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A Solvothermal Route to Nanocrystalline Cu_7Te_4 at Low Temperature

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Nanocrystalline Cu_7Te_4 was directly synthesized by the reaction of $CuCl_2 \cdot 2H_2O$ and tellurium in an autoclave with ethylenediamine as solvent at 160°C for 10 h. X-ray powder diffraction patterns, X-ray photoelectron spectra, and transmission electron microscope images show that the products are hexagonal Cu_7Te_4 phase and well crystallized with an average size of about 15 nm. The solvent ethylenediamine played an important role in the synthesis of nanocrystalline Cu_7Te_4. The reaction mechanism was proposed. © 1999 Academic Press

Key Words: **nanocrystalline; Cu_7Te_4; ethylenediamine; solvothermal process.**

1. INTRODUCTION

The tellurides represent a class of compounds that exhibit a wide range of physical and chemical properties (1). In addition to the salt-like compounds, some tellurides show metallic properties while others have strong covalent bonds. In recent years the structures of a large number of tellurium-rich tellurides have been reported whose anionic networks are characterized by homonuclear Te–Te bonds. Tellurides are attractive materials for thermoelectric applications due to their very high thermopower values and ability to yield both p and n type materials by doping (2, 3). The efficiency of these materials also depends on properties like electrical resistivity (σ) and thermal conductivity (K) (4). An improvement of the efficiency for thermoelectric applications of these materials is possible by microstructural control involving reduction of grain size. Since a major part of thermal conductivity is controlled by phonon conduction, introduction of large amounts of grain boundaries leads to scattering of phonons and significant decrease in the conductivity (5, 6). In order to develop more efficient thermoelectric materials it is important to find a method that can provide very fine particles. A major focus of recent work has been the development of different routes to these interesting materials (7).

Transition-metal tellurides can be made in a variety of ways, the most straightforward of which is the combination of the elements at elevated temperatures (8–10). This process requires elevated temperature and inert atmosphere protection and is of relatively long duration. It is difficult to get nanoscale materials by using this traditional solid state reaction. A low-energy approach is the precipitation of metal tellurides from aqueous solution of the metal cation by use of H_2Te (11). This method includes the use of a very toxic reagent and H_2Te is very unstable at room temperature, resulting in impurity of the product. Molecular precursor methods have been developed by a number of groups for bulk materials or coatings (12, 13). Recently, Henshaw *et al.*, reported that some metal tellurides could be obtained through the reaction of tellurium with elemental metals in liquid ammonia at room temperature in a pressure vessel, but they only got the mixtures of $Cu_{2.74}Te_2$, CuTe, and $Cu_{2-x}Te$ by the reaction of tellurioum with copper (14). Sridhar and Chattopsdhyay synthesized the hexagonal Cu_2Te by mechanical alloying from elemental powders (15). Ohtani and co-workers also obtained the $Cu_{2-x}Te$ and Cu_3Te_2 by mechanical alloying from elemental powders (16).

Materials chemists have always been looking for considerably milder conditions for materials preparation. The solvothermal pathway is a newly developed route, which does not require organometallic or toxic procurers and is carried out at low temperature. Various kinds of nanocrystalline materials have been obtained by using a solvothermal process at a relatively low temperature (17, 18). In this work, we report a novel solvothermal route to nanocrystals of Cu_7Te_4 at a temperature as low as 160°C. The solvent ethylenediamine takes an important place in the formation of nanocrystalline Cu_7Te_4.

2. EXPERIMENTAL

The solvent of ethylenediamine was put into a Teflon liner autoclave of 100-ml capacity until 85% of its volume was filled. Then appropriate amounts of $CuCl_2 \cdot 2H_2O$

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(7 mmol) and tellurium (4 mmol) were added to the autoclave successively. The autoclave was sealed and maintained at 160°C for 10 h and then cooled to room temperature naturally. The precipitate was filtered and washed with distilled water and absolute ethanol several times to remove the by-products. The product was dried in vacuum at 60°C for 4 h.

The obtained products were characterized by X-ray power diffraction (XRD) patterns, using a Japan Rigaku D/max-γA X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The scan rate of $0.05° \mathrm{s}^{-1}$ was applied to record the patterns in the 2θ range of 10–70°. Further evidence for the purity and composition of the product was obtained by the X-ray photoelectron spectra (XPS) of the product. The XPS was collected on an ESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Mg$K\alpha$ X-ray as the excitation source. To examine the morphology and particle size of the products, transmission electron microscope (TEM) images were taken on a Hitachi Model H-800, using an accelerating voltage of 200 kV.

3. RESULTS AND DISCUSSION

A typical XRD pattern of the sample prepared through solvothermal process is shown in Fig. 1. All the reflections in the pattern can be indexed to the hexagonal Cu_7Te_4 phase with lattice parameters $a = 8.335$ Å and $c = 7.211$ Å, which are close to the reported data for hexagonal Cu_7Te_4 (JCPDS No. 18-456). The broadening of the XRD reflection indicates the small size of the product. The crystalline size of the sample is about 15 nm, as calculated from the half-width of diffraction peaks using the Scherrer formula.

Figure 2 shows the XPS spectra of the sample. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C_{1s} to 284.60 kV. The two strong peaks at 932.4 and 572.7 eV correspond to Cu ($2p$) and Te ($3d$) binding energy (19), respectively, for Cu_7Te_4. No obvious peak for copper oxide (933. 7 eV for Cu2p3/2 in CuO and 935.1 eV in $Cu(OH)_2$) or tellurium oxide (575.7 eV for Te3d in TeO_2 and 576.6 eV in TeO_3) is observed. The quantification of peaks gives the ratio of Cu to Te of 63.41:36.29, which is almost consistent

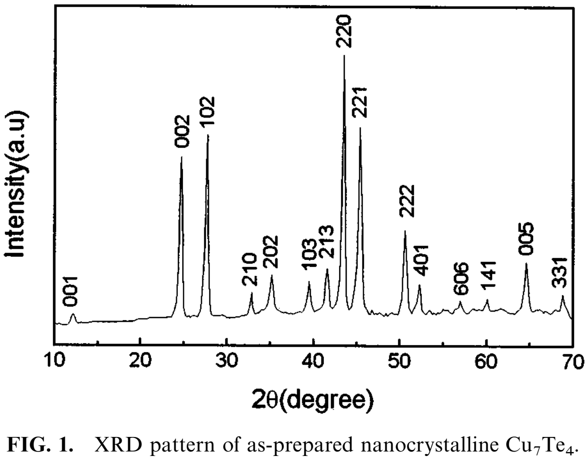

FIG. 1. XRD pattern of as-prepared nanocrystalline Cu_7Te_4.

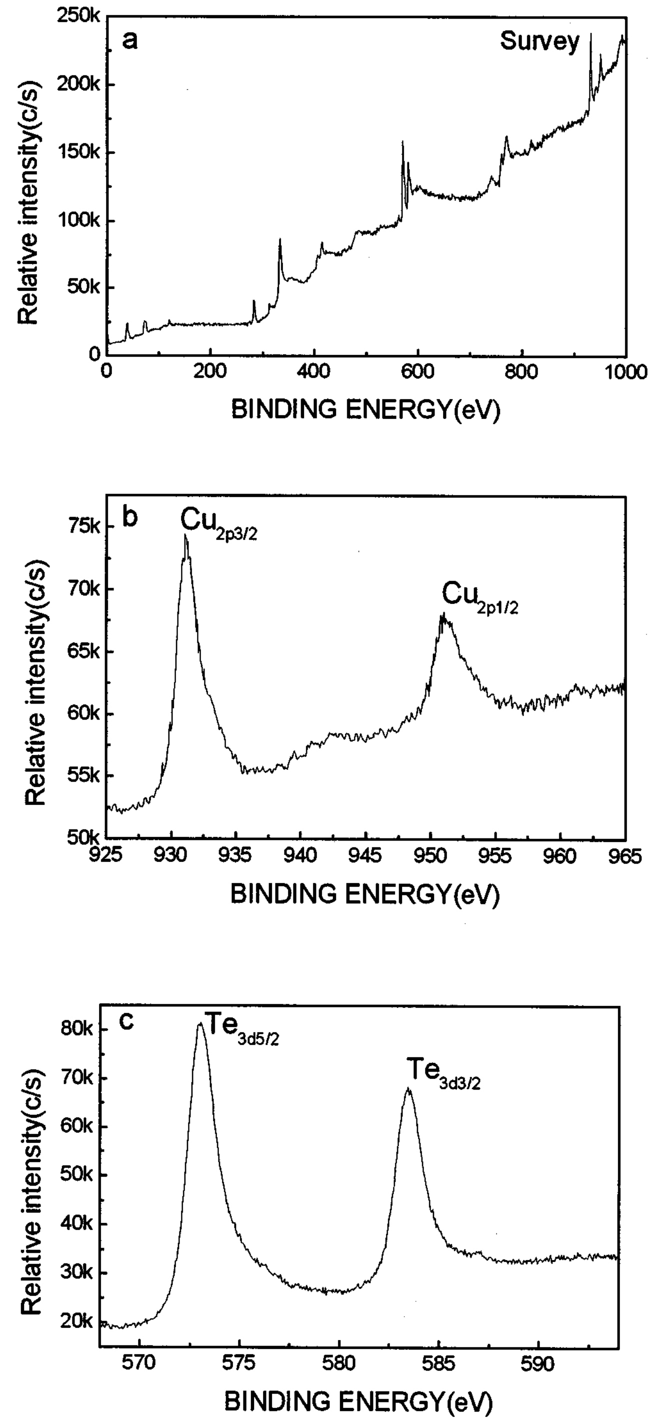

FIG. 2. XPS analysis of nanocrystalline Cu_7Te_4.

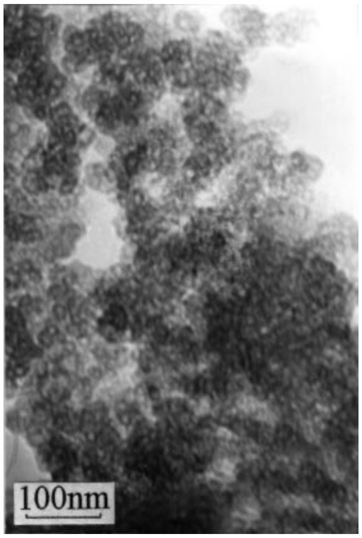

FIG. 3. TEM image of as-prepared nanocrystalline Cu_7Te_4.

with the formula of Cu_7Te_4. The particle size and the morphology of Cu_7Te_4 were observed by TEM (Fig. 3). The image shows that the products consist of homogeneous particles with an average diameter near 15 nm, which is close to the particle size calculated from XRD.

In this process, ethylenediamine was selected as the solvent because of its excellent donor solubility to many metals, which makes it possible to bind to and stabilize metal polytellurido intermediates (20). The solvent in the solvothermal process also acts as the absorber to release the excess heat produced in the reaction. Being a strongly polarizing solvent, ethylenediamine greatly enhances solubility, diffusion, and crystallization, but still provides reaction conditions mild enough to leave molecular building blocks to participate in the formation of the solid state phase. On the other hand, the viscosity of the solution is related to the critical temperature of solvent. In our process, the critical temperature of ethylenediamine (318°C) is lower than that of water (374°C). The diffusion of ions in ethylenediamine at 160°C will be more rapid because of its lower viscosity. This leads to acceleration in the solubility of starting materials and in the following crystal growth. When other solvents, such as benzene or diethylamine, were tested in our experiments, the results showed that the tellurium did not react with copper chloride. The experimental results show that ethylenediamine is an optimum solvent in such solvothermal processes due to the cooperation of the strong polarity and the bidentate ligands of ethylenediamine.

Different molar ratios of $CuCl_2 \cdot 2H_2O$ and tellurium were tried in our experiments. When the molar ratio was 3 : 2 the product was not the Cu_3Te_2 which we expected to get but rather was the mixture of Cu_7Te_4 and excess tellurium unreacted, which was detected by XRD. The XRD also showed that when the molar ratio was 2 : 1 the product was not the expected phase of Cu_2Te but only the hexagonal phase of Cu_7Te_4. When we selected CuI substituting for $CuCl_2$, we also obtained the Cu_7Te_4 nanoparticles. The reason may probably be that the copper cations can form a stable intermediate and the hexagonal Cu_7Te_4 is the most stable phase in ethylenediamine under this experimental condition. Our experiments confirm the appearance of that stable intermediate in the solvothermal process. The influences of the temperature and the reaction time were studied because they acted on the reaction activity of tellurium, the rate of the decomposition of the complex, and the following formation of Cu_7Te_4 in the system. When the thermal treatment temperature was 140°C, the complex could be formed and detected by the XRD patterns. However, we failed to identify the new phase from the present JCPDS patterns. Further heat treatment of the complex at 180°C can produce pure Cu_7Te_4. The tellurium, transition metal, and some donor solvent can form organometallic complexes, which have been reported and studied extensively (20–22). Thus it is reasonable to infer the unidentified intermediate as a complex of Cu, Te, and ethylenediamine. When the temperature was lower than 120°C, even the intermediate could not be formed and the tellurium remained unreacted due to its lower reactivity under this temperature. In brief, the optimum condition for preparing Cu_7Te_4 nanoparticles was at 160°C for 10 h in ethylenediamine.

4. CONCLUSIONS

In summary, nanocrystalline Cu_7Te_4 was directly synthesized through the reaction of $CuCl_2 \cdot 2H_2O$ and tellurium by solvothermal process in ethylenediamine at a relatively low temperature (160°C). XRD, XPS, and TEM examinations show the products are pure hexagonal Cu_7Te_4 phase and well crystallized with an average particle size of 15 nm. By choosing a suitable system, it is reasonable to expect that this simple one-step solvothermal route can be extended to obtain other nanocrystalline tellurides.

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