ESRF	**Experiment title:** A XANES spectroscopy study of the $LaNi_{1-x}Mn_xO_{3+y}$ perovskites.	**Experiment number**: HE-498
Beamline: ID26	**Date of experiment**: from: 04/02/1999 to: 15/02/1999	**Date of report**: 31/08/2000
Shifts: 24	**Local contact(s)**: Christophe Gauthier	*Received at ESRF:*

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Report:

X-ray absorption spectroscopy has been used to study the oxidation state and the local structure around the transition metal atoms, Ni and Mn, in $LaNi_{1-x}Mn_xO_{3.x}$ perovskites. Several samples (x=0.1, 0.25, 0.5, 0.75 and 0.9), obtained from different synthetic procedures, have been analysed. The experiments have been carried out at the beam line ID 26 at the E.S.R.F. (Grenoble, France). Absorption spectra have been recorded in both, transmission and fluorescence modes, at room temperature, obtained equivalent spectra in the two cases.

Figure 1(a) shows the Mn K-edge XANES spectra for the $LaNi_{1-x}Mn_xO_{3.x}$ (x=0.25, 0.5 and 0.75) compounds and Figure 1(b) shows the Ni K-edge spectrum of the $LaNi_{0.5}Mn_{0.5}O_{3.08}$ sample, in comparison with those of the reference compounds considered for the Mn^{3+} ($LaMnO_3$), Mn^{4+} ($CaMnO_3$), Ni^{2+} (Pr_2NiO_4) and Ni^{3+} ($LaNiO_3$), respectively.
All the Mn K-edge spectra show similar features, being the edge position placed between the $LaMnO_3$ and $CaMnO_3$ ones, in agreement with previous results reported for the Mn valence state in the mixed-valence manganites[1]. XANES spectra at the Ni K-edge also point to a mixed valence state for the Ni ions in these systems, but the chemical shift between Ni^{2+} and Ni^{3+} (about 2 eV) is smaller than the one found between Mn^{3+} and Mn^{4+} (about 4.4 eV).

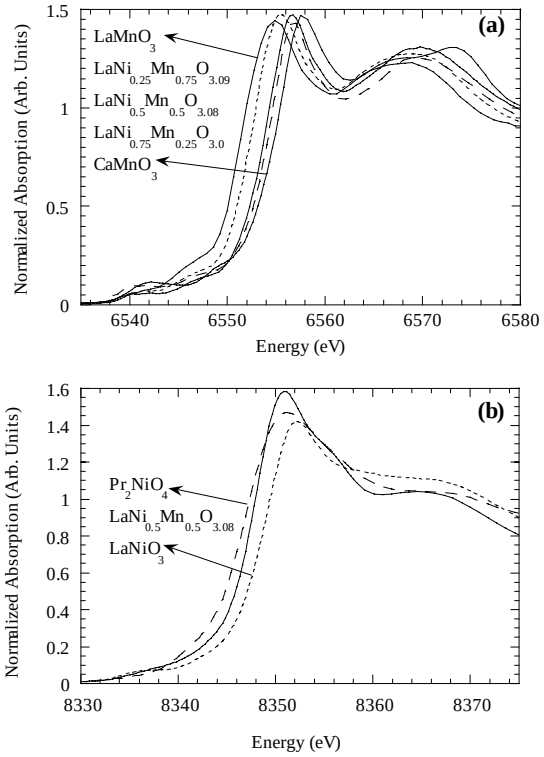

Figure 1. (a) Normalized Mn K-edge XANES spectra of $LaNi_{1-x}Mn_xO_{3.x}$ (x=0.25, 0.5 and 0.75) compounds at room temperature. (b) Normalized Ni K-edge XANES spectra of the $LaNi_{0.5}Mn_{0.5}O_{3.08}$ compound at room temperature.

The local structure has been investigated by means of the EXAFS technique[2]. The first coordination shell analysis at the Mn K-edge indicates a contraction of the MnO_6 octahedra along the $LaNi_{1-x}Mn_xO_{3.x}$ series by increasing the Ni content. Accordingly, an expansion of the NiO_6 octahedra is found at the Ni K-edge by increasing the Mn content up to x=0.5. This result agrees with the presence of an effective electronic transfer among Mn and Ni metal transition atoms, as it has been already suggested by the analysis of the respective XANES spectra.

Moreover, the EXAFS analysis also reflects the structural change observed in this series from a rhombohedral perovskite (x>0.5) to a orthorhombic perovskite (x<0.5), obtained from the crsytallographic study[3].

References

[1] G. Subías, J. García, M. G. Proietti and J. Blasco, *Phys. Rev. B* **56** (13), 8183 (1997).

[2] M. C. Sánchez, G. Subías, J. Pérez-Cacho, J. García and J. Blasco, *Proceedings of the XAFS XI conference*, Japan (2000), to be published in Journal of Synchrotron Radiation.

[3] J. Blasco, M. C. Sánchez, J. Pérez-Cacho, J. García, G. Subías and J. Campo, (2000), submitted to *Chem. Mat.*