

## Passage from T-Type to T'-Type Arrangement by Reducing $R_4Ni_3O_{10}$ to $R_4Ni_3O_8$ ( $R = La, Pr, Nd$ )

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For the first time a triple-layer T'-type arrangement has been stabilized in mixed-valence  $Ni^{1+}/Ni^{2+}$  nickelates  $R_4Ni_3O_8$  ( $R = La, Pr, Nd$ ). These compounds are obtained by reducing mixed-valence  $Ni^{2+}/Ni^{3+}$  oxides  $R_4Ni_3O_{10}$ , the  $n = 3$  members of the Ruddlesden–Popper-type series  $R_{n+1}Ni_nO_{3n+1}$ . In the same way that  $R_4Ni_3O_{10}$  adopts the triple-layer structure intermediate between single-layer T-type and perovskite structures,  $R_4Ni_3O_8$  can be considered as the triple-layer intermediate between the T' and so-called infinite-layer structural types. The compounds  $R_4Ni_3O_8$  ( $R = La, Pr, Nd$ ) are black semiconductors and they are stable in air at room temperature. The passage from  $R_4Ni_3O_{10}$  to  $R_4Ni_3O_8$  is reversible by reduction/oxidation under hydrogen/oxygen at moderate temperature. It is expected that a similar reduction process can occur in triple-layer  $La_4Cu_3O_{10}$ . © 1992 Academic Press, Inc.

T-structure (Fig. 1, upper part,  $n = 1$ ) and T'-structure (Fig. 1, lower part,  $n = 1$ ) are typical structural arrangements of single-layer hole-doped (1) ( $La_{2-x}A_xCuO_4$ ,  $A = Ba^{2+}, Sr^{2+}$ ) and electron-doped (2) ( $Nd_{2-x}Ce_xCuO_4$ ) superconductors, respectively. Several studies have been devoted to trying to understand the different factors involved in the stabilization of these structures (see, for instance, Ref. (3) and references therein). Recently (4), a cuprate with nominal composition  $La_2CuO_{4+\delta}$  with T'-structure has been obtained after reducing, then reoxidizing at low temperature the conventional T-type  $La_2CuO_4$ . T-type arrangements have been known for a long time in many first series transition metal binary oxides, but so far copper was the only one

for which a T'-type arrangement was observed.

Much effort has been devoted to trying to detect superconductivity in other metallates isostructural with superconducting cuprates, with a report of success concerning the nickelate  $La_{2-x}Sr_xNiO_4$  with a T-structure (5). In a slightly different approach, stabilizing mixed-valence  $Ni^{1+}/Ni^{2+}$  (electronic configuration  $3d^9/3d^8$ ) oxides with structures similar to those of hole-doped high- $T_c$  superconducting cuprates (mixed-valence  $Cu^{2+}/Cu^{3+}$ , electronic configuration  $3d^9/3d^8$ ) could be of importance for testing the prominent role of copper in the onset of superconductivity. Layered mixed-valence +2/+3 nickelates of the Ruddlesden–Popper-type (6) series  $R_{n+1}Ni_n$

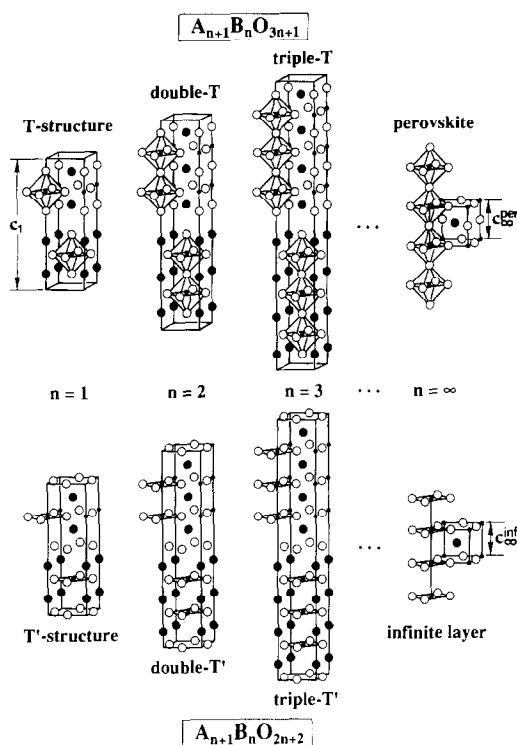


FIG. 1. (Upper part) The Ruddlesden-Popper (6) structural type series, based on T-type arrangements and encountered in several rare earth and alkaline earth metallates. (Lower part) The equivalent series based on T'-type arrangements encountered in rare earth cuprates and/or nickelates (up to now:  $n = 1$  in cuprates  $R_2\text{CuO}_4$  ( $R = \text{La, Pr, Nd, Sm, Eu, Gd,}$  and Ce- and Th-doped compounds) (21) and palladate  $\text{La}_2\text{PdO}_4$  (22),  $n = 2$  not yet encountered,  $n = 3$  in nickelates  $R_4\text{Ni}_3\text{O}_8$  ( $R = \text{La, Pr, Nd,}$  this work),  $n = \text{infinite}$  in cuprates  $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$  (23) and  $\text{Sr}_{1-x}\text{R}_x\text{CuO}_2$  ( $R = \text{Pr, Nd}$ ) (24) and nickelate  $\text{LaNiO}_2$  (11)). The present study emphasizes the reversible passage from upper to lower structural type in triple-layer rare earth nickelates by reduction/oxidation under hydrogen/oxygen. The values of  $c_1$  and  $c_\infty$  for perovskite (per) and infinite-layer (inf) structures as discussed in the text are indicated on the figure. Full circles = cations (large = A, small = B); open circles = oxygen.

$\text{O}_{3n+1}$  (7-9) (Fig. 1, upper part) were good precursors for such a purpose: reducing them would lower both the nickel's oxidation state and its coordination number (10-12). The present Letter reports the exist-

tence of a T'-type arrangement in triple-layer nickelates  $R_4\text{Ni}_3\text{O}_8$  ( $R = \text{La, Pr, Nd}$ , Fig. 1, lower part,  $n = 3$ ) obtained by the reduction of  $R_4\text{Ni}_3\text{O}_{10}$  with triple-layer T-type arrangement (Fig. 1, upper part,  $n = 3$ ).

The compounds  $R_4\text{Ni}_3\text{O}_{10}$  ( $R = \text{La, Pr, Nd}$ ) were synthesized from a stoichiometric mixture of oxides prepared by thermal decomposition of nitrates. The samples were pressed into pellets and fired at temperatures ranging from 950°C in 1 atm oxygen ( $R = \text{Nd}$ ) to 1050°C in air ( $R = \text{La}$ ). The total firing time varied from several days ( $R = \text{La}$ ) to several weeks ( $R = \text{Pr, Nd}$ ), with several intermediate regrindings and repressings. To my knowledge, the existence of  $\text{Nd}_4\text{Ni}_3\text{O}_{10}$  was not reported before.

The reduction of the previous samples was carried out on a thermogravimetric (TGA) balance in flowing hydrogen (99.99% purity) and hydrogen diluted in nitrogen (6%  $\text{H}_2$ , 94%  $\text{N}_2$ ). Results depend on the rare earth and the gas composition. Figure 2 displays the most striking TGA measurements obtained on  $\text{La}_4\text{Ni}_3\text{O}_{10}$ . The reduction in pure hydrogen (Fig. 2a) occurs through two steps, implying the loss of one, then another, oxygen atom per formula unit, before decomposition to a mixture of  $\text{La}_2\text{O}_3$  and metallic nickel at higher temperature. When reduced in diluted hydrogen (Fig. 2b), the first step only is achieved before decomposition, while in praseodymium and neodymium nickelates, the second step only is clearly observed. When long-run annealings, typically 1 to 3 days, are performed, the reduction temperature is lowered to about 300°C; then the decomposition occurs above 400°C.

Assuming oxidation states +3 and -2 for rare earth and oxygen, respectively, the average formal oxidation states of nickel in  $R_4\text{Ni}_3\text{O}_{10}$ ,  $R_4\text{Ni}_3\text{O}_9$ , and  $R_4\text{Ni}_3\text{O}_8$  are +2.66, +2, and +1.33, respectively. While  $R_4\text{Ni}_3\text{O}_{10}$  have metallic behavior,  $R_4\text{Ni}_3\text{O}_9$  and  $R_4\text{Ni}_3\text{O}_8$  are semiconductors and they

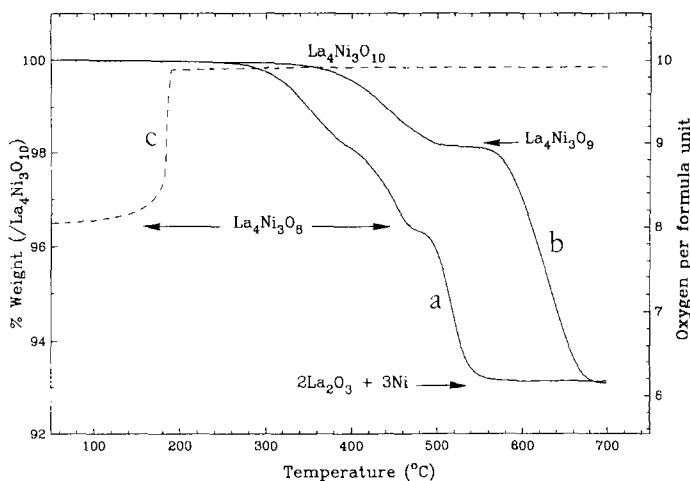


FIG. 2. Thermogravimetric analyses of  $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$  ( $\delta = 0$  and 2) performed on a Perkin-Elmer System 4 equipment upon heating (heating rate  $10^\circ\text{C}/\text{min}$ ) in the following atmospheres: (a)  $\text{La}_4\text{Ni}_3\text{O}_{10}$ , under pure hydrogen; (b)  $\text{La}_4\text{Ni}_3\text{O}_{10}$ , under diluted hydrogen (6%  $\text{H}_2$ , 94%  $\text{N}_2$ ); (c)  $\text{La}_4\text{Ni}_3\text{O}_8$ , under oxygen.

are stable in air at room temperature. Annealing the reduced forms in oxygen leads back to the original Ruddlesden-Popper phases (Fig. 2c). These nickelates are all black in color.

X-ray powder diffraction patterns of the lanthanates, together with their cell parameters and peaks indexation, are given in Fig. 3. Upon reduction to  $R_4\text{Ni}_3\text{O}_8$ , the most drastic effect is observed on the  $c$  parameter, which shrinks by about  $2 \text{ \AA}$  while  $a$  and  $b$  slightly increase. This is a strong indication that lost oxygens were originally apical. Two types of apical oxygens are present in  $R_4\text{Ni}_3\text{O}_{10}$  (see Fig. 4a), central apical oxygen O2 linking  $\text{NiO}_2$  layers, and external apical oxygen O4 belonging to the  $RO$  layers. The loss of O2 is in quantitative agreement with the  $c$  parameter reduction. Considering that triple-layer compounds are intergrowths between single-layer and infinite-layer compounds along  $c$ , the relationship  $c_3 = c_1 + 4c_x$ , where indices denote the number of layers between  $RO$  slabs (see Fig. 1 and 4), should be verified. With  $c_1 = 12.60 \text{ \AA}$  (13) and  $c_x = 3.84$  and  $3.38 \text{ \AA}$  for perovskite

$\text{LaNiO}_3$  (14) and infinite-layer  $\text{LaNiO}_2$  (11), respectively, one obtains  $c_3 = 27.96$  and  $26.12 \text{ \AA}$  for  $\text{La}_4\text{Ni}_3\text{O}_{10}$  and  $\text{La}_4\text{Ni}_3\text{O}_8$ , respectively. These values are in very good agreement with the observed  $c$  parameters (Fig. 3, caption). The crystal structure expected for  $R_4\text{Ni}_3\text{O}_8$  is simply obtained by removing atoms O2 from the structure of  $R_4\text{Ni}_3\text{O}_{10}$  (Fig. 4b). Note its close relationship with the structure of the high- $T_c$  superconductor Tl-2223 (15): the same kind of atomic arrangement, with rare earth replacing barium and calcium, and nickel replacing copper, but without double-TiO layers.

As the intermediate phase  $\text{La}_4\text{Ni}_3\text{O}_9$  appeared to be very poorly crystallized (Fig. 3), probably due to a disorder of vacancies in the structure, efforts were primarily devoted to the structural refinement of better crystallized  $R_4\text{Ni}_3\text{O}_8$ , from X-ray powder diffraction patterns. Starting from the model given in Fig. 4b, space group  $I4/mmm$ , the refinement (16) converges toward a solution which confirms the loss of apical oxygen O2, with a distance of  $3.31 \text{ \AA}$  between successive  $\text{NiO}_2$  layers: about the same as that

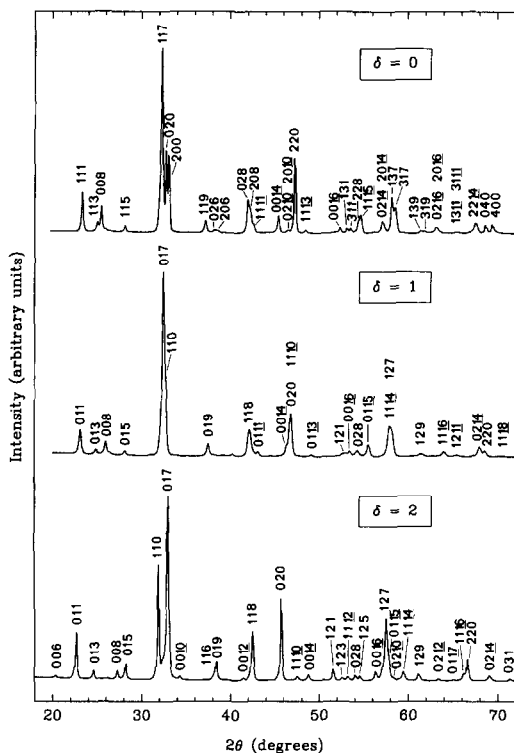


FIG. 3.  $\text{CuK}\alpha$  X-ray powder diffraction patterns of  $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$  ( $\delta = 0, 1, 2$ ):  $\text{La}_4\text{Ni}_3\text{O}_{10}$ , orthorhombic,  $a = 5.4145(3) \text{ \AA}$ ,  $b = 5.4638(3) \text{ \AA}$ ,  $c = 27.984(2) \text{ \AA}$ ;  $\text{La}_4\text{Ni}_3\text{O}_9$ , tetragonal,  $a = b = 3.8863(2) \text{ \AA}$ ,  $c = 27.452(2) \text{ \AA}$ ;  $\text{La}_4\text{Ni}_3\text{O}_8$ , tetragonal,  $a = b = 3.9678(2) \text{ \AA}$ ,  $c = 26.108(1) \text{ \AA}$ .

observed in  $\text{LaNiO}_2$  (11). However, this solution was not totally satisfying because of a marked tendency of apical oxygen O4 to be shifted toward the nickel atom at an unphysical distance of about 1  $\text{\AA}$ . When fixed at a more reasonable, but arbitrary distance of 2  $\text{\AA}$ , the thermal parameter of O4 increases dramatically, or its occupation rate tends toward zero, an indication of the absence of oxygen on this site. The missing atom was located by Fourier difference synthesis (17). The main residue ( $18e^-/\text{\AA}^3$ ) was located on site 4d ( $0, \frac{1}{2}, \frac{1}{4}$ ) of space group  $I4/mmm$ , at very reasonable distances of any surrounding cation. When oxygen (called

O5) is placed on this site, reliability is markedly lowered. Table I gives the results of the profile refinement for  $\text{Nd}_4\text{Ni}_3\text{O}_8$ , the best crystallized compound. The structural arrangement of  $\text{La}_4\text{Ni}_3\text{O}_8$  and  $\text{Pr}_4\text{Ni}_3\text{O}_8$  are essentially the same and will be presented elsewhere (18).

The structure of  $R_4\text{Ni}_3\text{O}_8$  is shown in Fig. 4c. Oxygen atoms form a cubic arrangement, like anions in the fluorite structure. All nickel atoms are in square planar coordination, while all rare earth atoms are in elongated cubic coordination.

Thus, during the reduction process, only apical oxygens suffer changes, two of them (per formula unit) being removed, the two others being shifted (Fig. 4). The origin of the migration of apical oxygen O4 could be related to the preference of both  $\text{Ni}^{2+}$  and  $\text{Ni}^{1+}$  for square planar, rather than square pyramidal, coordination. More work is needed in order to fully elucidate the migration process through the intermediate

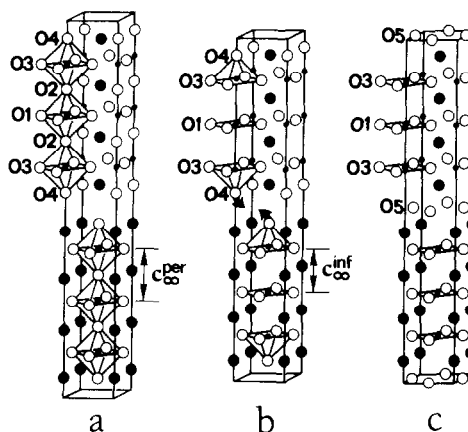


FIG. 4. The crystal structure of  $R_4\text{Ni}_3\text{O}_{10}$  ( $R = \text{La}, \text{Pr}, \text{Nd}$ ) (a) and of the reduced forms  $R_4\text{Ni}_3\text{O}_8$  as expected (b) and effectively observed (c). The thick arrows emphasize the migration of oxygen O4 toward oxygen position O5 (site 4d of space group  $I4/mmm$ ). The values of  $c_z$  for perovskite (per) and infinite-layer (inf) structures as discussed in the text are indicated on the figure. Full circles = cations (large = R, small = Ni); open circles = oxygen.

TABLE I  
REFINED CRYSTAL STRUCTURE OF Nd<sub>4</sub>Ni<sub>3</sub>O<sub>8</sub>

Atom	Site	x	y	z	B(Å <sup>2</sup> )
Nd1	4e	0	0	0.4339(1)	0.49(3)
Nd2	4e	0	0	0.2984(1)	0.34(3)
Ni1	2a	0	0	0	0.4(2)
Ni2	4e	0	0	0.1248(2)	0.5(1)
O1	4c	0	$\frac{1}{2}$	0	-0.1(4)
O3	8g	0	$\frac{1}{2}$	0.1250(4)	0.8(3)
O5	4d	0	$\frac{1}{2}$	$\frac{1}{4}$	0.9(5)

Average distances:  $d_{\text{Ni-O}} = 1.959 \text{ \AA}$ ;  
 $d_{\text{Nd-O}} = 2.526 \text{ \AA}$

Note. Space group *I4/mmm*,  $a = b = 3.9171(1) \text{ \AA}$ ,  $c = 25.307(1) \text{ \AA}$ . Refinement within the range  $20^\circ < 2\theta < 140^\circ$ , including 150 reflections (no excluded regions), with 27 refined parameters (including 6 background parameters). Conventional reliability factors:  $R_p = 0.131$ ,  $R_{wp} = 0.162$ ,  $R_{\text{Bragg}} = 0.040$ ,  $R_F = 0.027$ .

$R_4\text{Ni}_3\text{O}_9$  stage. The existence of  $R_4\text{Ni}_3\text{O}_8$  suggests, besides the Ruddlesden–Popper series  $A_{n+1}B_n\text{O}_{3n+1}$ , the outline for a new structural series, with formula  $A_{n+1}B_n\text{O}_{2n+2}$  and structures shown on Fig. 1, lower part. Attempts to prepare an  $n = 2$  member by reducing  $\text{La}_3\text{Ni}_2\text{O}_7$  were unsuccessful up to now, leading to a partially reduced compound with approximate formula  $\text{La}_3\text{Ni}_2\text{O}_{6.4}$ .

A structural arrangement such as the one of  $R_4\text{Ni}_3\text{O}_8$ , that is to say, an  $n = 3$  intermediate between single-layer T'-type and infinite-layer type, had never been observed before, even in cuprates. Moreover it is the first time that a T'-type arrangement has been stabilized outside the field of cuprates. It gives the opportunity to stress the relevance of indirect low-temperature synthesis conditions, beside more conventional high-temperature direct routes, for the stabilization of new structural types with potentially interesting properties. For instance, if the existence of Ruddlesden–Popper-type series in cuprates (19) is confirmed, one can wonder whether the reduction of  $\text{La}_4\text{Cu}_3\text{O}_{10}$  under hydrogen at low temperature could

lead to a  $\text{La}_4\text{Cu}_3\text{O}_8$  form isostructural to  $\text{La}_4\text{Ni}_3\text{O}_8$ . If yes, it would be a triple-layer counterpart of the single-layer electron-doped superconductor  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ . A study along this line is currently in progress.

Finally, the existence of stable  $\text{Ni}^{1+}/\text{Ni}^{2+}$  layered oxides is expected to be of interest by itself and in connection with the recent observations of fractional Meissner effect and anomalous resistivity transition in reduced forms of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  (see, for instance, Ref. (20) and references therein).

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