Journal of Solid State Chemistry **147,** 679–681 (1999)
Article ID jssc.1999.8492, available online at http://www.idealibrary.com on IDEAL®

LETTER TO THE EDITOR

Ambient Temperature Synthesis of Spinel Ni_3S_4: An Itinerant Electron Ferrimagnet

A. Manthiram[1] and Y. U. Jeong

Texas Materials Institute, ETC 9.104, The University of Texas at Austin, Austin, Texas 78712

Communicated by J. M. Honig June 4, 1999; in revised form August 6, 1999; accepted August 27, 1999

Ni_3S_4 crystallizing in the cubic spinel structure has been synthesized by an ambient temperature reaction between aqueous nickel chloride and sodium dithionite solutions. The product has been characterized by X-ray diffraction, thermogravimetric analysis, and electrical resistivity, Seebeck coefficient, and magnetic measurements. Ni_3S_4 is metastable and it begins to decompose above 100°C. Ni_3S_4 is metallic and it exhibits itinerant electron ferrimagnetism. © 1999 Academic Press

1. INTRODUCTION

Nickel oxides with $Ni^{2+/3+}$ and $Ni^{3+/4+}$ couples have drawn considerable attention during the past decade (1–4) after the discovery of high temperature superconductivity in copper oxides. The near equivalence of Ni:3*d* and O:2*p* energies in nickel oxides with higher formal oxidation states for Ni have also created much interest with respect to the location of holes in the Ni:3*d* versus O:2*p* bands (5). However, nickel sulfides with higher formal oxidation states have been investigated relatively to a lesser extent mainly because of the difficulties in accessing the phases.

Although a number of binary nickel sulfides such as $Ni_{3+x}S_2$, Ni_3S_2, Ni_4S_{3+x}, Ni_6S_5, Ni_7S_6, Ni_9S_8, NiS, Ni_3S_4, and NiS_2 have been reported (6), only a few sulfides such as NiS and NiS_2 have been investigated extensively. For example, NiS forms two polymorphs: a low temperature millerite phase and a high temperature NiAs-type phase. The NiAs-type phase exhibits a first-order antiferromagnetic semiconductor to metal transition around 260 K (7). NiS_2, on the other hand, adopts the pyrite structure and exhibits semiconducting properties (8). NiS_2 has been suggested to be a Mott–Hubbard insulator and a substitution of Se for S causes a semiconductor to metal transition for $x > 0.5$ in $NiS_{2-x}Se_x$ (9).

Ni_3S_4 with a possible substitution of a small amount of Fe for Ni occurs in nature as a mineral, polydymite, with the cubic spinel structure (10). However, synthesis of single phase Ni_3S_4 in the laboratory is rather difficult due to the instability of Ni_3S_4 at higher temperatures (6, 11). Solid state reactions of $Ni + S$, $NiS + S$, or $NiS + NiS_2$ at 200–300°C for 6–8 months have yielded Ni_3S_4 along with NiS and NiS_2 impurities (11). Although other sulfides such as Ni_3S_2 and NiS could be obtained readily by a mechanical milling of Ni and S powders in a hardened stainless-steel vial sealed in a glove box, Ni_3S_4 could not be produced by such a procedure (12). Attempts to produce Ni_3S_4 by pulsed laser on nickel disks that are in contact with sulfur-containing liquids have resulted in a significant amount of NiS impurity (13). Homogeneous precipitation by a reaction between nickel nitrate and ammonium sulfide solutions at 80°C followed by heat treatment at 100°C in a mixture of 20% H_2S–80% H_2 has shown a few broad reflections corresponding to Ni_3S_4 (14). However, the product produced by such a procedure decomposes to well-crystalline $NiS_{1.03}$ and NiS (millerite) on heat treating at 200°C in a mixture of 20% H_2S–80% H_2. These results clearly reveal that it is difficult to synthesize single phase Ni_3S_4.

The properties of Ni_3S_4 are not known because of the difficulties to synthesize Ni_3S_4 and the lack of single phase samples. We present in this Letter an ambient-temperature, solution-based procedure to synthesize well-crystalline Ni_3S_4. The crystal chemistry, compositional analysis, and electrical and magnetic properties of Ni_3S_4 are presented.

2. EXPERIMENTAL

Ni_3S_4 was synthesized by adding 150 mL of 1 M sodium dithionite ($Na_2S_2O_4$) solution from a burette to 50 mL of 0.25 M nickel chloride solution under constant stirring while maintaining the pH at 3 by adding drops of hydrochloric acid. The solid formed was filtered, washed several

---

[1] To whom correspondence should be addressed.

0022-4596/99 $30.00

times with deionized water, and allowed to dry at room temperature. The product was then characterized by X-ray powder diffraction. Sulfur content was determined by oxidizing Ni_3S_4 to NiO in a thermogravimetric analyzer (TGA) in a flowing mixture of 75% N_2 and 25% O_2. Four-probe electrical resistivity and Seebeck coefficient measurements were carried out with pressed pellets as the sample could not be sintered at higher temperatures. Magnetic properties were measured with a SQUID magnetometer.

3. RESULTS AND DISCUSSION

The X-ray powder diffraction pattern shown in Fig. 1a reveals the formation of single phase Ni_3S_4 at ambient temperature. The pattern could be indexed on a cubic spinel structure with a lattice parameter of 9.478(50) Å, which is in close agreement with that reported for the naturally occurring polydymite (11). TGA data reveal a composition of $Ni_3S_{4.02}$. Figure 1b shows the X-ray diffraction pattern recorded after annealing the Ni_3S_4 sample in an evacuated sealed glass tube at 150°C for 12 h. The data clearly reveal that Ni_3S_4 is unstable to heat treatment and it decomposes to NiS (millerite) and $NiS_{1.03}$, which is in agreement with that found recently by Olivas *et al.* (14). This observation demonstrates the necessity of ambient temperature procedures to access the metastable Ni_3S_4.

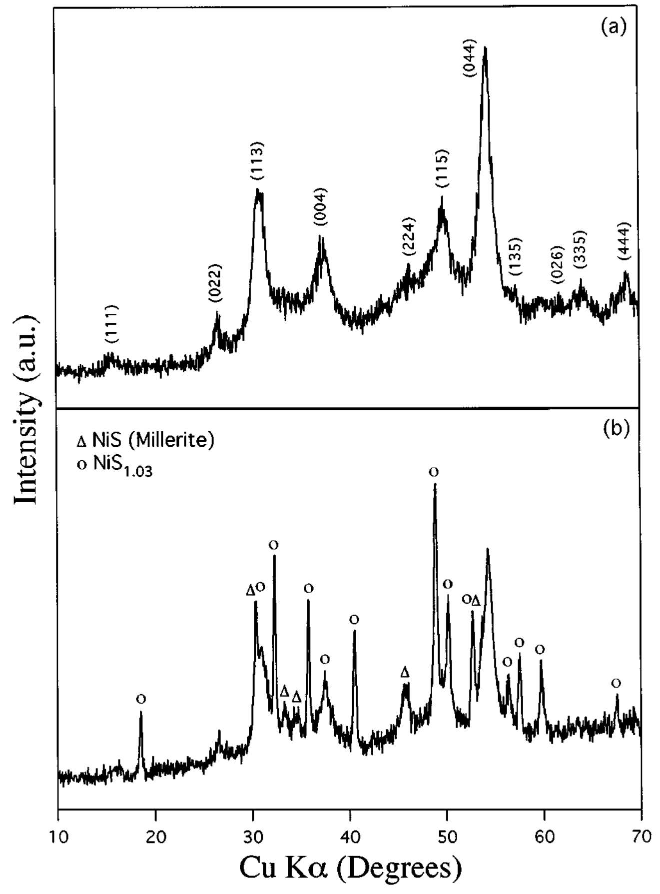

FIG. 1. X-ray diffraction patterns of (a) as-prepared Ni_3S_4 and (b) after heating the as-prepared Ni_3S_4 in an evacuated glass tube at 150°C. In (b), the reflections corresponding to the remaining Ni_3S_4 are not marked.

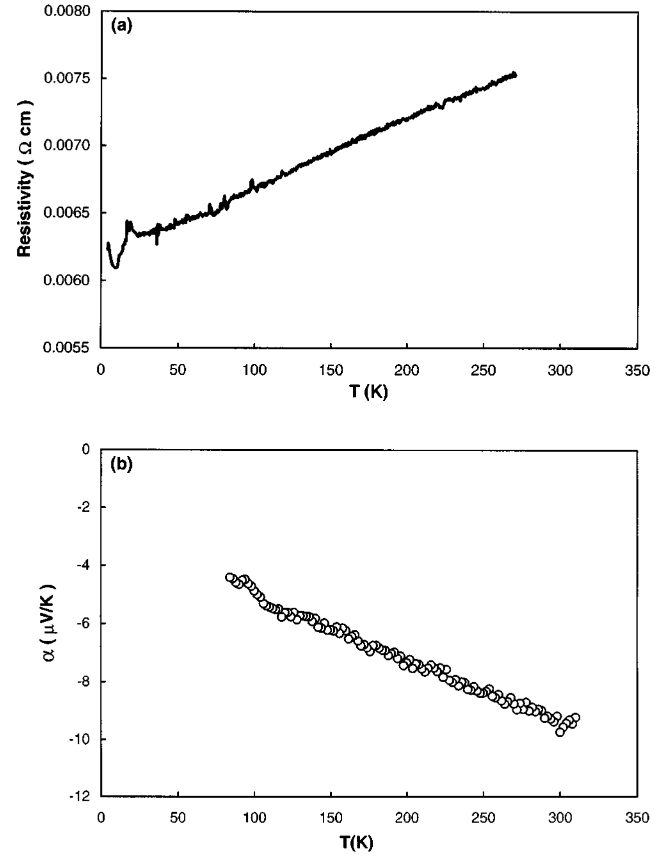

FIG. 2. Variations of (a) electrical resistivity and (b) Seebeck coefficient of Ni_3S_4 with temperature.

The accessibility of single phase Ni_3S_4 has enabled us to study its electrical and magnetic properties. Figure 2 shows the variations of electrical resistivity and Seebeck coefficient α of Ni_3S_4 with temperature. The data reveal that Ni_3S_4 is metallic and the predominant carriers are electrons. The small value of α is consistent with metallic behavior. It is interesting to note that the sample shows good metallic behavior without much degradation from grain boundary effects even though the measurements were carried out with pressed pellet without sintering; the absolute value of resistivity in Fig. 2a may decrease for sintered specimens, but Ni_3S_4 begins to decompose above 100°C. The metallic behavior reveals a strong covalent mixing between the Ni:3*d* and S:3*p* orbitals.

Figure 3a shows the variation of inverse molar magnetic susceptibility of Ni_3S_4 with temperature. The data reveal ferrimagnetic behavior with a Curie temperature $T_C \approx 20$ K.

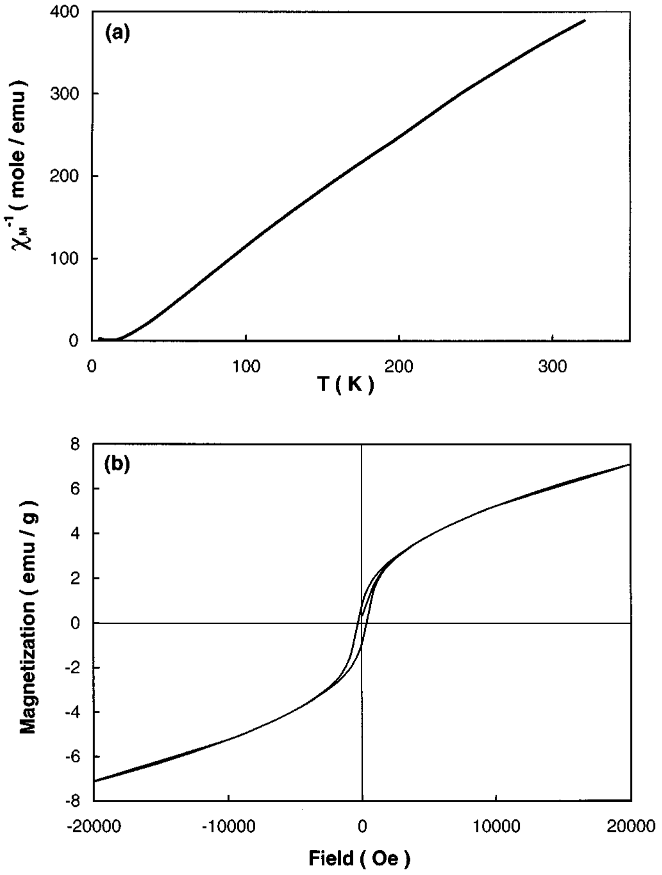

FIG. 3. Variations of (a) inverse molar magnetic susceptibility of Ni_3S_4 with temperature and (b) magnetization with applied field (hysterisis loop) at 5 K for Ni_3S_4.

The downward curvature before T_C in Fig. 3a clearly distinguishes ferrimagnetic behavior from ferromagnetic behavior. The hysterisis loop recorded at 5 K (Fig. 3b) further confirms the spontaneous magnetization at lower temperatures $T < 20$ K. Ni_3S_4 has a coercive field of about 320 Oe. The occurrence of ferrimagnetic behavior for Ni_3S_4 can be understood from the spontaneous alignment of the octahedral and tetrahedral site moments of the spinel lattice in the opposite directions.

The electrical and magnetic data clearly reveal that Ni_3S_4 is an itinerant electron ferrimagnet. Although a few examples of itinerant electron ferromagnet such as CrO_2, $SrRuO_3$, and $CuCr_2S_4$ are known, Ni_3S_4 appears to be the first example of an itinerant electron ferrimagnet, to our knowledge. The analogous spinel sulfide Co_3S_4 is a metallic Pauli paramagnet (15–17) and Fe_3S_4 is a ferrimagnetic ($T_C = 570$ K) semiconductor with a low resistivity of 10^{-1}–10^{-3} ohm cm (17–19). The effective magnetic moment ($\mu_{eff} = 1.47$ μ_B per Ni) calculated from the slope in Fig. 3a in the temperature range 100–320 K suggests less than one unpaired electron per Ni in Ni_3S_4. The observed magnetic moment is lower than that expected based on the formal valence of 2.67+. The lower magnetic moment may be due to an overlap of the Ni:3*d* and S:3*p* energies and a strong covalent mixing between them. The observed itinerant electron ferrimagnetism is a result of strong covalence in Ni_3S_4.

3. CONCLUSIONS

Single phase Ni_3S_4 crystallizing in the cubic spinel structure has been synthesized successfully by an ambient-temperature solution-based procedure. Ni_3S_4 is metastable and unstable to heat treatment. The properties of Ni_3S_4 have been measured for the first time and it exhibits itinerant electron ferrimagnetism.

ACKNOWLEDGMENT

Financial support by the Welch Foundation Grant F-1254 is gratefully acknowledged.

REFERENCES

1. R. J. Cava, B. Batlogg, T. T. Palstra, J. J. Krajewski, W. F. Peck, Jr., A. P. Ramirez, and L. W. Rupp, Jr., *Phys. Rev. B* **43,** 1229 (1991).
2. J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldo, and C. Niedermayer, *Phys. Rev. B* **45,** 8209 (1992).
3. K. Sreedhar, M. McElfresh, D. Perry, D. Kim, P. Metcalf, and J. M. Honig, *J. Solid State Chem.* **110,** 208 (1994).
4. Z. Zhang and M. Greenblatt, *J. Solid State Chem.* **117,** 236 (1995).
5. J. Zaanen and G. A. Sawatzky, *J. Solid State Chem.* **88,** 8 (1990).
6. C. N. R. Rao and K. P. R. Pisharody, *Prog. Solid State Chem.* **10,** 207 (1976).
7. E. Barthelemy, O. Gorochov, and H. McKinzie, *Mater. Res. Bull.* **8,** 1401 (1973).
8. T. A. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue, and W. J. Siemons, *Inorg. Chem.* **7,** 2208 (1968).
9. J. M. Honig and J. Spalek, *Chem. Mater.* **10,** 2910 (1998).
10. D. Lunqvist, *Arkiv. Kemi. Mineral. Geol. A* **24,** 21 (1947).
11. G. Kullerud and J. R. A. Yund, *J. Petrology* **3,** 126 (1962).
12. T. Kosmac, D. Maurice, and T. H. Courtney, *J. Amer. Ceram. Soc.* **76,** 2345 (1993).
13. V. M. Anischik, M. I. Markevich, F. A. Piskunov, and V. A. Yanushkevich, *Thin Solid Films* **261,** 183 (1995).
14. A. Olivas, J. Cruz-Reyes, M. Avalos, and S. Fuentes, *J. Vac. Sci. Technol. A* **16,** 3515 (1998).
15. R. J. Bouchard, P. A. Russo, and A. Wold, *Inorg. Chem.* **4,** 685 (1965).
16. R. F. Heidelberg, A. H. Luxem, S. Talhouk, and J. J. Nanewicz, *Inorg. Chem.* **5,** 194 (1966).
17. Landolt-Bornstein Tabellen, Group III, Volume 27a, p. 292, Springer-Verlag, Berlin, 1988.
18. J. M. D. Coey, M. R. Spender, and A. H. Morrish, *Solid State Commun.* **8,** 1605 (1970).
19. M. R. Spender, J. M. D. Coey, and A. H. Morrish, *Can. J. Phys.* **50,** 2313 (1972).