

Sonochemical Synthesis of Nanocrystalline Silver Tellurides Ag_2Te and Ag_7Te_4

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In this paper, we report a simple and clean method of producing nanocrystalline silver tellurides in organic solvent systems by high-intensity ultrasonic irradiation at room temperature. Ag_2Te and Ag_7Te_4 are prepared in an ethylenediamine system and an ethanol system, respectively. The products were mainly characterized by X-ray powder diffraction and transmission electron microscopy. The ultrasonic irradiation and the solvents are both important in the formation of products. The possible mechanism of the nanocrystalline Ag_2Te formation in ethylenediamine under high-intensity ultrasonic irradiation is also discussed. © 2001 Academic Press

INTRODUCTION

Recently, there has been growing interest in nonmagnetic compounds such as silver chalcogenides, Ag_2Se and Ag_2Te , due to their large magnetoresistance (MR) effect (1, 2). These materials have outstanding properties such as MR values up to 200% at 40 kOe and room temperature, linear field dependence of MR down to 100 Oe, almost flat temperature dependence of MR at room temperature, and low resistance in the range of milliohm per centimeter (3).

Traditionally, metal tellurides are synthesized by the elemental reaction at elevated temperature, typically 500–600°C, in evacuated tubes (4), or by reaction of aqueous metal–salt solutions with toxic and malodorous gas H_2Te (5). Parkin *et al.* (6) reported a method for the synthesis of metal chalcogenides by a reaction between metal and chalcogen in liquid ammonia at room temperature. However, no single product except the mixture of Ag_2Te with 5–10% Ag_7Te_4 was obtained by this method. Then they reported a new method to synthesize pure Ag_2Te crystals by elemental reaction in *n*-butylamine (7). The solvothermal route also can be used to synthesize silver chalcogenides; however, the dominant product was silver with minor silver telluride

when preparation of pure silver telluride was attempted (8). With increased interest in nanostructured inorganic materials, reducing the reaction temperatures of synthesis has become a research goal for both chemists and materialists. Here we report a new and simple sonochemical synthesis of nanocrystalline silver tellurides (Ag_2Te and Ag_7Te_4) in different organic solvent systems at room temperature.

The use of ultrasound to enhance chemical reaction in liquid–solid heterogeneous systems has become increasingly widespread. In heterogeneous, liquid–solid reactions, ultrasound has been demonstrated to increase the reactivity of metal powders by as much as 100,000-fold (9). A variety of nanosized but often amorphous metals, alloys, and carbides have been produced from metal carbonyls under high-intensity ultrasonic irradiation (10). Recently, sonochemical synthesis has been widely used to prepare selenides. This method can be used to prepare $\text{Cu}(\text{Ag},\text{Pb})\text{Se}$ (11), and ZnSe (12). It also can be combined with electrochemical deposition to prepare CdSe (13) and PbSe (14). However, to our knowledge, this is the first time that silver tellurides have been prepared by ultrasonic irradiation at room temperature.

EXPERIMENTAL SECTION

In a typical experimental procedure, Ag_2Te can be prepared from a stoichiometric mixture of tellurium (0.300 g, 2.34 mmol) and AgNO_3 (0.795 g, 4.68 mmol), all with nominal purity greater than 99.8%. The reagents were loaded into a 100-ml reactor that was then filled with anhydrous ethylenediamine up to 80% of the total volume. The reactor was designed to ensure that the horn tip was immersed into the solution consistently to the same depth (10 mm). The sealed reactor was kept in a circulating water bath to maintain the temperature of the bulk solution at $20 \pm 5^\circ\text{C}$ and was irradiated with a high-intensity ultrasonic probe (Model, 1.5 cm Ti horn, 20 KHz, 100 W/cm²) for 3 h. The precipitate was filtered and washed several times with distilled water and absolute ethanol to remove

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the by-products. The product was dried under vacuum at 60°C for 4 h. In the case of the preparation of Ag_7Te_4 , the ethylenediamine solvent was substituted by ethanol, and the used reagents were a stoichiometric mixture of tellurium (0.205 g, 1.60 mmol) and AgNO_3 (0.476 g, 2.80 mmol).

The phases and the crystallographic structures of the products were determined by X-ray powder diffraction (XRD) using a Japan Rigaku D/max- γ A X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). A scan rate of $0.05^\circ \text{ s}^{-1}$ was applied to record the patterns in the 2θ range of $10\text{--}70^\circ$. The morphology and size of the prepared products were observed in transmission electron microscopy (TEM) images, which were taken on a Hitachi Model H-800, using an accelerating voltage of 200 kV. Elemental analyses were carried out with an ICP emission spectrograph.

RESULTS AND DISCUSSION

The XRD patterns of Ag_2Te and Ag_7Te_4 as prepared are shown in Figs. 1A and 1B, respectively. In each pattern, all peaks are consistent with those of standard samples. The cell constants measured from the pattern in Fig. 1A are $a = 8.18 \text{ \AA}$, $b = 8.94 \text{ \AA}$, $c = 8.07 \text{ \AA}$, and $\beta = 112.8^\circ$, which are consistent with the reported data for monoclinic Ag_2Te (15). In Fig. 1B, the measured cell constants are $a = 13.51 \text{ \AA}$ and $c = 8.48 \text{ \AA}$, which are close to the reported data for hexagonal Ag_7Te_4 (16). Elemental analysis by ICP emission spectra shows the presence of Ag and Te in 2.015:1 and 6.987:4 ratios in Ag_2Te and Ag_7Te_4 products, respectively. The preceding results show that the products prepared in ethylenediamine and ethanol are pure crystalline Ag_2Te and Ag_7Te_4 , respectively. Products prepared by high-intensity ultrasonic irradiation are often in an amorphous form (10, 17), but the products synthesized in our experiments are both crystalline. Ultrasonic waves that are intense enough to produce cavitation can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition. In our process, AgNO_3 can dissolve in ethylenediamine and ethanol but tellurium can not; therefore, the reaction system is a heterogeneous system. It has been known that three different regions are formed during heterogeneous sonochemical process (18): (a) the inner environment (gas phase) of the collapsing bubble, where elevated temperature (several thousands of degrees) and pressure (hundreds of atmospheres) are produced; (b) the interfacial region where the temperature is lower than that in the gas-phase region but still high enough to induce a sonochemical reaction; and (c) the bulk solution, which is at ambient temperatures. Among these three regions, it appears that the current sonochemical reaction occurs within the interfacial region, yielding nanoparticles. This is because silver nitrate and tellurium are certainly involatile under normal conditions, but might well dissociate or produce radicals under the extreme

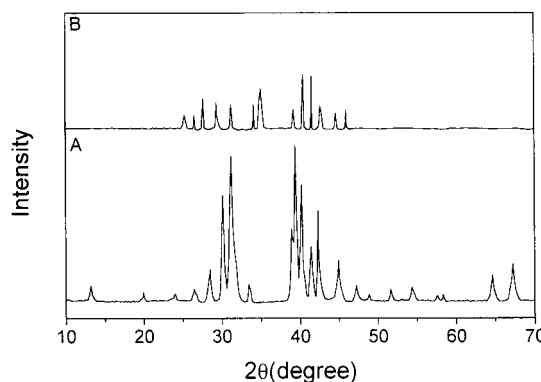


FIG. 1. XRD patterns of (A) Ag_2Te and (B) Ag_7Te_4 nanocrystals.

conditions of sonification. The reaction occurred within the interfacial region where the not very high quenching rate experienced by the product makes it possible to produce crystalline nanoparticles. Certainly, the crystallization of final products is also related to the solvent. Ethylenediamine can provide reaction conditions mild enough to enable molecular-building blocks to participate in subsequent formation of the solid-state phase and greatly enhance crystallization (19). That is why the crystallinity of Ag_2Te prepared in ethylenediamine is better than that of Ag_7Te_4 prepared in ethanol as shown in Fig. 1.

Figures 2A and 2B show the TEM images of Ag_2Te and Ag_7Te_4 , respectively. Both samples show spherical morphology; however, the diameter (about 20 nm) of Ag_2Te prepared in ethylenediamine is much smaller than that (about 50 nm) of Ag_7Te_4 prepared in ethanol. In ethylenediamine the Ag^+ can form a complex $[\text{Ag}(\text{en})_n]^+$ ($k = [\text{Ag}(\text{en})_2]/[\text{Ag}][\text{en}]^2 = 10^{7.7}$), the stability of which effectively reduces the growth of the particles. On the other hand, the viscosity of solvent is also important to the growth of the particles. During the formation of the final product, the competition between particle growth and nucleation is partially controlled by diffusion. For high-viscosity solutions, the rate of diffusion is low and the silver tellurides can form new nuclei before they migrate to the surface of nuclei. The time of nucleation and the length of the growth period of nuclei in different solution systems are not the same, giving particles with different sizes at the end of the growth process. The high viscosity of ethylenediamine (1.54 mPa/s at 25°C) makes the rate of diffusion slower than that of ethanol with low viscosity (1.06 mPa/s at 25°C). Therefore, the product size prepared in ethylenediamine is much smaller than that prepared in ethanol, as shown in Fig. 2. We also found that in the same solvent system the particle size increases with the sonication time. The increase of the particle size with sonication time can be explained in terms of the effect of acoustic cavitation on silver tellurides. The implosive collapse of a cavity on extended solid silver tellu-

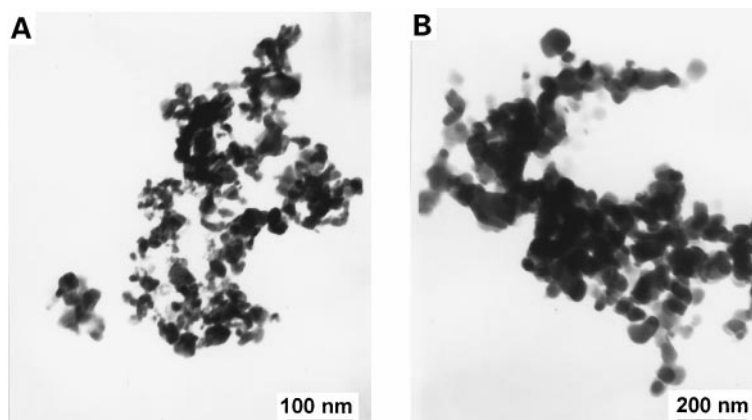


FIG. 2. TEM images of (A) Ag_2Te and (B) Ag_7Te_4 nanocrystals. Note the difference in the size bars.

ride surface in the liquid results in the formation of high-speed microjets of liquids as well as shock waves that drive the solid particles to high velocities, which leads to interparticle collisions. The collisions of the particles at high velocity result in increased local heating and condensation to form larger particles (20). The increase in size of the nanoparticles can also involve crystal growth. When the silver telluride nanoparticles formed, smaller particles had large numbers of dangling bonds, defect sites, or traps (21). During the reaction time, the surface states changed Dangling bonds, defect sites, or traps decreased gradually and particles grew.

In the process of preparing tellurides, both ultrasonic irradiation and solvent play important roles. Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule. In the liquid–solid solution, under ultrasonic irradiation the cavity collapsing near the extended solid surface of tellurium drives high-speed jets of liquid that impinge upon the surface. The impingement of the jet and related shock waves can create a localized erosion (which produces a newly exposed and highly reactive surface), improve mass transport, and cause particle fragmentation (which can substantially increase the surface of tellurium as brittle solids) (22). When the experiments were made at room temperature with low intensity or without ultrasonic irradiation, the XRD measurements show that the reactions did not occur at all even after prolonged periods of time. The high-intensity ultrasonic irradiation is necessarily fully responsible for these reactions. Solvent also plays an important role in the formation of the final products. The experiments show that the final products prepared in ethylenediamine and ethanol are monoclinic Ag_2Te and hexagonal Ag_7Te_4 , respectively. The formation of silver tellurides with different stoichiometries and phases is mainly related to the reducing capability of the solvent system the reaction conducted. Here the possible mechanism of the

formation of Ag_2Te in ethylenediamine under high-intensity ultrasonic irradiation is provided. Ethylenediamine was selected as the solvent due to its special properties, such as strong polarity, strong chelation, and certain solubility. As reported in the literature this organic liquid can generate free radicals upon ultrasonic irradiation (23); it is easy for ethylenediamine as a donor solvent. The formation of Ag_2Te might be through the attack of ethylenediamine on tellurium under high-intensity ultrasonic irradiation. To improve our understanding of the proposed mechanism in the ethylenediamine system, the following experiments were performed. Our experiments show that under high-intensity ultrasonic irradiation, tellurium can form a solution with ethylenediamine that remains stable in an open container for 1 day and then releases tellurium. Moreover, TEM shows that this released tellurium is in the form of nanorods with a diameter of about 25 nm and a length of about 100 nm. Compared with the raw material of tellurium with its microsize, there is a sharp decrease in the size of tellurium. However, the particles with microsize, cannot be significantly decreased in size under high-intensity ultrasonic irradiation in the absence of ethylenediamine, even after several hours of irradiation (24). So the nanosized tellurium might be formed by the slow release from the ethylenediamine solution. The released tellurium reacts with metal cation Ag^+ to form Ag_2Te at room temperature. However, tellurium cannot form a solution with ethanol under high-intensity ultrasonic irradiation even after many hours of irradiation. Further studies about the mechanism of the formation of Ag_7Te_4 in ethanol are underway.

CONCLUSION

In conclusion, nanocrystalline silver tellurides Ag_2Te and Ag_7Te_4 have been successfully prepared in ethylenediamine and ethanol systems, respectively, under high-intensity

ultrasonic irradiation at room temperature. XRD and TEM examinations showed that the products were pure monoclinic Ag₂Te and hexagonal Ag₇Te₄ and that they were well crystallized. This inexpensive and extremely reliable method can be easily controlled and is expected to be applicable to the preparation of other nanosized inorganic compounds. Further studies of the use of ultrasonic irradiation to prepare other tellurides and the mechanism are underway.

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