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Atomic-scale Control of Magnetism at the Titanite-Manganite Interfaces

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KEYWORDS:

ferroelectric field effect, orbital anisotropy, charge transfer, orbital hybridization, interfacial magnetic coupling, artificial multiferroic interface

1 **ABSTRACT:**

2 Complex oxide thin-film heterostructures often exhibit magnetic properties different from
3 those known for bulk constituents. This is due to the altered local structural and electronic
4 environment at the interfaces, which affects the exchange coupling and magnetic ordering.
5 The emergent magnetism at oxide interfaces can be controlled by ferroelectric polarization
6 and has a strong effect on spin-dependent transport properties of oxide heterostructures,
7 including magnetic and ferroelectric tunnel junctions. Here, using prototype
8 $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{BaTiO}_3$ heterostructures, we demonstrate that ferroelectric polarization of
9 BaTiO_3 controls the orbital hybridization and magnetism at heterointerfaces. We observe
10 changes in the enhanced orbital occupancy and significant charge redistribution across the
11 heterointerfaces, affecting the spin and orbital magnetic moments of the interfacial Mn and
12 Ti atoms. Importantly, we find that the exchange coupling between Mn and Ti atoms across
13 the interface is tuned by ferroelectric polarization from ferromagnetic to antiferromagnetic.
14 Our findings provide a viable route to electrically control complex magnetic configurations
15 at artificial multiferroic interfaces, taking a step towards low-power spintronics.

16 **INTRODUCTION:**

17 Multiferroics, compounds with two or more ferroic orders, have potential applications in
18 electric-field-controlled spintronic devices with ultralow energy consumption.¹⁻³ Owing to
19 the scarcity of single-phase materials with strong magnetoelectric coupling, investigation
20 of artificial multiferroic heterostructures, consisting of ferromagnetic (FM) and
21 ferroelectric (FE) layers, has received much attention.⁴⁻⁹ Extensive studies have focused on
22 the influence of FE polarization on magnetism via strain coupling,¹⁰⁻¹² interfacial-oxidized

1 state,⁹ exchange coupling,¹³ interfacial orbital reconstructions,¹⁴ interfacial bond
2 reconfiguration,⁸ carrier density modulation (charge transfer)^{6, 12, 15} or a combination of
3 these at heterointerfaces. For example, (i) Cui *et al.* have demonstrated a ferroelectric-
4 polarization control of interfacial orbital reconstruction and its effect on transport of
5 contacted films.¹⁴ (ii) Molegraaf *et al.* have proposed charge-density-driven magnetic
6 ground states.¹⁵ (iii) Bingham *et al.* have attributed the enhanced magnetocaloric effect to
7 the strain effect from ferroelectric capping layer.¹² (iv) Herklotz *et al.* have presented a
8 reversible control of interfacial magnetism through ionic-liquid-assisted polarization
9 switching.¹⁶ Still, however, there is limited understanding of the FE field effect on orbital
10 hybridizations affecting the interfacial magnetism and the exchange coupling, despite the
11 observation of interfacial magnetism in FM/FE systems.^{12, 17} Moreover, the control of
12 magnetic coupling and electronic structure at multiferroic interfaces deserves particular
13 attention, since they may directly influence spin-dependent transport properties¹⁸ and the
14 performance of practical oxide devices.⁶ The insight to the competition between charge
15 transfer due to valence imbalance and carrier-density modulation caused by the
16 ferroelectric field as well as the control of the interfacial magnetic coupling, therefore, is
17 warranted in realizing potential applications of multiferroic heterostructures.

18 Furthermore, the extensive studies of the magnetoelectric coupling in high-quality
19 thick piezoelectric or FE layers (even substrates) have shown that high electrical voltage is
20 essential for the magnetoelectric effect,^{10, 15} thus introducing other undesirable effects, such
21 as strain effect via electrostriction,¹⁰ oxygen vacancy migration¹⁹ and carrier modulation.²⁰
22 The multi-domain state in a thick FE layer also complicates the effect of FE polarization
23 on interfacial magnetism.²¹ To obtain the FE field effect, a series of samples with opposite

1 spontaneous FE polarization states but with the same strain state are needed. To avoid this
2 complexity we have fabricated the prototypical heterostructures of ferromagnetic
3 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and ferroelectric BaTiO_3 (BTO), carrying different polarizations
4 via interface engineering,^{22, 23} instead of using an applied electric field. To separate the
5 possible effect of the interface chemistry, another series of heterostructures, exhibiting no
6 FE polarization but having the same interface atomic-plane stacking sequence with that of
7 BTO thicker films, were fabricated and explored.

8 In this work, we demonstrate the ferroelectric field-dependent orbital hybridization
9 affecting magnetism and exchange coupling at LSMO/BTO heterointerfaces by means of
10 X-ray magnetic circular dichroism (XMCD). The changes of induced spin and orbital
11 magnetic moments at Ti and Mn atoms are associated with charge redistribution across the
12 heterointerfaces. Combining the atomic-resolution energy dispersive X-ray (EDX)
13 elemental maps and electron energy loss spectroscopy (EELS) data with aberration-
14 corrected scanning transmission electron microscopy (STEM) results, the charge
15 redistribution and the valence states at the LSMO/BTO interfaces are systematically
16 analyzed. The modulation of the interfacial exchange interaction from ferromagnetic to
17 antiferromagnetic coupling originates from the change of orbital occupancy, as shown by
18 X-ray linear dichroism (XLD) and theoretical calculations. These discoveries open the way
19 for the electrical modulation of interfacial properties, especially on spin-dependent
20 phenomena, at the atomic level.

21 RESULTS:

Control of ferroelectric polarization via interface engineering. We have in situ grown high-quality LSMO/BTO heterostructures on (001) SrTiO₃ (STO) substrates by pulsed laser deposition. For BTO, a thickness of 45-unit cells (u.c.) is chosen to keep sufficiently good FE properties with a single domain and fully strained state. For LSMO, a thickness of 5-u.c. is selected to ensure the collection of signal of interfacial layer using the total electron yield (TEY) measurements.^{24, 25} **Figure 1A** and 1B show the morphology of LSMO/BTO heterostructure terminated by TiO₂ and SrO. Clear atomic terrace separated by $\sim 0.40 \pm 0.05$ nm high step reveals a two-dimensional growth of films, which is further supported by in situ RHEED of various oxide materials (Figure S1). We obtained the SrO-terminated surface through depositing 1 u.c.-SrRuO₃ (SRO) layer on TiO₂-terminated STO substrates at high temperature and low oxygen pressure (Figure S1), benefiting from that highly volatile RuO₂-layer will be desorbed before the deposition of BTO film.²³ Out-of-plane piezoresponse force microscopy (PFM) images of BTO written by an electrical bias of $\sim \pm 6$ V at room temperature are shown in Figure 1C and 1D. Clear phase contrast of $\sim 180^\circ$ shows high quality and switchability of ferroelectric polarization in BTO films, which is further supported by the butterfly-like amplitude and hysteresis phase loop (Figure S2A, 2B). More importantly, we deduce that the ferroelectric polarization of BTO terminated by SrO, which is switched by positive electrical bias through Coulomb interaction between conductive tip and bound charges, is upward (**P_{up}**), whereas the ferroelectric polarization of BTO terminated by TiO₂ which is switched by negative electrical bias is downward (**P_{dn}**) as shown in Figure S3. Thus we could conclude that the preferential ferroelectric polarization in the as-grown BTO terminated by TiO₂ (SrO) has **P_{dn}** (**P_{up}**) state.^{22, 26} We also confirm that the 5-u.c. LSMO does not influence the original

orientation of ferroelectric polarization in BTO, as shown in Figure S2 (B-E). Concerning the effect of temperature on ferroelectricity of fully strained films, the remnant polarization (without electrical bias)²⁷ has an increasing trend with decreasing temperature, revealing no structural phase transition. On the other hand, theoretical calculations suggest that ultrathin BTO films keep the *c*-axis tetragonal structure, and FE polarization does not rotate at low temperature due to a compressive strain of -2.0 % imposed by epitaxy with STO substrate.²⁸ Hence, it's reasonable that BTO films retain single FE domain ($P_z > P_x = P_y = 0$) from room temperature to 80 K. Reciprocal space mappings (RSMs) shown in Figure 1E and Figure S4 suggest that both BTO films are coherently grown on TiO₂ and SrO terminated STO substrates. The as-grown films have a tetragonal structure under the compressive strain of -2.22 % (Table S1) and possess the almost same strained state (Lattice parameters: $a=b=3.905 \text{ \AA}$, $c=4.348 \text{ \AA}$, and tetragonality=1.11), as indicated by the same **L** values. In comparison with lattice parameters of BTO and STO, LSMO layers on top of them are under tensile strain (0.6 %), as shown in Figure S4C. Considering almost same strained BTO, we deduce that LSMO layers also have the same stress state except for the interfacial unit cell, being sensitive to FE field.

Figure 1. Ferroelectricity and structural characterization of LSMO/BTO heterostructures.

(A) and (B) The surface morphology of heterostructures on TiO_2 - and SrO -terminated STO substrates, respectively. The insets show the schematic illustrations of preferential ferroelectric polarization. The scale bar is $0.5 \mu\text{m}$. (C) and (D) Typical out-of-plane PFM phase images of 45-u.c. BTO with downward polarization ($\mathbf{P}_{\text{dn}}$) and upward polarization ($\mathbf{P}_{\text{up}}$), respectively. The square domains are written using a conductive AFM tip with $\pm 6\text{V}$ bias. The scale bar is $1 \mu\text{m}$. (E) In-plane asymmetric RSMs around the (013) and (-103) Bragg reflections of the heterostructures. (F) Typical atomic-resolution HAADF-STEM image of the heterostructure terminated by SrO along the [001] zone axis, together with a schematic illustration of termination transformation from TiO_2 to SrO by pre-depositing

one unit cell SrRuO₃ (SRO) on STO. The scale bar is 2 nm. The inset in the green rectangle shows the superposition of the magnified STEM image of the overlying area and Ti displacement vector maps (yellow arrow). The yellow scale bar is 40 pm. (G) and (H) A magnified image and false-color overlaid EDX elemental maps from an area marked with a cyan rectangle in (F), respectively. The scale bar is 1 nm.

Figure 1F and Figure S5 show typical cross-section scanning transmission electron microscopy (STEM) images of LSMO/BTO heterostructure on SrO terminated STO substrate, directly revealing the quality of film and ferroelectric displacement of Ti ions (D_{Ti}). The FE polarization can be roughly evaluated using the empirical linear relation ($P_s = \kappa * D_{Ti}$), where P_s represents the spontaneous polarization, and κ is a constant of 2.0 $\mu\text{C}/\text{cm}^2/\text{pm}$ used in the estimation of P_s for BTO, PTO, and BFO systems.²⁹ The FE polarization of BTO film is calculated to be about 50 $\mu\text{C}/\text{cm}^2$, close to the reported values of BTO film.³⁰ The clear contrast from the high angle annular dark field STEM (HAADF-STEM) images in Figure 1G shows the pre-deposited 1-u.c. SRO with Ru vacancies, further confirmed by EDX map in Figure 1H. Note that, Sr is brighter than Ru, unlike the perfect SRO crystal (Figure S13), which is associated with reducing scattering due to Ru vacancies. The same batch of LSMO/BTO heterostructures with TiO₂ termination are grown at the same conditions with that of the SrO terminated heterostructure, revealing the same strain state through synchrotron XRD (Figure S4) and STEM images (Figure S6). We, therefore, are able to manipulate the ferroelectric polarization of BTO under the same strained state only by engineering the interface chemical environment, without an external electric field.

1

2 **Figure 2.** Normalized X-ray absorption spectroscopy and X-ray magnetic circular
3 dichroism of the LSMO/BTO heterostructures at 80 K. (A) Schematic illustrations of the
4 LSMO/BTO heterointerfaces and arrangement of magnetic moment dependent on
5 ferroelectric polarization. (B) Principle of XLD and XMCD techniques, where GI and NI
6 represent grazing incidence (polarization $E//c$) and normal incidence X-ray (polarization

1 $E//ab$), respectively. (C) and (D) Mn- and Ti- $L_{2,3}$ edges XAS under ± 1 T in-plane
2 magnetic field and their XMCD of LSMO/BTO with a downward polarization. (E) and (F)
3 Mn- and Ti- $L_{2,3}$ edges XAS under ± 1 T in-plane magnetic field and their XMCD of
4 LSMO/BTO with an upward polarization. The arrows in the inset show the direction of the
5 total magnetic moment at Ti and Mn.

6 **Effect of polarization on the orbital hybridization and induced magnetism at**
7 **heterointerface.** X-ray absorption spectroscopy (XAS) and XMCD techniques are used to
8 probe the element-resolved magnetic moments in the heterostructures, taking advantage of
9 the elemental specificity and shallow probing depth of XAS in the total electron yield
10 (TEY) mode (details in methods and supporting information). **Figure 2** displays
11 normalized XAS and XMCD of Mn- and Ti- $L_{2,3}$ edges in LSMO/BTO heterostructures
12 with $\mathbf{P}_{\text{dn}}$ and $\mathbf{P}_{\text{up}}$ states (Figure 2A). The Mn XMCD signals in both samples with $\mathbf{P}_{\text{dn}}$
13 (Figure 2C) and $\mathbf{P}_{\text{up}}$ (Figure 2E) polarization are similar to the typical XMCD spectrum,
14 revealing robust Mn magnetism. In the BTO layer, the visible Ti XMCD signals (Figures
15 2D and 2F) indicate the presence of Ti magnetism at the heterointerfaces. Comparing the
16 XMCD spectra of the samples with $\mathbf{P}_{\text{up}}$ and $\mathbf{P}_{\text{dn}}$ polarizations, the former seems to show a
17 stronger signal. To gain a better insight into the influence of FE polarization on magnetism,
18 we qualitatively compare the integrals of the XMCD signals (Figure S7). The result shows
19 that the XMCD integrals for Mn is smaller for the $\mathbf{P}_{\text{dn}}$ state than that under $\mathbf{P}_{\text{up}}$ state. More
20 importantly, the XMCD integrals for Ti in the heterostructures with different FE
21 polarizations display the opposite sign, whereas that for Mn in both samples display the
22 same sign, which reveals the change of the exchange coupling between Mn and Ti. Though
23 effective magnetic moments, using the spin and orbital sum rules³¹ (details in supporting

information), are greatly underestimated due to the strong L_2 and L_3 edges overlap for Ti and Mn, we only focus on the relative magnitude and sign of the spin (s_z) and orbital (l_z) moments (Table S2). We find that magnetic moments of Mn and Ti have both spin and orbital contributions under $\mathbf{P}_{\text{up}}$ state resulting from strong orbital hybridization, contrary to the common belief that $3d$ transition metals should have a suppressed orbital moment owing to the quenched orbital angular momentum.

The macroscopic magnetic properties of multiferroic heterostructures (see Figures S8-S10) confirm the smaller magnetization under $\mathbf{P}_{\text{dn}}$ state than that under $\mathbf{P}_{\text{up}}$ state. As for the effect of FE polarization on the magnetic moment of Mn, there are two contributions affecting it. One is the valence change ($\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$) caused by the FE field through electrostatic doping.¹⁵ Electrostatic doping results in hole accumulation under $\mathbf{P}_{\text{dn}}$ state (more Mn^{4+}) and hole depletion under $\mathbf{P}_{\text{up}}$ state (more Mn^{3+}) due to the screening of FE polarization. The other one is the FE field effect on the exchange coupling which changes from FM ($\mathbf{P}_{\text{up}}$, large e_g population) to AFM ($\mathbf{P}_{\text{dn}}$, small e_g population) through the change of the e_g population.^{25, 32, 33} Surprisingly, a visible exchange bias is observed under $\mathbf{P}_{\text{dn}}$ state, which experimentally supports the existence of an AFM layer at the manganite/ferroelectric interface. The Ti magnetic moment is determined by the amount of transferred charge because of the interfacial hybridization between the Ti and Mn atoms. The hybridization of Mn and Ti is weaker in LSMO/BTO interface with $\mathbf{P}_{\text{dn}}$ state than that of the interface with $\mathbf{P}_{\text{up}}$ state suggested by the XAS of O- K edge (Figure S18). The charge transfer is further confirmed by EELS results in Figure 3. Comparing with other similar systems,^{16, 25} our system has a larger change in magnetism for 5 u.c.-LSMO. The possible

1 reason is a smaller magnetization and thickness in our system that could be fully affected
2 by the FE field effect.

3 To evaluate the effect of the interface chemistry on the magnetism of
4 heterostructures, we have examined another group of samples grown under the same
5 conditions, in which the thickness of BTO was decreased from 45 u.c. (much larger than
6 the critical thickness, good ferroelectricity) to 3 u.c. (lower than the critical thickness,³⁴
7 very weak ferroelectricity as shown in Figure S11), but retaining the same chemical
8 interface as for the samples in Figure 2. We found that Ti-*L* edge EELS throughout BTO
9 film (Figure S14) shows the decreasing concentration of Ti³⁺ from LSMO/BTO interface
10 to inner of BTO, suggesting that Ti³⁺ mainly appears at the interface. The XMCD spectra
11 in Figure S12 display similar signals for Mn and almost negligible signals for Ti. These
12 results suggest that the effects of the chemical properties at the interface would be too small
13 to play any meaningful role on induced interfacial magnetism. Comparing to bulk BTO,
14 which exhibits structural phase transitions,¹⁰ the ultrathin single crystal films in our work
15 are coherently grown on STO substrate (strain -2.0 %). These fully strained films maintain
16 the tetragonal structure in the range of 80 K-300 K due to the strong clamping effect of
17 substrate.^{30, 35} The effect of strain on the magnetism of LSMO films is weak, unlike that on
18 bulk BTO.

19 Note that a charge modulation mechanism of interfacial ferromagnetic magnetic Ti
20 in LaAlO₃/SrTiO₃³⁶ results from the polar discontinuity, and the theoretical calculations of
21 Fe/BTO bilayers involves the mechanism of ferroelectric-induced charge transfer.⁸ In the
22 structure of Fe/BTO used by S. Valencia *et al.* the magnetic Ti at the interface is resulting
23 from proximity effect and the finite magnetic moment is located at Fe and O atoms⁷.

1 However, in LSMO/BTO heterointerfaces, charge redistribution is determined by the
2 competition of charge transfer due to valence imbalance and carrier density modulation
3 due to the FE field. Hence, the present magnetic arrangement is different from that
4 discussed by Valencia *et al.*⁷ and Duan *et al.*⁸ where the alignment of magnetic moments
5 of Ti and Mn atoms is independent from the FE polarization and always antiparallel. The
6 interfacial magnetic coupling in this work is similar to the one modulated by strain in the
7 LaMnO₃/STO superlattice.³⁷ The critical difference is that exchange coupling between Ti
8 and Mn at the artificial multiferroic interface is controlled by FE field effect or electric
9 field.

1

2 **Figure 3.** STEM, EDX and EELS across the LSMO/BTO heterointerface. (A-E) under P_{dn}
3 state. (A) The HAADF image. The white dashed line represents the position of the
4 interface. The green dot-dashed line denotes the electron beam position for the EELS
5 spectra. The scale bar is 2 nm. (B) The atomic-resolution overlaid EDX elemental maps.
6 (C) EDX elemental profiles extracted from La-L (Cyan), Ba-M (Red), Mn-K (Pink), and

1 Ti-K (Green) edges. **(D)** Layer-resolved EELS spectra of Mn- $L_{2,3}$ edges (**Top**) and Ti- $L_{2,3}$
 2 edges (**Bottom**). The gray dashed lines mark the position of L_3 and L_2 peaks for Mn- $L_{2,3}$
 3 edges. The gray lines for Ti- $L_{2,3}$ edges represent experimental data, while the coloured lines
 4 are the fitted results by the fractional contribution of Ti^{4+} and Ti^{3+} . Reference spectra for
 5 Ti^{3+} (Red line) and Ti^{4+} (blue line) are shown at the bottom, taken from Ti_2O_3 powder and
 6 stoichiometric $SrTiO_3$ substrate, respectively. **(E)** The extracted $L_{2,3}$ ratio from EELS of
 7 Mn and the calculated Mn valence state vs. the distance from the surface. The gray dashed
 8 line shows the Mn valence state (3.3) in bulk LSMO (**Top**). The component of Ti from
 9 EELS of Ti- L edge vs. the distance from the interface (**Bottom**). The numbers in the inset
 10 represent the calculated Ti valence state. **(F-J)** under P_{up} state.

11 **Ti and Mn charge redistribution across the interfaces.** To probe charge
 12 redistribution/oxidization state near the LSMO/BTO heterointerfaces, we conduct atomic-
 13 resolution EDX mapping and EELS characterization atomic layer by atomic layer, as
 14 shown in **Figure 3**. The HAADF image and EDX mapping of LSMO/BTO heterostructure
 15 under P_{up} state in Figure 3A and 3B confirm that LSMO layer was coherently grown on
 16 the BTO layer, retaining the tensile state. From the bottom to the top across the interface
 17 the EELS signals gradually change from Ti- L edge to Mn- L edge, as shown in Figure 3D
 18 (**Top**). To quantitatively obtain the fraction of Mn^{3+} and Mn^{4+} , the $L_{2,3}$ peak area ratio
 19 (L_3/L_2) is evaluated from EELS of Mn through the Gaussian fitting of each individual Mn
 20 peak L_2 and L_3 , as shown in Figure S15, following Varela *et al.*'s work.³⁸ It can be seen
 21 that $L_{2,3}$ ratio decreases within 2 unit cells near the LSMO/BTO interface, indicating the
 22 increase of the Mn valence as shown in Figure 3E (**Top**). This agrees with the peak position
 23 shift seen in Figure 3D (**Top**). For the BTO layer, the Ti- $L_{2,3}$ edge spectra shown in Figure

3D (**Bottom**) were decomposed into a linear combination of the reference data for Ti^{3+} and Ti^{4+} as shown in Figure S16, following Ohtomo *et al.*'s work.³⁹ The fraction of Ti^{3+} gradually increases from the inner of the BTO to the LSMO/BTO interface, indicating the decrease of the Ti valence from +4 as shown in Figure 3E (**Bottom**). Quantitatively analyzing the EELS spectra of Mn and Ti, we argue the existence of charge redistribution, originating from the competition of valence imbalance $(-\text{BaO})^0-(\text{TiO}_2)^0-(\text{La/SrO})^{+0.67}-(\text{MnO}_2)^{-0.67}-$ and FE polarization discontinuity at the heterointerface. This valence imbalance may induce a charge transfer/oxygen vacancy,⁴⁰ whereas the FE polarization discontinuity may induce screening charges⁴¹ at the interface. Comparing to the LSMO/BTO heterointerface under $\mathbf{P}_{\text{dn}}$ state, $L_{2,3}$ ratio extracted from the EELS of Mn, shown in Figure 3I (**Top**), gradually decreases from the LSMO/BTO interface to surface, indicating the gradual increase of Mn valence as shown in Figure 3J (**Top**). Also, there is a more significant fraction of Ti^{3+} at the heterointerface, therefore, indicating a lower Ti valence. On one hand, both heterointerfaces under $\mathbf{P}_{\text{dn}}$ and $\mathbf{P}_{\text{up}}$ state have Mn and Ti valence change, in turn, leading to induced magnetism at the heterointerfaces. On the other hand, our EELS analysis indicates the affected thickness of Mn valence and change of Ti valence at LSMO/BTO heterointerface under $\mathbf{P}_{\text{up}}$ state are more significant than that at the heterointerface under $\mathbf{P}_{\text{dn}}$ state due to larger charge redistribution arising from the stronger Mn-O-Ti hybridization. This enhancement is caused by the FE field, resulting in a more considerable interfacial magnetism.

1

2 **Figure 4.** Normalized X-ray absorption spectroscopy and X-ray linear dichroism of the

3 LSMO/BTO heterostructures at 300 K. (A) and (B) Mn- and Ti- $L_{2,3}$ edge XAS and their

4 XLD for LSMO/BTO under $\mathbf{P}_{\text{dn}}$ state, respectively. The blue line and gray line represent

5 Ti- L edge XAS for the reference sample of SrTiO_3 and Ti_2O_3 , respectively. (C) and (D)

1 Mn- and Ti- $L_{2,3}$ edge XAS and their XLD for LSMO/BTO under $\mathbf{P}_{\text{up}}$ state, respectively.
2 The insets show the preferential orbitals of Ti and Mn under different polarization states,
3 respectively. (E) and (F) The orbital-resolved density of states (DOS) in the LSMO/BTO
4 heterostructure projected onto the interfacial Mn atoms at the LaO/TiO interface (E) and
5 the BaO/MnO interface (F).

6 **Mn-O bonds and orbital occupancy tuned by ferroelectric field effect.** Physical
7 properties (such as magnetic interaction and electrical transport) of 3d transition metal
8 oxides is delicately sensitive to the occupation of d orbitals.⁴² To understand the difference
9 of Mn-Ti exchange coupling at the LSMO/BTO heterointerfaces, therefore, we utilize
10 element-specific XAS and XLD (Figure 2B) to probe the electronic structure and orbital
11 occupancy. **Figure 4** shows the normalized XAS and XLD signals of Mn- and Ti- L edge
12 measured at 300 K, respectively. The preferential orbital of Mn under $\mathbf{P}_{\text{dn}}$ state is in-plane
13 ($d_{x^2-y^2}$ in Figure 4A), verified by a negative XLD integral in Figure S17. The orbital of Mn
14 under $\mathbf{P}_{\text{up}}$ is out-of-plane ($d_{3z^2-r^2}$ in Figure 4C) confirmed by a positive XLD integral in
15 Figure S17. However, both Ti preferential orbitals under $\mathbf{P}_{\text{dn}}$ (Figure 4B) and $\mathbf{P}_{\text{up}}$ (Figure
16 4D) states are out-of-plane ($d_{xz/yz}$), which is consistent with an elongated c axis under
17 compressive strain from the substrate (tetragonality of BTO is 1.1). The change of orbital
18 occupation tuned by ferroelectric field effect is further supported by the orbital-resolved
19 density of states (Figure 4E and 4F) based on density functional theory (DFT) calculations
20 (further details can be found in the Supporting Information). The structural distortion of
21 interfacial MnO_6 octahedra under a tensile strain from the BTO layer (Figure S4C and
22 Table S1) and the alteration of Mn-O bond from FE field is the primary origin of orbital

1 anisotropy. This configuration of orbital degeneration as determined by FE polarization is
 2 consistent with the theoretical predictions⁴³ and experimental observations.^{14, 44}

3
 4 **Figure 5.** Mn orbital occupation and interfacial magnetic couplings across the
 5 titanite/manganite interfaces. (A) and (B) Real-space charge density calculated in the
 6 energy window from $E_F - 0.94$ eV to E_F (E_F is the Fermi energy) at the LaO/TiO interface
 7 (A) and the BaO/MnO interface (B) in the LSMO/BTO heterostructure. The Mn-O bond
 8 lengths are indicated. (C) and (D) The sketches of the orbital hybridization between Mn
 9 and Ti via O. The black arrows represent the spin alignment based on the Goodenough
 10 rules. (E) and (F) Proposed interfacial spin configuration and magnetic coupling
 11 mechanism at the LSMO/BTO heterointerfaces. The center shows the charge redistribution
 12 at the interfaces. The black +/- symbols represent the screening charges induced by the
 13 ferroelectric bond charges.

14 DISCUSSION:

Combining the microscopic element-specific XMCD and XLD results, and the macroscopic magnetic properties with EELS analysis, we now turn to construct a picture of the mutual effects at the FE/FM interface regarding the charge redistribution, orbital anisotropy and possible interfacial magnetic arrangement between Mn and Ti moments. The charge redistribution originating from the competition of charge transfer/oxygen vacancy and FE screening charge at the interfaces leads to transferred electrons on the Ti d orbitals and thus an induced magnetism on the Ti atom. It is believed that the tensile stress from the substrate and the Jahn-Teller effect lead to a smaller Mn-O bond length (3.81 Å) along the out-of-plane than that along the in-plane⁴⁵ as shown in **Figure 5A**; thus electron occupation of the Mn $d_{x^2-y^2}$ orbital is energetically preferred. In the FE/FM heterostructure, the FE polarization effect should be considered as well. For the $\mathbf{P}_{\text{dn}}$ state, the FE field leads to a further reduction in the out-of-plane Mn-O bond length via distortion of oxygen octahedra,⁴³ therefore, electrons still preferably occupy the Mn $d_{x^2-y^2}$ orbital. On the contrary, for the $\mathbf{P}_{\text{up}}$ state, the FE field leads to a substantially elongated Mn-O bond (4.01 Å) along out-of-plane (Figure 5B) via overcoming the tensile stress from STO substrate; thus the Mn $d_{3z^2-r^2}$ orbital is preferentially occupied. The layer-resolved lattice parameters extracted from the STEM images (Figure S21) suggest that the out-of-plane lattice parameter (3.99 Å) of the first unit cell of LSMO close to the interface for $\mathbf{P}_{\text{up}}$ sample is indeed larger than that (3.80 Å) for the $\mathbf{P}_{\text{dn}}$ sample. Both the XLD and XMCD signals from the O- K edge (Figure S18 and S19) further confirm that the hybridization of Mn-O-Ti is stronger for the $\mathbf{P}_{\text{up}}$ state than that for the $\mathbf{P}_{\text{dn}}$ state. The hybridization between the Mn occupied $d_{x^2-y^2}$ orbital and the Ti $d_{xz/yz}$ orbital across the interface is very weak due to the larger Mn-Ti distance ($c+\delta$) in the heterostructure with $\mathbf{P}_{\text{dn}}$ state, where δ is ferroelectric

displacement of ions; thus the virtual hopping of electron is limited. According to the Goodenough-Kanamori rules,⁴⁶ the virtual hopping of electron from the occupied Ti orbital to the empty Mn $d_{3z^2-r^2}$ orbital determines the FM coupling between Mn and Ti as shown in Figure 5C. Also, for the $\mathbf{P}_{\text{dn}}$ state the small magnetic moment of Mn atom and a weak exchange bias (Figure S10) may be possibly due to the presence of an AFM layer at the interface.³³ We therefore propose that in the $\mathbf{P}_{\text{dn}}$ heterostructure, the exchange coupling between Mn atoms at the interface is AFM, whereas it is FM between Mn and Ti as shown in Figure 5E. On the contrary, in the $\mathbf{P}_{\text{up}}$ heterostructure, there is a strong overlap and hybridization across the interface between the occupied Mn $d_{3z^2-r^2}$ orbitals and Ti $d_{xz/yz}$ orbitals due to the reduced distance between Mn and Ti ($c-\delta$) as shown in Figure 5D. According to the Goodenough-Kanamori rules and the interfacial orbital hybridization,^{37, 47} magnetic moments of Ti t_{2g} electrons and the half-filled Mn bands should be AFM coupled at the interface as shown in Figure 5F. Interfacial AFM magnetic coupling in LSMO/LSCO⁴⁸ or LSMO/BFO,⁴⁹ LCMO/BFO⁵⁰ and LSMO/LFO¹⁸ have been previously reported, where the magnetic moments in Cu or Fe atoms are preexisting. However, in our samples, charge redistribution changes non-magnetic Ti^{4+} (d^0) in bulk BTO to magnetic Ti^{3+} (d^1) at heterointerface and magnetic coupling is tuned by the FE polarization, which is fundamentally different from the other studies.

CONCLUSION:

In summary, we have explored the ferroelectric field effect on the orbital hybridization and induced magnetism at the titanite-manganite heterointerfaces and showed that charge redistribution and changes in orbital occupancy play an important role. The element-specific XMCD spectra indicated that ferroelectric polarization controls spin and orbital

1 moments of the interfacial Mn and Ti atoms and affects the interfacial exchange
2 interaction. The combination of atomic-resolution STEM and EDX mapping with EELS
3 characterization provided a detailed picture of charge redistribution and changes in the
4 valence states across oxide heterointerfaces. Both XLD characterization and the calculated
5 orbital-resolved density of states confirmed the polarization dependent orbital occupancy,
6 activating ferroelectric control of the interfacial exchange coupling. Our findings
7 demonstrate a route to the electrical control of magnetic states and interactions at oxide
8 FM/FE heterointerfaces, which in turn, tunes the spin-dependent transport properties in
9 magnetic and ferroelectric tunnel junctions.

11 MATERIALS AND METHODS

12 *Sample Preparation:* All LSMO/BTO heterostructures were epitaxially grown on
13 atomically smooth (001) STO single-crystal substrates (CrysTec GmbH) by pulsed laser
14 deposition (PLD). 1 u.c.-SRO layer were pre-deposited on TiO₂-terminated STO substrates,
15 getting a SrO-terminated surface. After film growth, pure oxygen (typically 200 Torr
16 annealing for 1 hour) was introduced the PLD chamber, and the samples were cooled down
17 to room temperature at a cooling rate of 10 °Cmin⁻¹ to reduce oxygen vacancy.

18 *Sample Characterization:* The surface morphology, ferroelectricity of these as-grown
19 heterostructures were characterized by AFM and PFM on a commercial scanning probe
20 microscope (Asylum Research MFP-3D) instrument at room temperature. The crystal
21 structures and strain state were characterized by synchrotron-based X-ray diffraction at
22 room temperature. Microstructure, interfacial structure, element mappings, and EELS were
23 conducted by aberration-corrected STEM (FEI Titan G2 80-200 microscope equipped with

a Super-X EDX detector) at room temperature. The magnetization measurements at different temperatures were conducted by superconducting quantum interference device (SQUID). XAS signals were recorded from the total electron yield (TEY) current, which takes into account the surface sensitivity (with a 30 ° grazing angle) and element selectivity of the TEY mode. X-ray absorption spectroscopy (XAS) was conducted at room temperature and 80 K at beamline SINS (Surface, Interface and Nanostructure Science) of SSLS. The experimental configurations of X-ray linear dichroism (XLD) and X-ray magnetic circular dichroism (XMCD) are shown in Fig. 2b. The XLD signal is obtained by subtracting the intensities of the linear-polarized X-ray with vertical (I_c) polarization from horizontal (I_{ab}) polarization without magnetic field, that is, $XLD = (I_{ab} - I_c)$. The XMCD signal is the difference of the circularized X-ray absorption spectra taken in plus and minus 1 T in-plane magnetic field, that is, $XMCD = (I^+ - I^-)$.

Others: The detailed information of the film growth, characterization and DFT calculations are listed in Supporting Information.

ASSOCIATED CONTENT:

SUPPORTING INFORMATION:

The following files are available free of charge.

The detailed information of the film growth, characterization, determination of cation displacement vector, DFT calculations and the estimation of spin and orbital moments are listed in the supplementary section. (PDF)

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Author Contributions

These authors (^o) contributed equally to this work. H.W. and J.S.C.: conceived and designed this work and manuscript writing. H.W.: Sample preparation and characterization, data analysis. X.C., J.S.C., C.J.S. and G.M.C.: XAS characterization and data analysis. L.L.T. and E.Y.T.: Density functional calculation and data analysis; Z.R.L. and H.T.: HAADF-STEM and EELS experiment. J.X.W and Z.L.D.: HR-TEM experiment. H.Y.Y., and P.Y.: XRD. All authors contributed to the manuscript and the interpretation of the data.

Notes

The authors declare no competing financial interest.

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