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PAPER

Controlling magnetoelectric coupling by nanoscale phase transformation in strain engineered bismuth ferrite

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The magnetoelectric coupling in multiferroic materials is promising for a wide range of applications, yet manipulating magnetic ordering by electric field proves elusive to obtain and difficult to control. In this paper, we explore the prospect of controlling magnetic ordering in misfit strained bismuth ferrite (BiFeO₃, BFO) films, combining theoretical analysis, numerical simulations, and experimental characterizations. Electric field induced transformation from a tetragonal phase to a distorted rhombohedral one in strain engineered BFO films has been identified by thermodynamic analysis, and realized by scanning probe microscopy (SPM) experiment. By breaking the rotational symmetry of a tip-induced electric field as suggested by phase field simulation, the morphology of distorted rhombohedral variants has been delicately controlled and regulated. Such capabilities enable nanoscale control of magnetoelectric coupling in strain engineered BFO films that is difficult to achieve otherwise, as demonstrated by phase field simulations.

1. Introduction

The prospect of manipulating magnetic ordering by electric field in multiferroic materials has generated great excitement in the past few years;^{1,2} yet such magnetoelectric coupling proves elusive to obtain and difficult to control. Numerous multiferroic composites have been developed,^{3–7} though their magnetoelectric coupling is extrinsic, induced indirectly through the interaction between piezoelectric and magnetostrictive phases, and most of the studies have focused on magnetic induced electric voltage. While a variety of compounds have been discovered to exhibit magnetoelectric coupling,⁸ they usually function at temperatures much lower than room temperature, and their coupling effect is extremely small. Bismuth ferrite (BiFeO₃, BFO), however, is one of the rare multiferroic compounds that allows electric manipulation of magnetic ordering at room temperature.^{9–13} It is both

ferroelectric and antiferromagnetic at room temperature, having spontaneous polarization along one of the eight pseudocubic $\langle 111 \rangle$ axes and a magnetic easy plane perpendicular to the ferroelectric polar axis.^{10,14,15} As such, the magnetoelectric coupling in BFO has been realized by electric switching of ferroelectric domains, which in turn changes the magnetic easy plane. Such a magnetoelectric pathway, however, is difficult to control deterministically, since 71°, 109°, and 180° ferroelectric domain switching may all occur in a rhombohedral BFO, and it is not easy to choose one type of domain switching over the others to control the associated magnetic ordering.

It is well-known that the structure of epitaxial ferroelectric thin films can be engineered by misfit strain,^{16,17} and this has also been demonstrated in BFO films on LaAlO₃ (LAO) substrate, which turn out to be tetragonal-like monoclinic instead of rhombohedral,^{18–23} though other novel phases have also been reported.^{24–30} In fact, it is close to the so-called morphotropic phase boundary (MPB), where tetragonal-like monoclinic and distorted rhombohedral phases coexist.¹⁸ Such phase mixture can indeed be obtained by growing relatively thicker films, which partially relax the misfit strain, resulting in lamellar distorted rhombohedral variants in tetragonal-like matrix and a substantially higher piezoelectric response than either tetragonal or rhombohedral BFO.^{31,32} Even more interestingly, the tetragonal BFO exhibits C-type antiferromagnetism,^{33,34} while the distorted rhombohedral BFO is G-type antiferromagnetic.^{10,14,34} Oxygen octahedra tilting may lead to weak ferromagnetism in the rhombohedral BFO,^{14,35,36} though such mechanism does not exist for the tetragonal one.^{35,37} As a result, such a phase mixture introduces

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different magnetic orderings in the otherwise homogeneous tetragonal BFO films on LAO substrate.

It has been demonstrated that by applying opposite electric fields through a scanning probe microscope (SPM) tip, distorted rhombohedral variants can be erased and reintroduced in the phase mixture region, which in turn changes the underlying magnetic orderings, resulting in magnetoelectric coupling in strain engineered BFO.³⁶ While this is an exciting development, the process relies on the coexistence of the tetragonal and rhombohedral phase mixture, making it difficult to control—the film is predominantly tetragonal-like monoclinic, and the fraction of distorted rhombohedral phase is sensitive to film thickness and other deposition conditions. To overcome such difficulties, we explore the prospect of inducing and controlling different magnetic orderings in the phase pure tetragonal BFO films, using combined theoretical analysis, numerical simulations, and experimental characterizations.³⁸ Through careful thermodynamic analysis of strain engineered BFO, a pathway for field induced transformation from the tetragonal phase to the distorted rhombohedral one is identified, and realized by SPM experiment. By intentionally breaking the rotational symmetry of the tip induced electric field, it is also demonstrated that the morphology of the rhombohedral variants can be delicately controlled and regulated. Our key experimental findings have been reported in an earlier letter,³⁸ and in this paper we present our theoretical analysis and numerical simulations in detail, which we believe will have a wider range of implications in SPM probing and manipulation of functional materials. Furthermore, we explore the implications of such capability to magnetoelectric coupling, which is shown to enable delicate control and regulation of magnetic orderings in strain engineered BFO by electric field.

2. Phase structure and field induced transformation

Manipulating magnetic ordering in strain engineered BFO films requires delicate control of their phase structures, and this can be guided by thermodynamic analysis based on Landau–Devonshire theory modified for epitaxial films.^{17,39,40} For an epitaxial film under a biaxial misfit strain u_m and an electric field E_i ($i = 1, 2, 3$), its potential energy can be written as

$$G = \frac{u_m^2}{s_{11} + s_{12}} + \alpha_1^*(P_1^2 + P_2^2) + \alpha_3^*P_3^2 + \alpha_{11}^*(P_1^4 + P_2^4) + \alpha_{33}^*P_3^4 + \alpha_{12}^*P_1^2P_2^2 + \alpha_{13}^*(P_1^2 + P_2^2)P_3^2 - P_1E_1 - P_2E_2 - P_3E_3, \quad (1)$$

with

$$\alpha_1^* = \alpha_1 - u_m \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}},$$

$$\alpha_3^* = \alpha_1 - u_m \frac{2Q_{12}}{s_{11} + s_{12}},$$

$$\alpha_{11}^* = \alpha_{11} + \frac{1}{2(s_{11}^2 - s_{12}^2)} [s_{11}(Q_{11}^2 + Q_{12}^2) - 2s_{12}Q_{11}Q_{12}],$$

$$\alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{s_{11} + s_{12}},$$

$$\alpha_{12}^* = \alpha_{12} - \frac{1}{s_{11}^2 - s_{12}^2} [s_{12}(Q_{11}^2 + Q_{12}^2) - 2s_{11}Q_{11}Q_{12}] + \frac{Q_{44}^2}{2s_{44}},$$

$$\alpha_{13}^* = \alpha_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{s_{11} + s_{12}},$$

where P_i is the polarization component, α_1 , α_{ij} , and α_{ijk} are dielectric constants measured under constant stress, s_{IJ} ($I, J = 1, 2, \dots, 6$) is the elastic compliance constant measured at constant polarization, and Q_{IJ} is the electrostrictive coefficient that couples the elastic and electric field in ferroelectrics. All the coefficients used in the calculations are tabulated in ref. 41, and are assumed to be independent of temperature except the dielectric constant $\alpha_1 = (T - T_0)/2\varepsilon_0C$, where T_0 and C are the Curie–Weiss temperature and constant, and $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ Nm}^{-2}$ is the permittivity of free space. For homogeneous film with single domain and uniform distribution, the equilibrium polarization of the thin film can be determined from minimizing the free energy, $\partial G/\partial P_i = 0$, from which four sets of polarization are obtained, corresponding to four different phase structures, including paraelectric phase ($P_1^2 = P_2^2 = P_3^2 = 0$); tetragonal phase ($P_1^2 = P_2^2 = 0, P_3^2 \neq 0$), hereafter referred to as T-phase, which also includes tetragonal-like structure with a small magnitude of P_1 and P_2 compared to P_3 ; distorted rhombohedral phase ($P_1^2 = P_2^2 \neq 0, P_3^2 \neq 0$), hereafter referred to as R-phase; and orthorhombic aa-phase ($P_1^2 = P_2^2 \neq 0, P_3^2 = 0$). Notice that the distorted R-phase is actually a monoclinic phase. From these solutions, the piezoelectric coefficient of each individual phase can also be evaluated as detailed in ref 42.

We first consider the baseline structure of BFO in the absence of electric field, with its misfit-temperature phase diagram shown in Fig. 1(a). This is identical to the phase diagram constructed by Zeches *et al.*,¹⁸ where a MPB between T- and R-phases is observed around -4.3% at room temperature, though it does not completely agree with some recent experimental observations on the phase structure evolutions with respect to temperature.^{28,43} This could be due to the fact that the thermodynamic parameters, which require extensive reliable experimental data for fitting, might not always be accurate. However, the predicted phase structure at room temperature, which is what we focus on in this work, should be relatively reliable. Indeed, for epitaxial BFO films on LAO substrate, the misfit strain is calculated to be -4.3% , right at the MPB, suggesting the coexistence of T- and R-phases in the film. A perfect tetragonal structure would exist in an ideal epitaxial film, though various stress relaxation mechanisms will make the structure distorted toward either tetragonal- or rhombohedral-like monoclinic,^{22,33,43,44} depending on the extent of relaxations. Such a phase mixture is indeed confirmed by atomic force microscopy (AFM) topography mapping shown in Fig. 1(b), where lamellar R-phase variants (darker color) are observed in T-phase matrix (lighter color), though most of the region is predominantly T-phase. These lamellar variants tend to follow well defined orientations, presumably governed by mechanical and electric compatibilities across the interface, which is also verified by the phase field simulation shown in Fig. 1(c). The details of phase field methodology will be discussed in a later section.

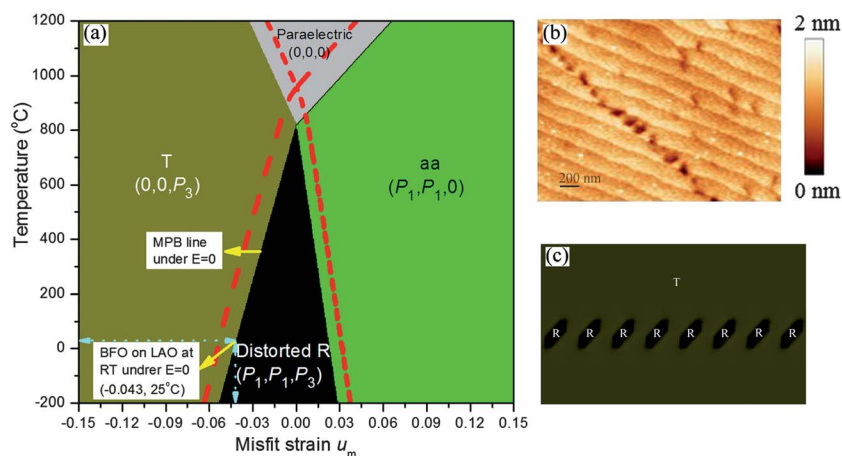


Fig. 1 Phase structure of strain engineered BFO; (a) misfit-temperature phase diagram, in the absence of electric field (solid line), and with an applied electric field of 2×10^7 [111] V m⁻¹ (red broken line); (b) AFM topography and (c) phase field simulation of lamellar R-phase variants in T-phase matrix; the simulation is carried out on a 64×64 grid with periodic boundary condition.

While strain can be engineered to control the phase structure of BFO based on the phase diagram shown in Fig. 1(a), for example by using different substrates or growing films of different thicknesses and thus partially relaxing the misfit strain to different extents, it is difficult to do after the film is deposited. Another option is to use electric fields, which can be easily applied. Since the out-of-plane electric field tends to stabilize the baseline T-phase, and we are interested in inducing and controlling magnetic ordering in R-phase, we explore the possibility of electric field applied along [111] axis instead. Quite encouragingly, under an applied electric field of 2×10^7 [111] V m⁻¹, the MPB does move left toward more compressive misfit strain, as shown by the red broken phase boundary in Fig. 1(a). This suggests that R-phase BFO is stabilized by an electric field along [111] axis, and thus it is indeed possible to transform the T-phase BFO to R-phase using such an electric field.

In order to examine the field induced phase transformation in strain engineered BFO in more detail, we construct the field-misfit phase diagram at room temperature, as shown in Fig. 2(a), with the baseline structure assumed to be $[00\bar{1}]$ polarized T-phase, and the distorted R-phase assumed to have $P_1 = P_2 > 8\% P_3$, corresponding to rotation of the polarization induced by the applied electric field.⁴⁵ It is observed that under a misfit strain of -4.3% , *i.e.* for a film on a LAO substrate, the T-phase BFO starts converting to the distorted R-phase at an electric field of 2.5×10^6 [111] V m⁻¹, and this critical electric field for the phase transformation is further reduced for thicker films with relaxed misfit strain. Associated with such a field induced phase transformation, the out-of-plane polarization decreases, and the in-plane polarizations increase, as shown in Fig. 2(b). The spontaneous polarization of T-phase in the absence of electric field is calculated to be $101 \mu\text{C cm}^{-2}$, which agrees well with some experimental data and first-principles calculations,^{45,46} but is smaller than some other reports.^{26,27} Such differences again might be resulted from some thermodynamic parameters that might not be very accurate, though it is not expected to change the prediction on qualitative behaviors. The polarization of corresponding R-phase with $P_1 = P_2 = P_3$ at the completion of TR transformation induced by the applied electric field is

$107 \mu\text{C cm}^{-2}$, which is slightly higher due to the electric field contribution, and the small difference suggests that TR transformation is completed *via* polarization rotation.⁴⁵ It is also noted that both in-plane and out-of-plane polarizations of T-phase BFO have been investigated recently,²⁶ and large in-plane polarization could exist. Indeed, according to Fig. 1(a) and 2(b), the in-plane polarization of T-phase BFO could continuously vary from 0 for a perfect T-phase to that of a perfect R-phase with $P_1 = P_2 = P_3$, depending on the exact magnitude of imposed misfit strain or external electric field, and such large in-plane polarization cannot be ignored. Furthermore, it is observed that the piezoelectric coefficient d_{33} increases with the applied electric field, as shown in Fig. 2(c), suggesting stronger amplitude in piezoresponse force microscopy (PFM). Notice that under an electric field along [111] axis, the $[00\bar{1}]$ -polarized T-phase may also be reversed, and an important observation from stability analysis is that the polarization reversal occurs at 8.9×10^8 [111] V m⁻¹, much larger than the field necessary for phase transformation, suggesting that phase transformation occurs before the polarization reversal. Single point spectroscopy PFM was performed to verify this, by applying a triangular waveform of increasing amplitude, as shown in the inset of Fig. 2(d), with the in-field response collected over a frequency band centred around the cantilever resonance. The spectrogram of the amplitude response collected during this experiment is shown in Fig. 2(d), top, with the corresponding phase information at the bottom. Small jumps in the cantilever resonance can be observed well before the phase flip, which is indicative of formation of R-phase before 180° polarization reversal of T-phase. Furthermore, the PFM amplitude does increase with the applied voltage, consistent with thermodynamic analysis.

3. Nanoscale control by scanning probe microscopy

While it is possible to transform the strain engineered T-phase BFO to R-phase by an electric field along [111] axis, applying such a multi-axial field is not trivial. Conductive SPM tip has been widely used to manipulate ferroelectric domain structures,^{47–49} yet most of these studies rely on the out-of-plane

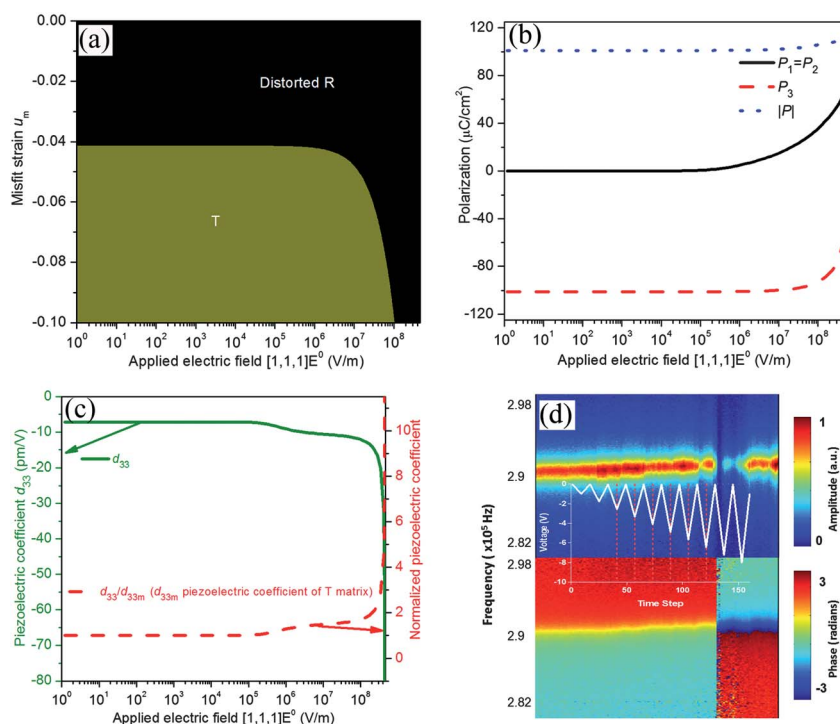


Fig. 2 Phase structure of strain engineered BFO at room temperature controlled by electric field; (a) field-misfit phase diagram; (b) polarization and (c) piezoelectric coefficient d_{33} versus electric field; (d) single point spectroscopy PFM experiment: amplitude (above) and phase (below) spectrogram captured while a DC waveform (inset, white) was applied to the sample at one point. Small shifts of the cantilever resonance can be seen well before the phase flip is observed, indicating that the phase transformation precedes polarization switching.

electric field directly underneath the SPM tip. Nevertheless, in-plane electric field also exists away from the SPM tip in addition to the out-of-plane component, making it possible to utilize such an in-plane electric field to induce phase transformation in T-phase BFO. To visualize this, we calculate the distribution of electric field induced by an SPM tip using image charge model,^{50,51} as shown in Fig. 3(a), with

$$\mathbf{E}^0 = -\nabla V, \quad (2)$$

$$V = \frac{Q}{2\pi\epsilon_0(\kappa + 1)} \frac{1}{\sqrt{(x_1 - x_1^0)^2 + (x_2 - x_2^0)^2 + (-x_3 + d)^2}},$$

where Q is the equivalent point charge determined by the voltage applied on the conductive tip, $(x_1^0, x_2^0, 0)$ is the tip location on the surface of thin film, κ is the effective dielectric constant of the film, and d is the spacing between the effective point charge and probed surface. The distributions of out-of-plane and in-plane electric field strengths are shown in Fig. 3(b) and (c). While the out-of-plane electric field decays rapidly away from the tip, the in-plane field shows a peak at $r = \sqrt{2}d/2$ away from the tip, and the magnitude of such an in-plane field can be as high as 38.5% of the maximum out-of-plane field right underneath the SPM tip. Meanwhile, the out-of-plane-field at this radius is 55% of the maximum field strength. This suggests that it is possible to use conductive SPM tip to convert T-phase BFO to R-phase, not directly underneath the SPM tip, but away from it instead, by taking advantages of the in-plane component of the electric field. This has indeed been confirmed by PFM studies, as shown by PFM amplitude mapping in Fig. 3(d), which was obtained by applying a -10 V pulse for 1 s through the SPM tip at a single point. It shows a circular switched

T-phase domain (dark) where the tip was placed, with four R-phase variants (white) surrounding the tip site forming a needle-like structure, hereafter referred to as R-phase rosette. Again, higher PFM amplitude is observed in R-phase variants, as we expected from thermodynamic analysis.

In order to regulate the morphology of magnetic R-phase rosettes in T-phase matrix for controlled magnetoelectric coupling, the mechanisms governing its formation have to be understood. To this end, we develop a phase field method to simulate the formation of R-phase variants in T-phase matrix. Ferroelectric variants are represented by their characteristic functions $\lambda_k(\mathbf{x})$, the distribution of which gives not only the morphology of phase variants, but also the distribution of transformation strain $\boldsymbol{\varepsilon}^*(\boldsymbol{\lambda})$ and spontaneous polarization $\mathbf{P}^*(\boldsymbol{\lambda})$,⁵²

$$\boldsymbol{\varepsilon}^*(\mathbf{x}) = \sum_k \lambda_k(\mathbf{x}) \boldsymbol{\varepsilon}^{(k)}, \quad \mathbf{P}^*(\mathbf{x}) = \sum_k \lambda_k(\mathbf{x}) \mathbf{P}^{(k)}, \quad (3)$$

where $\lambda_k(\mathbf{x})$ is the characteristic function of variant k

$$\lambda_k(\mathbf{x}) = \begin{cases} 1, & \mathbf{x} \text{ occupied by variant } k, \\ 0, & \text{otherwise,} \end{cases} \quad (4)$$

and $\boldsymbol{\varepsilon}^{(k)}$ and $\mathbf{P}^{(k)}$ are corresponding transformation strain and spontaneous polarization, respectively. The potential energy of the system occupying a region Ω thus is given by

$$\vartheta(\boldsymbol{\lambda}) = \int_{\Omega} [W_{\lambda}^{\text{gra}}(\nabla\boldsymbol{\lambda}) + W_{\lambda}^{\text{ani}}(\boldsymbol{\lambda}) + W^{\text{ela}}(\boldsymbol{\lambda}) + W^{\text{sum}}(\boldsymbol{\lambda}) - \boldsymbol{\sigma}^0 \cdot \boldsymbol{\varepsilon} - \mathbf{E}^0 \cdot \mathbf{P}] d\mathbf{x} + \frac{\epsilon_0}{2} \int_{\mathbb{R}^3} |\nabla\phi|^2 d\mathbf{x}, \quad (5)$$

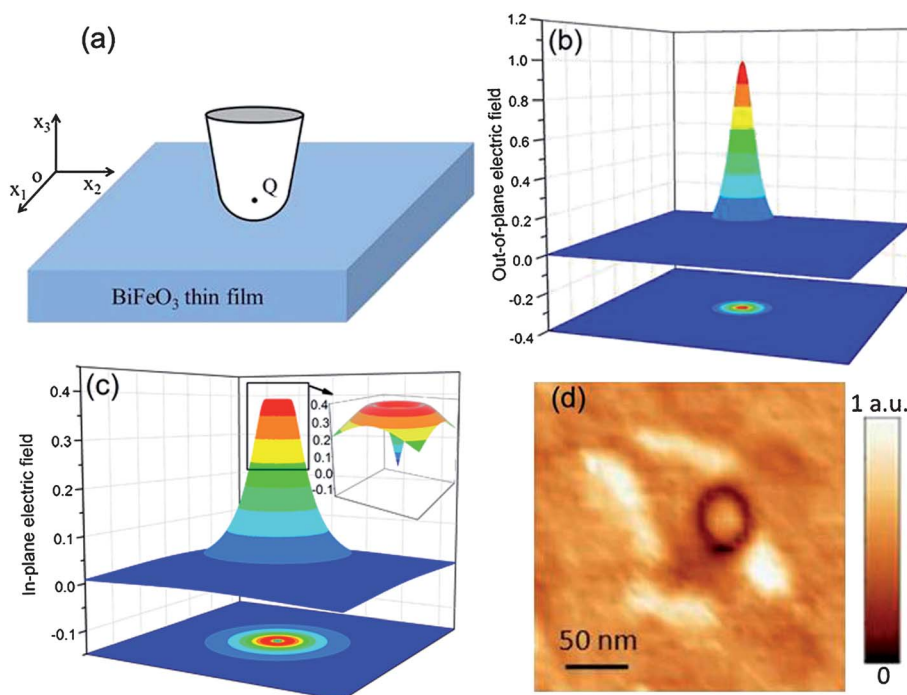


Fig. 3 Mapping of electric field under an SPM tip; (a) schematics of the SPM tip; (b) distribution of out-of-plane electric field E_3 ; (c) distribution of the in-plane electric field strength; (d) PFM amplitude image of R-phase rosette.

where σ^0 and E^0 are the applied stress and electric field, respectively, $W_\lambda^{\text{gra}} = A_\lambda^{\text{gra}} |\nabla \lambda|^2$ corresponds to the ferroelectric domain wall energy, $W_\lambda^{\text{ani}} = A_\lambda^{\text{ani}} \sum_k \lambda_k^2 (1 - \lambda_k)^2$ ensures the multiwell energetic structure minimized by λ_k at either 0 or 1, $W^{\text{ela}} = \frac{1}{2} [\epsilon - \epsilon^*(\lambda)] \cdot C [\epsilon - \epsilon^*(\lambda)]$ is the elastic energy density, $W^{\text{sum}} = A^{\text{sum}} \left[1 - \sum_k \lambda_k(x) \right]^2$ ensures that the summation of λ_k at any point is 1,⁵³ and the last term in eqn (5) is the depolarization energy. In eqn (5), the strain field ϵ is determined from transformation strain $\epsilon^*(\lambda)$ by solving mechanical equilibrium equation, while for polarization it is assumed that $P = P^*$ under the constrained theory.⁵² Notice that this is different from the constrained theory of magnetics,⁵⁴ as elastic strain in addition to transformation strain is allowed. As such, the ferroelectric domain pattern is completely specified by the characteristic function λ . The formation and evolution of the domain pattern are governed by the energy minimization with the following driving forces,

$$\mathbf{F} = -\frac{\delta \vartheta}{\delta \lambda} = 2A_\lambda^{\text{gra}} \nabla^2 \lambda - \frac{\partial W_\lambda^{\text{ani}}}{\partial \lambda} + C [\epsilon - \epsilon^*(\lambda)] \cdot \frac{\partial \epsilon^*(\lambda)}{\partial \lambda} - \frac{\partial W^{\text{sum}}}{\partial \lambda} + (\mathbf{E}^0 - \nabla \phi) \cdot \frac{\partial \mathbf{P}^*(\lambda)}{\partial \lambda}, \quad (6)$$

and the evolution is assumed to follow linear kinetic relation

$$\frac{\partial \lambda}{\partial t} = -L \frac{\delta \vartheta}{\delta \lambda} = L \mathbf{F}, \quad (7)$$

where L is the kinetic coefficient. These equations are solved numerically, with representative morphologies involving 4, 3, and 2

R-phase variants shown in Fig. 4(a–d). All these R-phase patterns have been observed in experiment, including rosette structure (a), U-shaped structure (b), parallel pair (c), and L-shaped pair (d), as highlighted in the AFM topography image in Fig. 4(e).

The good agreement between phase field simulations and AFM characterizations of R-phase variant morphology in T-phase matrix makes it possible to guide the morphology control through the phase field simulations. To this end, we notice that the electric field induced by the SPM tip has a rotational symmetry, as seen in Fig. 3, and in a perfect film, rosette involving 4 R-phase variants occurs, as shown in Fig. 4(a). Nevertheless, structures involving 3 and 2 R-phase variants are also observed in Fig. 4(e), presumably due to local defects that break the rotational symmetry. This suggests that the morphology of R-phase variants can be controlled by intentionally breaking the rotational symmetry, for example by

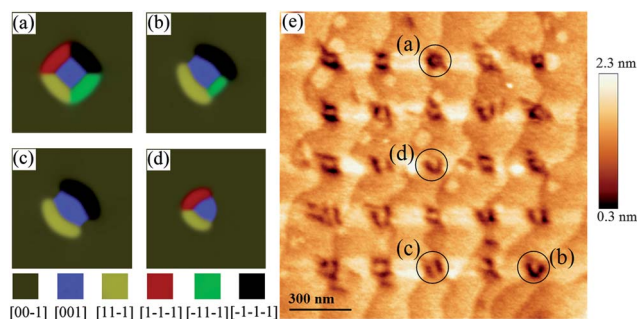


Fig. 4 Morphology of R-phase variants in T-phase matrix induced by an SPM tip; (a–d) phase field simulations and (e) AFM topography image.

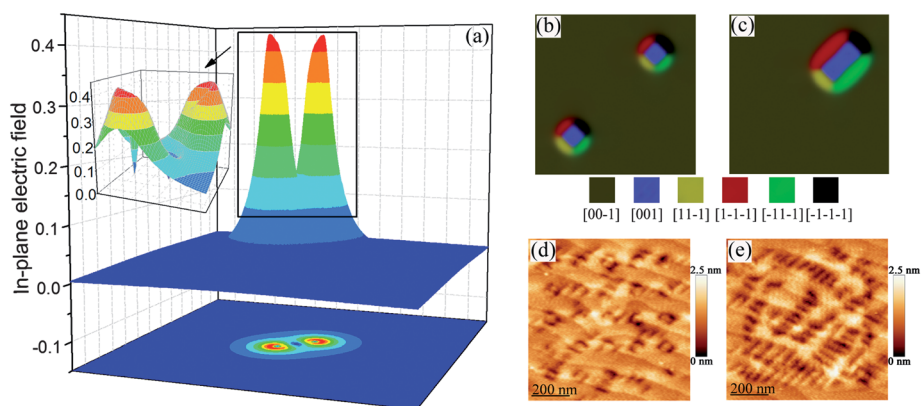


Fig. 5 Regulating the phase morphology by symmetry breaking; (a) superposition of the in-plane electric fields by two SPM tips; (b and c) phase field simulations and (d and e) AFM images of R-phase variants in T-phase matrix induced by SPM tips under different grid densities, 5×5 for (d) and 20×20 for (e) in a 700 nm^2 area, formed by applying pulses of -10 V for 1 s .

increasing grid density of the SPM tip and thus reducing their spacing. In particular, if in-plane electric fields from two SPM tips are superimposed on each other, rotational symmetry is broken when the spacing is sufficiently close, as seen in Fig. 5(a). This is supported by our phase field simulation, where two rosettes are observed in Fig. 5(b) when two SPM tips have a relatively large distance in between. With decreased distance, the two rosettes are collapsed into a lamellar structure involving mostly two R-phase variants, as shown in Fig. 5(c). While it is not easy to use multiple tips to impose electric fields simultaneously, sequentially scanning by a single tip will accomplish similar results. Indeed, the transition from rosette to lamellar structure with increased grid density is evident in AFM topography images shown in Fig. 5(d) and (e), confirming that R-phase

morphology can indeed be controlled by increasing grid density to break symmetry.

Another interesting aspect of symmetry breaking is that the tip induced electric field has infinite rotational symmetry, while the R-phase has 4-fold rotation symmetry, making the orientation of tip scanning relevant. In particular, when scanning the SPM tip with different angles but identical grid density, the resulting superimposed electric field will have different orientations from that shown in Fig. 5(a), which will then interact with the R-phase variants differently, as these variants have fixed crystallographic orientations. This makes it possible to manipulate and control the R-phase variants by altering SPM scanning angles, as demonstrated by the phase field simulation shown in Fig. 6(a) and (b), where the transition from rosette structure to lamellar structure is observed when the scanning angle is increased under constant tip spacing. This is also verified by AFM images shown in Fig. 6(c) and (d), confirming that the morphology of R-phase variants can indeed be controlled by varying scanning angles. In fact, such symmetry breaking could also be accomplished by a non-spherical tip.⁵¹

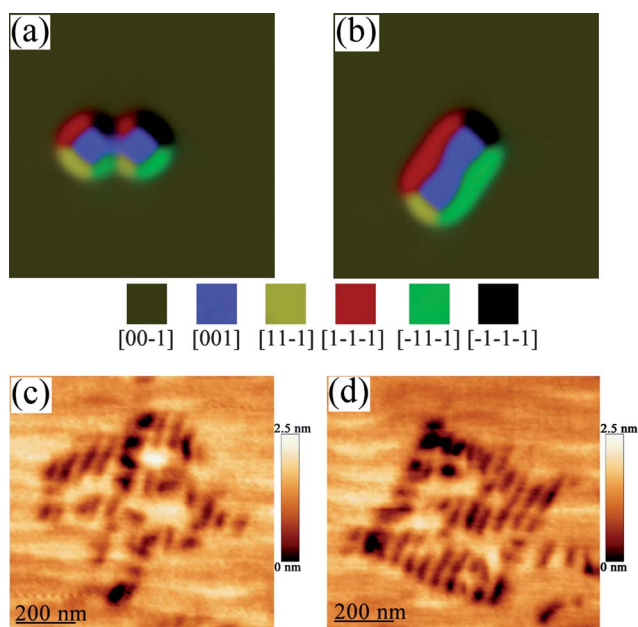


Fig. 6 Regulating the phase morphology by scanning angle; (a and b) phase field simulations and (c and d) AFM images of R-phase variants in T-phase matrix induced by SPM tips under different scanning angles, with (c) being 30° and (d) being 60° , obtained on an 8×8 grid across a 500 nm^2 area, with -10 V pulse for 1 s on each grid point.

4. Controlling magnetic ordering and magnetoelectric coupling

Having established the capability to control and regulate the morphology of R-phase variants in strain engineered BFO films, we explore the prospect of controlling and regulating their magnetic ordering *via* magnetoelectric coupling. Phase field simulations have been carried out, with additional terms from magnetic ordering included in the potential energy of eqn (5). One of the key contributions is the magnetic anisotropy energy

$$\int_{\Omega} W_m^{\text{ani}} dx = \int_{\Omega} \frac{A_m^{\text{ani}}}{2} \{2 - [m_a \cdot r(\lambda)]^2 - [m_b \cdot r(\lambda)]^2\} dx, \quad (8)$$

where r denotes the easy axis of spins, which depends on the particular ferroelectric variant, given by

$$r(\lambda) = \sum_k \lambda_k(x) r^{(k)}, \quad (9)$$

which governs the direction of magnetic moment. This magnetic anisotropy thus couples the ferroelectric (λ) and magnetic (m)

order parameters.⁵⁵ In other words, when ferroelectric variants are changed, magnetic anisotropy energy is changed accordingly, resulting in possible switching in magnetic orderings. To account for the antiferromagnetic ordering appropriately, magnetizations in two sub-lattices (\mathbf{m}_a and \mathbf{m}_b) are used under continuum approximation,^{10,14,55} with the antiferromagnetic energy given by

$$\int_{\Omega} W_m^{\text{af}} \, d\mathbf{x} = \int_{\Omega} \left[A_m^{\text{gra}} |\nabla \mathbf{m}_a - \nabla \mathbf{m}_b|^2 - A_m^{\text{af}} \mathbf{m}_a \cdot \mathbf{m}_b \right] \, d\mathbf{x}, \quad (10)$$

where the first term is magnetic domain wall energy, and the second term ensures that \mathbf{m}_a and \mathbf{m}_b are antiferromagnetically coupled. In addition, Zeeman's energy associated with the applied magnetic field \mathbf{H}^0 and magnetostatic energy associated with demagnetizing field have to be considered

$$\int_{\Omega} \left[-M_s \mathbf{H}^0 \cdot (\mathbf{m}_a + \mathbf{m}_b) \right] \, d\mathbf{x} + \frac{\mu_0}{2} \int_{\mathbb{R}^3} |\nabla \psi|^2 \, d\mathbf{x}, \quad (11)$$

where M_s is the magnetization, and the magnetostatic field is determined by solving Maxwell's equation. The evolution of magnetic spins is governed by Landau–Lifshitz–Gilbert type of rotational dynamics,^{56,57}

$$\frac{\partial \mathbf{m}_{a,b}}{\partial t} = -\gamma_g \mathbf{m}_{a,b} \times \mathbf{H}_{a,b}^{\text{eff}} - \delta \gamma_g \mathbf{m}_{a,b} \times (\mathbf{m}_{a,b} \times \mathbf{H}_{a,b}^{\text{eff}}), \quad (12)$$

with the effective magnetic field given by

$$\begin{aligned} \mathbf{H}_{a,b}^{\text{eff}} = & 2 \frac{A_m^{\text{gra}}}{M_s} (\nabla^2 \mathbf{m}_{a,b} - \nabla^2 \mathbf{m}_{b,a}) + \frac{A_m^{\text{af}}}{M_s} \mathbf{m}_{b,a} - \frac{1}{M_s} \frac{\partial W_m^{\text{ani}}}{\partial \mathbf{m}_{a,b}} \\ & + \mathbf{H}^0 - \nabla \psi. \end{aligned} \quad (13)$$

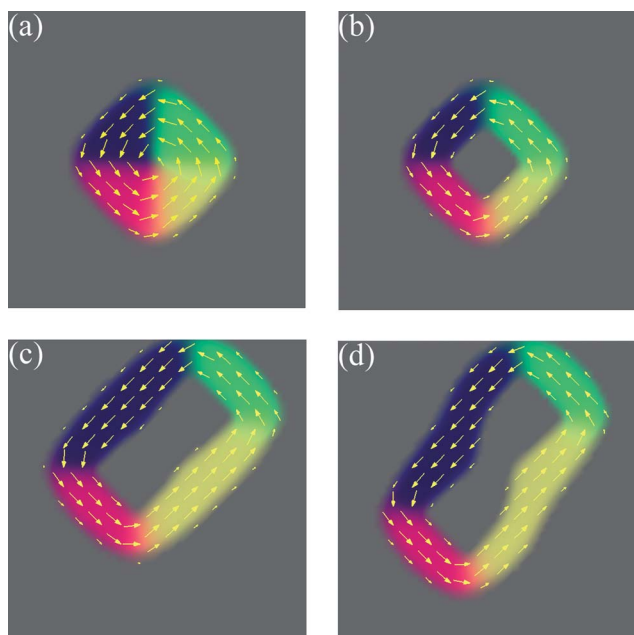


Fig. 7 Sublattice magnetic ordering in strain engineered antiferromagnetic BiFeO₃ controlled by an SPM tip; R-phase rosette in T-phase matrix before (a) and after (b) polarization reversal of T-phase, simulated on a 64 × 64 grid; and transition from R-phase rosette to lamellar structures controlled by grid density (c) and scanning angle (d), simulated on a 128 × 128 grid. Note that only the sublattice spin \mathbf{m}_a of R-phase is shown.

These equations are solved again numerically, and the resulting magnetic ordering of different R-phase structures in tetragonal matrix is shown in Fig. 7, where only spins of one sublattice of R-phase is given. While the incorporation of magnetic ordering has negligible influence on ferroelectric domain structures, the evolution of ferroelectric domains under external electric field results in substantial changes in magnetic ordering. Under the in-plane electric field from the SPM tip, R-rosette will be formed first before polarization reversal under the SPM tip, resulting in magnetic ordering as shown in Fig. 7(a). With further increase of electric field, the center of the R-rosette is transformed into reversed T-phase variant, and the magnetic ordering in the center reverse to that of T-phase, as seen in Fig. 7(b). Under increased grid density, or increased scanning angle, the R-phase rosette is converted into lamellar structures due to broken symmetry, and the magnetic domain structures are changed accordingly, as shown in Fig. 7(c) and (d). As a result, these simulations demonstrate the possibility of delicate control and regulation of magnetic ordering and magnetoelectric coupling in strain engineered BFO films by an SPM tip, which is accomplished indirectly through controlling and regulating field induced phase transformation by the SPM tip. Finally, it is also pointed that the antiferromagnetic ordering in BFO has little influence on its polarization distributions.

5. Conclusions

In summary, we have demonstrated electric-field control of magnetic ordering in strain engineered BFO films through combined theoretical analysis, numerical simulations and experimental characterizations. The magnetic R-phase BFO can be induced in the T-phase matrix by the SPM tip, and its morphology can be controlled and regulated by symmetry breaking. These point to a novel pathway to nanoscale control of magnetoelectric coupling in strain engineered BFO films. Future investigations include extending the simulation into three-dimensional configurations, and coupling our continuum phenomenological model with atomistic simulations, which would offer deeper insights into fundamental phase transformation mechanisms in strain engineered BFO films.

6. Method

A 20 nm thick sample of BiFeO₃ was grown on (001) LaAlO₃ with a 15 nm thick buffer layer of LaNiO₃ (to act as the bottom electrode), through pulsed laser deposition assisted with high pressure reflection high energy electron diffraction. The growth temperature is 700 °C and the growth pressure is 100 mtorr in oxygen. The growth mode was tuned to be layer-by-layer and then step flow modes. The sample was then studied using a commercially available scanning probe microscope (Asylum Research, Cypher model) equipped with NI PXI based band excitation controller to enable Band-Excitation (BE) measurements, with the data analyzed using MATLAB software (v7). Some images were also captured with a Veeco MultiMode AFM with Nanonis V controller. Image processing was carried out using WSxM v5.⁵⁸

The thermodynamic analysis was carried out using Landau–Devonshire phenomenological theory, and its numerical

simulations were implemented by a MATHEMATICA code.^{39,40} The phase field simulation was carried out using characteristic functions of variants and magnetic order as variables, and its numerical simulations were implemented by a FORTRAN code using fast Fourier transform on spatial scale and semi-implicit finite difference on temporal scale after normalization.^{55,59} The computation was two-dimensional (2D), with periodical boundary condition under plane strain approximation adopted. For single tip simulation, a 64×64 grid was used, while for multiple tips, the computation size was 128×128 .

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