EELS ASSESSMENT OF CATION MIGRATION IN (001) AND (110) LCMO LAYERS AS A FUNCTION OF LAYER THICKNESS

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Mixed-valence ferromagnetic manganite films, such as $La_{2/3}Ca_{1/3}MnO_3$ (LCMO), have been the object of much attention in recent years due to their potential applications in spintronics. However, expectations have been lowered by the negligible room-temperature magnetoresistance in tunnel junctions. Although the reasons for this behavior are not yet fully known, it has been suggested that they may be linked to electronic phase separation.

Electron energy-loss spectroscopy (EELS) allows direct determination of local Mn oxidation state at the nanometric scale and is thus the most suitable technique for direct evaluation of the spatial distribution of phase separation, if in fact a phase separation exists. In addition, elemental quantification can be carried out by EELS, offering chemical information at the nanometric scale. In particular, both the Mn L_3 edge onset and the Mn L_3/L_2 intensity ratio have been demonstrated to be correlated with Mn oxidation state. Mn L_3 EELS edge and Mn L_3 / L_2 edge intensity ratio can be determined using home-made program MANGANITAS [1, 2]. This is a MATLAB routine that reads the EEL spectrum file and recalibrates energy axis. Then, it performs a fitting of both the background and continuum signal and subtracts them. Finally, it estimates Mn L_3 edge onset, fits Gaussian curves to both Mn L_3 and Mn L_2 edges, and integrates the Gaussian curves, using integration ranges that have been chosen by quantification of LCMO reference bulk samples with controlled stoichiometry.

Several EELS studies on epitaxial (001) manganite thin films have been reported in literature. A Ca migration toward manganite free surface in (001) textured LCMO/STO/LCMO structures was reported [3], whilst other authors [4] found no cation migration in the LSMO ($La_{2/3}Sr_{1/3}MnO_3$) /STO/LSMO system but did find a weak decrease in the Mn valence near the interfaces, attributed to a transfer of electrons from STO to LSMO. It has been observed that in LCMO films grown on $LaAlO_3$ substrates, which are under compressive strain, the La^{3+} ions migrate toward the top layer surface [1].

On the other hand, very thin LCMO films seem to present an anomalous behaviour when compared to thicker films. In particular, they have been reported to have a different crystal structure [5].

Little attention has been paid, so far, to the crystallography, chemistry and electronic structure of (110) LCMO films, reported to display enhanced magnetic properties when compared to their (001) counterparts [6].

In the present work, a detailed (S)TEM-EELS characterization of (001) and (110) thin films of a wide rage of thicknesses will be presented. In particular, local deviations from layer nominal stoichiometry will be evaluated, and correlated with Mn oxidation state variation. Ca migration towards free surface in thicker LCMO films will be discussed as a stress relieving mechanism competing with other possible mechanisms, such as defect formation [2]. An anomalous thickness range (thinnest films) where a La migration towards free surface is promoted will also be discussed.

References:

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Figures:

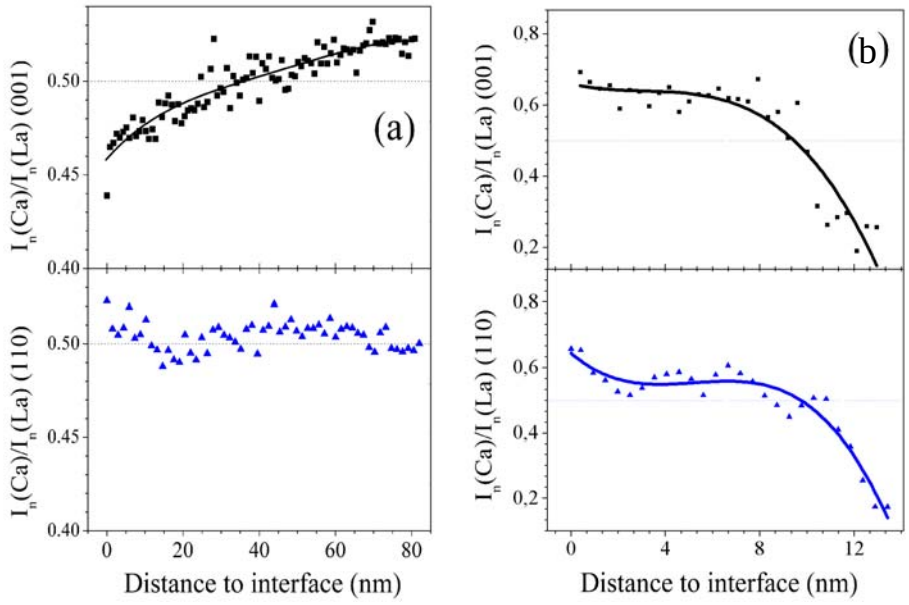

Fig. 1. (a) La/Ca ratio along (001) and (110) ~80 nm (a) and ~13 nm (b) thick LCMO films.