ESRF

Experiment title: Oxidation state of manganese and ruthenium in mixed valence $La_{1-x}Na_xMn_{1-y}Ru_yO_3$ manganite	Experiment number: 08-01-684

Beamline: BM08	**Date of experiment**: from: 8 September 2004 to: 11 September 2004	**Date of report**: 17 April 2005
Shifts: 6	**Local contact(s)**: **Dr. Chiara Maurizio**	*Received at ESRF:*

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Report:

The main objective of this study was to effectively determine the oxidation state of Ru and Mn in the samples $La_{1-x}Na_xMn_{1-y}Ru_yO_{3+\delta}$ with $x = 0.05$ and 0.15 and $y = 0.05$ and 0.15 considering also the effects of thermal annealings in pure oxygen and argon, i.e. the oxygen content variation.

The experiment were succesfully carried out on the BM08 beamline (GILDA) where the beam was always available and the beamline-staff support was very effective. XAS spectra were collected for all the sample at both Ru-K and Mn-K edeges. ΔE_0 (eV) Ru-K (agains the $CaRuO_3$ standard) and Mn-K trends (agains $LaMnO_3$ standard) *vs.* Ru content for all the series of samples are reported in Figure 1.

The main findings of our work can be summarized as follows:

1. The mean oxidation state of Ru ions is always $\leq +4$; while the one of Mn is never lower than +3, which can not be exaplined by considering the only reduction of Mn as a consequence of Ru doping;

2. XAS measurements clearly indicated that a simple Mn reduction is not the only mechanism involved in charge compensation when Ru is introduced in the manganite lattice. In particular, at a relatively low intrinsic hole doping ($x = 0.05$) a stronger influence of oxygen stoichiometry variation seems to play a considerable role in keeping the system neutral while at higher holes concentration a more direct electron exchange between Mn^{3+}/Mn^{4+} and Ru^{3+}/Ru^{4+} couples is present. In order to account

for the valence state variation observed we propose an additional compensation mechanism based on the following quasi-chemical equilibrium:

$$2Mn_{Mn}^{X} + 2RuO_2 \Leftrightarrow 2Ru_{Mn}^{\bullet} + O_O^X + \frac{1}{3}V_{Mn}''' + \frac{1}{3}V_{La}''' + Mn_2O_3$$
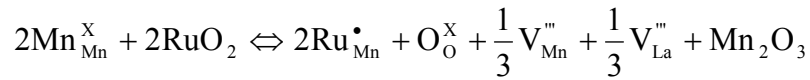
For both high and low Na doping both cases, the mechanisms involved assure to avoid a too strong manganese reduction. Moreover, an efficient redox system is present in the $x = 0.15$ samples which allows to keep the average Mn valence state nearly constant even though lower with respect to the Ru-free compound.
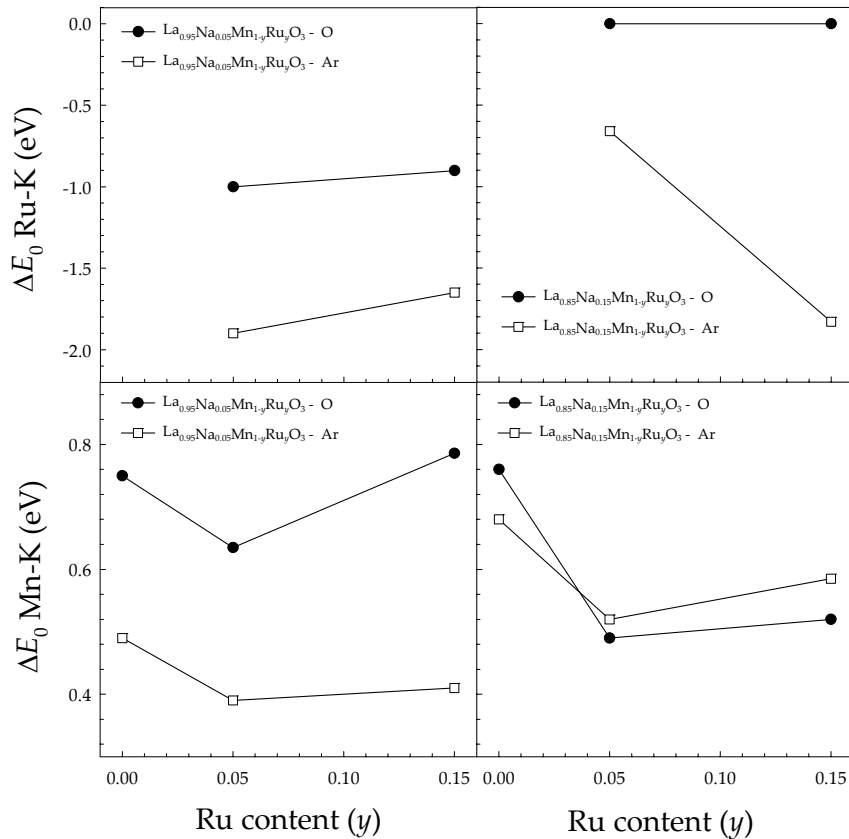

Figure 1

Publication derived from this work:

L. Malavasi, M.C. Mozzati, E. Di Tullio, C. Tealdi e G. Flor, "**Redox behaviour of Ru-doped manganites",** *Phys. Rev. B, in press* (2005)