High-pressure preparation and characterization of $(R,R')\text{NiO}_3$ ($R,R'=$ rare earths) perovskites: effect of the variance of the $R^{3+}$ ionic sizes

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Abstract. In this paper we describe some novel members of the $R\text{NiO}_3$ perovskites, containing $\text{Ni}^{3+}$ and presenting metal-insulator transitions coupled to a charge disproportionation effect. This phenomenon is observed in the insulating state as a subtle monoclinic distortion, due to the presence of two unequivalent Ni ions with different coordination environments, corresponding to expanded and contracted octahedra alternating in the three-dimensional network. Here we examine how the introduction of mixed rare-earth cations at the R sublattice affects the metal-insulator transition and the structural features, from high resolution neutron powder diffraction studies.

1. Introduction

High-pressure synthesis is well known to be an effective tool to stabilize transition-metal oxides in high-valence states (e.g. Mn(V), Fe(IV), Co(IV), Ni(III), Cu(III)) or intermediate-valence states (such as Cu(II)-Cu(III), Mn(III)-Mn(IV), Fe(III)-Fe(IV)) [1,2]. The stabilization of high oxidation states is achieved either under the high-pressure of an oxidizing gas, typically oxygen, or as a consequence of the compressive effect of the external pressure on the chemical bonds, favouring the shorter and more covalent bonds corresponding to the elevated valences. Happily, many solids synthesized at high-pressure-high temperature conditions (where they are thermodynamically stable) can be “quenched” to ambient conditions, where they are termodynamically metastable, yet they remain indefinitely kinetically stable. The heavy equipment usually required for high-pressure synthesis and the limited number of laboratories where this equipment is available justifies that many of these metastable oxides have only been superficially investigated, despite the exotic properties they may present such as superconductivity, metal behavior, metal-insulator transitions or colossal magnetoresistance. These phenomena are bound to the strong electronic correlations that they usually present.

In our research group we have paid much attention to a good number of metastable materials belonging to several families such as $R\text{NiO}_3$ ($R=$ rare earths) perovskites [3-14], $\text{Tl}_2\text{Mn}_2\text{O}_7$ pyrochlore and derivatives [15-23], $RC\text{u}_2\text{Mn}_4\text{O}_{12}$ ($R=$ rare earths) complex perovskite and derivatives [23-28], $\text{ABO}_3$ ($\text{A=}\text{Se, Te}; \text{B=}\text{divalent transition metals}$) perovskites containing p-block elements at A positions [29,30], etc. In the investigation of these oxides it has been decisive the use of neutron
diffraction, most of the times in powder samples. This technique has allowed us to access to structural details typically related to the octahedral tilting in perovskite structures, the oxygen stoichiometry and order-disorder of the oxygen sublattice, the distinction between close elements in the Periodic Table, the resolution of magnetic structures and, in general, the establishment of a correlation between the structure and the properties of interest.

A central theme in our research has been the systematic study of the metal-to-insulator (MI) transitions in the $R$NiO$_3$ ($R=$ rare earths) perovskites, that Torrance et al. [30] had interpreted as a function of the reduction and closing of the charge-transfer gap between O$^{2-}$ and Ni$^{3+}$ ions. The difficulty of preparation of these phases, associated with the presence of trivalent nickel, increases as the lanthanide radius diminishes, in such a way that the mentioned transport properties (and MI transitions) had only been investigated for $R$ between La and Eu. Since the pioneering work by Démazeau in 1971 [31], the phases for $R=$ Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, had not been prepared again. One of the most relevant results was the preparation of these materials under moderate pressures of 2 GPa, in closed gold capsules in the presence of KClO$_4$, in sufficiently large amounts to perform accurate neutron and synchrotron diffraction studies across the transitions. For YNiO$_3$ we described, for the first time, a charge disproportionation associated with the MI transition [4,5]. This effect is concomitant, in the insulator state, with an extremely subtle monoclinic distortion; in the crystal structure Ni atoms occupy two independent crystallographic sites with slightly different charge, $3+\delta$ and $3-\delta$. This effect is extensive to other small rare-earth members, from $R=$ Ho to $R=$ Lu [6,7]. In this work we have prepared new members of this family of perovskites with mixed occupancy of the $R$ positions by different rare-earths, mimicking the ionic radius of Er$^{3+}$ and Y$^{3+}$ found in the well-known ErNiO$_3$ and YNiO$_3$ perovskites, in order to get information about the evolution of the crystal structure and metal-insulator transitions in these novel materials and how they are affected by the intrinsic disorder at the $R$ site.

2. Experimental

The access at moderate pressures to the metastable $R$NiO$_3$ oxides requires the careful choice of the starting reactants. In order to synthesize the following four samples, Nd$_{0.09}$Tm$_{0.91}$NiO$_3$, Nd$_{0.32}$Lu$_{0.68}$NiO$_3$, Y$_{0.40}$Tm$_{0.60}$NiO$_3$, and Y$_{0.56}$Yb$_{0.44}$NiO$_3$, stoichiometric amounts of $R_2$O$_3$ ($R=$ Nd, Tm, Yb, Y) and Ni(OH)$_2$ were mixed up and ground with KClO$_4$ (30 % in weight), introduced into gold capsules (8 mm diameter, 10 mm length), sealed and placed into a cylindrical graphite heater. The reactions were carried out in a piston–cylinder press (Rockland Research Co.), at a pressure of 2 GPa at 900 °C for 20 min. The decomposition of KClO$_4$ provides an “in-situ” high O$_2$ pressure that is necessary to stabilize Ni$^{3+}$ ions. The raw products, obtained as dense, homogeneous pellets, were ground and washed in water, in order to dissolve KCl coming from the decomposition of KClO$_4$; then the powder samples were dried in air at 150 °C for 1 h. The final products were single phase to diffraction measurements.

The products were initially characterized by laboratory X-ray diffraction (XRD) (Cu Kα, $\lambda=$ 1.5406 Å). Neutron Powder Diffraction (NPD) diagrams were collected at the Institut Laue-Langevin (ILL) in Grenoble (France). The crystal structures were refined from high-resolution NPD patterns at the D2B diffractometer with $\lambda=$ 1.594 Å. The refinements of the crystal structures were performed by the Rietveld method [32], using the FULLPROF refinement program [33]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final runs: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors.

Differential Scanning Calorimetry (DSC) measurements were performed in a Mettler TA3000 system equipped with a DSC30 unit, in the temperature range from 25 °C to 590 °C. The heating and cooling rates were 10 °C·min$^{-1}$, using about 70 mg of sample in each run.
3. Results and Discussion

\((R,R')\)NiO\(_3\) samples were obtained as well crystallized powders. The X-ray patterns (Figure 1) are characteristic of monoclinic perovskites, space group \(P2_1/n\), showing sharp and well-defined superstructure reflections due to the tilting of the \(\text{NiO}_6\) octahedra. The unit-cell parameters are related to \(a_0\) (ideal cubic perovskite, \(a_0 \approx 3.8 \text{ Å}\)) as \(a \approx \sqrt{2}a_0\), \(b \approx \sqrt{2}a_0\), \(c \approx 2a_0\).

![XRD patterns](image)

**Figure 1.** XRD patterns (Cu Ka, \(\lambda = 1.5406 \text{ Å}\)) of \((R,R')\)NiO\(_3\) oxides.

A plot of the crystal structure is displayed in Figure 2.

The refinement of the crystal structures has been carried out from four NPD patterns acquired in the high-resolution diffractometer D2B at \(T= 295 \text{ K}\). The previously reported RT structures for \(RNiO_3\) (\(R= \text{Ho, Y, Er and Lu}\)) [6] were used as starting model. In the \(P2_1/n\) phase there are two crystallographically independent Ni positions (Ni1 and Ni2), as well as three kinds of non-equivalent oxygen atoms (O1, O2 and O3) all in general positions. \(\text{NiO}_6\) and \(\text{Ni2O}_6\) octahedra alternate along the three directions of the structure, in such a way that each \(\text{NiO}_6\) octahedron is linked to six \(\text{Ni2O}_6\) octahedra, and vice-versa. A minor NiO impurity was included as a second phase during the refinement, and vanadium metal, coming from the double-walled sample holder, as a third phase. Figure 3 illustrates the goodness of the structural refinement from NPD data at RT for \(\text{Nd}_{0.09}\text{Tm}_{0.91}\text{NiO}_3\), \(\text{Nd}_{0.32}\text{Lu}_{0.68}\text{NiO}_3\), \(\text{Y}_{0.40}\text{Tm}_{0.60}\text{NiO}_3\), \(\text{Y}_{0.56}\text{Yb}_{0.44}\text{NiO}_3\). Table 1 contains the structural parameters after the refinements. The main bond distances and bond angles are listed in Table 2.
**Figure 2.** View of the crystal structure of $R\text{NiO}_3$ ($R=$ rare earths) in the insulating monoclinic region below $T_{MI}$. Corner-sharing NiO$_6$ octahedra are fairly tilted in the structure to optimize R-O bond-lengths; two kind of NiO$_6$ octahedra (expanded and compressed) alternate in the 3D network.

**Figure 3.** Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles ($\lambda = 1.594$ Å) for Nd$_{0.09}$Tm$_{0.91}$NiO$_3$, Nd$_{0.32}$Lu$_{0.68}$NiO$_3$, Y$_{0.40}$Tm$_{0.60}$NiO$_3$, and Y$_{0.56}$Yb$_{0.44}$NiO$_3$ at RT. Second and third line of Bragg reflections corresponds to the NiO impurity and vanadium holder, respectively.
Table 1. Unit-cell, positional, thermal parameters and reliability factors after the refinements of the crystal structure of \((R,R')NiO_3\) \((R=\text{Nd, Y}; R'=\text{Tm, Yb, Lu})\) perovskites in the monoclinic \(P2_1/n\) space group, \(Z=4\), from NPD data at 295 K. \(<r_R>\) is the average ionic size of \(R\) and \(R'\) and \(\sigma^2\) the variance.

| \((R,R')\)NiO3 | \(\text{Nd}_{0.00}\text{Tm}_{0.91}\) | \(\text{Nd}_{0.32}\text{Lu}_{0.68}\) | \(\text{Y}_{0.40}\text{Tm}_{0.60}\) | \(\text{Y}_{0.50}\text{Yb}_{0.44}\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(T_{MI}\) heating (º C) | 304.9 | 287.4 | 312.9 | 313.2 |
| \(T_{MI}\) cooling (º C) | 302.9 | 284.6 | 309.8 | 309.9 |
| \(<r_R>\) | 1.004 | 1.019 | 1.004 | 1.004 |
| \(\sigma^2\) | 0.00108 | 0.00379 | 0.00015 | 0.00029 |
| \(a(\text{Å})\) | 5.1618(1) | 5.1608(1) | 5.1574(2) | 5.1563(2) |
| \(b(\text{Å})\) | 5.5004(1) | 5.4934(3) | 5.5079(2) | 5.5099(2) |
| \(c(\text{Å})\) | 7.3947(2) | 7.4006(4) | 7.3898(2) | 7.3881(3) |
| \(\beta\) | 90.122(4) | 90.232(6) | 90.106(4) | 90.104(4) |
| \(V(\text{Å}^3)\) | 209.95(9) | 209.81(2) | 209.92(1) | 209.90(1) |
| \(\text{R} 4e (x y z)\) | | | | |
| \(x\) | 0.9785(5) | 0.9770(8) | 0.9804(9) | 0.981(1) |
| \(y\) | 0.0737(3) | 0.0723(4) | 0.0753(4) | 0.0754(6) |
| \(z\) | 0.2491(1) | 0.2521(1) | 0.250(2) | 0.253(2) |
| \(B(\text{Å}^2)\) | 0.37(3) | 0.35(6) | 0.48(5) | 0.48(8) |
| \(\text{Ni}1\) | 2d \((1/2 \ 0 \ 0)\) | | | |
| \(B(\text{Å}^2)\) | 0.58(8) | 0.03(9) | 0.6(1) | 0.4(2) |
| \(\text{Ni}2\) | 2c \((1/2 \ 0 \ 1/2)\) | | | |
| \(B(\text{Å}^2)\) | 0.30(8) | 1.01(9) | 0.5(1) | 0.5(2) |
| \(\text{O}1\) | 4e \((x \ y \ z)\) | | | |
| \(x\) | 0.1031(5) | 0.1040(9) | 0.1019(8) | 0.102(1) |
| \(y\) | 0.4689(5) | 0.4671(8) | 0.4665(8) | 0.467(1) |
| \(z\) | 0.2446(9) | 0.249(1) | 0.244(1) | 0.2472 |
| \(B(\text{Å}^2)\) | 0.59(5) | 0.9788(1) | 0.52(7) | 0.6(1) |
| \(\text{O}2\) | 4e \((x \ y \ z)\) | | | |
| \(x\) | 0.7025(9) | 0.697(2) | 0.701(2) | 0.698(3) |
| \(y\) | 0.308(1) | 0.310(2) | 0.311(2) | 0.313(3) |
| \(z\) | 0.0503(8) | 0.053(1) | 0.051(1) | 0.051(2) |
| \(B(\text{Å}^2)\) | 0.44(8) | 0.77(13) | 0.58(13) | 0.7(2) |
| \(\text{O}3\) | 4e \((x \ y \ z)\) | | | |
| \(x\) | 0.1821(9) | 0.191(1) | 0.182(1) | 0.186(2) |
| \(y\) | 0.202(1) | 0.203(2) | 0.204(2) | 0.203(2) |
| \(z\) | 0.946288 | 0.950(1) | 0.947(1) | 0.947(2) |
| \(B(\text{Å}^2)\) | 0.73(9) | 0.60(13) | 0.54(13) | 0.4(2) |
| Reliability factors | | | | |
| \(\chi^2\) | 1.16 | 1.43 | 1.07 | 0.927 |
| \(R_p(\%)\) | 2.99 | 3.97 | 3.43 | 3.22 |
| \(R_{wp}(\%)\) | 3.75 | 5.01 | 4.35 | 4.03 |
| \(R_{exp}(\%)\) | 3.47 | 4.19 | 4.20 | 4.19 |
| \(R_I(\%)\) | 4.11 | 5.64 | 5.92 | 4.63 |

The occurrence of a MI transition in the RNiO3 perovskites was checked by DSC measurements. Figure 4 illustrates the DSC curves obtained during the heating and cooling runs for Y\(_{0.40}\)Tm\(_{0.60}\)NiO3. The heating process exhibits an endothermic peak centered at 313 ºC. The reverse transition, showing an exothermic peak, is observed during the cooling run at 310 ºC. By analogy with the DSC peaks...
observed for other rare-earth nickelates [6], the peaks shown in figure 4 can be assigned to the corresponding MI transition. The heat transfer accounts for the entropy and lattice energy gain due to the electronic delocalization. The $T_{MI}$ temperatures of the four samples are gathered in Table 1.

### Table 2. Main bond distances (Å) and selected angles (deg) for monoclinic ($RR'$)NiO$_3$ ($R$= Nd, Y; $R'$= Tm, Yb, Lu) perovskites at room temperature.

| $(R,R')$ | Nd$_{0.99}$Tm$_{0.01}$ | Nd$_{0.32}$Lu$_{0.68}$ | Y$_{0.40}$Tm$_{0.60}$ | Y$_{0.56}$Yb$_{0.44}$ |
|----------|-----------------|-----------------|-----------------|-----------------|
| Ni1 octahedra | | | | |
| Ni1 – O1 (x2) | 1.971(6) | 1.946(9) | 1.972(9) | 1.947(14) |
| Ni1 – O2 (x2) | 2.023(6) | 2.023(9) | 2.039(9) | 2.039(16) |
| Ni1 – O3 (x2) | 2.021(5) | 1.980(8) | 2.025(7) | 2.005(23) |
| <Ni1 – O> | 2.005(6) | 1.983(9) | 2.012(8) | 1.997(14) |
| $\Delta d^{104}$ | 1.44 | 2.52 | 2.06 | 3.62 |
| Ni2 octahedra | | | | |
| Ni2 – O1 (x2) | 1.892(6) | 1.924(9) | 1.888(9) | 1.910(14) |
| Ni2 – O2 (x2) | 1.902(5) | 1.921(9) | 1.896(8) | 1.906(16) |
| Ni2 – O3 (x2) | 1.930(6) | 1.943(8) | 1.920(8) | 1.937(15) |
| <Ni2 – O> | 1.908(6) | 1.929(9) | 1.901(8) | 1.921(15) |
| $\Delta d^{104}$ | 0.71 | 0.26 | 0.51 | 0.87 |
| <Ni – O> | 1.956(6) | 1.956(9) | 1.956(8) | 1.959(14) |
| Ni1 – O1 – Ni2 | 146.3(3) | 146.0(4) | 146.4(4) | 146.6(6) |
| Ni1 – O2 – Ni2 | 147.8(2) | 145.7(4) | 146.9(3) | 146.1(7) |
| Ni1 – O3 – Ni2 | 145.3(2) | 147.7(3) | 146.0(3) | 146.3(6) |
| RO$_8$ polyhedra | | | | |
| R – O1 | 2.26783(8) | 2.266(5) | 2.244 | 2.248(8) |
| R – O1 | 3.057(4) | 3.054(6) | 3.063(6) | 3.064(9) |
| R – O1 | 2.236(4) | 2.238(6) | 2.236(6) | 2.231(9) |
| R – O2 | 2.418(8) | 2.44(1) | 2.434(1) | 2.463(18) |
| R – O2 | 2.283(8) | 2.23(1) | 2.27(1) | 2.246(18) |
| R – O2 | 2.588(9) | 2.58(1) | 2.57(1) | 2.543(19) |
| R – O3 | 2.578(9) | 2.60(1) | 2.57(1) | 2.592(19) |
| R – O3 | 2.255(8) | 2.29(1) | 2.281(1) | 2.298(18) |
| R – O3 | 2.446(8) | 2.42(1) | 2.44(1) | 2.424(16) |
| <R – O>$_{short}$ | 2.384(8) | 2.38(1) | 2.380(9) | 2.381(16) |
| <R – O> | 2.720(8) | 2.72(1) | 2.720(9) | 2.724(16) |

For all the studied $R$NiO$_3$ perovskites the MI transition occurs considerably above room temperature in such a way that at RT the structural data correspond to samples with a 100% of insulating fraction. The structural refinement in the monoclinic symmetry is unique and shows a crystallographic description completely comparable to those obtained for the smaller rare-earth $R$NiO$_3$ compounds ($R$= Ho, Er, Tm, Yb and Lu). In the insulating regime below $T_{MI}$, Ni1 and Ni2 sites alternate along the three crystallographic directions (Figure 2). As shown in Table 2, the mean Ni–O distance in the Ni1O$_6$ octahedron (e.g. 2.012(8) Å in Y$_{0.40}$Tm$_{0.60}$NiO$_3$) is considerably larger than in the Ni2O$_6$ polyhedron (1.901(8) Å) at RT; we obtain again the same picture of expanded and contracted NiO$_6$ octahedra alternating along the three axes (Figure 2), consequence of the charge...
disproportionation phenomenon in the insulating regime. The difference between both mean Ni-O distances is slightly higher (within the standard deviations) to that observed for the smaller rare earth nickelates \( (R = \text{Y}, \text{Ho}, \text{Er}, \text{Lu}) \) [7,8]. It is remarkable that the distortion of the NiO\(_6\) octahedra is much more pronounced than that of Ni2O\(_6\) octahedra; at RT the distortion parameter for Ni1, defined as \( \Delta_d = \frac{1}{6}\sum_{i=1,6}(d_{ij}-\langle d \rangle)^2 \) is 3.62 \( 10^{-4} \) for \( \text{Y}_{0.56}\text{Yb}_{0.44}\text{NiO}_3 \), whilst for Ni2 it is 0.87 \( 10^{-4} \). The observed static distortion is even higher than those found for the heaviest rare earths, falling in the interval \( \Delta_d = 0.8 - 1.7 \times 10^{-4} \) [7,8].

![Figure 4. DSC curves for \( \text{Y}_{0.40}\text{Tm}_{0.60}\text{NiO}_3 \) obtained on the heating and cooling runs.](image)

The proportions of \( R \) and \( R' \) in \( (RR')\text{NiO}_3 \) were chosen in such a way that three of them (\( \text{Nd}_{0.09}\text{Tm}_{0.91}, \) \( \text{Y}_{0.40}\text{Tm}_{0.60} \) and \( \text{Y}_{0.56}\text{Yb}_{0.44} \)) mimic the ionic size of \( \text{Er}^{3+} \) (\( r_i = 1.004 \) Å) and one of them (\( \text{Nd}_{0.33}\text{Lu}_{0.68} \)) that of \( \text{Y}^{3+} \) (\( r_i = 1.019 \) Å). These substitutions usually result in size disorder or mismatch. This effect can be quantified by the variance of the A-site cation distribution, defined as \( \sigma^2 = \langle r^2 \rangle - \langle r \rangle^2 \) (\( r \) = ionic radius of R cation). Table 1 contains the mean ionic R radius and the variance calculated for all the samples. Figure 5 shows the linear dependence of the \( T_{\text{M}} \) with the variance. It is interesting to see that the compounds including Nd have a stronger deviation from the MI temperatures of \( \text{ErNiO}_3 \) (311 °C) and \( \text{YNiO}_3 \) (309 °C), as a result of the larger variance of the ionic sizes, involving large (\( \text{Nd}^{3+} \)) and small (\( \text{Tm}^{3+} \) and \( \text{Lu}^{3+} \)) ions, whereas the Y-containing compounds, with a smaller variance of ionic radius, show a much smaller deviation of the transition temperature with respect to the unmixed \( \text{ErNiO}_3 \) and \( \text{YNiO}_3 \) perovskites. In fact, the metal-transition temperature scales with the variance and not with the mean ionic radius of the R cations as shown in Fig. 5. A similar effect was described for manganese perovskites with colossal magnetoresistance [34], for which a sizeable decrease of ferromagnetic \( T_c \) upon disordering at the A positions was observed, and interpreted as coming from strain fields resulting from ordered or disordered oxygen displacements that are parameterized by the statistical mean and variance of the A cation radius. An analogous interpretation can be given here; the suppression of the MI transition observed when large and small rare earth cations randomly occupy the A sites is a result of oxygen displacements inducing an irregular Ni-O bond-length and Ni-O-Ni...
angle distribution across the crystal, which narrows the bandwidth of the conduction band and diminishes $T_{\text{MI}}$.

![Graph of $T_{\text{MI}}$ vs variance for different samples](image)

**Figure 5.** Variation of the $T_{\text{MI}}$ transition with the variance of the four studied samples. The line is guide to the eye.

4. Conclusions

Highly distorted $(RR')\text{NiO}_3$ perovskites, containing different rare-earth cations ($R = \text{Nd}, \text{Y}, \text{Tm}, \text{Yb}$) with diverse variance were prepared under high-oxygen pressure. The metal-insulator transition temperatures were determined by DSC measurements; they occur well above RT, with $T_{\text{MI}}$ ranging between 284 and 310 °C. The crystal structure at room temperature, studied from high-resolution neutron powder diffraction, shows that these oxides stabilize a charge disproportionation below $T_{\text{MI}}$ implying a separation of two kinds of $(\text{NiO}_6)$ octahedra (large $\text{Ni}_1\text{O}_6$ and small $\text{Ni}_2\text{O}_6$) described in a pseudo-orthorhombic unit cell, characterized by a subtle monoclinic distortion ($\beta$ between 90.23° and 90.10°) in the $P2_1/n$ space group. Whereas $(\text{Ni}_1\text{O}_6)$ octahedron is significantly distorted, $(\text{Ni}_2\text{O}_6)$ is much more regular. This is consistent with a scenario considering that the former contains more ionic Ni-O bonds and it is susceptible to experience a Jahn-Teller deformation, whereas the small $(\text{Ni}_2\text{O}_6)$ octahedron is constituted by more covalent Ni-O bonds. The analysis of the variance of the rare-earth distribution at the A positions shows that those perovskites containing rare earths with very different ionic sizes (large variance) exhibit a substantial reduction of the MI transition temperature, as a consequence of the irregular Ni-O bond-length and Ni-O-Ni angle distribution across the crystal, which narrows the bandwidth of the conduction band.

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