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Supplementary Information

Strong perpendicular exchange bias in epitaxial $La_{0.7}Sr_{0.3}MnO_3$:$BiFeO_3$ nanocomposite films through vertical interfacial coupling†

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†*Electronic Supplementary Information (ESI) available: Supporting HRTEM images and physical property measurement results are available.*

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Section 1. Experimental section

Sample preparation

The LSMO:BFO composite targets with different composition ratios were prepared by a conventional ceramic sintering method. In brief, a stoichiometric mixture of high purity La_2O_3, $SrCO_3$ and MnO_2 powders were ground, pressed and then sintered at 1200 ℃ in air for 24h to synthesize $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) powders. The BFO powders were prepared from the stoichiometric mixture of high purity Bi_2O_3 and Fe_2O_3 with 5 mol% excess of Bi_2O_3 for compensation of Bi loss and sintered at 700 ℃ in air for 3h. The calcined LSMO and BFO powders were then reground and mixed in different ratios and pressed into disks and subsequently sintered at 1300 ℃ in air for 12h to make the composite targets. The thin film deposition was conducted by a standard pulsed laser deposition method. The LSMO:BFO VAN films were grown on (001) single-crystal $SrTiO_3$ substrates at 700 ℃ in 100 mTorr of oxygen by pulsed laser deposition (PLD) with a KrF laser (Lamda Physik, λ = 248 nm). The growth rate for the VAN films is ~0.5 Å/s. The target to substrate distance is 5 cm. The repetition rate is 10 Hz and the laser energy density is 2.2 J/cm^2. After deposition, samples were cooled down in an oxygen pressure of 500 Torr at a cooling rate of 5 ℃/min. The LSMO:BFO films with different compositions were obtained by changing the target composition.

Microstructure characterization and property measurements

The high-resolution X-ray diffraction (XRD) was carried out with a PANalytical Empyrean diffractometer using Cu-K_α radiation. The conventional low-magnification and high-resolution transmission electron microscopy (TEM) and energy-dispersive X-ray

spectroscopy were performed using a FEI Tecnai G^2 F20 microscope operated at 200 kV. Selected-area diffraction patterns (SAED) were also collected. For the high-resolution scanning TEM (STEM) analysis, an aberration-corrected FEI Titan microscope equipped with a high brightness Schottky-field emission electron source operated at 300 kV was employed. The magnetic measurements were conducted by the vibrating sample magnetometer (VSM) mode in a Physical Properties Measurement System (PPMS, Quantum Design). For the filed cooling (FC) and zero filed cooling (ZFC) measurements, the samples were cooled down from 300 K to target temperatures. The signals from substrates have been subtracted for all measured samples. Local piezoresponse force microscopy (PFM) measurements were conducted using a Pt/Ir-coated tip at optimized resonance frequency with an alternating current voltage of 0.5 V.

Section 2. TEM images and physical property measurements

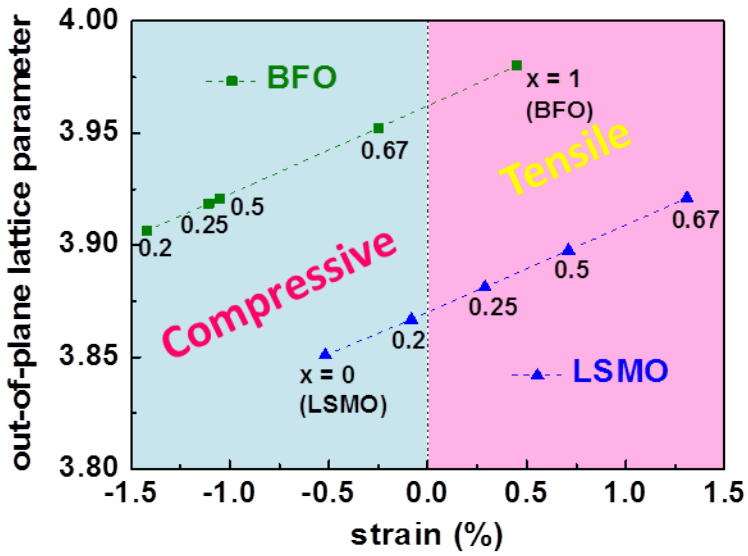

Fig. S1 Out-of-plane lattice parameter versus the vertical lattice strain in $L_{1-x}B_x$ films.

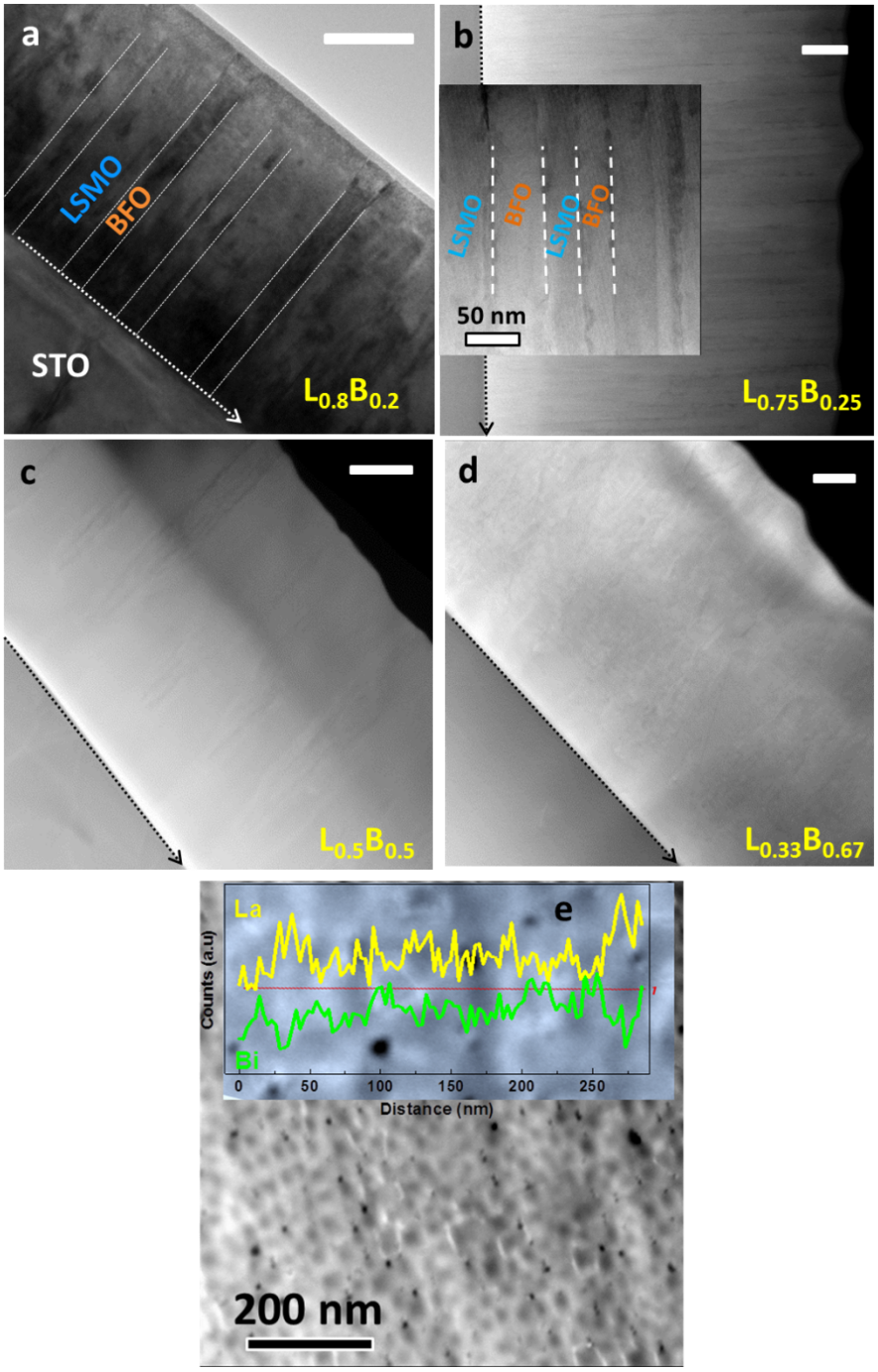

Fig. S2 (a)-(d) Cross-sectional (S)TEM images of $L_{1-x}B_x$ (x=0.2, 0.25,0.5,0.67) films. Scale bars are 100 nm. (**e**) Plan view STEM image of $L_{0.75}B_{0.25}$ VAN films showing a clear pillar-in-matrix morphology. The inset shows the EDS line results across a pillar-matrix region.

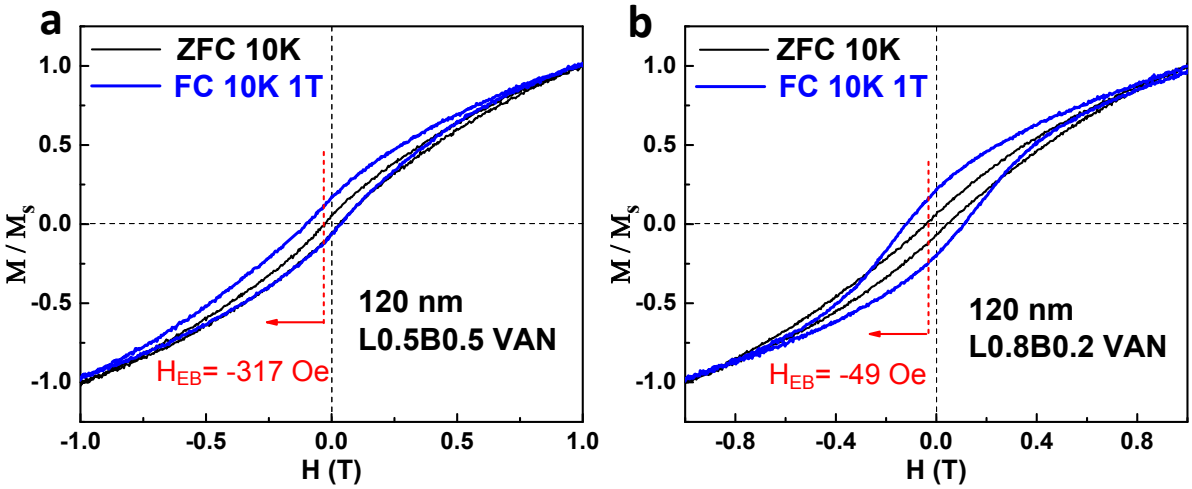

Fig. S3 Magnetization hysteresis curves of 120-nm-thick (**a**) $L_{0.5}B_{0.5}$ and (**b**) $L_{0.8}B_{0.2}$ VAN films measured at 10 K after field cooling from 300 K in +1 T (blue) and 0 T (black) field.

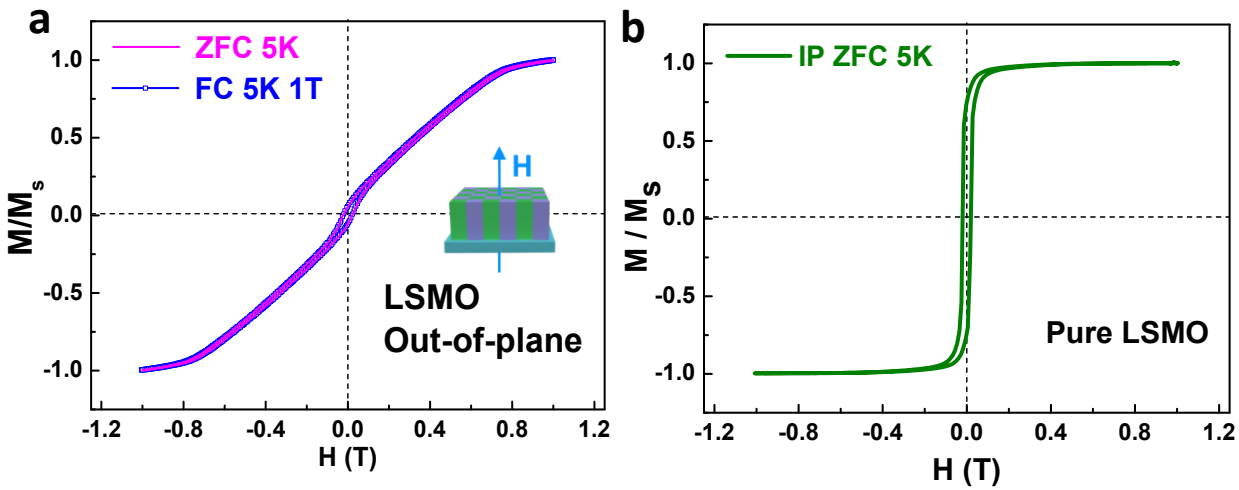

Fig. S4 (a) Magnetization hysteresis curves of pure LSMO (out-of-plane) measured at 5 K after ZFC (pink line) and FC (blue line with squares) procedure with an out-of-plane magnetic field. **(b)** IP magnetization hysteresis loop of pure LSMO measured at 5 K.

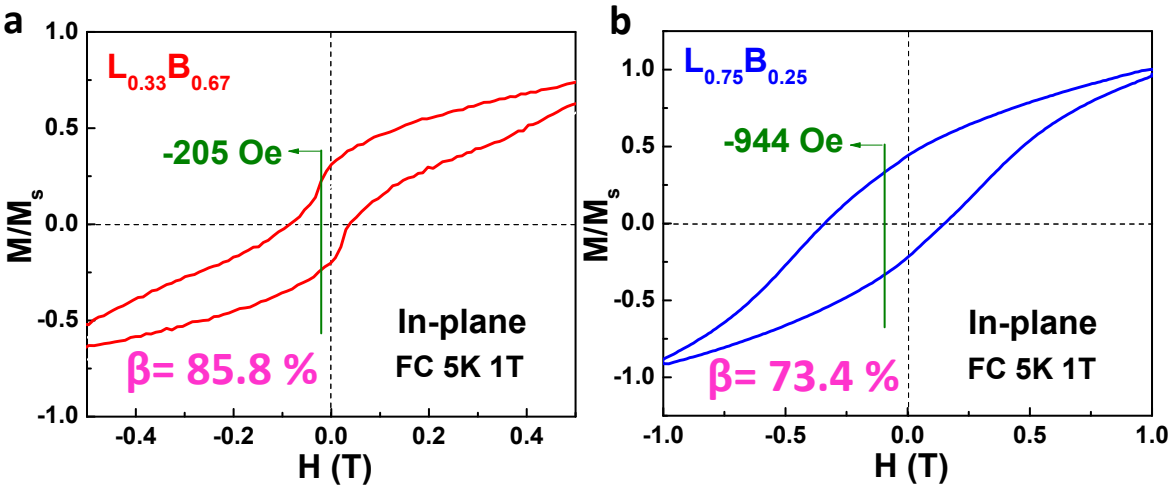

Fig. S5 Magnetization hysteresis curves of **(a)** $L_{0.75}B_{0.25}$ and **(b)** $L_{0.33}B_{0.67}$ VAN films measured at 5 K after field cooling from 300 K with +1 T field parallel to film surface.

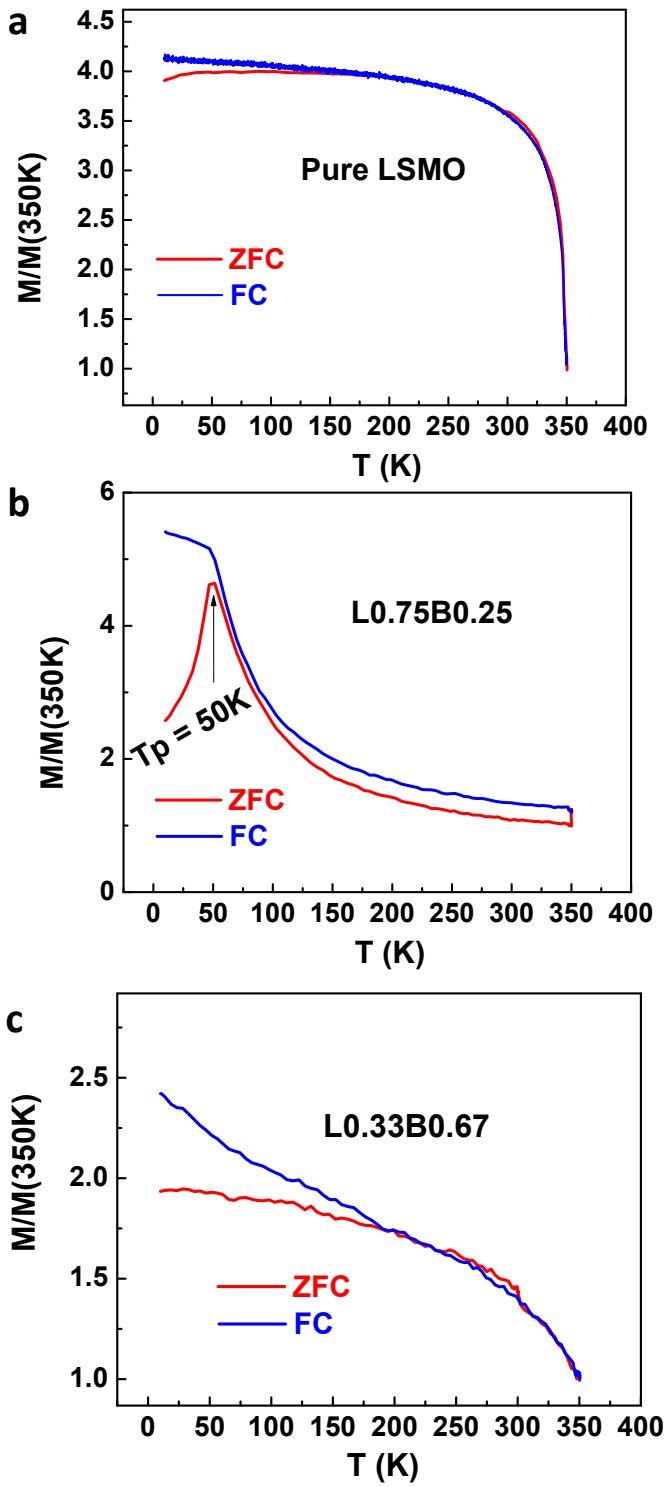

Fig. S6 (a)-(c) ZFC and FC M-T curves of pure LSMO, $L_{0.75}B_{0.25}$ and $L_{0.33}B_{0.67}$ films.

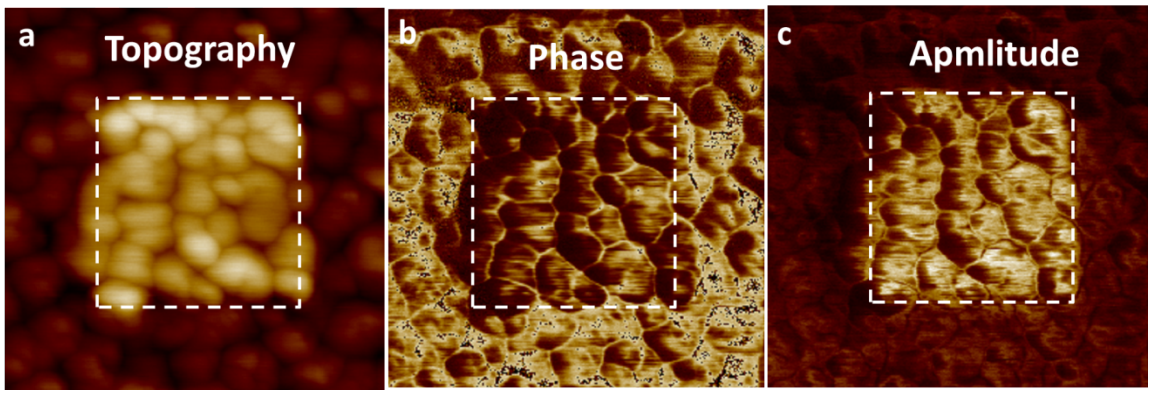

Fig. S7 (a)-(c) The simultaneously acquired PFM topography, phase and amplitude images on an area of 1.7x1.7 μm^2 of the $L_{0.33}B_{0.67}$ film after writing the central area (0.8x0.8 μm^2) with a 5 V tip bias.