into another structure. We had earlier reported<sup>[18]</sup> on the transition to an orthorho-

mibic phase in the Sm-substituted BFO thin film where the double polarization hysteresis loops have been observed. At the phase boundary, electromechanical properties including the piezoelectric coefficient  $d_{33}$  and the dielectric constant  $\varepsilon_{33}$  are substantially enhanced. The value of  $d_{33}$  at the boundary can be as high as 110 pm  $V^{-1}$ , which is nearly double that of previous values reported for undoped BFO thin films. This value is comparable to a value seen in single-domain PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> (PZT) thin films.<sup>[19]</sup> Such a material at the phase boundary is of substantial technological interest as a Pbfree piezoelectric for a variety of applications and hence leads to a set of fundamental key questions: 1) are there other compositions with similar behaviors, and 2) what is the mechanism behind the structural transition and the concomitant enhancement of piezoelectric properties? To this end, we have systematically investigated substitution of various trivalent RE<sup>3+</sup> into the A-site of BFO and discovered that there is a universal behavior with all RE<sup>3+</sup> dopants: the ferroelectric rhombohedral phase undergoes a structural transition to the paraelectric orthorhombic phase exhibiting the double hysteresis behavior, and there is concomitant enhancement in dielectric and piezoelectric properties at the transition. Using the first-principle calculation, we propose a model where the electric field induces the transformation from the paraelectric orthorhombic phase to the polar rhombohedral phase at the structural boundary, which results in the observed double hysteresis loop and the enhanced properties.

### 2. Results and Discussion

We have employed the thin-film composition spreads technique,  $^{\left[ 20\right] }$  which allows continuous and precise tracking of changes



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in structural and physical properties across phase boundaries.<sup>[21]</sup> The 200-nm-thick composition spreads of (Bi<sub>1-x</sub>RE<sub>x</sub>)FeO<sub>3</sub> are epitaxially grown on (001) SrTiO<sub>3</sub> (STO) substrates by pulsed laser deposition equipped with moving masks and a multi-target system. Here we focus on results with Sm, Gd, and Dy as the RE<sup>3+</sup> dopants to substitute for Bi3+ in the A-site of the perovskite structure. The ionic radii of these trivalent ions with a coordination number of twelve are  $Bi^{3+}$  (1.36 Å) > Sm<sup>3+</sup> (1.28 Å) > Gd<sup>3+</sup>  $(1.27 \text{ Å}) > \text{Dy}^{3+}$   $(1.24 \text{ Å}).^{[22]}$  For each composition spread with a different RE<sup>3+</sup> dopant, the dopant concentration is continuously varied from x = 0 (pure BFO) to a fixed value (typically x = 0.3) along the direction of the spread sample, as schematically shown in Figure 1a. Trivalent RE<sup>3+</sup> substitution is not expected to increase the leakage current because of the same valence state of Bi<sup>3+</sup>, unlike in a recent report where substitution of divalent Ca<sup>2+</sup> for Bi<sup>3+</sup> resulted in the electric conduction in BFO thin films.<sup>[23]</sup> In this report, we use scanning X-ray diffraction (XRD) extensively as the main tool to track and map the systemic change in structure as the phase transition takes place across each composition spread as shown in Figure 1a.

Scanning XRD of the spreads reveals that the RE<sup>3+</sup> substitution for Bi<sup>3+</sup> causes continuous evolution in the crystal structure. Figure 1b–d show typical 2D XRD images taken for a Dysubstituted BFO composition spread sample. They capture essential and common characteristics of the substitution-induced structural evolution we observe for all RE dopants studied. The key findings from the XRD patterns discussed below have also been corroborated by systematic selective area electron diffraction (SAED) patterns of individual samples (not shown) of selected compositions by transmission electron microscopy (TEM).<sup>[24,25]</sup> For pure BFO ( $x_{Dy} = 0\%$ , Fig. 1b), only (001) and (002) reflections from the film and the substrate are clearly observed confirming epitaxial growth of the film on the substrate. With increasing Dy concentration, extra diffraction spots begin to appear in addition to



**Figure 1.** 2D XRD images for Dy-substituted BiFeO<sub>3</sub> thin films. a) A schematic of XRD measurements of a  $(Bi_{1-x}RE_x)FeO_3$  composition spread with a 2D detector. b–d) 2D XRD images for the  $(Bi_{1-x}Dy_x)FeO_3$  composition spread film on (001) SrTiO<sub>3</sub> substrate. b)  $x_{Dy} = 0.$  c)  $x_{Dy} = 0.07$ . d)  $x_{Dy} = 0.1$ . The 2D XRD images are recorded in the  $2\theta - \chi$  plane with the incident X-ray beam parallel to the [100]<sub>STO</sub> direction. For (c) and (d), the spots with arrows belong to  $\frac{1}{4}$ {011} and  $\frac{1}{2}$ {010}, respectively. All spots are indexed by the pseudo-cubic-unit-cell notation.

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the fundamental spots. In Figure 1c, where  $x_{Dy} = 0.07$ , the spots with arrows in red that are assigned as  $\frac{1}{4}$ {011} have appeared. As the Dy concentration is further increased (Fig. 1d), the  $\frac{1}{4}$ {011} superstructure spots disappear and new superstructure spots (marked with yellow arrows) begin to emerge. These new spots correspond to the  $\frac{1}{2}$ {010} reflection spots, indicating that unit-cell doubling has taken place along the in-plane direction as compared to the rhombohedral BFO phase. From X-ray reciprocal space mapping (see Supporting Information, Fig. S1), we see that a film showing the  $\frac{1}{2}$ {010} spots is in an (pseudo-) orthorhombic structural phase with the unit cell having the dimensions of  $\sqrt{2a_{pc}} \times \sqrt{2a_{pc}} \times 2a_{pc}$ , where  $a_{pc}$  is the pseudo cubic lattice parameter. For  $x_{Dy} = 0.09$ , the lattice parameters are determined to be a = 5.44 Å, b = 5.61 Å, c = 7.81 Å, and  $\alpha = \beta = 90.0^{\circ}$ ,  $\gamma = 89.1^{\circ}$ .

It is important to point out that the diffraction patterns with the  $\frac{1}{4}$  {011} superstructure spots seen in Figure 1c closely resemble that of the well-established antiferroelectric (AFE) structure in PbZrO<sub>3</sub>,<sup>[26,27]</sup> where Pb<sup>3+</sup> is displaced in an anti-parallel manner along the  $\langle 011 \rangle$  direction and, as a result, the unit cell is quadrupled along the direction. The  $\frac{1}{4}$ {011} spots seen here have been previously reported for Sm-doped BFO<sup>[24]</sup> and Nd-doped BFO<sup>[28]</sup> and were shown to result from anti-parallel displacements of cations along the (011) direction. From high-resolution TEM observations and SAED patterns of the RE-substituted BFO thin films,  $[^{24,25}]$  it was found that the  $\frac{1}{4}$  {011}-related superstructure spots are seen only in isolated local domains in the films typically 10-20 nm in size and not in the entirety of the films, indicating that the structure associated with the spots is a minority phase. This is consistent with the fact that, in the composition range where the  $\frac{1}{4}$ spots are observed, macroscopic properties of the films are those consistent with a FE phase, and not an AFE phase, as we discuss below.

To further elucidate the sequence of structural evolution as a function of the substituting concentration, we plot the normalized intensities of the  $(0, \frac{1}{4}, \frac{7}{4})$  XRD spot (a  $\frac{1}{4}$  {011} spot) arising from the PbZrO<sub>3</sub>-type minority phase and the  $(0, \frac{1}{2}, 2)$  spot  $(a \frac{1}{2} \{010\}$  spot) due to the occurrence of the cell-doubling in the majority phase for Dy-substituted BFO in Figure 2a. The  $\frac{1}{4}$  {011} spot intensity peaks at 6% doping. Beyond this concentration, the  $\frac{1}{4}$ {011} spot decreases in intensity, while the  $\frac{1}{2}$ {010} spot gets enhanced as an indication of the structural phase transition taking place from the rhombohedral to the orthorhombic phase. The structural transition also is confirmed by evolution of the lattice parameters due to the Dy substitution as seen in Figure 2b. Also plotted in Figure 2c are the zero bias  $\varepsilon_{33}$  (blue rectangles) and maximum  $d_{33}$  (green rectangles), which show the peaking behavior at the structural boundary. The maximum value of  $\varepsilon_{33}$  is ~250, and the maximum  $d_{33}$  value at the peak is almost double the value for pure BFO thin films.

The observed structural evolution and the enhanced properties are found to be common to all three dopants as shown in Figure 3a, where we plot normalized intensities of the  $\frac{1}{4}$  and  $\frac{1}{2}$  XRD spots and  $\varepsilon_{33}$  as a function of each RE dopant composition (RE = Sm, Gd, Dy). A key observation here is that the composition of the structural transition shifts toward the larger composition values as the ionic radius of dopant becomes larger. For RE = Dy, which has the smallest ionic radius of the three elements, 8% doping is sufficient to induce the transition. On the other hand, for Sm, which has the largest radius of the three, 14% doping is necessary. This observation is attributed to a hydrostatic pressure effect caused by





**Figure 2.** Evolution of structural and electromechanical properties observed in Dy-substituted BiFeO<sub>3</sub> thin films. a) Normalized intensities of XRD spots— $(0, \frac{1}{4}, \frac{7}{4})$ , referred to as  $\frac{1}{4}$  spot, and  $(0, \frac{1}{2}, 2), \frac{1}{2}$  spot—as a function of Dy dopant composition. b) Lattice parameters determined by X-ray reciprocal space mappings using single-composition thin films. In the orthorhombic phase, the lattice parameters are calculated in terms of the pseudocubic unit cell notation for clarity. c) Composition dependence of maximum piezoelectric coefficient  $d_{33}$  (green) and zero-bias dielectric constant  $\varepsilon_{33}$  (blue). All data were taken at room temperature.

the smaller radii of the isovalent RE ions. It has been shown in BaTiO<sub>3</sub> that isovalent substitution for Ba<sup>2+</sup> by Sr<sup>2+</sup> results in the same changes in the lattice parameter and the Curie temperature as caused by an external hydrostatic pressure.<sup>[29]</sup> This hydrostatic



pressure effect caused by the chemical substitution is also the primary cause of the rhombohedral to orthorhombic structural phase transition here. The induced distortions, for example, the tilting of oxygen octahedral,<sup>[24]</sup> make the rhombohedral phase unstable and consequently stabilize the orthorhombic phase, shrinking lattice parameters as well as the overall volume of the unit cell (in the pseudocubic notation), which are confirmed by the evolution in lattice parameters in Figure 2b. Figure 3b captures the universal behavior common to all the RE dopants where the same data shown in Figure 3a are plotted together against the average Asite ionic radius  $r_{ave}$ . The curves collapse together, revealing an underlying common behavior as a function of the average ionic radius.

To rule out the possibility that the observed universal structural evolution results from some thin-film growth processes or substrate effects, we investigated the structural properties of 400-nm-thick Sm-substituted BFO thin films grown on various substrates under the same growth conditions. Figure 3c summarizes evolution of the normalized intensities of the  $\frac{1}{4}$  and  $\frac{1}{2}$  XRD spots and  $\epsilon_{33}$  with the Sm dopant composition for the films grown on (001) LSAT ((LaAlO<sub>3</sub>)<sub>0.3</sub>-(SrAl<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub>)<sub>0.7</sub>), (001) STO, and (110)<sub>ortho</sub> DyScO<sub>3</sub> (DSO) substrates. The key features of the observed structural evolution are found to be independent of the substrate. The  $\frac{1}{4}$  and  $\frac{1}{2}$  spot intensities switch over at the rhombohedral to orthorhombic structural phase transition. More importantly, the structural transition takes place at the same Sm composition of 14%. At the boundary,  $\epsilon_{33}$  also reaches the maximum for each sample. Note that the structural evolution observed for the 400-nm-thick sample on STO (the middle panel in Fig. 3c) reproduces the features seen in 200-nm-thick film (the bottom panel in Fig. 3a) well, indicating that the strain effect on the structural properties from the substrates is negligible. These results are direct evidence that the chemical pressure provided by the dopant is the origin of the observed change and that the growth



**Figure 3.** Universal structural properties for RE-substituted BiFeO<sub>3</sub> (RE = Sm, Gd, Dy). a) Normalized XRD intensities of  $(0, \frac{1}{4}, \frac{7}{4})$  (filled square, denoted as  $\frac{1}{4}$ , or  $\frac{1}{4}$  spot) and  $(0, \frac{1}{2}, 2)$  (open square, denoted as  $\frac{1}{2}$ , or  $\frac{1}{2}$  spot) XRD superstructure spots and  $\varepsilon_{33}$  at zero bias (black dot) as a function of RE dopant composition. b) All data in (a) are plotted against  $r_{ave}$ . The ionic radii in twelve coordination are 1.36 Å for Bi<sup>3+</sup>, 1.28 for Sm<sup>3+</sup>, 1.27 for Gd<sup>3+</sup>, and 1.24 for Dy<sup>3+</sup> [22]. This change in  $r_{ave}$  corresponds to the change in the Goldschmidt tolerance factor from 0.954 ( $r_{ave} = 1.36$  Å) to 0.947 ( $r_{ave} = 1.34$  Å) with 0.645 and 0.14 Å for the ionic radii of Fe<sup>3+</sup> and O<sup>2-</sup>, respectively. c) Normalized XRD intensities of the  $\frac{1}{4}$  and  $\frac{1}{2}$  XRD spots and  $\varepsilon_{33}$  at zero bias (black dot) plotted against the dopant compositions for 400-nm-thick Sm-substituted BFO grown on (001) LSAT, (001) STO, and (110)<sub>ortho</sub> DSO substrates. The trends observed here are also reproduced by individual composition films [24, 25].





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**Figure 4.** Phase diagram for RE-substituted BiFeO<sub>3</sub> (RE = Sm, Gd, Dy). a) Contour plots of intensities (counts per s) of  $(0, \frac{1}{2}, 2)$  ( $\frac{1}{2}$  spot, upper panel) and  $(0, \frac{1}{4}, \frac{7}{4})$  spots ( $\frac{1}{4}$  spot, bottom panel) as functions of temperature and  $r_{ave}$  for the Sm-substituted BiFeO<sub>3</sub> composition spread thin films. b) Proposed phase diagram for (Bi<sub>1-x</sub>RE<sub>x</sub>)FeO<sub>3</sub>. The black line represents the structural phase boundary between the rhombohedral (in blue) and the orthorhombic (in green) structural phases. At lower temperature side, the  $\frac{1}{4}$  spot is observed in the region in light blue. The double hysteresis loop behavior (see text and Fig. 5) emerges in the region in dark green.

processes or the substrate effect has little to do with the observed change in the structural properties.

To further investigate the phase stability and the role of the superstructures in determining the functional behavior, we also tracked the structural evolution as a function of temperature using the 2D XRD images across the composition spreads. In Figure 4a, we show contour plots of the  $(0, \frac{1}{4}, \frac{7}{4})$  and the  $(0, \frac{1}{2}, 2)$  XRD spot intensities as functions of temperature and the average ionic radius  $r_{ave}$  for the case of the Sm-substituted BFO thin films, in order to closely monitor the occurrence of the PbZrO<sub>3</sub>-type structure and the orthorhombic structure, respectively. The intensities are color-coded by the side bar. As the temperature is raised from room temperature, the  $\frac{1}{4}$  spot gradually decreases in intensity, while the  $\frac{1}{2}$  spot intensity gets enhanced. This indicates that on the higher temperature side, the orthorhombic phase is the stable phase. More importantly, the same rhombohedral to orthorhombic structural phase transition induced by RE substitution occurs with increasing temperature. Essentially the same contour plots of the  $(0, \frac{1}{4}, \frac{7}{4})$  and the  $(0, \frac{1}{2}, 2)$  XRD spot intensities are observed for the Dy-substituted BFO (see Supporting Information, Fig. S2), indicating again that the average ionic radius is the critical parameter that governs the structural properties of RE-substituted BFO. Based on this, we arrive at a universal phase diagram for REsubstituted BFO, as illustrated in Figure 4b. On the lower temperature side, the composition region in light blue where the local region gives rise to the  $\frac{1}{4}$  spot is seen to "bridge" the FE rhombohedral phase regions in blue and the orthorhombic phase in green. This bridging phase has been previously shown to result in lattice incommensuration at the rhombohedral-orthorhombic phase boundary.<sup>[24]</sup> As the temperature is elevated, the composition region with the  $\frac{1}{4}$  spot phase disappears, and the orthorhombic phase lies right adjacent to the FE region.

The fact that the structure related to the  $\frac{1}{4}$  spot are only seen in the local domains of the film probably indicates that in the composition region associated with the  $\frac{1}{4}$  spot, there are some other

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interactions competing with the ferroelectric one in the rhombohedral phase. Judging from the observation that the  $\frac{1}{4}$  spot originates from the antiparallel cation displacements, we believe that the competing interaction is analogous to the AFE state. The competition of the interactions disappears as the structure is changed into the orthorhombic phase, since in the orthorhombic phase neither FE nor AFE phases are stable as we discuss below.

The ferroelectric properties display concomitant evolution when the material undergoes the structural transition, and hence the ferroelectric properties of RE-substituted BFO also exhibit a universal behavior. This is shown in Figure 5 where room-temperature polarization hysteresis loops are plotted for various RE substituting concentrations such that the  $r_{ave}$  is the same for each group of curves. For each  $r_{ave}$ , the hysteresis loops collapse together, and the general shape and ferroelectric character of the hysteresis loop are constant. This indicates that the average ionic radius is the universal parameter to

describe not only the structural, but also the ferroelectric properties. As we cross the structural boundary drawn with a black line in Figure 4b, which is located at  $r_{ave} = 1.35$  Å at room temperature, the polarization hysteresis loop consequently exhibits a transition from single to double hysteresis loops with decreasing  $r_{\rm ave}$  as shown in Figure 5. The corresponding Goldschmidt tolerance factor for this  $r_{ave}$  is 0.9509. (For pure BFO, the tolerance factor is 0.954.) For the FE composition region immediately adjacent to the transition ( $r_{ave} > 1.35$  Å), the FE square-shaped hysteresis loops with saturated polarizations of  $70 \,\mu\text{C} \,\text{cm}^{-2}$  are observed. As one approaches the transition  $(r_{\rm ave} \sim 1.35$  Å), first the hysteresis loop becomes distorted and then develops into a fully developed doubled hysteresis loop beyond the transition ( $r_{ave} < 1.35$  Å). It is important to point out that in the orthorhombic phase, the value of saturated polarization remains relatively unchanged at  $\sim 70 \,\mu C \, cm^{-2}$ .

The evolution of the measured  $\varepsilon$ –*E* (dielectric constant–electric field) curve is also consistent (see Supporting Information, Fig. S3): the double-humped  $\varepsilon$ –*E* curve before the structural



**Figure 5.** Universal behavior in polarization hysteresis loops across the structural transition for RE-substituted BiFeO<sub>3</sub> thin films (RE = Sm, Gd, Dy). Room-temperature polarization hysteresis loops for 200-nm-thick RE-substituted BiFeO<sub>3</sub> thin films are plotted for  $r_{ave}$ . For each  $r_{ave}$ , the hysteresis loops collapse into a single curve. This clearly demonstrates universal behavior in ferroelectric properties of RE-substituted BiFeO<sub>3</sub>. The  $r_{ave}$  are calculated using 1.36 Å for Bi<sup>3+</sup>, 1.28 for Sm<sup>3+</sup>, 1.27 for Gd<sup>3+</sup>, and 1.24 for Dy<sup>3+</sup> [22].



transition develops into quadruple-humped curves beyond the transition. The same single-to-double hysteresis loop transition behavior is also seen as a function of the temperature as shown in Figure 6. We associate this transition with the rhombohedral-toorthorhombic structural transition using an increase in intensity of the  $\frac{1}{2}$ {010} XRD spot with temperature (Fig. 6a). Figure 6b-f displays the temperature dependence of the polarization hysteresis loops and  $\varepsilon$ -E curves measured for the 12% Sm-substituted BFO thin film whose average A-site ionic radius is 1.3505 Å. At room temperature (Fig. 6b), the square-shaped hysteresis loop and the corresponding two-humped  $\varepsilon - E$  loop are observed confirming the ferroelectric state of the film. As temperature is increased up to 175 °C, the hysteresis loop begins to get distorted and turns into a fully developed doubled hysteresis loop on the higher temperature side. Although high leakage current precludes us from attaining proper hysteresis loops at 175 °C, the transition from the single to double hysteresis loop is clearly seen in the  $\varepsilon$ -E curves. The temperature region where the double hysteresis loop is observed coincides with the region where the  $\frac{1}{2}$  spot is prominent. This is another confirmation that the double hysteresis loop is observed across the rhombohedral to orthorhombic transition boundary. These results further support the phase diagram depicted in Figure 4b as the universal behavior in A-site-substituted BiFeO<sub>3</sub> controlled by a single parameter, namely the average A-site ionic



**Figure 6.** Temperature-induced single-to-double hysteresis loop transition. a) Temperature dependence of the relative intensity of a  $(0, \frac{1}{2}, 2)$  XRD spot for 12% Sm-substituted BiFeO<sub>3</sub> thin films ( $r_{ave} = 1.3505$  Å). b–f) Evolution in polarization hysteresis loops and  $\varepsilon$ –*E* curves for the same sample as a function of temperature. The polarization hysteresis loops are measured at 25 kHz. The  $\varepsilon$ –*E* curves are obtained with an AC signal of 80 mV at 100 kHz. The corresponding temperatures are also marked in (a).



radius. The double hysteresis loop was found to remain intact after  $10^5$  cycles of application of switching field of  $\pm 625$  kV cm<sup>-1</sup>. Thus, we exclude the possibility that the double hysteresis loops is from either domain-wall pinning or aging-related phenomena as occasionally observed in some ferroelectric materials.<sup>[30,31]</sup>

To attain insight on the structural transition and the origin of the intrinsic double hysteresis behavior, we have performed firstprinciples total-energy calculations to identify low-energy structures of pure BFO that are potentially favorable with RE substitution on the Bi site. Using the G-type antiferromagnetic (AFM) cubic BFO lattice as a reference structure, we computed the phonon dispersion to identify unstable modes that act as generators of low-energy low-symmetry structures. Here, we focus on the zone-center polar mode  $\Gamma_4^-$ , the alternating polar displacement modes MAFE and XAFE, and the oxygen octahedron rotation modes  $R_4^+$  and  $M_3^+$ , as shown in Figure 7a. The ferroelectric bulk ground state R3c structure is obtained through combination of  $\Gamma_4^-[111]$  and  $R_4^+[111]$ , with a computed polarization of  $90 \,\mu\text{C} \text{ cm}^{-2}$  along [111]. For each structure considered, we optimize all lattice parameters as a bulk phase since it is unlikely that the epitaxial strain from the substrate plays an important role in the present samples as we showed in Figure 3c.

Initially, we explored the possibility that the orthorhombic phase

at RE concentrations just beyond the phase boundary is intrinsically antiferroelectric. To search for possible AFE structures in the BFO lattice, we have frozen in antiferroelectric MAFE and X<sub>AFF</sub> modes. Table 1 shows that the energy cost for the resulting structures relative to the ground state R3c phase is greater than 500 meV f.u.<sup>-1</sup> (f.u. = formula unit). In contrast, the structures obtained by freezing in various combinations of oxygen octahedron rotation modes are seen to be much more favorable. We also calculated the energy of BFO in the AFE Pbam type structure exhibited by PbZrO<sub>3</sub>. However, this structure is also found to be energetically unfavorable; in any case, it is observed only as a minority phase and primarily at RE concentrations below those of the phase boundary. The structure closest in energy to the ground state is the orthorhombic Pnma structure,<sup>[32]</sup> in agreement with the structures observed for paraelectric RE-ortho ferrite (RE = Sm, Gd, Dy) in bulk.<sup>[16,17,33-35]</sup> This structure, a very common one for perovskite oxides, is generated by combination of the oxygen octahedron modes  $R_4^+[110]$  and  $M_3^+[z]$ , which then induce an XAFE mode with alternating Bi displacements along the [110] direction.

In order to explain the occurrence of the double hysteresis behavior in the non-polar Pnma structure, we need to consider the effect of an applied electric field. Low fields will induce a linear polarization, determined by the Pnma dielectric response. At higher fields, one possibility is that the Pnma phase will behave as





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**Figure 7.** Theoretical investigation of stability of orthorhombic BiFeO<sub>3</sub> (BFO) lattice. a) Selected unstable modes of the G-type antiferromagnetic cubic perovskite reference structure of BFO. Small solid blue circles are oxygen atoms, open circles are Fe atoms, and solid black circles are Bi atoms. Green arrows show Bi displacements and red arrows show oxygen displacements (not to scale). b) Schematic of the energy functionals of the ferroelectric rhombohedral phase (solid line) and the nonpolar orthorhombic phase (dotted line) versus *P* near  $r_{ave\_critical}$ . For E = 0, the polar phase is higher in energy by  $\Delta U$ . For  $E > E_c$ , the polar phase is lower in energy than the non-polar phase. c)  $E_c$  of the double hysteresis loops for Sm-substituted BFO. The solid (and becoming dotted) black line shows the theoretical result with the values  $r_{ave\_critical} = 1.35$  Å and  $P = 70 \,\mu$ C cm<sup>-2</sup> taken from experiment. The experimental values for  $E_c$  are obtained from the double hysteresis loop at each  $r_{ave}$ , as seen in the inset. The theory line is in agreement with the general behavior of the experimental values. The part of the theory line is dotted to indicate that below some critical average ionic radius, we expect there to be a departure from the behavior predicted using our simple model.

a conventional antiferroelectric, with a discontinuous transition to a polar phase where the alternating cation displacements of the  $X_{AFE}$  mode align due to the field. The space group resulting from the combination of  $R_4^+[110]$  and  $M_3^+[z]$  and uniform Bi displacement along [110] is Pmc2<sub>1</sub>. Optimization of BFO in this structure yields, as shown in Table 1, a phase with unit cell volume 59 Å<sup>3</sup>, polarization of 84  $\mu$ C cm<sup>-2</sup>, and energy 66 meV f.u.<sup>-1</sup> above the ground state. The electric field required to reach this phase is estimated by equating the energy density of the polar phase 66 meV f.u.<sup>-1</sup>/59 Å<sup>3</sup> to its electric energy gain  $-E \cdot P$ . The result E = 2 MV cm<sup>-1</sup> is much larger than the field scale for

unlikely scenario. Our first-principles analysis shows that instead, at a much lower electric field, there is a structural transition from the non-polar orthorhombic Pnma back to the polar rhombohedral phase, and this is responsible for the double hysteresis loop. This is schematically depicted in Figure 4b. In this model, we define  $E_c$  to be the electric field necessary to drive the nonpolar orthorhombic phase to the polar rhombohedral one. We estimate  $E_c$  by approximating the difference in energy between Pnma and R3c structure per volume ( $\Delta U$ ) as a linear function of the average A-site ionic radius rave:

the double hysteresis loop, making this an

$$\Delta U(r_{\rm ave}) = \Delta U_0 - k(r_{\rm ave} - r_{\rm Bi})$$
(1)

verage ionic radius, we where k is a constant and  $\Delta U = 14 \text{ meV}/59 \text{ Å}^3$  is the computed energy density difference at  $r_{\text{ave}} = r_{\text{Bi}} = 1.36 \text{ Å}$  (pure BiFeO<sub>3</sub>). Since the energy difference is zero at the critical average ionic radius  $r_{\text{ave}} = c_{\text{ritical}}$ , we calculate

$$k = \Delta U_0 / (r_{\text{ave}\_\text{critical}} - r_{\text{Bi}})$$
<sup>(2)</sup>

**Table 1.** Low-energy alternative structures of G-type antiferromagnetic BiFeO<sub>3</sub>. The alternative structures are specified by the modes that combine to produce the given space group symmetry. The structures are fully optimized, except for the cases of P4/mbm and I4/mcm, for which only the atomic displacements were optimized with fixed lattice parameters corresponding to an ideal cubic perovskite lattice constant  $a_0 = 3.847$  Å. Lattice constants (a,b,c) are given in Å. V denotes volume of the unit cell and  $\Delta U$  is the difference in energy with respect to the rhombohedral R3c BiFeO<sub>3</sub> ground state per five-atom formula unit.

Space Group	Modes	Lattice constants [Å]	V [Å <sup>3</sup> f.u. <sup>-1</sup> ]	$\Delta U~[{ m meV}~{ m f.u.}^{-1}]$
Pm3m		(3.847, 3.847, 3.847)	56.94	861
P21/m	$X_{AFF}([\overline{1}10])$	(3.936, 3.936, 7.684) $\gamma = 86.3^{\circ}$	59.40	573
Cmmm	M <sub>AFE</sub> ([110]&[010])	(7.890, 7.858, 3.796)	58.85	538
P4/mbm	M <sub>3</sub> <sup>+</sup> ([001])	(5.440, 5.440, 3.847)	56.96	425
l4/mcm	R <sub>4</sub> <sup>+</sup> ([100])	(7.694, 5.440, 5.440)	56.96	354
R <del>3</del> c	R <sub>4</sub> <sup>+</sup> ([111])	(5.389, 5.389, 5.389) $\alpha = \beta = \gamma = 61.6^{\circ}$	57.34	208
Cmcm	M <sub>3</sub> <sup>+</sup> ([001]), R <sub>4</sub> <sup>+</sup> ([100])	(7.706, 7.732, 7.736)	57.62	173
P4mm	$\Gamma_{4}^{-}([001])$	(3.677, 3.677, 4.643)	62.78	159
Pbam	$\Gamma_{25}, R_{25}, (\frac{1}{2}, \frac{1}{2}, 0) \frac{\pi}{a} \sum_{3}, (110) \frac{\pi}{a} M'_{5}$	(5.480, 11.162, 7.680)	58.73	153
Pmc2 <sub>1</sub>	$M_3^+([001]), R_4^+([110]), \Gamma_4^-([110])$	(5.519, 5.511, 7.720)	58.71	66
Pnma	M <sub>3</sub> <sup>+</sup> ([001]), R <sub>4</sub> <sup>+</sup> ([110])	(5.372, 5.589, 7.690)	57.71	14
R3c	$\Gamma_4^-([111]),  R_4^+([111])$	(5.525, 5.525, 5.525) $\alpha\!=\!\beta\!=\!\gamma\!=\!59.8^\circ$	59.31	0



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An applied electric field favors the polar phase with nonzero polarization *P* by the coupling energy  $- E(r_{ave}) \cdot P$ , so that

$$E_{\rm c}(r_{\rm ave}) = (\Delta U_0/P)((r_{\rm ave} - r_{\rm Bi})/(r_{\rm ave\_critical} - r_{\rm Bi}) - 1) \tag{3}$$

For Sm substitution, with  $r_{ave\_critical} = 1.35$  Å and  $P(r_{ave\_critical}) = 70 \,\mu\text{C cm}^{-2}$  taken from experiment, the calculated  $E_c(r_{ave})$  is in good agreement with experimentally determined values, as seen in Figure 7c. The increase in  $E_c(r_{ave})$  with decreasing  $r_{ave}$  originates from the energy difference between the Pnma and the R3c phases, which becomes larger as the dopant composition is increased. The fact that the value of the saturated polarization for the double hysteresis loop changes smoothly through the transition supports the idea that the electric-field-induced metastable phase is the substituted R3c phase.

An important consequence of this sequence of electric-fieldinduced phase transformation events is the enhancement of  $d_{33}$  at the boundary. Similar electric-field-induced transformation and the resulting enhancement of piezoelectric response have been observed in Pb-based ferroelectric materials at morphotropic phase boundaries<sup>[1-5]</sup> such as  $Pb(Zr,Nb)O_3$ -PbTiO<sub>3</sub>,  $Pb(Zr,Ti)O_3$ , and Pb(Mg,Nb)O<sub>3</sub>-PbTiO<sub>3</sub>. We believe that the enhancement in the electromechanical properties we see in the present REsubstituted BFO thin films<sup>[13]</sup> is of similar nature. At the structural boundary of the substituted BFO, the lattice strain caused by the structural transformation is estimated to be  $\sim 1\%$  based on the difference in the lattice parameter 0.04 Å along the [001]<sub>STO</sub> direction between the rhombohedral and the orthorhombic phase (Fig. 2b). Taking into account a small spread in  $E_c$  present in samples due to local variation in dopant concentration (estimated to be  $\pm 1\%$  or better), the 1% strain corresponds to 750–1000 pm  $V^{-1}$ . This value is up to an order of magnitude larger than our observed  $d_{33}$  value of 110 pm V<sup>-1</sup> at the boundary.<sup>[18]</sup> Given that some degree of hysteresis is expected at the electric-field-induced transition, and that the clamping effect is known to significantly reduce  $d_{33}$  in epitaxial thin films compared to bulk,<sup>[36]</sup> we believe the agreement is not unreasonable. We have previously also observed occurrence of nanodomains at this critical Sm composition.<sup>[24]</sup> The nanodomains are also expected to be playing a role in enhancing the piezoelectric properties. Our model suggests that unclamped single crystals with precisely tuned composition at this boundary should exhibit an extremely large piezoelectric response. To date, however, such studies have not been possible due to the leakage problem and the difficulty in controlling the composition with high accuracy in BiFeO<sub>3</sub> single crystals.<sup>[7]</sup>

# 3. Conclusions

We have observed universal behaviors in structural and ferroelectric properties in RE-substituted BFO materials (RE = Sm, Gd, Dy) by systematically tracking their structural and ferroelectric properties across composition spreads. As the RE concentration is increased, the rhombohedral ferroelectric phase undergoes a phase transition to a paraelectric orthorhombic phase, exhibiting a double hysteresis loop with a high saturated polarization of 70  $\mu$ C cm<sup>-2</sup>. This behavior is universally observed for all RE dopants studied, and is described as a function of the average A-site ionic Makrials Views www.MaterialsViews.com

radius. Using the first principles calculations, we propose that the electric-field-induced structural transformation from the orthorhombic to rhombohedral phase is the origin of the double hysteresis loop and the concomitant enhancement of the electromechanical properties across the structural transition. Because chemical-modification-induced structural transitions are not be uncommon, the present observation of enhanced electromechanical properties due to an electric-field-induced transition in a simple perovskite-based system provides a guideline for search of other piezoelectric materials with enhanced properties at first-order structural transitions.

# 4. Experimental

Epitaxial ( $Bi_{1-x}RE_x$ )FeO<sub>3</sub> thin films (RE = Sm, Gd, Dy) were fabricated on (001) LSAT, (001) SrTiO<sub>3</sub>, and (110)<sub>ortho</sub> DyScO<sub>3</sub> substrates by pulsed laser deposition (Pascal Inc.). For composition spreads, composition gradient from x = 0 to x = 0.3 was created over a 6 mm length along one direction of the sample. Sintered ceramic targets of Bi1.1FeO3 and (RE)FeO3 were ablated with an excimer KrF laser with a wavelength of 248 nm (Thin Film Star). Temperature and oxygen pressure were kept at 590  $^\circ\text{C}$  and 25 mTorr during the depositions. 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 was 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, the X-ray beam was focused to a 0.5 mm diameter. For electrical characterization, an epitaxially-grown SrRuO3 layer was used as the bottom electrode. A 100-nm-thick Pd layer was sputtered and patterned by a lift-off process into  $50\,\mu m$  by  $50\,\mu m$  top electrode pads at room temperature. Polarization hysteresis loops were measured at 25 kHz with a Radiant Premiere II loop analyzer. Dielectric constant-electric field curves were taken with an HP 4275A LCR meter with an AC signal of 80 mV at the frequency of 100 kHz. The values of the maximum  $d_{33}$  values were obtained using piezoforce microscopy with a Pt/Ir coated cantilever at room temperature.

First-principles calculations were performed using the density functional theory within the local spin-density approximation (LSDA)+U method as implemented in the Vienna Ab-initio Simulation Package VASP-4.6 [37,38]. We used the Liechtenstein [39] implementation of rotationally invariant LSDA+U with effective on-site Coulomb interaction U = 5 eV and the effective on-site exchange interaction J = 1 eV to treat the localized d electron states in Fe [40]. We used projector-augmented wave potentials (PAW) [41,42] and explicitly treated 15 valence electrons for Bi,  $5d^{10}6s^{2}6p^{3}$ , 14 for Fe,  $3p^63d^64s^2$ , and 6 for O,  $2s^22p^4$ . For most structures generated by X, M, and/or R modes (including Pnma), we use a  $\sqrt{2} \times \sqrt{2} \times 2 a_0$ supercell with a  $6 \times 6 \times 4$  Monkhorst-Pack k-point grid [43]. For the rhombohedral R3c and orthorhombic Pbam structures, the Monkhorst-Pack grids are  $6 \times 6 \times 6$  and  $4 \times 2 \times 3$ , respectively. The cutoff energy for the plane wave basis set is 800 eV. Gaussian broadening of the partial occupancies for each wavefunction is 0.05 eV. To search for the lowest energy structure in a given space group, we perform structural relaxation with the conjugate gradient algorithm and relax the ions until the Hellmann–Feynman forces are less than  $10^{-3}$  eV Å<sup>-1</sup>. Calculations of the phonon dispersion for ideal cubic perovskite G-type antiferromagnetic (AFM) BiFeO3 are performed with the frozen phonon method in a  $\sqrt{2} \times \sqrt{2} \times 2 a_0$  supercell with a  $4 \times 4 \times 2$  Monkhorst-pack grid and an energy cutoff of 550 eV. Phonon frequencies obtained at  $\Gamma$ , R, M, and X are interpolated in the full Brillouin zone using the Anaddb package in ABINIT. We calculate polarization and Born effective charges  $q_{Bi} = 6.2$ ,  $q_{Fe} = 3.9$ ,  $q_{O_{\perp}} = -2.5$ ,  $q_{O_{\parallel}} = -3.4$  |e| (the parallel direction being along the Fe-O-Fe bond) by the Berry phase method [44,45], where we use a  $3 \times 3 \times 3$ Monkhorst-pack grid in self consistent and k-point mesh twice as dense in the polarization calculations, respectively. We estimate polarization in the polar Pnma (Pmc2<sub>1</sub>) using  $\vec{P} = \sum q_i \vec{u}_i$  where  $q_i$  is the Born effective charge





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for the *i*-th ion and  $\vec{u}_i$  is its displacement with respect to the ideal perovskite position.

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