

## Evidence for Room-Temperature Multiferroicity in a Compound with a Giant Axial Ratio

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In the search for multiferroic materials magnetic compounds with a strongly elongated unit-cell (large axial ratio  $c/a$ ) have been scrutinized intensely. However, none was hitherto proven to have a switchable polarization, an essential feature of ferroelectrics. Here, we provide evidence for the epitaxial stabilization of a monoclinic phase of BiFeO<sub>3</sub> with a giant axial ratio ( $c/a = 1.23$ ) that is both ferroelectric and magnetic at room temperature. Surprisingly, and in contrast with previous theoretical predictions, the polarization does not increase dramatically with  $c/a$ . We discuss our results in terms of the competition between polar and antiferrodistortive instabilities and give perspectives for engineering multiferroic phases.

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The rich physics of ferroelectric materials arises from the interplay between their electronic and structural degrees of freedom [1]. A great research effort is currently made to take further advantage of this interplay and discover novel ferroelectrics with better or additional properties. First, in order to obtain ferroelectrics with larger polarizations, an active route focuses on perovskites with strongly elongated unit cells [2], i.e., a large axial ratio (ratio of the long to the short axis of the pseudocubic unit-cell  $c/a$ ) [3]. Indeed, this structural property is expected to result in a polar charge distribution with a large dipolar moment. Systems with giant axial ratios have been sought after either in single-phase perovskites or in solid solutions, mostly by *ab initio* methods. Materials predicted to exhibit giant axial ratios include BiYO<sub>3</sub> ( $c/a = 1.376$ ) [3], BiScO<sub>3</sub> ( $c/a = 1.285$ ) [3] and Bi<sub>2</sub>ZnTiO<sub>6</sub> ( $c/a = 1.21$ ) [4], to be compared with  $c/a = 1.059$  for the prototypical ferroelectric perovskite PbTiO<sub>3</sub> [5].

Another research route focuses on magnetic ferroelectrics (multiferroics [6]) that, because of the magnetolectric cross-coupling between the magnetic and ferroelectric order parameters [7], open the door for novel spintronics devices [8–10]. More recently, the combination of these two approaches lead to the discovery of magnetic polar materials with giant axial ratio. Two known examples are PbVO<sub>3</sub> and BiCoO<sub>3</sub>. PbVO<sub>3</sub> [11] has a  $c/a = 1.23$  and a large dipolar moment of 101  $\mu\text{C}/\text{cm}^2$  as inferred from the refined atomic positions using an ionic model. Antiferromagnetic or ferromagnetic ordering of V<sup>4+</sup> ions was pre-

dicted [11,12] but unconfirmed by recent experiments [13]. PbVO<sub>3</sub> films have also been grown, with an even larger  $c/a$  of 1.32 [14] and indications of antiferromagnetism below  $\sim 100$  K [15]. For BiCoO<sub>3</sub>, the reported  $c/a$  is 1.27 [16] and the material is antiferromagnetic below 470 K [16].

Despite this flurry of compounds with a giant axial ratio and their large predicted polarization [2], experimental evidence for a genuine ferroelectric behavior has not hitherto been provided. In fact, while a polar state can be inferred from structural data or optical techniques, additional experiments are required to demonstrate ferroelectricity, i.e., the presence of a switchable polarization. So far, ferroelectric polarization vs electric field  $P(E)$  loop measurements in compounds with a giant axial ratio have proven unsuccessful. This may be because of strong leakage [11,16,17] due to extrinsic factors such as defects or to small band gaps [2,11,18]. Furthermore, in compounds with giant axial ratio not only  $P$  is expected to increase significantly but also the coercive field, that may then exceed the breakdown field. From the absence of a definitive proof of ferroelectricity, it is still unclear whether such compounds are promising as novel ferroelectrics with application potential.

In this Letter, we show that phases with a giant axial ratio can indeed be ferroelectric. Using both local and macroscopic techniques we report a clear ferroelectric behavior in epitaxial thin films of a monoclinic polymorph of BiFeO<sub>3</sub> (BFO) with a giant axial ratio (BFO is a well-

known multiferroic but with a rhombohedral R3c structure in the bulk [19]). This phase can be stabilized via epitaxial growth onto  $\text{LaAlO}_3$  (LAO) and has a  $c/a$  ratio of 1.23. Furthermore, this phase is antiferromagnetic at 300 K and is thus the first example of a room-temperature multiferroic with a giant axial ratio. We discuss the key role played by the slight monoclinic distortion in making this phase switchable as opposed to previous purely tetragonal compounds.

BFO films were grown by pulsed laser deposition onto (001)-oriented LAO substrates at  $580^\circ\text{C}$  and  $6 \times 10^{-3}$  mbar [20]. For electrical measurements, a 11-nm-thick  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  (LSMO) buffer was intercalated between BFO and LAO [21]. On x-ray diffraction (XRD)  $\theta$ - $2\theta$  scans obtained on such BFO heterostructures [Fig. 1(a)] only (00 $l$ ) peaks from the substrate, the BFO and the LSMO layer are visible, indicative of textured growth. The positions of the (00 $l$ ) peaks yield an out-of-plane parameter for BFO of  $c = 4.67 \pm 0.01$  Å for all three films, irrespective of the BFO thickness  $t$ . Strikingly, this  $c$  value is much larger than the pseudocubic cell parameter of bulk BFO ( $a_{\text{bulk}} = 3.96$  Å [19]) and than typical out-of-plane spacings for fully strained BFO films grown on  $\text{SrTiO}_3$  (STO) substrates ( $c = 4.08$ – $4.10$  Å) [22–24].  $\phi$ -scans [see Fig. 1(b)] reveal that the BFO films are epitaxial but that two variants are present and separated by  $\sim 1.5^\circ$ . This indicates that BFO does not crystallize in a

tetragonal space group but in a monoclinic one. In the reciprocal-space map shown in Fig. 1(c) the spots corresponding to BFO and LAO appear at virtually the same in-plane reciprocal-space parameter, indicating that the in-plane parameter of BFO is very close to that of LAO, i.e.,  $a \approx 3.79$  Å. This corresponds to  $c/a = 1.23$  for BFO in these samples.

High-resolution transmission electron microscopy images collected for the 56 nm (not shown) and 7 nm-thick BFO layers confirm the epitaxial growth; see Fig. 2(a). Quantitative measurements of the deformation by the GPA method [25] were used to measure the deformation of the BFO film compared to the LAO reference. Figures 2(b) and 2(c) present images of the deformation perpendicular and parallel to the growth axis, respectively. For both samples, the deformation value is around 23% in the growth direction and nearly null in the perpendicular direction. This confirms that the  $c/a$  ratio is 1.23 at a local scale. This value was measured on several areas of the sample evidencing the homogeneity of the deformation.

The structural data indicate that the  $c/a$  ratio in these films is thus much larger than that reported for films grown on STO (up to  $c/a \approx 1.04$  [22–24]). Although the lattice mismatch between BFO and LAO (4.8%) is enhanced compared to the one between BFO and STO (1.4%), simple elastic considerations alone cannot explain a strain-induced  $c/a$  ratio of 1.23. Indeed, within this simple

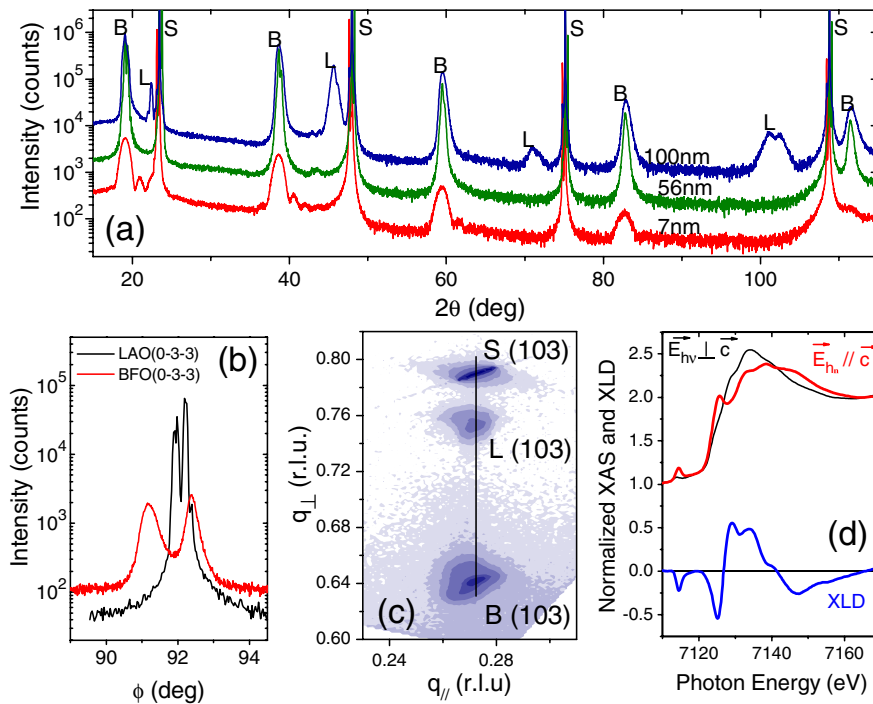


FIG. 1 (color online). (a)  $2\theta$ - $\omega$  scans for 7 and 56 nm single films and a 100 nm film grown on a LSMO buffer. (b)  $\phi$ -scans of the (0 $\bar{3}$ 3) reflections for a 56 nm film (the (30 $\bar{3}$ ) reflection is very similar). (c) reciprocal-space map for a BFO(100 nm)/LSMO || LAO sample. The line in (c) is a guide to the eye. S, B, and L are for LAO, BFO, and LSMO, respectively. (d) X-ray absorption spectra for two orthogonal direction of the incident linearly polarized beam and x-ray linear dichroism at the Fe  $K$  edge for a 56 nm BFO film.

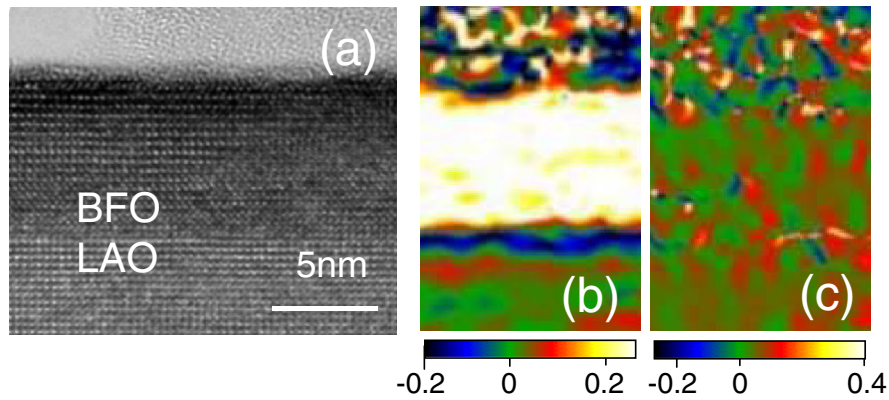


FIG. 2 (color online). (a) High-resolution transmission electron microscopy image in the  $[100]$  zone axis of a 7 nm BFO film. (b) and (c) are images of the deformation perpendicular and parallel to the growth axis, respectively. Color scales in (b) and (c) correspond to a displacement relative to the LAO cell size.

picture a maximum  $c/a$  of only 1.16 (using  $a = 3.79$  Å and a Poisson ratio  $\nu = 0.39$  [22,23]) is in principle achievable for BFO films fully strained on LAO. Furthermore, the  $c/a$  ratio of 1.23 is retained for films as thick as 100 nm, while in BFO films grown on better matched STO the increase in elastic energy upon increasing film thickness triggers structural relaxation at  $t = 40\text{--}70$  nm [22,23]. Therefore, the data either suggest that the BFO in our films corresponds to a different phase of BFO with an intrinsic in-plane parameter well matched to that of LAO, or that imposing such a large compressive strain strongly reduces another energy term that compensates for the huge increase in elastic energy. We will discuss this latter possibility later on.

Leaving aside for now the slight monoclinic distortion suggested by the  $\phi$ -scans, the structure of the BFO in our films is in fact reminiscent of highly distorted metastable tetragonal ( $P4mm$ ) BFO phases predicted by first-principles calculations by Ederer *et al.* [26] ( $a = 3.665$  Å and  $c = 4.655$  Å,  $c/a = 1.27$ ), Ravindran *et al.* [27] ( $a = 3.7859$  Å and  $c = 4.8525$  Å,  $c/a = 1.28$ ) and Ricinschi *et al.* [28] ( $a = 3.67$  Å and  $c = 4.64$  Å,  $c/a = 1.26$ ). Importantly, all these phases have been predicted to exhibit a large polar moment, up to  $150$   $\mu\text{C}/\text{cm}^2$  [26,28], which makes them very attractive for many applications. However, their energy is larger than that of the stable rhombohedral  $R3c$  phase by some hundreds of meV per unit-cell [27], and they are thus unlikely to form in bulk. On the other hand, the smaller lattice mismatch between LAO and these phases may favor their stabilization through epitaxial growth.

To get more insight into the structure of this highly distorted BFO, we have performed room-temperature x-ray absorption spectroscopy (XAS) and x-ray linear dichroism (XLD) measurements at the Fe  $K$  edge ( $1s \rightarrow 4p$  empty state transitions) at the ESRF ID 12 beamline, in grazing incidence and fluorescence yield detection mode. XLD is the difference between the XAS spectra recorded

for two orthogonal linear polarization vectors of the x-ray beam ( $\vec{E}_{hv} \perp \vec{c}$  or  $\vec{E}_{hv} \parallel \vec{c}$ ). XAS spectra for horizontal ( $\vec{E}_{hv} \perp \vec{c}$ ) and vertical ( $\vec{E}_{hv} \parallel \vec{c}$ ) polarizations and XLD spectra are plotted in Fig. 1(d). The main striking feature is a huge difference between the spectra for the two orthogonal beam polarizations. This difference directly reflects the anisotropy of the local coordination geometry of the Fe atoms. The preedge region is particularly interesting as in the case of noncentrosymmetric environment it is related to the  $1s \rightarrow 3d$  quadrupole transitions and  $1s \rightarrow 3d4p$  hybridized states dipole transitions. These transitions are allowed for a distorted octahedral system. Therefore the high amplitude of the XLD peak at the preedge reveals the strong distortion of the octahedral symmetry, as predicted for  $\text{PbVO}_3$  [29]. The overall amplitude of the XLD and especially that of the preedge peak are much larger than those obtained for BFO films grown on STO [30], reflecting the large difference in the axial ratio.

Having established that BFO films epitaxially grown on LAO(001) have a strongly elongated unit-cell potentially translating in a highly polar charge distribution, we now turn to investigate whether this dipole can be switched by an electric field. To circumvent possible leakage problems, we have first addressed this issue by PFM experiments [Figs. 3(a) and 3(b)]. The out-of-plane (OP) and in-plane (IP) signals were measured simultaneously. While the OP signal was found homogeneous, domain contrast was observed in the IP one [see Fig. 3(a)], indicating that the material is polar with a polarization vector not oriented along the  $c$  axis but having a finite IP component. IP rotation PFM experiments (not shown) revealed that the polarization is contained in a  $(110)$  plane, at some angle from the film normal. This is at odds with the situation found in  $P4mm$  systems (in which  $P$  is along the  $c$  axis) but consistent with the monoclinic symmetry inferred from XRD. To access the ferroelectric character of BFO in these films, we then poled a  $2 \times 2$   $\mu\text{m}^2$  square at a voltage of  $-8$  V and then rewrote a  $1 \times 1$   $\mu\text{m}^2$  square in the same

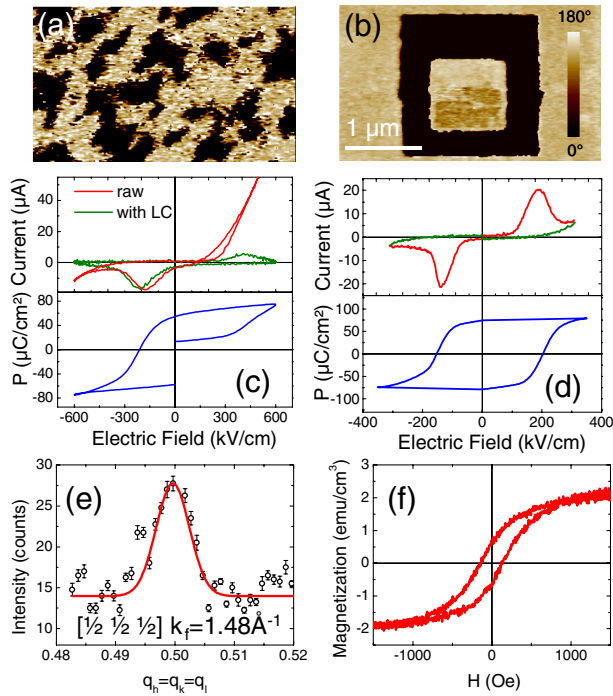


FIG. 3 (color online). (a) IP-PFM phase contrast of the as grown BFO (cantilever oriented along the [100] direction). The OP response is fully homogeneous. (b) OP-PFM phase after switching a  $2 \times 2 \mu\text{m}^2$  central square with  $V = -8 \text{ V}$  applied to the scanning tip (the initial state of polarization was down), and switching back a  $1 \times 1 \mu\text{m}^2$  central square with  $V = +8 \text{ V}$ . (c) and (d) Current and polarization versus electric field for BFO (c) and Mn-BFO (d) films. (e) Neutron diffraction spectrum and (f) field dependence of the magnetization at 300 K.

area at +8 V [Fig. 3(b)]. From this image it is clear that the OP piezoresponse phase can be reversibly switched from  $\sim 0^\circ$  to  $\sim 180^\circ$ , which is a first qualitative demonstration of the ferroelectric character. More quantitative information on the ferroelectric character was obtained by performing standard  $P(E)$  loop experiments with an aixACCT TF analyzer 2000. In the case of pure BFO, measurements were hampered by the high leakage level [see Fig. 3(c)]. Partial substitution with 5% of Mn allows to decrease the leakage [31] and to measure a  $75 \mu\text{C}/\text{cm}^2$  polarization along the [001] direction for this 60 nm film [32]. These measurements clearly confirm the ferroelectric character of this phase. The values found for the polarization ( $75 \mu\text{C}/\text{cm}^2$  along [001]) and the piezoelectric coefficient ( $d_{\text{eff}} = 30 \text{ pm}/\text{V}$ ) are in the range of those reported for BFO films grown on STO [33]. Such relatively modest values are startling in view of the high axial ratio generally associated, at least theoretically, with an enhanced polarization (e.g.,  $150 \mu\text{C}/\text{cm}^2$  for the  $P4mm$  phase of BFO [26,28], i.e., a factor of 2 larger than what we measure).

Before discussing this apparent contradiction, we present the magnetic properties of a 56 nm film grown directly on LAO. Neutron diffraction measurements were performed at 300 K at the Laboratoire Léon Brillouin.

Figure 3(e) shows the  $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$  peak due to the presence of a  $G$ -type antiferromagnetic ordering, as in bulk BFO [34] or in BFO films grown on STO [22,35]. A weak ferromagnetic moment is also present, reflecting a slight spin canting; see the magnetization hysteresis loop of Fig. 3(f).

Along with the ferroelectric characterization, these magnetic data indicate that the BFO phase stabilized on LAO represents the first example of a multiferroic with giant axial ratio. However, there is a significant difference between this phase and other predicted ferroelectrics with a giant axial ratio: its crystal structure is not strictly tetragonal, but tetragonal with a slight monoclinic distortion. This provides further degrees of freedom for the polarization direction and amplitude related to the rotation of the oxygen octahedra. In perovskites, polar instabilities and antiferrodistortive rotations of the oxygen octahedra usually compete with each other to determine the ground state [36]. We propose that the coexistence of both instabilities in our monoclinic BFO films is the key to their ferroelectric nature as well as to their moderate polarization.

To confirm this hypothesis, we performed direct *ab initio* calculations (at 0 K) similar to those of Ederer *et al.* [26], as well as simulations using the effective Hamiltonian approach of Kornev *et al.* [37] at 300 K of a BFO film epitaxially grown on LAO and under short-circuit electrical boundary conditions. These computations both unambiguously show that monoclinic (ferroelectric and antiferrodistortive)  $Cc$  and  $Cm$  phases are energetically more favorable than the purely tetragonal  $P4mm$  phase. This provides a successful explanation as to why the polarization is not strictly aligned along the [001] direction but contained in the (110) plane. This also allows to explain why largely compressed BFO films remain ferroelectric, that is, their polarization can still be switched in spite of their giant axial ratio. Indeed, in strictly tetragonal ferroelectrics,  $P$  is oriented along the  $c$  axis and increasing  $c/a$  increases not only  $P$  [2] but also the electric field  $E_c$  needed to switch  $P$  from  $P \parallel [001]$  to  $P \parallel [00\bar{1}]$ . For very large  $c/a$  ratios,  $E_c$  may thus exceed the breakdown field, disqualifying the material as a genuine ferroelectric. However, in nontetragonal ferroelectrics more than two polarization directions are energetically stable [33], so that switching from one to the other may be achieved through intermediate states, decreasing  $E_c$  and potentially allowing to switch the polarization direction. We note that preliminary PFM experiments are consistent with only  $109^\circ$  switching.

An important pending question is how to control the competition between both instabilities to engineer ferroelectrics and multiferroics with enhanced properties. While our results validate the exploration route aiming at materials with a giant axial ratio, they also suggest that antiferrodistortive instabilities should be taken into account and that the search should not be only focused on  $P4mm$  systems. In the precise case of  $\text{BiFeO}_3$ , the possi-

bility to play with both handles jointly or separately (via, e.g., strain or superlattice engineering [38]) may allow us to tune finely the polarization, the magnetic properties, the ordering temperatures, and eventually the magnetoelectric coupling.

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