ESRF	**Experiment title:** ***Operando* X-ray absorption spectroscopy characterization to understand the switching mechanisms in $La_{1-x}Sr_xMnO_{3+\delta}$ memristors in top-top configuration**	**Experiment number**: MA-4802
Beamline: ID12	**Date of experiment**: from: 29/06/2021 to: 05/07/2021	**Date of report**:
Shifts: 18	**Local contact(s)**: Dr. Fabrice Wilhelm wilhelm@esrf.fr	*Received at ESRF:*

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Report:

Objective

This experiment aimed to get direct insight into the mechanism involved in Resistive Switching (RS) phenomenon in manganite thin films ($La_{1-x}Sr_xMnO_{3\pm\delta}$, LSM) by X-ray absorption Near-Edge Spectroscopy (XANES). Experiments were carried out on devices biased and programmed at different resistance states (virgin, high and low resistance states) and under *operando* conditions (i.e. *in situ* electrical bias of the device under the beam). Additionally, different regions of interest of the device were measured. Moreover, LSM thin films annealed under different conditions were measured to serve as internal comparison with the measurements conducted on the devices.

Experimental

The photon source is the APPLE-II type helical undulator HU-38 at the fundamental harmonic of its emission. The annealed samples were measured in the 2nd experimental hutch (EH3) under vacuum and at T = 298K in a top-up 7/8+1 multibunch filling mode for better beam stability and nearly constant beam current of 196 mA. The intensity detector used was a silicon photodiode and the total fluorescence yield (TFY) was collected in backscattered geometry (detector plane at 90° respect the beam vector). Particularly, the Mn K-edge was measured in grazing incidence configuration.

The operando measurements were performed in the 3rd experimental hutch (EH3) (with the chopper stopped) at atmospheric pressure in open air and at T = 298K. Two silicon drift detectors[1] were used to collect the partial fluorescence yield (PFY) in backscattering configuration. A 10 μm thick Cr foil was used to reduce elastic scattering (20 μm thick Co foil for Ni K-edge). Beam spot size of ~5 um was achieved using 2 Be parabolic lenses with a radius of curvature of 50 μm (focal image distance ~1.6 m) and it was used for precise XANES mapping. Spot size of 200 μm was achieved by changing the secondary slits and it was used for low-photon density XANES over large areas. Polyscans were done in the 6521.9 – 6622.9 eV energy range. In order to improve sensitivity and for time-resolved *operando* measurements (scale of seconds), spectra were also acquired

[1] Each silicon drift detector is a SiriusSD with an on-chip active area of 100 mm^2 equipped with a low capacitance primary aplification device (RaySpec) coupled to Falcon-X processors (XIA LLC).

at fixed energy close to the Mn K-edge inflection point. A Keithley 2410 sourcemeter was used to apply bias to the device (voltage applied on Ti contact and Pt contact grounded).

Results

The data presented in the following section serves as proof of trend. Further data analysis and careful data treatment will be done to finely determine Mn oxidation state before publishing any result.

LSM system

Table 1 summarizes the samples that were measured during the experiment. All of them were measured in HU-38 and the specified edge. Additionally, the samples with devices were measured 4 HU-38 for mapping and operando experiments. However, only sample 10 did not saturate the detector and allowed proper characterization.

	Samp. N	Film	Substrate	Comments	Film thickness (nm)	Size (mm^2)	Edge	Comments
Cube	3	LSM 20	$Si_3N_4/SiO_2/Si/SiO_2/Si_3N_4$	Oxidized	20	5x5	Mn K	
	4	LSM 20	$Si_3N_4/SiO_2/Si/SiO_2/Si_3N_4$	Reduced	20	5x5	Mn K	
	7	LSM 50	$Si_3N_4/SiO_2/Si/SiO_2/Si_3N_4$	Oxidized	21	5x5	Mn K	
	8	LSM 50	$Si_3N_4/SiO_2/Si/SiO_2/Si_3N_4$	Reduced	21	5x5	Mn K	
Devices	9	LSM 50	$LaAlO_3$ (LAO)	As dep.	21	10x10	Mn K	SDD saturation
	10	LSM 20	$Si_3N_4/SiO_2/Si/SiO_2/Si_3N_4$	As dep.	10	10x10	Mn K	SDD Mapping of devices
	13	LSM 50	$SrTiO_3$ (STO)	As dep.	21	10x10	Ti K	SDD saturation

Table 1. Summary of the samples measured by XANES.

Ex situ measurements of LSM films: the annealed samples were measured *ex situ* to correlate chemical composition with annealing conditions and for further comparison with devices (next point). As shown in Figure 1, the overall Mn oxidation state of the samples annealed in oxidizing conditions is larger than that of the equivalent samples (i.e. same Sr substitution) annealed under reducing atmosphere. At given annealing conditions, the samples with lower Sr substitution (LSM20, x=0.2) exhibit a lower Mn oxidation state.

Preliminary mapping of pristine device Ti/LSM20\Pt: using a beam size of 5 um, XANES spectra was acquired at different regions of interest of a pristine device (contact size 200x200 μm^2 separated 50 μm). The position of Mn K-edge is practically the same under the Ti contact (position 1 and 2). The same applies for the 'exposed' LSM film (position 3 and 4). The oxidation state of the Mn under the Pt contact is close to that of the exposed LSM film and at the same time, similar to the oxidized LSM20. However, the position of the K-edge under the Ti contact is largely shifted indicating strongly reduced Mn.

Mapping of devices at different resistance states: several devices were programmed (outside the hutch) at high and low resistance states (i.e. HRS and LRS, respectively). However, no difference was observed by XANES between the different resistance states. Figure 3 shows the particular case of Mn K-edge under the Ti contact. Moreover, it was found out that the I-V (and R-V) characteristics of the device after being exposed to the beam are different and the cycling sense does not allow programming LRS. Hence, the beam might be injecting current into the device and the resistive switching response cannot be triggered as in standard laboratory conditions. Different conditions were tested to solve this issue: removing tips and cables from the device, diluting the photon density of the beam, grounding the insulating Si_3N_4 substrate (scratch substrate to reach Si layer and silver paste bridge until mass). Only a low photon density beam of 200 um (density /40) allowed obtaining similar results however, no difference was yet observed and operando measurement remained unachievable.

Other samples with devices could not be measured as the SDD detector saturates due to Ti and La elements present in the substrates, $SrTiO_3$ and $LaAlO_3$, respectively, when measuring Mn K-edge. At this point, other resistive switching devices were measured (shift 17 and 18). In these devices, the memristive active layer is La_2NiO_4 and the substrate is Pt.

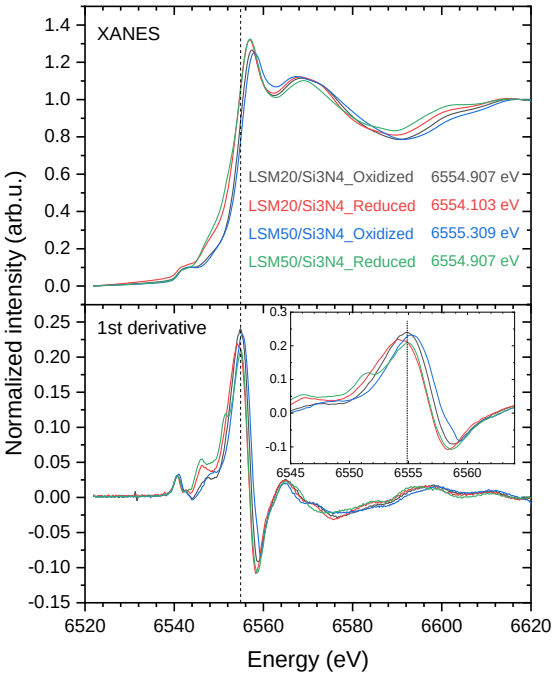

Figure 1. XANES spectra of annealed LSM thin films.

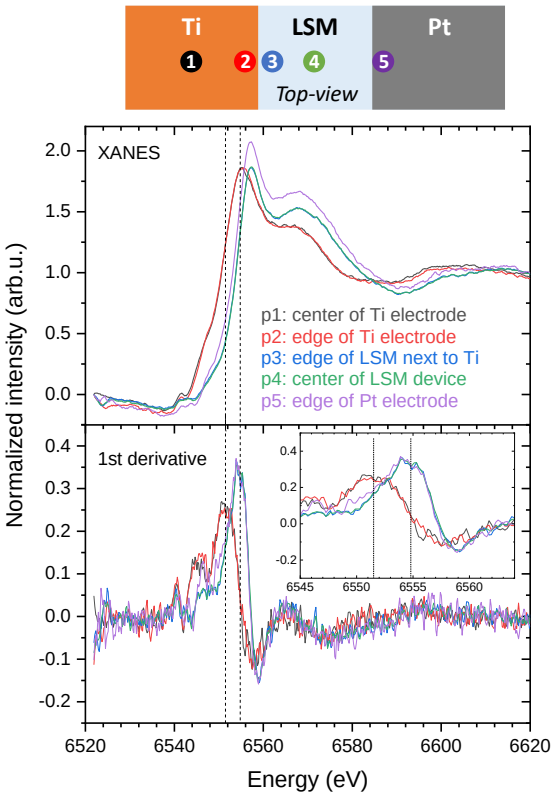

Figure 2. XANES mapping of pristine device Ti/LSM20/Pt.

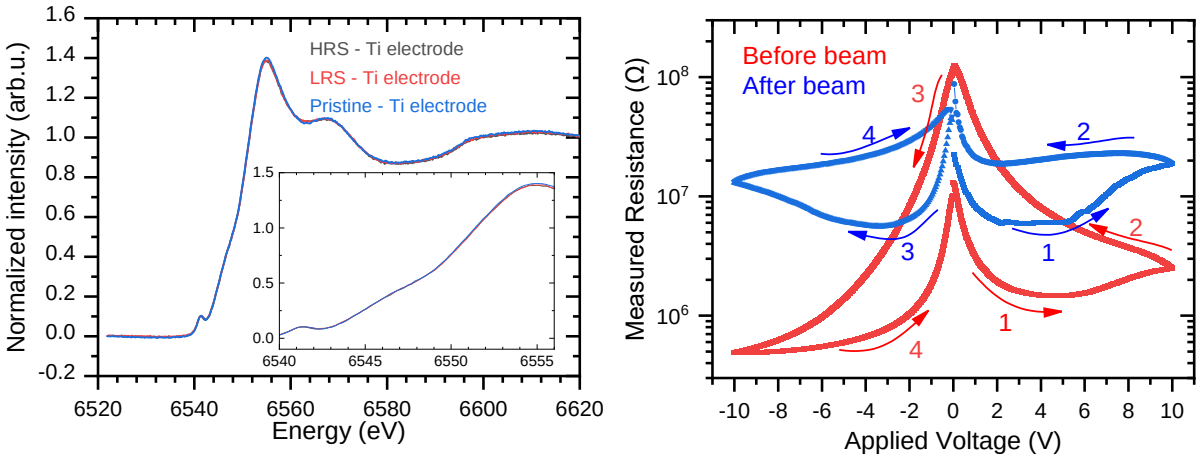

Figure 3. Left: M K-edge XANES spectra under Ti contact for devices programmed ex situ at different resistance states. Right: comparison of RV characteristics for the same device before and after being exposed to the beam.

L2NO4 system (back-up)

A 100x100 µm^2 TiN/L2NO4/Pt memristive device was used in this section. Its sketch is shown in Figure 4. La_2NiO_4 film was deposited on Pt/TiO_2/SiO_2/Si/SiO_2 substrate. TiN was then evaporated on top of L2NO4.

Preliminary *ex-situ* measurements of the TiN/$La_2NiO_{4+\delta}$(L2NO4)/Pt memristor: XANES spectra at the Ni-K edge of pristine La_2NiO_4 film without TiN electrode (black curve) and with TiN electrode on top (red curve) are shown in Figure 5. There seems to be a shift of the Ni-K edge towards lower energy when the La_2NiO_4 has TiN electrode on top. This could be to the uptake of oxygen from La_2NiO_4 memristive layer into TiN during its evaporation, even at room temperature.

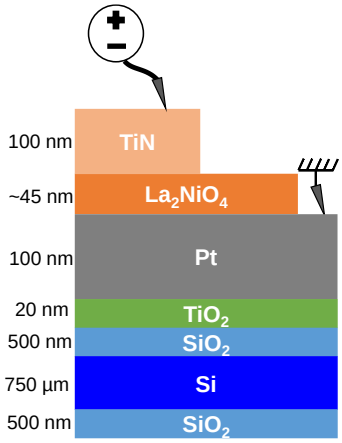

Figure 4. Sketch of TiN/L2NO4/Pt memristive device

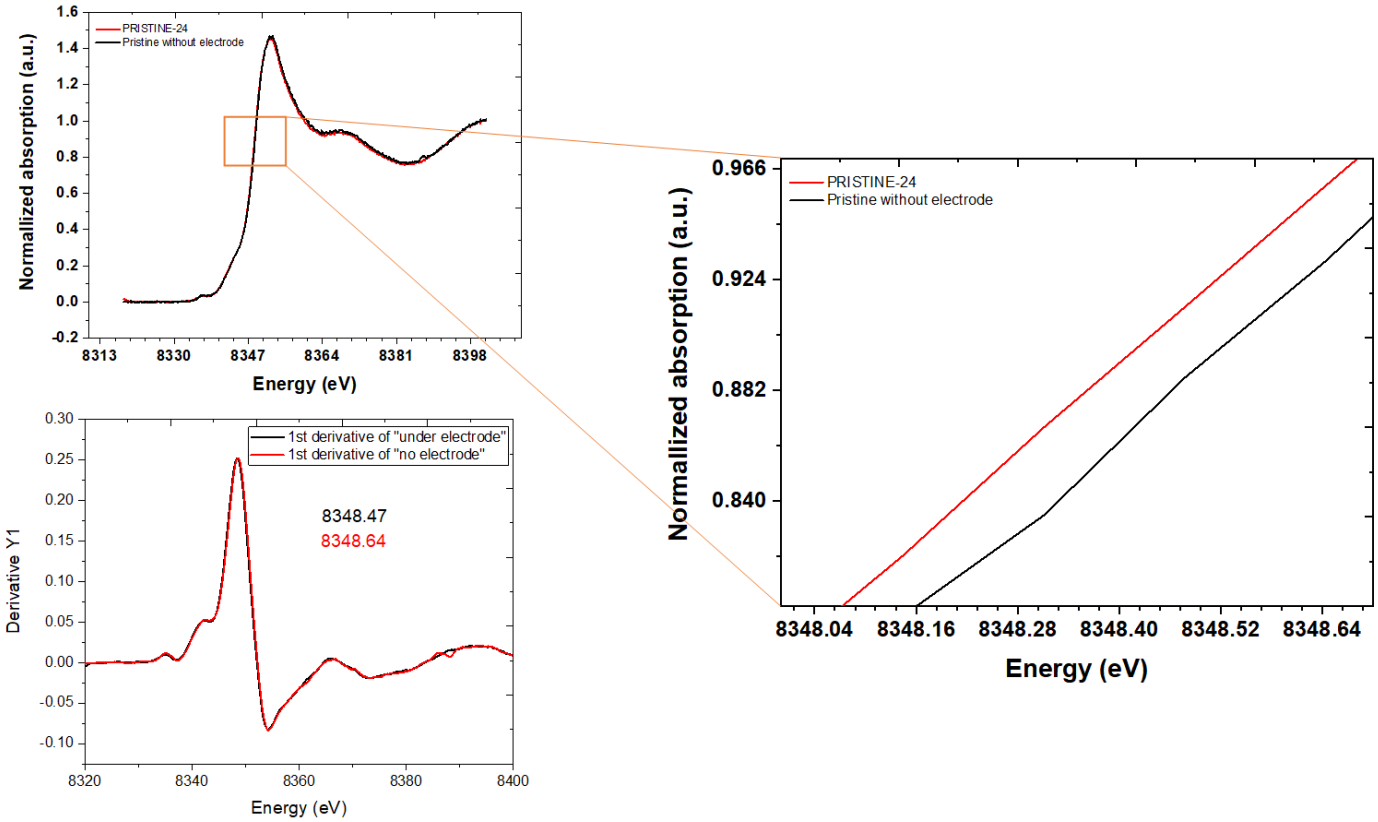

Figure 5. XANES spectra of L2NO4 film without TiN electrode (black curve) and with TiN electrode (red curve)

Preliminary o*perando* measurements of TiN/L2NO4/Pt memristive device: a 100x100 µm^2 device was used. Firstly, a XANES spectrum was carried out to find the Ni-K edge position (8348.64) (see Figure 6a and Figure 6b). Then, the X-ray absorbance was recorded vs time at the energy corresponging to the Ni-K edge position (8348.64) (see Figure 6c) while I(V) sweeps were applied to the device (see Figure 3d). The results clearly show an increase/decrease of the number of counts, which is related to two Ni oxidation states corresponding to two resistance states of the device. The intensity of signal was higher when the device was biased in positive polarity, indicating La_2NiO_4 has less oxygen, and thus that oxygen would drift and might be accumulating within TiN electrode. In contrast, when a negative is applied, the Ni-K edge shifted back to its initial signal intensity, pointing towards a back-drift of oxygen into the La_2NiO_4 memristive layer. This observation is reversible and coincides with the switching of the device.

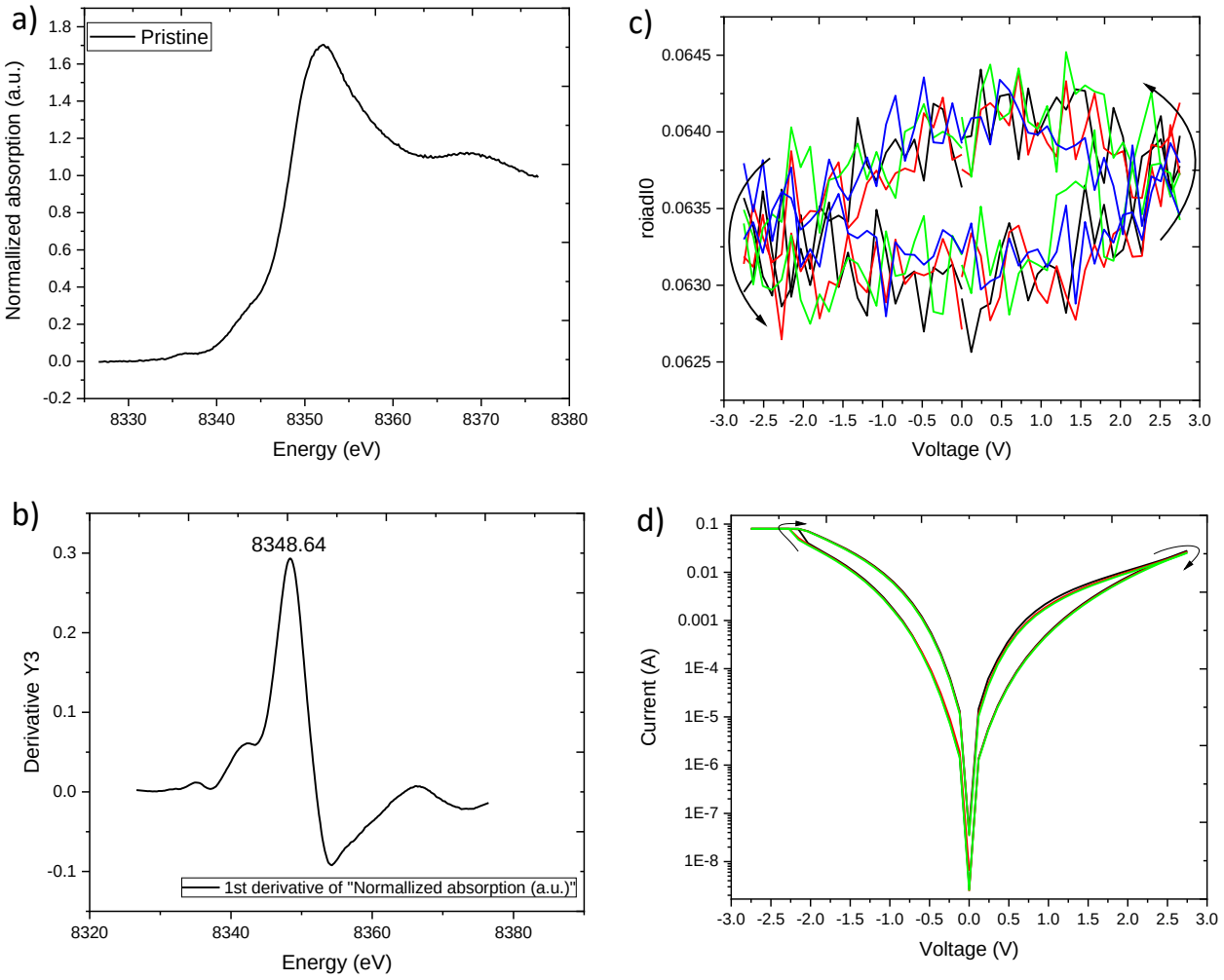

Figure 6. (a) XANES spectrum at the Ni K-edge obtained for TiN/L2NO4/Pt device at pristine state and (b) its derivative curve indicating Ni-K edge position. (c) operando XANES spectra recorded through (d) five I(V) sweeps

Conclusions

LSM system

The XANES experiments carried out in beamline ID12 have allowed to observe differences in the Mn K-edge of different samples related to changes in their oxidation state. Ex-situ measurements on samples annealed in different gas atmospheres have shown the effective change of oxygen content and concominant oxidation/reduction of Mn. Taking advantage of the small beam spot size (5 μm), XANES was acquired at different regions of interest within a device Ti/LSM20\Pt. The oxidation state of the Mn seems to be similar for that of the uncovered LSM and under the Pt contact. However, the Mn under the Ti contact is strongly reduced which suggest oxygen migration towards Ti to form TiO_x interlayer (x<2).

Mapping of devices at different resistance states was carried out, but no shift was observed for equivalent regions of interest. This might be related to the lack of Resistive Switching phenomena observed on the devices under (or that were exposed to) the beam. Their IV characteristics were different than those that were not exposed to the beam. Different conditions were assessed to have reliable RS but, unfortunately, none of them was successful. Further data analysis and device characterization will be carried out to extract conclusions, and to establish a connection between the resitance state and XANES (ex-situ and *operando*) measurements.

L2NO4 system (back-up)

The results allowed a preliminar characterization of the variation of the Ni-K edge position (valence state change) in *ex-situ* and *operando* modes. Both types of measurements suggest that the oxygen movement could play a key role in the resistive switching behavior. First, oxygen could be spontaneously uptaken when TiN is evaporated on top of La_2NiO_4. Next, the reversible change of Ni oxidation states (due to the oxygen ions' drift) during the resisitive switching process could be related to be the switching mechanism.