JOURNAL OF SOLID STATE CHEMISTRY **114**, 294–296 (1995)

# BRIEF COMMUNICATION

# Electrochemical Synthesis of Ferromagnetic $LaMnO_3$ and Metallic $NdNiO_3$

R. Mahesh, K. R. Kannan, and C. N. R. Rao[1]

*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

Received August 26, 1994; accepted September 7, 1994

**While $NdNiO_{3-\delta}$ prepared ordinarily is highly oxygen-deficient and exhibits a metal–insulator transition at low temperature, it has been possible to prepare nearly metallic $NdNiO_{3-\delta}$ ($\delta = 0.05$) by electrochemical oxidation. On progressive electrochemical oxidation, orthorhombic, insulating $LaMnO_3$ transforms to a rhombohedral and then to a cubic structure. The last two phases are ferromagnetic and exhibit metal–insulator transitions.** © 1995 Academic Press, Inc.

Perovskite oxides of the general formula $LaMO_3$ ($M$ = transition metal) exhibit a wide range of electrical and magnetic properties (1, 2). Thus, stoichiometric $LaNiO_3$ is metallic while $LaMnO_3$ is an insulator. The properties of $LaNiO_3$ have been investigated extensively in the literature (3, 4) and there is considerable interest in those of $NdNiO_3$. $NdNiO_3$ was first prepared under high oxygen pressures by Demazeau *et al.* (5). Since nickel compounds with Ni in the +3 state are basically unstable, a low-temperature sol–gel method was employed by Vassiliou *et al.* [6] to prepare $NdNiO_3$ with a rhombohedral structure ($a$ = 5.40 Å, $\alpha$ = 60.5°). The material so prepared showed a transition from metallic to insulating behavior around 130 K. The transition was associated with thermal hysteresis due to the first-order nature of the transition. Lacorre *et al.* (7) and Garcia-Muñoz *et al.* (8) have studied the metal–insulator (M–I) transition in orthorhombic $NdNiO_3$ synthesized under moderate pressures. It appears that $NdNiO_3$ prepared even at low temperatures is oxygen-deficient. By employing low-temperature low-oxygen-pressure methods, Garcia *et al.* (9) have prepared $NdNiO_{3-\delta}$ with $\delta$ in the range 0.1–0.2.

$LaMnO_3$ is an interesting material which, when suitably substituted with a divalent ion such as Ca or Sr, as in $La_{1-x}Ca_x(Sr)_xMnO_3$, becomes ferromagnetic at a specific $x$ value and exhibit a M–I transition close to the ferromagnetic Curie temperature (1, 10). Verelst *et al.* (11) have shown that $LaMnO_3$ transforms from the orthorhombic to the rhombohedral and then to the cubic structure, depending on the $Mn^{4+}$ content. The temperature of the M–I transition, as well as the ferromagnetic $T_c$, accordingly increases with the $Mn^{4+}/Mn^3$ ratio.

We considered it to be rewarding to prepare stoichiometric $NdNiO_3$, which might be metallic, as well as cubic $LaMnO_3$ with a high $Mn^{4+}$ content, which would be ferromagnetic, by employing a suitable low-temperature route using electrochemical oxidation, which has proved successful in preparing oxygen-excess $La_2CuO_4$ and other materials (12, 13).

We have carried out electrochemical oxidation in 1 $N$ KOH solution using a cell described schematically in Fig. 1. The working electrode was a polished pellet of the sample of 2 mm thickness and 8 mm diameter fixed onto a groove in the rotating disc electrode (1000 rpm). Electrical contact was established using silver paste, which was then separated from the electrolyte with silicon rubber. The counterelectrode was a thin platinum foil of 0.5 mm thickness and 10 mm diameter. A Hg/HgO electrode standardized with reference to NHE ($E^0$ = +0.1 V) served as the reference electrode. The oxidation was carried out under an anodic potential of 650 mV for different polarization periods. The pellets were removed from the cell, washed with water and acetone, and dried.

By the procedure of Vassiliou *et al.* (6), we first prepared $NdNiO_{3-\delta}$ with $\delta$ = 0.12. The powder XRD pattern of this sample (Fig. 2a) could be indexed on a rhombohedral unit cell with $a$ = 5.396(4) Å and $\alpha$ = 60.40(4)°. The resistance of this sample (by 4-probe measurements) exhibited a M–I transition at around 150 K (Fig. 3a). A well-sintered pellet of this material was subjected to electrochemical oxidation. After oxidation for 24 hr, the sample became more metallic (Fig. 3b), with a lower M–I transition temperature. Oxidation for 48 hr rendered the material nearly metallic down to 100 K, with an essentially constant value of resistance down to 20 K (Fig. 3c). The

[1] To whom correspondence should be addressed.



0022-4596/95 $6.00

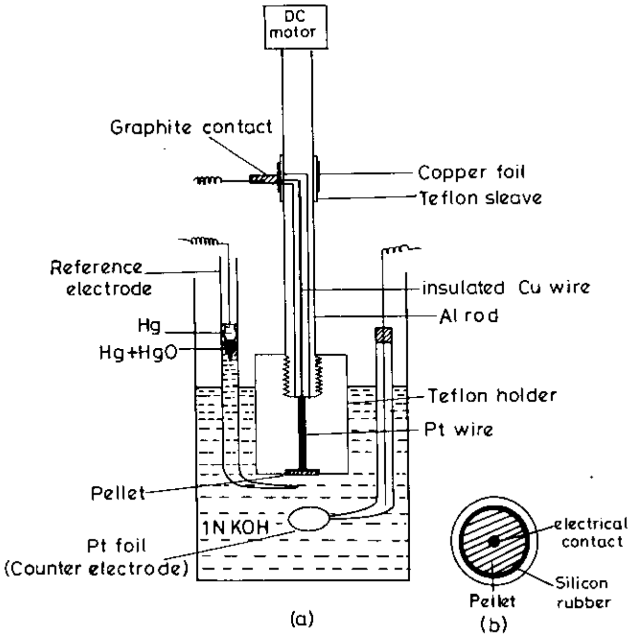


FIG. 1. Schematic diagrams of (a) the electrochemical cell and (b) the rotating disc electrode.

composition of this sample, as determined by thermogravimetric analysis and by iodometric titrations, was $NdNiO_{2.95}$. This sample also has a rhombohedral structure ($R\bar{3}c$), with unit cell parameters $a$ = 5.414(5) Å and $\alpha$ = 60.18(7)°. The rhombohedral angle suggests that the material is close to becoming cubic with a Ni–O–Ni angle of 180°. Interestingly, the resistance of this sample did not show any thermal hysteresis.

Orthorhombic $LaMnO_3$ ($a$ = 5.543 Å, $b$ = 5.494 Å, and $c$ = 7.805 Å) was prepared by the sol–gel procedure using citric acid and ethylene diamine with a solution of lanthanum and manganese nitrates. The powder obtained after decomposition of the gel at 773 K for 6 hr was pressed into a pellet and heat-treated at 1470 K in air for 24 hr. The resulting sample contained 12% $Mn^{4+}$, as determined by redox titrations. On electrochemical oxidation of the sample for 24 hr the structure changed to rhombohedral ($a$ = 5.478 Å, $\alpha$ = 60.55°). We obtained the cubic structure ($a$ = 7.788 Å) after further oxidation (Fig. 4). While orthorhombic $LaMnO_3$ was insulating and paramagnetic, the rhombohedral and cubic samples are ferromagnetic and exhibit M–I transitions at around 170 and 215 K, respectively, just below the corresponding ferromagnetic Curie temperatures. Further studies on oxidized $LaMnO_3$ samples are in progress.

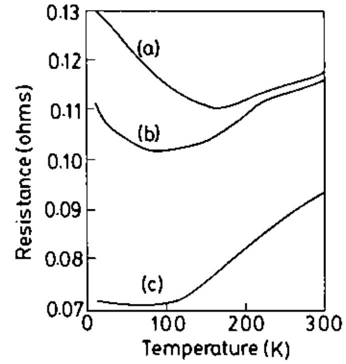


FIG. 3. Electrical resistance of $NdNiO_{3-\delta}$ (a) before oxidation, (b) after electrochemical oxidation for 24 hr, and (c) after electrochemical oxidation for 48 hr.

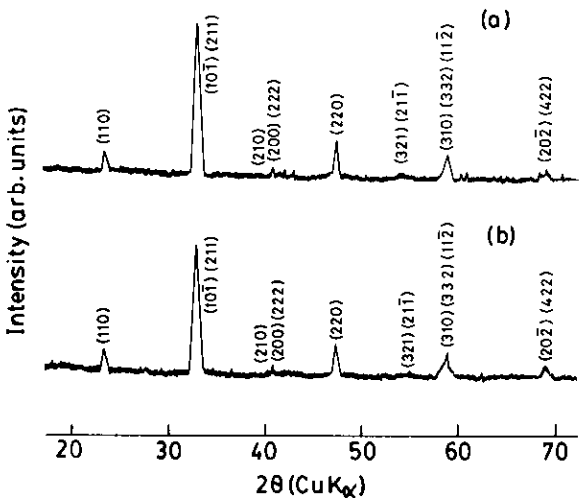


FIG. 2. X-ray diffraction patterns of $NdNiO_{3-\delta}$ (a) before oxidation ($\delta$ = 0.12) and (b) after oxidation ($\delta$ = 0.05).

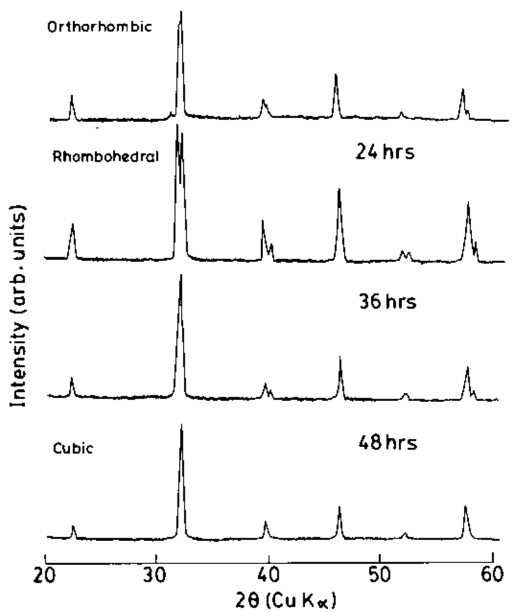


FIG. 4. Changes in the X-ray diffraction pattern of $LaMnO_3$ on progressive electrochemical oxidation.

## REFERENCES


1. J. B. Goodenough, *Prog. Solid State Chem.* **5,** 149 (1971).
2. C. N. R. Rao, *Annu. Rev. Phys. Chem.* **40,** 291 (1989).
3. N. Y. Vasanthacharya, P. Ganguly, J. B. Goodenough, and C. N. R. Rao, *J. Phys. C* **17,** 2745 (1984).
4. K. Sreedhar, J. M. Honig, M. Darwin, M. McElfresh, P. M. Shand, J. Xu, B. C. Crooker, and J. Spalek, *Phys. Rev. B* **46,** 4382 (1992).
5. G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **3,** 582 (1971).
6. J. K. Vassiliou, M. Hornbostel, R. Ziebarth, and F. J. Disalvo, *J. Solid State Chem.* **81,** 208 (1989).
7. P. Lacorre, J. B. Torrance, J. Pannetier, A. I. Nazzal, P. W. Wang, and T. C. Huang, *J. Solid State Chem.* **91,** 225 (1991).
8. J. L. Garcia-Muñoz, J. Rodriguez-Carvajal, P. Lacorre, and J. B. Torrance, *Phys. Rev. B* **46,** 4414 (1992).
9. J. Garcia, A. Gonzalez, M. J. Sanchis, M. D. Marcos, E. Martinez, F. Sapina, D. Beltran, and A. Beltran, *Solid State Ionics* **63–65,** 52 (1993).
10. E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100,** 549 (1955).
11. M. Verelst, N. Rangavittal, C. N. R. Rao, and A. Rousset, *J. Solid State Chem.* **104,** 74 (1993).
12. J. C. Grenier, A. Wattiaux, J. P. Doumerc, P. Dordor, L. Fournés, J. P. Chaminade, and M. Pouchard, *J. Solid State Chem.* **96,** 20 (1992), and references cited therein.
13. N. Casan-Pastor, P. Gomez-Romero, A. Fuertes, J. M. Navarro, M. J. Sanchis, and S. Ondono, *Physica C* **216,** 478 (1993).