

Identification of a New Strontium Ni(III) Oxide Prepared in Molten Hydroxides

JEONGHEE LEE AND GARY F. HOLLAND*

*Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112*

Communicated by J. M. Honig, April 23, 1991

The compound $\text{Sr}_5\text{Ni}_4\text{O}_{11}$ was prepared at atmospheric pressure from potassium hydroxide melts, by slow cooling from 700°C. All observed lines in the powder X-ray diffraction pattern were indexed according to a hexagonal unit cell, with $a = 9.480(1) \text{ \AA}$, $c = 7.815(4) \text{ \AA}$. The idealized formula $\text{Sr}_5\text{Ni}_4\text{O}_{11}$ corresponds to a formal oxidation state of Ni^{+3} . From magnetic susceptibility measurements, the observed high temperature Curie constant is consistent with the low spin $t_{2g}^6 e_g^1$ configuration. Electrical conductivity measurements exhibit linear behavior of $\ln \rho$ vs $1/T$ over the range 270–350 K, indicating semiconducting behavior with a bandgap of $0.5 \pm 0.1 \text{ eV}$ and room temperature resistivity $\sim 10^5 \text{ \Omega-cm}$. © 1991 Academic Press, Inc.

Introduction

The Ni(III) center is a particularly informative probe of interatomic interactions in metal oxides because it displays an unusual sensitivity to its nearest neighbor environment and the spacing between nickel ions. This can lead to delocalized metallic behavior in one system, e.g., LaNiO_3 or LaSrNiO_4 (1, 2), while structurally similar ones exhibit localized insulating behavior, as in LaBaNiO_4 (3), or temperature-dependent mixed behavior, as in NdNiO_3 (which undergoes a metal/nonmetal transition at 120 K) (4). Recent work on mixed valent nickel(II,III) oxides of the formula types $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Ln}_{2-x}\text{Sr}_x\text{NiO}_4$ ($\text{Ln} = \text{La}, \text{Nd}$) indicate that upon reaching some critical concentration of Ni(III), semiconduc-

tor-metal or transitions to superconducting behavior can be observed (5–7).

We report here the isolation and preliminary results of the characterization of a new strontium nickel oxide containing formally trivalent nickel, with idealized empirical formula $\text{Sr}_5\text{Ni}_4\text{O}_{11}$. This material has been prepared without resorting to the high oxygen pressures typically required for stabilization of Ni(III) oxides. The low temperatures and high oxygen activity possible in solvents such as molten KOH offer an attractive alternative to high pressure synthesis of high oxidation state transition metal compounds. Hydroxide media have been used effectively for the low temperature preparation of two metastable superconducting phases, $\text{La}_2\text{CuO}_{4+\delta}$ and $(\text{Ba}, \text{K})\text{BiO}_3$ (8–10), as well as the stabilization of highly oxidized nickel(III) and copper(III) species, e.g., ANiO_2 ($A = \text{Li}, \text{Na}$) (11) and $\text{Al}_6\text{Ba}_4\text{Cu}_{24}\text{O}_{84}$ (12).

* To whom correspondence should be addressed.

Experimental

The compound $\text{Sr}_5\text{Ni}_4\text{O}_{11}$ was prepared under atmospheric pressure from potassium hydroxide melts, by slow cooling from 700°C. In a typical preparation, 0.59 g (4 mmol) strontium carbonate and 0.075 g (1 mmol) nickel oxide were combined with 11.2 g (200 mmol) reagent grade potassium hydroxide and transferred to an alumina crucible; the reaction mixture was heated to 700°C and held for 12 h, then cooled slowly to room temperature over approximately 15 h. Distilled water was used to extract KOH and any soluble material from the cooled reaction mixture, and solid product was isolated by suction filtration. This product tended to form as long, lustrous black needles, some up to 1 cm in length, with well-defined hexagonal faceting. These crystals showed no adverse effects to water work-ups, and maintained their luster indefinitely.

X-ray powder diffraction studies were performed on a computer-interfaced Rigaku Miniflex diffractometer with $\text{CuK}\alpha$ radiation, using step-and-count techniques. Composition was determined by wavelength dispersive microprobe analysis of single crystals, using a Cameca/SX electron beam microprobe, calibrated against commercially available SrTiO_3 and NiO single crystal standards for quantitative analysis. Thermogravimetric analyses were performed on a DuPont 2200 Thermal Analyzer in 5% H_2 /Ar. Magnetic studies were performed on a Quantum Design SQUID magnetometer at UC Berkeley/Lawrence Berkeley Laboratory. The powdered sample was loaded into a calibrated Kel-F (poly(chlorotrifluoroethylene)) container and the measured magnetization corrected for core and container diamagnetism (13). The electrical conductivity was measured in the range $270 < T < 350$ K by four-probe techniques with silver paint contacts and gold lead wires; temperature was controlled with

an Air Products Displex closed cycle He refrigerator.

Results and Discussion

The highest quality crystals of $\text{Sr}_5\text{Ni}_4\text{O}_{11}$ were obtained by first predrying KOH by heating at 700°C in air for 12 hr and cooling to room temperature, followed by addition of the binary oxides, reheating, and slow cooling. These observations correlate with the enhanced solubility of Ni^{2+} as the solvated oxyhydroxide complex $[\text{Ni}(\text{O})_2(\text{OH})_4]^{6-}$ in basic (dry) hydroxide media, as discussed by Tremillon and coworkers (14, 15). Preparations in air atmospheres, saturated with water vapor, gave no evidence of product formation. The ternary product was found to form only when reaction temperatures were 600°C or higher. Analogous reactions with barium produced the ternary BaNiO_3 with Ni(IV) rather than a similar Ni(III) oxide (16).

Least squares refinement of powder X-ray diffraction data, Fig. 1, leads to the indexing of all observed lines according to a hexagonal unit cell, $a = 9.480(1)$ Å, $c = 7.815(4)$ Å (see Table I). The cell type and corresponding cell parameters were confirmed by precession photographs. This diffraction pattern is similar to data reported for two polycrystalline phases, previously identified as SrNiO_3 and $\text{Sr}_2\text{Ni}_2\text{O}_5$; both of these phases were prepared by solid state reaction under 1–50 atm oxygen (17, 18). However, the pattern in Fig. 1 exhibits several low angle lines not reported for either of the reported phases, indicating that the present compound is a structurally related material. Detailed single crystal structural studies have thus far been thwarted by crystallographic twinning.

Microprobe analysis gave an empirical formula of $\text{Sr}_{4.96}\text{K}_{0.1}\text{Ni}_4\text{O}_{11.0}$. Thermal gravimetric analyses were undertaken to better characterize the oxygen content of this ma-

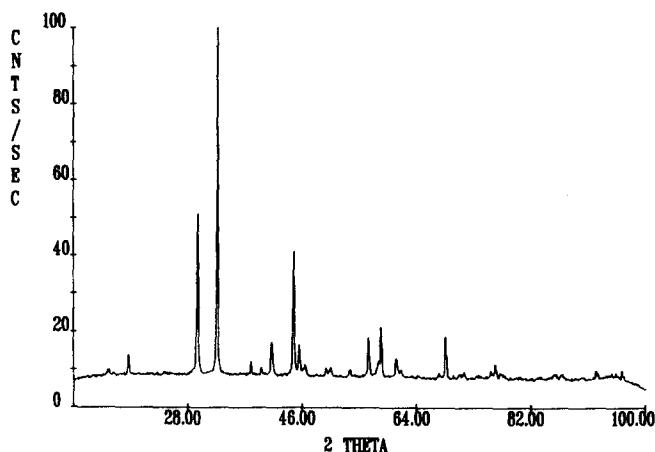


FIG. 1. X-ray powder diffraction pattern of polycrystalline $\text{Sr}_3\text{Ni}_4\text{O}_{11}$; $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$). This pattern can be indexed as hexagonal cell, $a = 9.480(1) \text{ \AA}$, $c = 7.815(4) \text{ \AA}$.

terial. The weight loss for this reduction process corresponds to an overall stoichiometry (based on the metals analysis from microprobe) of $\text{Sr}_{4.96}\text{K}_{0.1}\text{Ni}_4\text{O}_{10.62}$, and a formal oxidation state of $\text{Ni}^{2.8+}$. This suggests the idealized formula $\text{Sr}_3\text{Ni}_4\text{O}_{11}$ if one assumes potassium is present as an impurity or minor dopant; the idealized formula corresponds to a formal oxidation state of +3 for the nickel.

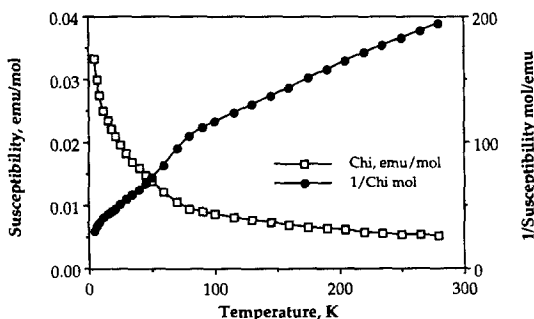


FIG. 2. Magnetic susceptibility (left axis) and inverse magnetic susceptibility (right axis) as functions of temperature for polycrystalline $\text{Sr}_3\text{Ni}_4\text{O}_{11}$, 5 kG applied field. Least squares fitting of $T > 100 \text{ K}$ data indicates linear Curie-Weiss fit, $C = 2.28 \text{ emu-K/mol Sr}_3\text{Ni}_4\text{O}_{11}$ and $\Theta = -166.9 \text{ K}$. Data at 40 kG are qualitatively similar.

Magnetic susceptibility studies on polycrystalline $\text{Sr}_3\text{Ni}_4\text{O}_{11}$ show that this material is paramagnetic over the temperature range 5–280 K and in fields from 5 to 40 kG (Fig. 2). The magnetic susceptibility at 5 K varied linearly with applied field, indicating the presence of isolated magnetic centers at low temperatures. At temperatures above 100 K, plots of χ^{-1} vs temperature are linear, yielding a Curie constant of $C = 0.570 \text{ emu-K/mol Ni}$, and a Weiss constant $\Theta = -166.9 \text{ K}$ at 5 kG; 40 kG data are qualitatively similar. Below 100 K, there is a transition to behavior characteristic of a lower spin multiplicity, with χ^{-1} vs temperature linear over this entire range. The observed high temperature Curie constant rules out the possibility of high-spin Ni^{3+} , and is more consistent with the low spin $t_{2g}^6 e_g^1$ configuration (assuming O_h coordination geometry), a feature common to all Ni(III) oxides studied thus far (2, 19, 20), with the exception of BaLaNiO_4 (3). The measured Curie constant is significantly greater than the spin-only value predicted for a simple $S = 1/2$ system; a similar discrepancy has been observed in several other nonmetallic Ni(III) oxides (2, 19, 20), but its origin is as

TABLE I
INDEXING OF X-RAY POWDER DIFFRACTION
DATA, $\text{Sr}_5\text{Ni}_4\text{O}_{11}$ ^a

d_{obs}	d_{calc}	hkl	I/I_0
5.708	5.658	101	1.8
4.744	4.735	110	8.1
3.657	3.631	201	1.4
3.017	3.014	112	76.2
2.738	2.734	300	100
2.367	2.367	220	3.7
2.276	2.274	310	3.3
2.192	2.184, 2.199	311,203	10.0
2.027	2.025	222	47.5
1.991	1.994	213	13.6
1.957	1.954	004	4.7
1.828	1.829	321	4.5
1.805	1.806	114	3.1
1.711	1.713	313	3.1
1.628	1.627	412	19.6
1.606	1.605	501	2.2
1.589	1.590	304	7.3
1.578	1.578	330	27.1
1.523	1.520	421	11.2
1.508	1.507	224	2.6
1.367	1.367	600	20.2
1.329	1.329	431,423	1.8
1.319	1.320	414	1.8
1.287	1.290, 1.287	602,106	1.2
1.235	1.235	611	2.9
1.140	1.137, 1.141	620,226	1.2
1.133	1.133	442	2.6
1.119	1.120	604	2.2
1.068	1.068	353	2.6
1.051	1.050, 1.053	127,614	1.4
1.041	1.041	451	1.6
1.033	1.034, 1.033	307,630	3.1

^a Based on a hexagonal unit cell, $a = 9.470(1)$ Å, $c = 7.815(4)$ Å.

yet unclear. The Weiss constant extracted from the low temperature magnetic data indicates that the dominant Ni–O–Ni exchange interactions are antiferromagnetic in nature. These two factors ($C_{\text{obs}} > C_{\text{calc}}$, Θ large and negative) suggest strong Ni–O–Ni interactions and may signal incipient metalization.

Electrical conductivity measurements, performed on pressed pellets of polycrystal-

line material, exhibit linear behavior of $\ln \rho$ vs $1/T$ over the range 270–350 K, indicating semiconducting behavior with a bandgap of 0.5 ± 0.1 eV. Room temperature resistivities ($\sim 10^5$ Ω-cm) were 10–1000 times greater than observed for other semiconducting Ni^{3+} oxides. The unusually high resistivity may be due to very low electronic mobility or trapping of the conduction electrons at crystal defects.

In conclusion, we have synthesized a new Ni(III) oxide with formula $\text{Sr}_5\text{Ni}_4\text{O}_{11}$, using potassium hydroxide melts at atmospheric pressure. As prepared, this material is a paramagnetic semiconductor. Studies are underway to elucidate the single crystal structure and further characterize the unusual magnetic and electrical transport properties of this material. Doping of aliovalent metal ions (e.g., La^{3+} , Rb^+) is being investigated to determine their effect on the transport properties of this new Ni(III) oxide. Further work is in progress to explore the generality of this synthetic procedure for the preparation of other highly oxidized nickel oxides.

Acknowledgments

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research. The authors thank M. Geselbracht for the SQUID magnetic susceptibility data, P. VerNooy for the precession photographs as well as for several helpful discussions, and Prof. Bill Nash for assistance with the microprobe experiments. We also thank Prof. John B. Goodenough for useful discussions concerning the magnetic behavior. J.L. thanks the University of Utah for a University Graduate Research Fellowship.

References

1. J. B. GOODENOUGH, N. F. MOTT, M. POUCHARD, G. DEMAZEAU, AND P. HAGENMULLER, *Mater. Res. Bull.* **8**, 647 (1973).
2. G. DEMAZEAU, M. POUCHARD, AND P. HAGENMULLER, *J. Solid State Chem.* **18**, 159 (1976).
3. G. DEMAZEAU, J. L. MARTY, B. BUFFAT, J. M. DANCE, M. POUCHARD, P. DORDOR, AND B. CHEVALIER, *Mater. Res. Bull.* **17**, 37 (1982).

4. J. K. VASSILIOU, M. HORNBOSTEL, R. ZIEBARTH, AND F. J. DISALVO, *J. Solid State Chem.* **81**, 208 (1989).
5. Z. KAKOL, J. SPALEK, AND J. HONIG, *J. Solid State Chem.* **79**, 288 (1989).
6. B. W. ARBUCKLE, K. V. RAMANUJACHARY, Z. ZHANG, AND M. GREENBLATT, *J. Solid State Chem.* **88**, 278 (1990).
7. Y. TAKEDA, R. KANNO, M. SAKANO, O. YAMAMOTO, M. TAKANO, Y. BANDO, H. AKINGA, K. TAKITA, AND J. B. GOODENOUGH, *Mater. Res. Bull.* **25**, 293 (1990).
8. W. K. HAM, G. F. HOLLAND, AND A. M. STACY, *J. Amer. Chem. Soc.* **110**, 5214 (1988).
9. L. F. SCHNEEMEYER, J. K. THOMAS, T. SIEGRIST, B. BATLOGG, L. W. RUPP, R. L. OPILA, R. J. CAVA, AND D. W. MURPHY, *Nature* **335**, 421 (1988).
10. J. P. WIGNACOURT, J. S. SWINNEA, H. STEINFINK, AND J. B. GOODENOUGH, *Appl. Phys. Lett.* **53**, 1753 (1988).
11. L. D. DYER, B. S. BORIE, AND G. P. SMITH, *J. Amer. Chem. Soc.* **76**, 1499 (1954).
12. P. D. VERNOOY, M. A. DIXON, F. J. HOLLANDER, AND A. M. STACY, *Inorg. Chem.* **29**, 2837 (1990).
13. The magnetization of the sample was obtained by subtracting the magnetization due to the container from the measured magnetization; the magnetization of the container was 2-3 orders of magnitude smaller than the sample magnetization. The measured susceptibility was also corrected for core diamagnetism: O'Connor, C. J. *Prog. Inorg. Chem.* **29**, 203 (1982).
14. B. TREMILLON, *Pure Appl. Chem.* **25**, 395 (1972).
15. J. GORET AND B. TREMILLON, *Electrochim. Acta* **12**, 1065 (1967).
16. J. LEE, K. J. GREENWOOD, AND G. F. HOLLAND, manuscript in preparation.
17. Y. TAKEDA, T. HASHINO, H. MIYAMOTO, F. KANAMARU, S. KUME, AND M. KOIZUMI, *J. Inorg. Nucl. Chem.* **34**, 1599 (1972).
18. R. J. MARCISAK AND L. KATZ, *J. Solid State Chem.* **24**, 295 (1978).
19. G. DEMAZEAU, A. MARBEUF, M. POUCHARD, AND P. HAGENMULLER, *J. Solid State Chem.* **3**, 582 (1971).
20. A. WICHAINCHAI, P. DORDOR, J. P. DOUMERC, E. MARQUESTAUT, M. POUCHARD, AND P. HAGENMULLER, *J. Solid State Chem.* **74**, 126 (1988).