Local structure and oxidation state of Mn and Ni atoms in $LaNi_{1-x}Mn_xO_{3+\delta}$ perovskites

M. C. Sánchez,[a]* G. Subías,[a] J. Pérez-Cacho,[a] J. García[a] and J. Blasco[a]

[a]*Instituto de Ciencia de Materiales de Aragón, C.S.I.C.-Universidad de Zaragoza, CL Pedro Cerbuna 12, 50009 Zaragoza, Spain.
Email:csanchez@posta.unizar.es*

X-ray absorption spectroscopy has been used to study $LaNi_{1-x}Mn_xO_{3+\delta}$ perovskites (x= 0.1, 0.25, 0.5, 0.75, 0.9). We have analysed both, the oxidation state and the local structure around the transition metal atoms. XANES spectra of these samples suggest a mixed valence state for both transition metal atoms. The Mn K-edge is shifted to high energies as the Ni content is increased up to x=0.5. The opposite behavior is found instead, for the Ni K-edge. Samples with x=0.5 and x=0.25 present the Mn K-edge at the same energy but the absorption features are different for both samples. The local structure has also been studied by means of the EXAFS technique. The first coordination shell nicely reflects the structural change observed in this series from rhombohedral perovskites (x>0.5) to orthorhombic perovskites (x<0.5). The changes in the local structure for Ni and Mn atoms agree with the variation of the oxidation state observed in the XANES spectra.

Keywords: mixed valence, charge transfer, mixed oxides.

1. Introduction

Mixed (transition metal / rare earth) oxides have been widely studied due to their various electrical and magnetic properties (Tsuda, N. *et al.*, 1991). Nowadays, doped manganese perovskites have attracted attention because of the discovery of colossal magnetoresistance (Coey *et al.*, 1999). The doped $RE_{1-x}A_xMnO_3$ (RE= rare earth, and A= Ba, Sr, Ca) oxides, which are mixed-valence compounds with nominal Mn^{3+} and Mn^{4+}, develop a paramagnetic to ferromagnetic transition coupled to a large decrease of the resistivity for a determined range of x. The ferromagnetic ground state was interpreted in the past by means of the double-exchange interaction (Zener, 1951) but recent studies put in evidence that further interactions, such as the electron-phonon coupling, must be taken into account (Millis *et al.*, 1996). The presence of magnetoresistance properties has stimulated the research in other kind of oxides. In particular, ferromagnetic oxides with Mn in a mixed valence state seem to be good candidates to show magnetoresistance.

Goodenough *et al.* (1961) have reported that ternary oxides $LaMe_{1-x}Mn_xO_3$ (Me = Ni, Co) are ferromagnetic. Blasse (1965) suggested that the ferromagnetism is governed by the positive super-exchange interaction between Ni^{2+} (or Co^{2+}) and Mn^{4+} ions via the oxygen anions. However, spectroscopic studies on $LaMn_{1-x}Co_xO_3$ samples suggest a mixture of Mn^{3+} and Mn^{4+} in this series and a double-exchange mechanism is proposed for these compounds (Park *et al.*, 1997). Accordingly, the electronic configuration of the transition metal atoms in these perovskites is an open matter. Similar conclusions can be deduced for the

electronic configurations of $LaNi_{1-x}Mn_xO_3$ materials. They appear to depend on the synthesis route, while those from the high-temperature solid-state method are reported (Blasse, 1969; Asai *et al.*, 1979; Sonobe *et al.*, 1992) to have Mn^{4+} and Ni^{2+}, those from low-temperature precursor routes are reported (Vasanthacharya *et al.*, 1984) to have Mn^{3+} and Ni^{3+}. Therefore, the study of the local structure and the oxidation state of the transition metal atoms is desirable in order to understand the intrinsic properties of this series. We report here a spectroscopic study of several $LaNi_{1-x}Mn_xO_3$ samples. The aim of this work is to test the oxidation state of the transition metal atoms (Ni, Mn) and to investigate the evolution of the different local structures along the series. We have studied several samples obtained from different synthetic procedures and an oxygen content well defined.

2. Experimental

The preparation and characterization of $LaNi_{1-x}Mn_xO_3$ (x=0, 0.1, 0.25, 0.5, 0.75, 0.9, 1) samples have been reported elsewhere (Blasco *et al.*, 2000). The oxygen content of the samples was determined from thermogravimetric analysis in a reducing atmosphere (Ar/H_2 = 95/5). The heating rate was 10ºC/min up to 950º C. The samples studied in this work have the following chemical compositions: $LaNiO_3$, $LaNi_{0.9}Mn_{0.1}O_{3.02}$, $LaNi_{0.75}Mn_{0.25}O_{3.0}$, $LaNi_{0.5}Mn_{0.5}O_{3.08}$, $LaNi_{0.25}Mn_{0.75}O_{3.09}$, $LaNi_{0.25}Mn_{0.75}O_{2.97}$, $LaNi_{0.1}Mn_{0.9}O_{3.13}$, $LaNi_{0.1}Mn_{0.9}O_{3.0}$, $LaMnO_{3.0}$.

X-ray absorption measurements were carried out at beam lines 7.1 and 8.1 at S.R.S. (Daresbury) and at beam line ID26 at E.S.R.F. (Grenoble). The SRS storage ring was operating at 2 GeV with an average current of 150 mA. The ESRF storage ring was operated at 6 GeV with a maximum stored current of about 190 mA. The radiation was monochromatized using a double Si(111) crystal. Harmonic rejection was performed by slightly detuning of the two crystals. The energy resolution, $\Delta E/E$, was estimated to be about 2×10^{-4}. Ionization chambers were used to detect the incident and transmitted flux at SRS while silicon photo-diodes were used at ESRF. The absorption spectra were recorded in both, the transmission and fluorescence modes at room temperature and equivalent spectra are obtained in both cases. This allows us to discard any significant contribution to our spectra arising from the La L_I-edge.

The extraction of the XANES spectra was carried out using standard procedures (Koninsberger *et al.*, 1988). In order to compare different samples, the XANES spectra were normalized to the high energy of the spectrum after background subtraction. The experimental EXAFS signal has been also extracted from the raw data following standard procedures (Koninsberger *et al.*, 1988).

3. Results

3.1 XANES

Fig 1(a) shows the Mn K-edge XANES spectra of $LaNi_{0.75}Mn_{0.25}O_{3.0}$, $LaNi_{0.5}Mn_{0.5}O_{3.08}$ and $LaNi_{0.25}Mn_{0.75}O_{3.09}$ compounds. They are compared with those of $LaMnO_3$ and $CaMnO_3$ samples. All the spectra show similar features, as expected for compounds with a similar perovskite structure. The main difference among the spectra is the energy position of the Mn absorption edge. The edge for $LaNi_{1-x}Mn_xO_{3+\delta}$ samples is placed between the $LaMnO_3$ and $CaMnO_3$ ones. Taking the absorption edge position as the inflection point of the edge in Fig

magnetic materials

1(a), a chemical shift of 4.4 eV is obtained between $LaMnO_3$ and $CaMnO_3$ (i.e. between Mn^{3+} and Mn^{4+}). This value nicely agrees with the reported ones in the literature (Subías *et al.*, 1997). Accordingly, a chemical shift of 1.5 eV is obtained for $LaNi_{0.25}Mn_{0.75}O_{3.09}$ compound while both, $LaNi_{0.5}Mn_{0.5}O_{3.08}$ and $LaNi_{0.75}Mn_{0.25}O_{3.0}$ exhibit the same chemical shift of 3.3 eV. The presence of a systematic shift in the absorption edge position has been correlated with the valence state of Mn atoms in manganites (Subías *et al.*, 1997). Considering a linear relationship between them, we find an oxidation state of $Mn^{+3.34}$ for the $LaNi_{0.25}Mn_{0.75}O_{3.0}$ sample and of $Mn^{+3.77}$ for $LaNi_{0.5}Mn_{0.5}O_{3.08}$ and $LaNi_{0.75}Mn_{0.25}O_{3.0}$ compounds. This result suggests a mixed valence state for transition metal atoms in these systems. Therefore, the rough ionic formulae for these samples would be $LaNi^{+2.7}_{0.25}Mn^{+3.34}_{0.75}O_{3.09}$, $LaNi^{+2.55}_{0.5}Mn^{+3.77}_{0.5}O_{3.08}$ and $LaNi^{+2.74}_{0.75}Mn^{+3.77}_{0.25}O_{3.0}$, respectively. XANES spectra at the Ni K-edge also points out to a mixed valence for the Ni ions in these systems, as it can be observed in Fig 1(b). Here, we compare the XANES spectra of the $LaNi_{0.5}Mn_{0.5}O_{3.08}$ sample with those of Pr_2NiO_4 and $LaNiO_3$ samples. The chemical shift between Ni^{3+} and Ni^{2+} is smaller than the one found between Mn^{3+} and Mn^{4+} (2 eV for Ni^{3+}/Ni^{2+}). Moreover, the absorption edge position for $LaNi_{0.5}Mn_{0.5}O_{3.08}$ is also located between Pr_2NiO_4 (Ni^{2+}) and $LaNiO_3$ (Ni^{3+}).
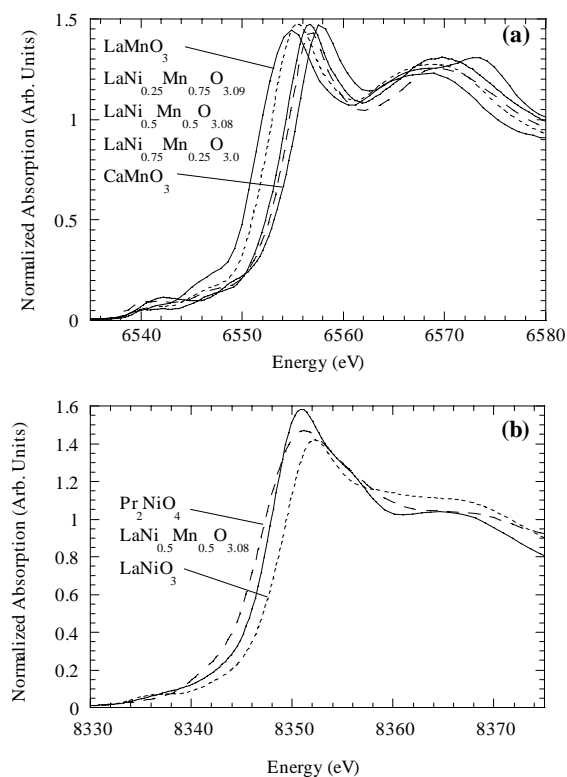

Figure 1
(a) Normalized Mn K-edge XANES spectra of $LaMnO_3$, $LaNi_{0.75}Mn_{0.25}O_{3.09}$, $LaNi_{0.5}Mn_{0.5}O_{3.08}$, $LaNi_{0.75}Mn_{0.25}O_{3.0}$ and $CaMnO_3$ compounds. (b) Normalized Ni K-edge XANES spectra of Pr_2NiO_4, $LaNi_{0.5}Mn_{0.5}O_{3.08}$, and $LaNiO_3$ compounds.

Finally, we want to focus on the absorption spectra of $LaNi_{0.75}Mn_{0.25}O_{3.0}$ and $LaNi_{0.5}Mn_{0.5}O_{3.08}$ samples. There is some works casting doubts on the existence of single phases for $LaNi_{1-x}Mn_xO_3$ compounds with $x \leq 0.5$. Blasse *et al.* (1965) suggest a

mixture of $LaNiO3$ and $LaNi_{0.5}Mn_{0.5}O_3$ for this sample. Our study shows a similar edge position for both, $LaNi_{0.75}Mn_{0.25}O_{3.0}$ and $LaNi_{0.5}Mn_{0.5}O_{3.08}$ but the resonances above the absorption edge are clearly different. This fact seems to confirm the existence of a solid solution in the $LaNi_{0.75}Mn_{0.25}O_{3.0}$ sample because the same absorption spectra at the Mn K-edge would be expected for both, a pure $LaNi_{0.5}Mn_{0.5}O_3$ compound and a solid solution of $LaNi_{0.5}Mn_{0.5}O_3$ and $LaNiO_3$ ones.

1.2 EXAFS

EXAFS measurements have been carried out on selected $LaNi_{1-x}Mn_xO_3$ samples in order to study the local structure around both, Mn and Ni atoms. Figure 2(a) displays the Fourier transform of the k-weighted EXAFS spectra at the Mn K-edge, taken between 2.8 and 12 $Å^{-1}$. The intensity of the first peak, related to the first oxygen coordination shell, rises as the Mn content decreases, pointing out to a reduction of the distortion of the MnO_6 octahedra. The decrease of the MnO_6 distortion could be ascribed to the disappearing of the static Jahn-Teller distortion of the $LaMnO_3$ and to the diminution of the orthorhombic distortion in the unit cell, as the Mn content decreases. According to the crystallographic results (Blasco *et al.*, 2000), $LaNi_{1-x}Mn_xO_3$ samples with x>0.5 exhibit an orthorhombic unit cell, while samples with x<0.5 show a rhombohedral unit cell. Interestingly, $LaNi_{0.5}Mn_{0.5}O_{3.08}$ develops a structural phase transition from rhombohedral to orthorhombic structure with decreasing temperature at around 300 K. The rhombohedral unit cell has a regular MnO_6 octahedron. Moreover, the increase of the intensity of the peak related to the second coordination shell as the Mn content decreases can also be ascribed to the decrease of the orthorhombic distortion in the unit cell.
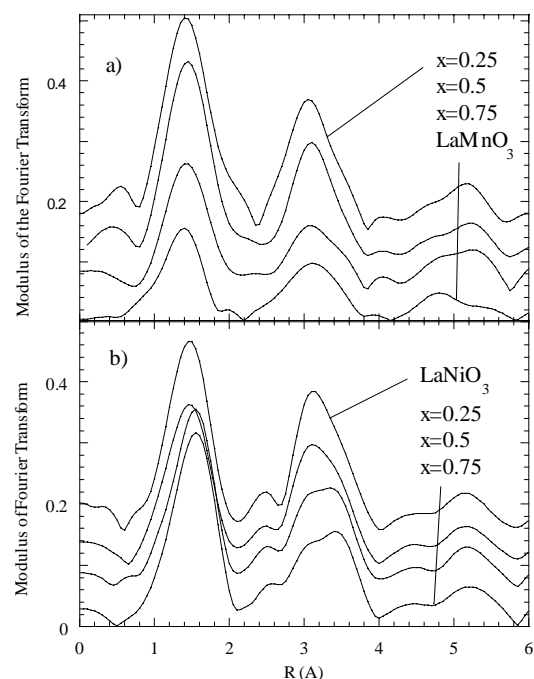

Figure 2
Fourier transform of the EXAFS spectra of $LaNi_{1-x}Mn_xO_3$ compounds (a) at the Mn K-edge and (b) at the Ni K-edge at room temperature.

Figure 2(b) shows the Fourier transform at the Ni K-edge, taken between 2.6 and 12 Å^{-1}. Similarly to the Mn K-edge EXAFS study, one can notice a decrease in the peak's intensities correspondient to the first and second coordination shells as the Mn content increases. This result suggests the presence of local distortions in the rhombohedral cell induced by the Mn addition.

The first coordination shell EXAFS contribution was extracted by Fourier Filtering of the spectra between 1 and 2 Å at the Mn K-edge and between 0.8 and 2 Å at the Ni K-edge. The information about the Mn-O bond distribution was obtained by least square fitting of the k-weighted filtered spectra. We used the Mn-O pair signal extracted from the $CaMnO_3$ spectrum as reference for the Mn K-edge analysis and the Ni-O pair signal extracted from $LaNiO_3$ spectrum for the Ni K-edge analysis. The best-fit parameters obtained for the first coordination shell are summarized in table 1.

Table 1

EXAFS parameters of the first oxygen coordination shell for a selected set of samples at room temperature at both, Mn and Ni K-edges. D (×N) are the interatomic Mn-O (or Ni-O) distances, N being the coordination number. $\Delta\sigma^2$ is the Debye-Waller factor referred to the value for $CaMnO_3$ sample (Mn K-edge) or $LaNiO_3$ sample (Ni K-edge). R is the best fit residual factor normalized by the difference between the number of independent points of the spectra and the number of fit parameters (Lytle *et al.*, 1989).* Analysed using theoretical phases and amplitudes of the FEFF code (Rehr *et al.*, 1991).

Sample	D (Å)	$\Delta\sigma^2 \times 10^{-3}$ (Å²)	R
Mn K-edge			
$LaMnO_3$	1.94(×4)	-0.20	0.01
	2.21(×2)	8.50	
$LaNi_{0.1}Mn_{0.9}O_{3.13}$	1.94(×6)	2.6	0.03
$LaNi_{0.1}Mn_{0.9}O_{3.0}$	1.95(×6)	6.2	0.007
$LaNi_{0.25}Mn_{0.75}O_{2.97}$	1.95(×6)	2.3	0.007
$LaNi_{0.5}Mn_{0.5}O_{3.08}$	1.92(×6)	-2.3	0.02
$LaNi_{0.75}Mn_{0.25}O_{3.0}$	1.92(×6)	-1.1	0.07
Ni K-edge			
$LaNiO_3$*	1.93	3.6	0.002
$LaNi_{0.9}Mn_{0.1}O_{3.02}$	1.93	0.6	0.001
$LaNi_{0.75}Mn_{0.25}O_{3.0}$	1.95	2.5	0.001
$LaNi_{0.5}Mn_{0.5}O_{3.08}$	2.05	0.0	0.003

The static Jahn-Teller distortion of stoichiometric $LaMnO_3$ sample is well resolved. Instead, the first oxygen coordination shell for the rest of the samples can be reasonably simulated with a single Mn-O distance. This result suggests a strong diminution of Mn^{3+} concentration in these samples in agreement with the XANES study. Moreover, the Mn-O distance decreases as the Mn content does. We note the presence of negative Debye-Waller factors in the fits of $LaNi_{0.75}Mn_{0.25}O_3$ and $LaNi_{0.5}Mn_{0.5}O_{3.08}$ samples. This fact points out to a lower Mn-O distortion in these samples than that of the reference compound ($CaMnO_3$). We note that $LaNi_{0.75}Mn_{0.25}O_3$ and $LaNi_{0.5}Mn_{0.5}O_{3.08}$ samples have a rhombohedral unit cell while $CaMnO_3$ has an orthorhombic one.

The opposite results can be obtained from the local structure around the Ni atom. We notice an increase of the Ni-O distances as the Mn content increases. It is noteworthy that the evolution of the interatomic distances, shown in table 1, suggest an expansion of the NiO_6 octahedra in the $LaNi_{1-x}Mn_xO_3$ series by increasing x up to x=0.5. Accordingly, there is a contraction of the MnO_6 octahedra from $LaMnO_3$ down to x=0.5. This result is in agreement with a Mn oxidation and a Ni reduction, as deduced from the XANES spectra.

We have only observed slight differences in the local environment between Ni and Mn atoms in the local, although both atoms

occupy randomly the same crystallographic site. We note that the crystallographic distance is similar to the average of both local environments (Blasco *et al.*, 2000). The chemical shift at the Mn K-edge achieve its maximum value for x=0.5. This sample also shows the maximum Ni-O distance and consequently, the minimum oxidation state for the Ni atom.

Finally, we also notice the effect of oxygen excess in the local structure. The oxidation of these samples produces a decrease of the unit cell volume and in some cases, a structural change. Then, the oxidized samples show a unit cell of higher symmetry (Blasco et al., 2000). In this way, the $LaMn_{0.9}Ni_{0.1}O_{3.11}$ compound shows a lower average Mn-O distance than the $LaMn_{0.9}Ni_{0.1}O_{3.0}$ one.

4. Conclusions

Our results suggest a mixed valence state for both, Ni and Mn atoms, in the whole $LaNi_{1-x}Mn_xO_3$ series. XANES spectroscopy shows a chemical shift in both absorption K-edges. In addition, the first coordination shell studied by EXAFS spectroscopy indicates a contraction of the MnO_6 octahedra together with an expansion of the NiO_6 ones along this series. This fact agrees with the presence of Mn^{3+y} and Ni^{3-z} ions and consequently, with the presence of an effective electronic transfer among Mn and Ni metal transition atoms.

References

Asai, K., Sezikawa, H. & Iida, S. (1979). *J. Phys. Soc. Japan* **47**(4), 1054-1060.

Blasco, J., Sánchez, M. C., Pérez-Cacho, J., García#, J., Subías G. & Campo J. (2000). *Chem. Mat.* Submitted.

Blasse, G. (1965). *J. Phys. Chem. Solids* **26**, 1969-1971.

Coey, J. M. D., Viret, M. & VonMolnar, S. (1999). *Adv. Phys.* **48**(2), 167-293.

Goodenough, J. B., Wold, A., Arnott, R. J. & Menyuk, N. (1961). *Phys. Rev.* **124**(2), 373-384.

Koningsberger, D. C. & and R. Prins, R. (1988). *X-ray absorption Techniques of EXAFS, SEXAFS and XANES*. Ed. Wiley, New York.

Lytle, F. W., Sayers, D. E. & Stern E. A. (1989). *Physica B* **158**, 701-722. Appendix to the report on the international workshop on Standards and Criteria in Absorption X-ray Spectroscopy, March 7-9, 1998.

Millis, A. J., Littlewood P. B. & and Shraiman, B. L. (1996). *Phys. Rev. Lett.* **76**, 3392-3394.

Park, J.-H., Cheong, S-W. & Chen, C. T. (1997). *Phys. Rev. B* **55**(17), 11072-11075.

Rehr, J. J., Mustre de Leon, J., Zabinsky, S. I. & Albers, R. C. (1991). *J. Am. Chem. Soc.* **113**(14), 5135-5140.

Sonobe, M. & Asai, K. (1992). *J. Phys. Soc. Japan* **61**(11), 4193-4203.

Subías, G., García, J., Proietti, M. G. & Blasco, J. (1997) *Phys.Rev. B.* **56**(13), 8183-8191.

Tsuda, N., Nasu, K., Yanase A. & Siratori K (1991). *Electronic conduction in oxides*, Springer Series in Solid-State Sciences, Ed. Springer-Verlag, Heidelberg.

Vasanthacharya, N. Y., Ganguly, P., Goodenough, J. B. & Rao, C. N. R. (1984). *J. Phys. C: Solid State Phys.* **17**, 2745-2760.

Zener, C. (1951) *Phys. Rev.* **82**, 403-405.