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2004 J. Phys.: Condens. Matter 16 S1277

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# Crystal growth of NdNiO<sub>3</sub> perovskite under high oxygen pressure

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Received 21 January 2004

Published 26 March 2004

Online at [stacks.iop.org/JPhysCM/16/S1277](http://stacks.iop.org/JPhysCM/16/S1277)

DOI: 10.1088/0953-8984/16/14/040

## Abstract

Well-shaped single crystals of NdNiO<sub>3</sub> perovskite have been grown for the first time under high oxygen pressure conditions, in a belt-type press at 4 GPa. The reaction took place in sealed platinum capsules, in the presence of KClO<sub>3</sub> as the oxidizing agent. It seems that the choice of hydroxides of the cations involved as departure reagents is crucial for the success of the crystal growth, via water vapour transport reactions. The perovskite has been characterized by x-ray diffraction, scanning microscopy and differential scanning calorimetry measurements, suitable to identify the metal–insulator transition. The transition temperature of the as-grown crystals, of 191.2 K in the heating run, is significantly lower than that reported for powder NdNiO<sub>3</sub> materials. This suggests a better metallicity of the present crystals, probably due to an improved oxygen stoichiometry associated with the much stronger oxidizing conditions utilized for its preparation.

## 1. Introduction

The family of RNiO<sub>3</sub> perovskites (R = rare earths) offers an excellent opportunity to study a metal-to-insulator (MI) transition in narrow  $\sigma^*$  band oxides, in which the bandwidth can be significantly varied as the  $e_g(\text{Ni})-2p_\sigma(\text{O})$  covalent mixing is progressively reduced from R = La to Lu. The complete series of rare-earth nickelates RNiO<sub>3</sub> (R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Lu) was first described by Demazeau *et al* in 1971 [1], who prepared these metastable materials under high pressure of 6 GPa. Lacorre *et al* [2] described the existence of metal-to-insulator transitions for the Ni perovskites with R = Pr, Nd, . . . , Eu, as a function of temperature and the size of the rare-earth cation, measured in powder samples prepared under moderate O<sub>2</sub> pressure of 20 MPa. They present orthorhombic symmetry (space group *Pbnm*) both above and below the MI transition. The subtle structural changes accompanying the metal–insulator transition [3] do not imply a symmetry change. The insulating phase

becomes magnetically ordered below  $T_N$  and the corresponding phase diagram as a function of the tolerance factor was mapped out [4, 5]. The magnetic ordering of Ni below  $T_N$  [6–8] is defined by an unexpected propagation vector  $\mathbf{k} = (1/2, 0, 1/2)$ , which implies that ferromagnetic (FM) and antiferromagnetic (AFM) Ni–O–Ni couplings alternate along the three pseudocubic axes. The materials containing  $R^{3+}$  cations smaller than  $Dy^{3+}$  present a rather rich phenomenology associated with the MI transition, including the occurrence of a charge disproportionation (CHD) of  $Ni^{3+}$  cations associated with the electronic localization in  $YNiO_3$  ( $T_{MI} = 582$  K) [9–12]. In the delocalized carrier regime, above  $T_{MI}$ , the structure is orthorhombic ( $Pbnm$ ), similar to that of  $RNiO_3$ ,  $R = Pr, Nd$ . Below  $T_{MI}$  the symmetry changes to monoclinic ( $P2_1/n$ ).

All of the preceding findings have been studied for polycrystalline  $RNiO_3$  samples, since the growth of single crystals had not been possible so far, given the difficulties inherent to the high pressure preparation of these materials. The lack of availability of single crystals has delayed an in-depth comprehension of the subtle mechanisms driving the electronic properties of these fascinating perovskites. In this work we describe the growth under pressure, for the first time, of single crystals of  $NdNiO_3$ , with an average size of 50–100  $\mu\text{m}$ . The preliminary characterization of this material, by x-ray diffraction, scanning microscopy and differential scanning calorimetry (DSC) measurements, is also reported.

## 2. Experimental details

Single crystals of the  $NdNiO_3$  perovskite were grown as follows. About 0.60 g of a stoichiometric mixture of  $Nd(OH)_3$  and  $Ni(OH)_2$  was ground together with 0.24 g of  $KClO_3$ . The mixture was put into a platinum capsule, sealed and placed in a graphite heater. The reaction was carried out in a belt-type press (1000 ton), at a pressure of 4 GPa for 15 min at 900 °C; this was followed by slow cooling from 900 to 600 °C in 1 h. The product was washed in water to dissolve the KCl and then dried in air at 150 °C for 1 h. This procedure yielded  $NdNiO_3$  crystals conformed as well-shaped needles of up to 100  $\mu\text{m}$  in size. Alternative procedures using mixtures of  $KClO_3 + KCl$  as a flux and heating at 800 °C followed by slow cooling down to 500 °C did not lead to crystals, but to a compact  $NdNiO_3$  microcrystalline powder.

X-ray powder diffraction (XRD) patterns were collected for phase identification and to assess phase purity, using Cu  $K\alpha$  radiation in a Siemens D-501 goniometer controlled by a DACO-MP computer. A room temperature structural refinement was performed from XRD data from crushed crystals. The diagram was recorded by step-scanning from 10° to 100° in  $2\theta$ , in increments of 0.05° and with a counting time of 4 s for each step. The XRD pattern was analysed by the Rietveld method, using the FULLPROF program [13]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. No regions were excluded in the refinement. In the final run the following parameters were refined: background coefficients, zero point, half-width, pseudo-Voigt and asymmetry parameters for the peak shape; scale factors, positional and unit-cell parameters. The isotropic thermal factors were set to 0.3 and 0.7  $\text{\AA}^2$  for metal and oxygen atoms, respectively, and an overall thermal factor was also refined.

DSC measurements were performed in a Mettler TA3000 system equipped with a DSC30 unit, in the temperature range from 143 to 283 K. The heating and cooling rates were 10 °C  $\text{min}^{-1}$ , using about 70 mg of sample.

Scanning electron microscopy (SEM) micrographs were taken using a Philips XL30 microscope at an accelerating voltage of 25 kV, and magnification values up to 6500 $\times$ . The  $NdNiO_3$  SEM images were taken for as-grown uncoated crystals, stuck on a carbon coated adhesive film.

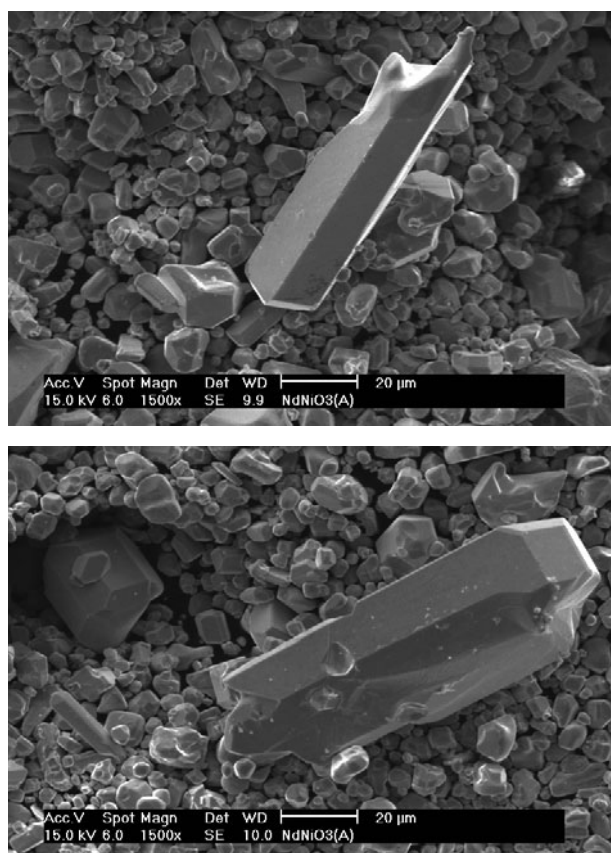
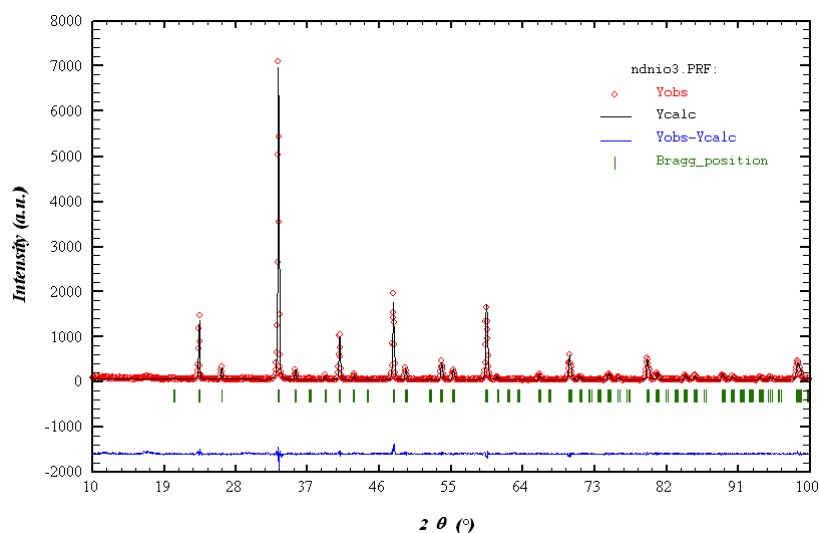


Figure 1. Scanning electron micrographs of as-grown NdNiO<sub>3</sub>, taken at a magnification of 1500 $\times$ .

### 3. Results and discussion

Figure 1 shows two SEM pictures showing the characteristic shapes and sizes of the as-grown crystals. There are a large number of small crystals (also well conformed) with average sizes 5–10  $\mu\text{m}$ , and some large crystals, with sizes up to 100  $\mu\text{m}$ , with well-defined prismatic shapes with truncated edges. They are presumably single crystals, although further confirmation is required.

The XRD diagram obtained from crushed crystals is characteristic of a perovskite, showing sharp, well-defined superstructure reflections corresponding to an orthorhombic distortion of the aristotype (ideal cubic perovskite,  $\mathbf{a}_0 \approx 4 \text{ \AA}$ ) with unit-cell parameters related to  $\mathbf{a}_0$  as  $\mathbf{a} = \sqrt{2}\mathbf{a}_0$ ,  $\mathbf{b} = \sqrt{2}\mathbf{a}_0$ ,  $\mathbf{c} = 2\mathbf{a}_0$ . The structural refinement at room temperature was performed by the Rietveld method taking as starting parameters those reported in [3]. The structure was refined in the conventional orthorhombic  $Pbnm$  space group, with Nd and Ni atoms placed at 4c and 4d positions, respectively, and two independent positions for oxygens, O1(4c) and O2(8d). The final atomic coordinates, unit-cell parameters and discrepancy factors after the refinement are included in table 1. Figure 2 illustrates the good agreement between observed and calculated XRD profiles for NdNiO<sub>3</sub> perovskite. No impurities were detected in the XRD diagram.



**Figure 2.** Observed (circles), calculated (solid curve) and difference (at the bottom) XRD profiles for NdNiO<sub>3</sub> at 295 K. The series of tick marks indicates the positions of the allowed Bragg reflections for NdNiO<sub>3</sub>.

(This figure is in colour only in the electronic version)

**Table 1.** Room temperature structural parameters for NdNiO<sub>3</sub>. (Note:  $a = 5.3903(6)$  Å,  $b = 5.3787(5)$  Å,  $c = 7.6097(8)$  Å; space group  $Pbnm$ ,  $Z = 4$ .  $B_{\text{overall}} = -0.08$  Å<sup>2</sup>.  $R_p = 8.28$ ,  $R_{\text{wp}} = 11.2$ ,  $R_{\text{exp}} = 9.49$ ,  $R_1 = 4.52\%$ ;  $\chi^2 = 1.39$ .)

Atom	Site	$x/a$	$y/b$	$z/c$	$B$ (Å <sup>2</sup> )
Nd	4c	0.9929(9)	0.0356(4)	0.25	0.3
Ni	4b	0.5	0	0	0.3
O1	4c	0.067(8)	0.496(4)	0.25	0.7
O2	8d	0.712(6)	0.281(7)	0.037(4)	0.7

Figure 3 illustrates the DSC curves for NdNiO<sub>3</sub> crystals, obtained during the cooling and heating runs. The cooling process exhibits a sharp exothermic peak centred at  $-87.4$  °C (185.8 K). The reverse transition, showing an exothermic peak centred at  $-82.0$  °C (191.2 K), is observed during the heating run. These peaks can be assigned to the MI transition in NdNiO<sub>3</sub> perovskite. These values are slightly lower than that previously reported for NdNiO<sub>3</sub> powder samples, of 200 K. This indicates an extended domain of the metallic region in the present crystals, down to lower temperatures, perhaps due to an improved oxygen stoichiometry. It is important to underline that all of the preceding studies on the metal–insulator transition of the former members of the RNiO<sub>3</sub> perovskites ( $R = \text{Pr, Nd, Sm, Eu}$ ) have been performed on powder samples prepared and oxygenated at moderate oxygen pressures of 20 MPa [2]. This is in contrast with the much more strongly oxidizing conditions used in the present work: 4 GPa in the presence of O<sub>2</sub> produced by the *in situ* decomposition of KClO<sub>3</sub>. The thermal hysteresis observed by means of DSC in figure 3 suggests that the transition is first order for this single-crystalline material. The heat transfer accounts for the entropy and lattice energy gain due to the electronic delocalization.

A more complete characterization of the present crystals, including a scheduled study by means of synchrotron x-ray diffraction, aiming to unravel the possible coupling of structural

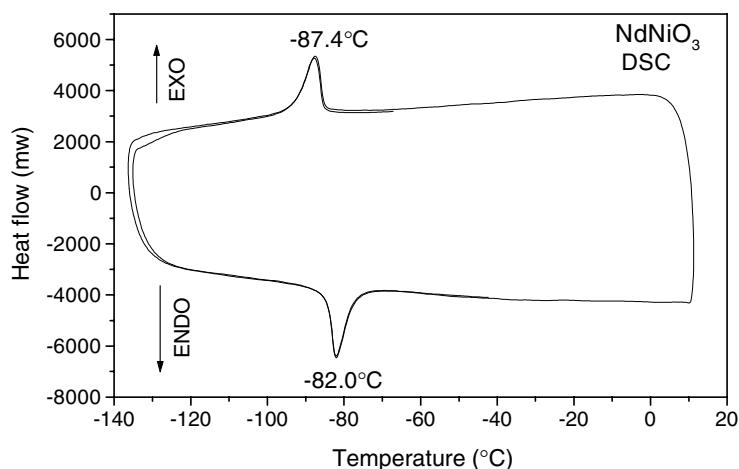


Figure 3. DSC curves for NdNiO<sub>3</sub> obtained in the cooling and heating runs.

modifications upon the MI transition and the nature of the unusual and unexplained magnetic structure at low temperature is under way.

#### 4. Conclusions

We have demonstrated the possibility of preparing well-shaped NdNiO<sub>3</sub> crystals, under high oxygen pressure in a belt-type press. We believe that the use of starting reactives in the form of hydroxides is crucial for the crystallization of the perovskite, perhaps through water vapour transport-driven reactions. The use of fluxes was not successful, in the temperature and pressure ranges studied.

#### Acknowledgments

We thank CICYT, project MAT2001-0539, for financial support and the Spanish Ministry of Science and Technology and CNRS for funding the CSIC/CNRS project 2002FR0001.

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