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Synthesis and Crystallographic Characterization of the Mixed-Valence Reduced Nickelate $La_{1.6}Sr_{0.4}(Ni^{+I},Ni^{+II})O_{3.47}$

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The new mixed-valence nickelate $La_{1.6}Sr_{0.4}(Ni^{+I},Ni^{+II})O_{3.47}$ was prepared by low-temperature reduction of the oxide $La_{1.6}Sr_{0.4}NiO_{4.10}$ at 670 K under hydrogen. This strongly reduced nickelate—65% Ni^{+I}—is stable in air, at room temperature. The crystallographic characterization points to an orthorhombic unit cell: $a = 3.8728(6)$ Å, $b = 3.7242(6)$ Å, $c = 12.767(2)$ Å. Structure calculations evidence an oxygen-deficient K_2NiF_4-type structure. The oxygen vacancies are found only in the "NiO_2" equatorial planes, leading to a lowering of the nickel coordination. The main feature is the occurrence of Ni–O squares systematically orientated along the c-axis.

Introduction

The striking similarity between $La_{2-x}Sr_xCuO_4$ (*1, 3*) and $La_{2-x}Sr_xNiO_4$ (*4–6*), with respect to both their structure and their magnetic properties, has stimulated very recent work on the latter compound, owing to the understanding of the superconductivity phenomenon in this kind of oxide (5–7). The authors announced the onset of superconductivity in reduced forms of $La_{2-x}Sr_xNiO_4$ compounds, obtained under particular conditions of annealing and thermal cycling.

In addition to magnetic considerations involving the high spin state of the Ni^{+II} ion, one may wonder whether the Ni^{+I} ion, which is isoelectronic with the Cu^{+II} ion, can occur under these low partial oxygen pressures. As a matter of fact, some years ago, low-temperature reduction of $LaNiO_3$ under hydrogen leads before total reduction to new ternary oxides such as $La_2Ni_2O_5$ and $LaNiO_2$ (*8–10*). A pure monovalent nickel phase was obtained for $LaNiO_2$. Therefore, with respect to the above results, it was very interesting to reproduce the same reduction experiments on K_2NiF_4-type lanthanum–strontium nickelates.

In this way, our paper reports the synthe-

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sis of a mixed-valence $La_{1.6}Sr_{0.4}(Ni^{+I}, Ni^{+II})O_{3.5}$ compound. The crystallographic characterization of this new compound was then performed. The main result is related to the ordering of the oxygen vacancies. They are exclusively distributed in the equatorial "NiO_2" planes, leading to the formation of Ni–O squares, which are systematically orientated along the *c*-axis.

Experimental

The initial powder was obtained by a modified sol/gel route (*11*) using lanthanum nitrate, nickel nitrate, and strontium carbonate as precursors. The aqueous solution containing *n* equivalents of citric acid per each charged M^{n+} metal (three for La^{+III}, two for Ni^{+II} or Sr^{+II}) and ammonia up to pH 7 is gelled by *in situ* formation of an organic polymer network: the polyacrylamide gel. This solution was then calcinated at 900°C in air, the resulting powder being black, light, and chemically homogeneous. A first annealing in an alumina crucible was realized at 1000°C under a continuous oxygen flow for 10 hr. A second calcination at 1150°C in air, for 3 hr, gave monophasic samples as proved by X-ray phase analysis (Cu*Kα* radiation).

The reduction of the sample was performed using the same method and experimental devices as those used in the study of the reduction of $LaNiO_3$ (*8*, *10*). A measured amount of hydrogen was circulated over the sample at a reduced pressure in an all-glass loop by a magnetically activated pump (frequently used in catalysis works); the extent of reduction was calculated from the volume of oxygen consumed per equivalent weight of the oxide.

Results and Discussion

Reduction

Oxygen content of the as-prepared samples: reduction at 900 K. First, the total oxygen content of the compound was measured by reduction at 900 K. To eliminate all traces of organic matter, the sample was heated for 12 h at 900 K in flowing dry oxygen, followed by evacuation at the same temperature for 2 h. Reduction was then carried out at the same temperature, until a plateau was reached (in 1 hr). Raising the temperature did not further change this stationary state, between the sample and the gas phase. During the reduction step, all the hydrogen appeared as water. X-ray diffraction (under vacuum) showed a mixture corresponding to the addition of the patterns of La_2O_3, SrO, and metallic Ni. At this stage, using as a model the chemical formula $La_{1.6}Sr_{0.4}NiO_{4+x}$, the reduction process is formulated as follows:

$$La_{1.6}Sr_{0.4}NiO_{4+x} + (1.2 + x)H_2 \rightarrow \tfrac{4}{5}La_2O_3 + \tfrac{2}{5}SrO + Ni + (1.2 + x)H_2O.$$

The consumption of H_2 was found to be 29.16 cm^3 (10^{-3} moles), corresponding to $x = 0.1 \pm 0.005$. Therefore, the composition of the starting material is $La_{1.6}Sr_{0.4}NiO_{4.1}$.

Existence of a stable oxidation state lower than (+II): reduction at 670 K. The reduction at 670 K was performed as previously at 900 K (Fig. 1). In the very first minutes, we observed an abrupt change of the slope, just before reaching a plateau, corresponding to a volume of 14.1 cm^3 of H_2 (see the insert in Fig. 1). The chemical formula was then calculated to be approximately $La_{1.6}Sr_{0.4}NiO_{3.8}$. The oxide $La_{1.6}Sr_{0.4}NiO_{4.1}$, which is black, turned to dark yellow. At this stage, this color is likely to be related to the existence of the only (+II) valence state of nickel.

After more than 1 day (1600 min), a plateau was reached, which can be ascribed to a thermodynamically metastable state. The chemical formula of this reduced compound is $La_{1.6}Sr_{0.4}NiO_{3.47}$. As its color is black, a mixed-valence state of nickel is very likely to occur. *It is important to emphasize the stability of this reduced oxide in air at room temperature.*

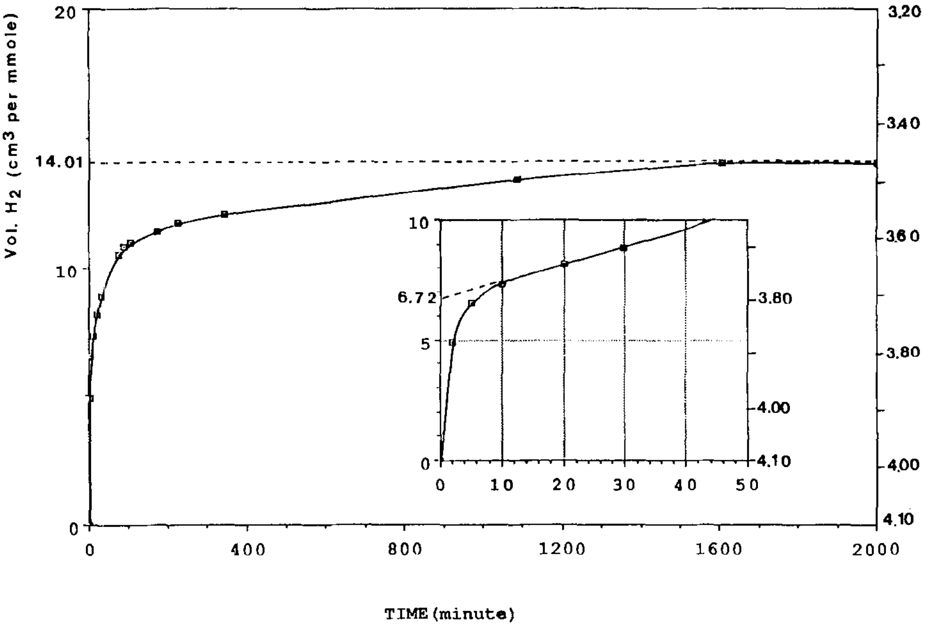

FIG. 1. Volume of H_2 consumed, as a function of time, per micromole of oxides or of oxygen content (2.8 + x, right scale). The insert shows, on a larger time scale, the initial part of the curve.

Because doubly charged oxygen is regarded as the most probable hypothesis under reducing conditions, a mean valence of nickel smaller than (+II), 1.34, is obtained. Magnetic susceptibility measurements were performed on this sample. As is also found for $LaNiO_2$ (*12*), a ferromagnetic-type behavior is observed in the temperature range 4.2 K $< T <$ 300 K. From the data, it cannot be excluded that Ni^0 atoms are present in $La_{1.6}Sr_{0.4}NiO_{3.47}$; however, it does not exceed 3% of the nickel sites and is below the detection limit of X-ray diffraction. Nor did transmission electron microscopy give indications of precipitates. It is therefore clear that the charge of the nickel is between I and II as a result of the simultaneous occurrence of Ni^{+I} (65%) and Ni^{+II} (35%) in order to satisfy the electroneutrality. It is important to recall that monovalent nickel has already been discovered by one of us (*8–10*) in the oxygen defect perovskite $LaNiO_2$.

It is worthwhile to note that Ni^{+I} cannot be stabilized by the same procedure as that performed on a lanthanum nickelate whose composition is $La_2NiO_{4.18}$. Only the first stage, obtained before the total reduction, is observed, as a dark yellow compound (probably Ni^{+II}). Conversely, when the reduction is made on a defective compound—on both the lanthanum and oxygen sites—such as $La_{1.85}NiO_{3.87}$, our results point to the presence of a small amount of Ni^{+I}. This can be interpreted in the following way:

(i) Starting from an oxidized lanthanum nickelate $La_{2-y}NiO_{4+\delta}$ or $La_{2-x}Sr_xNiO_{4+\delta}$—i.e., with both Ni^{+II} and Ni^{+III}—the occurrence of the first stage in the reduction is probably related to a pure Ni^{+II} phase. As these phases probably show, to some extent, an oxygen-deficient state, i.e., $La_{1.85}NiO_{3.775}$ or $La_{1.6}Sr_{0.4}NiO_{3.8}$, the occurrence of oxygen vacancies allows one to get a further step in the reduction process, i.e., the stabilization of some amount of Ni^{+I}.

(ii) In La_2NiO_4 or La_2NiO_{4+x}, Ni^{+I} cannot be stabilized because the charge of the lanthanum site is too high. By decreasing it—by means of substitution of strontium on lanthanum sites or by lanthanum vacancies—a reduction in the nickel valency down to +I is likely to occur.

Crystallographic Characterization

The reduced nickelate $La_{1.6}Sr_{0.4}NiO_{3.47}$ was characterized from its X-ray powder pattern. A strong similarity with that of the oxidized phase $La_{1.6}Sr_{0.4}NiO_{4.1}$ warrants an indexation in a closely related unit cell; more precisely, the systematic splitting of the ($h00$) and ($h0l$) lines is ascribed to the lack of tetragonal symmetry. Consequently, a satisfactory indexation of all the diffraction lines is obtained using an orthorhombic unit cell, whose parameters after a least-squares procedure are:

$$a_R = 3.8728(6)\ \text{Å};\ b_R = 3.7242(6)\ \text{Å};\ c_R = 12.767(2)\ \text{Å}.$$

(We preferred not to keep the conventional set of cell parameters $b > a > c$ in order to ensure an easy comparison with the K_2NiF_4 tetragonal cell type).

As an expected result, the unit cell volume decreases from 185.4 Å^3 for the oxidized phase $La_{1.6}Sr_{0.4}NiO_{4+x}$ to 184.1 Å^3 when the oxygen content is lowered as in the reduced phase. Comparing the values of a_R, b_R, and c_R with those of the tetragonal cell (oxidized phase), i.e., $a_0 = 3.819(1)$ Å, $c_0 = 12.709(2)$ Å, points out the influence of the oxygen nonstoichiometry: from one part, a_R and b_R are respectively larger and smaller than a_0 and from another part c_R slightly increases in the reduced compound. Therefore, the anisotropy of the geometrical characteristics is modified, taking into account the existence of both oxygen vacancies and partial reduction of nickel to the (+I) state.

TABLE I

ATOMIC PARAMETERS OF THE K_2NiF_4-TYPE STRUCTURE OF $La_{1.6}Sr_{0.4}NiO_{3.50}$ AFTER REFINEMENT

Atom	Position	x	y	z	B(Å^2)	Occupancy factor N
La, Sr	4(i)	0	0	0.3610(5)	0.4(1)	1.0
Ni	2(a)	0	0	0	2.4(2)	1.0
O(1)	4(i)	0	0	0.173(2)	4.2(3)	1.00(2)
O′(2)	2(b)	0.5	0	0	0.7(3)	0.85(2)
O″(2)	2(a)	0	0.5	0	0.5(3)	0.65(2)

Note. Total oxygen content: 3.5 per unit formula. $RI = \Sigma|I_o - I_c|/\Sigma I_o = 0.052$.

Structure Calculations

Structure calculations were carried out from the intensities of X-ray powder diffractograms using 38 (hkl), i.e., 28 independent reflections in a refinement procedure which is detailed in the following. The only limiting condition on (hkl), $h + k + l = 2n$, deduced from X-ray diffractograms and confirmed from electron diffraction, is consistent with the choice of the most symmetrical space group *Immm*.

As the main structural problem to solve is the oxygen nonstoichiometry, i.e., the localization of oxygen vacancies (here possibly owing to the large extent of oxygen vacancies: 0.5/4), the refinement procedure was successively applied to:

(i) atomic parameters of La, Sr (statistically distributed) and "axial" oxygen O(1);

(ii) occupancy factors of the three sets of oxygen: O(1), O′(2), O″(2), coupled with their isotropic thermal parameters.

An unambiguous result is obtained in this way: the oxygen vacancies are exclusively distributed in the equatorial "NiO_2" planes. Moreover, a significant trend to their ordering is evidenced as 70% are found over the O″(2) set of oxygen positions. The results are reported in Table I.

In order to ensure the validity of these results—especially the occupancy factor of O′(2) and O″(2)—a comparison of the *RI* confidence factors obtained for several other occupancy factors coupled with the

TABLE II

COMPARISON OF SEVERAL OXYGEN DISTRIBUTIONS OVER O'(2) AND O''(2) SITES COUPLED WITH THE CORRESPONDING ISOTROPIC THERMAL FACTOR B(Å^2)

Occupancy	Statistical	O'(2) order	O''(2) order
N[O'(2)]	0.75	1	0.5
$B'2$	<0	0.3	<0
N[O''(2)]	0.75	0.5	1
$B''2$	2.1	<0	5.0
RI	0.057	0.068	0.094

corresponding thermal parameters is shown in Table II. It must be stated that in any case and even for the statistical distribution, unrealistic thermal factors are systematically observed: each time, one of them is negative, which means a lack of electron density. Always concerning the thermal factors, once more, the O(1) axial oxygen exhibits a large thermal motion—B = 4.2 Å^2. The significance of this phenomenon cannot be found in an excess of oxygen O(1): as a matter of fact, any decrease in the O(1) occupancy factor leads to a corresponding increase in the RI confidence factor. An anisotropic motion of O(1) in the (La,Sr)–O layers is likely to occur as in numerous K_2NiF_4-type nickelates and cuprates (*13, 14*). This is another point of interest which is under investigation by our group and concerns crystal chemistry and the chemical and physical properties of these oxides. Especially, O^- species must be considered in these layers (*15*), at least for oxidized compounds. Finally, a rather large thermal factor is equally observed for nickel atoms; this is an unusual trend; however, it has been observed before for copper atoms in the oxygen-deficient K_2NiF_4 structure of $Ba_2CuO_{3.3}$ (*16*)—B_{Cu} = 3.1 Å^2.

The most striking feature in the defect structure of the reduced nickelate $La_{1.6}Sr_{0.4}NiO_{3.47}$ is the lowering of the coordination of Ni atoms with respect to the VI octahedral coordination. This can surely be related to the occurrence of both Ni^{+I} and Ni^{+II}, as expected from the chemical point of view. Up to now, Ni^{+I} has only been known in the IV (square) coordination in the defect perovskite $LaNiO_2$ (*8–10*).

In $La_{1.6}Sr_{0.4}NiO_{3.5}$ Ni–O squares, with or without an additional oxygen (IV + I square pyramidal coordination) are observed, with a systematic orientation along the c-axis; as a consequence of the ordering of oxygen vacancies, 70% of these squares are parallel to the a-axis and 30% to the b-axis (Fig. 2). They are both irregular: Ni–O(1) = 2.21 Å and Ni–O'(2) = 1.94 Å (70%), Ni–O''(2) = 1.86 Å (30%). This anisotropy cannot be ascribed to Ni in its (+I) state—in $LaNiO_2$, squares are regular with Ni–O close to 1.98 Å—but must be considered as a common feature of the K_2NiF_4-type structure.

These results are rather exceptional regarding the crystal chemistry of perovskite-like nickelates and, generally speaking, of nickel mixed oxides. Conversely, satisfactory structural relationships are found with analogous cuprates. Here we emphasize two main features which concern:

(i) $YBa_2Cu_3O_7$: square-coordinated Cu^{+II} and (or) Cu^{+III} link two successive "BaO" layers and are alternatively parallel to the a- and b-axis (*17*);

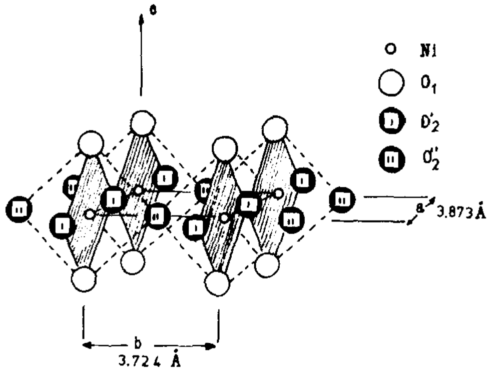

FIG. 2. Schematic drawing of the oxygen defect octahedral layers in the structure of $La_{1.6}Sr_{0.4}NiO_{3.5}$. Hatched squares show the most probable orientation (70%) along the a-axis.

(ii) $Ba_2CuO_{3.3}$: this oxidized barium cuprate (Cu^{+II} and Cu^{+III}) shows a defect K_2NiF_4-type structure (*16*) i.e., an orthorhombic cell and a nearly statistical distribution of oxygen vacancies in the "CuO_2" equatorial planes.

Therefore, new similarities in the crystal chemistry of the perovskite-like cuprates and nickelates are evidenced by our results: this time, it is in terms of a large amount of oxygen vacancies, which are located only in the equatorial "MO_2" planes. This enrichment of the data concerning the Ni mixed oxides, compared to the well-known identical features for the Cu mixed oxides, leads to the following conclusions:

(i) the crystal chemistry of Ni^{+I} is expected to be very close to that of Cu^{+II}, owing to the isoelectronic structure of these d^9 ions; thus, anisotropic coordinations, originating in a strong Jahn–Teller effect, are frequently observed.

(ii) the valence states of Ni and Cu in these perovskite-like oxides are entirely different. From one part strongly reduced compounds (Ni) and from another part highly oxidized compounds (Cu) have been prepared. The simultaneous occurrence of such opposite trends should be considered of primary importance in the triggering of unusual electronic properties, responsible for the superconducting behavior of many of these oxides.

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