

# Preparation of $\text{Cu}_{2-x}\text{Te}$ and $\text{HgTe}$ by Using Microwave Heating

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**A new method for the preparation of nanophased tellurides is described. It employs microwave heating for the synthesis of  $\text{Cu}_{2-x}\text{Te}$  and  $\text{HgTe}$ . The copper telluride prepared by this method was a complex of  $\text{Cu}_{2-x}\text{Te}$  and ethylenediamine, which decomposes into pure  $\text{Cu}_{2-x}\text{Te}$  following annealing at 280°C. A mechanism for the microwave-assisted formation of the tellurides is proposed.** © 2000 Academic Press

unique reaction effects stemming from microwave irradiation, such as rapid volumetric heating and the consequent dramatic increase in reaction rates. In this paper, we present a preparation method for late transition metal and main group metal tellurides that uses a microwave-assisted, pressureless solventothermal reaction. We present syntheses of two compounds,  $\text{HgTe}$  and  $\text{Cu}_2\text{Te}$ , obtained by this technique.

## INTRODUCTION

Tellurides of the late transition metals and main group elements are a class of solid state materials that have attracted much recent interest, due to their intriguing thermoelectric, semiconducting, and optical properties. They have already found applications in many fields, including nonlinear optic detectors, photorefractive devices (1), permanent magnets, catalysis (Nitro process and Mitsubishi processes) (2), photovoltaic solar cells, and optical storage media (3).

Originally, tellurides were prepared by simple combination of the elements followed by heating to very high temperatures for a prolonged period of time. This method was successfully used for preparation and characterization of many binary tellurides (4).  $\text{H}_2\text{Te}$  has been used as a tellurating agent; it suffers, however, from the drawbacks of extreme toxicity and a tendency to yield Te at room temperatures due to disproportionation to  $\text{H}_2 + \text{Te}$  (5). Another very promising method (6) uses Zintl ions of nominal composition  $A_2\text{Te}_n^-$ , where  $A$  is an alkali metal, and the  $\text{Te}_n^{2-}$ , as a tellurating agent (7–9). Recently, many publications have appeared (10, 11) in which a solventothermal method has been described. Many new Te-containing phases were synthesized at moderate pressure and temperatures, using different amines as solvents (10, 11). The solventothermal method requires, relatively high pressures and prolonged heating to obtain the desired product, however.

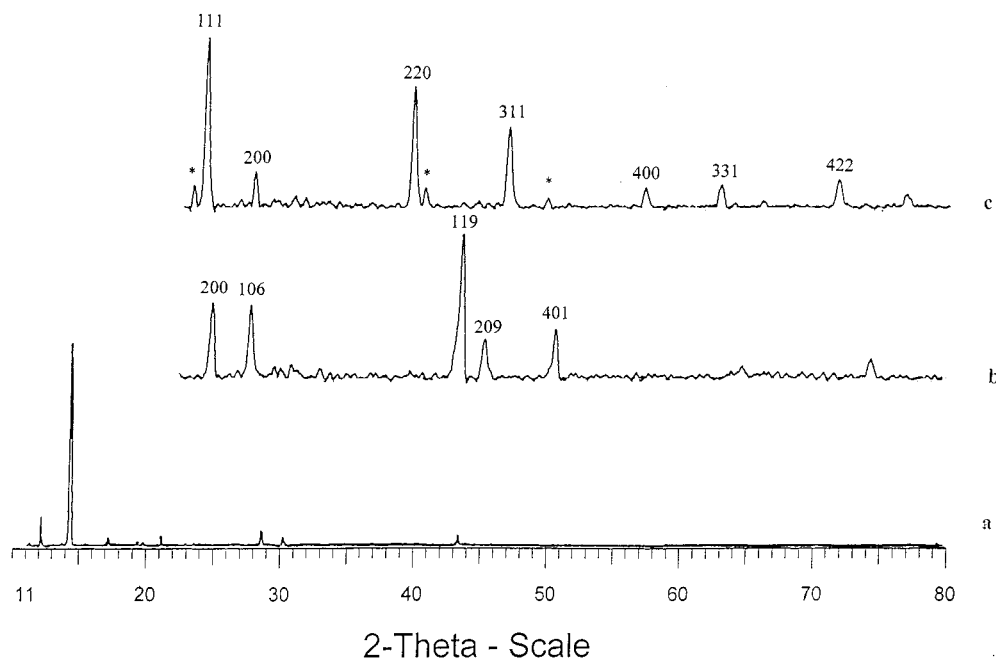
Solid-state synthesis by microwave heating is a relatively new technique in chemistry (12, 13), which has shown very rapid growth in its application to material science due to the

## EXPERIMENTAL

Elemental Te, copper (+I) acetate, mercury (+II) acetate and ethylenediamine (en) were all purchased from Aldrich in the highest available purity. X-ray diffraction patterns of the products were recorded on a Bruker AXS D8 advance powder X-ray diffractometer using  $\text{CuK}\alpha$  radiation. EDX measurements were performed on an X-ray microanalyzer (Oxford Scientific) built on a JEOL JSM-840 Scanning electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos Analytical AXIS, HIS, 165, ULTRA (Kratos Analytical). TGA analysis was done with a Mettler TG-50/SDTA851 in a temperature range of 30 to 600°C, at a heating rate of 5°C per minute, in an argon atmosphere. DSC measurements were conducted on a Mettler DSC-30 with a heating rate of 5°C/min. Transmission electron micrographs (TEM) were obtained by employing JEOL-JEM 100SX microscope. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid piece of 400 mesh (Electron Microscopy Sciences) coated with carbon film and were allowed to dry in air. The microwave oven reflux system has been described elsewhere (14).

In order to fabricate  $\text{Cu}_2\text{Te}$ , 0.1 g (0.786 mmol) of Te was mixed with 0.284 g (1.56 mmol)  $\text{Cu}(\text{OAc})$  and 40 ml of ethylenediamine. The mixture was placed in the microwave reflux system, and reaction was carried out in the open air for 1 h. The microwave oven followed a working cycle of 6 s on, 4 s off (= 60% power). The resulting powder was placed through several cycles of washing with acetone, centrifugation, and drying *in vacuo*. The product was then annealed by heating at 280°C under Ar for 2 h.

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**FIG. 1.** Powder XRD patterns of (a) unannealed crystalline precursor for  $\text{Cu}_{2-x}\text{Te}$ . (b) Weissite ( $\text{Cu}_{2-x}\text{Te}$ ) prepared by annealing of the as-prepared organometallic crystalline precursor. (c) XRD powder of unannealed coloradoite ( $\text{HgTe}$ ). The stars represent impurities of unreacted Te.

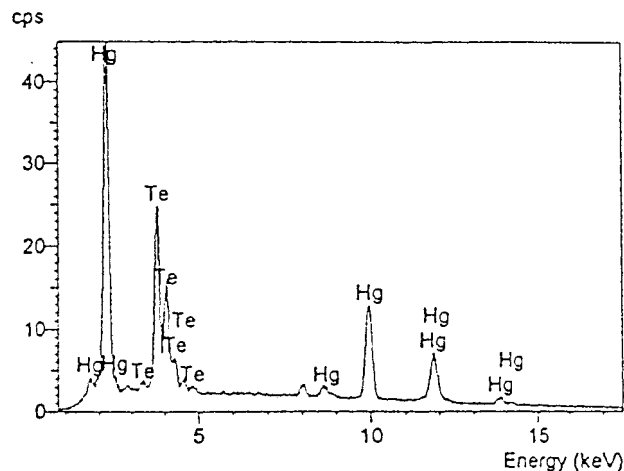
In order to fabricate  $\text{HgTe}$ , the stoichiometric quantities of mercury (II) acetate and tellurium were mixed with ethylenediamine. The mixture was refluxed in the microwave system for 2 h at 70% power. The subsequent treatment was identical to that of  $\text{Cu}_{2-x}\text{Te}$ .

## RESULTS

The XRD patterns of the initial, and of the annealed, products are shown in Figs. 1a and 1b. The diffraction pattern of the as-prepared product shows very strong and clear peaks at relatively low angles ( $2\theta < 45^\circ$ ). We could not assign the diffraction peaks to elemental Te or to any known compound of Cu, including metallic Cu. We believe that the initial product is an organometallic crystalline complex of ethylenediamine with copper and tellurium, based on the known propensity of ethylenediamine to complex with metal cations, and on the EDX result described below (10). The XRD pattern of the annealed compound is depicted in Fig. 1b. The Miller indices of the diffraction peaks are marked. The experimental spectrum closely matches the literature spectrum for  $\text{Cu}_{2-x}\text{Te}$  (Weissite, in PDF2 No. 10-0421). The crystallite size of the  $\text{Cu}_{2-x}\text{Te}$  prepared in the present experiment is 50 nm, as calculated by the Debye-Scherrer equation. The XRD patterns yields unit cell parameters for the hexagonal unit cell ( $P3m1$ ) of  $a = b = 8.3 \text{ \AA}$ ,  $c = 21.7 \text{ \AA}$ , which are in very good agreement with the published data for  $\text{Cu}_{2-x}\text{Te}$  (15). The atomic ratio of the Cu:Te calculated from the EDX results, is 1.93:1, which is in

good agreement with the stoichiometry of Weissite. The EDX spectrum of the initial (unannealed) Cu-Te-en compound (not shown) indicates that it has the same Cu:Te stoichiometry, demonstrating that the as-prepared product is indeed a complex of  $\text{Cu}_{2-x}\text{Te}$  and serves as the source for  $\text{Cu}_{2-x}\text{Te}$  upon its decomposition.

The initial product of reaction of Te with  $\text{Hg}(\text{OAc})_2$  was found to be  $\text{HgTe}$  in the crystalline coloradoite phase (PDF2 No. 32-0665). Calculation of the unit cell parameters (Fig. 1c) yields  $a = b = c = 6.47 \text{ \AA}$  for the fcc ( $F-43m$ ) phase, in good agreement with published data (16). The EDX

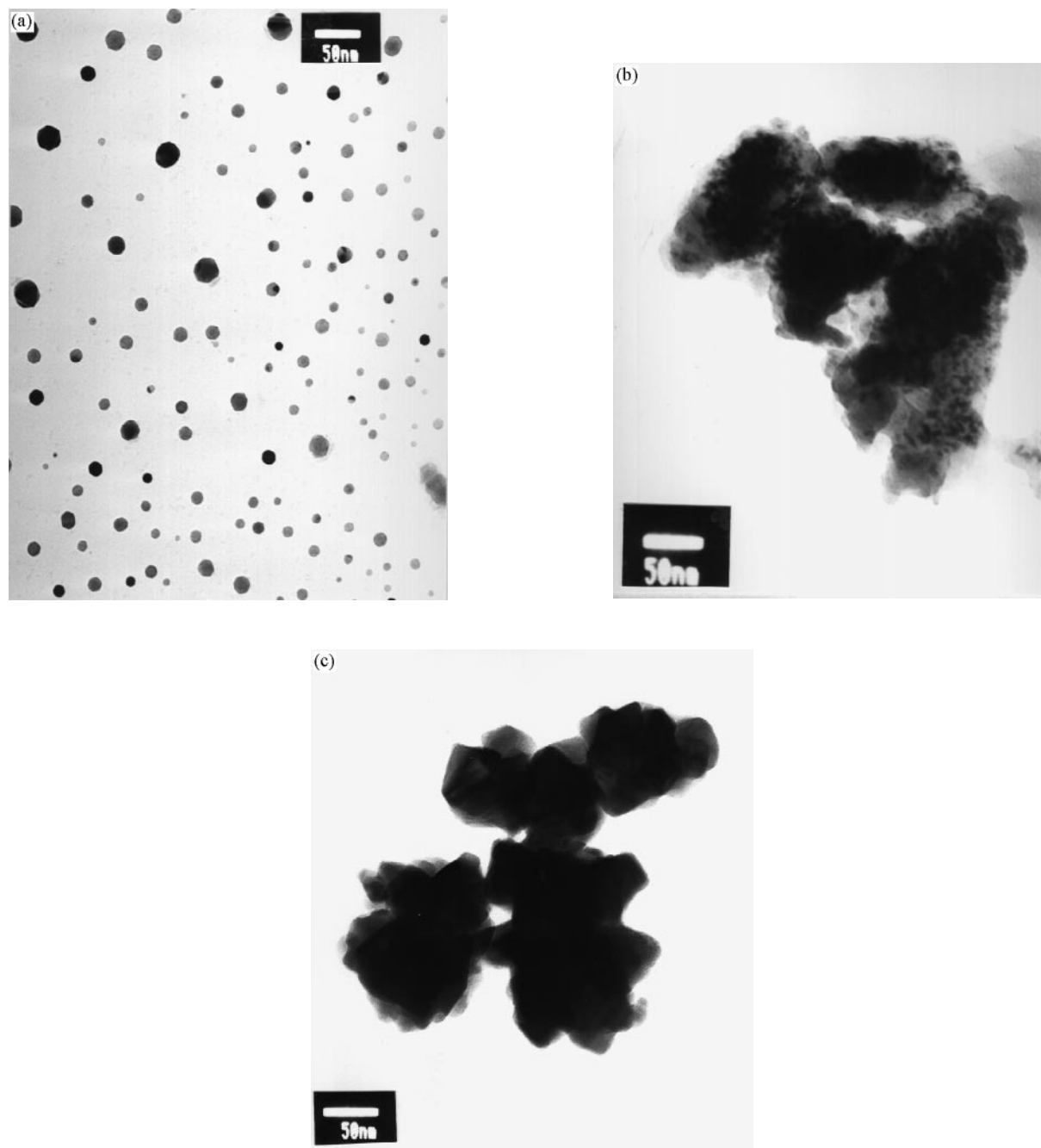


**FIG. 2.** EDX spectrum of the  $\text{HgTe}$ .

spectrum of the HgTe is shown in Fig. 2. It indicates an atomic ratio of Hg:Te of 1:1.09, which is consistent with the above-mentioned formula. The calculated size of the HgTe particles, based on the Debye-Scherrer formula, is 40 nm.

TEM pictures of  $\text{Cu}_{2-x}\text{Te}$  prior and after annealing and of HgTe are shown in Figs. 3a–3c, respectively. For  $\text{Cu}_{2-x}\text{Te}$ , individual spherical nanoparticles whose diameter is 20–40 nm (Fig. 3a) dominate the product, with

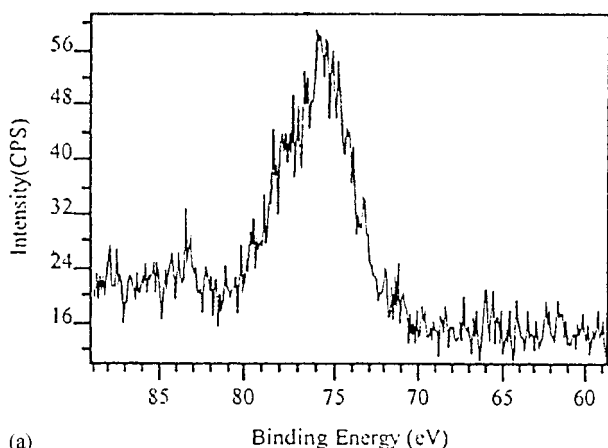
a small amount of aggregates of  $\sim 100$ – $140$  nm. Upon annealing, a change in the particle shape from spherical to elliptical and a growth in the dimension of the individual  $\text{Cu}_{2-x}\text{Te}$  particles to  $\sim 60$ – $100$  nm is observed (see Fig. 3b). Since the annealing was performed at a relatively low temperature, only minor aggregation was observed. The TEM picture of the HgTe (Fig. 3c) sample shows that the particles are cubic, in keeping with the face-centered cubic structure



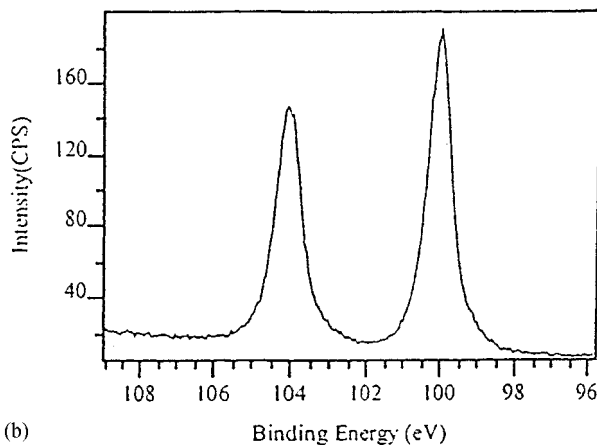
**FIG. 3.** TEM picture: (a) spherical nanoparticles of unannealed  $\text{Cu}_{2-x}\text{Te}$ ; (b) annealed  $\text{Cu}_{2-x}\text{Te}$ ; (c) cubic aggregates of HgTe.

determined from the XRD data. The dimensions of the nanoparticles are  $\sim 45$  nm, with some aggregates of  $\sim 400$  nm also observed.

Figure 4a illustrates the XPS spectra of the Cu  $3p$  transition of unannealed  $\text{Cu}_{2-x}\text{Te}$ . In addition to the bands assigned to the Cu  $3p$  and Te  $3d$  transitions, we observe very strong peaks for C at 286 eV and N at 394 eV. Their presence is further evidence for our proposed structure of this material as a Cu-Te-en complex. The measured atomic ratio of C:N is 2:1, which does not fit the expected 1:1 ratio of ethylenediamine. This deviation may be because XPS primarily monitors concentrations at the surface of the examined particle, which may not be representative of the sample as a whole. High-resolution XPS spectra of  $\text{HgTe}$  are shown in Fig. 4b. The intense doublets observed at 100 and 104 eV are assigned to the  $4f_{7/2}$  and  $4f_{5/2}$  transitions of Hg, respectively. The doublet at 572 and 582.6 eV correspond to Te  $3d$  transitions. The elemental ratio of Hg:Te calculated on the basis of XPS spectra is approximately to 1:1.1.



(a)



(b)

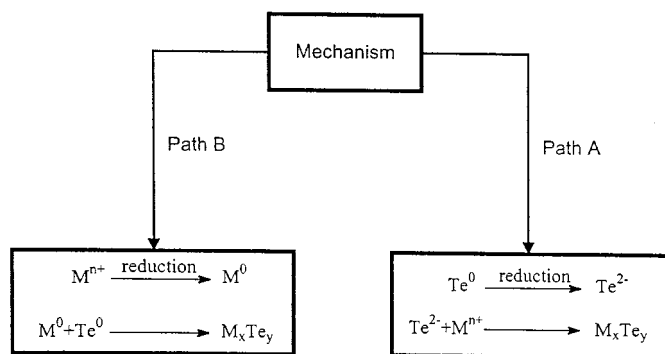
FIG. 4. XPS spectra: (a) Cu  $3p$  transition peak in the unannealed  $\text{Cu}_{2-x}\text{Te}$ ; (b) Hg  $4f_{7/2}$  and  $4f_{5/2}$  transition in  $\text{HgTe}$ . Elemental ratio of Hg:Te calculated on the basis of XPS spectra is approximately to 1:1.1.

The unannealed tellurides were also analyzed by TGA-MS. A loss of 53% of the weight of the unannealed  $\text{Cu}_{2-x}\text{Te}$  sample occurs at  $360^\circ\text{C}$ . A mass spectral analysis of the material lost demonstrated that this weight drop corresponds to loss of en ( $61 \text{ amu} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$ ). A much smaller (5%) weight loss is observed for the unannealed  $\text{HgTe}$  in the same temperature region. This mass loss  $\text{HgTe}$  is due to the evaporation of metallic Hg, produced as a result of the reduction of  $\text{Hg}^{2+}$  ions by en; no en was detected during TGA-MS of  $\text{HgTe}$ .

## DISCUSSION

In the literature, a few examples of the preparation of chalcogenides using microwave irradiation have been reported (17–19). In all cases, the method was based on the mixing of the metallic powders and heating them in a microwave oven. All of the reactions were highly exothermic and fast. Te is generally less reactive than other chalcogenides; however, as mentioned above, special conditions or reagents are needed for generation of  $\text{Te}^{2-}$  (5). Our results show that microwave heating can activate Te toward telluride formation under surprisingly mild conditions.

Two reasonable mechanisms can be proposed for the formation of the tellurides by microwave irradiation (see Scheme I). First, there can be a direct interaction between the tellurium and the microwave radiation. There are many examples in the literature (20–22) of microwave radiation, being used to heat metallic powders to very high temperatures, even if they are dispersed in a low-boiling-point solvent (14). Since Te has some metallic character (resistivity  $\rho = 2 \times 10^{-6} \mu\Omega \text{ cm}$ ), its heating can be a major driving force for the reaction. To check the validity of this argument, the controlled heating of powdered tellurium was carried out in a microwave oven. Its heating rate was moderate, and after 10 min the temperature reached  $118^\circ\text{C}$  (which is, incidentally, the boiling point of ethylenediamine). The preparation of the tellurides required a reaction time of



SCHEME I. Possible mechanisms for the formation of  $\text{Cu}_{2-x}\text{Te}$  and  $\text{HgTe}$ .

1 to 2 h and we therefore can anticipate that Te will reach temperatures higher than 118°C, causing interfacial overheating of the solvent and facilitating the solventothermal reaction with ethylenediamine. At an elevated temperatures the ethylenediamine can reduce the Te to  $\text{Te}^{2-}$ , which subsequently reacts with the metallic ion.

A Second possibility is based on the observation that in microwave boiled solvents, the solvents themselves can undergo profound overheating (20, 23–25). This localized overheating effect can reach 13–26°C in the case of organic solvents (26). Such an increase in the boiling point has been known to result in an approximately eightfold reaction rate enhancement; the exact magnitude of this overheating effect for ethylenediamine is still unknown, however. Such overheating effects are similar to the solventothermal reactions of ethylenediamine (10), where the high pressure that is developed increases the reduction power of the solvent. As a result of such overheating, the metal ion could be reduced to the metal in the zero oxidation state. Such metallic particles will strongly interact with microwave radiation (they are much better absorbers of microwave radiation than Te), yielding very high temperatures, which will enhance the reaction rate of the metal with Te. Thus the microwave irradiation leads to a classical solid state reaction between the metal and the tellurium. These two proposed mechanisms are presented in Scheme I.

Research is underway to assess the relative importance of solvent overheating and microwave-induced “solid state reaction” in the microwave-assisted synthesis of metal tellurides.

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