JOURNAL OF SOLID STATE CHEMISTRY **74**, 233–238 (1988)

Oxygen Excess in Layered Lanthanide Nickelates

D. J. BUTTREY,* P. GANGULY,† J. M. HONIG,* C. N. R. RAO,†
R. R. SCHARTMAN,* AND G. N. SUBBANNA†

**Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and †Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

Received April 29, 1987; in revised form July 19, 1987

Density measurements on large single-crystal specimens of $La_2NiO_{4+\delta}$ and $Pr_2NiO_{4+\delta}$ show that oxygen nonstoichiometry arises from the presence of excess lattice oxygen. X-ray photoelectron spectra as well as X-ray absorption edge studies provide no evidence for the existence of Ni^{3+} in these oxygen-excess nickelates under the conditions of the measurements. Transmission electron microscopy has revealed a novel type of exsolution process of the stoichiometric phase out of nonstoichiometric La_2NiO_4 during heating in CO_2 at 870 K for 3 h. An interpretation of the results in terms of the existence of peroxide species within the conducting layers is proposed. © 1988 Academic Press, Inc.

Introduction

Oxides of the type A_2BO_4 possessing the K_2NiF_4 structure or closely related structures have long been known to exhibit a significant range of nonstoichiometry in oxygen content (*1–5*). The nature of the deviations from the ideal O/(2*A* + *B*) stoichiometry has, however, remained unresolved. In many cases, presence of Ruddlesden–Popper phase intergrowths, deviations in the 2/1 *A*/*B* ratio, or variable valence of the *B* ion have been cited as being associated with the defect structure (*5–8*). Recent characterization of single crystals of the lanthanide nickelates, $La_2NiO_{4+\delta}$, has revealed that large deviations in nonstoichiometry ($\delta > 0$) cannot be attributed to the presence of intergrowth phases or deviations in the metal atom ratio (*9*). It therefore remains to be established whether the oxygen nonstoichiometry is associated with the presence of vacancies in stoichiometric proportions on the metal atom sublattice [i.e., $(A_2B)_{1-x}O_4$] or with the presence of interstitial oxygen in the lattice (i.e., $A_2BO_{4+\delta}$). Ganguly (*10*) pointed out that sufficient space exists in the lattice to permit excess oxygen to be incorporated as a peroxide species (see also below).

The importance of deviations from ideal stoichiometry in characterizing the structural features and physical properties of these layered materials has become apparent in a number of studies over the past few years (*1, 11, 12*). The very recent intense interest in the high temperature superconductivity of substituted lanthanum cuprates has led to the recognition of the importance of stoichiometry in determining T_c (*13–15*). A detailed investigation of the defect structure of existing materials of this type is clearly necessary for the full understanding of their fascinating and widely varying properties.

In the present study measurements of the

0022-4596/88 $3.00

density of lanthanide nickelate single crystals are used in conjunction with X-ray lattice parameters, XPS, *K*-absorption edge, and TEM studies to distinguish between the metal-deficient and oxygen-excess models for the defect structure. The consequences of this study are discussed in terms of the influence on transport and magnetic behavior.

Materials

Starting materials for the crystal growth of Ln_2NiO_4 ($Ln \equiv$ La, Pr) were La_2O_3 (99.99%), Pr_2O_3 (99.9%), and NiO (99.999%). La_2O_3 was dehydrated by heating at 1000°C in air for 24 h and cooling under vacuum. Iodometric titration and reduction in hydrogen were combined to determine the extent of nonstoichiometry and hydration in Pr_2O_3 (*9*).

Stoichiometric proportions of Ln_2O_3 or Pr_2O_3 and NiO were prereacted in air by grinding, followed by sintering in a nickel crucible for 24 h. The material was then air quenched, ground, and fired a second time. With this starting material, single crystals were grown by the radiofrequency skull melting technique (*9*). One sample of La_2NiO_4 was prepared by ceramic techniques starting with the component oxides (*16*).

Crystal characterization included the determination of the degree of nonstoichiometry by iodometric titration. The Ln/Ni ratio was determined by titrations with EDTA and was found to be 2.00 ± 0.01 (*9*). Laue back-reflection photographs verified the single-crystal nature of the samples. No evidence of additional phases was detected by polarized light microscopy, X-ray powder and electron diffraction, or high-resolution lattice imaging.

Density Measurements

The Archimedes method was used to determine the density of $Ln_2NiO_{4+\delta}$ crystals by weighing a sample in air and in a liquid of known density to determine the sample volume.

The procedure closely followed that of Cawrthorne and Sinclair (*17*). A Cahn 2000 microbalance was used for all mass determinations. Doubly deionized water was used as the immersion liquid.[1] The temperature of the water was measured so that accurate values of its density could be obtained.

The single largest source of error in this experiment arises from surface tension forces on the sample support wire at the air–liquid interface. It is crucial that surface tension forces be minimized when determining the difference between the sample support weight in water with and without a sample. To this end, several of Cawrthorne and Sinclair's (*17*) recommendations were followed. A small amount of a wetting agent was used to reduce the surface tension effects. The latter were minimized by use of very-small-diameter tungsten support wires. The wire was cleaned by dipping in 6 *M* HCl, in alcoholic KOH, and in ethanol, and was then dried.

Because of the surface tension forces, it is difficult to estimate the absolute error in the density measurement. Therefore, the density of a standard (99.99% Ni) was measured to check the accuracy of our results. The agreement between the expected density of 8.90 g/cm^3 and our determinations was always better than ±0.025 g/cm^3.

Table I shows the experimentally determined density, along with the theoretical density predicted using lattice parameters for the two defect types. On this basis one concludes that oxygen interstitials are the dominant defect type.

[1] As noted by Cawrthorne and Sinclair (*16*), liquids of higher density would be expected to give more accurate results, but this is not the case because of an observed increase in convection currents with the increase in the density of the liquid.

TABLE I

DENSITY DATA AND LATTICE PARAMETERS FOR NONSTOICHIOMETRIC La_2NiO_4 AND Pr_2NiO_4

Defect model	Lattice parameter (Å)	ρ_{th} (g/cm³)	ρ_{ex} (g/cm³)
$(La_2Ni)_{1-x}O_4$ ($x = 0.01325$)	$a = 5.480$	6.915	7.02
$La_2NiO_{4+\delta}$ ($\delta = 0.053$)	$c = 12.67$	7.006	
$(Pr_2Ni)_{1-x}O_4$ ($x = 0.0228$)	$a = 5.469$	7.156	7.30
$Pr_2NiO_{4+\delta}$ ($\delta = 0.091$)	$c = 12.31$	7.324	

X-ray Photoelectron Spectra and *K*-Absorption Edge Studies

X-ray photoelectron spectra of nonstoichiometric La_2NiO_4 and Pr_2NiO_4 (for which δ fell in the range 0.05–0.12 as estimated by iodometry) prepared by the ceramic method (*16*) and by skull melting (*1*, *9*) exhibited two distinct O(1*s*) signals close to 530 and 532 eV (Fig. 1). These signals remained even after the samples were etched in ultrahigh vacuum. We assign the 530-eV feature to the O(1*s*) level of the oxide ion. The 532-eV feature may arise from carbonate, O^{1-}, or O_2^{2-} species. Since the signal remains after Ar^+ etching and heating (i.e., after cleaning *in situ*) we suggest that the signal may be due to O^{1-} or to O_2^{2-}, probably the latter. It should be noted that metal perovskites in general exhibit an O_2^{2-} signal near 532 eV. For example, the presence of peroxide species has recently been inferred (*18*) in $La_{1.8}Sr_{0.2}CuO_4$ and in $YBa_2Cu_3O_7$. Since XPS is a surface technique, evidence based on O(1*s*) binding energies alone would be insufficient. We have examined the Ni(2*p*) spectra of the nickelates as well. The Ni(2*p*) signal of La_2NiO_4 could not be studied since the La(3*d*) and Ni(2*p*) signals could not be separated. The Ni(2*p*) spectrum of Pr_2NiO_4 shows a symmetric peak due to Ni^{2+} with no evidence for a shoulder or a peak due to Ni^{3+} on the higher binding energy side (Fig. 1). These XPS results thus suggest that peroxide-type species may be present in oxygen-excess La_2NiO_4 and Pr_2NiO_4 but provide no evidence for the

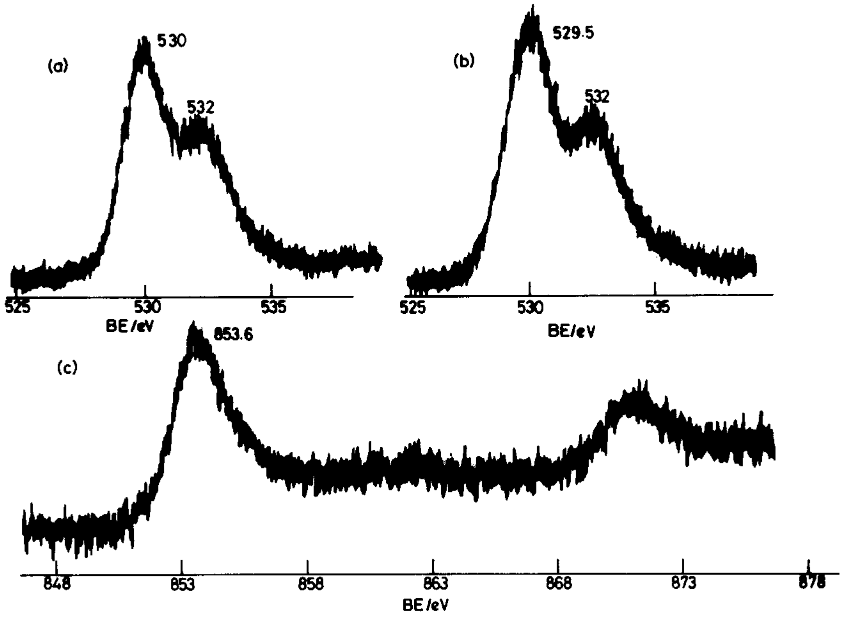

FIG. 1. X-ray photoelectron spectra of (a) O(1*s*) in La_2NiO_4 after etching, (b) O(1*s*) in Pr_2NiO_4 after etching, and (c) Ni(2*p*) in Pr_2NiO_4.

presence of Ni^{3+} ions under the conditions of the experiment.

To further confirm whether Ni^{3+} is present in oxygen-excess La_2NiO_4 and Pr_2NiO_4, we carried out Ni *K*-absorption edge measurements. The results are summarized in Table II. The parent compound NiO, with Ni only in divalent state, exhibits a chemical shift, ΔE, of 6.7 eV. In $LaNiO_3$ and $LaSrNiO_4$, where only Ni^{3+} is present, the chemical shift is close to 11 eV. In $La_3Ni_2O_7$ with 50% of Ni in the 3+ state, ΔE is 8.4 eV. In La_2NiO_4 prepared by the skull method as well by the ceramic method, with an apparent oxygen excess of $\delta = 0.05$–0.12 as determined by iodometry, the chemical shifts remain in the range 6.3–6.7 eV. Similarly, Pr_2NiO_4 exhibits chemical shifts in the range 6.3–6.8 eV. These results further suggest that Ni^{3+} is unlikely to be present in significant amounts in oxygen-excess nickelates.

The manner of accommodating the peroxide ion in La_2NiO_4 or Pr_2NiO_4 is worthy of comment. In La_2NiO_4, there are two types of oxygen; one of them, O_I, bonded to Ni having the coordinates (0.5, 0, 0) and the other, O_{II}, having the coordinates (0, 0, *z*), $z = 0.16$. There is a third possible position, O_{III}, with coordinates (0.5, 0, 0.25) which is vacant. The O_{II} and O_{III} cannot be occupied simultaneously by oxide ions; however, the space available is more than sufficient to accommodate peroxide ions. The composition $La_2NiO_{4.125}$ seems to be unique. This phase is stable when heated in air up to relatively high temperatures. The composition should be specified by $La_2Ni^{2+}O^{2-}_{3.875}(O_2^{2-})_{0.125}$ (rather than by $La_2Ni^{2+}_{0.75}Ni^{3+}_{0.25}O^{2-}_{4.125}$), wherein 1/16th of the O_{II} sites is occupied by O_2^{2-} ions.

TABLE II

Ni *K*-Adsorption Edge Data on Lanthanide Nickelates and Model Ni Compounds

Compound	Chemical shift, ΔE (eV, ±0.7 eV)
NiO	6.7
$LaNiO_3$	11.0
$LaSrNiO_4$	10.8
$La_3Ni_2O_7$	8.4
La_2NiO_4 (ceramics)	6.8
La_2NiO_4 (skull)	6.3
Pr_2NiO_4 (ceramic)	6.4
Pr_2NiO_4 (skull)	6.7

Transmission Electron Microscopy

We have carried out transmission electron microscopic studies on La_2NiO_4 containing apparent oxygen excess. When the samples were heated close to 870 K in a CO_2 atmosphere for 3 h, the bright-field images showed the emergence of dark, oriented regions (Fig. 2a) possibly due to exsolution of the stoichiometric phase. Since the lattice dimensions of the stoichiometric as well as the nonstoichiometric phases are similar, we believe this phenomenon, wherein the stoichiometric phase emerges in this manner from the nonstoichiometric phase, to be novel. High-resolution images (Fig. 2b) show that there is no major transformation in the solid, the lattice spacings being essentially the same throughout the entire crystal.

Discussion

The above data have forced us to suggest that nonstoichiometry in lanthanum and praseodymium nickelates results from the presence of excess oxygen in the lattice, most likely in the form of peroxide species. The existence of $(O_2)^{-2}$ species as defects in the Ni–O basal planes is contrary to the generally held view that nickel exists in a mixed valence state in the lanthanide nickelates. Furthermore, carbonate ions are unlikely to remain under the conditions of the experiments, quite aside from the fact that it would be difficult to accommodate such bulky units in the lattice. The suppression

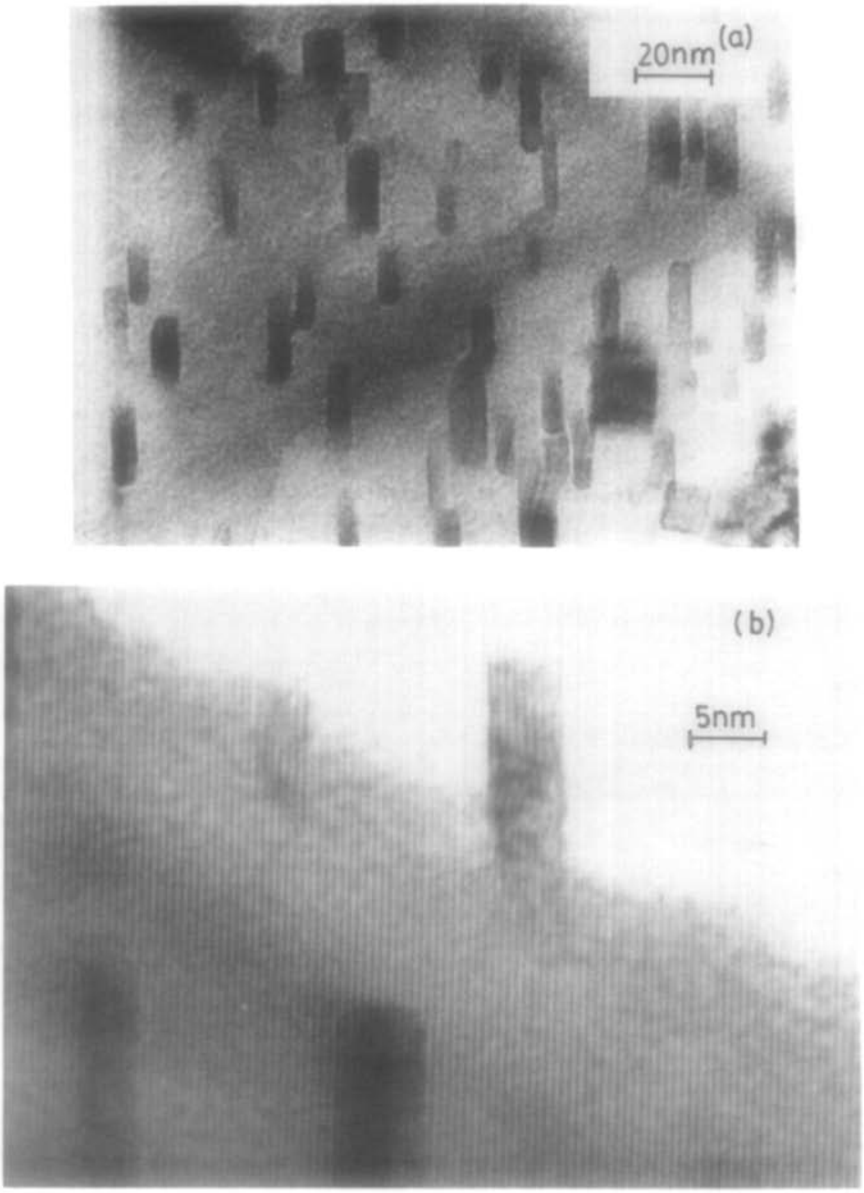

FIG. 2. (a) Bright-field image of La_2NiO_4 (samples heated at 870 K for 3 h in CO_2 atmosphere). (b) HREM image indicating that the lattice spacings are the same in the entire crystal (beam direction ⟨010⟩).

of magnetic ordering (*11, 12*) and the increase in resistivity within the basal plane (*1*) with increasing δ may be understood, in terms of the present model, as due to the disruption of superexchange interactions and to the increased localization of carriers. This model is also consistent with an observed increase in the c/a ratio with an increase in δ (19, 20).

In light of the above discussion, the influence of oxygen nonstoichiometry on the physical properties of the lanthanide nickelates is not surprising. While the generalization of this defect structure to other oxides in this family has yet to be demonstrated, it has direct relevance to the interpretation of their interesting properties, such as the recently reported high-temperature superconducting behavior in the alkaline earth-doped lanthanum cuprate systems.

Acknowledgment

This research was supported by NSF Grant INT 83-12855.

References

1. C. N. R. Rao, D. J. Buttrey, N. Otsuka, P. Ganguly, H. R. Harrison, C. J. Sandberg, and J. M. Honig, *J. Solid State Chem.* **51,** 266 (1984).
2. P. Ganguly and S. Ramasesha, *Magn. Lett.* **1,** 131 (1980).
3. N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **39,** 120 (1981).
4. J. B. Goodenough and S. Ramasesha, *Mater. Res. Bull.* **17,** 383 (1982).
5. P. Odier, M. Leblanc, and J. Choisnet, *Mater. Res. Bull.* **21,** 787 (1986).
6. J. Fontcuberta, G. Longworth, and J. B. Goodenough, *Phys. Rev. B* **30,** 6320 (1984).
7. J. T. Lewandowski, R. A. Beyerlein, J. M. Longo, and R. A. McCauley, *J. Amer. Ceram. Soc.* **69,** 699 (1986).
8. J. Drennan, C. P. Tavares, and B. C. H. Steele, *Mater. Res. Bull.* **17,** 621 (1982).
9. D. J. Buttrey, H. R. Harrison, J. M. Honig, and R. R. Schartman, *J. Solid State Chem.* **54,** 407 (1984).
10. P. Ganguly, *in* "Advances in Solid State Chemistry" (C. N. R. Rao, Ed.), p. 135ff, Indian National Science Academy, New Delhi (1986).
11. D. J. Buttrey, J. M. Honig, and C. N. R. Rao, *J. Solid State Chem.* **64,** 287 (1986).
12. D. J. Buttrey and J. M. Honig, *J. Solid State Chem.* **72,** 38 (1988).
13. C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58,** 405 (1987).
14. R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, *Phys. Rev. Lett.* **58,** 408 (1987).
15. C. N. R. Rao and P. Ganguly, *Curr. Sci.* **56,** 47 (1987).
16. P. Ganguly and C. N. R. Rao, *Mater. Res. Bull.* **8,** 405 (1973).
17. C. Cawrthorne and W. D. J. Sinclair, *J. Phys. E* **5,** 531 (1972).
18. D. D. Sarma, K. Sreedhar, P. Ganguly, and C. N. R. Rao, *Phys. Rev.,* in press; D. D. Sarma and C. N. R. Rao, *J. Phys. C,* in press.
19. P. Odier, Y. Nigara, and J. Coutures, *J. Solid State Chem.* **56,** 32 (1985).
20. D. J. Buttrey, Ph.D. thesis, Purdue University (1984).