

Ni K-Edge XANES Studies of Hole Doped $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ and Reduced $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_y$

M. Jiménez-Ruiz, C. Prieto, A. de Andrés, J.L. Martínez, J.M. Alonso, M. Vallet-Regí* and J.M. González-Calbet**

Instituto de Ciencia de Materiales de Madrid (C.S.I.C.) Cantoblanco, Madrid 28049, Spain

* *Dep. Química Inorgánica y Bioinorgánica, Fac. Farmacia, Universidad Complutense, Madrid 28040, Spain*

** *Dep. Química Inorgánica, Fac. Ciencias Químicas, Universidad Complutense, Madrid 28040, Spain*

Abstract. In the present work we have analyzed the Ni K-edge XANES of two series of families in order to determine their Ni oxidation state: i) the hole doped $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ ($0.2 \leq x \leq 0.8$); and ii) the reduced $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_y$ ($0.2 \leq x \leq 0.5$ and $3.5 \leq y \leq 3.79$). The Ni K-edge XANES shows an increase of Ni(III) content with the Sr concentration for the hole doped samples. Additionally, the reduced family shows the disappearance of Ni(III), a decrease of Ni(II) with respect to the non-reduced one and an increase of Ni(I).

1. INTRODUCTION

An approximation to superconductivity is the study of non-superconducting compounds which are structurally similar to superconductors. This is the case of the Ln_2NiO_4 family, where the presence of Ni inhibits this interesting transport property.

In the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ family the hole doping is introduced through an oxygen excess and through the substitution of the rare earth by a divalent cation (Ca, Sr). The structural changes have been studied by X-ray and electron diffraction [1], for $x=0.2$ this system undergoes a structural transition from *Fmmm* orthorhombic to *I4/mmm* tetragonal. In both cases, Ni atoms remain octahedrally coordinated (NiO_6), as it has recently shown in an oxygen K-edge X-ray absorption study of the isostructural compound La_2NiO_4 [2], where the NiO_6 octahedron has predominantly the $3d^8$ configuration (Ni^{2+}). X-ray absorption measurements have also been performed in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, where the O K-edge XANES [2] shows that doping holes have $\text{O}2p$ character, while the Ni K-edge [3] analysis indicates that these holes have a mixed $\text{O}2p$ and $\text{Ni}3d$ character. A comparison between Ni K-edges of NiO and NdSrNiO_4 has been carried out in the last study to estimate the weight of the $\text{Ni}3d$ holes, being this value of 35%.

The structural changes in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_y$ ($0 \leq x \leq 0.8$, $3.38 \leq y \leq 4$) reduced system have been studied with X-ray and electron diffraction [1]. All this family present orthorhombic symmetry, for $3.8 \leq y \leq 4$ with *B112/n* spatial group and for $3.45 \leq y \leq 3.75$ with *Immm*. It has been observed the existence of twin domains due to different rotation axes of the octahedron. According to neutron diffraction data [4], the anionic vacancies basically concentrated in the twin boundaries in order that Ni atoms are in a plane square environment (NiO_4) and the oxidation state should be lower than +2.

2. EXPERIMENTAL

Samples were prepared by heating in air the corresponding oxides at different temperatures between 1300-1450° C for a Sr content between $0.2 \leq x \leq 0.8$. The reduced samples were obtained by heating the oxidized precursor at moderated temperatures in a controlled H_2 atmosphere during 15 to 24 hours. X-ray Absorption experiments were carried out at the XAS-3 beamline at DCI storage ring (Orsay) with an electron beam energy of 1.85 GeV and an average current of 250 mA. Data were collected by using a fixed exit monochromator with two flat Si (311) crystals and detection was made using two gas filled ion chambers. Energy resolution was estimated to be about 2 eV by the Cu foil 3d near edge feature. The energy calibration was monitored using the Cu foil sample, it was taken as 8991 eV at the first maximum above the edge.

3. RESULTS AND DISCUSSION

3.1 $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ ($0.2 \leq x \leq 0.8$) family

Fig. 1 presents the evolution of the normalized XANES spectrum at the Ni K-edge as the Sr content increases, showing the following tendency:

- An increase of the A-labeled feature corresponding to the $1s \rightarrow 3d$ transition, (see the inset of Fig. 1). This is consistent with an increase in the $\text{Ni}3d$ holes amount. For an absorber with inversion symmetry this is a forbidden dipolar transition, however the quadrupolar one is allowed. In these compounds the octahedra distortion is very small, so in average the local inversion symmetry is preserved [5]. For this reason the increase of A-feature has an electronic origin rather than a structural one, since the empty 3d density of states increases.
- The B- and D- features are present in every compound. They are characteristic of Ni(II) existence and associated with $|3d^9 \underline{L}_z\rangle \rightarrow |3d^9 \underline{L}_x\rangle$ and $|3d^8\rangle \rightarrow |3d^8 \underline{L}_x\rangle$ transitions, respectively.
- The fundamental state of Ni(III) can be described as a mixed configuration of $|3d^7\rangle$ and $|3d^8 \underline{L}_z\rangle$ states. The C-feature corresponds to the $|3d^8 \underline{L}_z\rangle \rightarrow |3d^8 \underline{L}_x\rangle$ transition and it has been observed in RNiO_3 compounds by M. Medarde *et al.* [6], therefore some Ni^{3+} amount appears to compensate the charge.

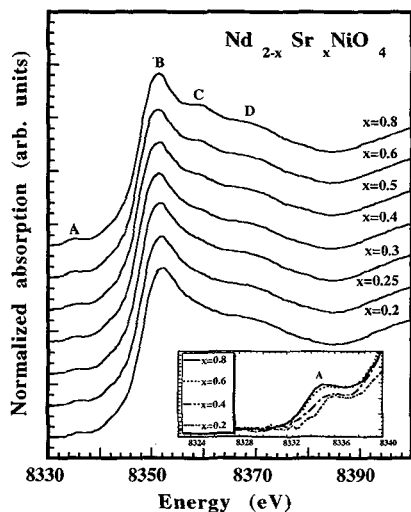


Figure 1: Normalized XANES spectra at the Ni K-edge of $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ family with $0.2 \leq x \leq 0.8$. Inset is the amplified A-feature.

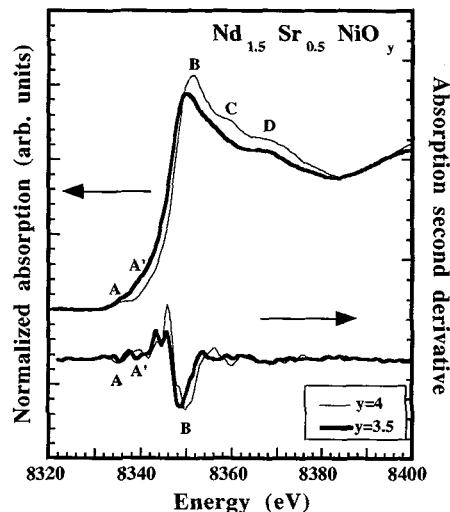


Figure 2: Normalized XANES spectra at Ni K-edge of $\text{Nd}_{1.5}\text{Sr}_{0.5}\text{NiO}_y$ ($y=4$ and $y=3.5$) and the absorption second derivative of each spectrum.

3.2 $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_y$ ($0.2 \leq x \leq 0.5$ and $3.5 \leq y \leq 3.79$) family

Ni K-edge X-ray absorption studies have been carried out on the reduced family in order to compare their spectra with the non-reduced ones with the same Sr amount. Although Fig. 2 only shows the Ni K-edge of $\text{Nd}_{1.5}\text{Sr}_{0.5}\text{NiO}_y$ for $y = 3.5$, $y = 4$ and the corresponding second derivative, the same behaviour for the rest of Sr amount is observed:

- The energy edge for $y = 3.5$ is about 2 eV lower than for $y = 4$. This is consistent with a decrease of the Ni oxidation state in the reduced one in relation with $\text{Nd}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$, in which some Ni^{3+} appears with the holes introduced by the Sr.
- The complete disappearance of the C-feature, associated with Ni(III) presence. Although the A-feature still appears in the reduced one, it has a lower magnitude than the $y=4$ compound, so there are more Ni3d holes in $\text{Nd}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ than in $\text{Nd}_{1.5}\text{Sr}_{0.5}\text{NiO}_{3.5}$, what is in agreement with the decrease of the Ni oxidation state for the reduced family.
- The B-feature intensity is lower for the $y=3.5$ than for the $y=4$ compound. This means that the $3d^9\text{L}$ configuration (Ni^{2+}) has less weight in the reduced one.
- The absorption second derivative of the reduced compound (Fig. 2) presents an additional minimum at 8339.1 eV (A' -feature) that is not present in the $y=4$ compound. This feature has been observed in square plane coordination of Ni(I) [7], situated at the same energy, and corresponds to the $3d^84s^1 \rightarrow 3d^84s^14p^1$ transition. Based upon that, the additional feature could be explained as the presence of Ni(I) in the reduced compound with a square plane environment, being this result in agreement with those previously obtained by J. M. Alonso [1] with other technics.

4. CONCLUSIONS

We have performed a Ni K-edge XANES study in the $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ ($0.2 \leq x \leq 0.8$) and $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_y$ ($0.2 \leq x \leq 0.5$ and $3.5 \leq y \leq 3.79$) families in order to determine the Ni oxidation state. The Ni K-edge XANES study of the first family shows qualitatively an increase of the Ni(III) amount as x increases. On the other hand, the comparison between the reduced family $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_y$ and the corresponding non-reduced one with the same Sr amount, shows the disappearance of Ni(III), a decrease of Ni(II) and an increase of Ni(I) content in the reduced family. This increase of Ni(I) amount would be associated with the presence of twin domains due to the different rotation axes of the NiO_6 octahedron, where the anionic vacancies are concentrated, so the Ni atoms are in a plane environment.

References

- J. M. Alonso. Ph. D. thesis. Universidad Complutense de Madrid (1993).
- P. Kuiper, J. van Elp, G. A. Sawatzky, A. Fujimori, S. Hosoya and D. M. de Leeuw, Phys. Rev. B, **44**, 4570 (1991). J. Zaanen, C. Westra and G. A. Sawatzky, Phys. Rev. B, **33**, 8060 (1986).
- Z. Tan, S. M. Heald, S. W. Cheong, A. S. Cooper y A. R. Moodenbaugh, Phys. Rev. B, **47**, 12365 (1993).
- M. Medarde. Ph. D. thesis. Universidad de Barcelona (1992).
- J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre and J. B. Torrance, Phys. Rev. B, **46**, 4414 (1992).
- M. Medarde, A. Fontaine, J. L. García-Muñoz, J. Rodríguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi and P. Lacorre, Phys. Rev. B, **46**, 14975 (1992).
- L. R. Furenliid, M. W. Renner and E. Fujita, Physica B, **208 & 209**, 739 (1995).