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# Microwave-Assisted Polyol Synthesis of $CuInTe_2$ and $CuInSe_2$ Nanoparticles

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Nanoparticles of the $CuInTe_2$ (CIT) and $CuInSe_2$ (CIS) alloys have been prepared using the microwave-assisted polyol method. In this simple and quick reaction the polyol is both the solvent and the reducing agent. XRD studies show that nanoparticles of CIT and CIS are formed in the body-centered tetragonal structure and their average diameters are ∼94 and ∼83 nm, respectively. Electron microscopy studies show that these formed particles are poorly aggregated with a mean diameter of 100 and 85 nm, respectively. The products have been characterized by different analytical techniques, and the electronic properties have been measured using photoacoustic spectroscopy (PAS).

## Introduction

Some members of the Cu−III−$VI_2$ family of chalcopyrite semiconductors continue to receive considerable attention due to their potential applications in optoelectronic devices.[1] In recent years, solar cells based on $CuInSe_2$ (CIS) have been reported with efficiency around 17%.[2] This compound is a subject of intense research since it holds the promise of high performance combined with low cost. Recently, it was also suggested that $CuInTe_2$ (CIT), another member of the Cu−III−$VI_2$ family, could also be a very efficient solar-cell material.[3] $CuInSe_2$ can be prepared by several methods such as evaporation,[4] decomposition of organometallic precursors,[5] electrodeposition,[6] metal reactions with $H_2Se$,[7] microwave-assisted solid-state reaction involving pure metal powders,[8a−c] and a few other techniques.[8d]

A few techniques have been applied for the preparation of nanoparticles of CIS. The first report was by Gurin,[9] who has prepared aqueous and nonaqueous colloids of a series of ternary semiconductor compounds. Malik and co-workers[10] conducted the synthesis of tri-*n*-octylphosphine oxide (TOPO)-capped $CuInSe_2$ nanoparticles using a two-step reaction from $InCl_3$ and CuCl in tri-*n*-octylphosphine (TOP), followed by injection into TOPO at 100 °C. Tri-*n*-octylphosphine selenide (TOPSe) was then added to the reaction mixture at the elevated temperature of 250 °C. Three solvothermal reactions were described by Qian's group.[11a−c] Li et al.[11a] prepared $CuInSe_2$ nanowhiskers and nanoparticles at 180 °C using $CuCl_2$, $InCl_3$, and Se as reagents. Jiang et al.[11b] synthesized $CuInS_2$ nanorods at 280 °C through

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elemental solvothermal reactions. In the last solvothermal work,[11c] Qian extended the solvothermal pathway to the chalcopyrite quaternary semiconductor $CuIn(Se_xS_{1-x})_2$ nanocrystallites with composition $x$ ranging from 0 to 1 using $CuCl_2 \cdot 2H_2O$, $InCl_3 \cdot 4H_2O$, Se, and S as reagents. They have also investigated the effect of different solvents on the formation of the product. Ethylenediamine (en), diethylamine, pyridine, and benzene were examined as solvents in an autoclave sealed and maintained at 180 °C for 15 h. The method described by Basol[12] is based on the preparation of the Cu−In alloy in the first stage. The alloy is ball-milled and then selenized in a $H_2Se-N_2$ (5−95%) gas mixture. A few papers describe the preparation of bulk $CuInTe_2$.[13] However, we could not find a paper reporting on the preparation of nanoparticles of CIT. This paper will therefore be the first report of the synthesis of CIT nanoparticles.

The electronic properties of the semiconductor nanoparticles are influenced by their stoichiometric composition, morphology, and impurities, which are dependent on the method and conditions of preparation. Nevertheless, the above-mentioned methods have disadvantages, for example, the need for special reagents such as $H_2Se$, which is a very hazardous gas.[12] The application of the solvothermal method requires special high-pressure equipment, and the impurity levels can be sometimes very high. Frequently, the reaction time is long, and taking more than 1 day.[11]

In our continuing effort to prepare semiconducting nanoparticles, we have developed a general method, the so-called microwave-assisted polyol method, which is general and very efficient. The polyol method was developed in the 1980s by Fievet et al. for the preparation of the finely divided metal powders of easily reducible metals (such as precious metals and copper) and a few less reducible metals (cobalt and nickel).[14] In the polyol process a powdered inorganic metallic compound is suspended in a liquid polyol (ethylene glycol, di- or triethylene glycol, or a mixture of few glycols). The starting compound must be soluble in polyol (generally it is the acetate salt of the corresponding metal, but other soluble salts could also be used). The solution is stirred and heated until the boiling temperature of the solvent is reached. A complete reduction of these compounds can be achieved within a few hours (for the more reducible metals), and the metal recovered is a finely divided powder. The resulting powder is composed of spherical particles with a mean size of 1−10 $\mu$m, depending on the nature of the metal and the reaction conditions.[14,15] In these reactions the polyol acts, at first, as a solvent for the starting compounds due to its rather high dielectric constant. Subsequently, the polyol reduces the metallic cation to the metallic form in the liquid phase, at which stage nucleation and growth of the metallic phase occurs. The mechanism of the reduction by the polyol is still unclear.[16] Prior to our application of microwave heating to the polyol reactions, the following disadvantages were present in this method:[14] (a) Micrometer size particles were prepared rather than nanometer size. (b) Only easily reducible metallic powders were prepared. (c) No binary or ternary compounds were synthesized. (d) A relatively high level of impurities was detected (especially carbon). (e) Prolonged reaction times were required.

We found that due to the high dipole moment of the glycol molecules they are very efficient absorbers of microwave radiation. The absorption leads to the heating of the glycol. The microwave-assisted polyol method was found to be a superior technique for the preparation of binary and ternary chalcogenide nanoparticles in comparison with other methods.[17,18] We summarize the advantages of the microwave-assisted polyol method: (a) The reactions are conducted at normal atmospheric pressure and at the boiling temperature of the solvent. (b) The method is suitable for microwave and sonochemical reactions.[19] (c) Nanoparticles with a diameter of a few nanometers can be prepared.[17] (d) It is possible to prepare ternary phases and pseudoternary phases (alloys).[18] (e) Shorter reaction times are required. (f) The products show a very low level of impurities. (g) Tellurides can be prepared by this method (both binary and ternary). (h) Very simple reagents are used as precursors. (i) There are excellent reproducibility and high yields of products. (j) The method is not limited to the preparation of chalcogenide semiconductors (antimony-based binary phases are now under investigation). In this publication we present the application of the microwave-assisted polyol synthesis to the preparation of nanoparticles of two chalcopyrite semiconductors, $CuInTe_2$, and $CuInSe_2$. The former compound is prepared in the nanophase form for the first time. In addition these solid products are dissolved in 2-mercaptoethanol forming a colloidal solution.

## Experimental Section

**Materials.** All reagents were of the highest purity. Elemental Se, Te, and In, copper(I) chloride, triethylene glycol, tetraethylene glycol, and 2-mercaptoethanol were all purchased from Aldrich Co. and used without further purification.

**Instrumentation.** The X-ray diffraction patterns of the products were recorded by employing a Bruker AXS D8 Advance powder

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X-ray diffractometer (using Cu Kα $\lambda = 0.15418$ nm radiation at 40 kV/40 mA) with a secondary graphite crystal monochromator. The transmission electron micrographs (TEM) were obtained by employing a JEOL-JEM 100SX microscope, working at 100 kV accelerating voltage. High-resolution TEM (HR-TEM) images were obtained by employing a JEOL-3010 with 300 kV accelerating voltage. A conventional CCD camera, with a resolution of 768 × 512 pixels, has been used to digitize the micrographs. Image processing of these digital images has been performed using Digital Micrograph software. HR-TEM image calculation and electron diffraction indexing were performed using an EMS package.[20] High-resolution SEM (HR-SEM) images were recorded by employing a DSM 982 GEMINI digital field emission SEM (Zeiss) with 4 kV accelerating voltage. EDS measurements were conducted using an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 scanning electron microscope (JEOL). Elemental analysis (carbon) was done with an EA 1110 CHNS-O instrument. Differential scanning calorimetric analysis (DSC) was carried out on a Mettler Toledo TC 15, using nitrogen or argon as a purging gas, and the scanning rate was 5 °C/min. Thermogravimetric analysis (TGA) was done on a Mettler Toledo TGA/SDTA851 instrument using nitrogen or argon as a purging gas with a scanning rate of 5 °C/min. X-ray photoelectron spectra (XPS) were recorded using an AXIS HIS 165 ULTRA (Kratos Analytical, Inc.).

The electronic properties of the nanoparticles were measured using photoacoustic spectroscopy (PAS). Photoacoustic measurements were conducted employing a homemade instrument, which has been described elsewhere.[21] The signals, which are acquired as a function of wavelength, were normalized against the absorption of carbon black powder, the 100% absorber. The band gap is calculated by the "knee" method for all the samples.[22]

Microwave-assisted reactions were conducted in a Kenwood 900 W $2.45 \times 10^9$ Hz working frequency, domestic microwave oven, modified with a refluxing system. In all the experiments the microwave oven worked in the following cycling mode: on for 21 s; off for 9 s. The total power was always 900 W. This cycling mode was chosen to prevent the violent "bump" boiling of the solvent. All reactions were conducted under a flow of nitrogen.

**Preparation of $CuInSe_2$.** CuCl (0.098 g, 1 mmol) is dissolved in triethylene glycol (50 mL) by gentle heating in the microwave oven for approximately 1 min. The stoichiometric quantities of In (0.114 g, 1 mmol) and Se (0.158 g, 2 mmol) powder are then added. The system is purged for 10 min with nitrogen, and then the microwave reactor is turned on. The reaction is conducted for 1 h. To find out whether the particle size is concentration-dependent, experiments are also conducted with 0.2 mmol CuCl, 0.2 mmol In, and 0.4 mmol of Se powder in the same amount of triethylene glycol.

**Preparation of $CuInTe_2$.** The procedure is same as for $CuInSe_2$, the only difference being that instead of Se Te (0.255 g, 2 mmol) is used and triethylene glycol is changed to tetraethylene glycol. The reaction was conducted for 1 h. In the postreaction treatment in all the experiments, the products were centrifuged once at 9500 rpm with the mother liquid, to separate the powder from the liquid, and then washed a few times with ethanol at 20 °C at 9500 rpm. The products were then dried overnight under vacuum. Like the CIS, a similar dependence of the particle size on the concentration of the precursor solution was obtained for CIT. Reducing the concentration of the precursor solution by a factor of 5 yielded 50−60 nm size particles.

**Colloidal Solution.** To get a colloidal solution the solid products of CIS and CIT are dissolved in 2-mercaptoethanol by stirring and heating the solution to 50−60 °C overnight. A colloidal solution of CIS and CIT stable for 10 h is obtained. After this period a precipitate is observed. To prepare a grid for TEM measurements the colloidal solution was heated overnight to 110 °C. The heated solution was purged with dry air while stirring. We added a few drops of ethanol to the viscous liquid, the solution was sonicated for 10 min, and then a drop was removed and placed on the TEM grid.

## Results and Discussions

The chemical reaction that takes place under the microwave radiation is described in the following equation:

$$\mathrm{CuCl(polyol)} + \mathrm{In(polyol)} + 2\mathrm{CHAL(polyol)} \rightarrow \mathrm{CuInSe_2(s)} + 1/2\mathrm{Cl}_{2(g)} \quad (1)$$

Here the (polyol) symbol refers to a solution either in triethylene glycol or tetraethylene glycol and CHAL = Se or Te. To characterize the crystallographic structure of the as-prepared compounds, powder XRD analysis was employed. The PXRD patterns of the $CuInSe_2$ and $CuInTe_2$ are shown in Figure 1a,b, respectively. For the CIT, an almost pure phase is obtained (body-centered tetragonal structure; PDF No. 34-1498) with a very small impurity (<2%) level of $Cu_2Te$ (PDF No. 40-1325). The intensities of the peaks were in agreement with the standard pattern, which indicates the isotropic nature of the as-prepared particles. The Scherrer equation was used to calculate the particle dimensions.[23] The particle size of the CIT was ~94 nm (using the width of the peaks at $2\theta = 24.8$, 41.1, and 48.7°). Small impurity levels of $Cu_2Se$ (PDF No. 47-1448) were also detected for CIS (body-centered tetragonal; PDF No. 40-1487). The dimensions of the CIS particles, calculated by the Scherrer equation, are equal to ~83 nm (using the width of the peaks at $2\theta = 26.6$, 44.3, and 52.4°). The calculated lattice parameters for CIT are found as $a = b = 6.165$ Å and $c = 12.342$ Å. For CIS we calculated $a = b = 5.776$ Å and $c = 11.560$ Å. These results are in very good agreement with the previously published parameters.[11,13e] An additional analysis was conducted to verify the exact stoichiometry of the prepared compounds. Elemental analysis is especially important for the CIT, because of the systematic overlap of the peaks of the CIT phase with that of $In_2Te_3$ (PDF No. 33−1488) in the PXRD spectrum. In such cases EDS elemental analysis could help to distinguish between CIT and $In_2Te_3$. The stoichiometric ratio of Cu:In:Se in the CIS sample measured using EDS is 1.04:1:2.06, and for CIT the Cu:In:Te ratio is 1.03:1:2.07. For CIT, a small excess of Cu is observed from the EDS measurements. As a result of the EDS and XRD measurements, we could confirm that CIS and CIT phases are the as-prepared products.

The morphology of the as-prepared compounds was studied by TEM, SEM, and HR-SEM measurements. The

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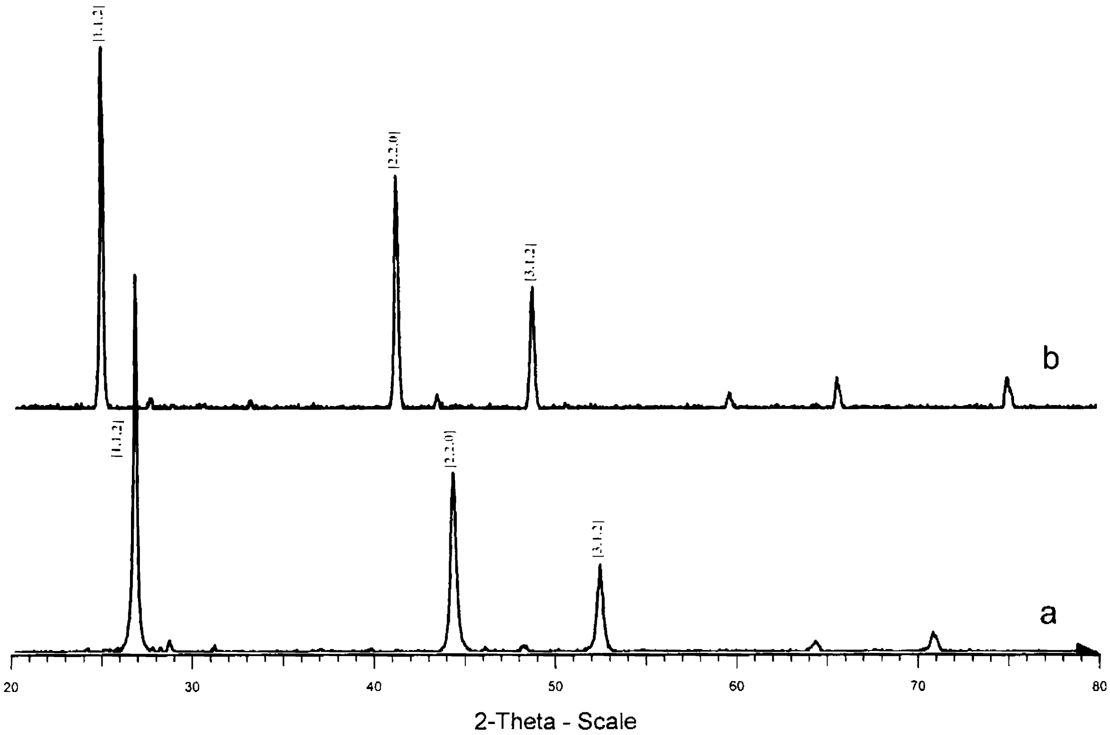

**Figure 1.** Powder XRD patterns of as-prepared body-centered tetragonal (a) CuInSe$_2$ prepared in triethylene glycol and (b) CuInTe$_2$ prepared in tetraethylene glycol.

TEM pattern of the CIT is shown in Figure 2a. CIT is prepared in the form of spherical aggregates, with a mean diameter of 100 nm, which are loosely aggregated. The presence of rings, and not points, in the electron diffraction pattern of the particles attests to the polycrystalline nature of the as-prepared CIT. The spheres are clearly not a single crystal. An HR-SEM picture of the CIT is shown in Figure 2b. Again, poorly aggregated spherical particles with a mean diameter of 100 nm are observed. This result is in agreement with the TEM measurements (see Figure 2a). The HR-SEM image of CIS is shown in Figure 2c. We observed spherical, nonaggregated particles with an average diameter of 85 nm. We have also found that by reducing the concentration of the precursor in the solution the particle sized is reduced. For example, reducing the concentration by a factor of 5 yielded 50 nm diameter particles of CIS.

To check whether the product is an aggregate of smaller particles we prepared a colloidal solution of CIS and CIT in 2-mercaptoethanol and examined the particle size of the dispersed particles by TEM. The TEM image of the colloidal solution of CIS is shown in Figure 2d. The picture reveals different morphological structures from those observed in the solid product. Of special interest are some nanorods, which are found all over the grid. The length of the rod was 300 nm, and its width was 35 nm. Small particles with an average size of ~30 nm were found glued to these rods. These nanorods were not observed in the TEM images of the as-prepared CIS and CIT solids. There is no question that the particles in the colloidal solution were less aggregated than in the as-prepared solids. However, some agglomerated particles were observed even in the picture of the colloidal product. The polycrystalline nature of the dissolved CIS was detected by electron diffraction measurements.

To study the structure of the individual nanospheres, the HR-TEM technique was used. An HR-TEM micrograph of the CIT is shown in Figure 2e. This image is taken on the edge of the spherical nanoparticle. It is impossible to do HR-TEM in the middle of the particles due to the thickness limitations of the HR-TEM method. The image is recorded along the [112] zone. We can clearly observe that the nanoparticles have a perfect arrangement of their atoms, in agreement with the tetragonal lattice of the CIT (PDF No. 34-1498). The distance between these lattice planes is 0.358 nm, which is very close to the distance between the planes obtained from the XRD (0.361 nm). Furthermore, on the surface of all CIT nanospheres an amorphous shell is observed. The thickness of this shell measured for many particles is approximately 1 nm. For the CIS an analogous shell was also observed, but its thickness was smaller ($<1$ nm). In CIS the shell was not found around all the nanoparticles.

To study the surface composition of the nanoparticles, and especially the shell observed for the CuInTe$_2$, we employ XPS technique. XPS analyzes the composition of the surface layer of the compound with a depth penetration of approximately 2−3 nm. In Figure 3a,b we illustrate the XPS spectra of the CIS and CIT, respectively. The binding energies obtained in the XPS analysis are corrected for specimen charging by referencing the C$_{1s}$ to 285.5 eV and are presented in Table 1. These binding energies are consistent with the energies observed in the previously published XPS spectrum of this compound.[11] The same is

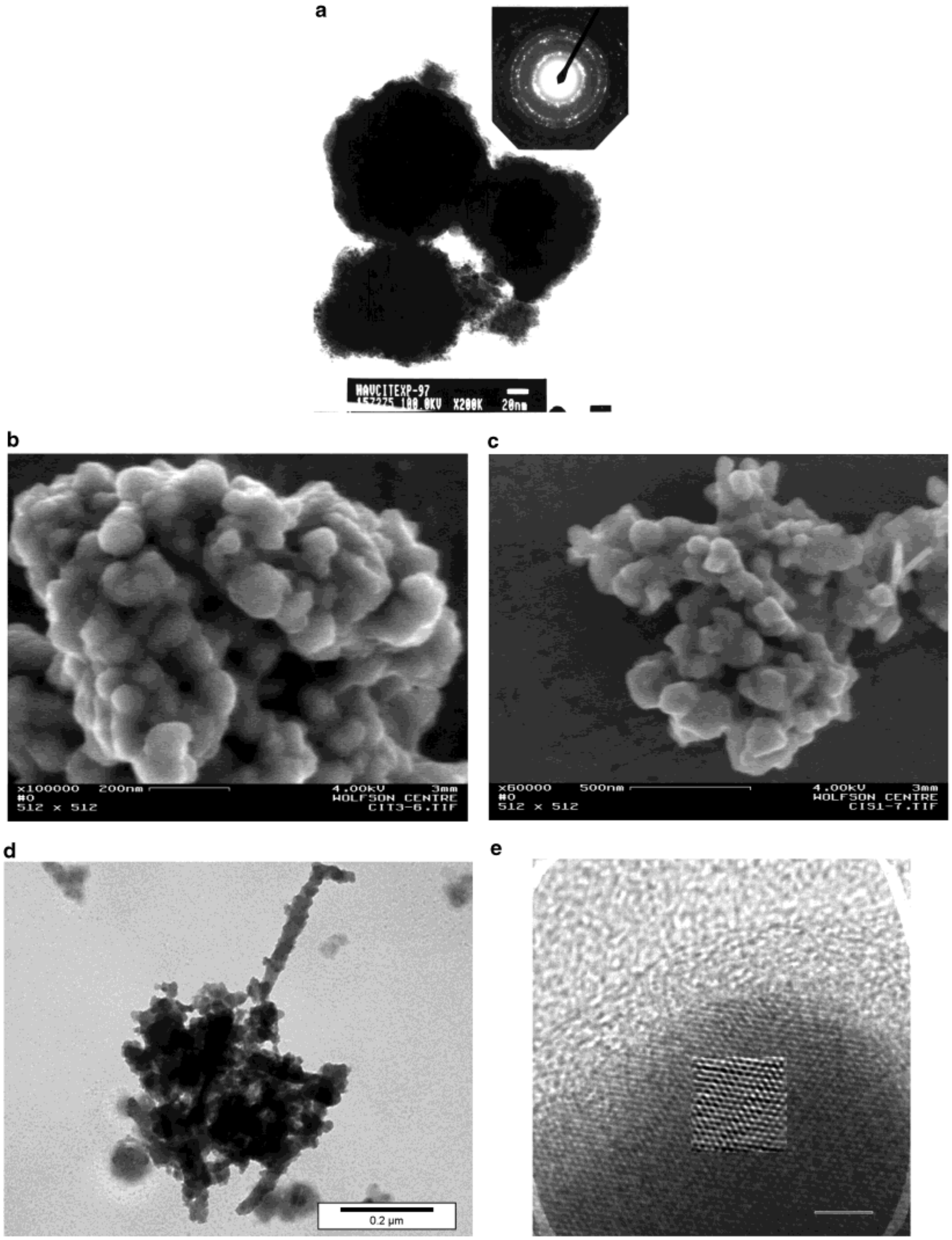

**Figure 2.** (a) TEM picture of as-prepared $CuInTe_2$ in the form of spherical aggregates (bar equals 20 nm). Insert: Selected area electronic diffraction pattern for CIT. (b) HR-SEM image of the as-prepared $CuInTe_2$ alloy (scale bar = 200 nm) (c) HR-SEM image of the as-prepared $CuInSe_2$ alloy (scale bar = 500 nm). (d) TEM image of a colloidal solution of solid $CuInSe_2$ nanoparticles. (e) HR-TEM image of the as-prepared $CuInTe_2$ alloy (bar equals 2.3 nm). Insert: FFT-filtered image of the lattice.

true for the binding energies of the different atoms in CIT.[24] For both CIS and CIT, the binding energies of Cu (Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are 932.5 and 952.2 eV, respectively) are in agreement with the published data and no satellite peaks due to $Cu^{2+}$ are observed. On the basis of the deconvolution analysis made for the Cu peaks (for both compounds), two kinds of oxidation states for copper were observed, $Cu^0$ and $Cu^+$. As a result of this analysis, we conclude that the shell is composed of metallic copper and below this shell is $CuInSe_2$ or $CuInTe_2$ (in both compounds the oxidation state of the copper is +1). These results are in agreement with the EDS measurements, where a small excess (3−4%) of Cu is observed for both compounds. The elemental copper is not observed in the XRD patterns since the Cu layer is amorphous (see HR-TEM Figure 2e). For both compounds oxygen and carbon impurity peaks are observed. The source

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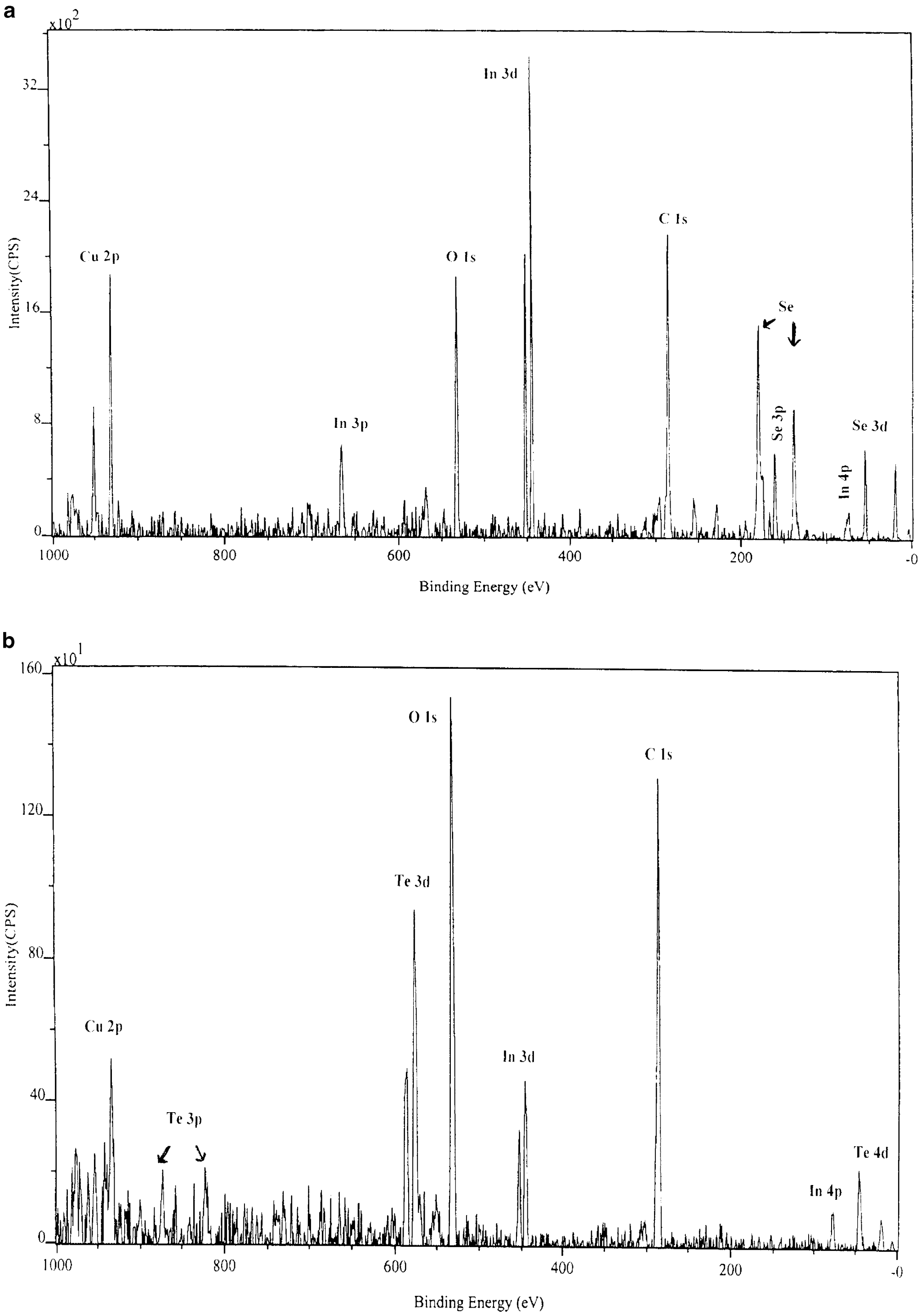


**Figure 3.** (a) XPS spectrum of the as-prepared $CuInSe_2$. (b) XPS spectrum of the as-prepared $CuInTe_2$.

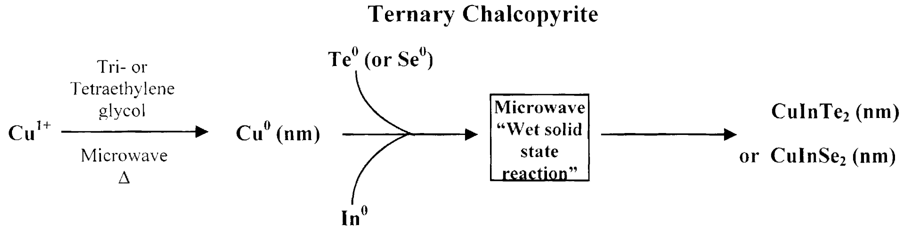
**Table 1.** Spin−Orbit Components and Respective Binding Energies (BE) of the Elements in $CuInTe_2$ and $CuInSe_2$

| | $CuInTe_2$ | | | | | $CuInSe_2$ | | |
|---|---|---|---|---|---|---|---|---|
| param | Cu | | In | | Te | In | | Se |
| spin−orbit component | $2p_{3/2}$ | $2p_{1/2}$ | $3d_{5/2}$ | $3d_{3/2}$ | 3d | $3d_{5/2}$ | $3d_{3/2}$ | 3d |
| BE (eV) | 932.5 | 952.2 | 445.0 | 452.8 | 576.4 | 445.0 | 452.5 | 55.0 |

for these carbonaceous impurities could be due to the presence of the chemically attached ethylene glycol molecules to the surface of the particles.

TGA and DSC were additional characterization methods by which the as-prepared products were studied. For both compounds very small decreases in weight are observed (<1%) in the 100−250 °C temperature range. This weight loss is attributed to the vaporization of the adsorbed carbonaceous species from the nanoparticles surface. To verify this suggestion we have carried out an elemental analysis study of carbon and hydrogen. It was found that the level of carbon and hydrogen impurities after the annealing for both compounds is less than 1%. This result proves our suggestion that the drop in weight in TGA is due

**Scheme 1.** Possible Mechanism for the Formation of $CuInTe_2$ and $CuInSe_2$ Nanoparticles



to the evaporation of organic molecules from the surface. The TPD (temperature-programmed desorption) analysis is conducted simultaneously with TGA measurements and reveals that the organic species desorbed from the surface of the nanoparticles are low molecular weight oligomers of ethylene glycol. The fact that this species is not washed out after an extensive washing procedure could suggest that these oligomers are chemically connected (chemisorbed) to the surface of the nanoparticles. This result confirms the XPS findings that the surface of the nanoparticles is modified by the chemically attached ethylene glycol moieties.

The photoacoustic spectra (PAS)[25] of CIS and CIT are shown in Figure 4a,b, respectively. The band gap for CIT was found to be 1.047 eV (1184.2 nm). This result shows that the as-prepared CIT is a semiconductor, and the measured band gap is close to the value of the bulk band gap measured by others (approximately 1 eV).[3] No blue shift due to size quantization is observed because of the relatively big diameter of the particles. The band gap measured for CIS (Figure 4a) is 1.06 eV (thin films of CIS have a band gap in the range 1.02−1.04 eV).[6c,26]

**Reaction Mechanism**. The main question regarding the preparation of $CuInTe_2$ and $CuInSe_2$ is the mechanism of their formation. In our previous work, we developed a simple method for the synthesis of nanosized binary chalcogenides (tellurides or selenides).[17,19] Binary chalcogenides were prepared via a glycol solution (such as ethylene glycol), the reactants being a metallic ion and the elemental chalcogenide. We proposed a two-step mechanism for this reaction, where the first step is the reduction of the metallic ion to the corresponding metallic state. This hypothesis is based on the observation that, in the absence of the elemental chalcogenide, pure metallic material is obtained. For irreducible metals such as Ti, no binary chalcogenide could be obtained. In the second step, these small metallic particles continue to absorb microwave radiation, and reduce the elemental chalcogenide to the binary compound. We call this reaction "wet solid-state reactions". The fact that the reduced metallic particles could react under microwave irradiation with chalcogenide led us to add another metallic element (that cannot be reduced by ethylene glycol) to the reaction mixture to form a ternary chalcogenide compound. To confirm this hypothesis we added an additional metallic element, indium. In this ternary system, copper(I) could easily be reduced, unlike all our attempts to reduce indium salts under the reaction condition, which were unsuccessful. This makes indium an ideal candidate for such a study. Thus, the $Cu^+$/In/Se system or Te resulted in CIS or CIT. These results give us partial confirmation of our hypothesis that the "wet

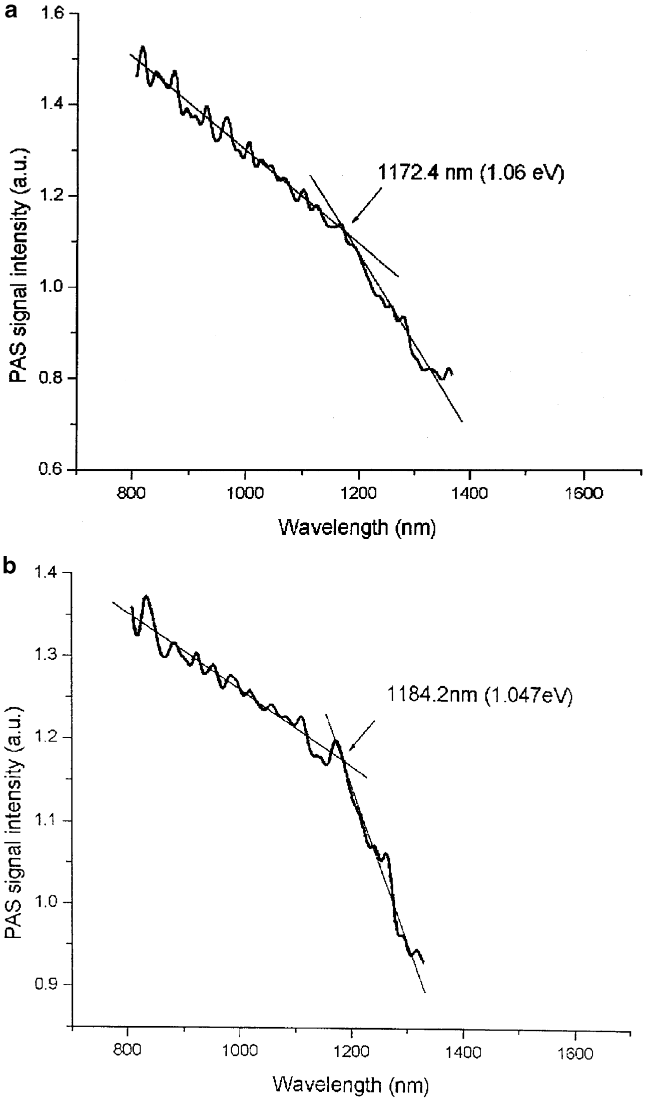


**Figure 4.** (a) Photoacoustic measurement of the as-prepared $CuInSe_2$ (energy gap $E_g = 1.06$ eV, 1172.4 nm). (b) Photoacoustic measurement of the as-prepared $CuInTe_2$ (energy gap $E_g = 1.047$ eV, 1184.2 nm).

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(25) The photoacoustic method consists of illuminating the sample with chopped monochromatic light in an airtight cell connected to a microphone. The light is absorbed and converted to heat. The chopped heat then flows to the surface of the sample where it produces an acoustic wave. The wave is detected with a lock-in voltmeter. The signal, which is acquired as a function of wavelength, is normalized against the absorption of carbon black powder, a 100% absorber. The instrument operates over the wavelength region 300−1600 nm. The spectrum is independent of the nature of the sample unlike reflectance spectroscopy, where the nature of the surface can have a marked effect on the spectrum. The photoacoustic spectra show features that are much better resolved than in the absorption spectra.

(26) Neelkanth, G.; Dhere, M.; Lourenco, C.; Ramesh, G. *Sol. Cells* **1984**, *13*, 59.

solid-state reaction" mechanism is fulfilled also for ternary compounds. A control experiment, where metallic copper powder, $In^{3+}$ salt, and Se (or Te) were reacted ($Cu/In^{3+}/Se$ or Te), did not result in the ternary chalcogenides (instead binary copper selenide was obtained). These experiments prove the applicability of the "wet solid-state" microwave reactions mechanism, for the ternary compound also (see Scheme 1).

## Conclusions

Nanoparticles of $CuInTe_2$ and $CuInSe_2$ are prepared for the first time using a microwave-assisted polyol method. These reactions required cheap and simple precursors and lasted only 1 h. The polyol solvents acted as both the solvents and the reducing agents. The products are characterized by different analytical techniques, and the electronic properties are measured using the photoacoustic method. The mechanism of the reactions is proposed.

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