



	Experiment title: High-resolution XANES spectroscopy in manganese perovskites $RE_{1-x}D_xMnO_3$ (RE:La, Tb, Pr, Nd; D:Ca, Sr).	Experiment number: HE-498
Beamline: ID 26	Date of experiment: from: 04/02/1999 to: 15/02/1999	Date of report: 31/08/2000
Shifts: 24	Local contact(s): Christophe Gauthier	<i>Received at ESRF:</i>
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Report:

The electronic state of the Mn atom in mixed valence manganites has been studied by means of high-resolution X-ray absorption spectroscopy at the Mn K-edge. The experiments have been carried out at the beam line ID 26 at the E.S.R.F. (Grenoble, France). Room temperature XANES spectra of $RE_{1-x}Ca_xMnO_3$ (RE:La, Tb; $x=0, 0.33, 0.5, 0.67, 1$) and $RE_{0.5}D_{0.5}MnO_3$ (RE:La, Tb, Pr, Nd; D:Ca, Sr) series were recorded simultaneously, both, measuring the total fluorescence yield (TFY) intensity and the Mn K_β fluorescence line intensity at the maximum of the emission peak (see figure 1). The spectra obtained by measuring the Mn K_β fluorescence show better edge resolution, beyond the broadening due to the core-hole lifetime. We noted that the TFY spectra could be obtained from the K_β fluorescence spectra by convolution with a Lorentzian function of about 0.8 eV width.

The spectral line shapes are similar in the two measurements modes for all the samples. However, the pre-edge structures are better resolved and the slope at the edge is sharper for the high-resolution XANES spectra. In order to determine the Mn valence state, we have also compared the high-resolution experimental spectra with the averaged spectra obtained by a weighted addition of the end-members ones ($LaMnO_3$ and $CaMnO_3$). Although the edge position is well reproduced, strong differences are found between the calculated and the experimental spectra, in particular, at the K absorption edge.

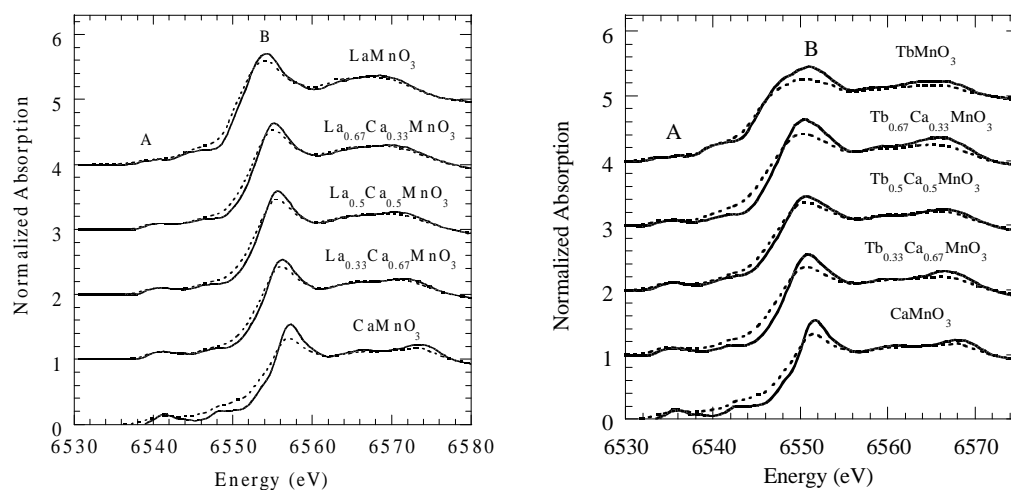


Figure 1. Normalized XANES spectra of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (left) and $\text{Tb}_{1-x}\text{Ca}_x\text{MnO}_3$ (right) series at room temperature, recorded by the total fluorescence yield (solid line) and the $\text{Mn K}\beta$ fluorescence line (dashed line).

The shape of the XANES spectrum also depends on the particular local structure of the absorbing atom. In order to check how small changes in the local structure affect to the XANES spectrum, we have also analyzed the high-resolution XANES spectra of several $\text{RE}_{0.5}\text{D}_{0.5}\text{MnO}_3$ samples with different rare earth or divalent cations, but keeping constant the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio equal to 1 (see figure 2).

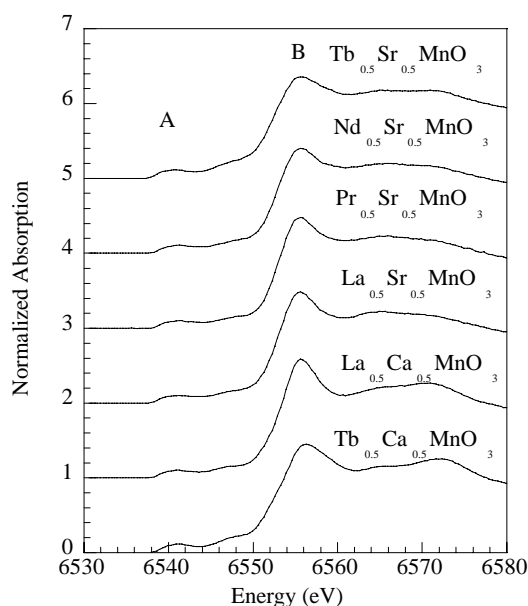


Figure 2. Normalized high-resolution XANES spectra recorded by the $\text{Mn K}\beta$ fluorescence line of the $\text{RE}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($\text{RE}=\text{La}, \text{Tb}, \text{Nd}, \text{Pr}$) and $\text{RE}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\text{RE}=\text{La}, \text{Tb}$) samples at room temperature.

Similar spectra are obtained for all the samples. Small variations in the intensity of the main resonance (K-edge) are found, but the main differences among the various spectra are related to the local structure, at energies above the absorption edge. Therefore, the absorption edge is the same for all these manganites and it could be used as a finger print of the electronic state of the Mn atom in these compounds. In consequence, the differences obtained for the main edge resonance between the experimental high-resolution and the simulated spectra cannot be associated to local structure effects.