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Preparation of $Cd_{1-x}Zn_xSe$ Using Microwave-Assisted Polyol Synthesis

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Selenides of the late transition metals are a class of solid-state materials that have attracted much interest recently, due to their intriguing semiconducting and optical properties. Applications of these materials include nonlinear optical detectors, photovoltaic solar cells, and laser screen materials.[1−3] Cd−Zn−Se is especially important because of the possibility of tuning its electronic properties by changing the Cd:Zn ratio.[4]

Various techniques were developed in order to synthesize selenides. Originally, chalcogenides were prepared by simple combination of the elements followed by heating to high temperatures for a prolonged period of time (in the standard procedure, alloy was obtained after heating for 24 h at 1273 K).[5,6] H_2Se has been used as a reagent, but its use is undesirable due to its extreme toxicity.[7] Thin films of these materials have been synthesized using vacuum techniques. The main disadvantage of vacuum techniques is the high cost of equipment and precursors.[8] Another very promising method uses Zintl ions of nominal composition A_2Se_n, where "A" is an alkali metal and the Se_n^{-2} is the Se source.[9] Recently, a solventothermal method has been described for their preparation.[10] Many new Se-containing phases have been synthesized at moderate pressure and temperatures, using different amines (especially ethylenediamine) as solvents. The solventothermal method requires relatively high pressures and prolonged heating to obtain the desired product, and in many cases, incorporation of amine into the resulting product was detected.

Solid-state synthesis by microwave heating is a relatively new and promising technique,[11,12] whose applications have been growing due to the unique reaction effects which microwave irradiation produces, such as rapid volumetric heating and the consequent increase in reaction rates. Recently, microwave heating was applied in the solution to the synthesis of binary chalcagonides nanoparticles.[13]

The current paper documents the extension of this method to the preparation of a ternary selenide. The synthesis of $Cd_{1-x}Zn_xSe$ with a composition of $x = 0.2$ using a microwave-assisted, pressureless solventothermal reaction is described, and the optical, thermal, and morphological properties of the product are presented.

In our experiments, all reagents were of the highest commercially available purity. Elemental Se, Cadmium acetate, Zinc acetate, and ethylene glycol were all purchased from Aldrich Co. and used without further purification. The X-ray diffraction patterns of the products were recorded by employing a Bruker AXS D8 Advance Powder X-ray Diffractometer (using Cu Kα $\lambda = 1.5418$ Å radiation). EDX measurements were made using an X-ray microanalyzer (Oxford scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). The transmission electron micrographs (TEM) were obtained with a JEOL-JEM 100SX microscope, working at a 100 kV accelerating voltage. High-Resolution TEM (HRTEM) images were taken on a JEOL-3010, at 300 kV. A conventional CCD camera, with a spatial resolution of 768×512 pixels, was used to digitize the micrographs. The digital images were processed using Digital Micrograph software. HRTEM image analysis and electron diffraction indexing were performed using an EMS package.[14] Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film. The grid was then air dried.

The electronic properties of the as-prepared and annealed materials are measured by photoacoustic spectroscopy (PAS). Photoacoustic measurements were conducted employing a home-made instrument, which has been described elsewhere.[15] The band gap is calculated by the "knee" method for both samples.[16]

Microwave assisted reactions were conducted in a Spectra-900 W microwave oven, with a 2.45 GHz working frequency. The oven was modified to include a refluxing system. In all experiments, the microwave oven was cycled as follows: on for 21 s, off for 9 s, with total power always at 900 W. This cycling mode was chosen in order to reduce the risk of superheating the solvent. All reactions were conducted under a flow of nitrogen.

Microwave Synthesis: zinc acetate (0.044 g) and cadmium acetate (0.213 g) were dissolved in 50 mL of basic ethylene glycol (pH = 10, pH adjustment is made with NaOH) by gentle heating using the cycling mode for approximately 1 min. Then, stoichiometric quantities of Se powder (0.079 g) were added. The system was purged for few minutes with nitrogen, and then the microwave oven was cycled as described above for 1 h. In the postreaction treatment, the product was centrifuged at 9 000 rpm once with the mother liquid, to separate the powder from the liquid. It was then washed few times with EtOH, at 20 °C and 9000 rpm. The product was then dried overnight under vacuum. The samples were annealed under nitrogen for 12 h at 550 °C.

The XRD patterns of the as-prepared and annealed products are shown in Figure 1a and b, respectively. For both cases, the resulting alloy is formed in the hexagonal (wurtzite) phase with lattice parameters $a = 4.273$ and $c = 6.962$ Å. These parameters are in agreement with previously published data regarding hexagonal $Cd_{1-x}Zn_xSe$ with $x < 0.4$ (2H).[5,17] The peaks of the XRD patterns of the as-prepared compound are broad, suggesting the formation of ultrafine particles. Particles size calculations employing the Scherrer equation yielded an average particle size of 5.8 nm.[18] For the annealed samples, an average size of 40 nm was calculated.

The morphology of the resulting nanoparticles was studied with TEM (see Figure 2). Poorly aggregated spherical particles are observed, with an average diameter of 6 ± 2 nm (100 particles

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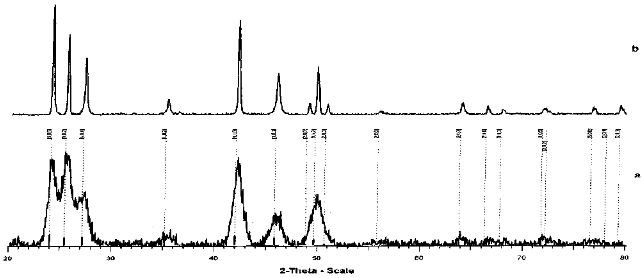

Figure 1. The XRD patterns: (a) the as-prepared and (b) annealed hexagonal $Cd_{0.8}Zn_{0.2}Se$ prepared in basic ethylene glycol.

Figure 2. The TEM picture of hexagonal $Cd_{0.8}Zn_{0.2}Se$ spheres. (Bar equals 16 nm).

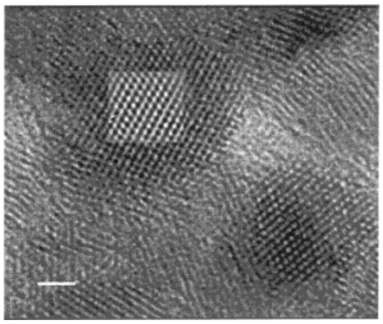

Figure 3. The HRTEM image of a hexagonal $Cd_{0.8}Zn_{0.2}Se$ nanoparticle (bar equals 15.7 Å); inset is an FFT filtered image of the lattice.

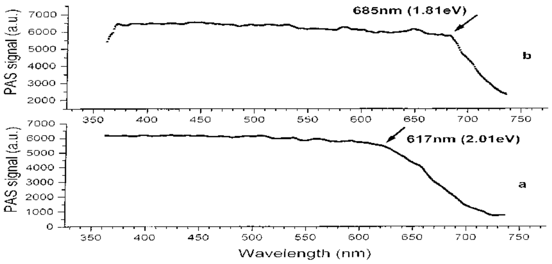

Figure 4. The Photoacoustic measurements of (a) the as-prepared $Cd_{0.8}Zn_{0.2}Se$ ($E_g = 2.01$ eV, 617 nm); (b) heated sample ($E_g = 1.81$ eV, 685 nm).

measured). This result is in agreement with the Scherrer XRD calculation. Electron diffraction patterns of the as-prepared alloy (data not shown) also demonstrate that the product is formed during the hexagonal (CdSe) polycrystalline phase. Both the annealed and as-prepared samples showed no aggregation.

An HR-TEM micrograph of the as-prepared product is shown in Figure 3. These micrographs confirm an average diameter of 5−7 nm. They point to the high crystallinity of the as-prepared material, which might be considered "nano-single crystals".

All of the observed particles were spherical. Since all of the particles are randomly oriented, every particle has a different zone axis. The particles contained in the rectangular area (see Figure 3) are oriented in the [101] zone axis. In this case, the interplanar distance equals 3.128 ± 0.083 Å, which is in agreement with published values for $Cd_{1-x}Zn_xSe$.[5,19,20]

The PAS spectra of the as-prepared and annealed samples are shown in Figure 4. Arrows on Figure 4 mark the energy of the band gap. The absorption edge of the as-prepared compound (2.01 ± 0.023 eV − 617 nm) is blue-shifted relative to the annealed sample (1.81 ± 0.023 eV − 685 nm). This blue shift is due to the smaller size of the as-prepared materials. The stoichiometry of $Cd_{1-x}Zn_xSe$ alloys can be calculated based on the linear relationship between the band gap energy and x. If the composition is accurately known, it can serve for the determination of the band gap.[21] However, this relationship is found to be based on the study of bulk materials. The involvement of nanosized particles and the blue shifts they cause complicate the use of this relationship for the determination of x. Therefore, the stoichiometry was determined with EDS measurements. The exact composition of the as-prepared alloy is found to be $Cd_{0.85}Zn_{0.15}Se$. For this composition, the calculated bulk band gap is 1.82 eV. This value determines that the observed blue shift is 0.19 eV, which is close to the 0.20 eV blue shift observed for nanoparticles of hexagonal CdSe.[22] The polyol method was previously applied to the synthesis of binary selenides using microwave heating. Normally, metal acetates such as Cd^{2+},[22,23] Pb^{2+}, Hg^{2+}, and Cu^{2+} [13] are reduced to the corresponding metals when selenium is not present in the ethylene glycol solution. However, in neutral solution, Zn^{2+} is not reduced to metallic Zn. Instead, ZnO is formed. In a basic polyol solution, Zn^{2+} was found to react with Se to form ZnSe. For this reason, Cd−Zn−Se was prepared in a basic polyol solution.

The probable mechanism for this reaction is a simultaneous reduction by the polyol of the Cd and Zn ions to the metallic clusters, which subsequently react by "solid-state microwave assisted solution reactions" with Se to form $Cd_{1-x}Zn_xSe$ alloys. Since we have never observed the formation of a pure phase of ZnSe, the first step in the proposed mechanism is probably the reduction of the ions and the formation of Cd and Zn metals. The mechanism of this reaction is still under study.

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