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Stabilization of Ni^+ in defect perovskites $La(Ni_{1-x}Al_x)O_{2+x}$ with 'infinite-layer' structure

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Abstract

$La(Ni_{1-x}Al_x)O_3$ perovskites have been prepared from citrate precursors, decomposed and annealed at 200 bar of O_2 pressure. The thermal analysis in H_2/N_2 flow of the members with $x=0.1$, 0.2 allowed us to identify two new oxygen deficient perovskite phases. At moderate temperatures (≈330°C) defect perovskites of general stoichiometry $La(Ni_{1-x}Al_x)O_{2.5+x/2}$, containing Ni^{2+}, have been stabilized. Although the term for $x=0$ ($LaNiO_{2.5}$) is monoclinic and shows a $2a_0\times2a_0\times2a_0$ superstructure (a_0 is the edge of the ideal perovskite unit, ≈4 Å), the materials for $x=0.1$, 0.2 exhibit a larger orthorhombic superstructure, $2\sqrt{2}a_0\times2\sqrt{2}a_0\times2a_0$. At higher temperatures (≈700°C) a further reduction process leads to a new defect phase for $x=0.2$, of composition $La(Ni_{0.8}Al_{0.2})O_{2.16(3)}$, in which the formal oxidation state for Ni is 0.9(1)+. The unit cell is tetragonal, $a=3.834(1)$, $c=3.876(1)$ Å, and the structure is closely related to the 'infinite layer' type, as shown from neutron powder diffraction data. The presence of some axial oxygens, probably coordinated to Al^{3+} cations, seems to stabilize the structure, acting as bridges between two adjacent layers.

Keywords: Al-doped $LaNiO_3$; Oxygen-defect perovskite; Infinite layer structure; Neutron powder diffraction

1. Introduction

Topotactic deintercalation of oxygen ions has been shown to be possible in the family of perovskites $RNiO_3$ (R=La, rare earth), giving rise to defect perovskites of composition $RNiO_{3-\delta}$ which show interesting magnetic properties. The structure of $LaNiO_{2.5}$, containing divalent Ni cations, has been recently described [1,2]. A defect perovskite of composition $LaNiO_2$, presenting the so-called 'infinite-layer' structure and containing monovalent Ni, was described some years ago [3]. This phase seems to be strongly unstable, and its preparation has been unsuccesfully tried by several research groups.

At present we show that the 'infinite-layer' structure can be stabilized by doping the Ni sublattice with Al^{3+} cations, in oxygen defect perovskites of nominal stoichiometry $La(Ni_{1-x}Al_x)O_{2+x}$. The samples have been characterized by thermal analysis, X-ray diffraction (XRD) and neutron powder diffraction (NPD).

2. Experimental

Black polycrystalline precursors of composition $La(Ni_{1-x}Al_x)O_3$ were previously prepared from citrate solutions of the involved cations, thermally decomposed and oxygenated at 1000°C under 200 bar of O_2, as reported elsewhere [4]. The present study deals with the products of the reduction of the samples with $x=0.1$, 0.2.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric (TG) curves were obtained in a TG50 unit, working at a heating rate of $10°C\ min^{-1}$, in a reducing $H_2(5\%)/N_2(95\%)$ flow of $0.3\ l\ min^{-1}$. About 50 mg of sample were used in each experiment.

The products were characterized by XRD using Cu Kα radiation, in a Siemens D-501 goniometer controlled by a DACO-MP computer, by step-scanning from 10 to 100° in 2θ, in increments of 0.05° and a counting time of 4 s each step.

The neutron powder diffraction diagram of $La(Ni_{0.8}Al_{0.2})O_{2.16}$ was collected at room temperature in the multidetector DN5 diffractometer at the Siloé reactor of the Centre d'Etudes Nucléaires, Grenoble. A wavelength of 1.344 Å was selected from a Cu monochromator. The 800 detectors covered a 2Θ range of 80°, from $2\Theta_i=18°$. The counting time was 4 h, using about 6 g of sample contained in a vanadium can.

The diffraction patterns were analyzed by the Rietveld method, using the FULLPROF refinement program [5]. A pseudo-Voigt function was chosen to generate the line

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shape of the diffraction peaks. FULLPROF enables both the conventional refinement of a proposed structural model as well as the matching of an observed diffraction profile without the previous knowledge of the crystal structure, except the approximate cell dimensions and space group symmetry. In the neutron refinement the angular 2θ range 42–45° was excluded due to electronic noise during the counting process.

3. Results and discussion

The precursor materials, La(Ni$_{1-x}$Al$_x$)O$_3$, x=0.1, 0.2, are monophased perovskites stoichiometric in oxygen, and show a rhombohedral distortion which decrease as the Al content (x) increases [4]. The XRD patterns of both compounds are shown in Figs. 1 and 2 In the precursor perovskites the oxidation state for Ni is 3+.

3.1. Thermal analysis in reducing conditions

In Fig. 3 the TG curves of La(Ni$_{1-x}$Al$_x$)O$_3$, x=0.1, 0.2 are shown, obtained in a reducing H$_2$/N$_2$ flow. The thermal analysis of the $x=0$ term is described in ref. [1]. Two main reduction steps can be distinguished: after the first one an oxygen deficient perovskite phase can be identified by XRD. This first reduction process can be written as

$$\mathrm{La(Ni_{1-x}Al_x)NiO_3} + (1-x)/2\,\mathrm{H_2} \rightarrow \mathrm{La(Ni_{1-x}Al_x)O_{2.5+x/2}} + (1-x)/2\mathrm{H_2O}\,.$$

For $x=0.1$, the corresponding reduced phase after the first weight loss could be obtained as a well-crystallized product by isothermal heating at 330°C for 1 h, under H$_2$/N$_2$ flow. The XRD pattern of this defect phase is shown in Fig. 1, together with that of the stoichiometric precursor. A composition of La(Ni$_{0.9}$Al$_{0.1}$)O$_{2.52}$ can be inferred from the observed weight loss. For $x=0.2$, a similar oxygen-deficient perovskite phase was identified after the first reduction process, of composition La(Ni$_{0.8}$Al$_{0.2}$)O$_{2.58}$. In both cases the compositions imply oxidation states close to 2+ for Ni.

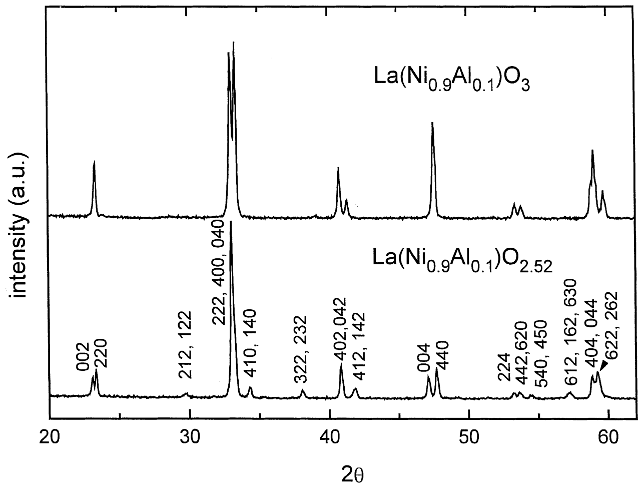

Fig. 1. XRD patterns of oxygen-stoichiometric La(Ni$_{0.9}$Al$_{0.1}$)O$_3$ and the defect perovskite La(Ni$_{0.9}$Al$_{0.1}$)O$_{2.52}$. The latter is indexed on the basis of an orthorhombic unit-cell with $a=10.8190(3)$, $b=10.7999(4)$ and $c=7.7061(1)$ Å.

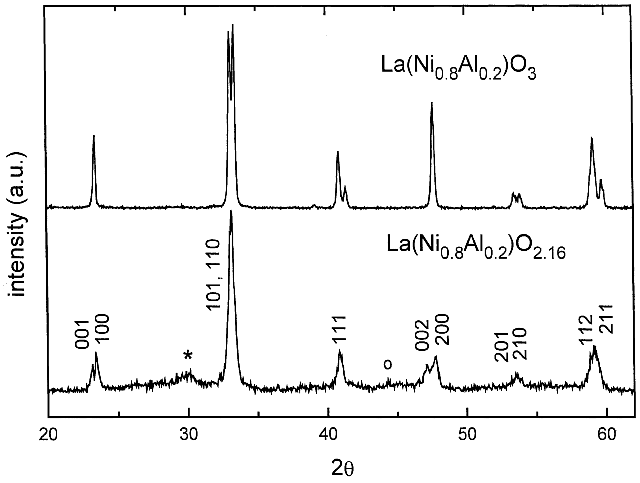

Fig. 2. XRD patterns of La(Ni$_{0.8}$Al$_{0.2}$)O$_3$ and reduced La(Ni$_{0.8}$Al$_{0.2}$)O$_{2.16(3)}$ perovskites. The Miller indices in the latter correspond to a tetragonal unit cell with dimensions $a=3.834(1)$, $c=3.876(1)$ Å. The star and the circle indicate, respectively, the most intense reflection of La$_2$O$_3$ and Ni metal impurity phases.

After the second reduction process (Fig. 3) the samples completely decompose by total reduction to Ni metal, according to the following equation:

$$\mathrm{La(Ni_{1-x}Al_x)O_{2.5+x/2}} + (1-x)\mathrm{H_2} \rightarrow 1/2\mathrm{La_2O_3} + (1-x)\mathrm{Ni} + x/2\mathrm{Al_2O_3} + (1-x)\mathrm{H_2O}\,.$$

However, the DTG curve of the second step of the $x=0.2$ sample shows a splitting suggesting that the reduction proceeds via an intermediate phase. By isothermal heatings at 700°C (for 1 h) we could isolate a strongly reduced perovskite-related phase, whose XRD pattern is shown in Fig. 2. Some impurities (La$_2$O$_3$ and Ni) are also present in the pattern. From the weight loss, the composition was determined to be La(Ni$_{0.8}$Al$_{0.2}$)O$_{2.16(3)}$. Assuming that Al^{3+} cations remain unreduced, the nominal valence for Ni in this material can be estimated as 0.9(1)+. To perform a NPD study, a 6 g sample was prepared by annealing the precursor perovskite at 600°C for 13 h in a H$_2$/N$_2$ flow.

3.2. Structural study

For comparative purposes, it is interesting to note that the stoichiometric perovskite for $x=0$ (LaNiO$_3$) gives LaNiO$_{2.5}$ as reduction product after the first step in the

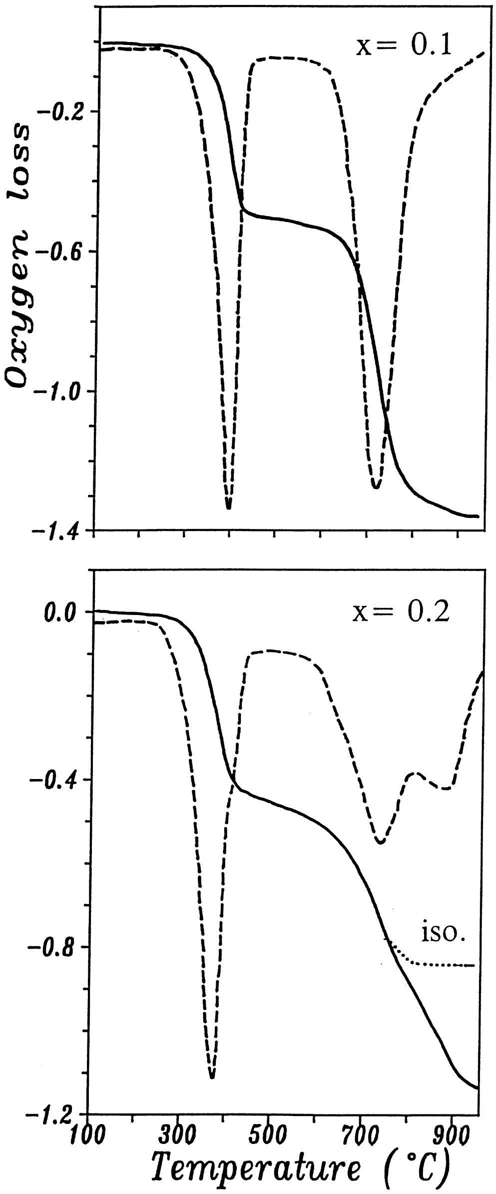

Fig. 3. TG (full lines) and DTG (broken lines) curves for $La(Ni_{1-x}Al_x)O_3$, $x=0.1$, 0.2. In the latter a stable phase with constant weight is isolated by isothermal heating at 700°C (dotted line).

corresponding TG curve. It can be described as a monoclinic superstructure of perovskite, with unit-cell parameters $2a_0 \times 2a_0 \times 2a_0$, with Ni^{2+} in both octahedral and square planar coordination [1,2].

For $x=0.1$, a defect perovskite $La(Ni_{0.9}Al_{0.1})O_{2.52}$ can be isolated after the first reduction step. The XRD pattern (Fig. 1) can be indexed in an orthorhombic unit cell with dimensions $2\sqrt{2}a_0 \times 2\sqrt{2}a_0 \times 2a_0$. The pattern matching (without structural model) leads to the refined unit-cell parameters $a=10.8190(3)$ Å, $b=10.7999(4)$ Å and $c=7.7061(1)$ Å. The *Pmmm* space group was considered. The discrepancy *R*-factors were: $R_p=8.85$, $R_{wp}=11.8$, $R_{exp}=10.32$, $R_I=2.22\%$, $\chi^2=1.30$. The precise tilting scheme of the (Ni,Al) coordination polyhedra in this complex superstructure is currently under study. For $x=0.2$, the similar oxygen-deficient perovskite phase $La(Ni_{0.8}Al_{0.2})O_{2.58}$ also shows an orthorhombic $2\sqrt{2}a_0 \times 2\sqrt{a_0} \times 2a_0$ superstructure. The refined unit-cell parameters are $a=10.8268(4)$ Å, $b=10.7979(3)$ Å, $c=7.7378(2)$ Å. *R*-factors: $R_p=10.1$, $R_{wp}=13.3$, $R_{exp}=10.17$, $R_I=2.00\%$, $\chi^2=1.19$.

By further reduction of the $x=0.2$ phase a new defect perovskite-related phase with stoichiometry $La(Ni_{0.8}Al_{0.2})O_{2.16(3)}$ was isolated. The XRD pattern was indexed in a tetragonally distorted perovskite unit cell with $\approx a_0$ edge dimensions. In order to check a possible departure of the mentioned symmetry, due to tilting of the (Ni,Al) coordination polyhedra, a NPD study was performed, taking advantage of the higher sensitivity of neutrons to the oxygen positions. The NPD pattern was correctly refined on the basis of the structural model of the so-called 'infinite-layer' structure, typified by $SrCuO_2$ [6]. The ideal ABO_2 infinite layer structure can be derived from the ABO_3 network by removing all the axial oxygens, in such a way that B cations are coordinated to four oxygens, in square planar configuration. The refinement was performed in the space group *P*4/*mmm*, with (Ni, Al) atoms at (0, 0, 0) positions, La at (1/2, 1/2, 1/2), O1 at (1/2, 0, 0) and O2 at (0, 0, 1/2), with a fixed occupation factor of 0.2. The impurity phases La_2O_3 and Ni metal were also included in a multipattern refinement. The unit-cell parameters of the main perovskite phase were $a=3.834(1)$, $c=3.876(1)$ Å.

In Fig. 4 the observed and calculated profiles are shown. In spite of the relatively large amount of impurities, and the rather poor crystallinity of the main phase, the reasonable agreement observed allows us to show evidence for the stabilization of a defect perovskite with a structure related to the 'infinite layer', containing monovalent Ni. In Fig. 5 a model of this structure is shown. We assume that Al^{3+} cations, distributed at random in the Ni^+ sublattice,

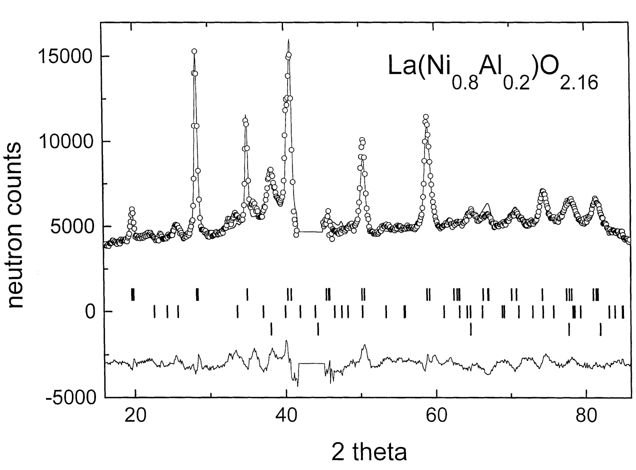

Fig. 4. Observed (circles) and calculated (full line) NPD profiles for $La(Ni_{0.8}Al_{0.2})O_{2.16(3)}$ at 295 K. The three series of tick marks correspond to the main tetragonal phase, La_2O_3 and Ni, respectively. Discrepancy factors: $R_p=4.39$, $R_{wp}=5.60$, $R_{exp}=1.31$, $R_I=10.2\%$.

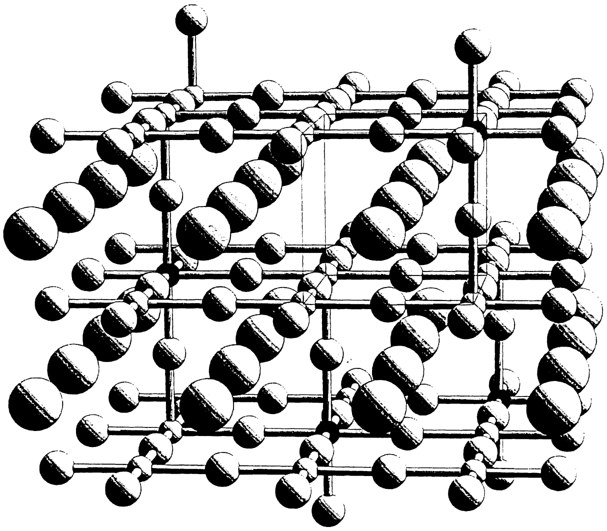

Fig. 5. View of the $La(Ni_{0.8}Al_{0.2})O_{2.16(3)}$ structure, related to the 'infinite layer' type, in which the presence of some axial oxygens seem to stabilize the structure. Small atoms are (Ni, Al); in this model Al^{3+} cations (dark) are always octahedrally coordinated to oxygens. Large atoms represent La.

keep the octahedral coordination even in this reduced phase. Ni^{+} cations are in both square planar and square pyramidal coordination to oxygens. Note that c axis is slightly larger than the a axis, unlike the tetragonal structure of $SrCuO_2$ [6] in which the unit cell is flattened because of the absence of all the axial oxygens, giving rise to a perfect square-planar coordination for Cu^{2+} cations. Also, $a>c$ in the tetragonal lattice is described for $LaNiO_2$ [3]. In the present case, the presence of some axial oxygen atoms, probably coordinated to Al^{3+} cations, are probably responsible for the larger value of the axial c parameter. The axial oxygens, acting as bridges between two adjacent infinite layers, seem to favour the stability of the crystal structure. For Al contents of $x=0.1$, our results suggest that the number of axial oxygens (0.1 atoms per formula unit) is not large enough to stabilize the infinite layer structure under the present preparation conditions. We are currently working in the synthesis of impurity-free phases in which Ni^{+} can be stabilized in defect perovskite structures.

4. Conclusions

Thermal treatments in reducing atmosphere of Al-substituted $LaNiO_3$ perovskites enabled the topotactic removal of oxygen atoms to give two structurally different defect perovskites. By annealing $La(Ni_{0.9}Al_{0.1})O_3$ at 330°C in H_2/N_2, an intermediate Ni^{2+}-containing defect perovskite $La(Ni_{0.9}Al_{0.1})O_{2.52}$ is identified, showing a $2\sqrt{2}a_0 \times 2\sqrt{2}a_0 \times 2a_0$ superstructure. A subsequent reduction of the $x=0.2$ phase, at 700°C in H_2/N_2, leads to a tetragonal material with a crystal structure closely related to the 'infinite-layer' type, as shown from NPD data. The oxygen stoichiometry, determined by thermal analysis, leads to the composition $La(Ni_{0.8}Al_{0.2})O_{2.16(3)}$, with a nominal valence for Ni of $0.9(1)+$. The presence of some axial oxygen atoms, probably coordinated to Al^{3+} cations, are thought to be responsible for the stability of the structure, acting as bridges between two adjacent infinite layers.

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