Solvothermal Coordination–Reduction Route to γ-NiSb Nanocrystals at Low Temperature

Yi Xie, Jun Lu, Ping Yan, Xuchuan Jiang, and Yitai Qian

Structure Research Laboratory and Laboratory of Nanochemistry and Nanomaterials, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

E-mail: yxie@ustc.edu.cn

DEDICATED TO PROFESSOR J. M. HONIG

A very mild synthesis of nanocrystalline γ-NiSb via a novel solvothermal coordination-reduction process is reported here. The reaction of the mixture of $NiCl_2$, antimony, and KBH_4 was carried out in ethylenediamine (en) at 140°C for 24 h. X-ray powder diffraction and transmission electron microscope images show that the products are hexagonal γ-NiSb phase and well crystallized with an average size of about 15 nm. The reaction proceeds through a metallic nickel intermediate. The morphology of the products was influenced markedly by the solvents, and a dendritic crystal of NiSb was obtained in diethylamine. The products were also investigated by UV/vis absorption, photoluminescence, X-ray photoelectron spectra, and Fourier-transform IR. © 2000 Academic Press

1. INTRODUCTION

Metal pnictides, which are well-known electronic and optoelectronic materials (1), have a wide variety of application such as displayers, satellite TV receivers, and optical fiber (2). In comparison with III–V semiconductors, transition metal pnictides have many special electrical. mechanical, and anticorrodating properties (3). Among them, nickel monoantimonide has been a great fascination for scientists because of its technological importance in secondary high-temperature batteries (4). γ-NiSb exhibits a hexagonal B8₁ (NiAs) (5) structure with cell constants $a = 3.9258$ Å, $c = 5.4378$ Å (6). This γ phase is formed by the interpenetration of three hexagonal sublattices: the (α) sublattice occupied by nickel atoms, the (β) sublattice occupied by antimony atoms, and the (δ) sublattice, which corresponds to vacant tetrahedral sites (7).

To date, considerable progress has been made in the synthesis of metal pnictide semiconductor crystallites. These syntheses include dehalosilylation and related reactions (8), solution–liquid–solid mechanism (9), and metal organic precursors' alcoholysis (9, 10). All of these methods are very useful and mild in comparison with traditional solid state reactions (usually above 1000°C), but there are some limitations to their utilities, especially for the preparation of binary metal antimonides. To our knowledge no antimonides can be obtained via the above methods, due to the difficulty of the formation of SbH_3 and the metal organic precursors of antimony. Recently, using solid state metathesis (SSM), Kaner and co-workers obtained GaSb and InSb at a high temperature of 550°C, where elemental Sb coexisted in the final products (11), which also confirms that the metal antimonides are not easy to form due to the relatively strong metallicity of the elemental antimony. Very recently, Gopalakrishnan and co-workers prepared binary metal antimonides by direct reduction of antimonate precursors with H_2 gas at a temperature of 500°C; however only $NiSb_2$ was reported to be obtained (12). In addition, the above methods either require relatively high temperature or use toxic and dangerous agents such as H_3Pn ($Pn = $ P, As), H_2, or metalorganic compounds. So, few literature has reported on the synthesis of pure-phase binary metal antimonides via a solution method to date.

In this work, we report a novel method for preparing antimonides of pure-phase γ-NiSb via a safe mild solvothermal process in ethylenediamine at a temperature of 140°C. The synthesis route is described as

$$NiCl_2 + Sb + KBH_4 \xrightarrow{\text{en}} NiSb + KCl + BH_3 + H_2.$$

$$[1]$$
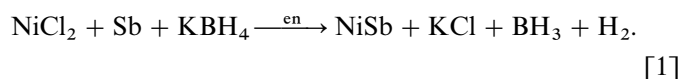
We call it the solvothermal coordination–reduction route. This route has a further advantage in that the reactants are readily available. Reduction of metal salts with hydroorganoborates has been used to prepare finely divided powders of metals and alloys (13)
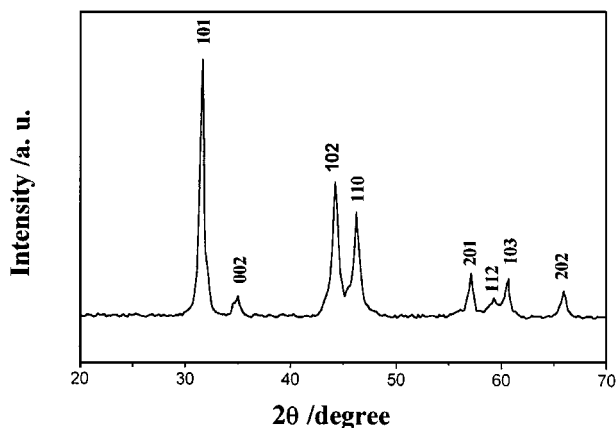
$$uMX_v + vM'(BR_3H)_u \rightarrow uM + vM'X_u + vBR_3 + (uv)/2H_2.$$

$$[2]$$
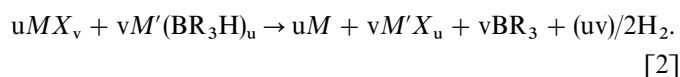
FIG. 1. XRD patterns of as-prepared nanocrystalline NiSb.

We have extended it to prepare CdSe (14) nanocrystals at room temperature, InP (15) nanocrystals at 80–160°C, and InAs (16) nanofibers at 160°C. Here we first obtained pure-phase nanocrystalline NiSb via a mild solution process by applying a potassium borohydride reducing route.

2. EXPERIMENTAL

All reagents were of analytical grade, and the nickel chloride was purified through refluxing in thionyl chloride ($SOCl_2$) for 45 min before used. A typical procedure is as follows: 40 ml of ethylenediamine, 0.609 g (5 mmol) of Sb, and 0.648 g (5 mmol) of $NiCl_2$ were added to a 50-ml flask, and then the mixture was ultrasonically mixed for 3 h before putting 0.538 g (10 mmol) of KBH_4 into the flask. The mixture was transferred to a Teflon-lined autoclave immediately. It was maintained at 140°C for 24 h, and then cooled to room temperature naturally. The black products were filtered out, washed with distilled water and absolute alcohol in subsequence, and then dried in vacuum at room temperature for 4 h.

X-ray powder diffractions (XRD) patterns were obtained on a Japan Rigaku D/Max γA rotating anode X-ray diffractometer with Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). Transmission electron microscope (TEM) measurements were made on a Hitachi H-800 with an accelerating voltage of 200 kV.

X-ray photoelectron spectra (XPS) were recorded on an ECSALab MKII instrument with Mg$K\alpha$ radiation as the exciting source. The binding energies obtained in the XPS analysis were corrected by referencing the C 1s peak to 284.60 eV.

The infrared (IR) spectra were recorded in the wavenumber range of 4000–400 cm^{-1} with a Nicolet Model 759 Fourier-transform infrared (FTIR) spectrometer, using a KBr wafer.

Room temperature UV/vis adsorption spectrum of the products dispersed in water were recorded using a Shimadzu UV-240 UV/vis spectrophotometer. Room temperature photoluminescence (PL) spectra of the products were recorded using a Hitachi 850 fluorescence spectrophotometer in reflection geometry.

3. RESULTS AND DISCUSSION

Reaction of $NiCl_2$, antimony, and potassium borohydride at 140°C in ethylenediamine resulted in black precipitates. XRD patterns of the samples are shown in Fig. 1. All the reflections can be indexed to the hexagonal γ-NiSb phase with the parameters $a = 3.9396$ Å and $c = 5.3367$ Å, which are very close to the reported data (6). The average crystalline size of NiSb estimated by the Scherrer equation based on the XRD linewidths is about 15 nm. TEM images for the samples are shown in Fig. 2a. The products are spherical grains with diameters of about 18 nm; the electron
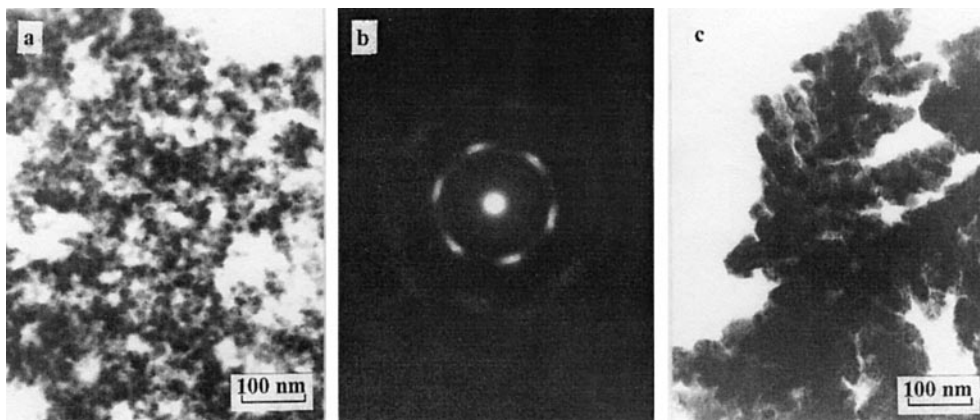

FIG. 2. (a) TEM image for NiSb nanocrystals prepared in ethylenediamine (en) at 140°C. (b) Selected area electron diffraction pattern for the products prepared in ethylenediamine (en) at 140°C. (c) TEM images for dendritic NiSb prepared in diethylamine at 140°C.

diffraction pattern (Fig. 2b) gave diffraction rings indexed to hexagonal NiSb.

The product purity and elemental composition were detected by XPS (Fig. 3). On the XPS spectra of the sample, the two strong peaks at 855.85 and 539.95 eV correspond to Ni 2p and Sb 3d binding energy. No obvious peaks for nickel oxide or antimony oxide are observed. The quantification of peaks gives the ratio of Ni to Sb of 1.08:1, which is almost consistent with the formula of NiSb. This result is also in agreement with the quantitative composition analysis via the energy-dispersive X-ray (EDX) analysis. The ratio of Ni to Sb is 1.06:1 from the EDX analysis.

The IR spectrum of the products did not show any characteristic peaks of ethylenediamine, indicating that the ethylenediamine was at most weakly bonded to the surface and readily removed by washing with ethanol.

The optimum condition, used for synthesizing nanocrystalline NiSb, is in the range of 140–160°C for 24 h. If the temperature is lower than 120°C or the time is less than 12 h, the formation of the nickel antimonide is incomplete or even cannot be initiated. However, if the temperature is higher or the reaction time is longer than the optimum conditions, the size of the as-prepared particles would become larger.

The reaction was deeply influenced by the coordinating ability of the solvents. In our system, ethylenediamine has strong coordinating ability similar to liquid ammonia (17) and n-butylamine (18). When we substituted ethylenediamine with benzene, heptane, and CCl$_4$, respectively, we found that in benzene, heptane, and CCl$_4$, no nickel antimonide can be obtained under similar conditions. Considering the difference in the coordinating ability of ethylenediamine from that of benzene, heptane, or CCl$_4$, we proposed a possible formation mechanism as follows:
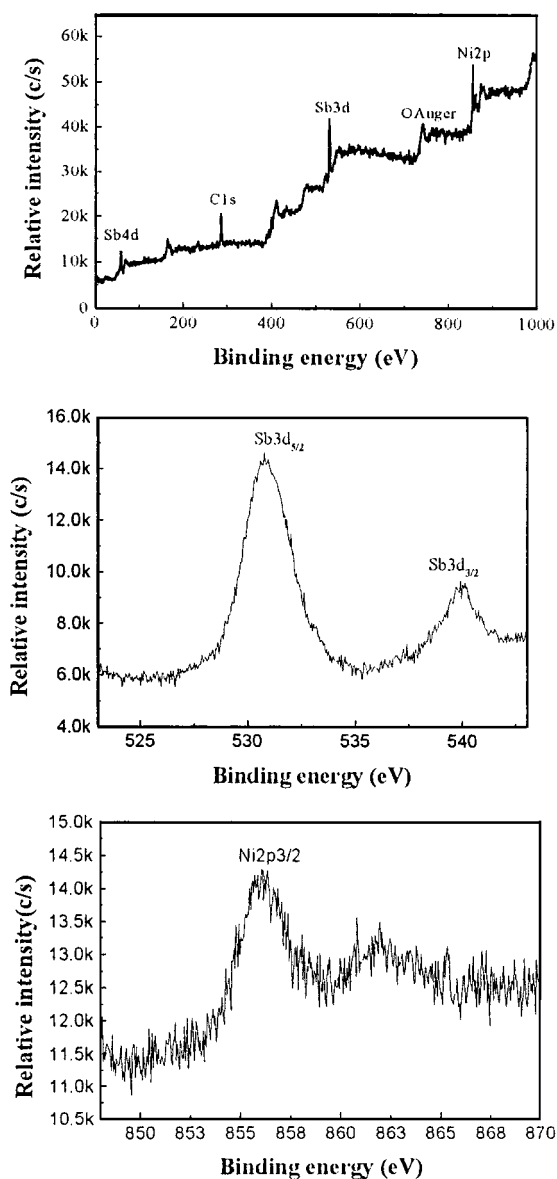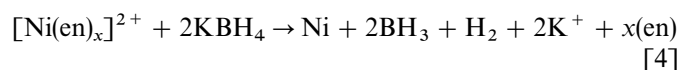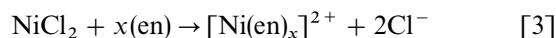
$$NiCl_2 + x(en) \rightarrow [Ni(en)_x]^{2+} + 2Cl^- \qquad [3]$$

$$[Ni(en)_x]^{2+} + 2KBH_4 \rightarrow Ni + 2BH_3 + H_2 + 2K^+ + x(en) \qquad [4]$$

$$Ni + Sb \rightarrow NiSb. \qquad [5]$$

The reaction mechanism can also be rationalized and the intermediate product is confirmed as nickel atom by the following experiments: if NiCl$_2$, Sb, KBH$_4$, and ethylenediamine were added together into a flask, mixed under ultrasonic treatment, and then maintained at 140°C for 24 h. We found that the product was not NiSb, but the mixture of metallic nickel and antimony powder, as confirmed by XRD results. Since, at room temperature, the freshly formed nickel atoms reduced by potassium borohydride under ultrasonic treatment cannot react with antimony, while gathering, they thus remained in the product. However, when the temperature is not lower than 140°C, the newly formed nickel atoms reduced by potassium borohydride are active enough to combine with elemental antimony immediately to form the final product of NiSb.

On the other hand, the morphology of the products was also influenced deeply by the solvents. Unexpectedly, we yielded a dendritic crystal of NiSb in diethylamine, which is shown in Fig. 2c and 2d. The dendritic structure is a fractal object, which had been proved by Nittmannm and Stanley several years ago (19).

Figures 4 and 5 show the UV/vis absorption spectrum and PL spectrum at room temperature of NiSb nanocrystals, respectively. The absorption spectrum was taken of a NiSb dispersion in water and showed an excitonic peak at about 385 nm, a significant blue shift from the bulk band
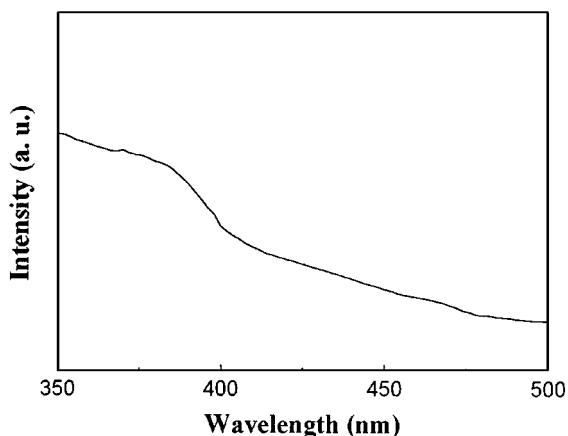

FIG. 3.   XPS analyses of as-prepared nanocrystalline NiSb.

FIG. 4. Absorption spectrum of as-prepared nanocrystalline NiSb.

gap of about 1.53 eV (810 nm). The PL (excitation at 360 nm) was taken in reflection geometry and showed an emission band at 400 nm.

4. CONCLUSION

In summary, pure-phase binary antimonide was first reported to be obtained through a solution route. The nanocrystalline NiSb was successfully synthesized via a novel solvothermal reaction of $NiCl_2$ with antimony and KBH_4 in ethylenediamine at a temperature of 140°C for 24 h. XRD and TEM examination showed that the products were well-crystallized hexagonal NiSb with an average size of 15 nm. We first obtained pure-phase binary antimonides through
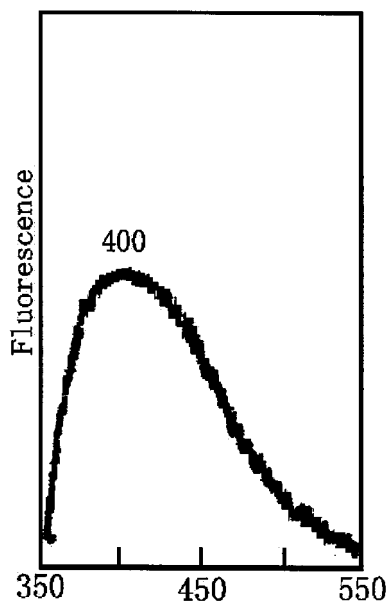

FIG. 5. Photoluminescence (PL) spectrum of as-prepared nanocrystalline NiSb.

a solution route. The reaction proceeds through a metallic nickel intermediate, and thus a coordination–reduction mechanism is proposed. It is proved that the solvents played an important role in this route, and a dendritic crystal was obtained in diethylamine. By choosing a suitable system, it is reasonable to expect that this safe, very mild route can be extended to obtain other metal antimonides.

REFERENCES

1. B. G. Streetman, "Solid State Electronic Devices," 3rd ed. Prentice Hall: Englewood Cliffs, NJ, 1990.
2. (a) A. C. Jones, *Chem. Soc. Rev.* 101 (1997); (b) T. J. Cumberbatch and A. Putuis, *Mater. Res. Soc. Symp. Proc* **164,** 129 (1990); (c) E. K. Bryne, L. Parkanyi, and K. H. Theopld, *Science* **241,** 332 (1988); (d) D. Gammon, E. S. Snow, B. V. Shanabrook, D. S. Kater, and D. Parks, *Science* **273,** 87 (1996).
3. J. C. Bailer, H. J. Emelius, R. Nyholm, and A. F. Trotman-Dickenson, "Comprehensive in Organic Chemistry," Vol. 2. Pergamon Press, Oxford, 1973.
4. J. Coetzer and V. I. Louw, Programme 3 patent holdings, PCT Int. Appl. WO94 23, 467 (Cl. H01M10/39) 13 Oct. 1994; ZA Appl. 93/2406, 02 Apr. 1993.
5. (a) N. Shibata, *Sci. Rept. Tohoku Univ.* **29,** 697 (1941); (b) A. Osawa and N. Shibata, *Met. Abstr.* **8,** 56 (1941); (c) L. A. Panteleimonov, A. Y. Khanna, I. G. Solokova, and T. I. Fedoseeva, *Vestn. Mosk. Univ. Ser. II; Khim.* **19,** 69 (1964).
6. Joint Committee on Powder Diffraction Standards (JCPDS), File No. 41-1439 NiSb.
7. R. Leubolt, H. Isper, and K. L. Komarek, *Z. Metallkd.* **77,** 284 (1986).
8. (a) M. A. Olshavsky, A. N. Goldstein, and A. P. Alivisatos, *J. Am. Chem. Soc.* **112,** 9438 (1990); (b) R. L. Wells, C. G. Pitt, A. T. Mephail, A. P. Purdy, S. Shafieezad, and R. B. Hallock, *Mater. Res. Soc. Symp. Proc.* **131,** 45 (1989).
9. (a) T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, *Science* **270,** 1791 (1995); (b) T. J. Trentler, S. C. Goel, K. M. Hickman, A. M. Viano, M. Chiang, A. M. Beatty, P. C. Gibbons, and W. E. Buhro, *J. Am. Chem. Soc.* **119,** 2172 (1997).
10. (a) E. K. Byrne, T. Dougals, and K. H. Theopold, *Mater. Res. Soc. Symp. Proc.* **131,** 59 (1989); (b) T. Dougals and K. H. Theopold, *Inorg. Chem.* **30,** 594 (1991).
11. R. E. Treece, G. S. Macala, L. Rao, D. Franke, H. Eckert, and R. B. Kaner, *Inorg. Chem.* **32,** 2745 (1993).
12. J. Gopalakrishnan, S. Pandey, and K. K. Rangan, *Chem. Mater.* **9,** 2113 (1997).
13. H. Bönnemann, W. Brijous, and T. Joussen, *Angew. Chem. Int. Ed. Engl.* **29,** 273 (1990).
14. W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, and Y. Qian. *J. Am. Chem. Soc.* **121,** 4602 (1999).
15. P. Yan, Y. Xie, W. Wang, F. Liu, and Y. Qian, *J. Mater. Chem.* **9,** 1831 (1999).
16. Y. Xie, P. Yan, J. Lu, W. Wang, and Y. Qian, *Chem. Mater.* **11,** 2619 (1999).
17. M. R. C. Symons, *Chem. Soc. Rev.* **5,** 337 (1976).
18. V. Dusastre, B. Omer, I. P. Parkin, and G. A. Shaw. *J. Chem. Soc. Dalton Trans.* 3505, (1997).
19. J. Nittmann and H. E. Stanley, *Nature* **321,** 663 (1986).