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Supporting Information

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Controlling Magnetic Properties at BiFe_{1-x}Mn_xO₃/ La_{2/3}Ca_{1/3}MnO₃ Interfaces by Tuning the Spatial Distribution of Interfacial Electronic States

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Figure S1 Magnetic hysteresis loops for the pure BFMO films record at 10 K in in-plane orientation after FC at +3 kOe



Figure S2 Magnetic hysteresis loops for the pure LCMO films record at 10 K in in-plane orientation after FC at 30 kOe, and the inset shows that record in the out-plane orientation after FC at 30 kOe.



Figure S3 The magnetic hysteresis loops of these samples in the out-of-plane directions after FC at +3 kOe at 10 K with an external field of ± 3 T.



Figure S4 Exchange bias field (H_{EB}) of the Mn-0%, Mn-20% and Mn-40% heterostructures as a function of temperature. The exponential fitting of the H_{EB} as a function of temperature is noted by the blue line.

The hysteresis loops of the BFMO/LCMO heterostructure measured at different temperatures show that both H_E decrease with increasing temperature, as shown in Figure S3, which shows the variation of the H_E with temperature from 5 K to 275 K. The H_E decreases almost monotonously with increasing temperature and becomes zero at about 150 K for Mn-0%

and Mn-40% heterostructures, but 50 K for Mn-20% heterostructure, which corresponds to conventional (Exchange bias) EB-blocking temperature (T_B). The relation between H_E and temperature can be described by the following formula: $H_E = H_0 \exp(-T/T_0)$, where H_0 is the extrapolation of H_E at 0 K and T_0 is a constant. As shown in Figure S4, H_E exponentially decays with increasing temperature. This is in agreement with the experimental results in perovskite manganite in recent reports such as FM/AFM of La_{1-x}Ca_xMnO₃/La_{1-y}Ca_yMnO₃ superlattices,^[1] LSMO/SrMnO₃^[2] and LSMO/NiO composite films.^[3] This kind of thermal activation of the FM interactions across the interfaces has been proposed to manipulate the EB effect in the manganite systems. It has been reported by Cai *et al.*^[4] that the random spin coupling can be established in the PM states even with the films.



Figure S5 Temperature dependence of magnetization for the BFMO films with the Mn content from 0% to 50%, measured in an in-plane magnetic field of 3 kOe.



Figure S6. EELS spectra of the O K edge, Mn $L_{2,3}$, and Fe $L_{2,3}$ across the BFMO/LCMO (Mn =

50%) interface.



Figure S7. The schematic energy diagram of the BFMO/LCMO heterostructures. (b) VBO values VS the valence states of Fe and Mn ions.

Figure S6(a) shows the schematic energy diagram of the BFMO/LCMO heterostructures. If we consider the BFMO and as wide band gap semiconductors and without considering the polarization charges, the band structure of the BFMO/LCMO heterostructure can be described as Figure 6(a). The knowledge of the valence band offset (VBO) (Figure 6(a)) at oxide heterostructures is of ultmost importance for the understanding and operating the local oxide interface environments, as the electronic transport properties are governed by the band alignments. The VBO is obtained by the following equation:^[5]

$$\Delta E_{VBO(A/B)} = (E_{CL(A-I)} - E_{CL(B-I)}) - [(E_{CL(A)} - E_{V(A)}) - (E_{CL(B)} - E_{V(B)})]$$

Where $\Delta E_{VBO(A/B)}$ is the VBO of the manganites relative to the cap layer of BFMO and LCMO (where A refers to the LCMO and B refers to BFMO), $E_{CL(A-I)} - E_{CL(B-I)}$ is the energy difference between Mn 2p and Fe 2p core levels (CLs) in the BFMO/LCMO heterostructure, $E_{CL(A)} - E_{V(A)}$ and $E_{CL(B)} - E_{V(B)}$ are the energy differences between the CLs and the valence band maximum (VBM) for the LCMO and BFMO inner layers, respectively. The shifts of the Fermi level position for the BFMO show a linear relationship with the Mn doping *x*. Thus, the Mn doping level determines the value of the VBO and the valence states.



Figure S7. Time dependence of the magnetization of the BFMO/LCMO heterostructure at 10 K in a field of 1000 Oe after ZFC from room temperature. The dots are experimental data and the solid lines are fits to a double-exponential equation.

At low temperatures, after a sudden change in magnetic field, the magnetic relaxation has been found to follow dominantly the usual logarithmic time dependence as reported by Panagiotopoulos *et al.*^[6] Figure S7 shows the time dependence of the magnetization at 10 K in a field of 1000 Oe after ZFC from room temperature. The magnetic relaxation is found to deviate from the usual logarithmic time dependence and follows a double-exponential equation: M(t) = $M(0) + M_1 e^{-t/\tau 1} + M_2 e^{-t/\tau 2}$, where, M(0), M_1 , M_2 , $\tau 1$, and $\tau 2$ are constants. For the Mn-0%, Mn-30%, Mn-40% and Mn-50% heterostructures, an initially relatively fast exponential relaxation (τ_1) is followed by a slower relaxation (τ_2) has been observed, as shown in Figure S7. During the ZFC process, the Fe-O-Mn double-exchange interaction FM clusters in the heterostructure are randomly frozen at low temperature. Firstly, the random spins of the interfacial FM clusters rapidly reorient to a more stable state in the direction of the external magnetic field due to the Zeeman interaction.^[7] With further increasing time, the magnetization continues to increase due to the strong exchange coupling between the spins of the AFM BFMO and the FM LCMO inner layers. For the Mn-20% and Mn-30% heterostructures, the magnetization remains almost unchanged with the increase of time. Thermal activation leads to the weak exchange coupling at the interface which makes it hard to separate the fast and slow relaxations. This is consistent with the experimental result of the weak *EB* for these samples.

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