K2NiF4 TYPE OXIDES : THE COMPOUNDS
La2-xSrxNiO4-y : CRYSTAL CHEMISTRY AND ELECTRICAL PROPERTIES

M. Khairy, P. Odier, J. Choisnet

To cite this version:

HAL Id: jpa-00225524
https://hal.archives-ouvertes.fr/jpa-00225524
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
K$_2$NiF$_4$ TYPE OXIDES : THE COMPOUNDS La$_{2-x}$Sr$_x$NiO$_{4-y}$ : CRYSTAL CHEMISTRY AND ELECTRICAL PROPERTIES

M. KHAIRY, P. ODIER and J. CHOISNET

Centre de Recherches sur la Physique des Hautes Températures, C.N.R.S., F-45045 Orléans Cedex, France

Résumé - La substitution du lanthane par le strontium dans La$_2$NiO$_4$ a été étudiée. Une famille d'oxydes mixtes de formulation La$_{2-x}$Sr$_x$NiO$_{4-y}$ a été obtenue à l'air avec un large domaine d'homogénéité (0 < x < 1.2). Les propriétés structurelles et électriques sont discutées à partir des résultats de diffraction X et de conductivité électrique. En particulier, nous mettons en évidence une forte corrélation entre la distortion géométrique des octaèdres de nickel et les propriétés électriques ($\sigma \approx 100 \Omega\cdot cm^{-1}$ pour 0.8 < x < 1).

Abstract - The substitution of lanthanum for strontium has been studied in La$_2$NiO$_4$. A family of mixed oxides with the formulation La$_{2-x}$Sr$_x$NiO$_{4-y}$ has been obtained with a wide homogeneity range (0 < x < 1.2). Structural and electrical properties are discussed from X ray diffraction results and electrical conductivity measurements. We show up especially a strong relationship between the geometrical distortion of the Ni octahedra and the electrical properties ($\sigma \approx 100 \Omega\cdot cm^{-1}$ for 0.8 < x < 1).

I - INTRODUCTION

Several oxides with the A$_2$BO$_4$ composition are isotype of the K$_2$NiF$_4$ family which essentially is an intergrowth of ABO$_3$ perovskite and sodium chloride A0 layers. Such mixed oxides as La$_2$CuO$_4$ (1) and La$_2$NiO$_4$ (2) show simultaneously a rather high electrical conductivity (about $10^3 \Omega\cdot cm^{-1}$) and a good thermal stability in air: La$_2$NiO$_4$ congruently melts at approximately 1700°C. The partial substitution of lanthanum by strontium in these two oxides has been studied. It results either in a non-stoichiometric compounds: La$_{2-x}$Sr$_x$CuO$_{4-y}$ (3) or in stoichiometric compounds: La$_{2-x}$Sr$_x$NiO$_4$ (4), depending on the preparation conditions. The copper compound exhibits an enhancement of the electrical conductivity to a value as high as $10^3 \Omega\cdot cm^{-1}$ for x = 1/3 (5) related to a large amount of Cu$^{III}$. Unlike this result, the values reported for the electrical conductivity of nickel based compounds are lower than that of pure La$_2$NiO$_4$ (4,6,7). This result is inconsistent with the increase in the Ni$^{III}$ content of the material expected after the Sr substitution. Accordingly the crystal chemistry and electrical properties of strontium substituted lanthanum nickelates has been reinvestigated on air prepared materials. More specifically, we emphasize the strong relationship between the geometrical distortion of the Ni octahedron and the electrical behaviour (semi-conductor or metallic), earlier evidenced in La$_2$NiO$_4$ (8)(11).

II - EXPERIMENTAL METHODS

The synthesis of mixed oxides La$_{2-x}$Sr$_x$NiO$_{4-y}$ has been carried out using mixtures of powders having the composition (2-x)/2 La$_2$O$_3$ + x SrCO$_3$ + NiO. The mixtures were calcined in platinum crucibles for 1h at 920°C followed by 15h at 1120°C all being conducted in air. This last heating was repeated with intermittent grinding twice or three times for 0.5 < x < 1.2. The products were air quenched after each firing. The compositions with x = 0.01, 0.2, 0.5, 0.6, 0.8, 1.0, 1.2 were air sintered at 1180°C after compacting the powder at 480 MPa in an isostatic press. Rods were thus machined for electrical measurements. The electrical measurements were performed in air between 20 and 900°C by the four probe technic under dc current. Platinum electrodes sintered at 800°C were used, which permit a good reproducibility of the data.
The crystallographic analysis was made using a Guinier Nonius camera. The diffractograms were recorded with a Philips powder goniometer with the CuKα radiation. Infrared spectra were obtained in transmission in the range 800-2000 cm⁻¹ with a Beckman 4250 spectrometer with the KBr disk technic.

III - RESULTS AND DISCUSSION

III-1 Crystallographic characterization of the compounds La₂₋ₓSrₓNiO₄₋ₓ.

A family of strontium lanthanum mixed nickelates was synthesised following the above described method. These compounds crystallize within the K₂NiF₄ isotypic family; a large homogeneity range is observed for the compounds La₂₋ₓSrₓNiO₄₋ₓ, x ranging between 0 and 1.2. The preparation in air prevents the full oxidation of Ni²⁺ in NiII and probably brings about a non-stoichiometric defect on the oxygen sublattice as previously shown up for the copper compounds (3). Two composition ranges can be distinguished from the X-ray patterns.

A: 0 < x < 0.8. The indexing has been made in a tetragonal cell with parameters very similar to those of La₂NiO₄: a ~ 3.8 Å and c ~ 12.7 Å. As indicated in an introductory paper (9) the a parameter progressively decreases with x while c increases, then c remains constant (0.5 < x < 0.7) and finally smoothly decreases. Consequently the c/a ratio displays a clear maximum reaching 3.335 for x = 0.8.

B: 0.8 < x < 1.2. The occurrence of extra-diffraction peaks which cannot be indexed in the previous tetragonal cell (a ~ 3.8 Å) and show an increasing intensity with x, is the signature of a superstructure. The same phenomenon has been yet observed for La₀.₈Sr₁₋ₓCuO₃₋₅ (3), its actual tetragonal cell being a₀ = 5a ~ 18.8 Å and c₀ = c ~ 12.9 Å. The same 5a x 5a tetragonal cell is also a good model for La₀.₈Sr₁₋ₓNiO₄₋ₓ: a₆ = 5a ~ 19.1 Å and c₆ = c ~ 12.4 Å, with the same indexation as for the copper compound. Nevertheless, this result should be confirmed by an electron diffraction study.

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.860(1)</td>
<td>12.672(2)</td>
<td>3.323</td>
</tr>
<tr>
<td>0.1</td>
<td>3.853(1)</td>
<td>12.679(2)</td>
<td>3.390</td>
</tr>
<tr>
<td>0.2</td>
<td>3.842(1)</td>
<td>12.690(5)</td>
<td>3.280</td>
</tr>
<tr>
<td>0.4</td>
<td>3.827(1)</td>
<td>12.710(2)</td>
<td>3.321</td>
</tr>
<tr>
<td>0.6</td>
<td>3.819(1)</td>
<td>12.723(3)</td>
<td>3.331</td>
</tr>
<tr>
<td>0.8</td>
<td>3.816(1)</td>
<td>12.715(4)</td>
<td>3.332</td>
</tr>
<tr>
<td>1</td>
<td>3.810(1)</td>
<td>12.709(5)</td>
<td>3.335</td>
</tr>
<tr>
<td>1.2</td>
<td>3.813(1)</td>
<td>12.708(5)</td>
<td>3.331</td>
</tr>
<tr>
<td>1.2(*)</td>
<td>3.824(1)</td>
<td>12.365(5)</td>
<td>3.234</td>
</tr>
</tbody>
</table>

Table I brings together a, c and the c/a ratio for all the compositions studied. The agreement between calculated and measured d_hkl values for La₀.₈Sr₁₋ₓNiO₄₋ₓ is good. Unlike the A range, the parameter a increases while an abrupt decrease of c occurs between x = 1 and 1.2. The c/a ratio sharply falls to 3.234 for x = 1.2. This trend must be related to a progressive ordering of oxygen vacancies in the (001) planes with simultaneously a decrease of the anisotropy of the NiO₆ octahedra.

III-2 Structural study of the compositions x = 0.5 and x = 0.8.

The crystal chemistry of these mixed oxides has been specified for the particular compositions x = 0.5 and x = 0.8 using 29 X-ray reflexions for the former (38 hkl).
and 17 (21 hkl) for the latter. The more symmetric space group, i.e. I4/mmm was chosen which involves the only limiting condition on (hkl): h+k+l = 2n.

The effect of stoichiometry was taken into account by searching the best refinement in two extreme cases: -i) fully oxidized NiIII (y=0) and -ii) fully non-stoichiometric compound with only NiII (y=x/2). In that particular case, the possibility of ordering oxygen vacancies on each oxygen family 0(1) and 0(2) (see table II) has been considered. After refinement of the atomic parameters, the z values of (La,Sr), Ni, 01 and 02 are reported in table III together with their isotropic thermal factor.

<table>
<thead>
<tr>
<th>Atoms sites</th>
<th>Stoichiometric model</th>
<th>Non stoichiometric model</th>
</tr>
</thead>
<tbody>
<tr>
<td>x y z</td>
<td>La1.5Sr0.5NiO4-y</td>
<td>La1.2Sr0.8NiO4-y</td>
</tr>
<tr>
<td>La 4(e)</td>
<td>z=0.3605(5) B=1.4(1)(A)^2</td>
<td>z=0.3599(6) B=0.9(2)(A)^2</td>
</tr>
<tr>
<td>Sr 4(a)</td>
<td>B=0.1(3)(A)^2</td>
<td>B=0.7(6)(A)^2</td>
</tr>
<tr>
<td>O(1) 4(e)</td>
<td>z=0.178 (4)</td>
<td>z=0.175 (5)</td>
</tr>
<tr>
<td>O(2) 4(c)</td>
<td>% 0 0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>y=0</th>
<th>y=0.25</th>
<th>y=0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0(1)</td>
<td>3.5(9)</td>
</tr>
<tr>
<td>B</td>
<td>0(2)</td>
<td>0.5(9)</td>
</tr>
</tbody>
</table>

RI = 0.077
RI = 0.053
RI = 0.088
RI = 0.072
RI = 0.066
RI = 0.051

Table III
Atomic parameters and RI discrepancy factors for La2-xSr0.8NiO4-y (x=0.5; x=0.8)
Stoichiometric and non-stoichiometric models.

Lanthanum and strontium are statistically distributed on the 4(e) sites. The confidence factors R2 are rather similar: 0.072-0.088 for x = 0.5 and 0.05-0.066 for x = 0.8 due to the relatively weak contribution of oxygen atoms to the X ray diffraction. However the thermal factor is of particular interest for discussing the structure. As an example in the non-stoichiometric model if R2 is slightly smaller when oxygen vacancies are located on the O(2) family i.e. in the (001) plane, the B(0(2)) becomes negative which is totally unrealistic. On contrary the R2 increases when the oxygen vacancies are located on the O(1) family. The stoichiometric model is thus considered as the more significant one; we however do not exclude the possibility of a weak non-stoichiometry with oxygen vacancies in the (001) plane.

The high value of the thermal factor B (0(1)): 3.5 to 4.8(Å)^2 for the stoichiometric model can be related to the strong anisotropy of the Ni octahedron having two long axial Ni-O(1) distances: 2.26 Å (x=0.5), 2.23 Å (x=0.8) and four short Ni-O(2) distances: 1.91 Å (x=0.5 and 0.8). The axial (La,Sr)-O(1) distance is very short: 2.26 Å and this suggests a competition between Ni-O(1) bonds and (La,Sr)-O(1) bonds, which can take into account the large axial thermal motion of O(1) atoms. A similar effect is observed in La2CuO4 (10): La-O(1)=2.37 Å, Cu-O(1) = 2.40 Å and a B(0(1)) = 4(Å)^2. We should emphasize that such a strong anisotropy of the (NiO4) does not exist in LaSrNiO4 obtained by Demazeau et al (6) (Ni-O(1) = 1.97 Å and Ni-O(2)=1.91 Å). The shortening of the axial Ni-O(1) distance could be due to the high pressure (100 MPa of O2) used during the synthesis. The enhancement of the anisotropy in our compounds is an interesting fact that further studies will probably clarify; it can be attributed either to a Jahn-Teller effect of the NiIII d ion or a pure geometrical distortion as observed in LaSrV04 (10), another strontium K2NiF4 type oxide.

The study of IR spectra (600-300 cm^-1) of La2-xSr0.8NiO4-y (0<x<0.8) gives further informations on the (La,Sr)-O(1) and Ni-O(2) bonds. As shown on Fig.1, two main features must be noticed. -i) The highest frequency band shifts to larger energies with the introduction of strontium (650-680 cm^-1). This is in agreement with the structural observations and the assignment of that band to the very short
Results of electrical measurements are plotted in Fig. 2. The resistivity variation with the temperature is given for various substitution rates: x = 0.01, 0.2, 0.5, 0.6, 0.8, 1, 1.2. The insert represents the conductivity (log $\sigma$) versus $1/T$ for $20^\circ C < T < 200^\circ C$. The following can be put forward: i) The resistivity decreases with the parameter x; the minimum value of $\rho = 1.10^{-2}\Omega\,\text{cm}$ ($\sigma = 100\Omega^{-1}\,\text{cm}^{-1}$) is obtained for x=0.8; ii) In the temperature range 20-900°C the compounds display a progressive transition from a semi-conducting behaviour to a metallic like state in the high temperature range. The activation energy in the semi-conductive regime, although not precisely determinable, gradually decreases from 0.086 eV for x=0.01 to zero for x=0.8 and the coefficient in the metallic state is very small for x>0.8.

The compounds having low substitution rates, i.e. x = 0.01 behave similarly to La$_2$NiO$_4$ (2,12.) but with a larger resistivity (twice at the $\rho_{\text{min}}$ of La$_2$NiO$_4$); for large x (> 0.8) the compounds are metallic like LaNiO$_3$ with also a larger resistivity. One of the major effects of substituting La by Sr is to oxidize Ni$^{\text{II}}$ in Ni$^{\text{III}}$ simultaneously the resistivity decreases (the conductivity increases) in proportion of the hole concentration carriers brought by the Ni$^{\text{III}}$. However, as pointed out previously, some non-stoichiometry exists on the oxygen sites which reduces the hole concentration by trapping electron holes or equivalently reducing some Ni$^{\text{III}}$ in Ni$^{\text{II}}$. The minimum resistivity occurs for x=0.8 while it is expected for x=1 corresponding to LaSrNiO$_4$ (all Ni in the Ni$^{\text{III}}$ state). For that particular composition the carrier concentration is in a first approximation equal to that of LaNiO$_3$; on the other hand the charge transport essentially takes place in the (001) plane (a perovskite layer of LaNiO$_3$) (13) and so the hole mobility is expected to be of the same order of magnitude than for LaNiO$_3$. The resistivity of LaSrNiO$_4$ should thus be comparable to that of LaNiO$_3$; it is in fact twice larger. One reason for a higher resistivity is the non-stoichiometry on the oxygen sites.
The tetragonal unit cell of La$_{2-x}$Sr$_x$Ni$_{0.4-y}$ is progressively elongated by the introduction of Sr. This is related to an increasing anisotropy of the Ni$_6$ octahedra in the (001) plane and to a particularly short (La,Sr)-O(1) bond in the c direction. The resistivity is decreased to a minimum value by the introduction of Sr, a metallic state being reached for La$_{1.2}$Sr$_{0.8}$Ni$_{0.4-y}$ which resistivity is only twice that of LaNi$_{0.3}$, but in a much stable environment.

In addition to the charge carrier influence, the structure has an important effect on the resistivity, especially the geometrical distortion of the Ni$_6$ octahedra. As a matter of fact, we can use the value of the c/a ratio as an imperfect measure of this distortion. So, the elongation of the unit cell (c/a ratio) is related to the hole transport as recently pointed out (8). In Fig. 3 is plotted the resistivity of La$_{2-x}$Sr$_x$Ni$_{0.4-y}$ at room temperature versus the c/a ratio of these compounds. The resistivity for $x = 0.01$ very well correlates with others if one takes the c/a value of La$_2$Ni$_{0.4}$ which is very reasonable. It appears that for semi-conducting compounds ($x < 0.6$) the resistivity decreases with increasing c/a; in other words the more elongated the Ni$_6$ octahedra are, the less resistive is the material. This correlation is in good agreement with the IR data and explains the low resistivity found by others for LaSrNi$_{0.4}$ (6, 11). It is interesting to notice that the more anisotropic material ($x = 0.8$) has the smaller resistivity. The composition $x = 0.6$ is at the border of a metallic state and very close to the minimum metallic conductivity as it can be calculated from the Mott’s theory (14). For larger $x$ the resistivity is metallic with a nearly null temperature coefficient (6, 8) while for smaller $x$ the temperature has a marked influence probably connected with the thermal deformation of the unit cell. All these general features are in agreement with the results obtained on similar compounds with copper; furthermore the stability with respect to the oxygen, is better than for the copper compounds.

**REFERENCES**