Anisotropic epitaxial stabilization of a low-symmetry ferroelectric with enhanced electromechanical response

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Piezoelectrics interconvert mechanical energy and electric charge and are widely used in actuators and sensors. The best performing materials are ferroelectrics at a morphotropic phase boundary, where several phases coexist. Switching between these phases by electric field produces a large electromechanical response. In ferroelectric BiFeO$_3$, strain can create a morphotropic-phase-boundary-like phase mixture and thus generate large electric-field-dependent strains. However, this enhanced response occurs at localized, randomly positioned regions of the film. Here, we use epitaxial strain and orientation engineering in tandem—anisotropic epitaxy—to create a low-symmetry phase of BiFeO$_3$ that acts as a structural bridge between the rhombohedral-like and tetragonal-like polymorphs. Interferometric displacement sensor measurements reveal that this phase has an enhanced piezoelectric coefficient of ×2.4 compared with typical rhombohedral-like BiFeO$_3$. Band-excitation frequency response measurements and first-principles calculations provide evidence that this phase undergoes a transition to the tetragonal-like polymorph under electric field, generating an enhanced piezoelectric response throughout the film and associated field-induced reversible strains. These results offer a route to engineer thin-film piezoelectrics with improved functionalities, with broader perspectives for other functional oxides.
regions induces polarization rotation, driving a phase transformation between the R’ and T’ polymorphs, leading to a large strain and enhanced electromechanical response.\(^\text{27,28}\)

In contrast with other MPB systems (such as PZT) where the bridging phase can be obtained at the correct composition, in typical mixed-phase BFO, separation into the R’ and T’ constituents is unavoidable.\(^\text{15}\) A monolithic film of the soft triclinic polymorph that is capable of reversible conversion to T’, and thus enhanced piezoelectric response, has remained elusive.

Here, we adopt an approach called anisotropic epitaxy using the highly miscut (310) LaAlO\(_3\) (LAO) substrate to demonstrate large-scale epitaxial stabilization of a highly strained, highly distorted R’ phase of BFO. Electromechanical measurements using an interferometric displacement sensor (IDS) demonstrate that the
untransformed phase alone has an intrinsic piezoresponse more than double that of standard R′-BFO. Spectroscopic measurements combined with first-principles-based calculations suggest that an applied electric field induces a reversible phase transition from the distorted R′ (that is, triclinic) phase to a T′ (that is, M2) phase, accompanied by elastic softening and an increase in the electromechanical strain.

**Establishing the basis for our approach**

In bulk ceramics and single crystals, MPBs are traditionally obtained through hydrostatic pressure, doping, intentionally induced defects and/or disorder. In epitaxial thin films, the mechanical and electrical boundary conditions are highly tunable. For instance, isotropic strain engineering can stabilize novel ferroelectric domain arrangements and structural phases, and various substrate orientations, such as (100), (110) and (111), yield (310)pc-oriented LAO substrates (nominal misfit strain of ~4.65 Å, characteristic of the T′ phase). For a 45° miscut, a, b and c are almost equal, indicative of the R′ phase. DFT calculations (lines in Fig. 1l) reproduce this trend and reveal that upon increase of the miscut from 15 to 20°, the c lattice parameter dramatically decreases, indicating the transition from the T′ to R′ phase. Indeed, this is observed experimentally: at a miscut of ~18.4° (310) orientation, the BFO film’s lattice parameters are halfway between the R′ and T′ polymorphs; c is ~4.30 Å and a remains clamped to the LAO substrate, while along the orthogonal [130]pc, in-plane direction, the film is partially relaxed. This anisotropic strain condition causes the symmetry to become triclinic (Supplementary Note 1), and this phase has the highest average strain in the a–b plane (~3.7%) of any pure R′ polymorph of BFO. We refer to this low-symmetry phase as ‘tri-BFO’.

The crystallography of tri-BFO on LAO (310) was examined with high-angle annular dark-field scanning transmission electron microscopy (STEM). A STEM image taken along the [001]pc zone axis (Fig. 2a) shows the clear miscut and several misfit dislocations at the substrate–film interface. The dislocation cores are clearly observed in the geometric phase analysis strain map of the boxed region (Fig. 2b; full strain maps and selected area electron diffraction in Supplementary Note 2). The STEM image collected along the orthogonal zone axis [130]pc (Fig. 2c) does not resolve individual atoms as the distance between the atomic columns is at the resolution limit (Supplementary Note 3); however, the corresponding geometric phase analysis strain map (Fig. 2d) confirms that the film is coherently strained along [001]pc. A map of the local polarization direction (Fig. 2e), extracted from the Fe atom displacement within the Bi cages from Fig. 2a, reveals the presence of two domains—a majority of right-down direction (Fig. 2f) and a minority of left-down direction (Fig. 2g). Piezoresponse force microscopy (PFM) imaging is consistent with these findings: the as-grown ferroelectric domain separation into the T′ and R′ polymorphs occurs at a miscut of 0°, the a and b lattice parameters are equal to that of the LAO, while the c parameter is ~4.65 Å, characteristic of the T′ phase. For a 45° miscut, a, b and c are almost equal, indicative of the R′ phase. DFT calculations (lines in Fig. 1l) reproduce this trend and reveal that upon increase of the miscut from 15 to 20°, the c lattice parameter dramatically decreases, indicating the transition from the T′ to R′ phase. Indeed, this is observed experimentally: at a miscut of ~18.4° (310) orientation, the BFO film’s lattice parameters are halfway between the R′ and T′ polymorphs; c is ~4.30 Å and a remains clamped to the LAO substrate, while along the orthogonal [130]pc, in-plane direction, the film is partially relaxed. This anisotropic strain condition causes the symmetry to become triclinic (Supplementary Note 1), and this phase has the highest average strain in the a–b plane (~3.7%) of any pure R′ polymorph of BFO. We refer to this low-symmetry phase as ‘tri-BFO’.

The structural characterization of low-symmetry phase

Epitaxial films of BFO were grown on (100)_pc-, (110)_pc- and (310)_pc-oriented LAO substrates (nominal misfit strain of ~4.5%; pc, pseudocubic) by pulsed laser deposition (Methods). The pseudocubic lattice parameters of the three films measured using X-ray diffraction (Methods) are presented in Fig. 1l (data points). At a miscut of 0°, the a and b lattice parameters are equal to that of the LAO, while the c parameter is ~4.65 Å, characteristic of the T′ phase. For a 45° miscut, a, b and c are almost equal, indicative of the R′ phase. The STEM image collected along the orthogonal zone axis [130]pc (Fig. 2c) does not resolve individual atoms as the distance between the atomic columns is at the resolution limit (Supplementary Note 3); however, the corresponding geometric phase analysis strain map (Fig. 2d) confirms that the film is coherently strained along [001]pc. A map of the local polarization direction (Fig. 2e), extracted from the Fe atom displacement within the Bi cages from Fig. 2a, reveals the presence of two domains—a majority of right-down direction (Fig. 2f) and a minority of left-down direction (Fig. 2g). Piezoresponse force microscopy (PFM) imaging is consistent with these findings: the as-grown ferroelectric domain arrangement is essentially single-domain along [130]pc (as expected from a highly miscut substrate), with uniform out-of-plane polarization (Fig. 2h). Although the two in-plane variants along the [001]pc direction are energetically degenerate, in this sample we observe only one of these variants (Fig. 2i), which is schematically shown in Fig. 2j. PFM switching experiments (Supplementary Note 3) reveal that out-of-plane polarization reversal also induces a change in the in-plane component along [130]pc, while the component of polarization along [001]pc is unchanged. This implies a 109° switch, as expected for a film grown on a substrate with a miscut along the [010] direction.

The structural analyses from X-ray diffraction and STEM thus indicate that the tri-BFO film is fully strained along [001]pc, while along [130]pc it is partially relaxed. This delicate balance of unequal strains imposed along each in-plane direction distinguishes our approach from conventional strain engineering and prevents phase separation into the T′ and R′ polymorphs, allowing us to strain the R′-BFO to its physical limits.

**Electromechanical response**

Having established the crystallography of tri-BFO, we now discuss its electromechanical response, which we measured on a sample with a thin (~2 nm) layer of La0.6Sr0.4MnO3 between the LAO substrate and the BFO film, which acts as a bottom electrode. La0.6Sr0.4MnO3 is expected to be a ‘bad metal’ in this thickness regime; however, its conductivity is sufficient to facilitate PFM characterization. The presence of the lower electrode induces an unavoidable relaxation in the BFO layer, such that a ~40–60 percent volume phase mixture of tri-BFO/R’-BFO is formed (Supplementary Note 1).
Before proceeding, we point out that obtaining a true and reliable measurement of the electromechanical response (and associated piezoelectric coefficient $d_{33}$) for very thin films is exceedingly difficult. One of the best currently available methods is through an atomic force microscope fitted with an IDS (Methods). This scanning probe technique uses laser interferometry to measure the precise displacement of the tip, and when correctly implemented, unlike traditional optical-beam-deflection-based PFM measurements of $d_{33}$ values, is mostly unaffected by electrostatic contributions. In our crystal geometry, the electric field was applied along [013]$_{pc}$, which denotes the strain in the [010] direction. This is not strictly along the ‘3’ direction of the film’s crystal structure, we use $d_{33}$ to denote this out-of-plane piezoresponse.

Using IDS-coupled atomic force microscope methods, we first consider the spatial dependence of piezoresponse loops measured across the sample surface. The data were collected on a 30 $\times$ 30 grid of points over a $2 \times 2 \mu$m$^2$ region of the film, where OFF-field and ON-field piezoresponse loops were measured (full data in Supplementary Note 4). Despite minimizing electrostatic effects in our measurements, we observe marked differences between the OFF-field and ON-field IDS measurements. For instance, while the OFF field shows typical displacements of 40–60 pm V$^{-1}$, the ON-field response reaches enormous values above 200 pm V$^{-1}$ in some spatial locations. Due to the IDS method’s ability to strongly minimize electrostatic effects, large differences between OFF-field and ON-field measurements may suggest a field-induced phase transition. (Although IDS-coupled piezoresponse measurements are largely unaffected by electrostatic forces, and although we have to the best of our ability eliminated other sources of measurement artefacts, we cannot rule out all possible sources of spurious signals.) Nevertheless, the OFF-field response is repeatable such that we can assert with confidence that it is a true representation of the tri-BFO piezoresponse below any critical field that induces a transition. We therefore restrict our following discussion of the measured $d_{33}$ constant to OFF-field measurements (further details in Supplementary Note 4).

Figure 3a shows the piezoelectric displacement as a function of applied bias, with the corresponding phase loop (Fig. 3b) for a representative point. We observe clear indications of ferroelectric switching and note that the maximum OFF-field piezoresponse of $\sim$50–60 pm V$^{-1}$ is quite remarkable for a clamped 20-nm-thick film. To contextualize the response of the tri-BFO sample, we next compare the IDS-coupled piezoresponse for ‘standard’ R’-phase BFO (grown on (100) SrTiO$_3$) and tri-BFO films over a 1.5 $\times$ 1.5 $\mu$m$^2$ area. Figure 3c.d presents the surface topography and IDS-measured $d_{33}$ response (measured at 1 V; making the units of $d_{33}$ thus picometre per volt) for the standard R’ sample (Fig. 3c), contrasted with the...
response of tri-BFO (Fig. 3d). At first glance, the tri-BFO sample shows an increased $d_{33}'$ response, with values approaching 60 pm V$^{-1}$, in line with the loops of Fig. 3a. Shown in Fig. 3c, frequency histograms of these piezoelectric measurements were fitted with two Gaussians to describe (1) the bulk domain piezoelectric (2) the lower response of the domain walls. These histograms reveal a marked positive shift in the piezoelectric peak centre (that is, the median value) for tri-BFO (Fig. 3f) when compared to the standard R′-BFO sample (Fig. 3e). The spatially averaged IDS-measured $d_{33}'$ value for tri-BFO is 23.4 pm V$^{-1}$, compared to 9.6 pm V$^{-1}$ for the standard R′-BFO film (Supplementary Note 4), implying a strong enhancement caused by an electric-field-induced transition at BFO R′–T′ phase boundaries.

A representative BEPS spectrogram of the tri-BFO film taken at a single spatial location and magnified around the field-induced phase transition (Fig. 3f) reveals that during the ON-field bias application, there is a distinct decrease (that is, softening) of the resonant frequency (of 2 kHz or 0.5%), suggesting a change in the elastic modulus. In the context of our IDS measurements and previous reports, we interpret this shift as a suggestion of a field-induced phase transition from tri-BFO (Fig. 3i) to T′-BFO (Fig. 3j). The spatial mapping of BEPS (measured over 2 μm$^2$) shows that the softening is observed everywhere, albeit with some spatial variation (not shown here). Finally, fatigue testing shows that ferroelectric switching occurs for >10,000 driving cycles (Supplementary Note 5); however, the softening behaviour decays after several hundred cycles.

**Suggestions of a field-induced phase transition**

To corroborate the suggestions of a field-induced phase transition from the IDS-coupled PFM, we used band-excitation piezoelectric spectroscopy (BEPSS) Methods on a 2 × 2 μm$^2$ region of 30 × 30 points. At each d.c. bias voltage step in the triangle wave (Fig. 3g), the frequency dependence of the electromechanical response of the sample is measured (purple lines and inset in Fig. 3g). A systematic and reproducible change in this contact resonance frequency is strongly suggestive of a modification of the elastic properties of the material and has previously been used to demonstrate elastic softening caused by an electric-field-induced transition at BFO R′–T′ phase boundaries.

**Insight from first-principles calculations**

To gain further insight into tri-BFO, 0K DFT and 300K first-principles-based effective Hamiltonian calculations were performed (Methods and Supplementary Notes 6 and 7).
Figure 4 presents the DFT-computed polarization and octahedral tilting as a function of applied electric field, while Fig. 4d–f focuses on the electromechanical and elastic response (comparison with measurements in Fig. 3). For the zero-field state, DFT finds a triclinic (P1) structure, characterized by non-equal components of the polarization vector $\mathbf{P}$ along the pseudocubic axes ($p_a, p_b, p_c$; Fig. 4a). The angle subtended by $\mathbf{P}$ with the [001] direction is deduced (Fig. 4b). Similarly, the octahedral rotations ($\omega_a, \omega_b, \omega_c$; Fig. 4c) are also found to be unequal.

Regarding the electromechanical properties of tri-BFO at zero field, the computations determine $d_{33} \approx 110 \text{ pm V}^{-1}$, higher than the calculated values for typical R′-phase BFO (literature survey of piezoelectric coefficients for BFO in Supplementary Note 8). The computed elastic stiffness $C_{33}$ at zero field (Fig. 4f) is considerably lower than that of the R3c phase (129–150 GPa; ref. 41), indicating that it is intrinsically mechanically soft.

Next, under applied field (Fig. 4), two regions are distinguished by a critical field $E_c \approx 1.7 \text{ MV cm}^{-1}$. Upon increasing field, the in-plane components of the polarization decrease (Fig. 4a), and the octahedral rotations are completely suppressed along the $z$ direction and are reduced along the other two directions (Fig. 4c). This transition thus suggests a conversion from tri-BFO to the $T\prime$-phase. Notably, at $E_c$, the polarization undergoes a rotation of $-8^\circ$ (Fig. 4b). This field-induced transition is schematically illustrated in Fig. 3i,j.

These structural changes are accompanied by anomalous signatures in the electromechanical coefficients. The $d_{33}$ value diverges approaching the transition (with values up to 3,000 pm V$^{-1}$) and is accompanied by an abrupt increase in strain (Fig. 4c). Additionally, the elastic coefficient $C_{33}$ (Fig. 4f) systematically decreases upon approach to $E_c$, above which it rebounds and then increases towards saturation.

**Discussion and outlook**

Combining theoretical and experimental results, we draw key inferences vis-à-vis the implications of the elastic softening observed in this system. Elastic anomalies triggered by external fields at a phase transition have been observed for various materials.28,41. There are two alternative viewpoints to explain this effect: (1) softening of acoustic phonon modes triggered by a field-induced phase transition to a low-symmetry phase42, versus (2) the presence of an adaptive domain phase where a vanishing polarization anisotropy decreases the domain wall energy32,43. Irrespective of the model, the key factor is a flattening of the free-energy curve that allows polarization rotation (compare to the introduction). In the context of the rotator and extender piezoelectrics given by Davis et al.25, this would correspond to the former viewpoint.

Anisotropic epitaxy has broader perspectives than simply BFO and ferroelectric materials. For instance, in optically active oxides52,53, low-symmetry phases may harbour dramatically enhanced optical responses. While our anisotropic epitaxy studies on BiFeO$_3$ show corrugated surfaces, probably due to the reduced surface energy of the (100) and (110) facets of BFO compared to the (310) surface, further optimization of fabrication will overcome such hurdles.

In summary, we have used anisotropic epitaxy to craft a mechanically soft triclinic phase of BFO. This phase has an intrinsic $d_{33}$ response that is enhanced compared to typical R′-phase BiFeO$_3$ films. Furthermore, there is strong spectroscopic evidence of a field-induced phase transition that acts to magnify this piezoresistance to even larger values. Wider perspectives of the anisotropic epitaxy technique encompass concepts, such as anisotropy control in low-symmetry magnetic oxides and epitaxially metastable phases of multiferroics, that could be harnessed in next-generation oxide electronic devices.
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Methods

Epitaxial thin-film fabrication. BFO thin films were grown by pulsed laser deposition using a KrF excimer laser with wavelength 248 nm. The LAO substrates (with orientations (110), (310) and (100)) with 0.5 mm thickness were purchased from Shin-Etsu and were single-side polished with no specific surface treatment. The substrates were heated to 590 °C and the films grown in an oxygen partial pressure of 100 mtorr. The laser fluence was 1–2 J cm⁻², and the films were cooled to room temperature at 20 °C min⁻¹ in 5 torr of oxygen. To enable IDS measurements, a 2-nm-thick bottom electrode of conductive La0.67Sr0.33MnO3 was inserted between the LAO (310) substrate and the BFO film. The presence of this electrode layer modifies the stability regions of the tri-BFO phase such that a phase mixture of tri-BFO and R′-BFO is unavoidable; however, through careful tuning of growth parameters and electrode thickness, we obtained a 40±0.5% volume fraction between the tri-BFO and R′-BFO phases for a nominal film thickness of 20 nm. X-ray diffraction characterization of the mixed-phase sample is given in Supplementary Note 1.

Structural characterization. X-ray diffraction was performed using Cu Kα₁ radiation in 9 kW rotating anode Rigaku SmartLab and PANalytical X-ray Diffractometer systems. The lattice parameters of the pure tri-BFO and the mixed tri-BFO/R′-BFO films were determined by measuring reciprocal space maps around various reflections, as detailed in Supplementary Note 1.

STEM. The STEM specimens were prepared by tripod polishing followed by final cleaning with a Getaion precision ion polishing system. The STEM images were acquired on a double-tilted FEG Titan™ 80–300 FEG/STEM at 300 kV voltage with the convergence angle of 21 mrad. The STEM images were drift corrected for geometric phase analysis and local polarization direction maps. Additional STEM images are presented in Supplementary Note 2.

Ferroelectric domain characterization and IDS measurements. Standard PFM measurements were performed on a commercial atomic force microscope (Cypher, Asylum Research) to determine the as-grown in-plane and out-of-plane domain arrangements for both the pure tri-BFO film (grown directly on LAO (310)) and the mixed tri-BFO/R′-BFO film (grown on La0.67Sr0.33MnO3-buffered LAO (310)). The tips were Pt/Cr-coated probes (ElectriMulti75-G, BudgetSensors), and the excitation voltage was 500 mV for the in-plane and out-of-plane responses. Further PFM was carried out in an ambient environment on a commercial atomic force microscope (Cypher, Asylum Research) equipped with an in-house-developed band-excitation controller based on a National Instruments PXLe-6124 data acquisition card operating in Labview software. Pt/Ir-coated conductive Si probes (ElectriMulti75-G, BudgetSensors) were used for all measurements. The interferometric measurements were performed on the same Cypher atomic force microscope with an integrated quantitative laser Doppler vibrometer system (Polytec).

Theoretical calculations. DFT calculations were performed using the Vienna Ab-initio Simulation Package. The revised Perdew–Burke–Ernzerhof functional for solids was adopted, with Bi 6p5, Fe 3d4.5 and O 2p2 electrons considered as valence electrons. A typical effective Hubbard U parameter of 4 eV was applied to the valence electrons. A typical effective Hubbard $d$ electrons of Fe ions. The parameter of 4 eV was applied to the valence electrons. A typical effective Hubbard $d$ electrons of Fe ions. The parameter of 4 eV was applied to the valence electrons.

was obtained via $d_{\eta} = n/E_{\text{BFG}}$, where $\eta$ is the change of strain along the [013] direction. The phonon spectra shown in Supplementary Note 6 are calculated with PHONOPY using 4 x 4 x 4 supercells (each containing 320 atoms) and a single $k$ point located at the zone centre. Finally, the polarization was calculated using the modern (Berry-phase) theory of polarization.

Data availability

The data that support the findings of this study are available from the corresponding authors upon request.

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