Inorganica Chimica Acta, *140* (1987) 151–153

Non-stoichiometric Aspects and Physical Properties of La_2NiO_4 Oxide*

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Compounds having the general formula A_2BX_4, where A is the larger diamagnetic cation ($1.0 < r_A < 1.9$ Å), B is the smaller cation ($0.5 < r_B < 1.2$ Å) and X = O, F and Cl, adopt the tetragonal K_2NiF_4-type structure, Fig. 1. This structure can be visualized as containing alternating perovskite (ABX_3) and rock salt (AX) blocks along the *c*-axis, which results in nine-coordination for cation A and octahedral coordination for B.

Transition metal oxides which show this structure have been extensively studied because the antiferromagnetic interatomic interactions between the transition metal ions situated in the perovskite layers are nearly two-dimensional. Recently, it has been reported that metallic mixed oxides based on this structure show superconductivity with transition temperatures around 40 K [1]. Although different oxides with the Ln_2MO_4 (Ln = lanthanide cation, M = Co, Ni, Cu) formula have been considered as tetragonal K_2NiF_4-type, the semiconductor La_2NiO_4 is the only oxide which shows tetragonal symmetry [2]. Moreover, a broad range of lattice constants have been reported for this material, indicative of variations in composition. It has also been suggested that the physical properties are influenced by the presence of non-stoichiometry [3].

Experimental

The La_2NiO_{4+x} oxide was prepared by firing stoichiometric amounts of high purity La_2O_3 (99.99%) and NiO (99.99%) in air at 1350 °C for 72 h with two interruptions for regrinding. La_2O_3 was heated overnight at 1000 °C in air to remove moisture and CO_2. The La_2NiO_{4+x} oxide was reduced at 200 torr of hydrogen in a thermogravimetric apparatus based on a Cahn electrobalance.

Powder X-ray diffraction analysis was carried out in a Siemens D-500 diffractometer and the lattice parameters were refined by using silicon as internal standard. Electron diffraction patterns and micrographs were performed on a Siemens Elmiskop 102 microscope.

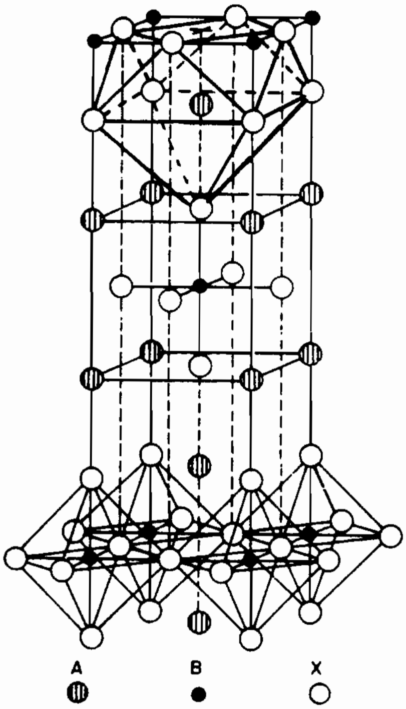

Fig. 1. Tetragonal K_2NiF_4-type structure of A_2BX_4.

Magnetic susceptibility measurements were made in the range 4.2–300 K using a Faraday apparatus.

The amount of Ni^{3+} was determined by iodometric titration.

Results and Discussion

Chemical analysis revealed the presence of about 5% of Ni^{3+} in the starting material La_2NiO_{4+x}, which shows the tetragonal K_2NiF_4-type structure (Table I and Fig. 2) and for this reason this phase should be formulated as indicated before.

The presence of extra spots superimposed on those corresponding to the tetragonal symmetry, observed in the electron diffraction pattern (Fig. 2b) have been assigned to a multitwinned phase; the corresponding electron micrograph, Fig. 2d, shows the presence of crystallographic planes in different orientations. Electron microscopy does not show evidence of intergrowth of $La_{1+x}Ni_xO_{3x+1}$ phases (Figs. 2c and 2d), mainly $La_3Ni_2O_7$, as has been proposed earlier in order to account for oxygen excess of this non-stoichiometric phase [4]. Cation vacancies or even twin planes could be also considered to accommodate this excess of oxygen.

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*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

TABLE 1. Lattice Parameters and Weight Loss (ΔW) for the Different Samples Obtained by Reducing La_2NiO_{4+x} Oxide in Hydrogen

Compound	Lattice constants (Å)				ΔW (%)
	a	b	c	γ	
La_2NiO_{4+x}	3.8703(3)	3.8703(3)	12.678(3)	90°	
La_2NiO_4 (1)	3.871(1)	3.871(1)	12.570(6)	90°	0.65
La_2NiO_4 (2)	3.886(5)	3.87(1)	12.55(3)	90°27′ (7)	0.80
La_2NiO_4 (3)	3.886(2)	3.889(2)	12.528(3)	90°50′ (1)	0.86

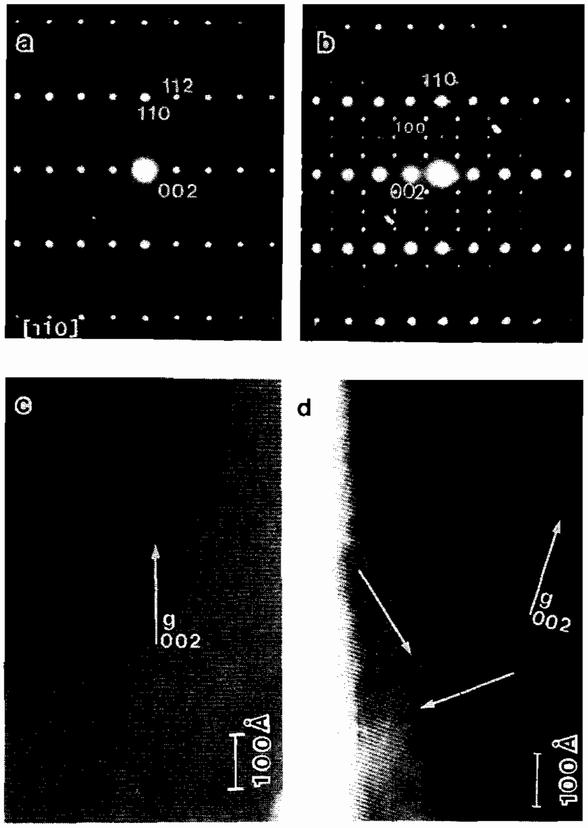

Fig. 2. Electron diffraction patterns corresponding to: (a) [110] zone axis of La_2NiO_{4+x}; (b) indexed as a multi-twinned phase; (c) and (d) electron micrographs of different crystals of La_2NiO_{4+x}.

When La_2NiO_{4+x} is reduced under hydrogen, the tetragonal ($h\bar{1}l$) reflections split into two, ($h\bar{1}l$) and ($h1l$), for weight loss values higher than 0.70%. The X-ray diagrams for these phases have been indexed in a monoclinic unit cell analogous to those assigned to Pr_2NiO_4 and Nd_2NiO_4 [5]. The lattice parameters a and b increase on going from the tetragonal La_2NiO_{4+x} to the monoclinic reduced samples, while the c parameter decreases to account for the increase in the Ni–O basal distances due to the presence of only Ni^{2+} in these reduced samples, as can be seen in Table I.

On the other hand, the reduced samples take in oxygen when they are exposed to air and become fully oxidized at 600 °C. These processes can be formulated according to:

$$La_2NiO_{4+x}(\text{tetragonal}) \underset{O_2 \text{ or air } 600\ ^\circ C}{\overset{H_2\ 430\ ^\circ C}{\rightleftharpoons}} La_2NiO_4(\text{monoclinic})$$

The magnetic susceptibility of the reduced sample, Fig. 3, is almost independent of the temperature, although a weak ferromagnetic component has been detected. It has been observed that this component disappears at 630 K [6], which corresponds to the Curie temperature of the nickel, indicative of the presence of some unreacted NiO in the starting material.

Transport properties are different from those reported earlier [7]; in fact, both oxidized and reduced samples are p semiconductors and the variation of the resistance against temperature (Fig. 4) probably indicates the presence of an acceptor level at 0.10 eV from the upper level of the conduction band in the case of the La_2NiO_{4+x}. However, for the reduced sample the experimental data fit two straight lines and this could be attributed to the presence of two acceptor levels at 0.06 eV and 0.15 eV from the upper level of the conduction band. These levels are nearly symmetric to the one in the starting material. Recently, the existence has been reported [8] of an orthorhombic phase for the reduced La_2NiO_4, only detected by neutron diffraction, which has been described by small displacements of the oxygen atoms of the K_2NiF_4 network, giving rise to two different distorted octahedra for the nickel atoms. A similar situation could take place

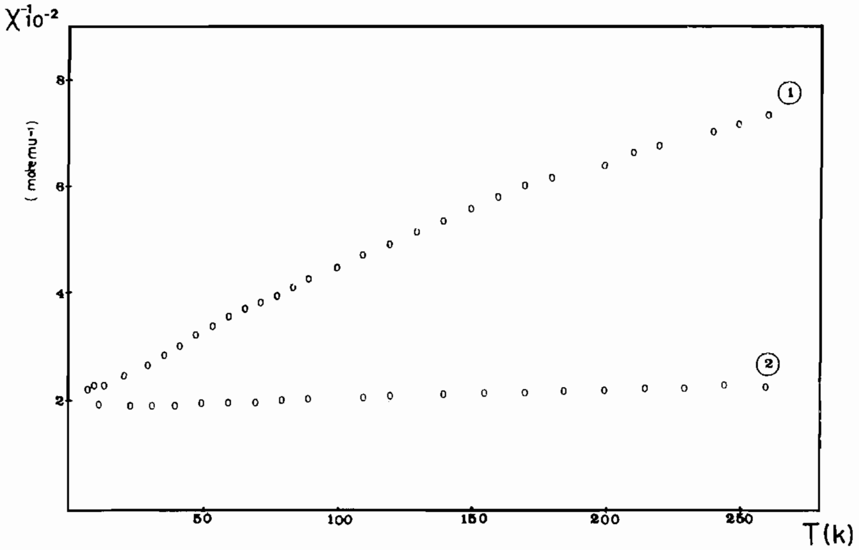

Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility for La_2NiO_{4+x} (1) and a reduced sample (2).

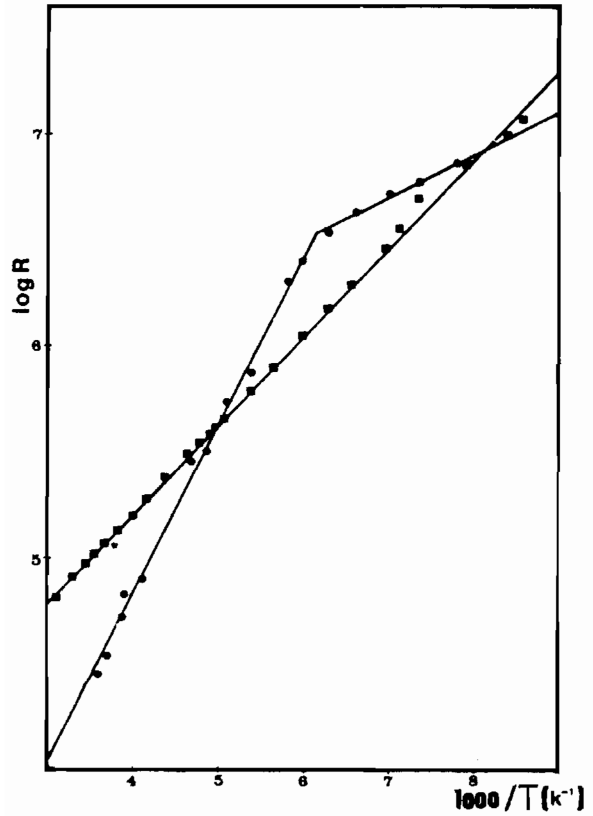

Fig. 4. Electrical resistence *vs.* reciprocal temperature for La_2NiO_{4+x} (■) and reduced sample (●).

in the monoclinic reduced phases and this could justify the presence of these two different acceptor levels.

Acknowledgements

We wish to thank Dr. L. C. Otero Diaz for valuable discussions. The authors acknowledge the Instituto de Quimica Inorganica, C.S.I.C. for use of its electron microscopy facilities.

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