Synthesis and Phase Transformation of IB-VIA Nonstoichiometric Nanocrystalline Tellurides by a Hydrothermal-Reduction Process

Jian Yang,*,† Shu-Hong Yu,*,†,1 Zhao-Hui Han*,† YiTai Qian,*,†,1 and Yu-Heng Zhang*

*Department of Chemistry and †Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

A convenient route to IB-VIA nonstoichiometric metal telluride nanocrystallites by a novel hydrothermal reaction of metal salts with tellurium in the presence of $N_2H_4 \cdot H_2O$ was established. The effects of molar ratio, temperature, and time on hydrothermal reactions and nonstoichiometric phases in the products have been investigated. Many interesting phases such as $Cu_{2.86}Te_2$, Cu_7Te_5, $Cu_{2-x}Te$, and Ag_7Te_4 were observed in the products at lower temperature. © 1999 Academic Press

IB-VIA compounds are extensively taken as superionic conductors and semiconductors (1–3) due to their mixed conduction, i.e., partly electronic conduction and partly ionic conduction. Furthermore, there are many interesting nonstoichiometric phases existing in the IB-VIA systems which are well suited for an investigation of the nonstoichiometric effect on their properties. Their relations on structure, phase transition, and homogeneity ranges are also the focus in the research. Therefore, IB-VIA compounds are attracting considerable attention (4–6).

Conventionally, metal tellurides are synthesized by solid–solid reactions including direct element reactions and solid–solid metathesis at elevated temperature, typically 600–900°C, in evacuated ampoules (7–9) or by the reactions of aqueous metal salts solutions with toxic and malodorous H_2E gas (10). In the past years, some novel techniques have been used to prepare them. For example, Hanus *et al.* obtained copper telluride with continuous wave Ar$^+$ laser beam assistance (3). Ohtani *et al.* reported a new pathway to them from the mixture of the elements by mechanical alloying using a high-energy ball mill (11). Recently, Parkin *et al.* (12, 13) reported a low-energy method for the synthesis of metal chalcogenides by element reactions in liquid ammonia at room temperature. However, the as-prepared powders were found to be the mixture of three phases of $Cu_{2.74}Te$, CuTe, and $Cu_{2-x}Te$ and two phases of Ag_2Te

and Ag_7Te_4. Later, Parkin *et al.* (14) improved the safety of reactions by using *n*-butylamine as solvent instead of liquid ammonia. The products were regarded as the predominant $Cu_{0.64}Te_{0.36}$ with a trace of Cu_4Te_3. After heating at 250–300°C, they transformed to the mixture of $Cu_{2-x}Te$ (Rickardite) and $Cu_{2-x}Te$ (Wessite). Our group has developed a new milder one-step route to metal chalcogenides such as Cd*E*, Pb*E*, and Bi_2E_3 (*E* = S, Se, Te) by the reactions of metal oxalate with chalcogens in organic solvents (15, 16).

In this paper, a convenient pathway to IB-VIA nonstoichiometric telluride nanocrystallites by a novel hydrothermal-reduction reaction was established. The influence of molar ratio, temperature, and time on hydrothermal reactions and nonstoichiometric phases in the products has been studied. Some interesting nonstoichiometric phases such as $Cu_{2.86}Te_2$, Cu_7Te_5, $Cu_{2-x}Te$, and Ag_7Te_4 were observed in the products at low temperature.

In a typical procedure, different molar ratios of analytical grade metal salts such as $CuCl_2$, $AgNO_3$ to tellurium were added into a Teflon-lined stainless autoclave which was filled with aqueous ammonia (25%, v/v) as solvent up to 80% of the capacity (50 ml) in the presence of hydrazine hydrate (85%, v/v). The autoclave was maintained in the temperature range of 160–200°C for 8–24 h and then cooled to room temperature naturally. The precipitates were filtered and washed with distilled H_2O several times and finally dried in vacuum at 50°C for 2 h. The powders were collected for characterization.

X-Ray powder diffraction patterns (XRD) were obtained on a Rigaku D/Max-γA X-ray diffractometer equipped with graphite monochromatized Cu*K*α radiation (λ = 0.154178 nm), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 10° to 60°. TEM images were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. X-Ray photoelectron spectra (XPS) were recorded on a VEGSCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg*K*α radiation as the excitation source.

[1] To whom correspondence should be addressed. Fax: + 86 0551 3631760. E-mail: shyu@ustc.edu.cn.

TABLE 1
Experimental Conditions and Results of the Reaction of $CuCl_2$ with Te

Molar ratio M to Te	Temperature (°C)	Reaction time (h)	Products
2:1	160	8	$Cu_{2-x}Te$
1.25:1	160	8	$Cu_{2.86}Te_2$, $Cu_{2-x}Te$
1:1	160	8	$Cu_{2.86}Te_2$, Cu_7Te_5,[a] $CuTe$,[a] Te[a]
1:1	200	12	$Cu_{2.86}Te_2$, Te[a]

[a] The minor phase in the product.

All the products were characterized by XRD. The experimental conditions and the results are summarized in Tables 1 and 2.

The reaction of $CuCl_2$ with Te in the presence of $N_2H_4 \cdot H_2O$ produced several interesting phases such as $Cu_{2-x}Te$(wessite), $CuTe$(vulcanite), Cu_7Te_5(rickardite), and $Cu_{2.86}Te_2$. After $CuCl_2$ and Te with their molar ratio equal to 2:1 reacted at 160°C for 8 h, the pure hexagonal phase $Cu_{2-x}Te$ with its average size of 10 nm was obtained as shown in Fig. 1a. There are no obvious differences with the molar ratio decreasing from 2:1 to 1.5:1, if other conditions were unchanged. However, when the molar ratio reduced to 1.25:1, the orthorhombic phase $Cu_{2.86}Te_2$ coexisted with the $Cu_{2-x}Te$ phase in the products as indicated in Fig. 1b. If the molar ratio kept decreasing to 1:1, the products could be indexed as the predominant $Cu_{2.86}Te_2$ phase together with a small amount of $CuTe$, Cu_7Te_5, and Te phases as shown in Fig. 1c. By prolonging the reaction time and/or increasing the reaction temperature, the content of Te and Cu_7Te_5 in the products decreased, while the content of CuTe in the product increased. This indicates that prolonging the reaction time and/or increasing the reaction temperature is favorable for the formation of CuTe. It is believed that the diversity of the product was caused by the nature of the reaction. In this route, metal ions can be reduced by hydrazine hydrate to elemental metal at room temperature; therefore, they will not be very uniformly dispersed in the solution. We believe that this uneven dispersion of the

TABLE 2
Experimental Conditions and Results of the Reaction of $AgNO_3$ with Te

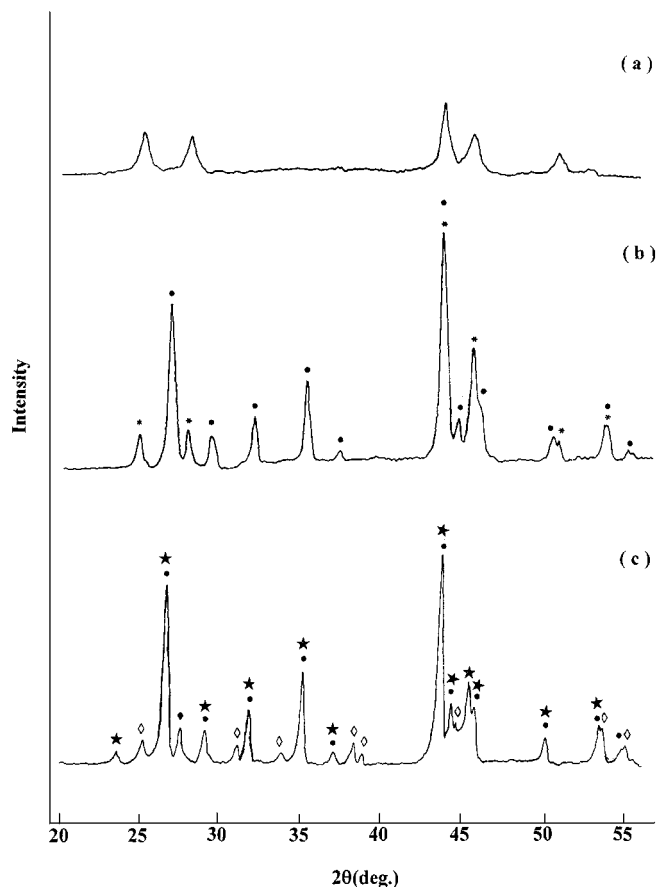| Molar ratio M to Te	Temperature (°C)	Reaction time (h)	Products
2:1	180	12	Ag_2Te, Ag
1.5:1	180	12	Ag_2Te, Ag,[a] Te[a]
1:1	180	12	Ag_2Te, Ag_7Te_4, Te
1:1	200	24	Ag_7Te_4

[a] Trace in the product.

FIG. 1. The XRD patterns of copper tellurides nanocrystallites produced at 160°C for 8 h: (a) Cu:Te = 2:1 (molar ratio), pure $Cu_{2-x}Te$ phase; (b) Cu:Te = 1.25:1, $Cu_{2-x}Te$ (∗), $Cu_{2.86}Te_2$ (●); (c) Cu:Te = 1:1, $Cu_{2.86}Te_2$ (●), CuTe (◇), Cu_7Te_5 (★), Te (◆).

reactants in the solution will result in the formation of different nonstoichiometric phases.

A similar situation also happened in the formation of silver tellurides. The experimental conditions and the results were summarized in Table 2. For instance, if $AgNO_3$ and Te with their molar ratio equal to 2:1 reacted at 180°C for 12 h, the product can be characterized as the monoclinic Ag_2Te phase and Ag according to the XRD patterns. When the molar ratio decreased from 2:1 to 1.5:1, the product is mainly Ag_2Te with a trace of Ag and Te as shown in Fig. 2a. If the reaction time is shortened, the content of Ag and Te in the product will rise, which implies that the reaction was not completed. On the contrary, increasing the time also did not improve the reaction. As the molar ratio kept reducing to 1:1, no Ag phase was detected in the powders, whereas the content of Ag_7Te_4 phase in the powders increased. If the reaction was kept at 200°C for 24 h, the pure monoclinic phase Ag_7Te_4 with its average size of 20 nm was obtained as shown in Fig. 2b.
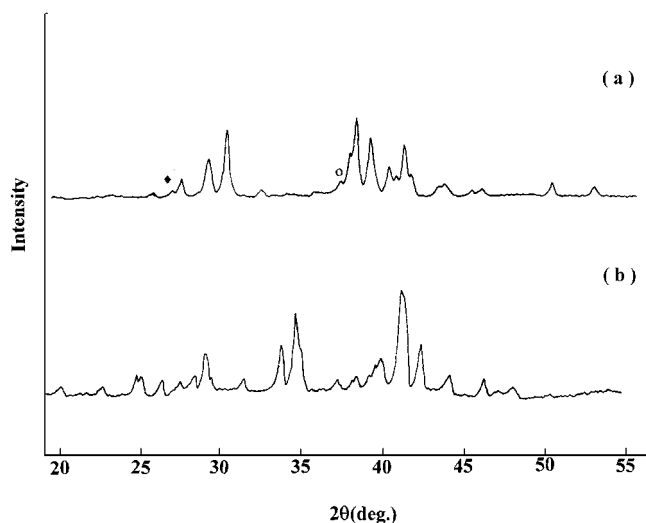
FIG. 2. The XRD patterns of silver tellurides produced at different conditions: (a) Ag : Te = 1.5 : 1 (molar ratio), prepared at 180°C for 12 h, Ag_2Te (undoted), Ag (○), Te (◆); (b) Ag : Te = 1 : 1, prepared at 200°C for 24 h, Ag_7Te_4.

A TEM image of $Cu_{2-x}Te$ powders synthesized at 160°C for 8 h (Fig. 3) indicates that products are composed of uniform spherical particles with sizes in the range of 5–15 nm, which is consistent with that determined by the XRD linewidth technique. XPS for $Cu_{2-x}Te$ reveals the binding energy value of Cu2p is 932.75 eV. The binding energy value of Te3$d_{5/2}$ is 572.50 eV and the kinetics energy value of the Te MNN Auger peak is 491.85 eV, which

FIG. 3. The TEM image of the pure hexagonal phase $Cu_{2-x}Te$ nanocrystallites.

demonstrated the formation of telluride (17). In as-prepared Ag_7Te_4, the binding energy peak of Ag3$d_{3/2}$ is at 367.90 eV and that of Te3$d_{5/2}$ is at 572.20 eV. But in these products, the binding energy peak observed at 575.80–575.90 eV is correspondent with the formation of TeO_2, which is believed to be from the surface oxidation of nanoparticles (18).

In summary, a novel route to IB-VIA nanocrystalline metal tellurides by a new hydrothermal-reduction reaction between metal salts and tellurium in the presence of $N_2H_4 \cdot H_2O$ was developed. The effects of the molar ratio, temperature, and time on nonstoichiometric phases in the products have been investigated. Some interesting nonstoichiometic phases such as $Cu_{2.86}Te_2$, Cu_7Te_5, $Cu_{2-x}Te$, and Ag_7Te_4 were observed in the products at lower temperature. The present method is expected to prepare other important transition metal nonstoichiometric chalcogenides.

REFERENCES

1. A. F. Wells, "Structural Inorganic Chemistry," 5th ed. Clarendon Press, Oxford, 1984.
2. S. Chandra, "Superionic Solid Principles and Applications." North-Holland, Amsterdam, 1982.
3. F. Hanus and M. Wautelet, *J. Appl. Phys.* **68,** 3307 (1990).
4. N. Vouroutzis and C. Manolikas, *Phys. Status Solidi A* **115,** 399 (1989).
5. S. N. Mostafa, S. R. Selim, and S. A. Soliman, *Electrochim. Acta* **38,** 1699 (1993).
6. N. Vouroutzis and C. Manolikas, *Solid State Commun.* **85,** 125 (1993).
7. R. Blachnik, M. Lasocka, and U. Walbrecht, *J. Solid State Chem.* **48,** 431 (1983).
8. R. A. Yakshibaev, N. N. Mukhamadeeva, and R. F. Almukhametov, *Phys. Status Solidi A* **108,** 135 (1988).
9. C. Kaito, Y. Saito, and K. Fujita, *J. Cryst. Growth* **94,** 967 (1989).
10. C. J. Warren, R. C. Haushalter, and B. Bocarsly, *J. Alloys Compd.* **229,** 175 (1995).
11. T. Ohtani, M. Motoki, K. Loh, and K. Ohshima, *Mater. Res. Bull.* **30,** 1495 (1995).
12. G. Henshaw, I. P. Parkin, and G. Shaw, *J. Chem. Soc., Chem Commun.* 1095 (1996).
13. G. Henshaw, I. P. Parkin, and G. Shaw, *J. Chem. Soc. Dalton Trans.* **2,** 231 (1997).
14. V. Dusastre, B. Omar, I. P. Parkin, and G. A. Shaw, *J. Chem. Soc. Dalton. Trans.* **19,** 3505 (1997).
15. S. H. Yu, Y. S. Wu, J. Yang, Z. H. Han, Y. Xie, Y. T. Qian, and X. M. Liu, *Chem. Mater.* **10,** 2309 (1998).
16. S. H. Yu, J. Yang, Y. S. Wu, Z. H. Han, Jun Lu, Y. Xie, and Y. T. Qian, *J. Mater. Chem.* **8,** 1949 (1998).
17. Perkin-Elmer Corporation, PHI 5300 Instrument Manual.
18. C. D. Wagner, *in* "Practical Surface Analysis" (D. Briggs and P. Seah, Eds.), 2nd ed., Vol. 1, Auger and X-ray Photoelectron Spectroscopy" Wiley, Chilchester, 1990.