Supporting Information

Magneto-electric coupling induced orbital reconstruction and

ferromagnetic insulating state in

PbZr_{0.52}Ti_{0.48}O₃/La_{0.67}Sr_{0.33}MnO₃ heterostructures

Chao Liu¹, Bangmin Zhang^{1,2}, Xiaoqian Yu¹, Xiaohan Wu¹, Pingfan Chen¹,

Ping Yang³, Xiaojiang Yu³, Jun Ding¹, Jingsheng Chen¹, Gan Moog Chow^{1*}.

¹Department of Materials Science & Engineering, National University of Singapore, 117575, Singapore.
²School of Physics, Sun Yat-Sen University, Guangzhou, Guangdong, 510275, China
³Singapore Synchrotron Light Source, National University of Singapore, 117603, Singapore.

*Corresponding author: Gan Moog Chow, E-mail: <u>msecgm@nus.edu.sg</u>

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Table S2 Summary of c lattice constant in LSMO

Table S3 Summary of fitting results for bond angle and length by half integer

diffraction

Reference

S1. PFM



Figure S1 PFM poling image and local piezoelectric response for different thickness of PZT: (a), (d) \sim 7 nm; (b), (d) \sim 30 nm; (c), (f) \sim 100 nm.

PFM poling image and local piezoelectric response for different thickness of PZT are displayed in **Figure S1**. From **Figure S1(a)** to (c), polarization direction of PZT layer keeps almost upward. From **Figure S1(d)** to (e), local piezoelectric response is better when PZT is thicker, suggesting a better ferroelectric property for thicker PZT layer.



Figure S2 XPS for Mn 2p core level in PZT/LSMO bilayer with different PZT thickness. (a) 0 nm (b) 5 nm (c) 20 nm (d) 30 nm and (e) 60 nm.

Valence state for manganese ion is determined by x-ray photoelectron spectroscopy using Al K_{α} X-rays. As shown in **Figure S2**, XPS signal for Mn 2p core level is collected and then fitted using Mn_{2p3/2}, Mn_{2p1/2}, Pb_{4p3/2} with XPSPEAK software. The reason to include the Pb 4p XPS peaks is that their energy levels are located in range of Mn 2p and they are regarded as satellite peaks during fitting process¹. The Pb content may arise from PZT layer or contamination from Pb evaporation during growth process, which is also verified by observation of Pb-4f XPS peaks. The Mn_{2p3/2} peak could be utilized to quantify the ratio for Mn³⁺ and Mn⁴⁺.² The Mn²⁺ is not considered here after considering the Mn-3s XPS peak separation. The Mn-3s peak separation due to spinorbital splitting is around 5.7~6.1 eV for Mn²⁺, 5.2~5.4 eV for Mn³⁺, 4.4 ~4.6 eV for Mn⁴⁺, around 5 eV for mixture of Mn³⁺ and Mn⁴⁺.³⁻⁴ The peak separations for our five samples are 5.11, 5.07, 5.15, 4.99 and 5.23 eV, as shown in **Figure S3**. The experiment evidence therefore supports the existence of a mixture of Mn^{3+} and Mn^{4+} . The fitting result and the deduced ratio are summarized in **Table S1**. Considering that XPS is a surface sensitive technique that might only detect averagely about 5 nm depth away from surface, the deduced ratio could not present the exactly precise ratio for Mn^{3+} and Mn^{4+} . However, it still can roughly suggest the relative change for the ratio for Mn^{3+} and Mn^{4+} . Therefore, relative change for Mn^{3+}/Mn^{4+} is reliable.



Figure S3 XPS for Mn 3s core level in PZT/LSMO bilayer with different PZT thickness. (a) 0 nm (b) 5 nm (c) 20 nm (d) 30 nm and (e) 60 nm.



Figure S4 Lscan along (00L) or (-10L) for PZT/LSMO with different PZT thickness. Green line is fitting result for LSMO peak. (a) 0 nm (b) 5 nm (c) 20 nm (d) 30 nm and (e) 60 nm.

As peak for LSMO is very close to that for NSTO, they can't be distinguished very clearly. By fitting L scan along (002) or (-103), exact peak position is extracted out. According to Bragg's law and the relative peak position in reciprocal space, c(film)*L(film) = c(substrate)*L(substrate) relationship is established. Based on this relationship, c lattice constant for LSMO layer is deduced. From Figure S4, green color peak refers to LSMO peak. And the deduced peak position and lattice constant is summarized in Table S2.

S4. Half integer diffraction



Figure S5 Selected half integer diffraction for PZT0nm/LSMO8nm heterostructure



Figure S6 Selected half integer diffraction for PZT5nm/LSMO8nm heterostructure



Figure S7 Selected half integer diffraction for PZT20nm/LSMO8nm heterostructure



Figure S8 Selected half integer diffraction for PZT30nm/LSMO8nm heterostructure



Figure S9 Selected half integer diffraction for PZT60nm/LSMO8nm heterostructure

Half integer diffraction peaks are measured to obtain octahedral rotation patterns. **Figure S5** to **S9** give selected half integer diffraction peaks for each sample. Rotation pattern for all samples are a⁻a⁻c⁻ according to Glazer classifying system⁵. Bond angle and bond length are deduced by fitting half integer peak intensity that is determined by oxygen atom arrangement in the crystal structure of LSMO. The fitting approach is developed using maple code based on the least square method, which has been used in our previous work.⁶ All fitting results are listed in **Table S3**.

S5. XLD measurement and analysis

XLD measurement geometry is shown in **Figure S10**. A linear polarized incident x-ray is perpendicular to the sample surface with the E-field vector parallel to the sample surface. Signal collected at this angle is labelled as I_{ab} . The other linear polarized incident x-ray has a grazing incident angle of 30° to the sample surface and the E-field vector intersecting with the sample surface at an angle of 60°. Signal collected at this angle is labelled as I_e . All the measurements were conducted at room temperature and no magnetic field was applied in order to avoid magnetization contribution to the XLD signal. All the signals were normalized using the same procedure. Each linear polarized XAS that include Mn L₃ and L₂ edges was normalized by fitting the background with a step function and then renormalizing the background step function to the range of 0 to $1.^7$ The XLD difference is obtained by $I_{ab} - I_e$. The XLD signal value was calculated by the integrated area intensity of XLD spectrum including Mn L₃ and L₂ edges^{8.9}, as shown in **Figure S11**. The integrated XLD intensities are -0.375, 0.655, 0.445, 0.544 when PZT is 0 nm, 5 nm, 30 nm and 60 nm, respectively.



Figure S10 XLD measurement geometry



Figure S11 Integral of XLD signal for PZT/LSMO bilayer with different PZT thickness.

Sample	$Mn_{2p3/2}(3+)$	Mn _{2p3/2} (3+)	$Mn_{2p3/2}(4+)$	Mn _{2p3/2} (4+)	${\rm Mn^{3+/}~Mn^{4+}}$	
	Position(eV)	Intensity	Position(eV)	Intensity		
LSMO8nm	641.40	12179±369	642.73	12499±387	0.9744±0.0445	
LSMO8nm /PZT 5 nm	641.36	10401±342	642.69	11411±371	0.9115±0.0507	
LSMO8nm /PZT20nm	641.39	8122±302	642.72	7584±300	1.0709±0.0506	
LSMO8nm /PZT30nm	641.33	9738±326	642.66	9561±335	1.0185±0.0476	
LSMO8nm /PZT60nm	641.29	8280±305	642.62	8795±327	0.9414±0.0556	

Table S1. Summary of fitting results for valence of Manganese ion

Sample	L ₀₀₂	L-103	<i>c</i> (Å)	
LSMO8nm	2.0290±0.0005		3.8490±0.0009	
LSMO8nm/PZT 5 nm		3.0016±0.0010	3.9031±0.0013	
LSMO8nm/PZT20nm		2.9834±0.0015	3.9270±0.0019	
LSMO8nm/PZT30nm		2.9743±0.0056	3.9381±0.0074	
LSMO8nm/PZT60nm		2.9869±0.0016	3.9220±0.0021	

 Table S2. Summary of c lattice constant in LSMO

Table S3.	Summary	of fitting	results for	bond ang	gle and l	length
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Sample	$\alpha_{in}(^{\circ})$	d _{in} (Å)	α _T (=β _T) (°)	$\alpha_{out}(^{\circ})$	d _{out} (Å)	γτ(°)	$d_{\rm in}/d_{\rm out}$
LSMO8nm	169.5±0.2	1.9607±0.0034	5.3±0.1	164.9±0.3	1.9414±0.0048	0±0.6	1.0099±0.0031
LSMO8nm /PZT 5 nm	161.7±0.3	1.9778±0.0049	7.4±0.1	159.2±0.3	1.9861±0.0049	5.4±0.1	0.9958±0.0034
LSMO8nm /PZT20nm	163.8±1.1	1.9723±0.0204	6.9±0.2	160.7±0.5	1.9917±0.0098	4.2±0.8	0.9903±0.0113
LSMO8nm /PZT30nm	167.5±1.1	1.9641±0.0202	5.5±0.2	164.6±0.6	1.9868±0.0094	2.8±0.9	0.9885±0.0112
LSMO8nm /PZT60nm	164.7±0.3	1.9701±0.0048	4.2±0.1	168.0 ±0.3	1.9745±0.0047	6.4±0.1	0.9977±0.0034

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