Low Temperature Synthesis of Ultrafine SnTe Powder in Ethanol Solvent

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(Received December 27, 1999; CL-991099)

Reaction of a tellurium alkaline ethanol solution and tin(II) tartaric acid complex produced ultrafine SnTe powder with a cubic phase. The XRD pattern indicated that the tellurium alkaline ethanol solution as a tellurium source, made the product crystallize well at 140 °C on reflux. The TEM image showed that the particle size was in the range of 0.25-0.50 µm. The mechanism of the formation of tin(II) telluride was discussed.

SnTe as a IV-VI compound, is a narrow band gap semiconductor of interest for use in infrared detectors.[1–3] It has the sodium chloride structure at high temperatures and makes a transition to a rhombohedral structure as the temperature is lowered, which shows ferroelectric behaviour.[4,5] SnTe is commonly synthesized by the solid state reaction of the elements at 850-900 °C in an evacuated and sealed tube.[6] When the same reaction happens in molten iodide (SnI_2), the temperature can be reduced to 400 °C.[7] Recently, a repeated "cold-pressing" (RP) technique activating the solid state reaction has been reported to give SnTe powders at room temperature.[8] The drawback is that the product quality is not easy to control. New preparation methods have concentrated on OMVPE and MOCVD routes, however organometallic and inorganometallic Sn-Te complexes must be synthesized beforehand as potential single source precursors for SnTe.[9–12] Liquid-phase synthesis appears to be advantageous for low temperature operation. A precipitation of metal chalcogenides has been obtained from aqueous solution of the metal ions by use of H_2E (E = S, Se or Te), which is highly toxic and makes the process relatively dangerous.[13] During the past several years, metal tellurides have been reported to be synthesized in non-aqueous solvents, such as in liquid ammonia or ethylenediamine, which requires careful manipulations.[14–16] Furthermore some products need post-treatment of annealing to be crystalline.

In this study, we report a mild preparation of ultrafine SnTe powder of 0.25-0.50 µm in ethanol solvent. A tellurium alkaline ethanol solution as a tellurium source, makes the product crystallize well at 140 °C on reflux. Tin(II) complex instead of tin(II) salt effectively avoids occurrence of impurities, such as tin hydroxide and oxides.

All reagents were of 99.9% purity from Shanghai Chemistry Co. and were used without further purification. Manipulations and reactions were carried out in air. The alkaline tellurium ethanol solution was prepared as follows: 0.001 mol of elemental Te and 20 g of KOH were added to 150 mL of ethanol solution at 140 °C on reflux. After about half an hour, elemental Te and KOH were dissolved completely and a deep purple solution was obtained. An ethanol solution of tin complex was prepared by 0.002 mol of $SnCl_2 \cdot 2H_2O$ dissolved in 5 mL of ethanol with 3 g of tartaric acid. Then the tin complex was added to hot alkaline tellurium solution through rapid stirring. A gray and black precipitate occurred at once. After being filtered and washed with distilled water, the precipitate was dried in a vacuum box at 50 °C for 4 hours. The obtained powder was identified by XRD. The X-ray powder diffraction (XRD) pattern was recorded on a MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized Cu Kα_1 radiation (λ = 1.54056 Å), employing a sampling width of 0.02°. The surface of the product was detected by X-ray photoelectron spectra (XPS) recorded on an ESCALab MKII instrument with Mg Kα X-ray as the excitation source. The morphology of the particles was observed by a Hitachi H-800 transmission electron microscope (TEM).

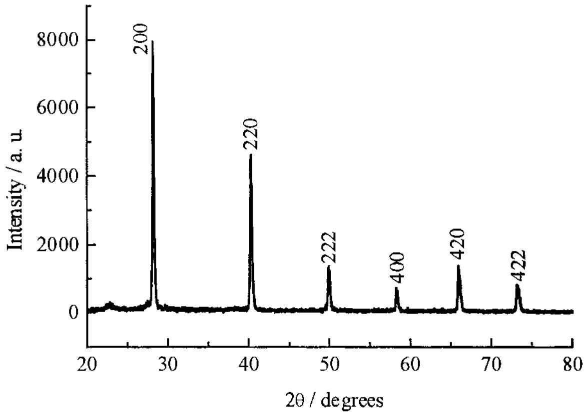

Figure 1. X-Ray powder diffraction (XRD) pattern of the sample:SnTe.

The XRD pattern of the product (Figure 1) shows that cubic SnTe (cell constant a = 0.63 nm) has been obtained, which matched literature pattern for tin(II) telluride.[17] No impurity phase was detected by XRD, nevertheless XPS result indicated that a small amount of tellurium oxide was observed, presumably from surface oxidation. Transmission electron microscopy (TEM) microphotograph (Figure 2) confirms that the product crystallizes well. The particles agglomerated slightly and the sizes of the particles are in the range of 0.25-0.50 µm.

In our route, the reactions take place as follows:

Dissolution of tellurium

$$3\ Te + 6\ KOH \leftrightarrow 2\ K_2Te + K_2TeO_3 + 3\ H_2O \qquad (1)$$
$$K_2Te + x\ Te \leftrightarrow K_2Te_{1+x} \qquad (2)$$

Precipitation reaction

$$K_2Te_{1+x} + Sn(tart) \rightarrow SnTe\downarrow + K_2(tart) + x\ Te \qquad (3)$$

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Figure 2. Transmission electron microscopy (TEM) micrograph of the sample: SnTe.

$SnCl_2 \cdot 2H_2O$ easily hydrolyzes in water and produces a precipitate of Sn(OH)Cl, but it can be dissolved in ethanol. Ethanol can also dissolve KOH.[18] Therefore ethanol is chosen as a solvent for the synthesis of SnTe. On the other hand tin(II) salt in alkaline solution will produce tin oxides. In our experiments, tin(II) complex instead of tin(II) salt effectively avoids occurrence of tin oxides, because tin(II) complex can be stable in alkaline solution. That has been confirmed by the XRD result of the final product.

It has been reported that tellurium is soluble and disproportionates to Te^{2-} and TeO_3^{2-} ions in NaOH or KOH aqueous solutions only at high alkali hydroxide concentrations and at high temperatures.[19,20] In our experiments, elemental Te and KOH are also dissolved easily in ethanol solvent by heat. The phenomena are similar to those reported in aqueous solvent.[19] The tellurium alkaline solution is a deep purple solution containing Te^{2-}, $[TeO_3]^{2-}$ and Te_{1+x}^{2-} ions. It is stable at high temperature with excessive OH^- ions. Simply cooling or dilution of the tellurium alkaline solution will make elemental Te precipitate again (reaction (1)). Therefore the volume of tin complex solution is much smaller than that of the tellurium source in order to avoid much cooling or dilution of the tellurium source. For the half-cell potential of $E°_{Te/Te^{2-}}$ is – 0.92 eV,[18] Te^{2-} has a high reductivity and is easily oxidized to elemental Te by air with decreasing temperature.

The freshly produced tellurium in reaction (3) is active and can dissolve in the excessive alkaline solution at once. The amount of reagent tin(II) chloride is excessive relatively to that of reagent elemental Te. Otherwise excessive Te will precipitate in the product in post-treatment of washing and be difficult to remove. In our experiments, no peak of elemental Te has been observed by XRD and XPS.

The influences of the concentration of KOH, reaction temperature and time on the formation of ultrafine SnTe powder were investigated. In our experiments, the optimum reaction condition was 140 °C on reflux for 40 minutes with 2.4 M of KOH solution. The concentration of KOH and the reaction temperature should be high enough for the formation of SnTe. Too low concentration of KOH and low temperature could not make elemental Te dissolved completely, which made the product contain Te as impurity. Too high concentration of KOH made the post-treatment of the final product difficult. It was observed that with 2.4 M of KOH solution, the tellurium alkaline ethanol solution was stable above 140 °C. For high temperature made the particle size of the final product larger, 140 °C was chosen as reflux temperature. Reaction time contained two parts. One was dissolving time of tellurium, which was longer than 30 minutes to make elemental Te dissolved completely. The other was the reaction time of equation (3) which was a rapid reaction and should be controlled about 10 minutes in our experiments. Long time made particles grow larger.

In summary, ultrafine SnTe powder has been successfully prepared through a reaction between a tellurium alkaline ethanol solution and tin(II) tartaric acid complex at 140 °C on reflux. The ethanol solvent and tin(II) complex effectively avoid occurrence of impurities, such as tin hydroxide and oxides. The product obtained with this technique does not need post-treatment of annealing.

We acknowledge the support of the National Natural Science Foundation of China.

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