

Experiment No: MA-3978

Beamline: ID12

18-24/07/2018

Study of resistive switching mechanisms of $\text{La}_{1-x}(\text{Sr})_x\text{Mn}_{1-y}(\text{Co})_y\text{O}_{3+\delta}$ thin films by combined operando XANES and XMCD measurements.

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OBJECTIVE

The objective of the experiment was to get a direct insight into the mechanisms involved in the Resistive Switching (RS) phenomenon of manganite thin films (i.e. $\text{La}_{1-x}(\text{Sr})_x\text{Mn}_{1-y}(\text{Co})_y\text{O}_{3+\delta}$) (LSMC) by X-ray Absorption Near-Edge Spectroscopy (XANES). Experiments were conducted on pre-polarized samples in different resistance states (after the SET and the RESET operation) and under *operando* conditions (i.e. *in-situ* biasing of the films).

EXPERIMENTAL

The *ex-situ* measurements were performed in the HU-38 under vacuum and $T=298$ K in a top-up 7/8 + 1 multibunch filling mode, which provides better beam stability and a nearly constant beam current of 200 mA. The intensity detectors used were (multi-anode) ion implanted silicon photodiodes. Particularly, the k-edge of Mn (and Co) were collected using a detector in back-scattering geometry ($\text{If}4\text{dI}\phi$) and a second diode mounted at 20° with respect to the incident beam to collect the fluorescence ($\text{If}3\text{dI}\phi$). The formal valence of Mn (and Co) were estimated from the inflection point after XANES spectra normalization using references from the literature (*Phys. Rev. B* 57 (1998) 10440, *Phys. Rev. B* 61 (2000) R9237(R) and *J. Phys. Conference Series* 430 (2013) 012102)

The *operando* measurements were performed in hutch 4 HU-38 (with the chopper stopped) at atmospheric pressure under air and $T=298$ K. A 100 μm -thick Al foil attenuator was inserted to minimize the radiation damage to the samples. Besides, a chromium filter was used to reduce the Ar signal from air. A small focal length of the beam (i.e. 50 μm in horizontal and 5 μm in vertical) was achieved using 3 beryllium compound refractive lenses with a curvature of 50 μm and 2 pinholes of 300 μm . A back-scattering detector was used. Polyscans were done in the 6529.50-6589.85 energy range. Finally, aiming to improve the sensitivity of Mn OS changes related to RS response, additional spectra were acquired fixing the energy close to the Mn inflection point.

RESULTS

***Ex-situ* measurements of the LMO system:** rhombohedral and orthorhombic LMO films, which both show resistive switching (RS) response, were measured *ex-situ* aiming to correlate the structure with the chemical composition of the films. As shown in **Fig.1**, Mn presents an oxidation state (OS) of +3.17 and +3.06 for rhombohedral and orthorhombic LMO films, respectively. Thus, the rhombohedral LMO film has a higher oxygen content than the orthorhombic one.

***Ex-situ* measurements of the LSMC system, showing RS (Fig.2a):** increasing the Co concentration, the OS of both Mn and Co, increases. Particularly, the OS increases up to $\sim +3.5$ and $\sim +2.6$ for Mn and Co, respectively. However, the global valence of the B cations in the perovskite structure (i.e. ABO_3) is reduced from $\sim +3.2$ to +3 (see **Fig.2b-c**).

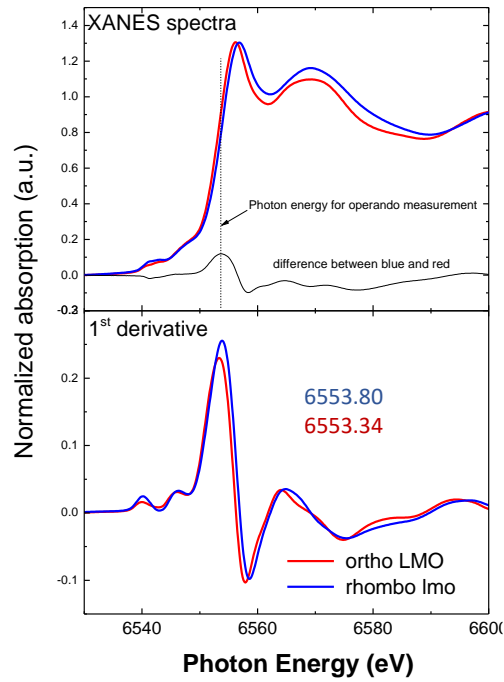


Fig.1: XANES of rhombo - and ortho - LMO films

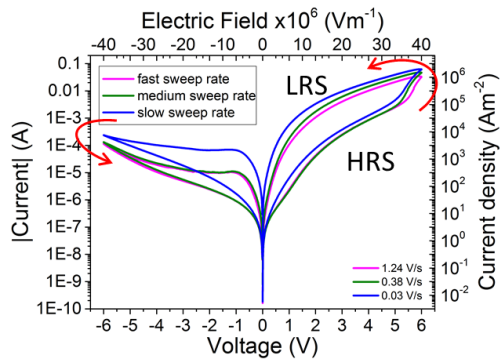


Fig.2a: RS characteristics in LSMC system

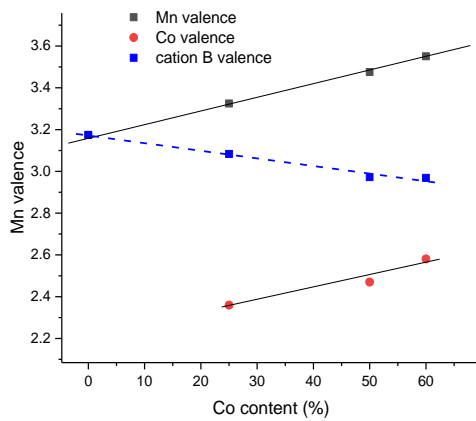
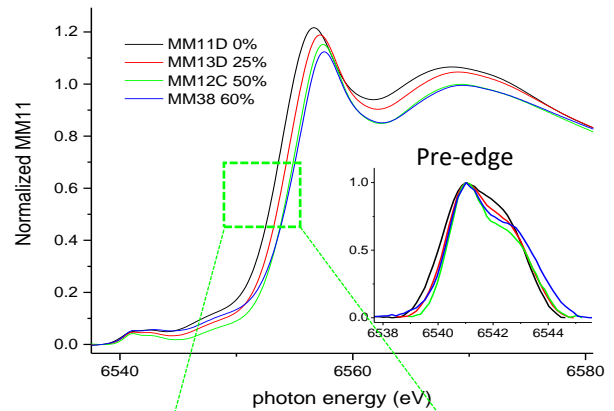


Fig.2b: Mn and Co oxidation states

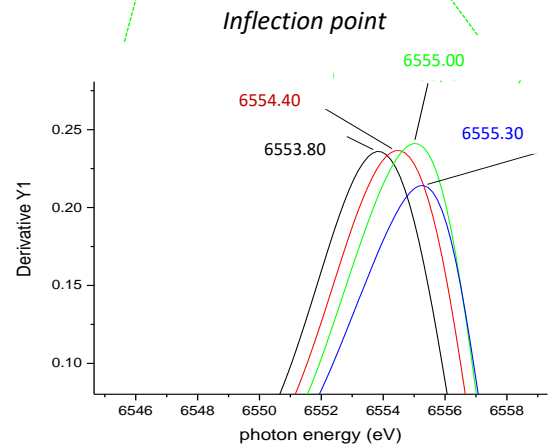


Fig.2c : Mn k-edge

Operando measurements of LMO-based ReRAM (mixture of phases, i.e. rhombo + ortho): a 100x100 μm^2 electrode which had already measured by HAXPES at Spring8 (under vacuum) was also polarized *in situ* under air (here at ID12) obtaining again the same RS response (see Fig.3a). The resistance state of LMO before switching (called ‘pristine’) was at 5 Ω and the Mn showed an OS of 3.17. The HRS (30-40 k Ω) was attained by sweeping in the positive bias. A XANES spectrum was recorded at HRS while the R value was read continuously. The OS of Mn at HRS decreased to 3.163. Next, the LRS (80 Ohms) was achieved by sweeping in the negative bias, and the Mn was reoxidized to 3.170 (see Fig.3b).

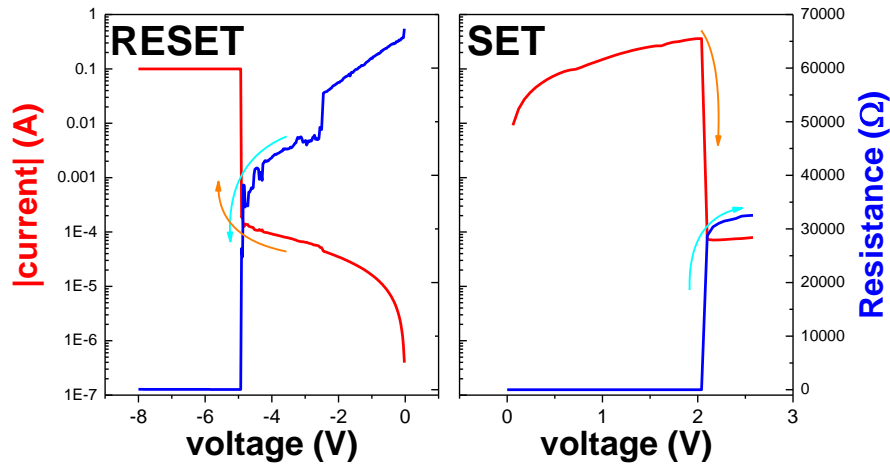
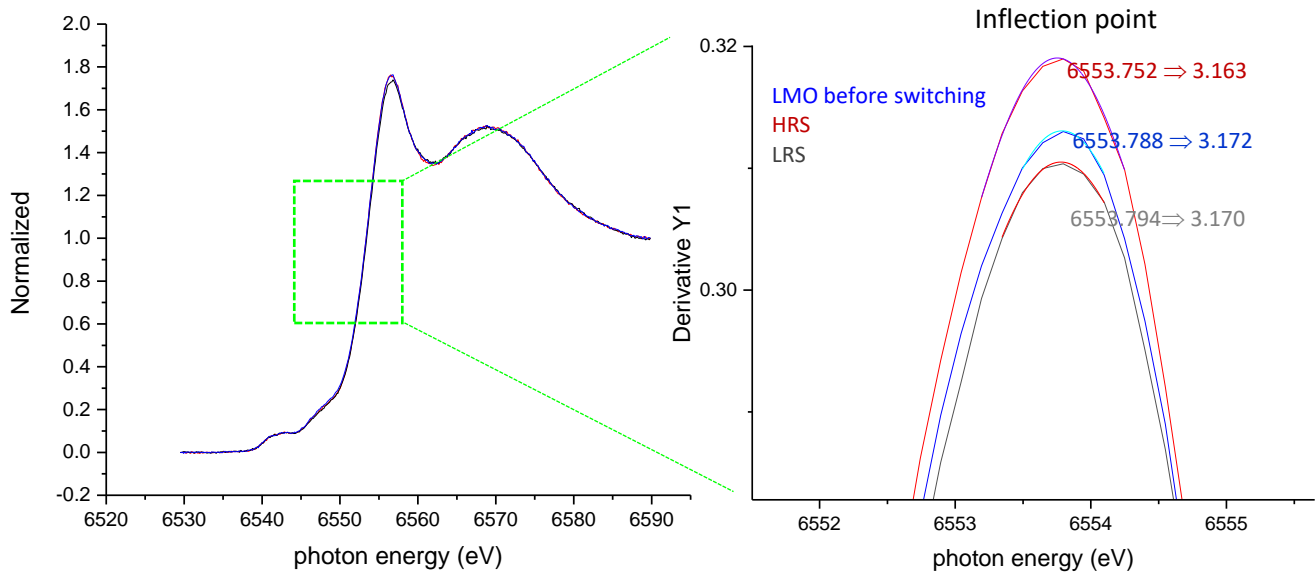


Fig.3a: polarization *in situ* under air in mixture-phases type LMO



References	
6553.34	Ortho
6553.80	Rhombo

Fig.3b: operando XANES spectra at different resistance states

Operando measurements of LMO-based ReRAM, orthorhombic-type: a pre-polarized electrode which had been electrically measured previously *ex-situ*, was polarized again *in situ* and under air at an intermediate resistance state ($\sim 2\times$ initial resistance value) (see **Fig. 4a**). The XANES spectra before and after switching were recorded, as well as the relaxation of the memory from the IRS to the initial state (i.e. LRS $\sim 5.5\Omega$), as detailed in blue, red and green dots in **Fig.4b**, respectively. After switching (at IRS), the intensity of signal was higher than the value attained in the initial state, which indicates a lower OS of Mn (in agreement with the results previously obtained). The relaxation in time suggests a low retention of this IRS.

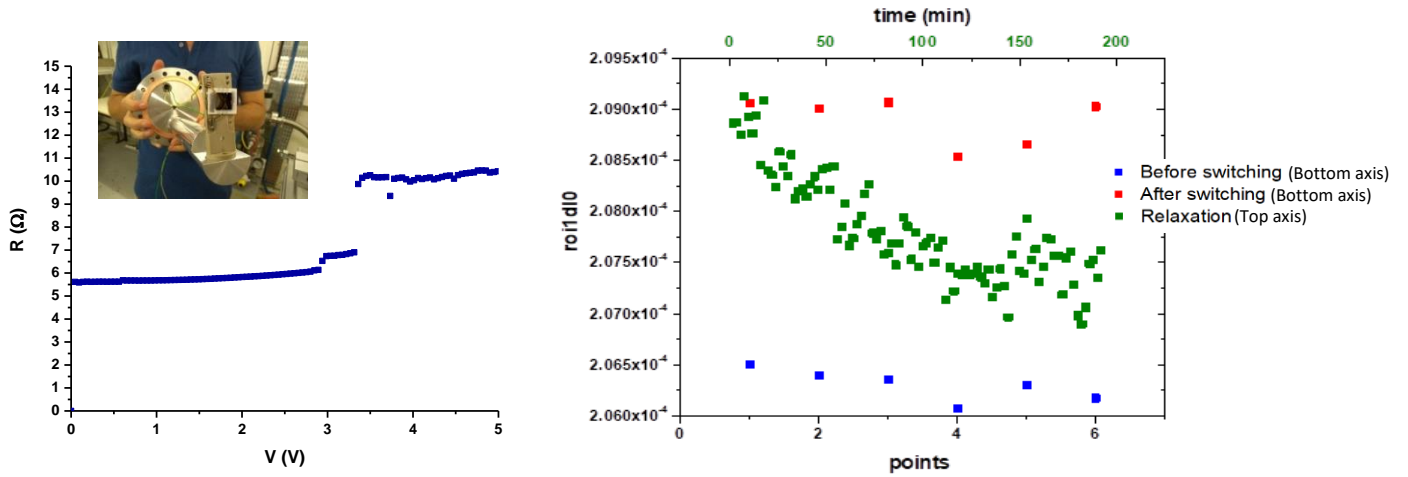


Fig.4: (a) polarization *in situ* of ortho-LMO film under air and (b) XANES response before and after switching, and relaxation as well.

CONCLUSIONS

The experiments carried out during 14 shifts in the beamline ID12 have allowed to characterize the evolution of the valence states of the Mn and Co species in LSM(C) during the RS process. *Ex-situ* and *operando* measurements suggest that Mn plays a crucial role in the switching response compensating the charge imbalance in the perovskite structure due to the oxygen ions' movement.

It is noteworthy to mention that it was decided not to perform the XMCD measurements due to the long spectra acquisition times required to obtain reliable data during *operando* measurements under air.