Strain-Driven Nanoscale Phase Competition near the Antipolar–Nonpolar Phase Boundary in Bi$_{0.7}$La$_{0.3}$FeO$_3$ Thin Films

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Supporting Information

ABSTRACT: Complex-oxide materials tuned to be near phase boundaries via chemistry/composition, temperature, pressure, etc. are known to exhibit large susceptibilities. Here, we observe a strain-driven nanoscale phase competition in epitaxially constrained Bi$_{0.7}$La$_{0.3}$FeO$_3$ thin films near the antipolar–nonpolar phase boundary and explore the evolution of the structural, dielectric, (anti)ferroelectric, and magnetic properties with strain. We find that compressive and tensile strains can stabilize an antipolar PbZrO$_3$-like Pbam phase and a nonpolar Pnma orthorhombic phase, respectively. Heterostructures grown with little to no strain exhibit a self-assembled nanoscale mixture of the two orthorhombic phases, wherein the relative fraction of each phase can be modified with film thickness. Subsequent investigation of the dielectric and (anti)ferroelectric properties reveals an electric-field-driven phase transformation from the nonpolar phase to the antipolar phase. X-ray linear dichroism reveals that the antiferromagnetic-spin axes can be effectively modified by the strain-induced phase transformation. This evolution of antiferromagnetic-spin axes can be leveraged in exchange coupling between the antiferromagnetic Bi$_{0.7}$La$_{0.3}$FeO$_3$ and a ferromagnetic Co$_{0.9}$Fe$_{0.1}$ layer to tune the ferromagnetic easy axis of the Co$_{0.9}$Fe$_{0.1}$. These results demonstrate that besides chemical alloying, epitaxial strain is an alternative and effective way to modify subtle phase relations and tune physical properties in rare earth-alloyed BiFeO$_3$. Furthermore, the observation of antiferroelectric-antiferromagnetic properties in the Pbam Bi$_{0.7}$La$_{0.3}$FeO$_3$ phase could be of significant scientific interest and great potential in magnetoelectric devices because of its dual antiferroic nature.

KEYWORDS: BiFeO$_3$, Bi$_{1-x}$La$_x$FeO$_3$, antipolar, phase competition, thin films

INTRODUCTION

By perching a ferroic material near a phase boundary, it is possible to produce large susceptibilities under application of small external stimuli (e.g., thermal, electric field, magnetic field, etc.). For instance, giant dielectric/piezoelectric responses are obtained in ferroelectrics near morphotropic phase boundaries (MPBs). The majority of work on MPB systems has focused on polar–polar boundaries, and there is little work on other systems, such as polar–antipolar and antipolar–nonpolar boundaries. However, as we expand the realm of material systems that we study, more exotic structural boundaries are being found. For example, the multiferroic BiFeO$_3$ is one of the most widely studied ferroic materials in recent years because of its strong room temperature magneto-electric coupling between the ferroelectric and antiferromagnetic ordering, which makes it a promising candidate for low-power nano-electric and spintronic devices. Despite exceptional interest and study, the use of BiFeO$_3$ continues to be limited by its high electrical leakage current. The relatively small band gap (~2.7 eV), partially occupied d orbitals, and propensity to form point defects that can dope the lattice with charge all contribute to the undesirable leakage. In turn, there has been research on doping/alloying BiFeO$_3$ to mitigate electronic leakage/conduction, thus enhance the ferroelectric properties, and also as a potential pathway, to improve other properties, including lowering coercivity and increasing piezoelectric response and magnetoelectric coupling. For example, A-site alloying with rare earth elements (e.g., Sm, Dy, etc.) has been shown to significantly reduce electronic conduction and to improve the piezoelectric response by emulating MPB-like behavior.

In this regard, considerable attention has been devoted to Bi$_{1-x}$La$_x$FeO$_3$ solid solutions. This is mainly because La$^{3+}$ and Bi$^{3+}$ have nearly the same ionic radii, which enables perturbation of the ferroelectric order without greatly impacting the magnetic B site. Until recently, however, the nature, and
even the exact number, of structural phase transitions as a function of lanthanum content is still an open question. This is mainly because most studies have focused on relatively low fractions of lanthanum addition ($x \lesssim 0.2$) in hopes of maintaining ferroelectricity while lowering the leakage and coercivity. For $x \lesssim 0.2$, bulk $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ maintains the parent $\text{R}3\text{c}$ symmetry and exhibits improved ferroelectric properties. As the lanthanum content increases, things get more interesting as there is a reported polar-to-nonpolar phase transition. As noted, there remains disagreement over the exact nature of this phase progression from the ferroelectric $\text{R}3\text{c}$ to the paraelectric $\text{Pm}ma$ end members. For instance, first-principles calculations have predicted a direct transition from the rhombohedral $\text{R}3\text{c}$ to the orthorhombic $\text{Pm}ma$ phase akin to a MPB-like transition with several quasi-energy-degenerate fractions of lanthanum addition ($x \lesssim 0.2$). Note that we will use cubic or pseudocubic indices ($\text{f}f$) to denote orthorhombic indices. Following growth, epitaxial $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ films are grown on a range of substrates producing epitaxial strains that range from $-0.7\%$ to $+1.1\%$. It is found that compressive strain stabilizes a single-phase, antipolar PbZrO$_3$-type $\text{Pbam}$ orthorhombic phase, that tensile strain stabilizes a single-phase, nonpolar $\text{Pm}ma$ orthorhombic phase, and that growth with essentially zero strain results in a self-assembled nanoscale mixture of the two orthorhombic phases, wherein the relative fraction of each phase can be modified with film thickness. Subsequent investigation of the dielectric and (anti)ferroelectric properties reveals an electric-field-driven irreversible phase transformation from the nonpolar to the antipolar phase. X-ray linear dichroism and exchange coupling studies further reveal that the antiferromagnetic-spin orientation in the $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ thin films and subsequently the magnetic anisotropy of a coupled ferromagnetic layer can be effectively tuned by the strain-induced phase transition.

## RESULTS AND DISCUSSION

$\text{Bi}_0.7\text{La}_{0.3}\text{FeO}_3$ (−90 nm)/$\text{SrRuO}_3$ (20 nm) bilayers were grown on SrTiO$_3$(001), DyScO$_3$(110)$_0$, and GdScO$_3$(110)$_0$ single-crystal substrates using pulsed-laser deposition (Materials and Methods). Note that we will use cubic or pseudocubic indices throughout this paper unless otherwise specified, and the subscript “O” denotes orthorhombic indices. Following growth, wide-angle $\theta$–$2\theta$ scan X-ray diffraction studies (Supporting Information, Figure S1) reveal that all $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ heterostructures are fully epitaxial and 001-oriented. Closer examination of the 002-diffraction condition of the $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ films reveals marked shifts in peak position, consistent with varying degrees of lattice parameter mismatch between the $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ film and the underlying substrate (Figure 1a). Consistent with the observed Laue oscillations and small full width at half-maximum in the $\theta$–$2\theta$ scans, all heterostructures (Figure 1b–g) show atomically smooth surface morphologies in atomic force microscopy (AFM). In the bulk, $\text{Bi}_0.7\text{La}_{0.3}\text{FeO}_3$ exhibits an orthorhombic structure at room temperature with lattice parameters of $a = 5.572$ Å, $b = 5.554$ Å, and $c = 7.864$ Å. Films grown on SrRuO$_3$-buffered $\text{SrTiO}_3$ (−0.7% lattice mismatch, Figure 1b,c) and GdScO$_3$ (−1.1% lattice mismatch, Figure 1f,g) substrates exhibit intrinsic nanoscale stripes in surface height with $3.4 \pm 0.3$ Å of height difference (corresponding to a $\sim0.4\%$ change in the out-of-plane thickness) between the (light) high and (dark) low regions. The relative fraction of high and low stripes shifts as the film thickness is increased, with the fraction of high regions growing as the film thickness is increased (Supporting Information, Figure S2). This stripe morphology and its thickness-dependent evolution are reminiscent of a strain-mediated, mixed-phase structure with enhanced electromechanical response in highly strained BiFeO$_3$ films and suggest that there could be strain-induced phase coexistence in heterostructures grown on DyScO$_3$.

Reciprocal space mapping (RSM) studies probed the strain state and the lattice parameters of the films. RSM studies about the 013-diffraction condition of the film and 013-diffraction condition of SrTiO$_3$ and 420$_y$-diffraction condition of the DyScO$_3$ and GdScO$_3$ substrates (Figure 2a–c) reveal two important points: (1) all heterostructures are essentially coherently strained to the respective substrates and (2) heterostructures grown on SrTiO$_3$ and GdScO$_3$ substrates exhibit only one phase (as illustrated by the single diffraction peak), whereas those grown on DyScO$_3$ appear to consist of two distinct phases (as indicated by the presence of two distinct diffraction peaks). We note that, in the latter case, elastic domains or twins could potentially give rise to multiple diffraction peaks. Below, we will describe additional studies that confirm that this diffraction pattern arises from two phases. The data together with additional RSM studies at different diffraction conditions (Supporting Information, Figures S3–S5) allow for the extraction of the unit-cell parameters for the various phases, which are thus summarized (Figure 2d); this includes two distinct phases for the films grown on SrTiO$_3$ and GdScO$_3$ and a mixture of phases on DyScO$_3$.
To further understand the nature of the crystal structures, various RSM studies were conducted to investigate quarter-order diffraction peaks (as their presence indicates a structure which is compatible with antipolar order).\(^{13,19}\) Focusing first on the compressively strained films grown on SrTiO\(_3\) substrates, RSM studies (Supporting Information, Figure S3c) reveal the presence of such quarter-order diffraction peaks. These results, combined with the extracted lattice parameters (Figure 2d), are consistent with reports in the literature of a PbZrO\(_3\)-type Pbam phase.\(^{\text{15,23,24,32,33}}\) Shifting our focus to the tensile-strained films grown on GdScO\(_3\) substrates, no evidence of quarter-order diffraction peaks was observed (Supporting Information, Figure S4d). This result combined with the extracted lattice parameters (Figure 2d) indicates a second orthorhombic phase that agrees closely with both the incommensurate Imma(00\(s\))00 superstructure and Pnma phases that have been previously observed.\(^{13,19,35}\) The Pnma phase is the most widely reported nonpolar phase in the rare earth-alloyed BiFeO\(_3\) system,\(^{13,19,35}\) but there has been some disagreement over whether the Imma(00\(s\))00 superstructure phase is an intermediate nonpolar phase. To further complicate phase identification, the Imma(00\(s\))00 superstructure phase was initially incorrectly indexed as a conventional Imma phase with secondary parasitic phases.\(^{29,30}\) This oversimplified assignment was subsequently amended based on the persistence of the superstructure peaks with varied synthesis conditions.\(^{19,30}\) A second Pn2\(_1\)a(00\(s\))00 superstructure has also been reported in bulk Bi\(_{0.7}\)La\(_{0.3}\)FeO\(_3\) and has been differentiated from the Imma(00\(s\))00 superstructure only by minute changes in the superstructure diffraction peaks.\(^{25,30}\) We can rule out the presence of either of the two superstructured phases because satellite peaks are not observed in the X-ray diffraction patterns (Supporting Information, Figure S1) nor in transmission electron microscopy (TEM) selected area electron diffraction (SAED, discussed later). The lack of both quarter-order and superstructure satellite diffraction peaks confirms that the tensile-strained heterostructures grown on GdScO\(_3\) are a single nonpolar Pnma phase.

Finally, we focus our attention on films grown on DyScO\(_3\) substrates which show evidence of seeming nanoscale phase coexistence. Synchrotron-based diffraction studies (Materials and Methods) reveal clear quarter-order peaks (Supporting Information, Figure S5b), indicating the presence of the compressively strained Pbam phase as observed in the heterostructures grown on SrTiO\(_3\). The uneven intensity distribution between the observed quarter-order peaks suggests that there is a preferred orientation, which is likely the result of the orthorhombic nature of the DyScO\(_3\) substrate.\(^{37}\) The lattice parameters of the second phase observed in the heterostructures grown on DyScO\(_3\) agree with an epitaxially strained Pnma phase, as observed in heterostructures grown on GdScO\(_3\) (Figure 2e). This observation is further supported by cross-sectional TEM imaging of heterostructures grown on DyScO\(_3\) (Figure 3a), which reveals bands of varying light and dark contrast on the same length scale as the stripes observed with AFM (Figure 1e). SAED patterns taken of the marked regions for the (b) Pnma and (c) Pbam phases. The superlattice ordering corresponding to the highlighted 1/4 (011) reflections (as marked by the arrows in c) indicates the antipolar structure with a space group of Pbam.

Figure 2. RSM studies about the (a) 013-diffraction condition of the SrTiO\(_3\) substrate and the 420\(s\)-diffraction conditions of the (b) DyScO\(_3\) and (c) GdScO\(_3\) substrates showing only a single peak for the SrTiO\(_3\) and GdScO\(_3\) heterostructures (confirming the presence of a single phase) but two clear diffraction peaks for films grown on DyScO\(_3\) substrates. (d) Experimentally extracted lattice parameters consistent with coexistence of the phases observed on SrTiO\(_3\) and GdScO\(_3\). The extracted lattice parameters agree well with (e) reported lattice parameters for both Pnma and Pbam phases.

Figure 3. (a) Transmission electron micrograph of the Bi\(_{0.7}\)La\(_{0.3}\)FeO\(_3\) heterostructure on SrRuO\(_3\)-buffered DyScO\(_3\), viewed along the substrate [001], revealing the presence of phase coexistence. SAED patterns taken of the marked regions for the (b) Pnma and (c) Pbam phases. The superlattice ordering corresponding to the highlighted 1/4 (011) reflections (as marked by the arrows in c) indicates the antipolar structure with a space group of Pbam.
of additional reflections in the diffraction pattern supports this conclusion as both superstructured phases would have clear superlattice spots. The second region, within a lighter contrast stripe, has a SAED pattern (Figure 3c), which is consistent with the RSM studies, where superlattice spots corresponding to the highlighted 1/4 (01̅1) reflections (as marked by the arrows, Figure 3c) indicate that the region exhibits an antipolar structure with a space group of Pbam. Thus, it appears that at small strains, as is the case for films grown on DyScO3 substrates, an intimate mixture of the two nanoscale phases is observed. This demonstrated ability to control phase stability using epitaxial strain in Bi0.7La0.3FeO3 has not been previously reported.

Because of the difference in structure between the compressively stabilized Pbam and tensile-stabilized Pnma phases, it is expected that heterostructures grown on SrTiO3 and GdScO3 will show antipolar and nonpolar electrical responses, respectively. The coexistence of both antipolar and nonpolar phases in heterostructures grown on DyScO3, however, begs the question as to whether one can electrically control the phases and if there is potential for unexpected electrical properties. Polarization—electric field hysteresis loops were measured at room temperature (Materials and Methods; Supporting Information Figure S6) but were inconclusive because of leakage currents obscuring the true loop shape. The issue is that even though lanthanum addition is known to increase the resistance of BiFeO3, the amount added herein also drives the electric fields (voltage) required to switch the material to such high levels that considerable leakage is observed. As such, additional electrical measurements were performed at 200 K to minimize the leakage behavior under the large fields required to saturate the response. Heterostructures grown on SrTiO3 (Figure 4a) and DyScO3 (Figure 4b) substrates exhibit pinched hysteresis loops regardless of the magnitude of the applied fields. This behavior is not unexpected considering the presence of the antipolar (and potentially antiferroelectric) Pbam phase in both cases. For heterostructures grown on GdScO3, however, the presence of the nonpolar Pnma phase results in a linear response at subcoercive fields but abruptly transitions to show the same pinched hysteresis loops above a threshold applied field (Figure 4c). These pinched hysteresis loops persist as the voltage is decreased below the coercive field and does not appear to relax back to the initially observed linear response after up to 2 h in zero bias, suggesting an irreversible phase transition from the nonpolar to the antipolar (and potentially antiferroelectric) phase. Such pinched hysteresis loops are observed in all heterostructure variants across a range of measurement frequencies (Supporting Information Figure S7).

To further verify the potential field-induced phase transition from the nonpolar Pnma to the antipolar Pbam phase, poling experiments were done using piezoresponse force microscopy on heterostructures grown on DyScO3 to track changes in surface morphology with applied bias (Figure 4d–f). The obtained height images demonstrate persistent transformation of the smaller out-of-plane lattice parameter minority Pnma phase (dark stripes) to the larger out-of-plane lattice parameter majority Pbam phase (lighter background) with the application of both positive and negative bias. A 11% (2%) and a 16% (10%) decrease in the fraction of low stripes from the as-grown state are observed after the application of −10 V (+10 V) (Figure 4e) and −20 V (+20 V) (Figure 4f), respectively. It is important to note that height images (Figure 4d–f) do not convey any information about the piezoresponse of the Bi0.7−xLaxFeO3 heterostructure. The piezoresponse data obtained during the measurements are consistent with the antipolar and nonpolar nature of the constituent phases. The only contrast in the piezoresponse data was observed in the poled areas and quickly dissipated after poling, which is consistent with transient charging due to the large applied voltage used in the poling study. On the basis of the significant change in relative fractions of light and dark regions after poling, it is concluded that a voltage-induced phase transformation takes place, driving the nonpolar Pnma phase (dark regions) to the antipolar Pbam phase (light stripes). To the best of our knowledge, this is the first experimental observation of an electric-field-driven nonpolar-to-antipolar phase transition in Bi0.7−xLaxFeO3. We note that although electric-field-driven nonpolar orthorhombic to polar rhombohedral phase transitions for other rare earth-doped BiFeO3 systems with higher chemical pressure (e.g., Dy and Sm) have been reported, such a field-driven transition has been dismissed in the case of low chemical pressure alloying with La because of the lack of nanoscale phase coexistence and the lack of observed d33 enhancement under applied bias. This said, first-principles calculations have predicted several low-energy metastable orthorhombic phases in Bi0.7−xLaxFeO3 and further
suggest that an electric field might be used to induce phase transformations between those nearly-energy-degenerate phases. Such predictions are consistent with our observations.

The observed pinched hysteresis loops and the potential for antiferroelectric-like behavior are further supported by capacitance/dielectric permittivity—voltage measurements (Figure 5a). The heterostructures clearly do not show the prototypical ferroelectric shape and instead are more reminiscent of antiferroelectric-like behavior. It is important to note that the heterostructures grown on GdScO3 are expected to show antiferroelectric-like behavior as the measurement started from negative bias, poling the sample into the antipolar (and potentially antiferroelectric-like) state for the remainder of the measurement. Heterostructures grown on SrTiO3 and DyScO3 are expected to show antipolar (and potentially antiferroelectric-like) behavior regardless of starting voltage because of their as-grown Pbam phase that is further reinforced by the applied bias. This is all consistent with what is expected for the antipolar Pbam phase. The dielectric constant of the Bi0.7La0.3FeO3 heterostructures (∼140) for heterostructures grown on both SrTiO3 and DyScO3, and ∼120 for the heterostructure grown on GdScO3: 10 kHz, (Figure 5b) is higher than that of a similarly grown BiFeO3 heterostructure (∼105, which is consistent with previous reports).

Thus, having shown that epitaxial strain can effectively tune the structural and electric properties of Bi1−xLa0.3FeO3, we now concentrate on how the strain affects the magnetic properties. Bulk BiFeO3 exhibits G-type antiferromagnetism with a superimposed long-wavelength cycloidal modulation and a Neél temperature \( T_N \approx 643 \) K, whereas bulk LaFeO3 is a simple G-type antiferromagnet with \( T_N \approx 750 \) K. It is reported that epitaxial strain or chemical alloying with rare earth elements can suppress the spin cycloid and drive a transition toward a homogenous weakly ferromagnetic order in BiFeO3. Angle- and polarization-dependent linear X-ray absorption spectroscopy (XAS) measurements were carried out on the Bi0.7La0.3FeO3 films to study the effect of strain on the antiferromagnetic order. The Fe \( L_{2,3} \) XAS spectral shape depends on the relative orientation of the polarization vector \( \vec{E} \) of the incoming X-rays, the crystallographic axes, and the antiferromagnetic-spin axis \( \vec{L} \). Representative pairs of absorption spectra [taken in normal incidence with \( \vec{E} \) parallel to [001] (orange curves), [010] (blue curves), [110] (red curves), and [110] (green curves)] are provided (Figure 6a−c). These studies demonstrate that strain and the resulting structural change can effectively tune the spin orientation of the films. For Bi0.7La0.3FeO3 heterostructures grown on SrTiO3 (Figure 6a), essentially no linear dichroism is revealed in the normal-incidence geometry, indicating that the antiferromagnetic-spin axis is likely along the out-of-plane [001]. For Bi0.7La0.3FeO3 heterostructures grown on DyScO3 (Figure 6b), large dichroism between X-ray with polarization lying along [001] and [110] is observed, whereas no dichroism is observed between X-ray with polarization lying along [110] and [110], indicating that the antiferromagnetic-spin axis is likely along the in-plane [001]. In contrast, for Bi0.7La0.3FeO3 heterostructures grown on GdScO3 (Figure 6c), large dichroism is observed between light with polarization lying along [110] and [110], whereas no dichroism is observed between light with polarization lying along [001] and [110], indicating that the antiferromagnetic-spin axis is likely along the in-plane [001].
in-plane [110]. These spectroscopic studies demonstrate that the antiferromagnetic-spin axis of the $Bi_0.7La_0.3FeO_3$ films is very sensitive to the strain and local structural distortion; therefore, a small change in the amount of strain could drive a significant amount of spin reorientation. This is probably due to a negligibly small magnetic anisotropy energy in Fe$^{3+}$, as a similar behavior has been observed in BiFeO$_3$ and Fe$_2$O$_3$.40–42

Exchange coupling of the $Bi_0.7La_0.3FeO_3$ layers with the ferromagnet $Co_{0.9}Fe_{0.1}$ provides further evidence for the significant effect of the strain-induced phase transition on the magnetic response. Pt (2.5 nm)/Co$_{0.9}Fe_{0.1}$ (2.5 nm) bilayers were grown on the $Bi_0.7La_0.3FeO_3$ films. Representative magneto-optical Kerr effect (MOKE) hysteresis loops taken from the Co$_{0.9}Fe_{0.1}$/Bi$_0.7La_0.3FeO$_3$ heterostructures reveal several important points: (1) All heterostructures show an enhancement of the coercive field of Co$_{0.9}Fe_{0.1}$, compared to Co$_{0.9}Fe_{0.1}$ grown on bare substrates (Supporting Information, Figure S8), indicating that a robust exchange coupling is established between the $Bi_0.7La_0.3FeO_3$ and Co$_{0.9}Fe_{0.1}$. (2) Isotropic response is observed for heterostructures/multilayers grown on SrTiO$_3$ (Figure 6d), whereas clear anisotropy is observed for heterostructures grown on DyScO$_3$ and GdScO$_3$. For heterostructures grown on DyScO$_3$ and GdScO$_3$, the ferromagnetic easy axis is along $[11\bar{0}]O$ and $[1\bar{1}0]$ respectively, indicating a perpendicular coupling between the antiferromagnetic-spin axis in $Bi_0.7La_0.3FeO_3$ and the ferromagnetic spin in the Co$_{0.9}Fe_{0.1}$ layers. (3) The exchange coupling between the antiferromagnetic-spin axis in $Bi_0.7La_0.3FeO_3$ and the ferromagnetic spin in Co$_{0.9}Fe_{0.1}$ is strong enough to overcome the substrate asymmetry. Without the $Bi_0.7La_0.3FeO_3$ layer, the easy axis of the Co$_{0.9}Fe_{0.1}$ film is always along $[00\bar{1}]O$ on the orthorhombic DyScO$_3$ and GdScO$_3$ substrates. In summary, these magnetic studies demonstrate that strain could effectively tune the antiferromagnetic-spin axis and, in turn, the magnetic anisotropy of an exchange-coupled ferromagnet.

## CONCLUSIONS

We have demonstrated that epitaxial strain can drive nanoscale phase competition at an antipolar–nonpolar phase boundary in antiferromagnetic $Bi_0.7La_0.3FeO_3$ thin films and that this coexistence has important implications for material properties. The nonpolar $Pnma$ phase, typically observed at higher lanthanum-concentration levels, is stabilized by the tensile strain imposed by the GdScO$_3$ substrate, whereas the compressive strain from the SrTiO$_3$ substrate stabilizes the antipolar PbZrO$_3$-like $Pbam$ phase. In the case of small strain, a self-assembled mixture of the two orthorhombic phases is observed. In this mixed-phase system, applied voltage can be used to transform the nonpolar phase to the antipolar phase; a phenomenon not previously observed in the $Bi_0.7La_0.3FeO_3$ system. Subsequent investigation of the magnetic properties reveals a strain-induced rotation of the antiferromagnetic-spin axis. This work provides insights into the complex and subtle nature of phase relations in the rare earth-alloyed BiFeO$_3$ system that could, in turn, allow for enhanced functionality.

## MATERIALS AND METHODS

### Film Growth

$Bi_0.7La_0.3FeO_3$ heterostructures were grown via pulsed-laser deposition in an on-axis geometry using a KrF excimer laser (Comex, Coherent) on 20 nm SrRuO$_3$/SrTiO$_3$(001), DyScO$_3$(110), and GdScO$_3$(110) single-crystal substrates (CrysTec GmbH). The SrRuO$_3$ films, to be used as a bottom electrode for subsequent electrical studies, were grown at a heater temperature of 700 °C, in a dynamic oxygen pressure of 100 mTorr, with a laser energy density of 1.2 J/cm$^2$, and a laser repetition rate of 15 Hz from a ceramic target of composition SrRuO$_3$. The BiFeO$_3$ films were grown at a heater temperature of 700 °C, in a dynamic oxygen pressure of 100 mTorr, with a laser energy density of 1.1 J/cm$^2$, and a laser repetition rate of 20 Hz from ceramic targets of composition Bi$_2$La$_2$Fe$_2$O$_7$. All substrates were adhered to the heater with Ag paint (Ted Pella, Inc.), and following growth, the heterostructures were cooled to room temperature at a rate of 10 °C/min in 700 Torr of oxygen.

### Structural, Chemical, and Physical Property Measurement

Following growth, a variety of techniques were used to probe the structural, electrical, and magnetic properties. Structural studies were performed using high-resolution X-ray diffraction and RSM (PANalytical, X’pertâ MRD). Synchrotron X-ray RSM studies were conducted at the Advanced Photon Source, Argonne National Laboratory, Sector 33-BM, using the Pilatus 100K detector. Cross-sectional TEM specimens were prepared using the standard procedure consisting of cutting, gluing, mechanical polishing, and ion milling. The ion milling process was performed on a Precision Ion Polishing System (PIPS, model 695, Gatan) with an incident ion angle of $5^\circ$ and an accelerating voltage of 3 kV using liquid N$_2$ to cool the stage. TEM investigations were carried out on a JEOL 3010 transmission electron microscope operated at 300 kV. Film morphology was imaged using AFM, with an MFP-3D microscope (Asylum Research). For electrical, dielectric, and ferroelectric studies, symmetric capacitor structures were fabricated by ex situ deposition of 80 nm thick SrRuO$_3$ top electrodes defined using a MgO hard-mask process.48 Ferroelectric polarization hysteresis loops were measured using a Precision MultiBerroferic Tester (Radiant Technologies), and dielectric and loss measurements were performed using an E4890 LCR meter (Agilent/Keysight) for frequencies up to 1 MHz. All electrical measurements were performed in a vacuum probe station (TPPX, Lakeshore) with a 336 temperature controller (Lakeshore) at room temperature or at 200 K to minimize leakage behavior. Magnetic hysteresis loop measurements were carried out using the longitudinal MOKE.48 X-ray spectroscopy measurements were carried out on beamline 4.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory. The measurements were performed in total-electron-yield geometry. The XLD measurements were obtained from the difference of horizontal and vertical polarized light absorption spectra. The X-ray beam was incident on the sample at an angle of 90° from the sample surface for normal incidence.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b02597.

Experimental growth and characterization methods, additional X-ray diffraction patterns and reciprocal space maps, information on thickness-dependent surface morphology development of mixed-phase films, and additional ferroelectric and magnetic measurement results (PDF)

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### Notes

The authors declare no competing financial interest.

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