A New Solvothermal-Reduction Pathway to Nanocrystalline MTe (M = Zn, Pb)

Jian Yang,[†,††] Shu-Hong Yu,[#†,††] Xue-Liang Yang,[†††] and Yi-Tai Qian[#†,††]
[†]*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
[††]*Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
[†††]*Department of Physics Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*

(Received May 10, 1999; CL-990368)

A novel solvothermal-reduction pathway (SRP) to nanocrystalline metal tellurides (MTe, M= Zn, Pb) has been established by the reaction of metal salts with tellurium in various solvents in the presence of hydrazine hydrate($N_2H_4 \cdot H_2O$) as a reducing agent. Nanocrystallites with different morphologies such as cube particles and similar-rectangular flakes were obtained under mild conditions. The effects of solvents and temperature on the reactions were investigated.

Due to their important physical, chemical properties,[1-6] and the extensive applications in many fields such as semiconductor, photovoltaic device, solar cell, and optical communication,[7] IVA-VIA and IIB-VIA tellurides nanocrystallites have attracted much attention.[8-10]

Usually metal tellurides are prepared either by solid state metathesis or direct elements reactions at the elevated temperature, typically 500-600 ℃, in evacuated tubes,[11,12] or by the reaction of aqueous metal salts solution with highly toxic and malodorous gaseous H_2Te.[13] In the past years, organicmetallic precursors also have been used to synthesize tellurides ultrafine powders or films by the technique such as CVD, MBE, and VPE.[14-16] However, organicmetallic compounds are expensive, toxic, and difficult to synthesize. Recently, Yu *et al.* [17-19] proposed a new one-step route to metal chalcogenides by the reactions of metal oxalates with chalcogens in organic solvents. Parkin et al.[20-22] developed a low-energy method by conducting element reactions in liquid ammonia at room temperature to produce crystalline metal chalcogenides. However, the reactions in liquid ammonia have been known to be explosive and no PbTe have been obtained in liquid ammonia unless heated in vacuum at 250 ℃. Although later they improved the safety of the reactions by using n-butylamine as solvent instead of liquid ammonia, the most important IIB-VIA tellurides can not be synthesized in this way.[23] As a mild chemical preparation, solvothermal synthesis has been widely used for many compounds.[24,25]

In this communication, a novel solvothermal-reduction process was reported to prepare nanocrystalline metal tellurides. Nanocrystallites with different morphologies such as cube and similar-rectangular flake were obtained under mild conditions. The effects of solvents and temperature on the reactions were investigated with emphasis on PbTe. Meanwhile, the reaction processes in ammonia solution were proposed. The reaction can be expressed as eqn(1):

$$M^{2+} + \mathrm{Te} + \mathrm{N_2H_4{\bullet}H_2O} \longrightarrow \mathrm{MTe} \quad (\mathrm{M = Zn, Pb}) \qquad (1)$$

In a typical procedure, different molar ratios of analytical grade metal salts such as $ZnCl_2$, PbF_2 to tellurium were added into a Teflon-lined stainless autoclave. Then it was filled with various solvents up to 80% of the capacity (40 ml) in the presence of hydrazine hydrate (3-4 drops, 85%, v/v). The autoclave was maintained in temperature range of 160-180 ℃ for 4.5-24 h, then cooled to room temperature naturally. The precipitates were filtered, washed with distilled H_2O several times and dried in vacuum at 70℃ for 2 h. At last the powders were collected up to characterize by X-Ray powder diffraction (XRD),[27] transmission electron microscopy (TEM),[28] selected area electron diffraction (SAED),[28] X-Ray photoelectron spectroscopy (XPS).[29]

Table 1. The experimental conditions and the results

Solvents	Molar ratio of M^{2+} to Te	Temperature /℃	Reaction time /h	Product Phase
Ammonia solution	3 : 1	180	24	ZnTe
Ammonia solution	1 : 1	160	4.5	β-PbTe (Altaite)
Ethylenediamine	1 : 1	180	12	

The experimental conditions and the corresponding results were summarized in Table 1. ZnTe powders synthesized at 180 ℃ for 24 h and PbTe powders synthesized at 160 ℃ for 4.5 h in ammonia solution can be indexed as pure phases (JCPDS Card File: ZnTe: No. 15-746; PbTe: No. 38-1435) according to their XRD patterns. Their lattice constants (ZnTe: a=6.090A, PbTe: a=6.463A) calculated from the XRD patterns were very close to the reported data in literature (JCPDS Card File: ZnTe: a=6.103A, PbTe: a=6.459A). Standard deviations of the observed lattice constants for ZnTe and PbTe are 0.2130% and 0.06193%, respectively. The average sizes of ZnTe and PbTe powders obtained from the scherrer formula based on the XRD linewidth were 50 and 30 nm, respectively.

When solvents were changed from glycerol to 1,6-diaminohexane, last to ethylenediamine under the same temperature, the concentration of PbTe in the products increased with the alkalescence of solvents increasing. It indicates that alkalescence of solvents is favorable for the formation of PbTe. This can be attributed to that alkalescence of solvents promote the reducing ability of $N_2H_4 \cdot H_2O$. Meanwhile increasing coordination ability of solvents avoids of the formation of hydroxides. So the solvents with stronger alkalescence and stronger coordination ability are of benefit to the reaction.

TEM image indicates that ZnTe powders consist of agglomerated particles with irregular shape, while PbTe powders prepared in ammonia solution (Figure 1a) are composed of uniform cubic-shaped particles with the average size of 40nm, which is consistent with the results from XRD patterns. However, PbTe powders prepared in ethylenediamine (Figure 1b) consist of similar-rectangular flakes. SAED pattern (Figure 1c) carried on the same sample shows that these flakes have high crystallitinity. This probably can be believed that the higher reaction temperature and time relative to ammonia solution improved the crystallization.

The XPS spectra of lead telluride showed that Te3d5/2 and Pb4f7/2 binding energies are 571.5 eV and 137.8 eV respectively, which is close to the corresponding values of tellurides in

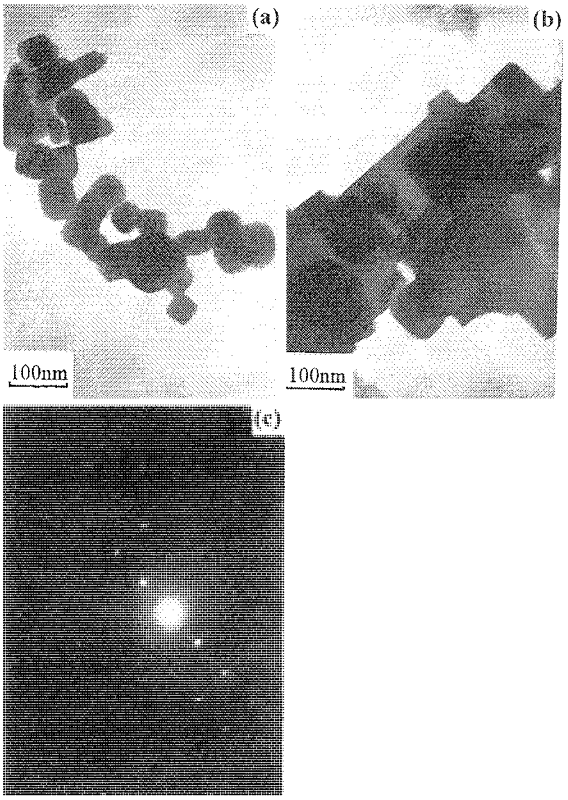

Figure 1. TEM images of PbTe powders under different conditions: (a) 160 ℃, 4.5 h , in ammonia solution; (b) 180 ℃, 12 h, in ethylenediamine; (c) SAED patterns carried on (b).

literature.[26] The molar ratio of Pb:Te according to XPS spectra is 57.5:42.5, which approaches the stoichiometry of PbTe.The as-prepared PbTe powders have been oxidation on the surface due to being exposed in air.[21]

Although Zn^{2+} and $N_2H_4 \cdot H_2O$ were in excess, the corresponding elemental metal was not detected by XRD in ammonia solution. This indicates that Zn^{2+} can not react with hydrazine hydrate, which also was demonstrated by the reaction of metal salts with hydrazine hydrate. So it is believed that the formation of ZnTe is not through direct elements combination but through solution-phase metathesis. This formation process of ZnTe in ammonia solution can be shown as eqn(2):

$$Te^{2-} + Zn^{2+} \longrightarrow ZnTe \qquad (2)$$

However, it was found that the formation process of PbTe seems more complicated due to the stronger oxidizing activity of Pb^{2+}. In the present system, Pb^{2+} would be reduced to element by $N_2H_4 \cdot H_2O$, which was demonstrated by the reaction of $N_2H_4 \cdot H_2O$ and PbF_2. When the reaction of PbF_2 and Te in the presence of $N_2H_4 \cdot H_2O$ was incomplete or PbF_2 was in little more excess of Te, elemental Pb was observed in the products. These results imply that in the formation process of PbTe through two competitive reaction routes as shown eqn (3) and (4), eqn (3) play a important roles in the production of PbTe.

$$Pb + Te \longrightarrow PbTe \qquad (3)$$

$$Pb^{2+} + Te^{2-} \longrightarrow PbTe \qquad (4)$$

Further study for its mechanism was in progress.

In summary, a convenient solvothermal-reduction route to metal tellurides nanocrystalline by the reaction of metal ion with tellurium in various solvents in the presence of reducing agents was successfully established. Nanocrystallites with different morphologies such as cube and similar-rectangular flake were obtained under mild conditions. The solvents with stronger alkalescence and stronger coordination ability are beneficial to the reaction. Meanwhile, the reaction processes in ammonia solution were proposed. This convenient technique has been successfully extended to synthesize other metal chalcogenides such as CdTe, HgTe, $Cu_{2-x}Te$, Ag_2Te.

We gratefully acknowledged the Chinese National Foundation of Natural Science Research, Anhui provincial Foundation of Natural Science, and the National Doctoral and Postdoctoral Foundation for their financial support.

References and Notes

\# Present address: Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China.
1 S. Mann, *Nature*, **322**, 119 (1988).
2 C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, **119**, 8706 (1993).
3 P. V. Braum, P. Osenar, and S. I. Stuopp, *Nature*, **380**, 325 (1996).
4 L. E. Brus, *Appl. Phys. A*, **53**, 465 (1991).
5 M. G. Bawendi, M. L. Steigerwald, and L. E. Brus, *Annu. Rev. Phys. Chem.*, **41**, 477 (1990).
6 Y. Wang and N. Herron, *J. Phys. Chem.*, **95**, 525 (1991).
7 A. J. Strausse, *Phys. Rev. Lett.*, **16**, 1193 (1966).
8 Y. A. Ugai, A. M. Sanoylov, and M. K. Sharov, *Thin Solid Films*, **336**, 196 (1998).
9 P. Ganitzer, A. Homer, M. Lucyshyn, B. Jamning, J. Oswald, D. K. Maude, and J. C. Portal, *Physica B*, **258**, 600 (1998).
10 L. V. Belyakov, I. B. Zakharova, T. I. Zubkova, S. F. Musikhin, and S. A. Rykov, *Semiconductors*, **31**, 76 (1997).
11 I. P. Parkin and A. T. Rowley, *Polyhydron.*, **12**, 2961 (1993); J. C. Fitzmaurice and I. P. Parkin, *Main Group Metal Chem.*, **17**, 7 (1994).
12 D. Arivuoli, F. D. Gnanam, and P. Ramasamy, *J. Mater. Sci. Lett.*, **7**, 711 (1988); C. Kaito, Y. Saito, and K. Fujita, *J. Cryst. Growth.*, **94**, 967 (1989).
13 L. C. Roof and J. W. Kolis, *Chem. Rev.*, **93**, 1037 (1993).
14 M. L. Steigerwald and C. R. Sprinkle, *J. Am. Chem. Soc.*, **109**, 7200 (1987).
15 M. Danek, S. Datnaik, K. F. Jensen, D. C. Gordon, D. W. Brown, and R. U. Kirss, *Chem. Mater.*, **5**, 1321 (1993).
16 A. C. Jones, *Chem. Soc. Rev.*, **1997**, 101.
17 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).
18 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).
19 S. H. Yu, Z. H. Han, J. Yang, R. Y. Yang, Y. Xie, and Y. T. Qian, *Chem. Lett.*, **1998**, 1111.
20 V. Dusastre, B. Omar, I. P. Parkin, and G. A. Shaw, *J. Chem. Soc., Dalton. Trans.*, **19**, 3505 (1997).
21 G. Henshaw, I. P. Parkin, and G. Shaw, *J. Mater. Sci. Lett.*, **15**, 1740 (1996).
22 G. Henshaw, I. P. Parkin, and G. Shaw, *Chem. Commun.*, **1996**, 1095.
23 G. Henshaw, I. P. Parkin, and G. A. Shaw, *J. Chem. Soc., Dalton. Trans.*, **2**, 231 (1997).
24 Y. Xie, Y. T. Qian, W. Z. Wang, S. Y. Zhang, and Y. H. Zhang, *Science*, **272**, 1926 (1996).
25 W. Z. Wang, Y. T. Qian, and P. Yan, *J. Am. Chem. Soc.*, in press.
26 Perkin-Elmer Corporation. PHI 5300 Instrument Manual, U.S.A.
27 X-Ray powders diffraction patterns was obtained on a Japan Rigaku D/Max-γA X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ=1.54178A), employing a scanning rate of $0.02^0 s^{-1}$ in the 2θ range from 10^0 to 60^0.
28 TEM images and selected area electron diffraction (SAED) patterns were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.
29 X-Ray photoelectron spectra (XPS) were recorded on a VEGSCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg-Kα radiation as the excitation source.