Supporting Information

Observation of oxygen pyramid tilting induced polarization rotation in strained BiFeO₃ thin film

Dongsheng Songᵃᵇ, Heng-Jui Liúᶜ, András Kovácsᵇ, Rafal E. Dunin-Borkowskiᵇ, Ying-Hao Chuᵈ, Jing Zhuᵃ⁺

ᵃNational Center for Electron Microscopy in Beijing, Key Laboratory of Advanced Materials (MOE) and The State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.
ᵇErnst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, D-52425 Jülich, Germany.
ᶜDepartment of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan.
ᵈDepartment of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan.

⁺Corresponding author: jzhu@mail.tsinghua.edu.cn
Experimental details

40 nm and 57 nm BFO thin films were epitaxially grown on (001)-oriented LAO single crystal substrates using pulsed laser deposition (PLD). TEM specimens were prepared using focused ion beam milling with a Ga ion beam at 30 kV beam energy on an FEI Helios NanoLab 400S workstation, followed by thinning with Ar ion milling in a Bal-Tec Res-120 ion beam milling system. The high-angle annular dark-field (HAADF-STEM) experiments were carried out at 200 kV with an FEI Titan G2 80–200 ChemiSTEM microscope equipped with a high-brightness Schottky field emission electron gun, a probe Cs corrector. Nano diffraction was performed at 300 kV with an FEI Titan 80–300 microscope equipped with a probe Cs corrector. Geometrical phase analysis (GPA) was carried out with the scripts written by in Digital Micrograph. The position of atom Fe and Bi are determined by performing the Gaussian fitting in the Mac TempasX software. The mapping of lattice parameters is calculated by measuring the distance of Bi atoms. The polarization mapping is plot by calculating the displacement of Fe atom from the center of four Bi atoms around it. All the calculations are conducted by a customed Matlab code.
Figure S1 Mixture of R-like and T-like phases in a BFO/LAO film of thickness 57 nm under [100] zone axis. (a) HRSTEM image showing stripe-like R-like and T-like phases. (e-g) show FFTs of the whole image, the T-like phase and the R-like phase, respectively. (b) Rotation map of the R-like and T-like phases. (c, d) In-plane ($\varepsilon_{xx}$) and out-of-plane ($\varepsilon_{yy}$) deformation measured using GPA.
Figure S2 Simulated electron diffraction patterns of the \textit{Cc} and \textit{Cm} phases. The upper row shows atomic models of the \textit{Cc} and \textit{Cm} phases viewed along different crystallographic directions. The lower row shows corresponding simulated electron diffraction patterns. The angles of the basis vectors determined from the simulations are shown below each figure.

**Identifying the \textit{Cm} and \textit{Cc} phase**

For the phase without extra $\frac{1}{2}$ (110) spots, there are two possible atomic models. One is the \textit{Cm} phase viewed along [010] as shown in Figure S2. In this direction, the oxygen pyramid tilting is along one direction, without the extra spots in Figure S2. The other is the \textit{Cc} phase, for which no extra spots are present along [100] or [010] in Figure 2(b), 2(d) and Figure S2. In order to exclude the possibility of the \textit{Cm} phase along [010], the angle between the basis vectors $a$ and $c$ was measured from Figure 2(b) and 2(e). The angle is 88.09° for the phase without extra spots, which is consistent with the \textit{Cc} phase along [100] or [010] (~87.91°). For the \textit{Cm} phase along [010], the angle is 86.58° in Figure S2. Therefore, the phase without the extra $\frac{1}{2}$ (110) spots is concluded to be the \textit{Cc} phase, which always exists in ultrathin BFO films on LAO$^{27,30}$. The stripe-like morphology with two \textit{T-like} phases, rather than a mixture of \textit{T-like} and \textit{R-like} phases, is observed at intermediate thicknesses of BFO on LAO.
Figure S3 Polarization mapping of the $C\!c$ and $C\!m$ phases in different areas under [100] zone axis to confirm that the large polarization rotation of the $C\!c$ phase is a common phenomenon in BFO/LAO thin films of thickness 40 nm. Meanwhile, the rotation angle of polarization is not homogeneous in the thin films.
Figure S4. Chemical composition of Cc and Cm phases by STEM-EELS. (a) STEM image of the stripe-like Cc and Cm phases. The green line indicates the area for line scanning by STEM-EELS. (b,c) EELS spectrum image of O K and Fe L3,2 edges after background subtraction, respectively. (d,e) EELS O K and Fe L3,2 edge extracted from the Cc and Cm phases as indicated by the red boxes in (b,c), respectively. (f) Atomic percentage of element Fe and O by EELS chemical quantification.