

Crystal Structure of NdNiO₃ at 123 and 292 K

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Well-shaped, small single crystals of the NdNiO₃ perovskite were grown 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 KClO₃ as oxidizing agent. It seems that the choice of hydroxides of the involved cations as precursor reagents is crucial for the success of the crystal growth, *via* water vapor transport reactions. NdNiO₃ was investigated by X-ray powder and single crystal diffraction at 123 and 292 K: GdFeO₃ type, *Pbnm*, $a = 538.10(7)$, $b = 537.91(7)$, $c = 760.26(10)$ pm, $wR2 = 0.0434$, 338 F^2 values, and 29 variables at 292 K. The low-temperature data gave no hint for a monoclinic distortion: *Pbnm*, $a = 537.91(8)$, $b = 538.49(8)$, $c = 760.02(12)$ pm, $wR2 = 0.0299$, 338 F^2 values, and 29 variables. At room temperature, the Ni–O distances vary from 193.9 to 194.2 pm, and the O–Ni–O angles cover the range from 89.5 to 90.5°. Similar small distortions are observed for the NiO₆ octahedra at 123 K. Due to the strong orthorhombic distortion, the neodymium atoms have only nine oxygen neighbors at Nd–O distances from 236.0 to 295.7 pm.

Key words: High-Pressure Syntheses, High Pressure
Crystal Growth, Crystal Structure

Introduction

RENiO₃ perovskites (RE = rare-earth), which contain trivalent nickel cations and which must be stabilized under high oxygen pressures [1], have been extensively studied in the last few years since they ex-

hibit metal-to-insulator (MI) transitions as a function of temperature that systematically varies with the rare-earth size [2–4]. The occurrence of these thermally driven MI transitions has been related to the closing of the charge-transfer gap, induced by the narrowing of the electronic bandwidth when temperature decreases [4, 5]. The degree of distortion of the structure determines the onset of electronic localization: for a given RE^{3+} size the NiO₆ octahedra are tilted in order to optimize RE –O bond-distances, giving rise to bent Ni–O–Ni angles determining the degree of overlapping of Ni 3*d* and O 2*p* orbitals and, therefore, the electronic bandwidth. For the less-distorted rhombohedral perovskite LaNiO₃, the degree of overlap is enough to ensure metallic behavior [6]; for RE^{3+} cations smaller than La³⁺ (RE = Pr, Nd, Sm...) the structure is orthorhombic and an abrupt change in the resistivity curves is observed at increasing temperatures: $T_{MI} = 130$ K (RE = Pr), 200 K (RE = Nd), 400 K (RE = Sm), *etc.* Metal-like behavior is only observed above T_{MI} .

Recently, the occurrence of a charge disproportionation (CHD) of Ni³⁺ cations associated with electronic localization was reported for YNiO₃ ($T_{MI} = 582$ K) [7]. In the delocalized carriers regime, above T_{MI} , the structure is orthorhombic (*Pbnm*), similar to that of RENiO₃, RE = Pr, Nd [4, 5]. Below T_{MI} the symmetry changes to monoclinic (space group $P2_1/n$) through a *translationengleiche* symmetry reduction. The monoclinic symmetry in the localized carrier regime is due to the existence of two types of alternating NiO₆ octahedra. They can be ascribed to two different charge states on Ni, or to Ni–O bonding states. It has been shown that the symmetry for the smallest RE^{3+} cations (RE = Ho, Y, Er, Tm, Yb and Lu) is also monoclinic at RT [8]. The evidence of two Ni³⁺ sites has been recently confirmed by Mössbauer spectroscopy using a low doping rate (1 to 2%) of ⁵⁷Fe³⁺ as Mössbauer probe into the YNiO₃, LuNiO₃ and TlNiO₃ structures [9, 10]. However, this lattice distortion occurring below T_{MI} has remained rather elusive for the largest cations RE = Pr, Nd, and Sm. Recently, electron microscopy and Raman scattering experiments have suggested a symmetry breaking at T_{MI} in NdNiO₃ [11].

Although RENiO₃ perovskite compounds have been known for many years, all the experiments aiming at a precise determination of the structures, including synchrotron and neutron diffraction, have been carried out

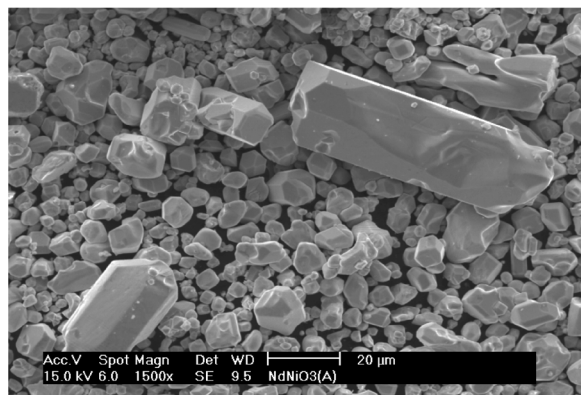


Fig. 1. As-grown single crystals of NdNiO₃.

on polycrystalline samples, except for a very recent work on 500-Å-thick thin films of NdNiO₃, performed to evaluate the possibility of a charge ordered state below the M-I phase transition [12, 13]. Both X-ray and neutron powder diffraction have not shown any sign of orbital ordering (superstructure reflections should be 10^4 times smaller than the largest nuclear reflection), which speaks in favor of a very small, if any, lattice distortion. We have now grown small single crystals of NdNiO₃ (Fig. 1), large enough to carry out diffraction experiments. With these high-quality single crystals it will be possible to test many ideas on the origin of magnetism in this compound and the very intriguing possibility of a *pure* orbital ordering; *i.e.*, without an accompanying lattice distortion. It is demonstrated that, split Bragg reflections due to a monoclinic distortion caused by a charge-disproportionated state below T_{MI} are not present.

Experimental Section

Synthesis

Single crystals of the NdNiO₃ perovskite were grown as follows: About 0.60 g of a stoichiometric mixture of Nd(OH)₃ and Ni(OH)₂ were ground together with 0.24 g of KClO₃. 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 tons), at a pressure of 4 GPa for 15 min at 1173 K, followed by slow cooling from 1173 to 873 K in 1 h. The product was washed in water to dissolve KCl and then dried in air at 423 K for 1 h. This procedure yielded well shaped NdNiO₃ crystals up to 100 μm in size. Alternative procedures using mixtures of KClO₃ + KCl as a flux, heating at 1073 K followed by slow cooling to 773 K did not lead to crystals, but to a compact microcrystalline NdNiO₃ powder.

Table 1. Crystal data and structure refinement for NdNiO₃, space group *Pbnm*, *Z* = 4, at 123 and 292 K.

Empirical formula	NdNiO ₃	NdNiO ₃
Molar mass [g/mol]	250.95	250.95
Temperature [K]	123	292
Unit cell dimensions [pm] (diffractometer data)	<i>a</i> = 537.91(8) <i>b</i> = 538.49(8) <i>c</i> = 760.02(12)	<i>a</i> = 538.10(7) <i>b</i> = 537.91(7) <i>c</i> = 760.26(10)
Volume [nm ³]	0.2202	0.2201
Calculated density [g/cm ³]	7.57	7.57
Crystal size [μm ³]	20 × 40 × 40	20 × 40 × 40
Absorption coefficient [mm ⁻¹]	31.6	31.6
<i>F</i> (000)	448	448
θ Range [°]	4 to 30	4 to 30
Range in <i>hkl</i>	±7, ±7, ±10	±7, ±7, ±10
Total no. reflections	2241	2219
Independent reflections	338 (<i>R</i> _{int} = 0.0384)	338 (<i>R</i> _{int} = 0.0364)
Reflections with <i>I</i> > 2σ(<i>I</i>)	321 (<i>R</i> _{sigma} = 0.0218)	323 (<i>R</i> _{sigma} = 0.0261)
Data/parameters	338 / 29	338 / 29
Goodness-of-fit on <i>F</i> ²	1.136	1.232
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0152 <i>wR</i> 2 = 0.0294	<i>R</i> 1 = 0.0188 <i>wR</i> 2 = 0.0432
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0167 <i>wR</i> 2 = 0.0299	<i>R</i> 1 = 0.0198 <i>wR</i> 2 = 0.0434
Extinction coefficient	0.0240(8)	0.021(1)
Largest diff. peak and hole [e/Å ³]	0.83 and −1.18	0.89 and −2.25

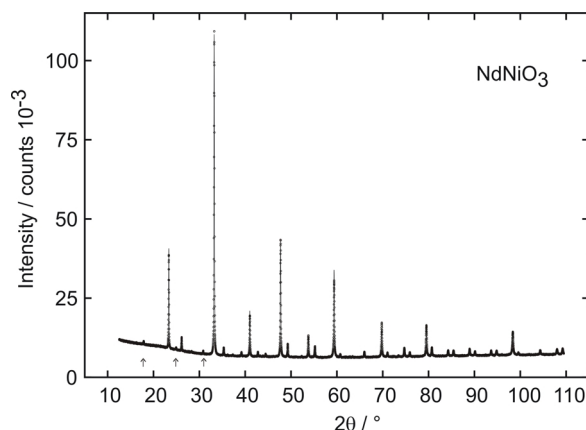


Fig. 2. X-ray powder diffraction diagram (Cu-K_{α1} radiation) of NdNiO₃. A minor amount of an unknown impurity phase is marked by arrows.

X-ray powder data and structure refinements

The polycrystalline product has been characterized through a powder pattern using a Stoe Stadi P powder diffractometer with Cu-K_{α1} radiation (λ = 154.0598 pm, Ge monochromator, silicon (*a* = 543.07 pm) as external standard). The measurement was performed in transmission geometry. The pattern is presented in Fig. 2. The powder data could readily be indexed on the basis of a GdFeO₃ type

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for NdNiO_3 at 123 and 292 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
123 K											
Nd	4c	0.00733(3)	0.96059(4)	3/4	27(1)	30(2)	28(2)	0	0	−3(1)	29(1)
Ni	4a	1/2	0	1/2	15(3)	20(2)	17(3)	−1(2)	0(2)	0(2)	17(1)
O1	4c	0.4278(6)	−0.0093(5)	1/4	76(13)	53(13)	35(14)	0	0	15(11)	55(6)
O2	8d	0.7869(3)	−0.2133(3)	0.4610(3)	45(9)	44(9)	63(9)	1(8)	13(8)	4(7)	51(4)
292 K											
Nd	4c	0.00669(4)	0.96382(6)	3/4	59(2)	68(2)	43(2)	0	0	−9(1)	57(2)
Ni	4a	1/2	0	1/2	36(4)	32(3)	25(4)	−2(2)	−1(2)	1(2)	31(2)
O1	4c	0.4296(7)	−0.0081(7)	1/4	106(17)	74(17)	25(17)	0	0	8(14)	68(7)
O2	8d	0.7847(5)	−0.2152(5)	0.4627(4)	74(11)	75(11)	75(11)	19(10)	12(10)	35(9)	75(5)

primitive orthorhombic unit cell with the lattice parameters $a = 538.59(1)$, $b = 538.59(1)$, $c = 761.69(1)$ pm. The sample showed three very weak additional reflections (marked by arrows in Fig. 2) corresponding to a non-identified impurity. The lattice parameters determined from the powders and the single crystals (Table 1) showed reasonable agreement.

Small platelet like crystals were selected from the sample and were first investigated on a Buerger precession camera equipped with an image plate system (Fujifilm BAS-1800) in order to establish both symmetry and suitability for intensity data collection. Intensity data were first collected at room temperature making use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo- K_{α} radiation (0.71073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the $\omega/2\theta$ mode. Empirical absorption corrections were applied on the basis of psi-scan data followed by spherical absorption corrections. The selection of single crystals was performed carefully in order to get an untwinned crystal for the low-temperature data collection. Keeping in mind the Bärnighausen tree for the various perovskite superstructures [14], the two *translationengleiche* symmetry reductions in going from the SrTiO_3 structure, space group $Pm\bar{3}m$, to the orthorhombically distorted GdFeO_3 type, space group $Pbnm$, twinning is highly probable. Indeed, some of the crystals showed twinning through the twin matrix 0 1 0, 1 0 0, 0 0 −1, and a few percent of a second domain were detected.

Room-temperature and low-temperature intensity data of an untwinned crystal were collected at 292 and 123 K on a Bruker AXS Smart Apex I with a rotating anode (graphite monochromatized Mo- K_{α} ; 50 kV, 150 mA) and a fixed detector distance of 50 mm. Ω -Scans were employed with a step width of 0.3° at three consequent φ -positions (0, 120, and 240°), thus allowing a ψ -scan absorption correction. The Ω -range was 180° i.e. $-90^\circ \leq \theta \leq 90^\circ$. A 30 s counting time was used for each frame. The data acquisition and the absorption correction were carried out with SAINT PLUS 6.28A and SADABS, respectively, supplied by Bruker-AXS.

			123 K	292 K
Nd:	1	O1	235.5(3)	236.0(4)
	2	O2	237.7(2)	238.8(3)
	1	O1	246.8(3)	248.6(4)
	2	O2	257.0(2)	257.7(3)
	2	O2	266.6(2)	266.9(3)
	1	O1	298.5(3)	295.7(4)
Ni:	2	O1	194.0(1)	193.9(1)
	2	O2	194.6(2)	194.1(2)
	2	O2	194.6(2)	194.2(2)
	2	Ni	194.0(1)	193.9(1)
	1	Nd	235.5(3)	236.0(4)
	1	Nd	246.8(3)	248.6(4)
	1	Nd	298.5(3)	295.7(4)
	1	Ni	194.6(2)	194.1(2)
	1	Ni	194.6(2)	194.2(2)
	1	Nd	237.7(2)	238.8(3)
	1	Nd	257.0(2)	257.7(3)
	1	Nd	266.6(2)	266.9(3)

Table 3. Interatomic distances (pm), in the structure of NdNiO_3 at 123 and 292 K. All distances within the first coordination spheres are listed. Standard deviations are given in parentheses.

The starting atomic parameters were deduced from an automatic interpretation of direct methods using SHELXS-97 [15] and the structures were refined using SHELXL-97 (full-matrix least-squares on F_o^2) [16] with anisotropic atomic displacement parameters for all sites. The final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinements are available.*

Discussion

The structure of NdNiO_3 has been refined from single crystal data at room temperature and at 123 K, well below the metal-insulator transition [3, 17]. Al-

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-416212 (NdNiO_3 123 K) and CSD-416213 (NdNiO_3 292 K).

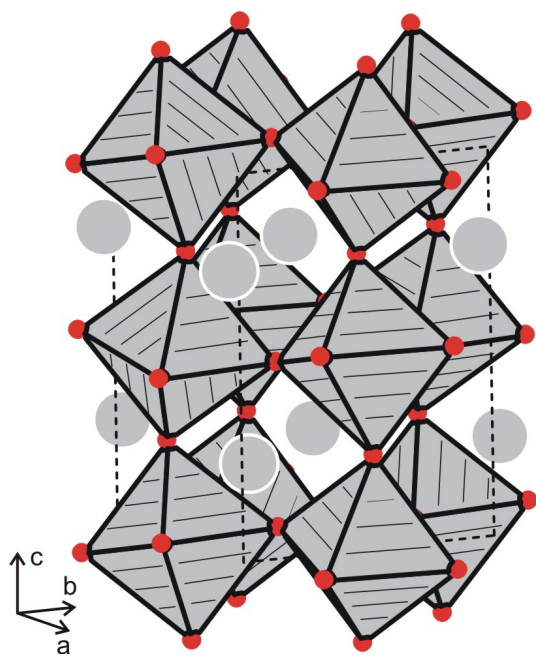


Fig. 3. The structure of NdNiO_3 (space group $Pbnm$). The three-dimensional network of corner-sharing NiO_6 octahedra is emphasized.

though neutron and synchrotron powder diffraction data clearly revealed a charge disproportionation and a lowering of the symmetry for YNiO_3 [7], there was no

hint for a monoclinic distortion for NdNiO_3 at 123 K. Both structure refinements revealed the orthorhombic GdFeO_3 type structure (Table 2, Fig. 3), space group $Pbnm$ (non-standard setting of $Pnma$). Most likely, the Nd^{3+} cations are too large for such a distortion.

At both temperatures, the NiO_6 octahedra are almost similar: 194.0–194.6 pm Ni–O; 88.7–91.3° O–Ni–O at 123 K and 193.9–194.2 pm Ni–O; 89.5–90.5° O–Ni–O at 292 K. The anisotropic displacement parameters gave no hint for a violation of the orthorhombic symmetry. A monoclinic distortion would result in a significant anisotropic behavior of at least the O2 atoms, since this 8d site would split into two fourfold sites in the lower symmetry space group. Furthermore, as in the case of YNiO_3 , this splitting would result in distinctly different Ni–O distances. In a nutshell, no deviation from the orthorhombic GdFeO_3 type symmetry is observed for NdNiO_3 based on X-ray single crystal data at 123 K.

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