Enhanced tunnelling electroresistance effect due to a ferroelectrically induced phase transition at a magnetic complex oxide interface

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**STEM-EELS and multiple linear least square (MLLS) fit**

To visualize spatial variability of chemical composition in the sample, we performed multiple linear least squares (MLLS) fittings to the EELS spectrum images obtained in the energy ranges of 4-130 eV (plasmonic and core-loss region). The representative spectra of the four components (after Fourier-log deconvolution), LSMO (top and bottom), BTO, and LCMO extracted from the four regions away from the interface are shown in Fig. S1. Each spectrum clearly differs in plasmonic energy, shape, and core-loss features. Applying the separate components to the MLLS fitting, the resulting fit coefficient map (Fig. 1b) shows clearly separated contrast associated with individual chemical phases.

**Figure S1**: Representative spectra of the four components showing distinctive features of individual layers in the multilayer structure for low-loss chemical mapping. The spectra were obtained after Fourier-log deconvolution. Each clearly shows core-loss edges of Ti M, Ca M, Mn M, Ba N, and La N at ≥ 35 eV.
**Out-of-plane lattice spacing**

We have determined the lattice spacing and the lattice distortion of BTO barrier from the cross sectional ADF STEM images. A sizable increase of the out-of-plane lattice spacing of the A-site (Ba) is seen for BTO. The measured lattice distortion is consistent with our first-principles calculation result shown in Fig. 4a, indicating a positive value (~ 0.2 Å) of the lattice distortion. The average value of the c-constant of the BTO is 4.09 ± 0.02 Å, signifying a strong tetragonal distortion of the strained ferroelectric layer characterized by $c/a = 1.047±0.005$.

![Figure S2: A-site lattice spacing along the out-of-plane direction obtained from cross-sectional ADF STEM data for the LSMO/BTO(3nm)/LCMO(1nm)/LSMO junction. The c-constant, $c = 3.818$ Å, of LSMO epitaxially strained to STO (the in-plane constant 3.905 Å) near the substrate was used for calibration (shown by the horizontal solid line in the plot). The c- lattice constant of LSMO is consistent with the out of plane lattice parameter determined by x-ray diffraction in a 10 nm LSMO thin films grown on STO substrate. Note that changes in the in-plane lattice spacing and B-site cation displacement are not significant due to epitaxial constraints, which are not shown here.](image-url)
Piezoresponse force microscopy (PFM) data

**Figure S3:** Temperature-dependent PFM amplitude hysteresis loops for a LSMO/BTO(3nm)/LCMO(2nm)/LSMO FTJ. The butterfly-like shape of the loops indicates that the BaTiO₃ layer is ferroelectric. With increasing temperature, the amplitude signal decreases.

**Figure S4:** Temperature-dependent PFM phase hysteresis loops for a LSMO/BTO(3nm)/LCMO(2nm)/LSMO FTJ. When the polarization direction of the ferroelectric BaTiO₃ layer reverses, the phase alters nearly by 180 degrees. For 100 K and 200 K measurements, the voltage was swept between –5 and +5 V. For room temperature measurements, a smaller sweeping voltage between –3 and 3 V was used due to the large leakage currents.
Temperature dependence of conductance

A significant increase in conductance is exhibited by all junctions at temperatures about 200K. This is evident from Fig. S5 which shows normalized conductances for junction J1-2 in both the upward and downward polarization states and junction J2 in the upward polarization state. Conductance per area in the semi-logarithmic scale is displayed in the inset of the figure. A similar conductance increase has been found for tunnel junctions with STO,\(^1\)-\(^4\) \(\alpha\)-Si\(^5\) and MgO\(^6\),\(^7\) barriers and explained by a thermally-activated inelastic conductance channel where conduction occurs through chains of localized states in the barrier.\(^8\) This conduction mechanism is strongly temperature dependent and with increasing barrier thickness evolves to a variable range hopping.\(^9\) As seen from Fig. S5, our data are reasonably well fitted using the Glazman-Matveev model\(^8\) of thermally activated conduction through localized states in the barrier at temperatures above \(\sim\)200 K for all junctions. The three curves shown in Fig. S5 are nearly identical above \(\sim\)200 K, indicating that at the high temperature range, the behavior is dominated by the defect-mediated inelastic conduction through BTO and the effect of the LCMO layer is not decisive.

**Figure S5**: Normalized conductance as a function of temperature. For junction J1-2, both the low and high resistance states are shown. For junction J2, only the low resistance state is shown because of a relatively small conductance difference between the two states. The conductance enhancement is seen at around 200K due to defect-mediated inelastic tunneling through localized...
states in the barrier. The solid line is a fit using the Glazman-Matveev model. The inset shows the conductance per area (1/RA) in the semi-logarithmic scale.

At lower temperatures, junction J1-2 in the low resistance state exhibits a qualitatively similar conductance variation as junction J2. This implies that adding LCMO does not affect much the temperature dependence when the polarization of BTO is pointing to the LCMO layer, indicating that LCMO in a metallic state. However, this behavior changes dramatically when the polarization is reversed so that junction J1-2 is now in the high resistance state. In this case the conductance variation as a function of temperature is largely determined by defect-mediated inelastic tunneling and can be reasonable well fitted by the Glazman-Matveev model over the whole temperature range (see Fig. S5). This behavior is consistent with a metal-insulator phase transition in LCMO which makes the tunneling barrier thicker, for which the transition to the defect-assisted tunneling regime occurs at lower temperatures.\(^5,6\)

Fig. S5 reveals that, for junction J1-2 in the low resistance state and junction J2, the conductance slowly decreases with increasing temperature in the temperature range \(\sim 100 – 200\text{K}\) and has a broad minimum at about 200K. This behavior has commonly been observed in manganite tunnel junctions, such as LSMO/STO/LSMO,\(^1,2\) LSMO/STO/Co,\(^3,4\) and LSMO/BTO/Fe/Co,\(^10\) mimicking a metal-insulator transition in the manganite\(^10\) with reduced ordering temperature near the interface.\(^2,4\) For junction J1-2 in the high resistance state, the defect mediated inelastic tunneling dominates the conduction so that the effect of magnetic ordering in the electrodes is not seen.

The defect-mediated inelastic tunneling itself reduces TER because the low resistance state exhibits a stronger increase in conductance with temperature, due to inelastic tunneling being less sensitive to polarization orientation. In addition, the enhanced conductance at elevated temperatures prevents poling the polarization state at a given voltage because the junction becomes too “leaky”. As the result, when measuring the resistance switching at elevated temperatures, the saturated ferroelectric state is not achieved. This behavior is similar for junctions with and without LCMO layer.
**I-V characteristics**

The **I-V** characteristics of our junctions show non-linear behavior, similar to junctions with the STO barrier.\textsuperscript{1,4,11-13} Due to the presence of defect mediated inelastic tunneling, using a direct tunneling model is not accurate even at low temperatures. Nevertheless, for the purpose of comparing our junctions with those based on a STO barriers, where strong defect mediated inelastic tunneling has also been present, we fitted our data at low voltage range using the asymmetric tunneling barrier model.\textsuperscript{14} The effective barrier height lies in the range of 0.1–0.4 eV for a number of junctions. This is similar to values obtained previously for the junctions with STO barriers.\textsuperscript{1,4,11-13} For junction J1-2, the fitting results indicate that when the resistance is changed from the low to high resistance state upon the ferroelectric polarization reversal, the barrier width is increased by about 1.5 nm. This change in the barrier width is consistent with the LCMO being metallic in the low resistance state and becoming insulating in the high resistance state.
Reproducibility of the TER effect over different junction areas and LCMO thicknesses

**Figure S6:** Resistance ($R$) as a function of pulsed poling voltage ($V_{\text{pulse}}$) measured at 10 mV and 80 K for a 10 × 10 μm² FTJ with 1 u.c. (~0.4 nm) LCMO at the top interface (J1-1) measured at $V = 0.1V$ and $T = 80K$. The solid lines are guide to the eye. The arrows indicate the direction of pulse sequence. A TER effect is ~4380%.

**Figure S7:** Resistance ($R$) switching in response to the pulsed poling voltage ($V_{\text{pulse}}$) for a FTJ with 5 u.c. (~2 nm) of LCMO at the top interface (J1-5) measured at $V = 0.1V$ and $T = 80K$. The solid lines are a guide to the eyes. The average TER value is 1070%.
**Reversed TER effect in junctions with a LCMO layer at the bottom interface**

**Figure S8:** $I$-$V$ curves for junction J3 with LCMO at the bottom interface at $T = 5\text{K}$ after the ferroelectricity was poled upward (blue) and downward (red). The arrows indicate the orientation of ferroelectric polarization. The sign of the TER is reversed in comparison with J1 series of samples due to the reversed charge doping effect, as the result of the LCMO layer being placed below the BTO layer. Inset shows the bias dependence of TER ratio of the junction obtained from the $I$-$V$ curves.

The reduced magnitude of the TER ratio in junction J3 as compared to junction J1 can likely be traced back to the inherent asymmetry in interface structures produced during growth. Indeed, even in FTJs without a La$_{0.5}$Ca$_{0.5}$MnO$_3$ layer (J2) we find a positive TER ratio, which probably arises due to changes in the profile of the depolarization potential after polarization reversal. In junction J3, therefore, the TER ratio is expected to be reduced due to the competition between the inherent asymmetry (positive TER) and the magnetoelectrically induced effect (negative TER).
References: