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Manipulating magnetoelectric energy landscape in multiferroics

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Magnetoelectric coupling at room temperature in multiferroic materials, such as BiFeO3, is one of the leading candidates to develop low-power spintronics and emerging memory technologies. Although extensive research activity has been devoted recently to exploring the physical properties, especially focusing on ferroelectricity and antiferromagnetism in chemically modified BiFeO3, a concrete understanding of the magnetoelectric coupling is yet to be fulfilled. We have discovered that La substitutions at the Bi-site lead to a progressive increase in the degeneracy of the potential energy landscape of the BiFeO3 system exemplified by a rotation of the polar axis away from the ⟨111⟩pc towards the ⟨112⟩pc discretion. This is accompanied by corresponding rotation of the antiferromagnetic axis as well, thus maintaining the right-handed vectorial relationship between ferroelectric polarization, antiferromagnetic vector and the Dzyaloshinskii-Moriya vector. As a consequence, La-BiFeO3 films exhibit a magnetoelectric coupling that is distinctly different from the undoped BiFeO3 films.

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Magnetoelectric multiferroics are materials which possess two or more order parameters simultaneously and, more importantly, exhibit coupling between the spin and charge degrees of freedom. Bismuth ferrite (BiFeO₃) is by far the most studied and characterized multiferroic in part because it exhibits robust order parameters—ferroelectricity (P), antiferromagnetism (L), a weak ferromagnetic moment (Mₐ) induced by canting of the antiferromagnetically aligned spins, and magnetoelastic coupling between these order parameters (P, L, Mₐ) well above room temperature. Because of the nature of its magnetoelectric coupling, BiFeO₃ holds significant promise to trigger the development of low-power consumption memory and logic devices. The strong spontaneous polarization in BiFeO₃, however, results in a correspondingly large coercive voltage [described by the classic Landau double-well (Fig. 1a)], which requires adjustment to enable low-voltage applications. Bulk BiFeO₃ has a ferroelectric polarization of ~90 μC/cm² pointing along the (111) pc (where pc refers to the pseudo-cubic notation) with a rhombohedrally distorted crystal structure (space group R₃c). Unlike most conventional displacive ferroelectrics (e.g., BaTiO₃ and PbTiO₃) which have polarization induced by the hybridization between the empty transition metal p orbital and the filled oxygen 2p orbital, the polarization in BiFeO₃ primarily originates from the stereo-chemically active lone pair in the form of the A-site Bi³⁺ 6s² electrons. This has motivated – because of the intimate connection with the polarization – extensive studies of chemical substitution of the A site of BiFeO₃ including using rare-earth elements such as La³⁺, Sm³⁺, and Dy³⁺ because of their similar ionic radius and isovalent chemistry to bismuth. A systematic change in ferroelectric ordering is indeed induced by rare-earth substitution for bismuth, including a reduction of the Curie temperature, formation of an antiferromagnetic phase, etc. On the other hand, isovalent chemical substitution of the A site is not expected to alter the antiferromagnetism in BiFeO₃ and, in fact, only minimal effects on the Néel temperature are reported. More importantly, however, is the impact of such rare-earth substitution for the evolution of the coupling mechanism between the magnetic and ferroelectric order. Despite having profound implications for material and device function, few studies have considered this. In turn, in the pursuit of the important technological question of how to enable low-voltage control of magnetism, foundational studies to unveil the correlation between P, L, Mₐ, and their switching pathways in, for example, rare-earth lanthanum-substituted BiFeO₃ (Bi₁₋ₓLaₓFeO₃) thin films are a key step towards addressing the material requirements for low-power spintronics.

### Results

**Polarization reduction and rotation in Bi₁₋ₓLaₓFeO₃.** To study the evolution of the order parameters, P, L, and Mₐ, under chemical pressure, we explore a model system consisting of (001) pc oriented (Bi₁₋ₓLaₓFeO₃ (x = 0, 0.1, 0.15, 0.2, and 0.3) thin films grown on a conducting layer of SrRuO₃ on insulating DyScO₃ (110) single crystal substrates (where O refers to orthorhombic indices), all grown by pulse-laser deposition (Methods). Rhombohedral BiFeO₃ can be thought of as exhibiting a pseudocubic perovskite unit cell which has been distorted along the (111) pc body diagonal resulting in a spontaneous polarization along that axis. On the other hand, in Bi₁₋ₓLaₓFeO₃, increasing amounts of lanthanum drives a suppression of the magnitude of and, possibly reorient, the polarization direction (Fig. 1b). As a consequence, chemical substitution could also provide a methodology to reduce the free-energy barrier for ferroelectric switching described by a classical Landau model (Fig. 1a) and experimentally demonstrated in polarization hysteresis loops (Fig. 1c). The polarization hysteresis loops, as a function of lanthanum content (Bi₁₋ₓLaₓFeO₃ with x = 0, 0.1, 0.15, 0.20, and 0.3), reveal a systematic suppression of remanent polarization (from 65 μC cm⁻² for x = 0 to 18 μC cm⁻² for x = 0.2) and a corresponding reduction of the average coercive field (from 158 kV cm⁻¹ for x = 0 to 106 kV cm⁻¹ for x = 0.2).

Reciprocal space maps (RSMs) about the 203 pc-diffraction condition of the films confirm the change in crystal structure (Supplementary Figs. 1, 2) and were used to extract the rhombohedral angles as well as the in-plane and out-of-plane lattice constants for this series of samples. We observe that the rhombohedral distortion decreases with lanthanum substitution while maintaining the imposed strain from the DyScO₃ substrate (i.e., all films are coherently strained to the substrate such that the in-plane lattice constant of the film remains the same despite changing the chemistry). This indicates that a phase transition occurs.

**Fig. 1 Ferroelectric ordering in Bi₁₋ₓLaₓFeO₃.** a Schematic for the energy landscape of the phase transition induced by lanthanum substitution in BiFeO₃ described by Landau theory. b Schematic for the ferroelectric polarization rotation (from BiFeO₃: [111] pc to Bi₉₀La₁₀FeO₃: [112] pc) and suppression of ferroelectric polarization induced by lanthanum substitution in BiFeO₃. c P-E measurements for different substitution levels of lanthanum in 100-nm-thick BiFeO₃ films. d The schematics illustrate the evolution of crystal symmetry of bismuth ferrite (rhombohedral) to lanthanum ferrite (orthorhombic).
transition from rhombohedral to orthorhombic can be driven by such a chemical substitution\textsuperscript{13}.

While it is clear that lanthanum substitution can reduce the magnitude of the measured polarization and the coercive field, the specific nature of this reduction (i.e., does it arise from polarization rotation, reduction of polarization magnitude, or some combination therein) remains to be determined. To directly visualize the nature of the change in polarization at the microscopic scale, we carried out high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, “Methods” section) imaging on both the Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} and BiFeO\textsubscript{3} thin films. From this, it is possible to extract quantitative local information about the direction of the polarization vector by measuring the displacement of the B-site cation (i.e., iron) to the mass center of the four cations at the unit-cell corners (i.e., bismuth and lanthanum) across each unit cell in the image (Fig. 2c). For BiFeO\textsubscript{3} (Fig. 2a), the extracted map of polarization (which is a projection upon a (100)\textsubscript{pc}) reveals a strong tendency for the polarization to point along a diagonal direction – consistent with polarization pointing along a [111]\textsubscript{pc} – but slightly tilted towards [001]\textsubscript{pc} (as shown in Fig. 2d). (This is intuitively expected in the 0.4% compressively strained BiFeO\textsubscript{3}, which should drive a rotation of the polarization towards the out-of-plane direction $\sim$10.9° from [111]\textsubscript{pc} as shown in Fig. 2d)\textsuperscript{18} In contrast, for the Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} (Fig. 2b), the extracted map of polarization (which again is a projection on a (100)\textsubscript{pc}) reveals a clear rotation of the polarization away from a [111]\textsubscript{pc} towards a [112]\textsubscript{pc} by $\sim$16.1° (the clockwise rotation is defined as positive direction), revealed by the histograms of measured polar vector directions across the entire area analyzed for both the BiFeO\textsubscript{3} and Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} (Fig. 2d). We also measured the polarization rotation of the 400-nm-thick BFO sample where the polarization only deviates $\sim$3.6° from [111]\textsubscript{pc} (Fig. 2d). For reference, the angle between the [111]\textsubscript{pc} and [112]\textsubscript{pc} in this projection is 19.4°.

This, in conjunction with the experimentally measured remanent polarization in BiFeO\textsubscript{3} and Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} projected along [001]\textsubscript{pc} (Fig. 1c), provides us with an estimate of the ferroelectric polarization for such a structurally distorted and chemically substituted, Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} film (the details are captured in the Supplementary Information Fig. 1). We calculate the ferroelectric polarization in Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} to be $\sim$44 µC cm\textsuperscript{-2}, i.e., a significant reduction from the spontaneous polarization of 90 µC cm\textsuperscript{-2} in pure BiFeO\textsubscript{3}. Thus, we conclude that incorporation of 15% lanthanum into the parent BiFeO\textsubscript{3} structure alters the nature of the polarization (i.e., both the magnitude and the direction of the polar vector), consistent with prior work\textsuperscript{14-16,19}.

Armed with an understanding from X-ray diffraction and STEM analyses on how the material structure is evolving, we turned to piezoresponse force microscopy (PFM, “Methods” section) for an analysis of the evolution of the mesoscale domain structure, which similarly reveals marked differences. The as-grown domain structure of 20-nm-thick BiFeO\textsubscript{3} features well-ordered stripe domain patterns (Fig. 3a), while that of 20-nm-thick Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} has no stripes, but exhibits a complex domain pattern (Fig. 3c). This is a consequence of weakened rhombohedral distortion (and a concomitant reduction in structural anisotropy), which is consistent with both the X-ray diffraction and STEM analyses above. In turn, one would expect that these crystal and domain structure differences will likely lead to corresponding differences in the mesoscale ferroelectric switching behavior – which can be probed via a combination of both

**Fig. 2 Atomic images, polarization mapping, and change of polarization in BiFeO\textsubscript{3} and Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} thin films.** a, b show the HAADF-STEM images of BiFeO\textsubscript{3} and Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3}, respectively, with the polarization mapping of the Fe atoms overlaid. The scale bar is 1 nm. c Schematic of ferroelectric polarization in BiFeO\textsubscript{3}/Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} unit cell. The vectors in (a, b) were extracted from the displacement of Fe\textsuperscript{3+} position to the mass center of four Bi\textsuperscript{3+}. d Histogram of polar distribution shows that the ferroelectric polarizations rotate 3.6°, 10.9° and 16.1° away from [111]\textsubscript{pc} in 400-nm-thick BiFeO\textsubscript{3} (gray), 80-nm-thick BiFeO\textsubscript{3} (red) and 80-nm-thick Bi\textsubscript{0.85}La\textsubscript{0.15}FeO\textsubscript{3} (blue), respectively.
lateral and vertical PFM (“Methods” section). For a 20-nm-thick BiFeO₃ heterostructure (Fig. 3b), for example, application of a −5 V DC voltage to the PFM tip reveals, as expected, classical 180° switching of polarization (i.e., reversed phase contrast in both the lateral and vertical PFM channels; Supplementary Information and Supplementary Figs. 3–6). For the same thickness Bi₀.₈₅La₀.₁₅FeO₃ heterostructure (Fig. 3d), however, 180° switching of the polarization cannot be achieved unless a voltage very close to the breakdown voltage (−10 V, 5 MV cm⁻¹) is applied. We capture the statistics of this difference in switching behavior in Fig. 3e, which shows histograms of the switching process as a function of voltage for both 20-nm-thick BiFeO₃ and Bi₀.₈₅La₀.₁₅FeO₃ thin films. The summary of the polarization switching angles for 20-nm-thick BiFeO₃ and Bi₀.₈₅La₀.₁₅FeO₃ thin films. f Schematic of ferroelectric polarization switching in Bi₀.₈₅La₀.₁₅FeO₃ thin film.

Probing magnetic order and magnetoelectric coupling in Bi₁₋ₓLaₓFeO₃. To address these questions, we used X-ray magnetic linear dichroism-photoemission electron microscopy (XMLD-PEEM) combined with PFM to establish the correlation between the order parameters in Bi₁₋ₓLaₓFeO₃ thin films. The geometry of the XMLD-PEEM experiment is shown with two angular dependences (α for the linear polarization of the X-rays and Φ for the azimuthal in-plane direction of the sample; Fig. 4a). Here we used two types of samples, BiFeO₃ and Bi₀.₈₅La₀.₁₅FeO₃, with two different thicknesses, 20 and 80 nm (see sample preparation details in the Method section). Typical of high-quality BiFeO₃ heterostructures, two-variant polarization, periodic stripe domains are observed for both 80 nm (Fig. 4b) and 20 nm (Fig. 4d) heterostructures. We performed electrical switching of the ferroelectric domain structure (shown in the box) and, by careful control of the applied bias to the PFM tip (Methods and Supplementary Information), we are able to obtain striped, two-variant domain structures after switching. Such a model system (both the 80- and 20-nm-thick BiFeO₃ heterostructures) provides the reference frame to study the antiferromagnetic ordering L. XMLD-PEEM is a powerful tool for the investigation of magnetic ordering for many ferromagnetic and antiferromagnetic systems.
with high spatial resolution and elemental specificity\textsuperscript{29–31}. This approach allows one to image the antiferromagnetic domains (Fig. 4c, e) with chemical specificity (here the images were taken at the iron $L_2$ edge; Methods). This specific energy (peak) was chosen for imaging because both antiferromagnetic and ferroelectric ordering contribute strongly to the dichroism at the iron $L_1$ edge while the dichroism at the $L_2$ edge is dominated by magnetic order\textsuperscript{25,32,33}. Consistent with previous studies, we observe a one-to-one correlation of ferroelectric and antiferromagnetic domains in both the 80- and 20-nm-thick BiFeO$3$ films due to the inherent coupling of polarization and magnetization in this material. By extracting the intensity of different $\alpha$ and $\Phi$ XMCD-PEEM images in different domains (see the analysis of the $L$ in Supplementary Information and Supplementary Figs. 7, 9), we find that the $L$ in both the 80- and 20-nm-thick BiFeO$3$ heterostructures is approximately parallel to a $\{\overline{1}1\overline{2}\}$pc before and after electrical switching.

Similar analysis was completed on the Bi$_{0.85}$La$_{0.15}$FeO$3$ heterostructures, which also show electrically switched antiferromagnetic domains with one-to-one correlation to the ferroelectric domains (Fig. 4f–i). Fitting of the XMCD intensity versus $\alpha$ and $\Phi$ in the antiferromagnetic domains for Bi$_{0.85}$La$_{0.15}$FeO$3$ (Supplementary Figs. 8–10), however, show that the $L$ in domain I is along $\approx [\overline{6}4\overline{1}]$pc and the $L$ in domain II is along $\approx [10\overline{2}]$pc, which means the $L$ rotates by $\approx 105^\circ$, consistent with the $P$ switching (Fig. 3). This also points to the fact that the easy magnetic plane for Bi$_{0.85}$La$_{0.15}$FeO$3$ is no longer in the $\{110\}$pc but most likely in the $\{111\}$pc (Supplementary Fig. 11). We attribute this change in the magnetic easy plane to the consequence of the rotation of the ferroelectric polarization in the Bi$_{0.85}$La$_{0.15}$FeO$3$ (Fig. 1). That is, as a consequence of the polarization in Bi$_{0.85}$La$_{0.15}$FeO$3$ pointing (approximately) along the $\{112\}$pc, $L$ and $MC$ are expected to follow the motion of the polarization accordingly (i.e., polarization is switched from, for example, $\{1\overline{1}2\}$pc to $\{2\overline{1}1\}$pc). Based on the ferroelectric data in Fig. 3 and the antiferromagnetic data in Fig. 4, one can calculate the canting moment direction, $MC$, using eq. (1). Our calculations indicate that the canted moment direction switched from $MC_{\text{II}}$ $\approx [-7 13 10]_{\text{pc}}$ to $MC_{\text{I}}$ $\approx [-251]_{\text{pc}}$ with the applied electric field in the Bi$_{0.85}$La$_{0.15}$FeO$3$ samples, while in BiFeO$3$ samples, the canted moment stays in the plane ($\{110\}$pc). This can be validated by exploring the coupling of the $MC$ to an external magnet. For example, an in-plane magnetized Co$_{0.9}$Fe$_{0.1}$ layer shows a progressively lower exchange coupling field, as illustrated in Supplementary Fig. 12, supporting the notion that the canted moment is tilting away from the in-plane direction towards the out-of-plane, as lanthanum is added. In contrast, a ferromagnetic multilayer with perpendicular magnetic anisotropy, such as Co/Pt multilayer, shows a stronger out-of-plane magnetic anisotropy on the Bi$_{0.85}$La$_{0.15}$FeO$3$ compared to the BiFeO$3$, Supplementary Fig. 13. Both these pieces of data provide substantiation that the out-of-plane magnetic exchange coupling is enhanced in the Bi$_{0.85}$La$_{0.15}$FeO$3$ sample; we attribute this enhancement to tilting of $MC$ as a consequence of lanthanum substitution in BiFeO$3$.

Magnetoresistance measurements and micromagnetic simulations. Having established the changes in $P$, $L$, and $MC$ as a function of lanthanum substitution as well as with electric field applied, captured schematically in Fig. 5a, we now proceed to ask the question: how do they impact the magnetotransport behavior of a spin-valve that is in magnetic contact with the Bi$_{0.85}$La$_{0.15}$-FeO$3$ surface. We deposited a spin-valve composed of Pt (2 nm)/Co$_{0.9}$Fe$_{0.1}$ (2.5 nm)/Cu (5 nm)/Co$_{0.9}$Fe$_{0.1}$ (2.5 nm) on the Bi$_{0.85}$La$_{0.15}$FeO$3$ surface and fabricated Hall-bar structures (Fig. 5b) to study the electrical-field dependence of magnetoresistance [$R(H)$] which is measured as the applied magnetic field, $H$, is swept from the positive value $H_{\text{max}}$ to the negative value $-H_{\text{max}}$ and back to zero field (sample preparation and device fabrication details are presented in the Methods section). We use the conventional form of magnetoresistance, defined as GMR (%) $= [R(H) - R(H_{\text{max}})] \times 100% / R(H_{\text{max}})$. To draw the distinction, we compare a pure BiFeO$3$ layer to the Bi$_{0.85}$La$_{0.15}$FeO$3$ layer of the same thickness, Fig. 5c–f. We support the experimental data through micromagnetic simulations (details presented in Supplementary Information and Method section).
the corresponding micromagnetic simulation in Fig. 5d. Similarly, the GMR hysteresis loop for the spin-valve on Bi$_{0.85}$La$_{0.15}$FeO$_3$ is shown in Fig. 5e, with the simulated data in Fig. 5f. For BiFeO$_3$, we observe the modulation of an exchange bias by the applied electric field, which is consistent with our previous study$^{34}$; on the other hand, for the Bi$_{0.85}$La$_{0.15}$FeO$_3$ case, we observe the modulation of exchange coupling, leading to a reduction of the GMR switching field at positive electric field (additional details presented in Supplementary Fig. 14).

We can now put the data presented in Figs. 3–5 together to present the following observations. The insertion of lanthanum into BiFeO$_3$ leads to a rotation of both $\mathbf{P}$ and $\mathbf{L}$ as well as their significantly different switching behaviors with an electric field. In the case of Bi$_{0.85}$La$_{0.15}$FeO$_3$, the rotation of $\mathbf{M}_C$ by $\sim 105^\circ$ amounts to an effective change in the magnetic anisotropy from essentially in-plane to essentially out-of-plane. This rotation of the magnetic anisotropy in Bi$_{0.85}$La$_{0.15}$FeO$_3$ explains the E-field modulation of the exchange coupling between the Co$_{0.9}$Fe$_{0.1}$ and the Bi$_{0.85}$La$_{0.15}$-FeO$_3$ layer that can be described by eq. (2). From Eq. (2), one can approximately derive the contributions to the energy of Co$_{0.9}$Fe$_{0.1}$ resulting from its interaction with Bi$_{0.85}$La$_{0.15}$FeO$_3$:

$$F_{\text{FM–AFM}} = \mu_0 H_{\text{eb}} M_s (\mathbf{m} \cdot \hat{\mathbf{m}}) + K_{\text{ex}} (\mathbf{I} \cdot \hat{\mathbf{m}})^2 \quad (2)$$

Here the lower-case symbols with a hat designate normalized vectors. Even though the values of exchange bias $H_{\text{eb}}$ and exchange coupling $K_{\text{ex}}$ can be expressed via the exchange energy, their phenomenological values are more reliable, since they account for non-idealities of the interface. From the expression of exchange coupling energy, we can foresee that once we can control the anisotropy in the ferromagnet through the magnetoelectric coupling in Bi$_{0.85}$La$_{0.15}$FeO$_3$, we will be able to switch its magnetization. This switch can be detected by measuring GMR in the spin-valve.

The micromagnetic simulations of the GMR stack (all the simulation details can be found in the Method and Supplementary Information) presented in Fig. 5d and f show a close resemblance to the experimental data and provide theoretical credence to these experimental observations above. Compared to the parent phase BiFeO$_3$, Bi$_{0.85}$La$_{0.15}$FeO$_3$ shows a very different magnetoelectric switching where the magnetic anisotropy (mainly the magnetic easy plane) can be controlled by electric field while BiFeO$_3$ has the same magnetic easy plane before and after the electric field is applied$^{35,36,34}$.

Discussion
In summary, we have discovered that the polarization vector in the BiFeO$_3$ system is systematically varied in both its magnitude and direction with respect to the crystal lattice, as the Bi$_{1-x}$La$_{x}$+3 is replaced by La$_{x}$+3. The rotation of the polar vector away from the $\langle 111 \rangle_{\text{pc}}$ direction and towards the $\langle 112 \rangle_{\text{pc}}$ direction appears to be critical in terms of understanding both the anisotropy energy of the polar phase as well as the response of the system to out of plane electric fields. In addition, we demonstrate the ability for electrical control the anisotropy of magnetoelectric coupling through a spin-valve/Bi$_{0.85}$La$_{0.15}$FeO$_3$ device. Our results fulfill the understanding of magnetoelectric coupling in chemically-modified BiFeO$_3$ thin films, and can trigger the new application of multiferroics.

Methods
Film growth. The oxide heterostructures Bi$_{0.85}$La$_{0.15}$FeO$_3$/SrRuO$_3$ or BiFeO$_3$/SrRuO$_3$ are grown on single-crystalline (110)$_{\text{p}}$ DyScO$_3$ by pulse laser deposition at 690–710 °C with focused laser fluence ~1.2 J cm$^{-2}$ under 100–160 mTorr oxygen pressure and cooled down to room temperature at 500 Torr oxygen pressure. After the cooling process, the oxide heterostructures were immediately transferred to high vacuum magnetron sputtering chamber with a base pressure $\sim 1 \times 10^{-7}$ Torr. The spin-valve structures we used in this article, are fabricated with Pt (2.5 nm)/Co$_{0.9}$Fe$_{0.1}$ (2.5 nm)/Cu (3–5 nm)/Co$_{0.9}$Fe$_{0.1}$ (2.5 nm), deposited by DC magnetron...
sputtering with argon pressure from ranging from 2 \times 10^{-3} to 7 \times 10^{-3} Torr under a static magnetic field of 200 Oe along the crystallographic [010] to establish the magnetic field. The Pt layer is deposited at the center of the top of the spin-valve as a capping layer to protect the top Co80Fe20 layer from oxidation, whereas the bottom SrRuO3 layer serves as a bottom electrode for ferroelectric switching. The chemical composition analysis can be found in Supplementary Fig. 15.

**Scanning transmission electron microscopy and polarization mapping.** TEM samples were prepared by mechanical polishing with an Allied Multitep followed by ion milling in a Gatan PIPS2. Samples were prepared so that the projected plane was (1,0,0). HAADF-STEM images were collected on a JEOL JEM-ARM300CF operating at 300 kV.

In quantifying the polarization, we used the pseudoscopic unit cell projected along the beam direction. The atomic polarization vector was calculated by measuring the displacements from the center of the four surrounding A/B site atoms in HAADF-STEM images. Each atom in the image is located accurately using gaussian fitting and the center of each unit cell is defined as the average position of the four atoms at the corners of the unit cell. Polarization mapping was performed on several images from different regions for the BiFeO3 and Bi0.85La0.15FeO3 samples. In bulk BiFeO3, the polarization in the (100) projection plane should appear along the unit cell diagonal, [010]. To determine the deviation of the average polarization angle from the diagonal, we combined the data from several images together to generate one distribution for each sample. A Gaussian distribution was then fit to quantify the mean and standard deviation of the polarization angle in each sample.

**Fabrication of spin-valve devices and magnetoelectric coupling measurements.** Conventional photolithography and Ar-ion milling were employed to pattern the Co80Fe20(2.5 nm)/Cu(5 nm)/Co80Fe20(2.5 nm) spin-valve devices of 15 x 5 µm². Subsequently, a 200 nm thick insulating amorphous LaAlO3 film was selectively deposited on the A/B site atoms using PLD. An Au film was used to isolate the spin-valve edges and contact pads from Bi0.85La0.15FeO3 to BiFeO3. The DM magnetron sputtering was used to deposit 230 nm thick Au film for electric contacts. The GMR responses of spin-valve devices were measured in current-in-plane configuration at constant current voltage with varying magnetic field. The magnetoelectric coupling measurements were conducted with the application of electric pulse (10–100 µs) across Bi0.85La0.15FeO3 films.

**Photoemission electron microscopy (PEEM).** X-ray imaging with variable circular and linear polarization at the Co and Fe L edges was performed at the PEEM3 end station of BL11.0.1 at the Advanced Light Source, Lawrence Berkeley National Lab. The sample was held at an angle of 60° with respect to the surface normal, and was mounted on an azimuthal rotation stage. The in-plane azimuthal angle of zero degrees is with x-rays incident along the in-plane [−100] direction (θ = 0°). The sample was held at a voltage of −18 kV to accelerate any photo-emitted and secondary electrons, proportional to the local x-ray absorption coefficient, through a series of electrostatic lenses and incident on an CCD detector with a phosphor-coated fiber plate as an amplifier. To probe antiferromagnetic orientation projections along the x-ray linear polarization axis, linear dichroism images at the Fe L2, A and B edges of 720.6 and 722 eV were taken at linear polarization axis angles between s- and p-polarization (s: θ = 90°; p: θ = 0°). For each polarization value, a pre-edge image at 718 eV was taken to normalize the on-edge images. A Gaussian distribution was then fitted and the center of each unit cell is defined as the average of the positions of the four atoms at the corners of the unit cell. To compensate for the ratio of the size to the exchange length in the ferromagnet, a lower value of the exchange stiffness was taken, Aex = 100 mJ/m². Other parameters: Msat = 1MA/m; magnetization of Co80Fe20, K = 5000 J/m³ - in-plane anisotropy in the bottom layer due to the exchange coupling, exchange bias HEB = 0 oe. The normalized vectors mentioned above and used in simulations were at positive applied voltage P1 = [0.4082 –0.4082 0.8165]; L1 = [0.8242 0.5494 –0.1374]; M2 = [−0.9325 0.7290 0.3668] and at negative applied voltage P1 = [−0.8165 0.4082 –0.4082]; L1 = [−0.4732 0.8944]; M2 = [−1.3651 −0.9129 −0.1826]. One can see that the projection of the canted magnetization on the shorter in-plane axis of the spin-valve is smaller than the long axis of the spin-valve. This explains why the manifestation of the exchange bias in the asymmetry of the hysteresis loop is smaller here than in ref. 11.

**Data availability**

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

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Author contributions

Y.-L.H. and R.R. designed the experiments and wrote this paper. Y.-L.H. carried out materials synthesis and characterization. D.V. conducted the micromagnet simulations on the magnetoelectric measurements. C.A. carried out the STEM measurements, analysis, and supervised by X. P. Y.-L.H and B.P performed device fabrication and electrical measurements. Y.-L.H., L.Z., H.-J.L., and Y.-H.C. performed the XRD measurements. Y.-L.H., M.R., and B.D.H. conducted the PFM measurements and analysis. J.C., M.Y., Z.Q.Q. and J.B. performed the magneto-optic measurements. Additional device processing, electrical measurements, and analysis were carried out by T.G., J.C., C.-C.L., and I.Y. R.V.C, Y.-L.H., and A.F. performed the XMLD-PEEM measurements and R.V.C provided analysis. J.I. performed the calculations for the ferroelectric switching energy. All authors made contribution to writing the manuscript. The work was conceived and guided by R.R. and L.W.M. All authors discussed results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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