

Oxygen Exchange in $\text{Pr}_2\text{NiO}_{4+\delta}$ at High Temperature and Direct Formation of $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$

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We have studied the stability of $\text{Pr}_2\text{NiO}_{4+\delta}$ under pure oxygen flow by *in situ* measurement of its weight versus T . Above 850°C a fast oxidation is observed corresponding to the ex-solution of PrO_y species and to the formation of metallic $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$. This reaction is not reversible. The quantity of exchanged oxygen, its fast kinetics, and the metallic behavior of the composite suggest that this material should have interesting applications for electrodes of solid oxide fuel cells. © 2000 Academic Press

INTRODUCTION

Layered perovskite structure has generated considerable interest (1) because of its important potential applications, for example in manganites (2) where giant magnetoresistance has been discovered in Ruddlesden–Popper (RP) phases. Some of these phases have an exceptional ability to exchange oxygen at high temperature (1, 3) and might be regarded as important materials for solid oxide fuel cells.

These phases have the general formula $A_{n+1}B_nO_{3n+1}$ in which n 2D layers of BO_6 corner-sharing octahedra are joined along the stacking direction and separated by AO layers. Their synthesis chemistry is generally time consuming due to sluggish reactivity, and it is difficult to reach pure phases. Intergrowths are frequently observed (4). It is then important to learn more about their chemistry, especially about their phase transformations at high temperatures. This is the general motivation of this short report.

Rare earth nickelates can also form RP phases that have been described in a number of papers (4–11), most of them concerning lanthanum-based compounds. We have studied recently the synthesis and electronic properties of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ (12). This compound behaves quite similarly to $\text{La}_4\text{Ni}_3\text{O}_{10}$ although the small ionic radius of the Pr^{3+} ion

might be at the origin of the crystalline distortions of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$, as is the case for Pr_2NiO_4 (13).

Earlier, Sullivan *et al.* (14) reported the formation of $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ at high temperature, at the boundary of the homogeneity field of Pr_2NiO_4 , the first member ($n = 1$) of the series. Pr_2NiO_4 can incorporate excess oxygen up to an extent controlled by structural strains (3, 15). In the pure compound, at high temperature, both oxygen excess and high thermal motion cause the apical oxygen to split into two sites leading to a statistical density map with a peanut shape (16). This suggests an intrinsic instability of this oxidized layer of “ PrO_y ”.

In this short paper, we report thermochemical investigations of $\text{Pr}_2\text{NiO}_{4+\delta}$ at high temperature by using a thermobalance which suggests above 850°C an ex-solution of PrO_y from $\text{Pr}_2\text{NiO}_{4+\delta}$, forming $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ as the main phase with a fast kinetic.

EXPERIMENTAL

Pr_2NiO_4 has been synthesized by a modified sol–gel route already described elsewhere (12, 17) and recently improved (18). It uses a gel precursor formed by entrapping a stabilized solution of the cation in a polymerized network of acrylamide. The gel is dried at 700°C in a ventilated oven and the resulting precursor is treated up to 1200°C under air with intermediate grinding. The final powder is very fine.

The variation of the oxygen content in $\text{Pr}_2\text{NiO}_{4+\delta}$ powders is followed versus temperature by TGA (TAG 24 from Setaram, Lyon, France) up to 1150°C under oxygen flow. The apparatus is very sensitive ($\pm 1 \mu\text{g}$) and has two symmetrical furnaces avoiding the need for gas density corrections that depend of T . The apparatus is able to resolve a very small variation of the excess oxygen stoichiometry $\Delta(\delta) \approx 0.002$. The oxygen flow is fixed at ~ 20 l/h, the heating and cooling ramps at 300 K/h.

X-ray diffraction ($\text{Cu } K\alpha$) is used to investigate the crystalline phases of the starting powders, of one sample

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quenched during the thermochemical investigation, and of the products at the end of the thermal cycle.

The resistivity is measured on sintered bars (>90% of the theoretical density) from 20°C to 1150°C in a furnace, under O₂ flow and then from room temperature to 4 K in an He bottle. The resistivity is measured in the four-probe configuration with sintered Pt electrodes.

RESULTS AND DISCUSSION

The synthesis of Pr₂NiO₄ under air forms samples having a high oxygen excess ($\delta \approx 0.22$) measured previously (14, 19) and checked again on the various samples studied in this report. This is done by measuring their weight loss during heating under Ar-H₂. The reduction is complete at 680°C and gives Pr₂O₃ + Ni. This value has been confirmed for some samples by iodometric titration. From many experiments, we know the characteristic shape of the weight variations versus T in Ar-H₂ and also in air for our samples. We can then appreciate the possible contributions of adsorbed contaminants such as H₂O, CO₂, etc. In the following experiments, these contributions are reduced to a negligible part. The oxygen exchange of a powdered sample (150–200 mg) of Pr₂NiO_{4.22} is then followed, upon heating and cooling, under pure oxygen flow. Several samples have been studied in the same way showing a reproducible behavior which is described now.

Figure 1 shows the relative weight variation versus T ; this is also expressed in terms of excess oxygen stoichiometry δ . From 200 to 850°C, the behavior is consistent with what is generally observed in this family of oxides (19, 20): the oxygen excess is reduced by increasing T , even under

oxygen flow. This loss of oxygen is small and occurs at a constant rate with T between 470 and 850°C where the composition reaches Pr₂NiO_{4.14}. A small anomaly is observed at 470°C attributed previously to an order-disorder phase transition involving interstitial oxygen (16).

Above 850°C, an upturn of the excess oxygen is evidenced. This new behavior has never been observed before in the lanthanum equivalent (20, 21). It is then perhaps characteristic of the praseodymium-based compound. The weight increases very rapidly evidencing a significant oxygen uptake between 850 and 1000°C. At the end of this process, the oxygen excess is more than twice the initial value. The oxygen uptake saturates above 1020°C and then is lost suddenly. At 1150°C, the oxygen stoichiometry reaches a value identical to the one extrapolated from 850°C. On cooling of the sample below 1150°C, the weight increases smoothly, and below 980°C the oxygen that was lost above 1150°C is suddenly picked up again. From 880 to 20°C, the oxygen stoichiometry increases continuously. Small anomalies are noticed at 850 and 250°C. The oxygen flow rate is an important ingredient of the phenomenon since a reduction of its value by a factor 10 shifts to higher T the onset of the reaction and decreases the oxygen uptake amount. No attempts have been made to further investigate the kinetic aspect of this reaction; we preferred to concentrate on its chemical nature.

From this, it is obvious that a more oxidized compound has been formed during this treatment. X-ray data provide clear evidence of the formation of Pr₄Ni₃O_{10-x} as the main phase. It is accompanied with PrO_y as a second phase. After this first experiment, in another study, we quenched the phases formed at 1030°C where the oxygen uptake

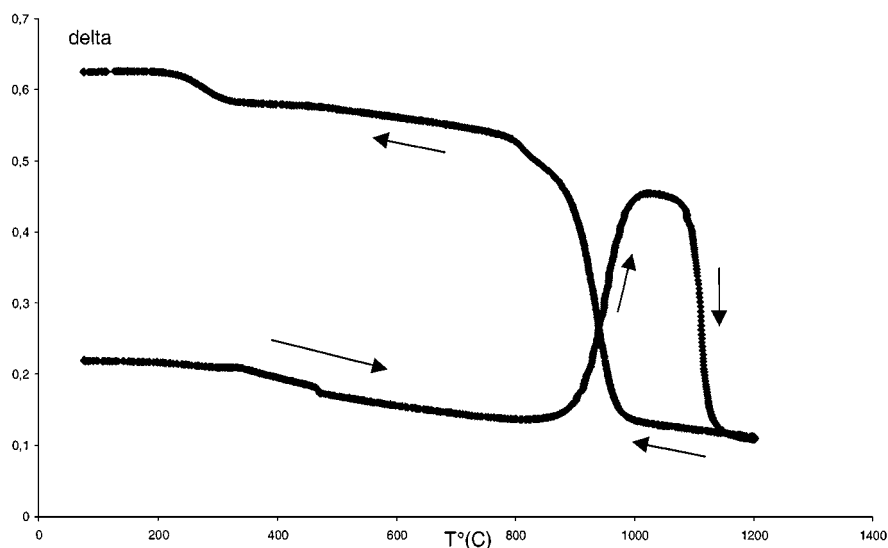


FIG. 1. Oxygen stoichiometry versus temperature in Pr₂NiO_{4+ δ} under pure oxygen flow (ambient pressure; oxygen flow, 20 l/h; heating and cooling ramp, 300°C/h).

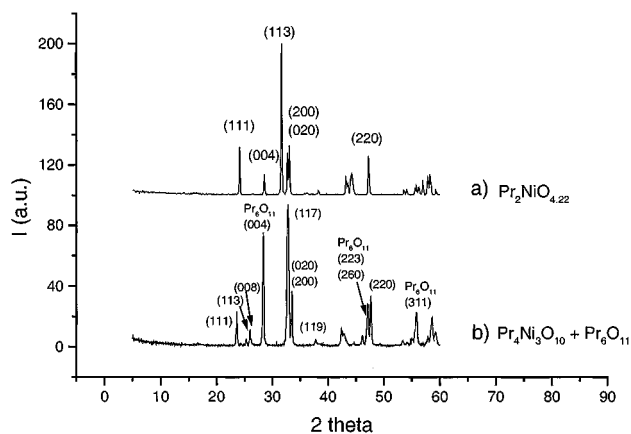


FIG. 2. (a) X-ray spectrum of $\text{Pr}_2\text{NiO}_{4.22}$, the starting product. (b) X-ray spectrum of the same sample quenched from 1030°C under oxygen flow. $\text{Pr}_2\text{NiO}_{4.22}$ has decomposed in $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ and PrO_y .

saturates. Figure 2 compares the initial product (Fig. 2a), i.e., $\text{Pr}_2\text{NiO}_{4.22}$, with the quenched sample (Fig. 2b). Figure 2b evidences a mixture of two phases. The main one has an X-ray spectrum similar to that of $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ shown previously by Zhang *et al.* (22). It can be indexed (although not perfectly) in the $Fm\bar{3}m$ space group and its unit cell parameters are $a = 5.365(5)$ Å, $b = 5.447(6)$ Å, $c = 27.500(1)$ Å. This compares well with previous determinations (22, 12), but the rather small c parameter points to an oxygen-deficient form (23).

The electrical resistivity of the $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ phase was shown to be metallic down to 4 K with an anomaly at 150 K (12, 23). We have also followed the resistivity of a ceramic of $\text{Pr}_2\text{NiO}_{4.22}$, *in situ*, during the same thermal treatment as the one discussed above. The resistivity follows a path

similar to that observed with the oxygen excess (Fig. 3). It passes through a minimum at 350°C (19) and decreases suddenly when the oxidation occurs at 850°C . Between 1100 and 1150°C the oxide loses its oxygen and consequently, the resistivity increases. On cooling the low resistivity is restored and it remains low down to 20°C and even down to 4 K, evidencing a metallic behavior. Obviously, the metallic $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ phase forms a percolated network in this two-phase compound produced by the transformation of $\text{Pr}_2\text{NiO}_{4.22}$.

These weight variations can be analyzed in the temperature range 850 – 1150°C assuming that oxygen exchanges are due to modifications of the oxygen stoichiometry in $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$ and PrO_y phases. The RP phases of rare earth nickelates or cuprates can accommodate oxygen non-stoichiometry to a large extent (1, 3, 23). They can be represented (23) by the general formula $A_{n+1}B_nO_{(2+p)n+2-p}$ ($p = 0, 1$). When $p = 0$ the structure is of T' type in which the B species has no apical oxygen and when $p = 1$ the structure is of T type. The controlled reduction of $\text{Ln}_4\text{Ni}_3\text{O}_{10}$ suggests a progressive transformation from T structure to T^* and then to T' structure by removing oxygen from the AO_y layer. The form $\text{Ln}_4\text{Ni}_3\text{O}_9$ has been identified in lanthanum-based nickelates (8, 23) but its structure, presumed to be T^* , has not been resolved yet. Note that the valence of Ni in this composition is strictly 2+. We have no reason to think that this composition exists only for La and might not be produced in the case of praseodymium. On the other hand the system PrO_y is well documented from the work of Hyde *et al.* (24). Altogether, these elements are now used to discuss the chemical transformations observed.

At 850°C , the actual stoichiometry reaches $\text{Pr}_2\text{NiO}_{4.137}$. Above this temperature, the fast weight increase indicates

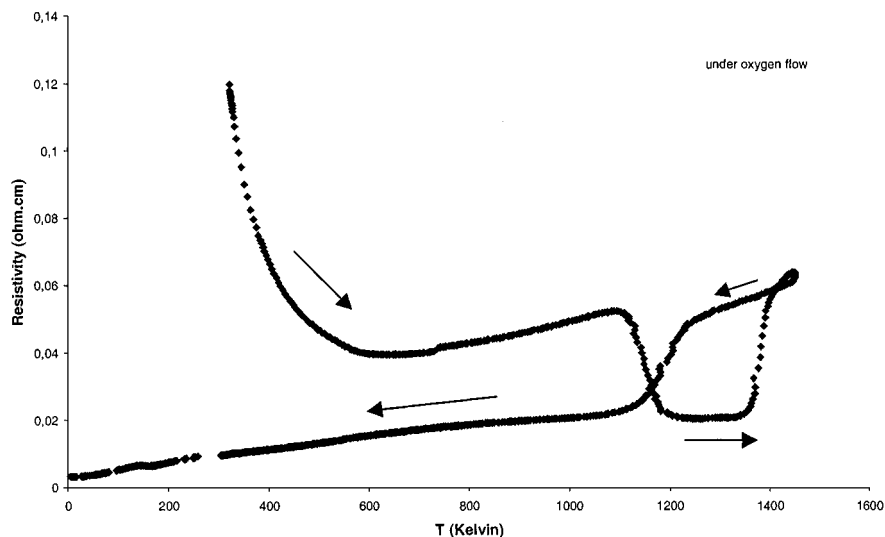
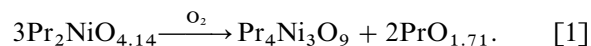


FIG. 3. *In situ* measurements of the resistivity versus T for $\text{Pr}_2\text{NiO}_{4+\delta}$ under pure oxygen flow (same kinetic conditions as for TGA).

a decomposition to a more oxidizable phase. From X-ray studies, PrO_y is produced in this decomposition. Taking into account the weight variations, if one assumes the formation of $\text{Pr}_3\text{Ni}_2\text{O}_7$, it should be accompanied with $\text{PrO}_{1.27}$. This is not realistic considering the equilibrium compositions of PrO_y (24). As said above, X-ray diffraction shows also the formation of $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$. Thus in agreement with the weight variations, it is reasonable to assume the formation of $\text{Pr}_4\text{Ni}_3\text{O}_9 + 2\text{PrO}_{1.706}$ at 850°C . This latter composition is very close to $\text{PrO}_{1.714}$, the ι phase of the system PrO_y (24). However, at an oxygen partial pressure of 0.8, this phase converts directly to the α phase containing more oxygen (PrO_y , with $1.778 < y < 1.833$) at around 800°C . In pure oxygen, as under our experimental conditions, by extrapolation of the equilibrium data, we expect the α phase to be stable above 900°C . It is then reasonable to assume that the native phase $\text{PrO}_{1.706}$ oxidizes to form $\text{PrO}_{1.8}$ between 850 and 1000°C . This is however a small contribution to the total weight gain between 900 and 1000°C which must then concern the RP phase. It is then plausible that $\text{Pr}_4\text{Ni}_3\text{O}_9$ also oxidizes in $\text{Pr}_4\text{Ni}_3\text{O}_{9.75}$. Upon heating above 1150°C , the $\text{Pr}_4\text{Ni}_3\text{O}_{9.75}$ loses its oxygen returning to $\text{Pr}_4\text{Ni}_3\text{O}_9$ while the α phase converts to the σ phase ($\text{PrO}_{1.6}$). The reverse path is observed upon cooling. The $\text{Pr}_4\text{Ni}_3\text{O}_9$ phase oxidizes below 1000°C to $\text{Pr}_4\text{Ni}_3\text{O}_{9.75}$ and is accompanied by $\text{PrO}_{1.8}$. The small anomalies at 850 and 300°C are due to the structural/compositional transformations of PrO_y phases. As a consequence $\text{Pr}_4\text{Ni}_3\text{O}_{9.75}$ is observed at room temperature accompanied by PrO_y . All this is in good agreement with earlier works (14). The resistivity data agree with that scheme.

All this suggests that above 850°C under pure oxygen and at ambient pressure, PrO_y is irreversibly expelled from the structure of $\text{Pr}_2\text{NiO}_{4+\delta}$. This transformation forms $\text{Pr}_4\text{Ni}_3\text{O}_9$ according to the reaction:



This reaction is quasi-topotactic since the structure, at least in the basal plane, is preserved. This perhaps explains the observed fast kinetics of this reaction because then it does not need nucleation (25). It is apparently not reversible but suggests that perhaps PrO_y could be exchanged by some smaller group. Such reaction is not observed at ambient pressure for $\text{La}_2\text{NiO}_{4.18}$ but only at high oxygen pressure, above 150 bar at $\sim 850^\circ\text{C}$, as observed in a recent experiment (26). The oxygen excess then reaches 0.2–0.24. Note that this limit can be reached under very oxidative electrochemical conditions and at room temperature, in $\text{La}_8\text{Ni}_4\text{O}_{17}$ (27).

The relative instability of praseodymium-based compounds might originate in the ability of Pr to form T'

structures (28), prefigured in the large delocalization of its apical oxygen at high temperature. This excessive oxidation of the PrO_y layer is relieved by the ex-solution of PrO_y and the consecutive formation of $\text{Pr}_4\text{Ni}_3\text{O}_9$.

CONCLUSION

We have studied at high temperature, *in situ*, the thermochemical properties of $\text{Pr}_2\text{NiO}_{4+\delta}$ under oxygen flow at ambient pressure. This compound picks up oxygen vigorously at 850°C and forms $\text{Pr}_4\text{Ni}_3\text{O}_9$ plus PrO_y that is expelled from the structure. This reaction seems to be triggered by the strongly anharmonic motion of the apical oxygen in $\text{Pr}_2\text{NiO}_{4+\delta}$ at high temperature. The high quantity of exchanged oxygen in this reaction, its fast kinetics, and the metallic behavior of the composite formed suggest that it might have some utility in electrode activity for solid oxide fuel cells.

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