Temperature-Driven Structural Phase Transition in Tetragonal-Like BiFeO₃

Wolter Siemons¹, Michael D. Biegalski², Joong Hee Nam¹,³, and Hans M. Christen¹*¹

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
²Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
³Optic and Electronic Ceramics Division, Korea Institute of Ceramic Engineering and Technology (KICET), Seoul 153-801, Republic of Korea

Received June 18, 2011; accepted July 20, 2011; published online August 8, 2011

Highly strained BiFeO₃ exhibits a “tetragonal-like, monoclinic” crystal structure found only in epitaxial films (with an out-of-plane lattice parameter exceeding the in-plane value by >20%). Previous work has shown that this phase is properly described as an $M_C$ monoclinic structure at room temperature [with a (010)pc symmetry plane, which contains the ferroelectric polarization]. Here, we show detailed temperature-dependent X-ray diffraction data that reveal a structural phase transition at ~100°C to a high-temperature $M_A$ phase [“tetragonal-like” but with a (110)pc symmetry plane]. These results indicate that the ferroelectric properties and domain structures of the strained BiFeO₃ are strongly temperature dependent.

© 2011 The Japan Society of Applied Physics

---

Bismuth ferrite (BiFeO₃, BFO) is the only known material that exhibits both magnetic and ferroelectric order at room temperature and has thus received much attention.¹ While the multiferroicity of this perovskite has been the subject of much interest, the ferroelectric and structural properties by themselves are fascinating. In fact, the ferroelectric polarization, which in the bulk points along the pseudocubic [111]pc direction, rotates towards the surface normal (i.e., the [001]pc direction) under mild compressive strain²,³ (here and in the following, the subscript “pc” is used to denote pseudocubic indices). This strain is imposed onto the film by its epitaxial relationship to a substrate such as SrTiO₃, with $a = 3.905$ Å (while for BFO, $a_{pc}^{bulk} \approx 3.96$ Å). The crystal structure of such films is described as monoclinic, and deviates little from that of the bulk analog. Therefore, we refer to this phase as rhombohedral-like (R-like).

A drastic change in crystal structure occurs when the compressive in-plane strain exceeds $\sigma \approx -4.5\%$ [which is achieved, for example, by epitaxial growth onto LaAlO₃ (LAO) substrates, $a_{pc} = 3.789$ Å]: the out-of-plane lattice parameter increases in steplike fashion by more than 20%, resulting in a monochromatically distorted structure that resembles a highly tetragonal unit cell (T-like).⁴⁻⁷ Interestingly, the change from the monoclinic R-like to the monoclinic T-like phase is accompanied by a significant symmetry change.⁸⁻¹⁰ To fully appreciate these differences, we “construct” the two different monoclinic structures by subjecting a hypothetical tetragonal unit cell to a shear distortion perpendicular to the long axis (and thus, in the case of BFO films, parallel to the film/substrate interface plane). As illustrated in Fig. 1, a shear distortion in the [100]pc direction results in a monoclinic structure for which the mirror (or glide) plane is parallel to the (010)pc plane. Neumann’s principle¹¹ dictates that the ferroelectric polarization is contained in this plane. Using the notation introduced by Vanderbilt and Cohen,¹¹ we refer to this phase as $M_C$. In contrast, a so-called $M_A$ structure is obtained when the hypothetical tetragonal unit cell is subject to a shear distortion along the [110]pc direction (see Fig. 1); the ferroelectric polarization then lies within the (110)pc plane. As has recently been shown,¹² the strain-induced R-like-to-T-like transition at room temperature is in fact an $M_A$-to-$M_C$ symmetry change, with the corresponding necessary change in the polarization orientation.

---

Fig. 1. Schematic drawing of monoclinic unit cells. (a) depicts an $M_C$ structure, in which $a \parallel a_{pc}$ and $b \parallel b_{pc}$ (where $a$ and $b$ are the proper monoclinic axes), and which can be seen as resulting from a shear distortion along the [100]pc direction. (b) shows the result of a shear distortion along [110]pc, requiring a doubled unit cell with the $a$ and $b$ axes rotated by 45° with respect to their pseudocubic counterparts. The smallest unit cells consistent with these shear distortions are shown and used to index the data in this paper, ignoring additional doubling of the cells due to antiferromagnetism and octahedral tilts.

---

¹E-mail address: christenhm@ornl.gov
The crystallographic \([00l]_{pc}\) direction at 25 and 175°C indexed RSMs. Observations of a doublet or triplet immediately distinguish the phase indicated by a star. In particular, there is no additional peak near 44° corresponding to excess bismuth oxides are labeled. The results of the maps containing the 103pc and 113pc reflections are shown in Figs. 3(a) and 3(b).] At room temperature [Fig. 3(a)], we find a triplet in the 103 map and a doublet for 113, which, by comparing with Table I, reconfirms the previously observed intermediary phase (near 43.4°).18)

The structural properties are studied on a sample grown from a sintered BFO target with 10% excess Bi by pulsed laser deposition (PLD) with a KrF excimer laser (248 nm) at 5 Hz. During deposition, a LAO substrate was kept at 700°C with 25 mTorr oxygen background pressure, resulting in a deposition rate of approximately 0.2 Å/pulse. The film analyzed in this work was approximately 300 nm thick.

X-ray diffraction measurements were performed on a PANalytical X′Pert thin-film diffractometer with Cu Kα radiation equipped with an Anton Paar hot stage. Diffraction patterns were obtained at 25°C intervals between 25 and 175°C. In Fig. 2(a), we show the diffraction pattern along the crystallographic \([001]_{pc}\) direction at 25 and 175°C. Besides the expected BFO and LAO peaks, there is a small contribution from an unassigned additional epitaxial phase that we discuss below (labeled with a star symbol), which is observed both at the 001pc and 002pc locations. Peaks corresponding to excess bismuth oxides are labeled. The additional peak near 44° results from the sample hot stage and is absent in measurements performed on the standard sample holder. Therefore, the data shows that our films are phase-pure with the exception of excess bismuth oxides and the temperature-dependent observation of the above-mentioned phase indicated by a star. In particular, there is no presence of the R-like BFO (which would be visible near 45.7°) or the recently observed intermediary phase (near 43.4°).18)

In Fig. 2(b), we focus on the evolution of the 004pc peak as a function of temperature. A clear phase transition is observed at 100°C: the peaks of the low-temperature phase (near 82.5°) diminish in intensity as the high-temperature phase appears. Intrinsic peak broadening makes it impossible to observe this splitting at lower angles, such as those investigated previously.16) However, it is clearly seen in Fig. 2(b) that higher-temperature peaks shift towards higher angles (i.e., smaller lattice parameters) with increasing temperature, consistent with our previous observations of a lower thermal expansion of BFO than of LAO.

To understand the nature of this phase transition near 100°C, we use RSMs through the 002pc, 103pc, and 113pc reflections. At all temperatures, the 002pc maps show only one peak for the film, confirming that the film’s (00L) planes are parallel to those of the substrate, as discussed above. [The results of the maps containing the 103pc and 113pc reflections are shown in Figs. 3(a) and 3(b).] At room temperature [Fig. 3(a)], we find a triplet in the 103 map and a doublet for 113, which, by comparing with Table I, reconfirms the previous observation8,9) of an \(M_C\) phase. From the peak positions, we find that \(a/b = 1.019(2), c = 4.67(2)\) Å, and \(β = 88.1(3)^{°}\). However, as the sample is heated above the phase transition temperature to 175°C, we find that the 103pc peak now shows a doublet and the 113pc peak a triplet. Inspection of Table I immediately indicates that the film at

### Table 1. Monoclinic diffraction peaks visible in the pseudocubically indexed RSMs. Observations of a doublet or triplet immediately distinguish between \(M_A\) and \(M_C\).

| RSM    | \(M_A\)       | \(M_C\)       |
|--------|---------------|---------------|
| 103pc  | 113, 113      | 103           |
|        | 113, 113      | 013, 013      |
| 113pc  | 203           | 113, 113      |
|        | 023, 023      | 113, 113      |

---

Fig. 2. X-ray \(θ-2θ\) scans for T-like BFO. (a) Scans through the 001pc and 002pc peaks of the BFO film and LAO substrate, at 25 and 175°C. The peak labeled with a dot results from the hot stage. The peaks labeled with a star are epitaxial peaks of a secondary room-temperature phase. Also indicated are peaks corresponding to excess bismuth oxide. (b) expanded view through the film’s 004pc peak at 25°C intervals upon heating. Curves are displaced vertically for clarity. At 100°C, the coexistence of two T-like phases is observed.
High temperature exhibits MA monoclinic phase, where the monoclinic distortion is along the [110]_pc direction. Confirming the consistency of this interpretation, we quantitatively inspect the splitting of the peaks in the normal ([001]_pc) direction of the RSMs: At 25 °C, we observe

\[ qz(113_m) - qz(113_m) = |qz(103_m) - qz(103_m)| \]

as expected. At 175 °C, the 113pc map corresponds to a higher-order monoclinic diffraction, and therefore,

\[ qz(113_m) - qz(113_m) = (1/2)|qz(203_m) - qz(203_m)|. \]

Thus, our data can reliably be interpreted as monoclinic \( M_A \) with \( a/b = 1.002(2), c = 4.672(2) \) Å, and \( \beta = 88.1(3)° \). Note that the deviation of \( \beta \) from 90° is much larger in both T-like phases than it is in the R-like structure where \( \beta \approx 89.5° \) is reported. In other words, the T-like phase has a large \( c/a \) ratio but is otherwise further from tetragonal than the R-like structure. We also note that two recent studies report results from x-ray diffraction and Raman spectroscopy or neutron scattering that are consistent with our observation of a structural phase transition near 100 °C, and those findings can now be attributed to the \( M_C \)-to-\( M_A \) symmetry change.

The temperature-induced change from one monoclinic structure to a different one has profound consequences for the ferroelectric properties of BFO films but is not strikingly different from what can be expected based on the current knowledge of BFO and related materials. As mentioned above, such transitions occur in Pb-based solid-solution ferroelectrics and in R-like BFO. In addition, previous calculations have shown the energetic proximity of several different crystalline structures within T-like BFO. There, it was also pointed out that the transformation from the \( M_C \) to the MA phase cannot be continuous—it requires the coexistence of an intermediate phase or the coexistence of two competing phases, and this coexistence is clearly observed here [Fig. 1(b)]. Therefore, in the intermediate temperature range (near 100 °C), the ferroelectric and structural properties will be highly sensitive to in-plane electric or elastic stimuli, as the projection of the ferroelectric polarization onto the in-plane direction differs between the coexisting \( M_A \) and \( M_C \). Thus, interesting new piezoelectric effects are expected, and there is hope that slight chemical modifications (doping) may lower the structural phase transition to room temperature, further increasing the practical utility of this material.

Finally, we note that the high-temperature \( M_A \) monoclinic phase approaches a higher symmetry than the room temperature \( M_C \) \( [b/a \) closer to unity, and thus also \( b_{pc} \approx a_{pc} \) with \( \angle(a_{pc}, b_{pc}) \approx 90° \). While changes in the ferroelectric and ferroelastic properties across the transition are still being investigated, these observations shed light on the formation of the domain structures in T-like BFO films. In fact, the high-temperature \( M_A \) phase (which we assume to be present at the growth temperature) exhibits a nearly square in-plane lattice, as required for good epitaxial match. This is not the case for the room-temperature \( M_C \) structure [with \( b/a = 1.019(2) \) as discussed above]. Clearly, this temperature-reversible change has to occur without the breaking of chemical bonds and will thus locally lead to large elastic strains. However, such strains cannot be fully accommodated within a monoclinic structure of the observed texture [i.e., having the (00L)-planes of the film parallel to those of the substrate]. Therefore, it is not surprising that an additional phase [indicated by a star symbol in Fig. 2(a)] occurs at low temperature.

To summarize, we observe a temperature-driven phase transition in tetragonal-like BFO from a monoclinic \( M_C \) phase at room temperature to a different (but still T-like) monoclinic phase of \( M_A \) symmetry. This will have significant consequences for the ferroelectric and ferroelastic properties of T-like BFO, as the symmetry constrains the in-plane component of the polarization to different orientations in these two phases (along [100]_pc at room temperature but along [110]_pc above 100 °C). The high-temperature \( M_A \) phase approaches a higher symmetry in its in-plane arrangement than its room-temperature \( M_C \) counterpart, with a nearly square lattice observed. Future work is needed to study the effect of this structural phase transition on optical, ferroelectric, and magnetic properties.

Acknowledgments W.S. and H.M.C. acknowledge support by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division. X-ray diffraction (M.D.B.) was supported by the Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Office of Basic Energy Sciences, US Department of Energy. J.H.N. was supported by the Republic of Korea, Ministry of Knowledge and Economy, Visiting Scientists Program, under IAN:16/642601, with the US Department of Energy.

1) J. Wang et al.: Science 299 (2003) 1719.
2) H. W. Jang et al.: Phys. Rev. Lett. 101 (2008) 107602.
3) D. H. Kim et al.: Appl. Phys. Lett. 92 (2008) 012911.
4) D. Rincschi et al.: J. Phys.: Condens. Matter 18 (2006) L97.
5) H. Bea et al.: Phys. Rev. Lett. 102 (2009) 217603.
6) R. I. Zeches et al.: Science 326 (2009) 977.
7) A. J. Hatt et al.: Phys. Rev. B 81 (2010) 054109.
8) Z. Chen et al.: Adv. Funct. Mater. 21 (2011) 133.
9) H. M. Christen et al.: Phys. Rev. B 83 (2011) 144407.
10) J. F. Nye: Physical Properties of Crystals (Oxford University Press, U.S.A., 1985).
11) D. Vanderbilt and M. Cohen: Phys. Rev. B 63 (2001) 094108.
12) C. J. M. Daumont et al.: Phys. Rev. B 81 (2010) 144115.
13) K. Saito et al.: Jpn. J. Appl. Phys. 45 (2006) 7311.
14) B. Noheda and D. E. Cox: Phase Transitions 79 (2006) 5.
15) H. Toupet et al.: Phys. Rev. B 81 (2010) 140101(R).
16) C. J. C. Bennett et al.: J. Mater. Res. 26 (2011) 1326.
17) B. C. Chakoumakos et al.: J. Appl. Phys. 83 (1998) 1979.
18) A. R. Damodaran et al.: Adv. Mater. 23 (2011) 3170.
19) I. C. Infante et al.: arXiv:1105.6016.
20) G. J. MacDougall et al.: arXiv:1107.2975.