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Abstract
The structural changes of SmNiO$_3$ under high pressure have been studied by means of x-ray powder diffraction with synchrotron radiation in a diamond anvil cell. The orthorhombic perovskite structure transforms into the less distorted $R\bar{3}c$ rhombohedral structure at a pressure of 26 GPa. The volume versus pressure data are well described by a single Murnaghan equation of state, which yields a bulk modulus of 167 GPa. At 2.5 GPa the cell parameter b undergoes a small abrupt contraction that we propose is related to the expected pressure-induced metallization.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The nickel perovskite family RNiO$_3$ (in which R is a rare earth ion or Y) is a very attractive system in which to study the relation between structural, electronic and magnetic degrees of freedom. The members of this family crystallize in the perovskite structure, and the degree of deviation from the ideal cubic perovskite gradually increases following the lanthanide contraction; while LaNiO$_3$ has rhombohedral $R\bar{3}c$ symmetry and shows metallic conductivity over the whole temperature range, the rest of the series is orthorhombic ($Pbnm$ space group) and shows a sharp insulator to metal transition, whose critical temperature T_{M-I} increases as the size of the rare earth ion decreases and the perovskite distortion increases. For example, $T_{M-I} = 200$ K for NdNiO$_3$, 400 K for SmNiO$_3$ and 600 K for LuNiO$_3$ [1]. The last members of the series with the smallest rare earth cation (R = Ho, Y, Er, Tm, Yb and Lu) have been reported [2] to present a small monoclinic distortion (space group $P2_1/n$, $\beta < 90.2°$) in the insulating regime. This arrangement implies two independent Ni positions and the presence of a Ni charge disproportionation ($2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$).

SmNiO$_3$ is insulating at ambient temperature, its insulator to metal transition temperature being 400 K [3]. However, its structure in the insulating regime has not yet been shown to be monoclinic; no reduction in the crystal symmetry across the insulator to metal transition has been detected, only a contraction of volume at the electronic delocalization as a result of a contraction of the Ni–O bond length and an increase of the Ni–O–Ni bond angle [4].

Pressure is a variable which allows a continuous modification of the interatomic distances and thus tuning of the lattice and electronic degrees of freedom. It has been shown [5, 6] that pressure favours the metallic state in the $RNiO_3$ system. A resistance study [7] of $SmNiO_3$ as a function of pressure reveals that at a pressure of 2.05 GPa (the highest pressure of that work), T_{M-I} is lowered from 400 K at ambient pressure to near room temperature. Here we present a study on the effect of high pressure on the structural properties of $SmNiO_3$.

2. Experimental details

$SmNiO_3$ was prepared by solid state reaction under 200 bar of O_2 pressure [8]. The resulting polycrystalline powder was studied at ambient temperature by means of angle-dispersive x-ray diffraction (wavelength of 0.4146 Å) at beamline ID09A of the European Synchrotron Radiation Facility (ESRF) in Grenoble. Pressures up to a maximum of 18 GPa in a first run and up to 38 GPa in the second were generated with membrane-type diamond anvil cells and measured by the ruby luminescence method [9]. Nitrogen was used as the pressure medium. Synchrotron x-ray diffraction patterns were recorded on image plates and then integrated [10] to obtain intensity versus 2Θ data. The diffraction data were analysed using the program FULLPROF [11].

3. Results and discussion

At ambient conditions $SmNiO_3$ crystallizes in the $GdFeO_3$ orthorhombic *Pbnm* structure, with Sm and O(1) at site 4c $(x, y, \frac{1}{4})$, Ni at 4b $(\frac{1}{2}, 0, 0)$ and O(2) in general 8d (x, y, z) positions. $SmNiO_3$ diffraction patterns can be refined as a single orthorhombic *Pbnm* phase up to a pressure of about 20 GPa. The parameters refined were the cell parameters, atomic positions, pseudo-Voigt peak shape factors, an overall temperature factor and polynomial background parameters. A small quantity of NiO impurity was detected and also included in the refinements. Figure 1 illustrates the pressure dependence of the orthorhombic lattice parameters up to the maximum pressure of 20 GPa at which a phase transition starts. The a cell parameter is plotted as triangles, b as circles and the c parameter is plotted as squares, normalized by a factor of $\sqrt{2}$ corresponding to a pseudocubic representation of the lattice. As pressure increases the orthorhombic distortion decreases; the a and b parameters approach each other until a pressure of about 12 GPa is reached when they cross. At this pressure point the a, b and $c/\sqrt{2}$ cell parameters have almost the same value, the metric of the structure being cubic. The structure however is still orthorhombic, as is evidenced in the diffraction pattern shown in figure 2(a), for example, by the presence of the (111) Bragg peak. As pressure continues to increase there is a crossover of the lattice parameters, a becoming larger than b and c, and the orthorhombic distortion increases again.

The ambient pressure compressibility $\beta_0 = \frac{1}{L_0}(\frac{\partial L}{\partial P})_{P_0}$ of a cell parameter L is obtained by simulating the volume V as L^3 in the Murnaghan equation of state

$$V = V_0 \left(1 + \frac{K' \cdot P}{K_0} \right)^{-1/K'}$$

and fitting the bulk modulus at ambient pressure K_0, its pressure derivative K' and the volume at ambient conditions V_0. The ambient pressure compressibility is related to K_0 as $\beta_0 = -\frac{1}{3K_0}$. We obtain a remarkable difference in compressibility between the b cell parameter, with a value of β_0 of $2.9(1) \times 10^{-3}$ GPa^{-1}, and the a and c cell parameters, with $\beta_0 = 2.0(1) \times 10^{-3}$ and $1.96(5) \times 10^{-3}$ GPa^{-1} respectively.
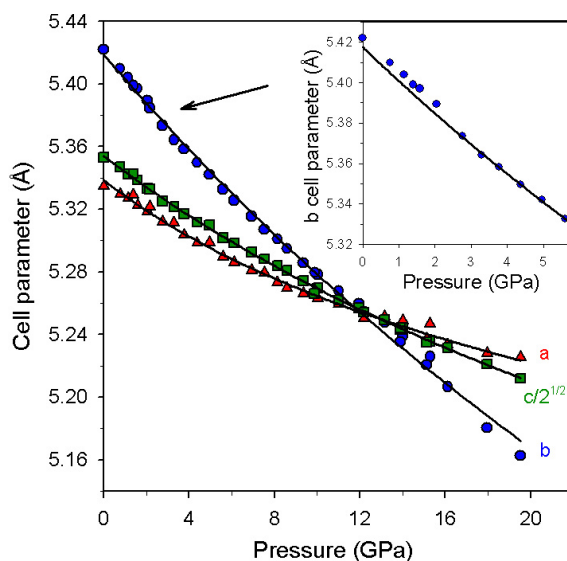
Figure 1. Lattice parameters of the orthorhombic phase of SmNiO$_3$ at ambient temperature as a function of pressure, fitted with Murnaghan-type equations. The arrow signals a small contraction of the b cell parameter at 2.5 GPa, also detailed in the inset.
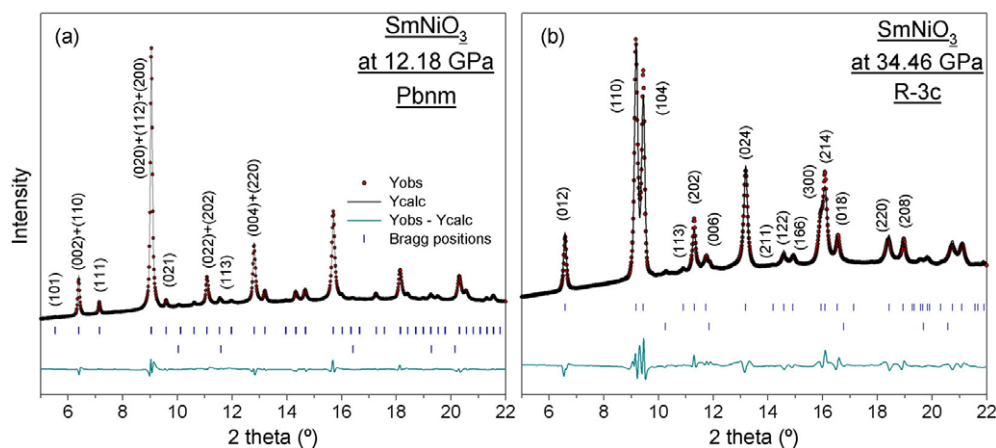

Figure 2. Rietveld refined diffraction patterns of SmNiO$_3$ showing the observed, calculated and difference patterns, and the Bragg peak positions of the SmNiO$_3$ phase and an impurity of NiO. (a) At 12.18 GPa the symmetry is orthorhombic, $Pbnm$, and (b) at 34.46 GPa it is rhombohedral, $R\bar{3}c$.

At a pressure of about 2.5 GPa the b cell parameter undergoes a small contraction; this is indicated by an arrow in figure 1, and can be seen more clearly in the inset, which shows a fit of the b cell parameter in which the pressure points below 2.5 GPa are not considered. This small contraction (about -0.08%) of the b cell parameter is similar to that found for the c parameter for YNiO$_3$ [12] and it could be related to the expected insulator to metal transition. However, higher resolution would be necessary to clearly determine the cell and volume contractions.
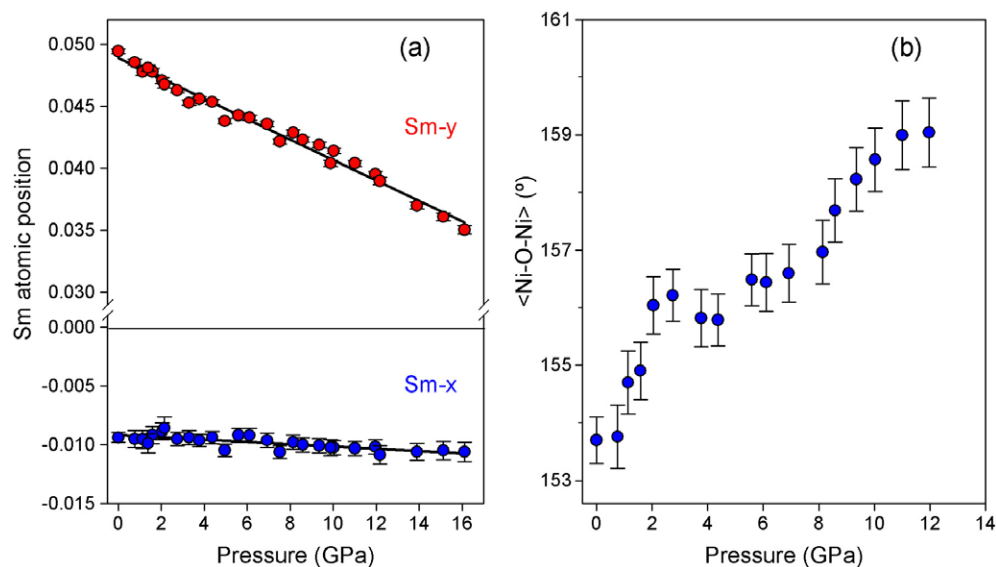
Figure 3. (a) The pressure dependence of the Sm atomic position in orthorhombic SmNiO$_3$. (b) Average Ni–O–Ni bond angle as a function of pressure.

Regarding the atomic structure, a clear evolution of the Sm atomic parameters towards the ideal positions has been found. While the Sm x atomic position remains practically constant throughout the pressure range studied, the Sm y atomic position gradually shifts towards the ideal position, as can be seen in figure 3(a). Despite the difficulties encountered in the refinement of the oxygen atomic positions, which are due to the small scattering power of oxygen compared to nickel and samarium, a clear decrease of the NiO$_6$ octahedral tilt upon application of pressure has been found; the average Ni–O–Ni angle is plotted in figure 3(b) for the lowest pressures, showing that the angle has increased by 5° at 12 GPa. This increase in symmetry is further confirmed at higher pressures by a phase transition towards a rhombohedral space group. This high pressure phase has been identified as having the same structure as that of LaNiO$_3$ at ambient conditions, rhombohedral with space group $R\bar{3}c$. There is an extensive two-phase coexistence region of about 10 GPa. A Rietveld refined pattern of the rhombohedral phase is presented in figure 1(b). Referring the $R\bar{3}c$ structure to the hexagonal setting, Sm occupies the position 6a $(0, 0, \frac{1}{4})$, Ni the position 6b $(0, 0, 0)$ and O is on the 18e $(x, 0, \frac{1}{4})$ position. The only free atomic parameter is then the x oxygen position, its deviation from the ideal $\frac{1}{2}$ value determining the tilt angle of the NiO$_6$ octahedra about the threefold axis of the ideal cubic structure. At 34.36 GPa for example, $a = 5.1757(3)$ Å, $c = 12.166(1)$ Å and for oxygen $x = 0.562(2)$, resulting in a Ni–O–Ni angle of 159.9(1)°.

The volume per formula unit versus pressure data are presented in figure 4. Only one Murnaghan equation of state has been used for both the orthorhombic and rhombohedral phases, by calculating the volume per formula unit (or a cubic equivalent volume), the orthorhombic *Pbnm* cell having four formula units, while there are six in the rhombohedral $R\bar{3}c$ cell. A bulk modulus K_0 of 167 GPa is obtained. Vertical dashed lines in figure 4 indicate the regions of stability of both phases and also the coexistence region. The patterns in the double-phase region have been refined fixing the structure to the values before and after the transition respectively for the orthorhombic and rhombohedral phases. The sample was laser annealed at 28 GPa in
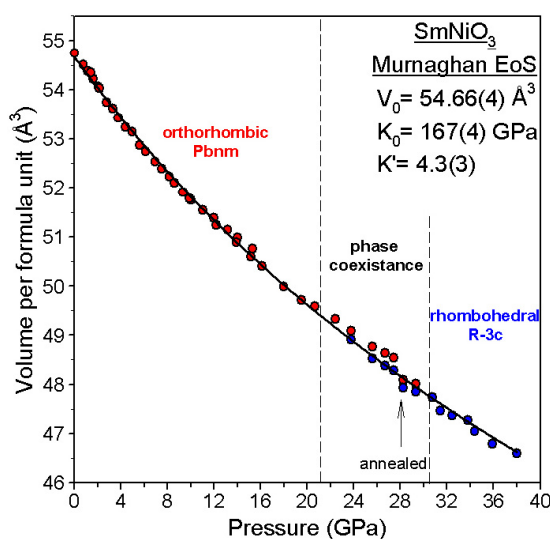
Figure 4. Volume per formula unit versus pressure. The solid curve is a Murnaghan equation of state fit to the data with the results of the fit shown in the inset. Vertical dashed lines indicate the regions of stability of the orthorhombic and rhombohedral phases.

order to release stresses and improve the hydrostaticity, resulting in an improved pattern with smaller peak widths and also a decrease in the cell volume.

4. Conclusions

In the temperature regime, SmNiO$_3$ undergoes an insulator to metal transition at the temperature of 400 K that is concomitant with an orthorhombic to orthorhombic phase transition (no monoclinic distortion has yet been reported for SmNiO$_3$ in the insulating regime), in which abrupt changes in the cell parameters occur; the cell contracts at the metallization temperature, mainly through the contraction of the b cell parameter [4] and as a consequence of the sudden decrease in Ni–O bond length.

In the pressure regime we have found a small contraction of about -0.08% in the b cell parameter at about 2.5 GPa that we propose is related to a pressure-induced metallization. At higher pressures SmNiO$_3$ undergoes an orthorhombic to rhombohedral phase transition that is unrelated to the expected metallization, as this transition is also present for metallic NdNiO$_3$ [13] and PrNiO$_3$ [14].

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