

Microstructure-electromechanical property correlations in rare-earth-substituted BiFeO₃ epitaxial thin films at morphotropic phase boundaries

Ching-Jung Cheng,^{1,a)} Daisuke Kan,^{2,b)} Varatharajan Anbusathaiah,¹ Ichiro Takeuchi,² and Valanoor Nagarajan¹

¹*School of Materials Science and Engineering, University of New South Wales, New South Wales 2052, Australia*

²*Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA*

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Structure-electromechanical property correlations in rare-earth (RE)-substituted (001) BiFeO₃ (BFO) epitaxial thin films have been investigated. Quantitative piezoelectric coefficient (d_{33}) and dielectric constant (ϵ_{33}) measurements, in conjunction with selected area electron diffraction, reveal that the enhancement in d_{33} and ϵ_{33} at the morphotropic phase boundary (MPB) of the RE-substituted films (RE=Dy³⁺, Gd³⁺, and Sm³⁺) is correlated with the presence of a competing intermediate antipolar phase with the rhombohedral ferroelectric and nonpolar orthorhombic phase. This leads to a complex nanoscale phase coexistence at the MPB. Extending the studies to RE=La³⁺ case, we find the nanoscale phase coexistence to be less pronounced. This explains the lack of increase in d_{33} for the La³⁺-substituted BFO films, in contrast to the Dy³⁺, Gd³⁺, and Sm³⁺-substituted films. © 2010 American Institute of Physics. [doi:10.1063/1.3520642]

BiFeO₃ (BFO) has recently attracted immense scientific attention as an environmentally friendly Pb-free piezoelectric.^{1,2} Recently, we reported on the discovery of a morphotropic phase boundary (MPB) in Sm³⁺-substituted BFO by combinatorial thin-film synthesis strategy.³ This particular boundary represents a structural transition from the ferroelectric rhombohedral phase to an orthorhombic phase exhibiting a double hysteresis in polarization versus electric field (P - E) loops at an approximate composition of Bi_{0.86}Sm_{0.14}FeO₃, with enhancements in the dielectric constant ϵ_{33} and out-of-plane piezoelectric coefficient d_{33} (Refs. 3 and 4). Subsequent investigations using smaller trivalent A-site rare-earth (RE³⁺) dopants (RE=Dy, Gd, and Sm) revealed that the structural transition and concomitant change in the ferroelectric properties occur independently of the RE dopant species. Furthermore, the composition of this boundary was able to be tuned by the systematic variation in the average A-site ionic radius. This showed that the chemical pressure effect provided by the substitution is the driving force leading to the formation of the boundary.⁵

While the origin of the enhanced electromechanical response was theoretically proposed to be an electric-field induced transformation from the orthorhombic phase to the polar rhombohedral phase,⁵ the picture of the MPB in terms of its microstructural makeup that facilitates such a transformation has not been discussed. It is of fundamental interest to investigate whether there is a common “structural fingerprint” irrespective of the type of the RE dopant, whose occurrence would substantially enhance the electric-field induced electromechanical susceptibilities. This particular goal of identifying a unifying structural correlation for the enhanced electromechanical properties at the MPB forms the motivation of this letter. We find a clear evidence of a nano-

scale phase mixture for MPBs created by the substitution of Bi³⁺ ions with smaller RE dopants, (here Dy³⁺, Gd³⁺, and Sm³⁺), composed of the parent BFO rhombohedral lattice, an intermediate antipolar PbZrO₃ (PZO)-like phase,⁶ and a cell-doubled orthorhombic phase. We propose that this nanoscale phase mixture acts as a facile platform for the electric-field induced phase transformation. In contrast, for dopants such as La³⁺, whose ionic radius is comparable to that of Bi³⁺, there is no clear signature of the nanoscale phase coexistence at the phase boundary, and consequently, no enhancement in d_{33} is observed.

The set of films used here were fabricated on SrTiO₃ (STO) substrates in an analogous way to our previous study.⁵ The cross-sectional transmission electron microscope (TEM) specimens were prepared by focused ion beam microscopy (FEI, Nova 200 Nanolab) followed by the “lift-out” technique by a micromanipulator. All electron diffraction patterns were recorded at the same exposure time on a 200 kV TEM (Philips, CM 200) with a double-tilt holder. The diffraction patterns labeled here are indexed using the pseudocubic notation. It should be noted that the 200 nm thick films on STO are almost entirely or at least partially relaxed,³ and thus, the epitaxial strain is playing a little role.⁵

We begin by examining the dielectric response of Dy³⁺, Gd³⁺, and Sm³⁺-substituted BFO thin films. Figure 1(a) shows the ϵ_{33} - E hysteresis loops for three representative Dy³⁺-substituted BFO compositions. These compositions (6%, 8%, and 10%) were selected to illustrate the clear evolution in the loop shape as a function of the dopant composition: from the typical ferroelectric double-humped ϵ_{33} - E curve (6%) through the MPB composition (8%) to a quadruple-humped curve (10%) beyond the MPB. The same trend was observed for the RE=Sm³⁺ (Ref. 5) and Gd³⁺ cases. The presence of the four humps in the ϵ_{33} - E loop for compositions in the paraelectric orthorhombic phase is supported by the corresponding observation that these compositions also show a double hysteresis in the P - E loops.⁵ We

^{a)}Electronic mail: ching-jung@unswalumni.com.

^{b)}Present address: Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan. Electronic mail: dkan@sci.kyoto-u.ac.jp.

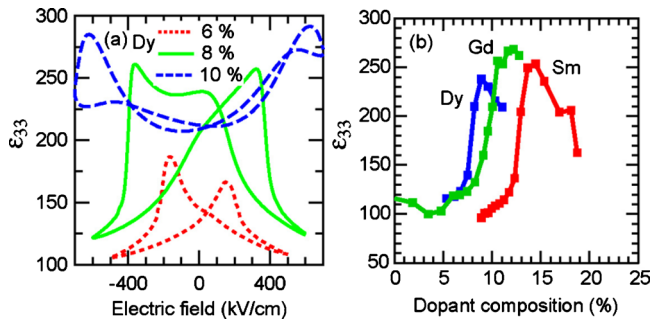


FIG. 1. (Color online) (a) ϵ_{33} - E loops for 6%, 8%, and 10% Dy³⁺-substituted BFO films displaying the enhancement of dielectric constant. It reaches a maximum value of ~ 250 as one approaches the MPB. The loops were measured with an ac voltage of 80 mV at 100 kHz. (b) ϵ_{33} vs composition for Dy³⁺, Gd³⁺, and Sm³⁺-substituted BFO films at zero applied field showing a peak at their respective MPB concentrations.

note that the clear double-hysteresis P - E (quadruply humped ϵ_{33} - E) loops are only shown in the nonpolar orthorhombic phase well beyond the MPB, where no PZO-like structural phase is observed (as discussed in Fig. 3). There is a continuous enhancement of the dielectric constant reaching maximum values of 250 at the phase boundary compositions of 8% for Dy³⁺, 12% for Gd³⁺, and 14% for Sm³⁺ as plotted in Fig. 1(b). The dielectric leakage current (not shown) is also found to be reduced toward the MPB composition. This confirms that the observed increase in the dielectric constant is not due to the increased leakage.

Figure 2(a) shows the d_{33} loops for Dy³⁺-substituted BFO for the same dopant concentrations in Fig. 1(a). Figure 2(b) plots the d_{33} values as a function of the dopant composition for Dy³⁺, Gd³⁺, and Sm³⁺-substituted BFOs. We plot here high field (400 kV/cm) values to highlight the maximum d_{33} values measured. The remanent d_{33} (i.e., zero-field) values were typically 20% lower. At the MPB compositions, an enhancement in the piezoelectric response is observed for all three dopants with the value reaching 110 pm/V for the Sm-substituted case. For compositions beyond MPB, there is not only a drastic drop in the d_{33} response but also a change in the shape of the loop.

Next, we performed selected area electron diffraction (SAED) experiments to explore microscopic links between structural changes and the aforementioned evolution in the functional properties (Figs. 1 and 2). In Fig. 3, we show [100] zone axis diffraction patterns (ZADP) taken for

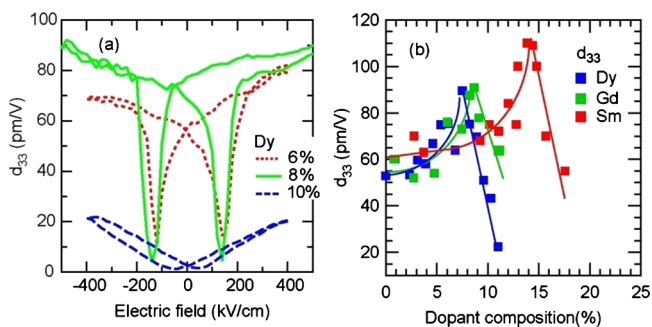


FIG. 2. (Color online) (a) Piezoelectric coefficient d_{33} vs electric-field hysteresis loops for 6%, 8%, and 10% Dy³⁺-substituted BFO films. Compositions were chosen to allow direct visual comparisons of the piezoelectric response as one straddles across the MPB. (b) Piezoelectric coefficient d_{33} for Dy³⁺, Gd³⁺, and Sm³⁺-substituted BFO films at 400 kV/cm as a function of RE concentration. The lines are a guide to the eye to highlight the peaking of d_{33} .

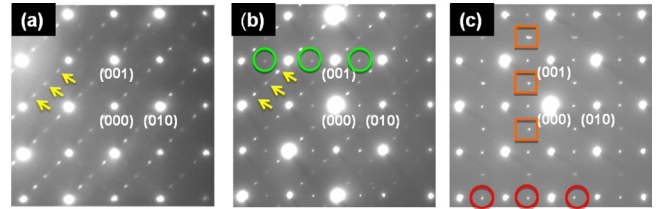


FIG. 3. (Color online) SAED analysis for Dy³⁺-substituted BFO thin films: (a) shows the pattern with 1/4{011} spots (arrowed) before MPB, (b) shows the pattern with the coexistence of 1/4{011} (arrowed) and 1/2{010} (circled) spots at MPB, and (c) shows the pattern with 1/2{010} (circled) and 1/2{011} (boxed) spots in the cell-doubled orthorhombic structural phase beyond MPB. Identical series of patterns were also obtained for the Gd³⁺ and Sm³⁺-substituted samples.

Dy³⁺-substituted BFO at the compositions similar to the samples in Figs. 1(a) and 2(a). Figures 3(a)–3(c) correspond to the compositions before the MPB, at the MPB, and beyond the MPB, respectively. The first significant change (from the typical [100] ZADP for undoped BFO) is the appearance of 1/4{011} reflections [Fig. 3(a)]. These 1/4 spots (marked by arrows) are due to antipolar PZO-like clusters (~ 10 – 20 nm in size), which have risen from A-site cations displaced in an antiparallel fashion along the [011] direction. This gives rise to the quadrupling of the unit cell with dimensions of $\sqrt{2}a \times 2\sqrt{2}a \times 2a$, where a is the pseudocubic perovskite lattice parameter.⁷ Recent atomic displacement measurement of the antipolar phase has revealed that it is actually a lamellar of highly dense ferroelectric domains with alternating polarizations.⁶ It is important to point out that the PZO-like phase only appears in compositions before or at the MPB,⁶ and these compositions before the MPB that show the PZO-like phase do not show a double hysteresis P - E loop⁵ or four humps in ϵ_{33} - E loop or d_{33} - E loop (Figs. 1 and 2). Therefore, we conclude that the antipolar PZO-like phase does not possess the long-range order to influence the macroscopically observed hysteresis loops.

At the MPB composition [Fig. 3(b)], the picture is more complex with the coexistence of the parent rhombohedral ferroelectric phase, antipolar PZO-like phase (marked by arrows in yellow), cell-doubled orthorhombic paraelectric phase (circles in green). This is in remarkable agreement to the previously shown data for Sm³⁺-substituted BFO,⁴ and we also find the same structural evolution to occur for the Gd³⁺-substituted BFO case. We also note that this complex pattern is found for the entire film, not restricted to local regions unlike the PZO-like phase in Fig. 3(a). The strong lattice interactions between ferroelectric rhombohedral, cell-doubled orthorhombic, and an intermediate PZO-like phase (shown by intense diffraction spots) can lead to lattice incommensuration at the MPB,⁴ which provides a “facile platform” for an electric-field induced phase transformation. A similar scenario has been proposed for the well-known Pb-based MPB piezoelectrics^{8–10} where such a nanoscale phase mixture has been associated with a low-energy pathway for a polarization transition between the different polar axes, which results in enhanced piezoelectric properties.^{11,12} Therefore, we can conclude that the occurrence of such complex phase coexistence is the underlying structural fingerprint for the enhanced electromechanical properties observed for BFO substituted by the smaller RE dopants.

With more Dy³⁺ dopant added into the BFO system, cell-doubled orthorhombic phases signified by 1/2{010} (circled)

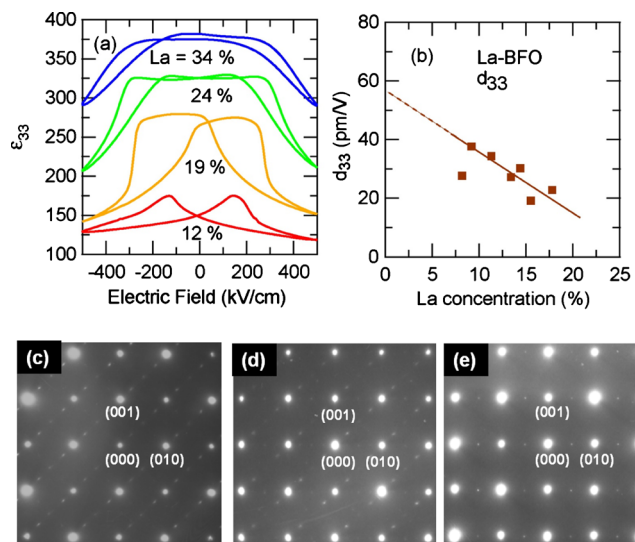


FIG. 4. (Color online) (a) ϵ_{33} - E loops for La^{3+} -substituted BFO across the structural boundary; (b) piezoelectric coefficient d_{33} for La^{3+} -substituted BFO at 400 kV/cm as a function of the La^{3+} concentration; (c) [100] ZADP of 14% La^{3+} -substituted BFO showing $1/4\{011\}$ spots; (d) [100] ZADP 23% La^{3+} -substituted BFO showing coexistence of weak $1/4\{011\}$ and $1/2\{010\}$ spots; and (e) [100] ZADP 26% La^{3+} -substituted BFO showing $1/2\{010\}$ spots only.

and $1/2\{011\}$ (boxed) reflections are observed throughout the entire sample [Fig. 3(c)]. The occurrence of both $1/2\{010\}$ and $1/2\{011\}$ reflections signifies that the orthorhombic phase is similar to the Sm^{3+} -substituted BFO with analogous crystallographic structural features.⁴

We have also investigated the La-substituted BFO thin films. Figure 4 summarizes our findings for the $\text{RE}=\text{La}^{3+}$ case, which reveals that there is no enhancement of the piezoelectric coefficient d_{33} in spite of a structural transition. We find that the rhombohedral to orthorhombic structural phase transition occurs at 23% La^{3+} , a much higher concentration compared to the smaller RE dopants discussed previously and with distinct differences in both functional and structural properties. Figure 4(a) shows the ϵ_{33} - E loops for a series of La^{3+} -substituted (001) BFO films across the structural boundary. No sharp quadruply-humped loop is observed as one crosses the boundary, which is in contrast to the case for $\text{RE}=\text{Dy}^{3+}$ in Fig. 1(a). In Fig. 4(b), we plot the d_{33} at 400 kV/cm for the La^{3+} -substituted BFO films as a function of La^{3+} concentration. The d_{33} value shows a monotonous decrease (down to almost zero) as one approaches the phase boundary, showing that there is no distinct increase in the electromechanical properties as opposed to the other smaller RE cases [seen in Fig. 2(b)], which is in agreement to previous reports.^{13,14}

We have examined the [100] ZADP of the three La-substituted BFO compositions across the phase boundary, i.e., before [Fig. 4(c); 14% La substitution], at phase boundary [Fig. 4(d); 23%], and for the orthorhombic phase [Fig. 4(e); 26%]. The diffraction patterns at the two ends of our composition series display certain features ($1/4$ ordering $\rightarrow 1/2$ ordering) similar to the Dy^{3+} -substituted BFO thin films (Fig. 3). The presence of $1/4$ superstructure spots indicates that a phase to isostructural PZO certainly forms initially. SAED patterns similar to our findings have also been observed in 20% La^{3+} -substituted BFO thin films on (entirely different) Si substrate,¹³ and thus any strain effects from the

underlying substrate as a cause can be excluded. However, the key difference between the La^{3+} -substituted system and the smaller RE^{3+} substituted systems is found in the ZADP for the phase boundary composition [Fig. 4(d)]. Here, the phase coexistence is distinctly weak as revealed by much fainter superstructure spots. The $1/2\{010\}$ spots are barely visible, which implies that the microstructural platform that would facilitate direct lattice interactions between the antipolar PZO-like phase and the rhombohedral/orthorhombic phase is absent here. Thus, the required domain mixture in order to facilitate electric-field induced transformation does not occur: no peak in the electromechanical properties is observed [comparing Fig. 4(d) to Fig. 3(b)]. Beyond the structural transition [Fig. 4(e)], superstructure reflections have almost disappeared with much weaker intensity of $1/2\{010\}$ reflections only. The absence of the $1/2\{011\}$ reflections beyond the structural transition implies that the structure of the La^{3+} -substituted BFO has a dimension of $a \times a \times 2a$, instead of $\sqrt{2}a \times \sqrt{2}a \times 2a$ as observed for the Dy^{3+} -substituted case in Fig. 3(c).

In summary, we report a correlation between the occurrence of a nanoscale phase coexistence and the enhanced electromechanical properties observed for (smaller) RE-substituted BFO MPB systems. We believe that this unique microstructure provides a facile platform that mediates the previously proposed electric-field phase transition from the orthorhombic phase to the ferroelectric rhombohedral phase. In contrast, we find that for La^{3+} (a same sized RE^{3+} ion as Bi^{3+}), there is a distinct lack of this phase coexistence and, consequently, the absence of enhancement in the electromechanical response.

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