

Engineering exchange bias at the interface of self-polarized ultrathin ferroelectric BaTiO₃ and ferromagnetic La_{0.67}Sr_{0.33}MnO₃

Tuhin Maity^{1,2,3,*}, Manisha Bansal^{2,†}, Nives Strkalj^{1,4}, Kapildeb Dolui¹, Di Zhang⁵, Zihao He⁵, Guillaume F. Nataf^{1,§}, Adam Lovett¹, Massimo Ghidini^{1,6,7}, Sarnjeet S. Dhesi⁶, Ping Lu⁸, Haiyan Wang⁵, Weiwei Li^{1,9,†} and Judith L. MacManus-Driscoll^{1,‡}

¹Department of Materials Science and Metallurgy, *University of Cambridge*, Cambridge, CB3 0FS, UK

²School of Physics, *Indian Institute of Science Education and Research*, Thiruvananthapuram, 695551, India

³CAMRIE and CHPC, *Indian Institute of Science Education and Research*, Thiruvananthapuram, 695551, India

⁴Center for Advanced Laser Techniques, *Institute of Physics*, 10000 Zagreb, Croatia

⁵School of Materials Engineering, *Purdue University*, West Lafayette, Indiana, USA

⁶*Diamond Light Source, Harwell Science and Innovation Campus*, Chilton, Didcot, OX11 0DE, UK

⁷Department of Mathematics, Physics and Computer Science, *University of Parma*, 43124 Parma, Italy

⁸*Sandia National Laboratories*, Albuquerque, New Mexico 87185, USA

⁹College of Physics, MIIT Key Laboratory of Aerospace Information Materials and Physics, State Key Laboratory of Mechanics and Control for Aerospace Structures, *Nanjing University of Aeronautics and Astronautics*, Nanjing 211106, China



(Received 20 March 2024; revised 11 September 2024; accepted 4 October 2024; published 13 November 2024)

We investigate the emergence and optimization of conventional exchange bias (EB) in ultrathin (<10 nm) ferroelectric (FE) BaTiO₃ (BTO)/ferromagnetic (FM) La_{0.67}Sr_{0.33}MnO₃ (LSMO) epitaxial bilayers without an antiferromagnetic (AFM) material. The EB originates from the electronic orbital reconstruction at the FE-FM interface due to the ferroelectric polarization. We achieve maximum EB of approximately 42 Oe with single-domain polarization in nine-unit-cell-thick BTO, setting the BTO thickness above the critical threshold for ferroelectricity yet below the thickness of strain relaxation and multidomain breakdown. Furthermore, the LSMO layer needs to be thick enough to sustain both the FM layer and polarization-induced AFM spin configuration at the LSMO/BTO interface, yet as thin as possible to enable the EB loop shift. The temperature, training, field, and thickness dependence of the EB confirm that the LSMO/BTO interface exhibits conventional EB despite its unconventional origin. Using x-ray magnetic circular dichroism, scanning transmission electron microscopy, and density-functional-theory calculations, we confirm that the macroscopic EB effect originates from the interfacial AFM spin configuration in LSMO driven by FE-induced *d*-orbital modifications in interfacial Mn ions. Thus, we engineer strong interfacial EB coupling in artificial multiferroics without a conventional AFM material by controlling FE polarization, highlighting the potential for advanced spintronic applications.

DOI: [10.1103/PhysRevApplied.22.054035](https://doi.org/10.1103/PhysRevApplied.22.054035)

I. INTRODUCTION

Engineering charge and spin degrees of freedom in atomically perfect lattice-matched interfaces of transition

metal perovskites has enabled advances in spintronics research. New ferroic states emerge at the interfaces of artificial multiferroics by either introduction of magnetization into the ferroelectric (FE) layer [1] or introduction of polarization in the ferromagnetic (FM) layer [2,3]. The direction of FE polarization towards or away from the interface with the FM layer plays a crucial role in modifying the active *d*-orbital electronic states at these interfaces [4,5]. For instance, FE polarization has been shown to induce crystal and electronic reconstructions at the FM-FE interface leading to magnetic reconstruction within the FM layer [6–10]. Such magnetic reconstruction at atomically sharp interfaces can result in multiferroic, magnetoelectric, and exchange bias (EB) couplings [11,12].

*Contact author: tuhin@iisertvm.ac.in

†Contact author: w1337@nuua.edu.cn

‡Contact author: jld35@cam.ac.uk

§Present address: GREMAN UMR7347, CNRS, University of Tours, INSA Centre Val de Loire, 37000 Tours, France

¶These authors contributed equally.

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

Conventional EB—a lateral shift of the magnetic hysteresis (MH) loop in the negative (positive) field direction when cooled in a positive (negative) field through the Neel temperature (T_N)—is often observed at the interface of FM [e.g., $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO)] and antiferromagnetic (AFM) (e.g., BiFeO_3) layers [13]. However, apart from a conventional FM-AFM interface, EB is also observed to arise from an unconventional origin in the absence of a distinct AFM layer, such as in a paramagnetic LaNiO_3 and FM LaMnO_3 superlattice [14], FM LSMO and non-magnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ heterostructures [15], and single-phase FM films [16,17]. Such EB emerges from orbital reconstruction, charge transfer, or inhomogeneous magnetic phases, and which holds significance for various modern nanoscale micromagnetic device applications such as spin valves, spin filters, quantum magnets, etc. [18–20]. Some reports have also shown EB in artificial multiferroic FM-FE bilayer structures due to the formation of a few-nanometer-thick magnetic dead layer or antiferromagnetic layer between the heterointerfaces of FE and FM layers [21,22]. On the other hand, some reports of magnetoelectric states at the FE-FM interface have demonstrated the formation of the AFM spin configuration ($\uparrow\downarrow$) in the interfacial magnetic layer from FE polarization [7–10], but without showing its effect on the macroscopic EB. Therefore, there is still a lack of understanding of the nature and optimization of the strength of macroscopic magnetic effects such as EB arising at such interfaces from the FE polarization. Furthermore, the optimization of FE polarization and individual layer thicknesses to obtain tunable EB have not been shown so far. Properties of both FE and FM layers are highly sensitive to thickness in the ultrathin regime (<10 nm), yet critical in obtaining a significant EB. For example, polarization and magnetization in ultrathin perovskite FE and FM are only stabilized above a critical thickness. Furthermore, FE often exhibits a multidomain state with lower net polarization at thicknesses above strain relaxation [23].

In this report, we engineer a conventional strong EB coupling (approximately 40 Oe at 2 K) at the interface of fully strained, epitaxially grown ultrathin (<10 nm) FM LSMO and FE BaTiO_3 (BTO) bilayers on TiO_2 -terminated SrTiO_3 (STO) substrates in the absence of a conventional AFM material. The EB increases with decreasing thickness (t_{FM}) of LSMO to a maximum of 42 Oe for $t_{\text{FM}} \sim 7$ -unit-cell (u.c.) LSMO. Similarly, the EB is maximized for an optimized BTO thickness of 9 u.c., but decreases below the FE critical thickness ($3/4$ u.c.), below which the film is nonpolar [24]. Interestingly, the EB also decreases for higher BTO thicknesses (25 u.c.) due to the formation of a multidomain state and thus lower net polarization. We further consolidate the microscopic picture of the EB at the LSMO/BTO interface in optimized heterostructures. We show a proximity effect between interfacial Ti and Mn atoms by x-ray magnetic circular

dichroism (XMCD) measurements at 2 K. We observe that the Ti^{4+} ions in BTO show ferromagnetism that is switchable on reversing the direction of the magnetic field. Experimental scanning transmission electron microscopy (STEM) observations and density-functional-theory (DFT) calculations reveal crystal-structure changes at the interface: an approximate 4% displacement of Ti^{4+} ions away from the interface promoting the displacement of Mn^{4+} ions towards the interface in the interfacial (2–3 u.c.) interlayer of the LSMO layer. DFT calculations unambiguously identify that polarization in BTO modifies the d -orbital occupancy of interfacial Mn and leads to an AFM spin configuration of Mn^{4+} ions at the FM-FE interface. The strong EB effect (approximately 40 Oe at 2 K) is thus attributed to the coupling of the FE-induced interfacial AFM interlayer in LSMO and adjacent FM layer in LSMO. Overall, a strong interfacial conventional EB is engineered in LSMO/BTO bilayer films by thickness optimization in the absence of a conventional AFM material from strain-induced polarization.

II. RESULTS AND DISCUSSION

We deposited bilayer films (L_nB_mS and B_mL_nS) of LSMO (L) and BTO (B) (n and m are the number of unit cells of LSMO and BTO, respectively) on TiO_2 -terminated STO substrate (S) by pulsed laser deposition (PLD) (details in Appendix A). For L_nB_mS , BTO was first deposited on the STO substrate and then LSMO was deposited on top of the BTO. For B_mL_nS , films were deposited in the reverse order. X-ray diffraction (XRD) measurements and high-resolution high-angle annular dark-field (HAADF) STEM images confirm the epitaxial growth of the films (see Appendix B, Fig. 6). To understand the effect of thickness on the interfacial magnetic properties, we investigated samples (L_nB_9S) with five different thicknesses of LSMO ($n = 4, 7, 14, 28$, and 50 u.c.) with a fixed thickness of BTO ($m = 9$ u.c.). We also deposited reference samples $B_{25}L_{14}S$ with thicker BTO (25 u.c.) and $B_3L_{14}S$ with thinner BTO (3 u.c.) with a fixed thickness of LSMO (14 u.c.) to study the impact of BTO thickness.

Despite the absence of a conventional antiferromagnetic layer, we observed a significant EB in L_nB_9S/B_9L_nS ($n \leq 14$) bilayers. The minimum step of measurement was taken to be 2 Oe to accurately measure the EB. EB decreased with increasing LSMO thickness (t_{FM}) [Figs. 1(a) and 1(b) and see Appendix C, Fig. 8], closely following $H_E \propto t_{\text{FM}}^{-1}$ [25]. $L_{14}B_9S$ exhibits no EB shift as LSMO loses ferromagnetism at such low thicknesses [26]. However, L_7B_9S and $L_{14}B_9S/B_9L_{14}S$ show the most prominent EB of approximately 40–50 Oe. The MH loop for L_7B_9S shows noise as the magnetic moment is too low for the sensitivity of the superconducting quantum interference device (SQUID). Hence, we considered sample $L_{14}B_9S$ for the detailed magnetic study.

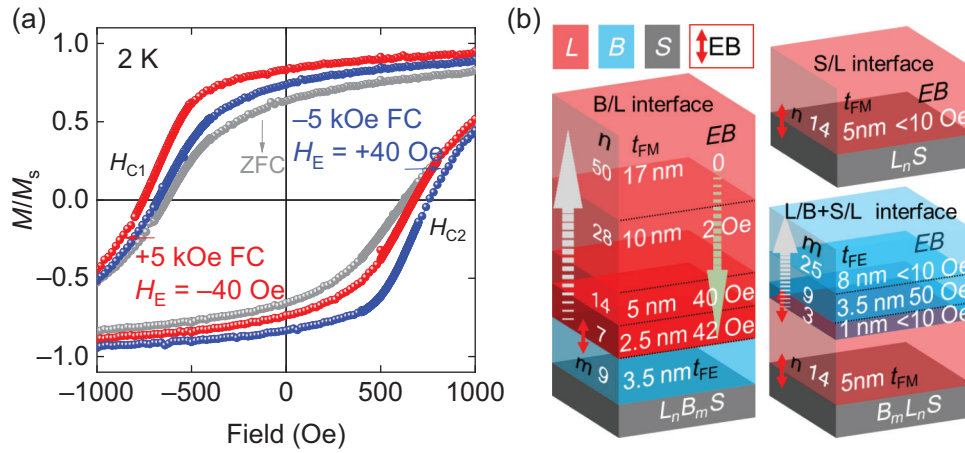


FIG. 1. (a) Significant exchange bias (EB) is observed for $L_{14}B_9S$ [where L represents $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), B represents $BaTiO_3$ (BTO), S represents $SrTiO_3$ (STO), and the subscripts are the number of unit cells]. FC denotes field cooled and ZFC denotes zero-field cooled. (b) EB increases with decreasing thickness t_{FM} of LSMO. The EB ($H_E \sim 50$ Oe) is higher when LSMO is deposited on STO i.e., $B_9L_{14}S$, than when BTO is deposited on STO ($H_E \sim 40$ Oe), i.e., $L_{14}B_9S$. $H_E \sim 8$ Oe is observed when only LSMO is deposited on STO i.e., $L_{14}S$.

We next investigated how the EB depends on BTO thickness, considering $B_mL_{14}S$ samples with 9-u.c.-thick BTO (approximately 50 Oe) and two reference samples with 25- and 3-u.c.-thick BTO layers. We observed very low EB (≤ 11 Oe) in $B_{25}L_{14}S$ with thicker (25 u.c.) and $B_3L_{14}S$ with thinner (3 u.c.) BTO, emphasizing the importance of an optimized thickness of BTO. To investigate the cause of the EB changes with BTO thickness in LSMO/BTO bilayers, we evaluated the polarization and domain state by piezoresponse force microscopy (PFM) measurements. We studied samples with the bottom LSMO electrode, which was necessary to perform PFM measurements. The $B_9L_{14}S$ sample with optimal EB is single-domain polarized upwards in the as-grown film, away from the interface with LSMO, and the polarization could be reversibly switched by applying a voltage (± 4 V) [Fig. 2(a)]. This suggests that screening sources such as the p -type carriers in LSMO could be governing the polarization direction away from the LSMO/BTO interface. The $B_{25}L_{14}S$ with reduced EB shows an as-grown multidomain structure, likely resulting from strain relaxation leading to the flexoelectric effect becoming dominant in determining the polarization direction (see Appendix D, Fig. 12 and Ref. [27]). The line profiles of the phase images further confirm that 9-u.c. BTO on LSMO [Fig. 2(b)] has only two contrast levels: P_{up} (as-grown and poled at +4 V) and P_{down} (poled at -4 V), whereas 25-u.c. BTO on LSMO (see Appendix D, Fig. 12) has three contrast levels: multidomain (as-grown), P_{up} (poled at +8 V), and P_{down} (poled at -8 V). Therefore, the 9-u.c. BTO is single-domain as-grown and 25-u.c. BTO is multidomain as-grown. To additionally confirm the multidomain behavior of thicker BTO, we performed optical second-harmonic

generation (SHG) [Fig. 2(d)]. The SHG polarizer (α) data for analyzer $\beta = 90^\circ$ shows that the SHG response at 90/90 which is most sensitive to out-of-plane polarization, is stronger for 9-u.c. BTO than for 25-u.c. BTO, indicating that 9-u.c. BTO has a higher net polarization value. Since this is contrary to what one expects from size effects, we confirmed using SHG that the 25-u.c. BTO is multidomain. Finally, the $B_3L_{14}S$ sample shows no PFM response and insignificant EB. These PFM measurements emphasize the importance of polarization in the FE layer for EB optimization. Polarization magnitude and domain state are stabilized by strain and screening. The epitaxial growth on STO induces a uniform strain [compression in-plane (IP) and tension out-of-plane (OP), confirmed by the geometric phase analysis (GPA) discussed later] in the BTO that induces strong OP FE polarization up to the relaxation thickness [28,29]. The strong single-domain OP FE polarization away from the interface can only be observed for thicknesses above the FE critical thickness of approximately 4 u.c. in BTO [30], but below the strain-relaxation thickness of approximately 10 nm. Hence, to obtain FE polarization away from the LSMO/BTO interface, we optimized BTO thickness to $m = 9$ u.c. Thus, we call this strain-induced ferroelectricity “self-polarized” as the BTO is single-domain OP polarized in the film without the application of an electric field. Thus, the direction-specific BTO self-polarization plays a key role in the stabilization of the EB in $L_{14}B_9S$ and $B_9L_{14}S$ [27,31], making them the focus of our study.

We compared $L_{14}B_9S$ and $B_9L_{14}S$ samples to understand the role of interfaces (LSMO/BTO and LSMO/STO) on the EB. At 2 K, the EB shifts for $L_{14}B_9S$ and $B_9L_{14}S$ are $H_E \sim 40$ Oe and $H_E \sim 50$ Oe, respectively, for both

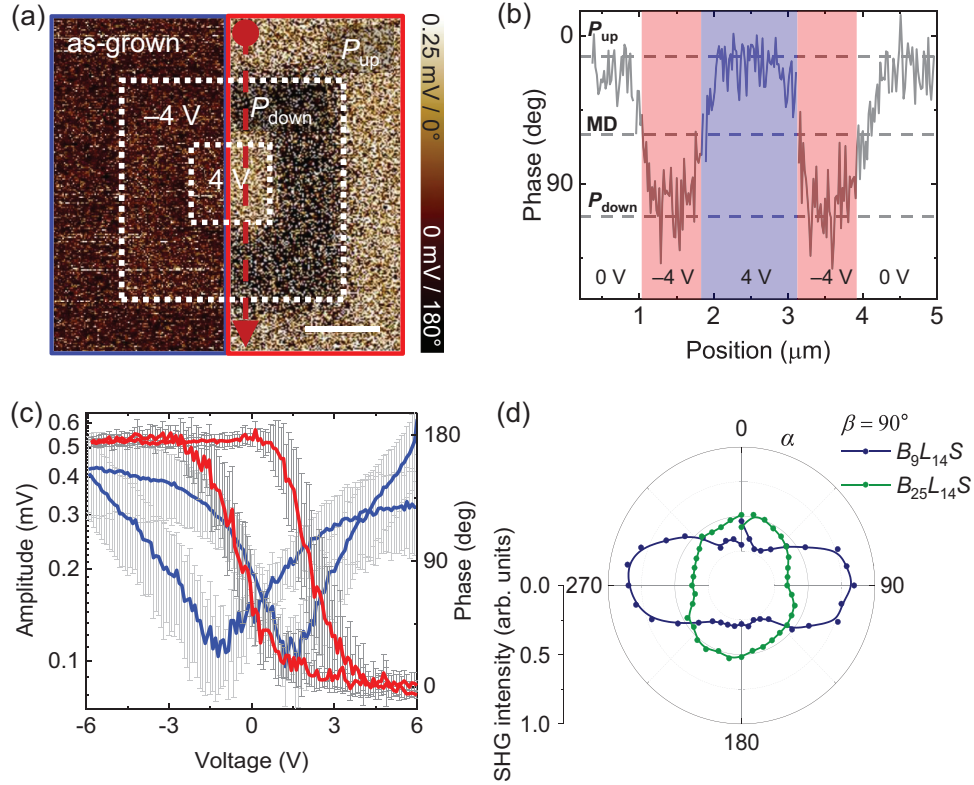


FIG. 2. (a) Amplitude (left half) and PFM phase (right half) contrasts for as-grown ($5 \times 5 \mu\text{m}^2$), after -4 V writing ($3 \times 3 \mu\text{m}^2$) and $+4 \text{ V}$ rewriting ($1 \times 1 \mu\text{m}^2$) at room temperature. Scale bar is $1 \mu\text{m}$. (b) Line profiles extracted along 30 pixels [as marked with red in (a)] of the phase image. The 9 u.c. BTO on LSMO has only two contrast levels: P_{up} – as-grown and poled $+4 \text{ V}$, and P_{down} – poled -4 V . (c) Piezoresponse measured on BTO (9 u.c.)-LSMO (14 u.c.)-STO at room temperature shows the amplitude (blue) and phase (red) with bias voltage. (d) The SHG polarizer (α) for $\beta = 90^\circ$ is shown for BTO layers of 9 u.c. and 25 u.c. thickness.

positive and negative bias field [Fig. 1 and as given in Appendix C, Figs. 9(a) and 9(c)]. The higher EB in $B_9L_{14}S$ is due to the additional EB from the interface of LSMO/STO [16,32]. We confirmed this with a single layer of 14-u.c. LSMO film ($L_{14}S$), which shows an EB of $H_E \sim 8 \text{ Oe}$. For the same reason, we observed an EB of $H_E \sim 11 \text{ Oe}$ in $B_{25}L_{14}S$ from the LSMO/STO interface. Saturation magnetization (M_S) is also reduced from approximately 300 emu/cm^3 (approximately $1.8 \mu_B/\text{Mn}$) in the $L_{14}S$ film to approximately 200 emu/cm^3 (approximately $1.2 \mu_B/\text{Mn}$) in the bilayer films ($L_{14}B_9S/B_9L_{14}S$) due to the pinned, uncompensated exchange-coupled spins at the interface of BTO and LSMO [33]. Hence, we mainly focused on $L_{14}B_9S$ to elucidate the effect of the LSMO/BTO interface in obtaining an unconventional EB without an AFM.

The $L_{14}B_9S$ film shows the field-cooled (FC) H_C (approximately 720 Oe) to be approximately 90 Oe higher than the zero-field-cooled (ZFC) H_C (approximately 630 Oe), ascribed to strong interfacial coupling under the bias field (H_{cool}) [34,35]. The average remanence magnetization (M_R) is also increased by 20% from

ZFC to FC due to the modified magnetic state at the interface, which is discussed later. Further, Fig. 3(a) shows both H_E and H_C monotonically decrease with temperature and reach zero above approximately 150 K [which matches with the blocking temperature (T_B) of $L_{14}B_9S$, $T_B \sim 140 \text{ K}$ (see Appendix C, Fig. 9(b))]. Note that the Curie temperature (T_C) of 5-nm LSMO film is around 250 K [36].

The EB training effect shows monotonically decreasing H_E and H_C with increasing repeating cycles (N), indicating spin rearrangement at the interface [Fig. 3(b)]. After the sixth cycle, H_E is saturated. This fits well with the empirical law, $H_{E^n} = H_{E^\infty} + kN^{(-0.5)}$ with $k = -26.9 \text{ Oe}$ and $H_{E^\infty} = -11.8 \text{ Oe}$, confirming pure AFM spin rearrangements and a clear signature of the conventional EB effect at the LSMO/BTO interface [37]. Further, for bias field (H_{cool}) variation, the H_E increases monotonically to $H_E = 50 \text{ Oe}$ until $H_{\text{cool}} \sim 3 \text{ kOe}$ and then gradually decreases for $3 \text{ kOe} \leq H_{\text{cool}} \leq 20 \text{ kOe}$ [Fig. 3(c)]. This behavior of H_E over H_{cool} is attributed to interfacial magnetic interactions being overcome by the Zeeman energy after reaching a depinning threshold field [38]. Above

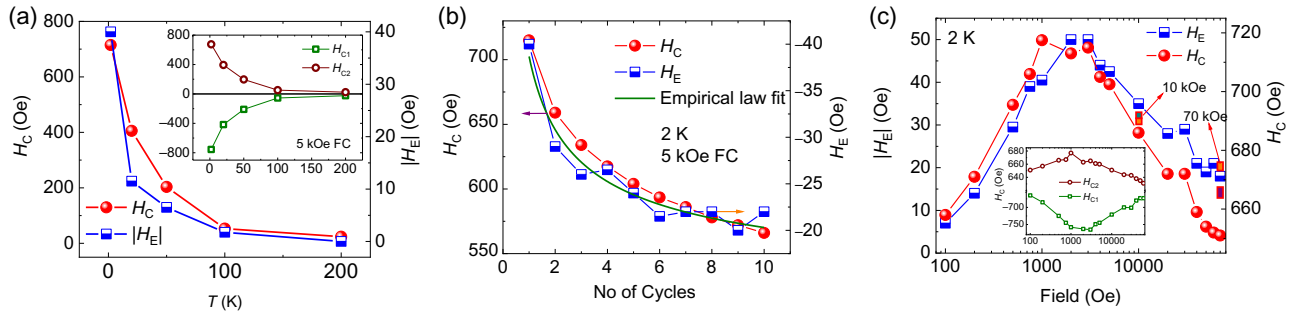


FIG. 3. (a) EB vanishes for temperatures higher than $T_B \sim 140$ K. (Inset) H_{C1} and H_{C2} show systematic change with temperature. (b) Training effect on EB shows H_E and H_C decrease with increasing cycle number up to sixth cycle. (c) H_E and H_C increase until $H_{cool} \sim 3$ kOe where they reach the maximum and then decrease. The H_{C1} change dominates over H_{C2} (inset). Red-bordered data points show the impact on H_E and H_C of varying the loop tracing field range ($H_S = \pm 10$ kOe and ± 70 kOe).

20 kOe, the changes are not significant. To verify the effect of loop tracing field range ($\pm H_S$), we measured the MH loops with $H_S = \pm 10$ and ± 70 kOe for $H_{cool} = 10$ kOe and a 70 kOe bias field, respectively, and found that the field range does not have any appreciable impact on H_E [Fig. 3(c), red-bordered data points]. This confirms that the ± 5 kOe field range and the ± 5 kOe bias field are suitable for investigating this complex EB system. Although the field range does not affect the H_E noticeably, the H_C is slightly increased for the higher field range owing to the existence of an unusual AFM component at the interface, showing high magnetic anisotropy, which is modified at higher magnetic fields. The bias field effect is more in H_{C1} than H_{C2} [inset Fig. 3(c)]. The training effect shows similar behavior (see Appendix C, Fig. 10). This is due to the nonswitchable exchange-coupled magnetic anisotropy created at the interface, which favors the bias field direction [17,39,40]. Hence, the temperature dependence, training effect, and field dependence on EB together confirm that the LSMO/BTO interface exhibits conventional EB effects, despite its unconventional origin.

We further investigated the crystal and electronic structure changes at the LSMO/BTO interface to consolidate the microscopic picture of the EB in optimized heterostructures. To identify the origin of the AFM layer in the EB coupling, element-specific magnetic measurements were carried out. The L_7B_9S sample ($H_E \sim 50$ Oe) was chosen, as this film was sufficiently thin that the LSMO/BTO interface was amenable to the x-ray beam. The XMCD signal and magnetic polarization of the Mn sites show a prominent XMCD spectra over the $L_{2,3}$ edges as well as magnetic hysteresis (as shown in Appendix C, Fig. 11) at 2 K, similar to the typical XMCD spectrum, confirming robust Mn magnetism [41]. In the BTO layer underneath the $n = 7$ u.c. LSMO, the observed Ti XMCD signal at 2 K indicates a net magnetic moment on the Ti sites (originally nonmagnetic) [Fig. 4(c)] [1,42]. The magnetism of Ti is switchable from one direction (M_{Ti}^+) to the opposite (M_{Ti}^-) direction with magnetic field (± 20 kOe), similar to Mn. When the

field is removed, the intensity of the Ti spectra decreases, similar to M_R^{Mn} , suggesting remanence magnetization on the Ti sites (M_R^{Ti}). The Ti XMCD spectrum vanishes at 300 K. Owing to signal-to-noise limitations, it was not possible to obtain a direct MH loop for the Ti sites. XMCD integrals indicate that the magnetic orientation of both Ti and Mn is in the same direction (see Appendix C, Fig. 11). Therefore, while magnetized Ti does not contribute to AFM, it does confirm the proximity effect between Ti and Mn atoms. This suggests an interface-induced AFM phase in the Mn sites, that is, within the single LSMO layer.

Next, we performed a GPA analysis from a high-resolution STEM image of the bilayer film [Fig. 5(a)]. The epitaxial film has 2.2% compressive and 0.87% tensile IP strain on the BTO and LSMO, respectively. The IP strain map shows perfect lattice matching with the substrate. For volume conservation, the IP strain results in the OP strain of the BTO/LSMO film lattice based on the OP GPA maps. The OP strain is different within approximately 5 nm of the STO substrate compared with that in the rest of the heterostructure. Within this 5 nm, approximately 3.5 nm is BTO film, which is highly elongated in the OP direction due to the higher lattice mismatch with STO. Surprisingly, 4 u.c. (< 1.5 nm) of the LSMO film are also structurally different in terms of OP strain compared to the rest of the LSMO film. This suggests structural distortions in the LSMO interfacial unit cells adjacent to the polarized BTO. As reported before, an EB can occur due to nonuniformity in the magnetic layer, such as a magnetically modified interfacial pinned layer in a strained epitaxial manganite thin film near the substrate, distinct from the rest of the film [16]. Typical thicknesses of such interfacial pinned layers are between 5 and 10 nm (for 50–60-nm-thick LSMO films) and the observed EB is approximately 20 Oe at 2 K [16,17]. According to our GPA analysis, OP strain is different in only 4 u.c. of LSMO and thus it is unlikely that such a thin LSMO layer can be solely responsible for the observed high EB. In the thinnest LSMO/BTO film with EB where the LSMO layer is only 7 u.c., it is not feasible to

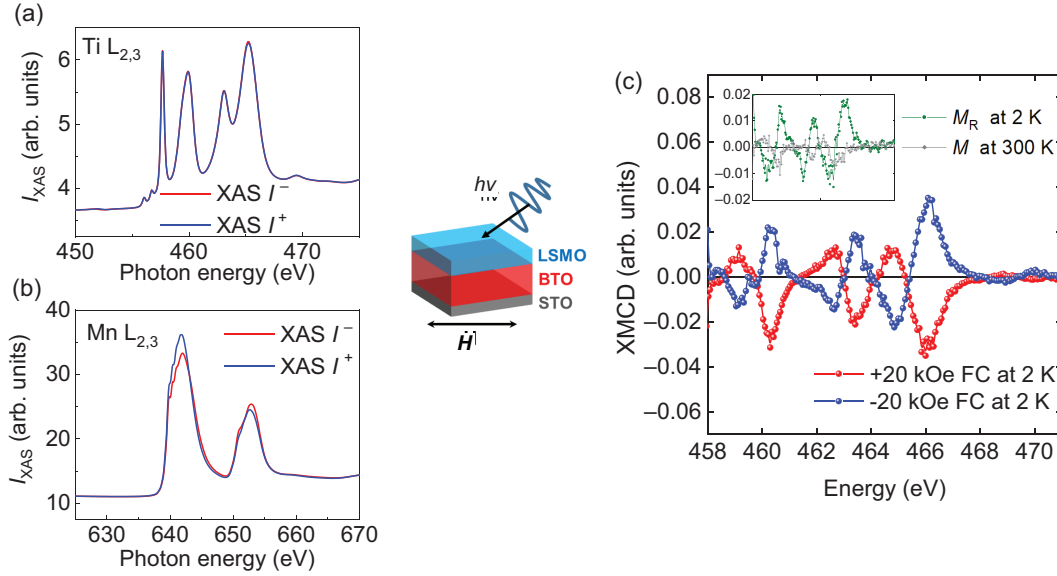


FIG. 4. (a) and (b) XAS of Ti- $L_{2,3}$ and Mn- $L_{2,3}$ edges at 2 K after cooling down from 300 K under -20 kOe magnetic field. I^+ and I^- indicate left- and right-circularly polarized light. (c) XMCD spectra over the Ti $L_{2,3}$ edge at 2 K after cooling from 300 K with ± 20 kOe bias field show a net magnetic moment on the Ti sites, switchable by applying an opposite magnetic field. (Inset) When the bias field (-20 kOe) is removed after cooling, a remanence magnetization (M_R^{Ti}) is observed. The XMCD has no signal at 300 K with ± 20 kOe field applied.

have both a pinned or canted region (approximately 4 u.c., based on GPA analysis) and a bulk region (the remaining approximately 3 u.c.) of the film for EB coupling, since a minimum of 3–4-u.c. LSMO is required to form FM domains [43]. Concomitantly, we do not observe any hysteresis in a 4-u.c. LSMO film. Furthermore, in previous reports of EB in thicker films resulting from a pinned surface or canted spin layer, a significant change in M_S from ZFC to FC was observed [16], contrary to the present observation [see Appendix C, Fig. 9(a)]. Certainly, the complex EB is due to orbital reconstructions at the LSMO interface induced by the polarization and not by the strain change in the LSMO alone.

To elucidate the role of BTO at the interface with LSMO for obtaining the EB effect, we studied the LSMO/BTO interface using HAADF STEM. The high-resolution HAADF STEM image shows that Ti atoms are displaced away (by approximately 4%) from the interface, as expected for an FE layer [Fig. 5(b) upper panel]. Surprisingly, the interfacial Mn atoms additionally displace towards the interface from their centrosymmetric positions. To investigate the distortions of the MnO_6 octahedra near the interface, we performed DFT calculations (computational details in Appendix E). An appropriate polarization (approximately 4%) in the BTO pointing away from the LSMO was considered for calculations in the LSMO/BTO heterostructure to simulate the PFM and STEM observations. The DFT results confirm that the OP Mn—O bond length at the interface shrinks by

approximately $0.23 \text{ \AA}$ (approximately 4.36%) as compared to the IP bond length in FE BTO/LSMO [Fig. 5(b) lower panel]. This increases the OP distance between the first two interfacial Mn atoms, reducing the electron spin hopping and leading to spin localization within individual Mn atomic orbitals. Eventually, the double-exchange mechanism is suppressed and the AFM superexchange interaction can then dominate between the first two Mn atoms near the interface [10,44]. The formation of the AFM layer in LSMO also decreases M_S in bilayers compared to LSMO/STO as observed in magnetic measurements. Furthermore, our energetics calculations found that the ground-state spin configuration of the interfacial Mn atoms transforms from the FM state to the AFM state only when the BTO is FE. For centrosymmetric BTO (C BTO), the interfacial LSMO is most stable in a FM configuration, emphasizing the importance of ferroelectricity.

The projected density of states (PDOS) depicts double degeneracy for the interfacial Mn- e_g orbitals, i.e., $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ when BTO is kept centrosymmetric (C BTO/LSMO heterostructure). In contrast, when BTO is ferroelectric (FE BTO/LSMO), the MnO_6 octahedral distortions lift the degeneracy, i.e., $d_{x^2-y^2}$ becomes more occupied than $d_{3z^2-r^2}$ to suppress the Coulomb repulsion [Fig. 5(c)]. Further analysis of the PDOS shows that the degeneracy of interfacial Mn t_{2g} orbitals remains mostly unaffected by the polarization direction (see Appendix E, Fig. 13). Moreover, the e_g and t_{2g} orbitals of the third Mn atom from the interface remain almost doubly and

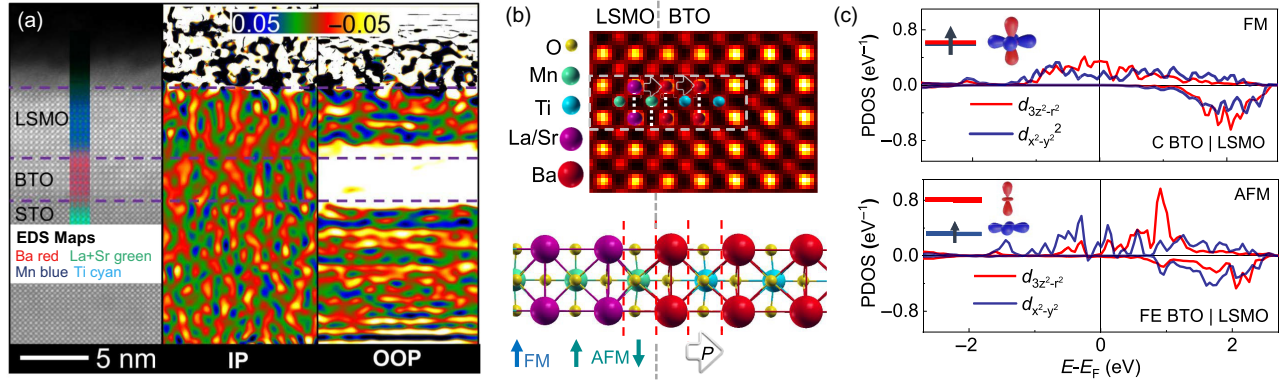


FIG. 5. (a) GPA shows fully IP strained LSMO and BTO films. BTO is highly elongated OP causing structural variation in the adjacent LSMO at the interface. (b) Upper panel: Displacement of Ti and Mn atoms (approximately 4%) observed in HAADF STEM data (white arrows are guides to the eyes). Lower panel: Enlarged view of the relaxed crystal structure for the FE BTO/LSMO system calculated from DFT calculations. The white arrow represents the direction of polarization of Ti in BTO. The green (blue) arrows represent the spin configurations of Mn (Ti), respectively. (c) PDOS of the interfacial Mn atom of C BTO/LSMO (upper panel) and FE BTO/LSMO (lower panel) for FM and AFM magnetic ground state configurations, respectively.

triply degenerate, respectively (see Appendix E, Fig. 13), implying that the effect of polarization extends up to two atomic layers of LSMO, supporting the GPA results. Further, we observe that a switchable magnetic moment ($>0.002 \mu_B$) is induced on the Ti in BTO due to the proximity effect, which is ferromagnetically ordered within the BTO and within the interfacial Mn atoms, in agreement with the XMCD results [2]. The induced magnetic moment ($0.002 \mu_B$) of Ti is significantly lower than the Mn moment (approximately $3 \mu_B$) and hence does not contribute to the observation of the EB in macroscopic magnetic measurements. Hence, the observed exchange bias originates dominantly from the interfacial and bulk LSMO sublayers. Furthermore, our calculations find no AFM coupling at the interface of the LSMO/STO heterostructure, which proves that the LSMO/STO with ultrathin LSMO cannot alone contribute to the observed strong EB. Therefore, our DFT calculations indicate that the interfacial AFM coupling is stabilized as a result of the OP FE polarization in the BTO layer, causing the EB effect in ultrathin LSMO/BTO bilayers.

III. CONCLUSION

In conclusion, we engineered an EB effect at the interface of ultrathin (<10 nm) epitaxial films of FM LSMO and FE BTO in the absence of any conventional AFM material. We optimized the LSMO and BTO thicknesses for the maximum EB (approximately 50 Oe) by considering the high sensitivity of magnetic and FE properties in the ultrathin regime. The EB significantly decreases for both thicker (25 u.c.) and thinner (3 u.c.) BTO, emphasizing the importance of single-domain polarization in an optimized thickness of BTO. As a result of the epitaxial strain in the ultrathin films, BTO is single-domain

self-polarized away from the interface in the absence of any external electric field. Furthermore, an optimal LSMO thickness of 7–14 u.c. allows for stabilization of both FM and AFM configurations. Though the observed EB is unconventional in origin, resulting from polarization-induced interfacial AFM spins, its nature is conventional in FM thickness, temperature, field, and training dependence. Element-specific XMCD confirms the presence of a switchable magnetic moment on the interfacial Ti sites of BTO at 2 K owing to the proximity effect with LSMO. We show a stabilized AFM phase due to the crystal and electronic structure distortion of interfacial Mn atoms driven by the BTO polarization, which enables the EB at the interface of epitaxial ferromagnetic and ferroelectric thin-film heterostructures. Our findings show a way to optimize reconfigurable interfacial magnetic states using ultrathin epitaxial film interfaces without external stimuli. This gives future opportunities for advanced energy-efficient multifunctional nanoscale magnetoelectric memory devices and sensors.

All the experimental and calculation data that support the findings of this study are available from the corresponding authors upon reasonable request. All the codes used for this study are available from the corresponding authors upon reasonable request.

ACKNOWLEDGMENTS

T.M. and J.L.M.-D. acknowledge funding from European Union Grant No. H2020-MSCA-IF-2016 (745886)-MuStMAM, the Isaac Newton Trust Grant No. RG96474. J.L.M.-D. also acknowledges funding from the Royal Academy of Engineering, CiET1819_24, the Leverhulme Trust Grant No. RPG-2015-017, EPSRC Grants No. /N004272/1 and No. EP/M000524/1. T.M., J.L.M.D.,

and N.S. acknowledge EU-H2020-ERC-ADG Grant No. 882929 EROS. T.M. and M.B. acknowledge SERB-SRG 2021/000423, IISER TVM CHPC, and the Prime Minister's Research Fellowship. N.S. acknowledges HORIZON-MSCA-2022-PF (Grant No. 101106176). G.F.N. acknowledges funding from the Royal Commission for the Exhibition of 1851 through the award of a Research Fellowship. The authors acknowledge Diamond Light Source for time on I06 under proposal MM22427. The authors acknowledge Thomas Forrest and Larissa Ishibe-Veiga for the help at Diamond Light Source. Sandia National Laboratories is a multiprogram laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy/National Nuclear Security Administration under Contract No. DE-NA0003525. This paper describes objective technical results and analysis. The TEM work at Purdue University was supported by the U.S. National Science Foundation (Grants No. DMR-2016453 and No. DMR-1809520).

T.M., W.L., and J.L.M.-D. conceived the experiments and supervised the research. W. L. made the samples and carried out the XRD and AFM characterizations. T.M. carried out magnetic properties' measurements. D.Z.,

Z.H., P.L., and H.W. performed STEM imaging and EDS mapping. N.S. performed the PFM measurements. T.M., W.L., G.F.N., A.L., M.G, and S.S.D. contributed to the XMCD measurements. M.B., K.D., and T.M. contributed to DFT calculation. T.M., M.B., and J.L.M.-D. contributed to the data analysis and wrote the manuscript. All the authors contributed to reviewing and revising the manuscript.

Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government.

APPENDIX A: SAMPLE PREPARATION

The samples were prepared by PLD. LSMO/BTO bilayer films were grown on TiO_2 -terminated STO (001) substrates. The layer-by-layer growth was controlled by the reflection high-energy electron diffraction technique. Two different combinations of LSMO/BTO and BTO/LSMO on TiO_2 -terminated STO (L_nB_mS and B_mL_nS , where n and m are the layer numbers of LSMO and BTO, respectively) were grown to understand the effect of the materials' interfaces. LSMO and BTO sublayers were deposited at 780 °C and 100 mTorr oxygen partial pressure

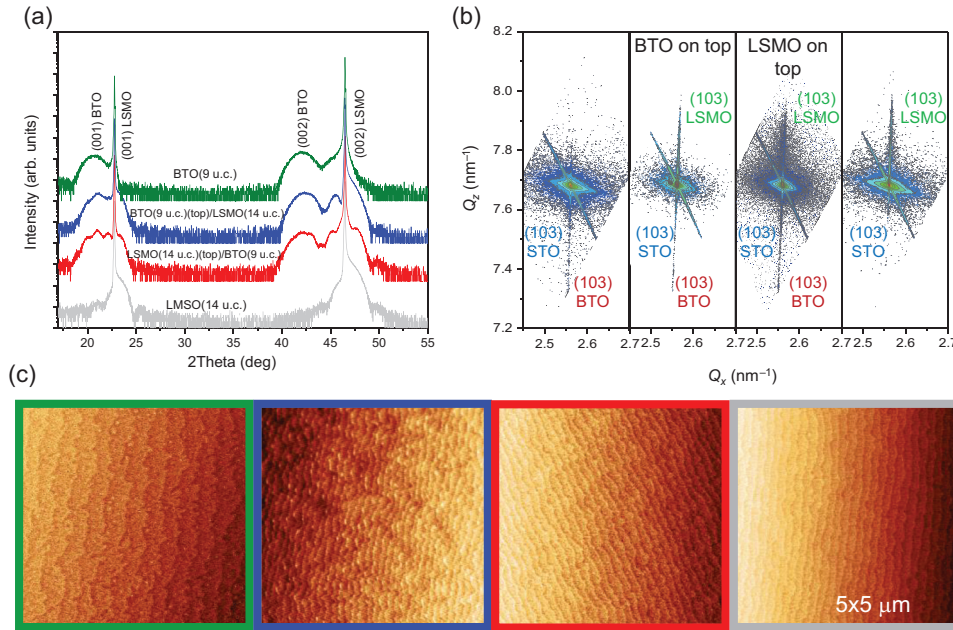


FIG. 6. Structural properties of the different films of this study. (a) The XRD intensity vs 2θ (b) and reciprocal space map show fully epitaxial growth of the samples, which is further supported by HRTEM images and GPA analysis. This clearly shows epitaxial behavior of the films where BTO and LSMO are fully strained by the STO substrate. (c) Atomic force microscopy images show the surface morphology of BTO and LSMO single and bilayer films (border colors are matched with the XRD plots). The atomic force microscopy image clearly shows atomic terrace separated by a step of approximately $4 \pm 1 \text{ \AA}$, which confirms two-dimensional epitaxial growth of the films. The layer-by-layer growth was controlled by reflection high-energy electron diffraction.

and 780 °C and 10 mTorr oxygen partial pressure, respectively, from the chemical stoichiometric ceramic targets by using the KrF excimer laser (248 nm) at a laser fluence of 2 J cm^{-2} . After growth, the films were cooled down to room temperature under an oxygen pressure of 300 Torr.

APPENDIX B: STRUCTURAL ANALYSIS BY XRD AND STEM

Film structures and surface morphologies were investigated by XRD using a high-resolution x-ray diffractometer (Empyrean, PANalytical, Netherlands) using Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) and atomic force microscopy, respectively (Fig. 6).

For structural investigation of the films by STEM, a FEI TitanTM G2 80–200 STEM with a Cs probe corrector and ChemiSTEMTM technology (X-FEGTM and SuperXTM EDS with four windowless silicon drift detectors), operated at 200 kV, was used. HAADF STEM imaging and STEM energy-dispersive x-ray spectroscopy (EDS) were used for structural and chemical analysis, respectively. EDS spectral image data were acquired in the STO [100] zone axis with an electron probe of size $<0.18 \text{ nm}$, convergence angle of 17.1 mrad , and current of approximately 100 pA. HAADF images were recorded under similar optical conditions using an annular detector with a collection range of 60–160 mrad. The atomic-scale STEM EDS maps indicate that the LSMO/BTO interface is quite sharp with possible atomic steps and without any significant diffusion

(see Fig. 7). There is a possibility of $<1.0 \text{ u.c.}$ intermixing (including both geometric and chemical effects), which is acceptable for the investigation [2,13].

APPENDIX C: MAGNETIC MEASUREMENTS

The magnetic measurements were carried out in a Quantum Design MPMS3 SQUID magnetometer. All samples were demagnetized at room temperature by a proper demagnetized protocol before each measurement. The superconducting magnet of the magnetometer was reset to remove any stray field in the magnetometer before each set of measurements. The magnetic field was always applied in-plane to the sample. For the EB measurement, the samples were cooled down from 350 to 2 K without a magnetic bias field and an MH loop was measured at 2 K. This is called the ZFC measurement. Then the sample was warmed up and cooled down from 350 to 2 K with a magnetic bias field (positive and negative) and an MH loop was measured. This is called the FC measurement. The field range of the MH loop was at least $\pm 5 \text{ kOe}$ to ensure the magnetic saturation of the samples. For the positive bias field (+FC), the MH loop measurement starts at $+5 \text{ kOe}$ and for the negative bias field (−FC), the MH loop measurement starts at -5 kOe . A small step size was taken near the origin to measure the EB shift precisely. The region near the origin of MH loop is enlarged to show the magnitude of the EB clearly (Fig. 2). The EB shift (H_E) was given by $(H_{C1} - H_{C2})/2$ while the

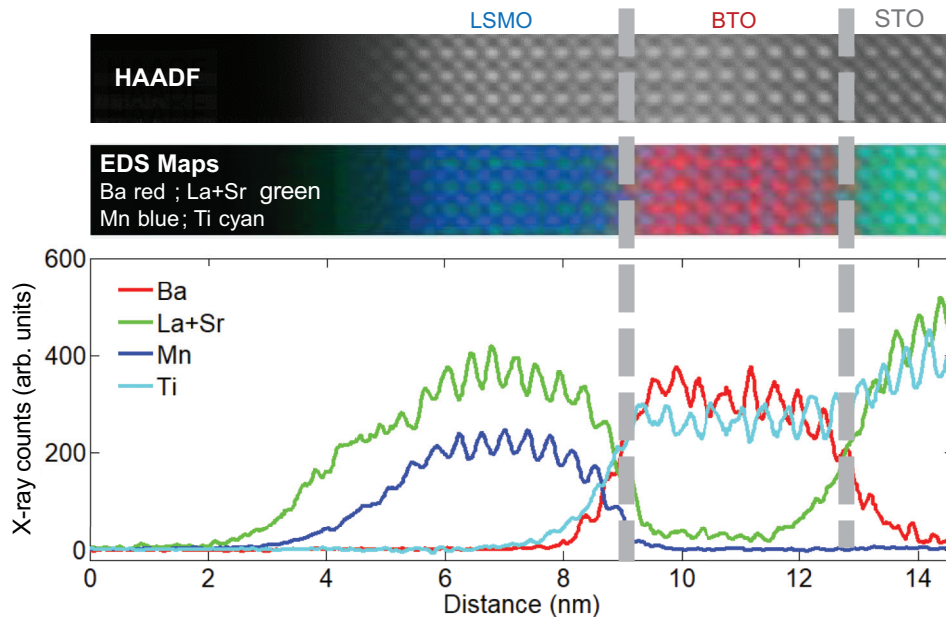


FIG. 7. Structural investigation by STEM. Cross-sectional high-resolution STEM image of LSMO($n = 14 \text{ u.c.}$)/BTO($m = 9 \text{ u.c.}$) on STO substrate grown by PLD. The EDS map shows the clean interface between LSMO and BTO. Since both BTO and LSMO are fully strained, the interfaces are not clearly visible in HAADF STEM image.

coercivity (H_C) was given by $(H_{C1} + H_{C2})/2$, where H_{C1} and H_{C2} were the magnetic fields (signs are included) corresponding to the field points in descending and ascending branches of the MH loop at which the magnetic moment reached zero. The observed EB is in the negative (positive) field direction when cooled with a positive (negative) bias field. Hence the observed EB is negative in type. The MT measurement was also carried out to identify the phase transition, if any (Fig. 9). The EB training effect was done where a number (N) of hysteresis loops were measured at 2 K after field cooling from 350 K with a 5 kOe bias field (Fig. 10). For bias field dependence on EB, the bias field was varied from 100 Oe to 70 kOe and MH loops were measured with a ± 5 kOe field range (Fig. 10).

The element-specific magnetism of the individual layers and its profile at the interfaces were investigated by XMCD at the Diamond Light Scattering, UK, beamline I06, using a 6 T superconducting vector magnet. $L_{14}B_{9}S$ was optimum for macroscopic magnetic measurements owing to a sufficiently large signal, whereas $L_7B_{9}S$ was optimum for XMCD measurements as the film was sufficiently thin ($L = 2.5$ nm or $n = 7$ u.c. and $B = 3.5$ nm or $m = 9$ u.c.) so that the LSMO/BTO interface was amenable to the x-ray beam, since the x-ray could only penetrate a depth of up to approximately 5 nm of the sample. X-ray

absorption spectroscopy (XAS) was conducted at 300 and 2 K. The XAS spectra were recorded by switching between left- and right-circularly polarized light. The XMCD signals were calculated from the difference between spectra taken with left- and right-circularly polarized light, i.e., $\text{XMCD} = (I^+ - I^-)$, where I^+ (I^-) is the parallel (antiparallel) alignment of photon helicity with respect to the applied magnetic field. The atomic magnetic moments were measured using total electron yield mode over the Mn or Ti $L_{2,3}$ edges with the spectra normalized to the incoming photon flux and the element-specific hysteresis loops were measured using fluorescence detection. The magnetic field was applied at an angle of 60° with respect to the sample normal. To confirm the sign reversal of XMCD, the magnetic field was applied in the opposite direction in order to ensure the magnetic origin of the XMCD signal.

APPENDIX D: FERROELECTRIC MEASUREMENTS

1. Piezoresponse force microscopy

The thin-film topography and piezoresponse were measured using a Bruker Multimode 8 atomic force microscope. Piezoresponse force microscopy and spectroscopy measurements were performed with Pt-coated NSC35 tips

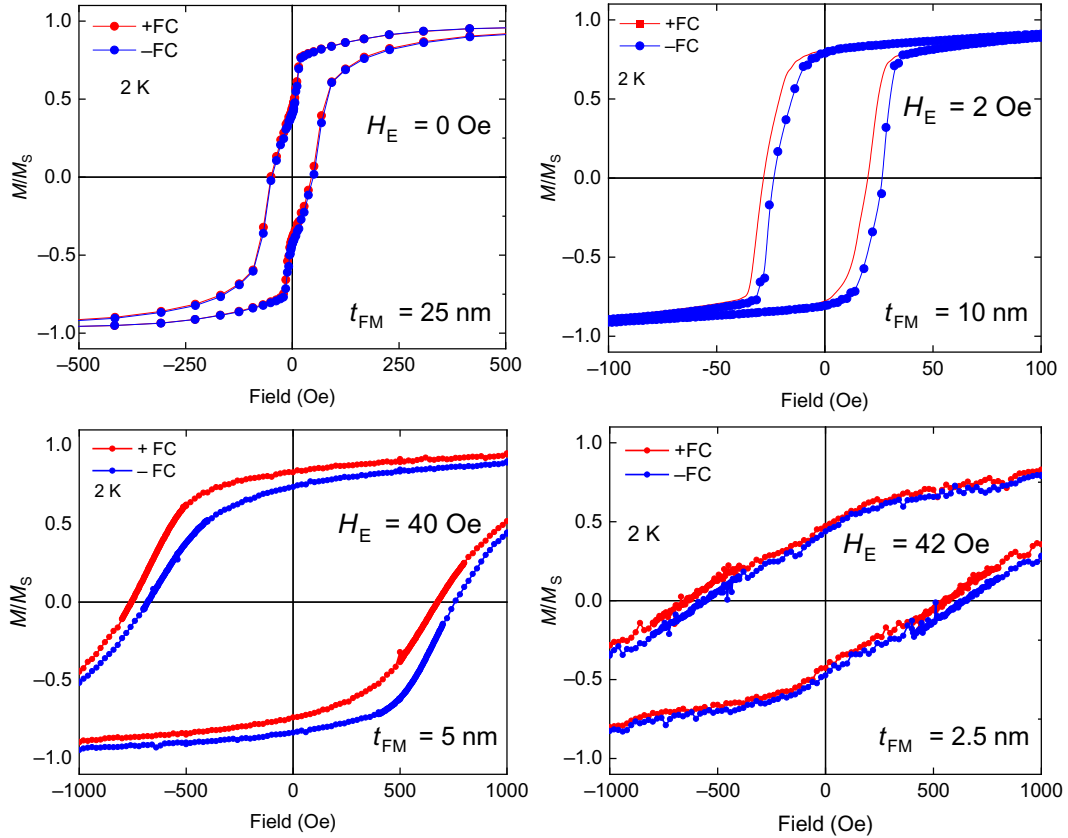


FIG. 8. FM thickness dependence (t_{FM}) of EB in L_nB_mS films. Four samples of LSMO ($t_{\text{FM}} = 17.5, 10, 5$, and 2.5 nm)/BTO/STO were investigated for EB. There is a trend of increasing EB with decreasing t_{FM} where thickness of BTO is kept constant at 3.5 nm.

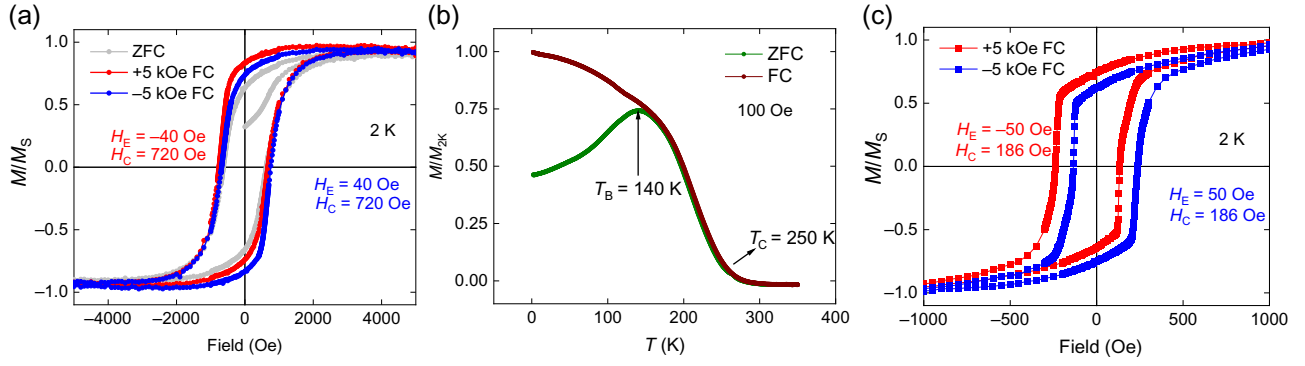


FIG. 9. Magnetic analysis for LSMO/BTO films. (a) ZFC and FC hysteresis loops of LSMO(5 nm)/BTO(3.5 nm)/STO at 2 K after cooling from 350 K under ± 50 kOe bias field, which show saturation of the loop at approximately 3 kOe. (b) The MT curve shows $T_C \sim 250$ K and $T_B \sim 140$ K. (c) Field-cooled hysteresis loops of BTO(3.5 nm)/LSMO(5 nm)/STO at 2 K showing an enhanced EB of 50 Oe.

(MikroMasch) and the PFM contrast was recorded in polar coordinates. We locally applied V_{dc} of ± 4 V to the sample while grounding the PFM tip and then detected the PFM response using a read V_{ac} of 1 V at 15 kHz in the same configuration. $B_m L_n S$ samples are chosen because of the presence of a bottom LSMO electrode.

2. Optical second-harmonic generation

A probe beam was produced using an amplified Ti:sapphire laser system operating at 800 nm with a pulse duration of 45 fs and a repetition rate of 1 kHz. This beam was converted to light with a 1200-nm wavelength via an optical parametric amplifier. The pulse energy was maintained at 15 μ J, with the beam focused to a spot size of 250 μ m in diameter. The SHG signal was detected using a monochromator set to 600 nm and a photomultiplier tube, with the SHG setup arranged in a 45° reflection geometry. The polarization of the incident fundamental wave was rotated to an angle α using a half-wave plate, and the frequency-doubled light was projected at a fixed polarization angle β via a Glan-Thompson prism. The

0° positions of the α and β angles were set along the normal of the setup plane. SHG measurements were conducted at room temperature. To ensure consistent SHG yield across different samples, equivalent alignment was confirmed using a common reference SHG signal, which was optimized to the same value for each sample before being filtered out from the measurements. The measured intensity was calibrated to sample thickness and is thus representative of net polarization.

APPENDIX E: DFT CALCULATIONS

DFT calculations were performed by using the QUANTUM ESPRESSO simulation package [46] based on the projector-augmented-wave method [47]. The Perdew-Burke-Ernzerhof parameterization [48] of the generalized-gradient approximation was used to describe the exchange correlation term. A plane-wave basis set with cutoff energy of 70 Ry and $8 \times 8 \times 1$ Monkhorst-Pack k -point grid were taken initially for relaxing the atomic coordinates until the force on each atom was less than 0.0005 hartree/bohr.

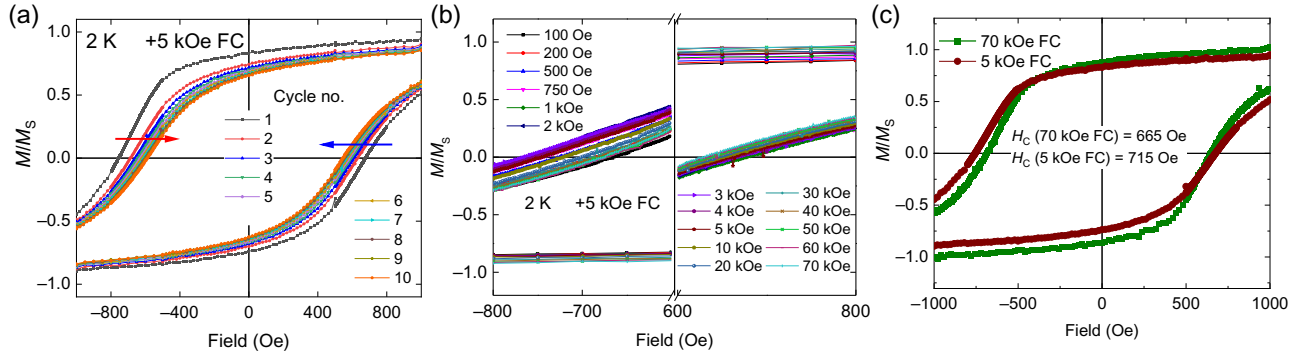


FIG. 10. Training, bias field, and loop tracing field effect. (a) The training effect measurement at 2 K after cooling the sample from 350 K under +50 kOe bias field. (b) The hysteresis loop measurements at 2 K after cooling from 350 K under different bias fields. (c) The hysteresis loops measured by different field ranges of 5 and 70 kOe, which show that H_C decreases at higher field ranges.

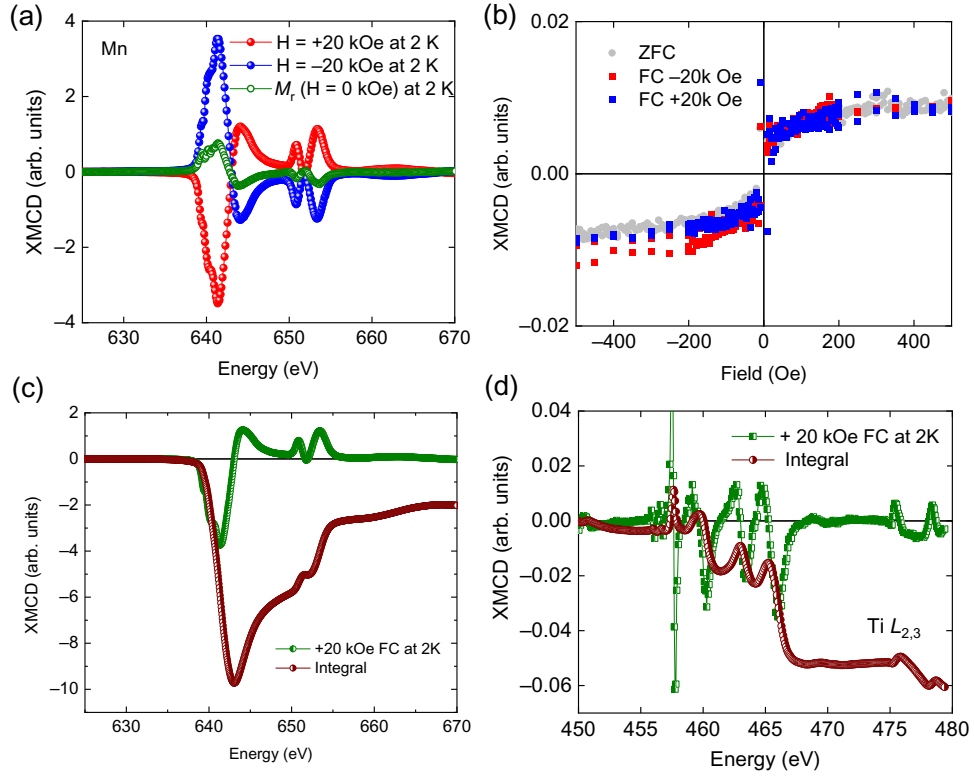


FIG. 11. XMCD measurements of L_7B_9S . (a) The XMCD spectrum of Mn at 2 K after cooling with ± 20 kOe bias field and after removing the field. (b) XMCD hysteresis loop measured for Mn at 2 K. (c), (d) The integrals of XMCD of Mn and Ti show that both the Mn and Ti magnetization are aligned in same direction. Sum rule analysis of the Mn $L_{2,3}$ edges indicates an orbital moment of $\mu_l = 0.037 \pm 0.015 \mu_B$ and a spin moment of $\mu_s = 0.68 \pm 0.03 \mu_B$ where the correction factor from [45] is used to correct the effects of the small Mn spin-orbit coupling on the spin moment. The finite Mn orbital moment arises from the strain imposed on the Mn^{4+} sites by the BTO film.

However, energetics and PDOS calculations were performed with the cutoff energy 125 Ry and a $15 \times 15 \times 1$ k -point grid. Collinear spins were used for the different

magnetic configurations. Strain was calculated from the experimental lattice constants of BTO, LSMO, and STO. Additionally, L_7B_9S was optimum for DFT calculations as

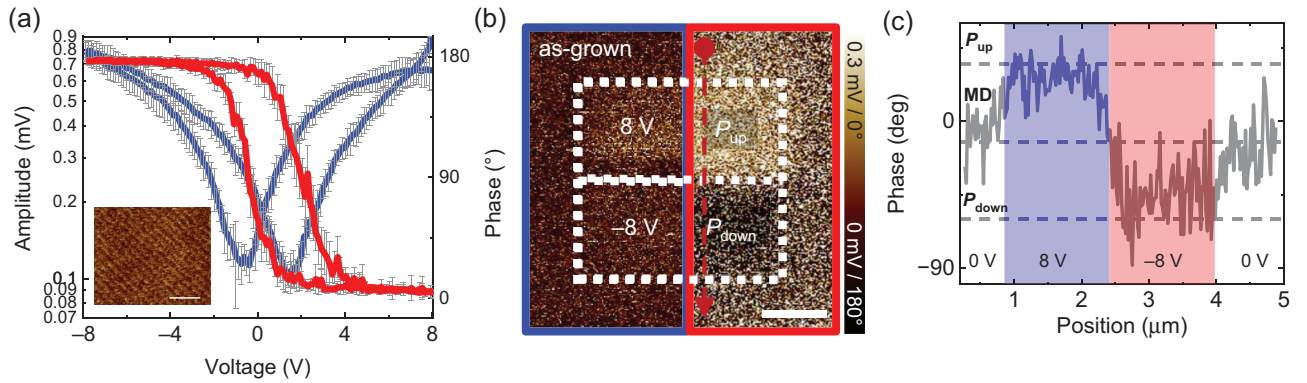


FIG. 12. Piezoresponse force microscopy for BTO/LSMO/STO film at room temperature. (a) Piezoresponse measured by PFM on BTO(25 u.c.)/LSMO(14 u.c.)/STO. Amplitude (blue) and phase (red) of the PFM signal as a function of bias voltage measured with 1 V read-out voltage. The inset atomic force microscopy image shows the surface morphology of the film. (b) Amplitude (left half) and phase (right half) contrasts for as-grown ($5 \times 5 \mu m^2$), after writing +8 V ($3 \times 1.5 \mu m^2$), and -8 V ($3 \times 1.5 \mu m^2$) at room temperature. Multidomain structure is observed in the as-grown film. Scale bar is 1 μm . (c) Line profiles extracted along 30 pixels [as marked with red in (b)] of the phase image. 25 u.c. BTO on LSMO has three contrast levels: multidomain (MD) (as-grown), P_{up} (poled at +8 V), P_{down} (poled at -8 V).

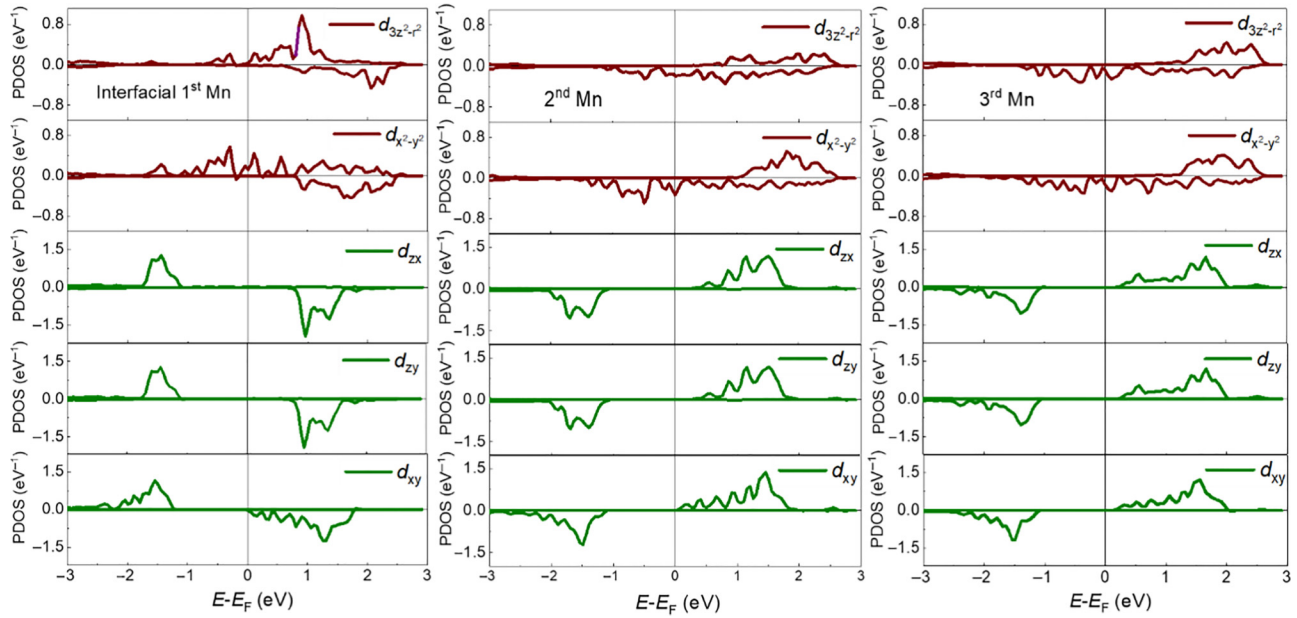


FIG. 13. PDOS calculations from DFT. The occupation of e_g and t_{2g} states are depicted for different Mn (first, second, and third layers of LSMO) atoms from the interface.

there were fewer atoms to simulate and hence required less computer-intensive calculations. The thickness of BTO and LSMO in the heterostructure corresponded to the experimentally grown sample (L_7B_9S) in which a large EB was observed. Therefore, the BTO/LSMO heterostructure consisted of $m = 8$ u.c. (approximately 3.2 nm) of BTO and $n = 7$ u.c. (approximately 2.5 nm) of LSMO. The common IP lattice constant of the heterostructure was taken to be the same as that of the STO, which simulated the compressive strain in BTO and a small tensile strain in LSMO, as they were grown onto a paraelectric STO substrate.

- [1] S. Valencia, A. Crassous, L. Bocher, V. Garcia, X. Moya, R. O. Cherifi, C. Deranlot, K. Bouzehouane, S. Fusil, A. Zobelli, A. Gloter, N. D. Mathur, A. Gaupp, R. Abrudan, F. Radu, A. Barthélémy, and M. Bibes, Interface-induced room-temperature multiferroicity in BaTiO_3 , *Nat. Mater.* **10** (10), 753 (2011).
- [2] Hangwen Guo, Zhen Wang, Shuai Dong, Saurabh Ghosh, Mohammad Saghayezhian, Lina Chen, Yakui Weng, Andreas Herklotz, Thomas Z. Ward, Rongying Jin, Sokrates T. Pantelides, Yimei Zhu, Jiandi Zhang, and E. W. Plummer, Interface-induced multiferroism by design in complex oxide superlattices, *Proc. Natl. Acad. Sci. U. S. A.* **114** (26), E5062 (2017).
- [3] Binbin Chen, Nicolas Gauquelin, Nives Strkalj, Sizhao Huang, Ufuk Halisdemir, Minh Duc Nguyen, Daen Jannis, Martin F. Sarott, Felix Eltes, Stefan Abel, Matjaž Spreitzer, Manfred Fiebig, Morgan Trassin, Jean Fompeyrine, Johan Verbeeck, Mark Huijben, Guus Rijnders & Gertjan Koster, Signatures of enhanced out-of-plane polarization in

asymmetric BaTiO_3 superlattices integrated on silicon, *Nat. Commun.* **13** (1), 1 (2022).

- [4] Hanghui Chen, Qiao Qiao, Matthew S. J. Marshall, Alexandru B. Georgescu, Ahmet Gulec, Patrick J. Phillips, Robert F. Klie, Frederick J. Walker, Charles H. Ahn, and Sohrab Ismail-Beigi, Reversible modulation of orbital occupations via an interface-induced polar state in metallic manganites, *Nano Lett.* **14** (9), 4965 (2014).
- [5] Bin Cui, Cheng Song, Haijun Mao, Huaqiang Wu, Fan Li, Jingjing Peng, Guangyue Wang, Fei Zeng, and Feng Pan, Magnetoelectric coupling induced by interfacial orbital reconstruction, *Adv. Mater.* **27** (42), 6651 (2015).
- [6] P. Yu, J.-S. Lee, S. Okamoto, M. D. Russell, M. Huijben, C.-H. Yang, Q. He, J. X. Zhang, S. Y. Yang, M. J. Lee, Q. M. Ramasse, R. Erni, Y.-H. Chu, D. A. Arena, C.-C. Kao, L. W. Martin, and R. Ramesh, Interface ferromagnetism and orbital reconstruction in $\text{BiFeO}_3 - \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures, *Phys. Rev. Lett.* **105** (2), 027201 (2010).
- [7] C. A. F. Vaz, J. Hoffman, Y. Segal, M. S. J. Marshall, J. W. Reiner, Z. Zhang, R. D. Grober, F. J. Walker, and C. H. Ahn, Control of magnetism in $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3/\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ multiferroic heterostructures, *J. Appl. Phys.* **109**(7), 07D905 (2011).
- [8] Han Wang, Xiao Chi, ZhongRan Liu, HengYau Yoong, LingLing Tao, JuanXiu Xiao, Rui Guo, JingXian Wang, ZhiLi Dong, Ping Yang, Cheng-Jun Sun, ChangJian Li, XiaoBing Yan, John Wang, Gan Moog Chow, Evgeny Y. Tsymbal, He Tian, and Jingsheng Chen, Atomic-scale control of magnetism at the titanite-manganite interfaces, *Nano Lett.* **19** (5), 3057 (2019).
- [9] J. D. Burton and E. Y. Tsymbal, Prediction of electrically induced magnetic reconstruction at the manganite/ferroelectric interface, *Phys. Rev. B* **80** (17), 174406 (2009).

- [10] F. Fang, H. Zhai, X. Ma, Y. W. Yin, Qi Li, and G. Lüpke, Interface magnetization transition via minority spin injection, *Appl. Phys. Lett.* **109** (23), 232903 (2016).
- [11] C. Menéndez, D. Chu, and C. Cazorla, Oxygen-vacancy induced magnetic phase transitions in multiferroic thin films, *npj Comput. Mater.* **6** (1), 76 (2020).
- [12] J. M. Hu, C. G. Duan, C. W. Nan, and L. Q. Chen, Understanding and designing magnetoelectric heterostructures guided by computation: progresses, remaining questions, and perspectives, *npj Comput. Mater.* **3** (1), 18 (2017).
- [13] S. M. Wu, Shane A. Cybart, P. Yu, M. D. Rossell, J. X. Zhang, R. Ramesh, and R. C. Dynes, Reversible electric control of exchange bias in a multiferroic field-effect device, *Nat. Mater.* **9** (9), 756 (2010).
- [14] M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez, and J. M. Triscone, Exchange bias in LaNiO_3 – LaMnO_3 superlattices, *Nat. Mater.* **11** (3), 195 (2012).
- [15] Sanaz Koohfar, Alexandru B. Georgescu, Aubrey N. Penn, James M. LeBeau, Elke Arenholz, and Divine P. Kumah, Confinement of magnetism in atomically thin $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures, *npj Quantum Mater.* **4** (1), 25 (2019).
- [16] Aiping Chen, Qiang Wang, Michael R. Fitzsimmons, Erik Enriquez, Marcus Weigand, Zach Harrell, Brian McFarland, Xujie Lü, Paul Dowden, Judith L. MacManus-Driscoll, Dmitry Yarotski, and Quanxi Jia, Hidden interface driven exchange coupling in oxide heterostructures, *Adv. Mater.* **29** (26), 1700672 (2017).
- [17] B. Cui, C. Song, G. Y. Wang, H. J. Mao, F. Zeng, and F. Pan, Strain engineering induced interfacial self-assembly and intrinsic exchange bias in a manganite perovskite film, *Sci. Rep.* **3** (1), 2542 (2013).
- [18] S. S. P. Parkin, K. P. Roche, M. G. Samant, P. M. Rice, R. B. Beyers, R. E. Scheuerlein, E. J. O’Sullivan, S. L. Brown, J. Bucchigano, D. W. Abraham, Yu Lu, M. Rooks, P. L. Trouilloud, R. A. Wanner, and W. J. Gallagher, Exchange-biased magnetic tunnel junctions and application to non-volatile magnetic random access memory, *J. Appl. Phys.* **85** (8), 5828 (1999).
- [19] Rui Wu, *et al.*, Self-biased magnetoelectric switching at room temperature in three-phase ferroelectric–antiferromagnetic–ferrimagnetic nanocomposites, *Nat. Electron.* **4** (5), 333 (2021).
- [20] S. Yan, D. J. Choi, J. A. Burgess, S. Rolf-Pissarczyk, and S. Loth, Control of quantum magnets by atomic exchange bias, *Nat. Nanotechnol.* **10** (1), 40 (2015).
- [21] Amitesh Paul, Christoph Reitinger, Carmine Autieri, Biplab Sanyal, Wolfgang Kreuzpaintner, Jaru Jutimoosik, Rattikorn Yimnirun, Francis Bern, Pablo Esquinazi, Panagiotis Korelis, Peter Böni, Exotic exchange bias at epitaxial ferroelectric-ferromagnetic interfaces, *Appl. Phys. Lett.* **105** (2), 022409 (2014).
- [22] Simon Hausmann, Jingfan Ye, Toshihiro Aoki, Jian-Guo Zheng, Jochen Stahn, Francis Bern, Binda Chen, Carmine Autieri, Biplab Sanyal, Pablo D. Esquinazi, Peter Böni, and Amitesh Paul, Atomic-scale engineering of ferroelectric-ferromagnetic interfaces of epitaxial perovskite films for functional properties, *Sci. Rep.* **7** (1), 10734 (2017).
- [23] Xiaoqian Yu, Lijun Wu, Bangmin Zhang, Hua Zhou, Yongqi Dong, Xiaohan Wu, Ronghui Kou, Ping Yang, Jingsheng Chen, Cheng-Jun Sun, Yimei Zhu, and Gan Moog Chow, Thickness-dependent polarization-induced intrinsic magnetoelectric effects in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ heterostructures, *Phys. Rev. B* **100** (10), 104405 (2019).
- [24] N. Strkalj, G. De Luca, M. Campanini, S. Pal, J. Schaab, C. Gattinoni, N. A. Spaldin, M. D. Rossell, M. Fiebig, and M. Trassin, Depolarizing-field effects in epitaxial capacitor heterostructures, *Phys. Rev. Lett.* **123** (14), 147601 (2019).
- [25] J. Nogués and I. K. Schuller, Exchange bias, *J. Magn. Magn. Mater.* **192** (2), 203 (1999).
- [26] M. Huijben, P. Yu, L. W. Martin, H. J. A. Molegraaf, Y-H Chu, M. B. Holcomb, N. Balke, G. Rijnders, and R. Ramesh, Ultrathin limit of exchange bias coupling at oxide multiferroic/ferromagnetic interfaces, *Adv. Mater.* **25** (34), 4739 (2013).
- [27] Rui Guo, Lei Shen, Han Wang, Zhishiuh Lim, Wenlai Lu, Ping Yang, Ariando, Alexei Gruverman, Thirumalai Venkatesan, Yuan Ping Feng, and Jingsheng Chen, Tailoring self-polarization of BaTiO_3 thin films by interface engineering and flexoelectric effect, *Adv. Mater. Interfaces* **3** (23), 1600737 (2016).
- [28] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Enhancement of ferroelectricity in strained BaTiO_3 thin films, *Science* **306** (5698), 1005 (2004).
- [29] Jinyan Zhao, Gang Niu, Wei Ren, Lingyan Wang, Guohua Dong, Nan Zhang, Ming Liu, and Zuo-Guang Ye, Self-polarization in epitaxial fully matched lead-free bismuth sodium titanate based ferroelectric thin films, *ACS Appl. Mater. Interfaces* **10** (28), 23945 (2018).
- [30] J. Junquera and P. Ghosez, Critical thickness for ferroelectricity in perovskite ultrathin films, *Nature* **422** (6931), 506 (2003).
- [31] P. Yu, W. Luo, D. Yi, J. X. Zhang, M. D. Rossell, C.-H. Yang, L. You, G. Singh-Bhalla, S. Y. Yang, Q. He, Q. M. Ramasse, R. Erni, L. W. Martin, Y. H. Chu, S. T. Pantelides, S. J. Pennycook, and R. Ramesh, Interface control of bulk ferroelectric polarization, *Proc. Natl. Acad. Sci. U. S. A.* **109** (25), 9710 (2012).
- [32] D. Schumacher, A. Steffen, J. Voigt, J. Schubert, Th. Brückel, H. Ambaye, and V. Lauter, Inducing exchange bias in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3-\delta}/\text{SrTiO}_3$ thin films by strain and oxygen deficiency, *Phys. Rev. B* **88** (14), 144427 (2013).
- [33] P. Yu, J.-S. Lee, S. Okamoto, M. D. Rossell, M. Huijben, C.-H. Yang, Q. He, J. X. Zhang, S. Y. Yang, M. J. Lee, Q. M. Ramasse, R. Erni, Y.-H. Chu, D. A. Arena, C.-C. Kao, L. W. Martin, and R. Ramesh, Interface ferromagnetism and orbital reconstruction in BiFeO_3 – $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures, *Phys. Rev. Lett.* **105** (2), 027201 (2010).
- [34] C. Leighton, J. Nogués, B. J. Jönsson-Åkerman, and I. K. Schuller, Coercivity enhancement in exchange biased systems driven by interfacial magnetic frustration, *Phys. Rev. Lett.* **84** (15), 3466 (2000).
- [35] M. D. Stiles and R. D. McMichael, Coercivity in exchange-bias bilayers, *Phys. Rev. B* **63** (6), 064405 (2001).

- [36] Ana Rakita, Nenad Nikolić, Michael Mildner, Johannes Matiassek, and Adelheid Elbe-Bürger, Effects of oxygen modification on the structural and magnetic properties of highly epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) thin films, *Sci. Rep.* **10** (1), 1 (2020).
- [37] C. Binek, Training of the exchange-bias effect: A simple analytic approach, *Phys. Rev. B* **70** (1), 014421 (2004).
- [38] L. Del Bianco, D. Fiorani, A. M. Testa, E. Bonetti, and L. Signorini, Field-cooling dependence of exchange bias in a granular system of Fe nanoparticles embedded in an Fe oxide matrix, *Phys. Rev. B* **70** (5), 052401 (2004).
- [39] T. Maity and S. Roy, Asymmetric shift of exchange bias loop in Ni-Ni(OH)_2 core-shell nanoparticles, *J. Magn. Mater.* **465**, 100 (2018).
- [40] T. Maity, S. Goswami, D. Bhattacharya, and S. Roy, Origin of the asymmetric exchange bias in $\text{BiFeO}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ nanocomposite, *Phys. Rev. B* **89** (14), 140411 (2014).
- [41] Di Yi, Jian Liu, Shang-Lin Hsu, Lipeng Zhang, Yongseong Choi, Jong-Woo Kim, Zuhuang Chen, James D. Clarkson, Claudy R. Serrao, Elke Arenholz, Philip J. Ryan, Haixuan Xu, Robert J. Birgeneau, and Ramamoorthy Ramesh, Atomic-scale control of magnetic anisotropy via novel spin-orbit coupling effect in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{SrIrO}_3$ superlattices, *Proc. Natl. Acad. Sci. U. S. A.* **113** (23), 6397 (2016).
- [42] Yaohua Liu, J. Tornos, S. Velthuis, J. Freeland, Hua Zhou, P. Steadman, P. Bencok, C. León, and J. Santamaria, Induced Ti magnetization at $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and BaTiO_3 interfaces, *APL Mater.* **4** (4), 046105 (2016).
- [43] M. Huijben, L. W. Martin, Y.-H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, and R. Ramesh, Critical thickness and orbital ordering in ultrathin $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films, *Phys. Rev. B* **78** (9), 094413 (2008).
- [44] J. B. Goodenough, Theory of the role of covalence in the perovskite-type manganites $[\text{La}, \text{M(II)}]\text{MnO}_3$, *Phys. Rev.* **100** (2), 564 (1955).
- [45] Cinthia Piamonteze, Piter Miedema, and Frank M. F. de Groot, Accuracy of the spin sum rule in XMCD for the transition-metal L edges from manganese to copper, *Phys. Rev. B* **80** (18), 184410 (2009).
- [46] P. Giannozzi, *et al.*, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* **29** (46), 465901 (2017).
- [47] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59** (3), 1758 (1999).
- [48] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77** (18), 3865 (1996).