Switchable photovoltaic response in hexagonal LuMnO₃ single crystals

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Hexagonal manganites, such as h -LuMnO₃, are ferroelectric with its polar axis along the hexagonal axis and have a narrow electronic bandgap (≈ 1.5 eV). Using Pt electrodes, h -LuMnO₃ single crystals display a strong rectification, characteristic of a Schottky diode, and a large photoresponse. It is found that the short circuit photocurrent J_{sc} along the polar axis is modulated (up to 25 %) by the direction of the ferroelectric polarization P , leading to a short circuit photocurrent loop that mimics the ferroelectric polarization, and by polarization back-switching. However, a non-switchable J_{sc} persists. Diffusion photocurrent is shown to dominate current-in-plane measurements and contributes to the non-switchable J_{sc} . This observation illustrates the dramatic role of the large optical absorption in hexagonal manganites. The accompanying optical dichroism shall challenge disentangling a genuine bulk photovoltaic response in h -LuMnO₃ single crystal contributing to the non-switchable J_{sc} . Epitaxial thin films may offer a suitable alternative.

Introduction

In the quest for all-oxide photovoltaics, the discovery of a substantial photocurrent (J_{sc}) in ferroelectric BiFeO₃ (BFO),^{1,2} having an energy gap $E_g \approx 2.71$ eV and absorbing at visible range, was a hallmark that stimulated revisiting the photoresponse of narrow gap polar materials. In conventional semiconductor photovoltaic devices, electron-hole pairs created by photon absorption, are extracted by an internal electric field (E_{in}) present at device interfaces and/or by diffusion, and the resulting open circuit photovoltage (V_{oc}) is limited by the energy gap.³ In recent years, attention is driven towards the so-called bulk photovoltaic effect (BPE), occurring in all non-centrosymmetric materials, and whose distinctive features on the short circuit photocurrent (J_{sc}) and open circuit voltage (V_{oc}) are: the photocurrent $J_{sc,BPE}$ flows in absence of any internal field, V_{oc} is not bounded by E_g and the $J_{sc,BPE}$ is found to be sensitive to the polarization (P) direction of the electric field of the incoming light.⁴ Indeed, although in BFO, V_{oc} was observed to be larger than the bandgap and firstly attributed to domain walls,⁵ the unique dependence of J_{sc} on light polarization angle^{6,7} allowed to assess its BPE origin, with amplitudes (Glass coefficients) that turned out to be in reasonable agreement with first principle calculations,⁸ although the detailed microscopic mechanisms of the observed photocurrent remain unsolved.^{9,10}

On general grounds, other than $J_{sc,BPE}$, the photocurrent contains drift (J_{drift}) and diffusion (J_{diff}) current contributions, being the first driven by the presence of internal electric fields (E_{in}) and the second by charge gradients whose origin is either inhomogeneous carrier generation and/or thermal gradients. In ferroelectric capacitor structures, the Schottky barrier (SB) and the depoling field (E_d) contribute to E_{in} , giving rise to asymmetric conducting diode-like response, and permitting E_{in} to be modulated, and even reversed, upon P switching. Indeed, polarization-switchable ferroelectric diode-like response and photocurrent was reported in BiFeO₃ single crystals¹ and thin films¹¹ which were also consistent with earlier reports using wider bandgap ferroelectrics (BaTiO₃, Pb(Zr,Ti)O₃).^{12,13} On the other hand, in strongly absorbing materials, gradients of photocarriers are unavoidable and, in presence of dichroism, J_{diff} may display a dependence on the light polarization, entangled with BPE. In any event, the presence of non-switchable fields, either associate to the SB or to the presence of an imprint fields (E_{imp}) or the occurrence of diffusion, may force J_{sc} to flow in a given direction thus allowing only for asymmetric switch of the photocurrent upon ferroelectric switching.^{12–14}

Beyond BiFeO₃, attention is nowadays driven to ferroelectrics having narrower bandgap and thus of greater potential interest, such as the hexagonal LMnO₃ and LFeO₃ (L = Lu, Y, Tb, etc.)¹⁵ having $E_g < 2$ eV.^{16–20} Experiments in thin films of (Y,Lu)MnO₃ and (Tb,Yb)FeO₃ indicated that J_{sc} was switchable by the polarization direction. On the light of the discussion above, it appears that the response of the measured hexagonal films was dictated by the modulation of interfacial Schottky barrier by the polarization direction, and the bulk photovoltaic contribution was not unveiled.

Herein, we aim at elucidating the photoresponse of hexagonal LuMnO₃ single crystals, sandwiched between Pt electrodes (Pt/LuMnO₃/Pt) with focus on disentangling the different contributions to the measured photocurrent in the visible range. It is found that the short circuit photocurrent J_{sc} is regulated by the polarization direction, mimicking the measured

polarization loop $P(E)$, as a result of the modulation of the SB. In addition, a non-switchable J_{sc} contribution exists. It is observed that the non-switchable J_{sc} response contains a strong diffusion term which originates from the fast light attenuation within the LuMnO_3 crystal and the concomitant charge gradients. Therefore, the optical dichroism of $h\text{-LuMnO}_3$ will be entangled with any bulk photovoltaic response compromising unravelling their relative weight. We shall argue that epitaxial thin films may constitute an appropriate alternative.

Experimental methodology

Single crystals of $h\text{-LuMnO}_3$ (LMO) were grown by high-temperature flux technique. The crystals are hexagonal-shaped platelets, of thickness $\approx 100\ \mu\text{m}$, with the hexagonal c -axis along the perpendicular to the largest faces. Crystals were chemically cleaned by using 6.5 % HNO_3 solution to remove flux-growth residues from surfaces. Data on several crystals are reported here, named Cry- n ($n = 1, 2, 3$ and 4), all displaying similar features. Pt electrical contacts were grown at room temperature by RF-sputtering. A stencil mask ($60 \times 60\ \mu\text{m}^2$) was applied for top Pt (Pt_{top} , 7 nm thick) electrodes for all crystals. The optical transparency of 7 nm Pt at 405 nm is of about 53.5 %.²¹ The bottom side of the $h\text{-LMO}$ crystals were either fully covered by a continuous Pt layer to be used as bottom electrode (Pt_{bot} , 7nm thick) when appropriate ($\text{Pt}_{\text{top}}/h\text{-LMO}/\text{Pt}_{\text{bot}}$), or left bare ($\text{Pt}_{\text{top}}/h\text{-LMO}$). The crystals with Pt_{bot} (Cry-1, Cry-4), were fixed on silicon substrates using silver paste, while the crystals without Pt_{bot} (Cry-2, Cry-3) were fixed on a Si substrate using an insulating varnish.

Ferroelectric measurements were performed on Pt/LMO/Pt crystals, using a TF Analyzer 2000 (AixACCT GmbH.). The $P(E)$ hysteresis loops were obtained in the Dynamic Hysteresis Mode (DHM) using the Dielectric Leakage Current Compensation (DLCC) when indicated.^{22,23} We ground Pt_{bot} and apply the voltage to Pt_{bot} , thus the upward direction $P^\uparrow$ is pointing from Pt_{bot} toward Pt_{top} , and the downward direction $P^\downarrow$ is pointing from Pt_{top} toward Pt_{bot} .

Current-Voltage (I - V) measurements were recorded by a Keithley 6517B Electrometer, using bipolar triangular excitation signals from +10 V to -10 V with ≈ 0.5 s integration time (the measurements takes ≈ 100 s, equivalent to 0.01 Hz, for 200 points). In the used configuration, called top-bottom (t-b) configuration, the excitation $V^{+/-}$ (non-grounded, NG) was applied to the Pt_{top} , while Pt_{bot} was grounded (G) as sketched in Fig. 1(a). In this configuration, positive current corresponds to positive charges flow towards Pt_{bot} . Data were recorded in dark or under illumination using a blue-violet laser source ($\lambda = 405$ nm) of 3.06 eV photon energy, larger than the LMO bandgap ($E_g \approx 1.5$ eV), and power density $I_p \approx 32\ \text{W}/\text{cm}^2$, fed by a CPX400SA DC power source (AimTTi Co.). The spot diameter (around $280\ \mu\text{m}$) is much larger than the electrodes size and larger than the inter-electrode distance, allowing uniform illumination of electrodes (Fig. 1(a)).

Results

Fig. 1. (a) Experimental installation for electrical measurements in t-b configuration. The yellow arrow denotes the flow of positive carriers from V-biased towards the grounded electrode. The blue arrow denotes the light propagation of wave vector k . (b) The $J(E)$ (right axis) and $P(E)$ (left axis) loops of a Pt/LMO/Pt sample (Cry-1), recorded in dark and under illumination (45° incidence), at 1 kHz using DHM with DLCC. (c) The J - V characteristic of a Pt/LMO/Pt sample (Cry-1) in dark and under illumination (45° incidence). The red arrows indicate the prominent photoresponse under illumination.

Fig. 1(b) shows the $J(E)$ loops of the LMO sample measured in t-b configuration and the corresponding $P(E)$ loops collected at 1 kHz in Cry-1. In $J(E)$ loops the ferroelectric switching current peaks are visible as a result from the ferroelectric nature of the sample. Data in Fig. 1(b) indicates that, in dark, the h -LMO crystal has a remanent polarization $P_r \approx 7.3 \mu\text{C}/\text{cm}^2$, which is somewhat larger than in LMO films ($\approx 5 \mu\text{C}/\text{cm}^2$)¹⁸ and other h -RMO single crystals (h - $\text{YMnO}_3 \approx 4.5 \mu\text{C}/\text{cm}^2$,²⁴ h - $\text{InMnO}_3 \approx 4.4 \mu\text{C}/\text{cm}^2$,²⁵ h - $\text{HoMnO}_3 \approx 5.6 \mu\text{C}/\text{cm}^2$).²⁶ The coercive field E_c is $\approx 5.3 \text{ kV}/\text{cm}$ and displays a shift along the negative voltage direction, reflecting the presence of an imprint field ($E_{\text{imp}} \approx 1.3 \text{ kV}/\text{cm}$) within LMO, pointing downwards. Although the top and bottom electrodes are both Pt, the presence of E_{imp} is commonly observed when using *ex-situ* deposited electrodes, while there is no E_{imp} in the measurements collected in the top-top configuration shown in Fig. S1(c). Fig. 1(b) also shows the $J(E)$ and $P(E)$ loops collected under illumination. Under illumination, the sample is more conductive and the $J(E)$ loop become leakier compromising the accuracy of the corresponding $P(E)$. However, the ferroelectric E_c and E_{imp} and the height of the ferroelectric switching current peak remain almost constant, indicating that changes of the ferroelectric properties under illumination, for instance due to heating effects, are not remarkable. As shown in Fig. 1(b), E_{imp} points downwards in Cry-1. It is worth noticing that the direction of E_{imp} differs among the crystals. For instance, in Cry-4, E_{imp} is observed to point upwards (Fig. S1(a)).

In Fig. 1(c) we show J - V data collected in the $V = \pm 10 \text{ V}$ voltage range in Cry-1, in dark and under illumination. The maximum electric field used in the J - V excursion ($E_{\text{max}} = 1 \text{ kV}/\text{cm}$ at $V = 10 \text{ V}$) is lower than E_c , which guarantees that the polarization is not switched by the applied voltage during data collection. It can be appreciated in Fig. 1(c), that in dark, there is substantial rectifying diode-like effect, blocking for $V > 0$ applied to the top Pt electrode (reverse bias). It indicates the presence of a Schottky-like barrier (SB) at the top $\text{Pt}_{\text{top}}/\text{LMO}$ interface. Due to its larger area, the bottom $\text{LMO}/\text{Pt}_{\text{bot}}$ interface has a lower resistance and the J - V is governed by the more resistive $\text{Pt}_{\text{top}}/\text{LMO}$ interface. The rectification at $V > 0$ observed in dark, implies the existence of an electric field (E_{in}) pointing downwards either at the Pt/LMO interface (E_{bi}) and/or within LMO, most likely the depoling field associated to its polarization (E_d) and a possible contribution from E_{imp} that we summarize as $E_{\text{in}} = E_{\text{bi}} + E_d + E_{\text{imp}}$. In Cry-1, E_{imp} and E_{in} are both pointing downwards. In contrast, in Cry-4, E_{imp} is upwards (Fig.

S1(a)), while its rectifying behavior still indicates that E_{in} is downwards (Fig. S1(b)). This observation suggests that E_{imp} does not dominate the rectifying character of the Pt_{top}/LMO junction. It will be show below (Fig. 2) that, instead, E_{in} is slightly modulated by E_d reflecting its contribution to the SB height.^{27,28}

Under illumination (Fig. 1(c)), the strong rectifying behavior of the Pt_{top}/LMO interface is suppressed and a large current flows in reverse bias. As the photoresponse of $Pt_{top}/LMO/Pt_{bot}$ is governed by the photoresponse of the exposed Pt_{top}/LMO interface and the exposure of the LMO/Pt_{bot} interface is negligible due to the relatively large thickness of the LMO crystal ($\approx 100 \mu m$). Indeed, the absorption coefficient of h -LMO at 405 nm is of about $\alpha \approx 5 \mu m^{-1}$,²⁹ thus the absorption is about 99 % in $1 \mu m$.

Searching for fingerprints of photovoltaic response and ferroelectric polarization effects in t-b configuration, we focus on the low field region of the J - V data of Fig. 1(c), zoomed in Fig. 2(a). It can be appreciated that under illumination (blue lines and symbols), the photovoltaic response is apparent with a short circuit current density J_{sc} ($\approx 6.6 \text{ mA/cm}^2$) and an open circuit voltage V_{oc} ($\approx -0.72 \text{ V}$). At $V = 0$ the photocurrent density increases significantly under illumination ($\Delta J = \frac{J_{sc} - J_{dark, V=0}}{J_{dark, V=0}} \approx 1.1 \times 10^4$), and the responsivity ($R = \frac{J_{sc} - J_{dark, V=0}}{I_p} \approx 0.2 \text{ mA/W}$, where I_p is the laser power density) is comparable to that used in self-powered photodetectors.³⁰ To unravel a possible role of the depoling field on the observed photovoltaic response, we pre-polarized the sample with a unipolar field (E_w) ($|E_w| = 15 \text{ kV/cm}$) higher than E_c , to set the polarization state and, after a delay time $\tau_d \approx 5 \text{ s}$, we recorded the J - V in each poling state. It can be seen in Fig. 2(a) that, whereas data recorded in dark (black line and symbols) does not show any perceptible dependence on the direction of pre-polarizing voltage, this is not the case under illumination. Indeed, it can be appreciated in Fig. 2(a) that for $E_w > 0$ ($P^\downarrow$), J_{sc} is larger than for $E_w < 0$ ($P^\uparrow$).

The modulation of J_{sc} (Fig. 2(a)) is rather modest ($\frac{J_{sc}^+ - J_{sc}^-}{J_{sc}^-} \approx 10 \%$, where J_{sc}^+ and J_{sc}^- are the short circuit current density after positive and negative poling). This is partially due to the back-switching of $P^\uparrow$ to $P^\downarrow$ in a time scale shorter than 5 s (time delay τ_d of measurements in Fig. 2(a)), implying that actual measurements are done almost in a $P^\downarrow$ state.¹³ Back-switching was already anticipated by the presence of downward imprint in this sample (Cry-1) and further confirmed by data in Supp. Infor. S2. The polarization-switchable ($J_{sc\text{-switch}}$) and the unswitchable ($J_{sc\text{-unswitch}}$) contributions to J_{sc} (V_{oc}) can be disentangled using:¹⁴

$$|J_{sc\text{-switch}}| = \frac{|J_{sc}^+ - J_{sc}^-|}{2}; \quad |J_{sc\text{-unswitch}}| = \frac{|J_{sc}^+ + J_{sc}^-|}{2} \quad [1]$$

Open circuit voltages can be treated in the same way. Herein, $|J_{sc\text{-switch}}| \approx 0.313 \text{ mA/cm}^2$, $|J_{sc\text{-unswitch}}| \approx 6.55 \text{ mA/cm}^2$; $|V_{oc\text{-switch}}| \approx 0.0174 \text{ V}$, $|V_{oc\text{-unswitch}}| \approx 0.723 \text{ V}$. These data show that polarization switching can only modulate J_{sc} and V_{oc} by some 10 % and 5 % ($|\frac{V_{oc}^+ - V_{oc}^-}{V_{oc}^-}|$) respectively, due to presence of the mentioned polarization back-switching process.

To minimize back-switching effects, we have measured out-of-plane J_{sc} by using a shorter

delay time ($\tau_d \approx 0.3$ s), after applying polarization-writing voltages (V_w) for 3 s, of different amplitudes and polarities, tracing a complete $P(E)$ loop, as schematized in Fig. 2(b).^{12,13} The recorded J_{sc} - E_w curve (Fig. 2(c)) demonstrates that J_{sc} can be now modulated by the ferroelectric polarization P by about ≈ 25 %. The switchable fraction increased to $|J_{sc-switch}| \approx 0.772$ mA/cm², with $|J_{sc-unswitch}| \approx 6.91$ mA/cm². The coercive field (≈ 2.5 kV/cm) in Fig. 2(c), is somewhat smaller than in Fig. 1(b) due to the different measuring frequencies, which is lower (≈ 2 mHz) in the J_{sc} - E_w experiments of Fig. 2(c) than in Fig. 1(b) (1 kHz). We have assessed that the switching peaks of $J(E)$ loops and the coercive fields, shift to higher electric fields when increasing frequency (Fig. 2(d)), as commonly observed in ferroelectrics.^{31,32}

Fig. 2. (a) Enlarged view of the J - V curves of a polarized Pt/LMO/Pt sample (Cry-1), recorded in dark and under illumination (45° incidence); “+” and “-” signify the application of positive and negative pre-polarizing voltage. (b) Diagram indicating the measuring protocol of the dependence of the short circuit J_{sc} on pre-polarization writing V_w amplitude; (c) corresponding J_{sc} - E_w characteristic (Cry-1, normal incidence). (d) The $J(E)$ hysteresis loops (Cry-1) recorded at various frequency without DLCC.

Finally, three features in J_{sc} - E_w loop (Fig. 2(c)) are worth noticing. First, J_{sc} - E_w is shifted towards $V < 0$, implying the presence of an internal electric field, such as imprint field, pointing downwards in agreement with the $P(E)$ loops (Fig. 1(b)). Second, importantly, J_{sc} remains always positive, that is: charge (positive) flows towards the ground, irrespectively on the depoling E_d direction which switches with P . This contribution is $J_{sc-unswitch}$ (≈ 6.91 mA/cm² for Cry-1) as identified above. This offset photocurrent is found always positive for all tested crystals, i.e. samples with different signs of E_{imp} show the same current offset sign (Fig. S3), which consequently, is not dictated by neither by E_{imp} nor E_d . Therefore, $J_{sc-unswitch}$ shall originate from E_{bi} at the LMO/Pt_{top} interface with a possible contribution from BPE. Third, the direction of the imprint field determines the cycling direction of the hysteresis J_{sc} - E_w curve. For samples with E_{imp} towards bottom electrode, as Cry-1 of Fig. 2(c), the hysteresis clockwise

($J_{sc}^+ > J_{sc}^-$, Fig. 2(a)). For samples with E_{imp} towards top electrode, as Cry-4 of Fig. S3(b), the hysteresis is anticlockwise ($J_{sc}^+ < J_{sc}^-$, Fig. S3(a)).

To elucidate the origin of $J_{sc-unswitch} > 0$, we explore in the following the possible role of a diffusive contribution ($J_{sc,diff}$) and BPE ($J_{sc,BPE}$) to the photocurrent. Due to the geometry of the experimental setup (Fig. 1(a)) and the notably short penetration depth of light in comparison to film thickness ($< 1\%$), we expect that in measurements described above, $J_{sc,drift}$ and $J_{sc,diff}$ will both contribute to the photocurrent. In contrast, in-plane photocurrent should minimize any $J_{sc,drift}$ contribution and thus:

$$J_{sc} = J_{sc,BPE} + J_{sc,diff} \quad [2]$$

Accordingly, we have measured the in-plane photoresponse J_{sc} of a LMO single crystal (Fig. 3(b)), having only top electrodes. Two adjacent electrodes separated by about $20\ \mu\text{m}$ (Fig. 3(a)), labelled TP1 and TP2) have been selected and the I - V curves are recorded. Experimental evidence of the contribution of the diffusion term to J_{sc} is demonstrated in Fig. 3, where we show the J_{sc} measured using a pair of adjacent Pt_{top} electrodes while scanning the laser beam from one electrode to the other (Fig. 3(a)). Data in Fig. 3(b), displaying the recorded in-plane photocurrent (J_{sc}) as a function of the position of laser beam (at 45° incidence), show that J_{sc} changes its sign from negative to positive when switching the illumination from grounded (G) to non-grounded (NG) electrode, as expected in presence of an excess of photocharges diffusing away from the illuminated spot. The inset in Fig. 3(b) indicates when the laser beam illuminates far away from both electrodes, the photovoltaic current (photogenerated carriers) detected tends to be zero.

Fig. 3. (a) Sketch of the measurement setup in top view, to record the in-plane short circuit photocurrent between a pair of adjacent top Pt electrodes as a function of the laser beam position. (b) J_{sc} as a function of laser beam position (Cry-2, 45° incidence) by scanning the laser beam from the grounded electrode to the non-grounded electrode. Inset: photocurrent measured in a larger scan on the beam position ($400\ \mu\text{m}$)

To further assess that only the illuminated electrode plays a role in the photoresponse and to make sure only one top electrode is under illumination (spot diameter $\approx 280\ \mu\text{m}$), we have recorded the in-plane photoresponse using a pair of electrodes, separated by $\approx 260\ \mu\text{m}$, (Fig. 4(a)). Experiments have been performed by illuminating either the non-grounded electrode (red stars in Fig. 4(b)) or the grounded one (blue circles in Fig. 4(c)). Data clearly show that (holes/electrons) photocarriers always flow towards the lowest/highest potential, and are generated under the illuminated electrode. Consistently, when reversing the bias

polarity of two top electrodes (left-G in Figs. 4(a,b,c) to right-G in Figs. 4(d,e,f), respectively), the photoconductance is observed at reversed illumination condition (Figs. 4(e,f)). This shows that the photoresponse occurs mainly at the illuminated electrode.

Fig. 4. (a) In-plane electric contacts configuration with the left electrode grounded. The J - V curves of a Pt/LMO/Pt sample (Cry-3) recorded in Fig. 4(a) configuration in dark and under illumination (45° incidence) of laser on (b) the right non-grounded electrode and (c) the left grounded electrode. (d) In-plane electric contacts configuration with the right electrode grounded. The J - V curves of a Pt/LMO/Pt sample (Cry-3) recorded in Fig. 4(d) configuration in dark and under illumination (45° incidence) of laser on (b) the left non-grounded electrode and (c) the right grounded electrode.

Therefore, it follows that the diffusive contribution to the photocurrent dominates in-plane measurements in strongly absorbing h -LuMnO₃ single crystals (so-called Dember effect) [see for instance Ji et al Nat. Mater. 18, 955–962 (2019)]. Moreover, in presence of dichroism, as in h -LuMnO₃ where the absorption coefficients ($\alpha // c$ and $\alpha \perp c$) are large and anisotropic,^{29,33} the rotation of the polarization direction of the light at oblique incidence should give an angular dependence to $J_{sc,diff}$, leading to a polarization-dependent additional Dember effect contribution, that unavoidably will be convoluted with any BPE photoresponse.

Summary and conclusions

We have measured the photoresponse of ferroelectric h -LuMnO₃ crystals along the hexagonal c -axis using Pt electrodes. We have observed a strong rectifying behavior which is largely suppressed under illumination. We have shown h -LuMnO₃ crystals display a photovoltaic response with a short circuit out-of-plane photocurrent J_{sc} that can be modulated by the ferroelectric polarization (up to 25 %), suggesting that depoling field contributes to modulate interface-Schottky barrier. The sign of the photocurrent cannot be switched by polarization reversal due to the presence of a non-switchable photocurrent contribution. Using in-plane photocurrent measurements we have evidenced the presence of a non-switchable diffusive photocurrent $J_{sc,diff}$, that originates from the large photoabsorption of h -LuMnO₃, that also contributes to the measured J_{sc} . The overruling presence of a diffusive term contributing to J_{sc} , associated to the large absorption (≈ 100 % attenuation in $1 \mu\text{m}$), and the reported optical dichroism of h -LuMnO₃ may challenge disentangle a genuine bulk

photovoltaic contribution to J_{sc} in available single crystals. Probably, epitaxial thin films offer appropriate alternatives towards disentangling bulk photovoltaic contributions in dichroic materials.

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Switchable photovoltaic response in hexagonal LuMnO₃ single crystals

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- S1. Polarization loops and rectifying behavior of an LMO crystal
- S2. Back-switching of polarization in LMO crystals
- S3. Photocurrent of an LMO crystal

S1. Polarization loops and rectifying behavior of an LMO crystal

In Fig. S1(a) below we show the $P(E)$ and $I(E)$ loops recorded on the Cry-4, exemplifying a $P(E)$ loop with a different sign of E_{imp} (upwards). Here the loops are right shifted, which is opposite to the behavior of Cry-1 (see Fig. 2(a) in the main text). We stress that crystals as taken from the growth bath are up/down randomly oriented. Therefore, in presence of a growth induced imprint, observation of E_{imp} of opposite sign is to be expected. Interestingly, as show in Fig. S1(b) the rectifying behavior is identical, that is blocking for $V > 0$, irrespectively on the direction of E_{imp} .

Fig. S1. (a) The $J(E)$ and $P(E)$ loops of a Pt/LMO/Pt sample (Cry-4), in t-b, recorded in dark and under illumination (45° incidence) at 1 kHz using DHM with DLCC. (b) The J - V characteristic of a Pt/LMO/Pt sample (Cry-4), in t-b, in dark and under illumination (45° incidence). The red arrows indicate the prominent photoresponse under illumination. (c) The I - E loops of a Pt/LMO/Pt sample (Cry-4) recorded in dark at 1 kHz without DLCC, where the black curve is measured in t-b configuration, the red and blue curves are measured in t-t configuration with different distance (D1 and D2, twice bigger than the sample thickness) between the two top electrodes.

The electric coercivity is the ability of a ferroelectric material to withstand an external electric field without becoming depolarized. In Fig. S1(c), the loops in top-top configuration are symmetric and the coercive field E_c' (12 kV/cm) is almost twice the value of E_c (8 kV/cm) in t-b configuration, which is attributed to the t-t configuration consists two capacitors in series through the conducting Pt_{bot} , and the configuration is virtually independent of the distance between top electrodes. Note that in this configuration two Pt_{top} electrodes are contacted (one is grounded and the other is biased) and that the Pt_{bot} is acting as short-circuit path between the mentioned two measured ferroelectric capacitors, which is not the case for the in-plane configuration used in Figs. (3,4) of the main text.

S2. Back-switching of polarization in LMO crystals

Fig. S2. (a) Voltage train pulses applied to write the polarization state and to read, where the shaded areas correspond to the measuring intervals, as the $J(E)$ curves shown in Figs. S2. (b,c). The I_2 - E , I_4 - E loops of Pt/LMO/Pt sample (b) Cry-1 and (c) Cry-4 recorded in dark at 1 kHz without DLCC, where the orange loop corresponds to the 2nd measuring pulse with upward initial $P^\uparrow$ state, and the green loop corresponds to the 4th measuring pulse with downward initial $P^\downarrow$ state.

Fig. S2(a) displays the $V(t)$ pulse sequence in DHM mode, four bipolar triangular excitation signals are applied to Pt_{top} with a delay time τ_d (1 s) between them, which can be used to explore polarization switching back. Fig. S2(b) shows the $J(E)$ recorded on Cry-1 sample during two measuring pulses (labelled 2,4 in Fig S2(a)) following ($\tau_d = 1$ s) the writing pulses (labelled 1,3 in Fig. S2(a)). If the sample remains at $P_r^\uparrow$ state after the latter half V^- writing pulse 1, a positive switching peak should be visible during reading step 2 at $V > 0$; whereas a reverse current switching peak should be visible at $V < 0$ in step 4. However, the corresponding J_2 - E loop (Fig. S2(b)) only contains a switching peak for $V < 0$ but not for $V > 0$, implying that after $\tau_d = 1$ s, the written $P^\uparrow$ with $V < 0$ has already been switched back to $P^\downarrow$. This proves that the sample has short polarization retention ($\tau_r < 1$ s) in $P^\uparrow$. The back-switching of $P^\uparrow$ to $P^\downarrow$ may be caused by the observed downward E_{imp} existing inside LMO that can switch the oriented polarization back to downward in 1 s.^{34,35} Consistent with the above observation, the J - V measurements of Fig. 3(a), collected with $\tau_d \approx 5$ s, do show a minimal dependence on polarization, because at the measurement time (τ_d) both pre-poled states are almost in an identical remanent polarization state ($P^\downarrow$).

Similarly, Fig. S2(c) shows the $J(E)$ recorded on Cry-4 sample, where the corresponding J_4 - E loop only contains an obvious switching peak for $V > 0$ but not for $V < 0$, implying that the sample has short polarization retention ($\tau_r < 1$ s) in $P^\downarrow$ caused by the observed upward E_{imp} existing inside LMO.

S3. Photocurrent of a LMO crystal

In Fig. S3(a) we show the J - V data recorded on Cry-4 together with the corresponding $J_{sc}(V_w)$ data (Fig. S3(b)) recorded during polarization cycles, measured using the protocol indicated in Fig. 3(b) (in the main text). It can be appreciated that E_{imp} is pointing upward (Fig S1(a), Fig S3(b) and Fig. S3(c)) and Pt_{top} /LMO is rectifying for $V > 0$, as in any other crystal, irrespectively on the E_{imp} direction.

Fig. S3(c) displays $J(E)$ loops recorded at different frequencies. It can be appreciated that the coercive fields increase with frequency as commonly observed in ferroelectrics.

Fig. S3. (a) Enlarged view of the J - V curves of a polarized Pt/LMO/Pt sample (Cry-4), recorded in dark and under illumination (45° incidence). (b) The J_{sc} - E_w characteristic (Cry-4, 45° incidence). (c) The $J(E)$ hysteresis loops (Cry-4) recorded at various frequency without DLCC.