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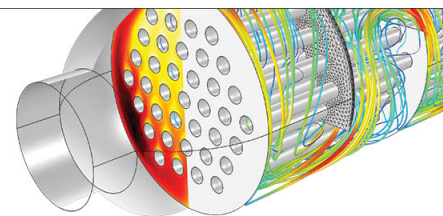
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# Ground state monoclinic ( $M_b$ ) phase in $(110)_c$ BiFeO<sub>3</sub> epitaxial thin films

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The lattice structure of  $(110)$ -oriented BiFeO<sub>3</sub> epitaxial thin layers has been identified by synchrotron x-ray diffraction. By using  $(221)$  and  $(2\bar{2}\bar{1})$  peaks in the  $(HHL)$  zone, a ground state monoclinic  $M_b$  phase has been observed with lattice parameters of  $(\beta; a_m/\sqrt{2}$  and  $c_m) = (89.35^\circ; 3.985$  and  $3.888 \text{ \AA})$ . These results demonstrate a change in phase stability from rhombohedral in bulk single crystals, to monoclinic in epitaxial thin films with two domain states whose polarization is slightly tilted away from  $[110]$  towards  $[111]$ . © 2006 American Institute of Physics. [DOI: 10.1063/1.2392818]

The average crystal lattice of BiFeO<sub>3</sub> bulk single crystals is a rhombohedrally distorted perovskite,<sup>1-7</sup> which belongs to the space group  $R3c$  ( $C_6^{3V}$ ). The unit cell parameters are  $a_r = 3.96 \text{ \AA}$  and  $\alpha_r = 0.6^\circ$ . Bismuth ferrite crystals are both ferroelectric and antiferromagnetic:<sup>1,8</sup> having a Curie temperature of  $T_c = 850 \text{ }^\circ\text{C}$ <sup>2,9,10</sup> and a Néel temperature of  $T_N = 370 \text{ }^\circ\text{C}$ .<sup>3,11</sup> Recently, epitaxial thin films of BiFeO<sub>3</sub> have been grown on SrTiO<sub>3</sub>.<sup>12</sup> Heteroepitaxy induces important structural changes. The lattice parameters of  $(001)_c$  epitaxial thin films are not the rhombohedral ones of bulk crystals, but rather have  $c/a > 1$ . Subsequently,  $(103)$  and  $(113)$  mesh scans taken in the  $(HOL)$  and  $(HHL)$  zones confirmed signatures of the monoclinic  $M_a$  structure with lattice parameters of  $(\beta; a_m/\sqrt{2}$ ,  $b_m/\sqrt{2}$ , and  $c_m) = (89.2^\circ; 3.907$ ,  $3.973$ , and  $3.997 \text{ \AA})$ .<sup>13</sup>

Heteroepitaxial BiFeO<sub>3</sub> films have also been grown on  $(110)_c$  SrTiO<sub>3</sub>.<sup>12</sup> Diffraction studies have indicated a monoclinic structure, whose lattice parameters are different than those of  $(001)_c$  films. However, this monoclinic structure of  $(110)_c$  films has not been satisfactorily identified. Three types of ferroelectric monoclinic phases are known,  $M_a/M_b$  and  $M_c$  that belong to space groups  $Cm$  and  $Pm$ , respectively.<sup>14-18</sup> The  $M_a$  and  $M_b$  unit cells have a unique  $b_m$  axis along the  $[110]$ , and are doubled and rotated  $45^\circ$  about the  $c$  axis with respect to the pseudocubic cell. The  $M_a$  and  $M_b$  phases belong to the same space group  $Cm$ : the only difference being that  $a_m/\sqrt{2}c_m < 1$  for  $M_a$ , but is  $a_m/\sqrt{2}c_m > 1$  for  $M_b$ .<sup>18</sup> The  $M_c$  unit cell is primitive having a unique  $b_m$  axis that is oriented along the pseudocubic  $[010]$ .

Usually, monoclinic symmetry leads to a very complicated domain configuration. However, for  $(110)_c$  epitaxial films, the  $(110)_c$  axis will be fixed by the substrate. This will result in a simplification of the domain configuration, which should give identifiable signatures in mesh scans. Critical to identification is that measurements should be performed in a scattering plane that contains the fixed axis. Ideally, we should measure the  $(001)$  Bragg peak directly in the  $(HHL)$  zone. However, the geometry of the film and substrate prevented such a measurement (the substrate would block either

the incident or the reflected x-ray beam, see Ref. 18 for details). Instead, we have measured  $(221)$  and  $(2\bar{2}\bar{1})$  peaks in the  $(HHL)$  zone. The  $(HHL)$  zone is defined by two primary wave vectors:  $(110)$  and  $(001)$ . Any Bragg reflection in the  $(HHL)$  zone can be decomposed into a linear superposition of these two vectors. With the  $(110)$  axis fixed, the splitting of the  $(001)$  axis can be directly mapped to all Bragg peaks in this plane containing a  $(001)$  component. A diagram is shown in Fig. 1, describing the scattering plane and the expected (Bragg) peak splittings. Our results show that the  $(001)$  axis split along the transverse direction in the  $(HHL)$  plane, suggesting a  $M_a/M_b$ -type structure. Detailed analysis on the lattice parameters demonstrates signature features of  $M_b$ .

We have grown phase-pure BiFeO<sub>3</sub> (BFO) thin films of  $2000 \text{ \AA}$  thickness by pulsed laser deposition onto  $(110)_c$

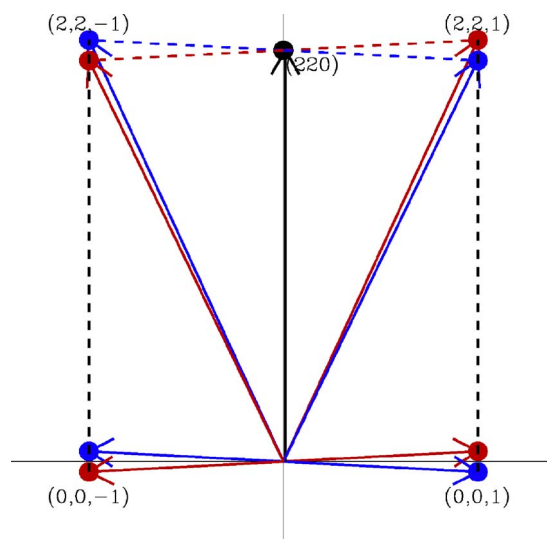


FIG. 1. (Color online) Schematic diagram showing the splitting of Bragg peaks in the  $(HHL)$  plane due to monoclinic distortion. The  $(110)$  direction, shared by both monoclinic domains A (red) and B (blue), is fixed by the substrate. The  $(001)$  direction, however, splits into two peaks along the  $(110)$  direction. Our measurements are performed near the  $(221)$  and  $(2\bar{2}\bar{1})$  Bragg peaks. Here the splittings due to domains A and B follow exactly the same patterns as the splittings around  $(001)$  and  $(0\bar{0}\bar{1})$  peaks.

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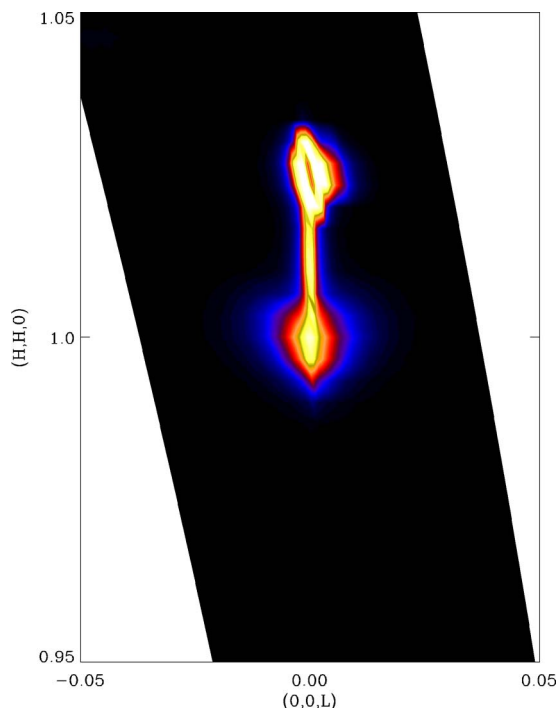


FIG. 2. (Color online) (110) mesh scan for (110)<sub>c</sub> BiFeO<sub>3</sub> epitaxial thin films taken in the (*HHL*) zone. The bright peak above the sample (110) peak is the substrate Bragg peak.

single crystal SrTiO<sub>3</sub> substrates. The conducting perovskite oxide electrode, SrRuO<sub>3</sub> (SRO),<sup>19</sup> was chosen as the bottom electrode due to the closest lattice mismatch with the BFO structure. Films of SRO of 500 Å were deposited at 600 °C in an oxygen ambient of 100 mTorr and followed by the BFO film, deposited at 670 °C in an oxygen ambient of 20 mTorr at a growth rate of 0.7 Å/s. Chemical analysis was carried out by scanning electron microscopy x-ray microanalysis, indicating a cation stoichiometry in the BFO films of ~1:1. Reciprocal lattice mapping was taken at the National Synchrotron Light Source at Brookhaven National Laboratory using beam line X22A. The x-ray energy was 10.2 keV, which cannot penetrate the substrate. Therefore, only reflective geometry can be used. Mesh scans were obtained about the (221) and (22 $\bar{1}$ ) peaks in the (*HHL*) zones. The units used in this letter are multiples of the reciprocal lattice unit  $a^* = 2\pi/a = 2\pi/3.985 \text{ \AA} = 1.577 \text{ \AA}^{-1}$ .

In Fig. 2, a (110) mesh scan is shown. The (110)<sub>film</sub> peak can be seen to be a sharp singlet, while the other sharp peak on the right side is the (110) peak from the SrTiO<sub>3</sub> substrate. The fact that the (110)<sub>film</sub> remains a singlet and is located along the radial direction of the (110) substrate peak, demonstrates that the (110) direction of the epitaxial grown BiFeO<sub>3</sub> layer is fixed along the (110) direction of the substrate. However, the (001) direction of the film is not fixed by the substrate. Rather the (221) and (22 $\bar{1}$ ) mesh scans, given in Figs. 3(a) and 3(b), respectively, clearly reveal splitting. The data show two domain states where the (001) of one of the domains rotates a little bit up away from the (001), whereas the (001) of the other domain tilts down. Since (001)+(220)  $\equiv$  (221) and (00 $\bar{1}$ )+(220)  $\equiv$  (22 $\bar{1}$ ), splitting of the (221) and (22 $\bar{1}$ ) peaks can entirely be attributed to the splitting of (001) and (00 $\bar{1}$ ). Thus one observes two peaks split along the transverse direction, that is, (*HHO*). This split-

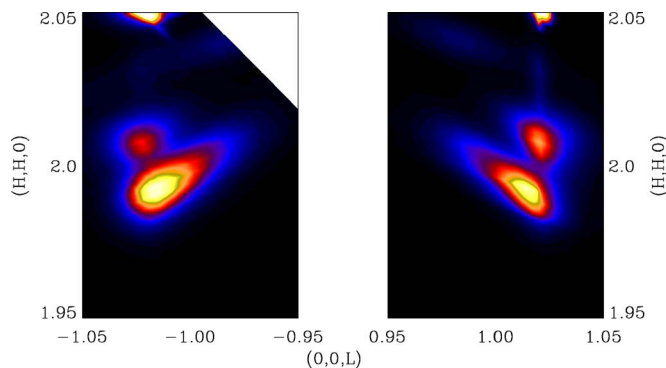


FIG. 3. (Color online) (221) and (22 $\bar{1}$ ) mesh scans for (110)<sub>c</sub> BiFeO<sub>3</sub> epitaxial thin films taken in the (*HHL*) zone. The bright peaks at the top border of the plots are substrate Bragg peaks.

ting reveals key signatures of the  $M_a/M_b$  structures in the mesh scans. Furthermore, the data in Figs. 3(a) and 3(b) show that  $a_m/\sqrt{2}c_m \cong 1.025$ , demonstrating that the stable monoclinic phase is  $M_b$ . Based on Figs. 2 and 3, we can calculate the lattice parameters as  $\beta = 89.35^\circ$ ,  $a_m/\sqrt{2} = 3.985 \text{ \AA}$ , and  $c_m = 3.888 \text{ \AA}$ .

Our results provide a confident identification that the stable structure of (110) BiFeO<sub>3</sub> films is the monoclinic  $M_b$ . A monoclinic  $M_b$  phase has recently been reported in (110) field-cooled crystals of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\% \text{PbTiO}_3$ .<sup>18</sup> However, our finding of a  $M_b$  phase in (110) BiFeO<sub>3</sub> films is unique in that it is the stable ground state in the zero-field-cooled condition. Fixing of the (110) favors an orthorhombic phase, while in bulk BiFeO<sub>3</sub> rhombohedral  $\langle 111 \rangle$  type polarizations are stable. Recent work on SrTiO<sub>3</sub> thin films<sup>20–22</sup> also show that epitaxial strain has significant effects on the structures of thin films. Similar effects have been observed in lead-based relaxors as well, where the near-surface region or “skin” layers have different structures than that of the bulk.<sup>23–26</sup> Our finding of the  $M_b$  phase confirms that, in the (110) epitaxial film, the resulting polarization indeed lies in the (*HHL*) plane, in between the [110] and [111] directions. It is also relevant to note the presence of a slight offset of one of the domains with respect to the other along the (00L) in the mesh scans. This offset is probably due to the strain of the films such that the two domains are not exactly mirrors of each other, but rather have slightly different monoclinic angles. The unit cell of this  $M_b$  phase is doubled with respect to the primitive pseudocubic one, where ( $c_m < b_m/\sqrt{2} < a_m/\sqrt{2}$ ) and where the polarization lies in the (*HHL*) plane. One in-plane lattice parameter ( $a_m/\sqrt{2} = 3.985 \text{ \AA}$ ) is fixed close to that of the SrTiO<sub>3</sub> substrate, whereas the out-of-plane parameter ( $c_m = 3.888 \text{ \AA}$ ) is unique to the film.

In summary, the lattice structure of (110)-oriented BiFeO<sub>3</sub> epitaxial thin layers has been shown to be the monoclinic  $M_b$ . Our results demonstrate a change in phase stability from rhombohedral in bulk single crystals to monoclinic in epitaxial thin films with two domain states whose polarization is just slightly tilted away from [110] towards [111].

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