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Synthesis and characterization of $NdNiO_3$ prepared by low temperature methods

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Abstract

$NdNiO_3$ has been prepared with an orthorhombic perovskite structure by a low temperature and low oxygen pressure method starting from a nickel(III) oxide precursor, β-NiO(OH). The compound $LaNiO_3$ has also been obtained by this method. This chemical-precursor-based synthesis overcomes problems related to the use of high oxygen pressures in the synthesis.

1. Introduction

The discovery of high temperature superconductivity [1] has led to a systematic study of the electronic and magnetic properties of simple oxides [2]. Indeed, rationalizing the behaviour of these relatively simple systems could provide us with a useful tool towards understanding the more complex behaviour displayed by the related high T_c superconductors. In particular, the study of the electrical properties acquires relevance if we consider that small changes in stoichiometry in, for example, the $La_{2-x}M_xCuO_4$ system [3] lead from antiferromagnetic insulator compounds to high temperature superconductors with metallic behaviour in the normal state. In this context the importance of the study of compounds that display metal-to-insulator transitions [4] is evident.

Recently, the existence of this kind of transition in rare earth nickelates, $RENiO_3$ (RE ≡ Pr, Nd, Sm), has been reported [5]. The observed trend in this series of compounds is a decrease in the temperature of the transition with an increase in the rare earth radius; in fact, the lanthanum compound is metallic down to 5 K. The synthesis of this type of compound has been mainly developed at high oxygen pressures (as high as 60 kbar for all rare earths except cerium, praseodymium and terbium [6]; starting from a mixture of nitrates, it is possible to obtain the lanthanum, praseodymium, neodymium and samarium compounds at 150–200 bar [5]). At low oxygen pressures, low temperature methods have been used to prepare $LaNiO_3$ [7] and $NdNiO_3$ [8] with a rhombohedral structure instead of the high pressure orthorhombic structure. The synthesis of $NdNiO_3$ from a mixture of hydroxides of nickel and the rare earth has also been described [9], but without reference to the detailed structural type.

In this paper we show that, starting from a nickel(III) oxide precursor, the compound $NdNiO_3$ can be prepared with an orthorhombic perovskite structure by a low temperature and low oxygen pressure method. This work has been developed in the framework of approaching the synthesis and characterization by "soft" preparations (alternative to the ceramic method) of superconducting oxides and related phases [10].

2. Experimental details

β-NiO(OH) was prepared as follows. A mixture of metallic powder nickel (3.5 g), sodium peroxide (8 g) and sodium hydroxide (3 g) was fired in a nickel crucible at 700 °C for 6 h. The resulting mixture of $NaNiO_2$ and sodium phases was washed with cold water until the disappearance of alkaline reaction [11]. Subsequent washing with an acidic solution allows the deintercalation of solvated alkaline ions from γ-NiO(OH) and yields β-NiO(OH) [12]. The nickel content was determined by thermogravimetric analysis.

The neodymium source compound was obtained by dissolving neodymium oxide in the minimum volume of concentrated nitric acid, followed by the addition of water. Slow evaporation of the solution yields a crystalline neodymium nitrate product. The neodymium content was determined by thermogravimetric analysis.

$NdNiO_3$ was obtained by firing, in an alumina boat, a stoichiometric mixture (from nickel and neodymium contents determined by analysis) of β-NiO(OH) and neodymium nitrate (freshly prepared) at 650 °C for 15 h in an oxygen atmosphere.

X-ray diffraction patterns were collected on a Siemens Krystalloflex 810 automatic diffractometer and on a Rigaku Geigerflex automatic diffractometer using

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Cu Kα radiation. The infrared spectra of β-NiO(OH) were recorded on a Perkin–Elmer 882 infrared spectrophotometer with KBr pellets in the range 500–4000 cm^{-1}.

Scanning electron microscopy (SEM) observations were performed by means of a Hitachi S-2500 microscope. Transmission electron microscopy (TEM) images were obtained with a Hitachi H-800 microscope.

3. Results and discussion

In this work we approach the synthesis of $NdNiO_3$ by a low temperature and low oxygen pressure method starting from nickel(III) precursors, namely β-NiO(OH) and a mixture of nickel and neodymium hydroxides.

With respect to the first precursor, the diffraction pattern of β-NiO(OH) was broad, which is indicative of poor crystallinity and corresponds to those reported in the JCPDS power diffraction file [13]. The infrared spectrum of this compound does not show the characteristic sharp OH stretching absorption associated with nickel(II) hydroxide which could be present as an impurity [14]. Figure 1 is an SEM image exhibiting the morphology of this compound. The particle size is inhomogeneous, but the micrograph clearly shows the layered nature of the compound, as can be expected from the "soft" chemical synthesis by exchange of Na^+ by H^+ from $NaNiO_2$ [12].

The X-ray powder diffraction patterns of $LaNiO_3$ and $NdNiO_3$ prepared by the first method are shown in Fig. 2. The more intense peaks correspond to the perovskite compounds, while small peaks corresponding to nickel and lanthanide oxides are observable mainly in the $NdNiO_3$ pattern. The $LaNiO_3$ pattern

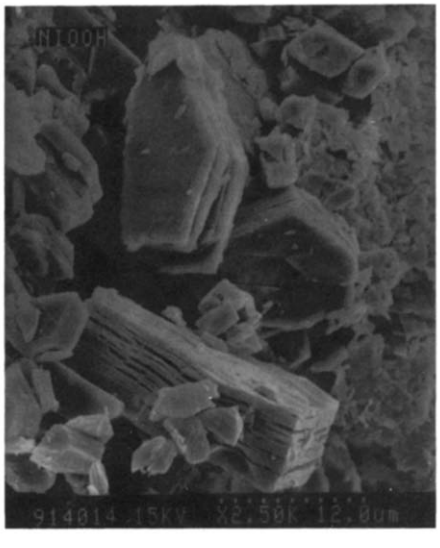

Fig. 1. SEM image of β-NiO(OH).

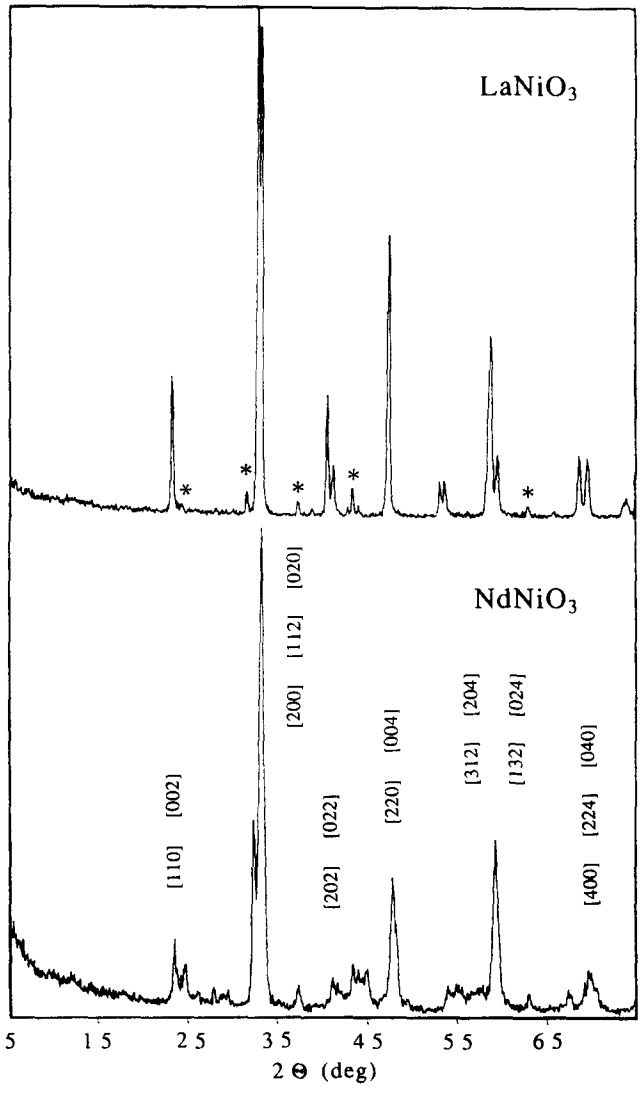

Fig. 2. X-ray powder diffraction patterns of $RENiO_3$ (RE ≡ La, Nd) obtained from β-NiO(OH). Peaks of $NdNiO_3$ are indexed; for clarity, impurity peaks are marked with an asterisk in $LaNiO_3$ pattern.

shows the characteristic splitting in the peaks that evidences the rhombohedral distortion of the perovskite structure. In Table 1 we report the indexation of the observed diffraction pattern of $NdNiO_3$ with the orthorhombic cell proposed by Lacorre *et al.* [5].

In Fig. 3 the electron diffraction pattern of $NdNiO_3$ along the [001] zone axis is shown. A careful examination of this pattern is consistent with an orthorhombic unit cell and the a/b ratio is estimated to be 1.003. This result shows unambiguously that this synthetic approach leads to an orthorhombic structure.

With respect to the second synthetic approach, the synthesis via hydroxide precursors is described elsewhere [9]. The diffractogram of this product is similar to that of the product obtained by the first synthetic method. Figure 4 shows an SEM image of $NdNiO_3$

TABLE 1. Indexation of the observed diffraction pattern of $NdNiO_3$ with the orthorhombic cell proposed by Lacorre *et al.* ($a = 5.3888$ Å, $b = 5.3845$ Å, $c = 7.6127$ Å) [5]

hkl	$2\Theta_{obs}$	d_{obs}	d_{calc}
110 002	23.4	3.80	3.81
200 112 020	33.2	2.70	2.69
202 022	41.1	2.19	2.20
220 004	47.8	1.90	1.90
312 204 132 024	59.2	1.56	1.55
400 224 040	69.7	1.35	1.35

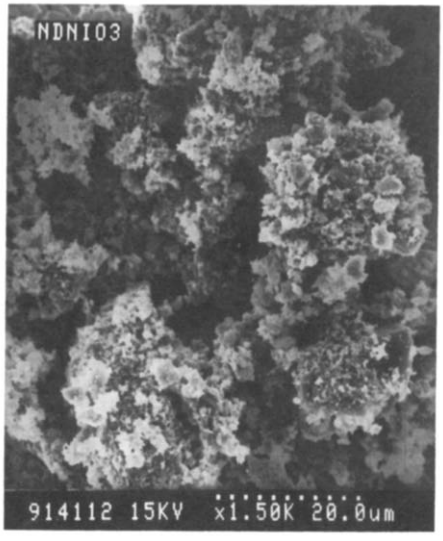

Fig. 4. SEM image of $NdNiO_3$ prepared from hydroxide mixture.

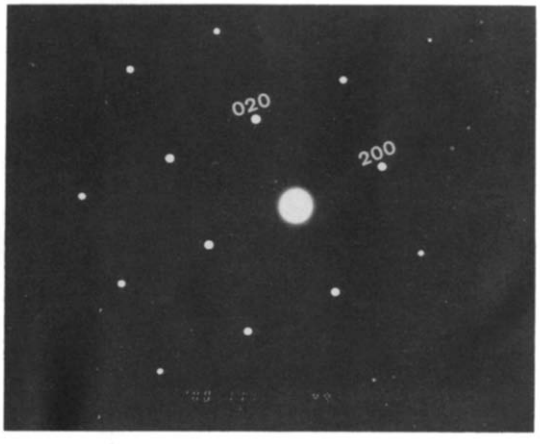

Fig. 3. Selected area diffraction pattern of $NdNiO_3$ along [001] zone axis.

obtained in this way. The product has a homogeneous and very low particle size, similar to that of the product obtained from β-NiO(OH).

4. Concluding remarks

In contrast with the work of Vassiliou *et al.* [8], which yields a rhombohedral form of $NdNiO_3$, we have developed a low temperature and low oxygen pressure synthetic route to this compound which allows us to obtain it with the orthorhombic (high pressure) structure, as evidenced by the electron diffraction pattern studies. We have shown that the other nickel(III) precursor method mentioned in the literature [9] seems also to yield the orthorhombic form.

It is interesting to point out that in both cases the products are obtained with nearly submicrometre particle sizes. This makes careful analysis of the powder X-ray diffraction patterns difficult owing to the broadening of the peaks. In addition to this particle size broadening, low temperature methods also yield products with mechanical strains, which also contribute to the broadening. These strains could be the origin of the appreciable hysteresis in resistivity measurements that has been observed in $NdNiO_3$ prepared by a low temperature method [8, 15].

More work is needed in order to understand why the different low temperature methods that avoid the use of high oxygen pressures seem to yield products with (slightly) different structures and to extend this strategy to other rare earth nickelates.

Acknowledgments

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