

THERMAL BEHAVIOR OF NANOCRYSTALLINE CADMIUM SELENIDES AND TELLURIDES

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Pseudobinary chalcogenides with the general formula $\text{CdSe}_x\text{Te}_{1-x}$ exhibit useful physical, chemical and semiconducting properties, which make them promising materials for applications in modern technology. In this article we present a simple and novel method for the preparation of nanocrystalline pseudobinary chalcogenides with the formula $\text{CdSe}_x\text{Te}_{1-x}$ ($x = 0.1$ and $x = 0.6$) by the solvothermal method from elemental precursors in ethylenediamine followed by heating on air or in nitrogen atmosphere. Preparing pseudobinary nanosized $\text{CdSe}_x\text{Te}_{1-x}$ from binary chalcogenides CdSe and CdTe without solution was not reported yet. By heating the as – prepared mixture of binary chalcogenides to 500 °C, nanosized $\text{CdSe}_{0.1}\text{Te}_{0.9}$ was prepared while at higher temperatures and prolonged heating times, the product was $\text{CdSe}_{0.6}\text{Te}_{0.4}$. The products were characterized by X-ray powder diffraction (XRD) and thermal analysis (TGA). The route employed in the present work is simple and controllable and could be used in preparing further semiconducting mixed metal chalcogenides.

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1. Introduction

Nanocrystalline cadmium chalcogenides have recently attracted much interest due to their unique thermoelectric, semiconducting and optical properties. It is known that semiconducting tellurides have already found applications as sensors or laser materials, optical filters, solar cells and in many other devices [1, 2]. Among these materials, cadmium telluride is particularly interesting due to its high photosensitivity [3], which makes it an excellent n-type window material in hetero-junction solar cells CdS/CdTe with efficiencies over 16% [4, 5]. The mixed pseudobinary compounds $\text{CdSe}_x\text{Te}_{1-x}$ are also a group of promising semiconductor material used for various applications like solar cells, photoconductors, thin film transistors etc. It has been reported that in these compounds, the band gap can be tuned between 1.0 and 1.7 eV by changing the value of x [6]. To date, research into pseudobinary ($\text{AB}_x\text{C}_{1-x}$) semiconductor nanocrystals has been limited [7]. An early method for the preparation of $\text{CdSe}_x\text{Te}_{1-x}$ by sintering mixtures of CdSe and CdTe has been reported [8], but like in most high – temperature methods, the size control is difficult. Most method used to prepare nanosized $\text{CdSe}_x\text{Te}_{1-x}$ use complex procedures, sophisticated equipment or rigid experimental conditions.

Murali et al. report the synthesis of $\text{CdSe}_x\text{Te}_{1-x}$ ($0 \leq x \leq 1$) with band gap values from 1.49 to 1.65 eV by the reaction of CdO with Se and Te in an aqueous oxalic acid solution [9] while Bailey and Nie reported a simple protocol to synthesize cadmium selenide telluride semiconductor quantum dots with different Se :

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Te molar ratios from CdO, Se and Te in a mixed hexadecylamine (HAD) / tri-n-octylphosphine oxide (TOPO) solvent [10]. The obtained products showed excellent NIR-emitting properties and broad absorption spectra coverage. Recently, Liang et al. prepared near – infrared emitting CdSeTe alloyed quantum dots capped with cysteine from cadmium chloride, selenium and tellurium powder through the incorporation of Se into CdTe nanocrystals in oxygen – free water under nitrogen [11] and studied their application for ultrasensitive Cu²⁺ sensing [12]. Most recently, Sathyamoorthy et al. prepared CdSe_xTe_{1-x} nanocrystals by a facile hydrothermal synthesis at relatively low temperatures [13]. In the present work, an attempt has been made to synthesize cadmium selenides, tellurides and ternary selenides/tellurides from elemental precursors by a simple solvothermal reaction followed by controlled heating of the obtained powders and to study the thermal behavior of the prepared nanoparticles.

2. Experimental

CdSe_xTe_{1-x} nanoparticles of different composition have been synthesized by a direct solvothermal reaction of high purity elemental cadmium (Cd, metals basis 100 mesh, 99.5%), selenium (Se, powder 100 mesh, 99.5%) and tellurium (Te, powder 200 mesh, 99.8%), all purchased from Aldrich, in ethylenediamine (p.a. 99%, Zorka Šabac).

In a typical procedure, 0.4593 g (= 4 mmol) of cadmium, 0.1616 g (= 2 mmol) of selenium and 0.2625 g (= 2 mmol) of tellurium were added to 100 ml of ethylenediamine (EDA) in a mixing Parr autoclave and maintained at 200 °C for 20 h with stirring during the heating period and then allowed to cool to room temperature. A black precipitate solution was collected, than centrifuged for 5 min at 7000 rpm and washed twice with distilled water and once with absolute ethanol to pH= 7. The black product was dried at 80 °C for 24 hours, cooled to room temperature and, after taking samples for X-ray diffraction analysis, heated up to 300, 500 and 600 °C for one and two hours on air and in nitrogen gas flow 100 ml/min.

In a control experiment, CdSe (99.99%, electronic grade, 10 μm) and CdTe (99.99%, metals basis, < 250 μm) produced by Aldrich, mixed in ratio 1:1, were also investigated and compared to particles prepared by the solvothermal synthesis.

The products were characterized with an AXS-Bruker/Siemens model D5005 X-ray powder diffractometer (XRD) equipped with a CuKα radiation source and a graphite monochromator (λ= 1.54178 Å). Thermal analyses (TGA/SDTA) were performed on a on a *Mettler Toledo TGA 851^e* system in static air and a nitrogen atmosphere (100 ml/min), both with a heating rate of 10K/min.

3. Results and discussion

The solvothermal reaction of Cd metal powder with elemental Se and Te was used to produce CdSe_xTe_{1-x} nanoparticles. Solvent and reaction temperature played a crucial role in controlling the nucleation and growth of binary nanoparticles CdE (E= Se, Te) in autoclave reactor.

Selenium is generally described as insoluble in handbooks and texts. Some studies of solubility of selenium under solvothermal conditions in organic solvents reported that a solution of selenium in ethylenediamine can be a useful selenium feedstock [14]. It is well known that ethylenediamine can chelate many metal cations, and even some anions as Se²⁻ and Te²⁻, to form polynuclear complexes with a simple chain fragment, furthermore, it is reduced under some conditions [15, 16, 17, 18].

Previous studies of binary quantum dots and bulk semiconductors have found that CdSe and CdTe nanocrystals can be prepared under similar conditions [19, 20]. Recent research indicates that elemental tellurium is considerably more reactive than selenium toward cadmium under rapid nucleation and growth conditions. Because of this difference in reactivity, the CdTe growth rate is approximately two times that of CdSe [10]. Therefore we expected in preparation of ternary chalcogenides CdSe_xTe_{1-x} from binary chalcogenides higher part of tellurium than selenium in CdSe_xTe_{1-x}.

The X- ray powder diffraction pattern in Fig. 1 shows that the products obtained by solvothermal reaction are binary chalcogenides in nanometer scale: cubic and hexagonal crystalline modifications of CdSe as well as CdTe and some unreacted cadmium. The average size of the nanoparticles was calculated using the Debye- Scherrer formula:

$$d_x = \frac{0,94 \cdot \lambda \cdot 57,3}{\beta \cdot \cos \theta} \quad (1)$$

Here, λ is the wavelength of the X – ray radiation, β the full – width at half – maximum (FWHM) of the corresponding peak and θ is the diffraction angle. The average size of cubic (c) CdSe was 13.2 nm, hexagonal (h) CdSe 35.0 nm and CdTe 25.6 nm.

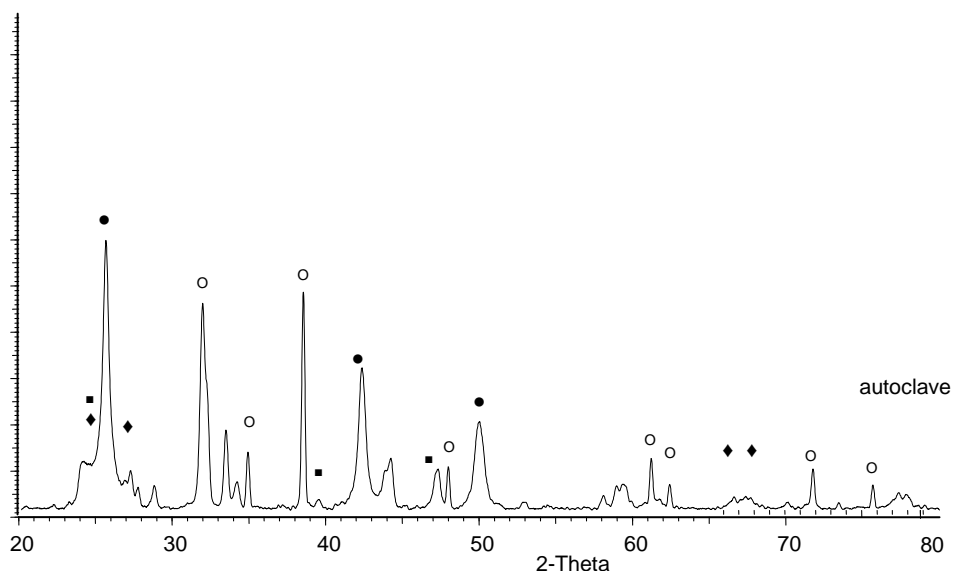


Fig. 1: X- ray diffraction pattern of solvothermally prepared CdSe and CdTe (■ CdTe, ● cubic CdSe, ◆ hexagonal CdSe, ○ Cd)

Binary chalcogenides are results of following reactions:



Where the E are chalcogene elements (E = Se, Te) and EDA is ethylenediamine. By heating the solvothermally prepared mixture of binary chalcogenides up to 600 °C in air or nitrogen flow we prepared ternary chalcogenides by the reaction:



The X-ray powder diffraction patterns of the ternary compound $\text{CdSe}_{0.1}\text{Te}_{0.9}$, synthesized by heating of the as – prepared mixture of the binary chalcogenides to 500 and 600 °C in air, are shown in Fig. 2. The strongest peaks can be classified as the (111), (220) and (311) reflections of cubic $\text{CdSe}_{0.1}\text{Te}_{0.9}$. The broadening of the peaks indicates that the particles are on the nanometer scale. The calculated particle size, calculated using the average of the (220) and (311) peaks, is 11.5 nm for $\text{CdSe}_{0.1}\text{Te}_{0.9}$ obtained at 500 °C and 20.1 nm for the product heated to 600 °C.

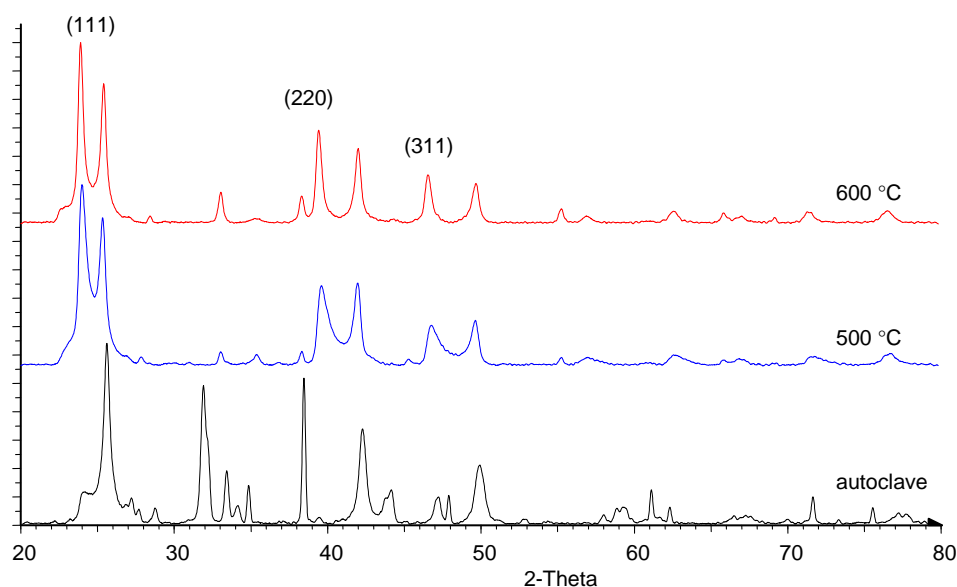


Fig. 2: X- ray diffraction pattern of prepared $\text{CdSe}_{0.1}\text{Te}_{0.9}$ at 500 and 600 °C

Fig. 3 shows the X-ray powder diffraction patterns of the ternary compound $\text{CdSe}_{0.6}\text{Te}_{0.4}$, obtained by heating the solvothermally prepared $\text{CdSe} / \text{CdTe}$ mixture at 500 °C for 2h and at 600 °C for 1h in air. The patterns correspond to (100), (002) and (110) peaks of hexagonal $\text{CdSe}_{0.6}\text{Te}_{0.4}$.

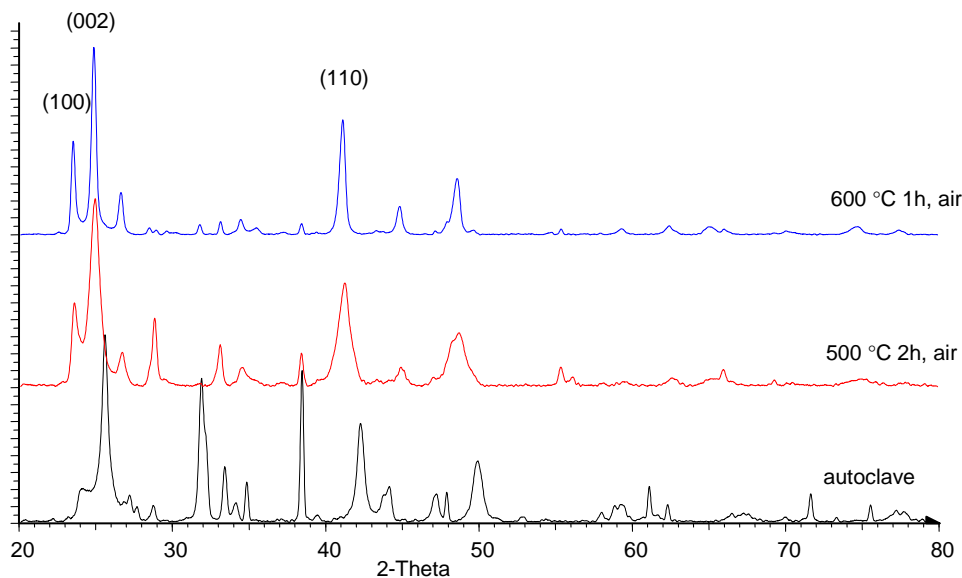


Fig. 3: X- ray diffraction pattern of as - prepared CdSe and CdTe and CdSe_{0.6}Te_{0.4} prepared by isothermal heating

Fig. 4 shows the X- ray powder diffraction patterns of CdSe_{0.6}Te_{0.4}, obtained by heating the solvothermally prepared mixture at 600 °C 1h on air and at 600 °C for 1h and 2h in nitrogen atmosphere. The broadening of the peaks in Fig. 4 indicates that the prepared particles heated on 600 °C for 1h in N₂ atmosphere are smaller (7.3 nm) than particles prepared on 600 °C for 1h in air (19.8 nm), that was also proved by calculations with Debye- Scherrer formula.

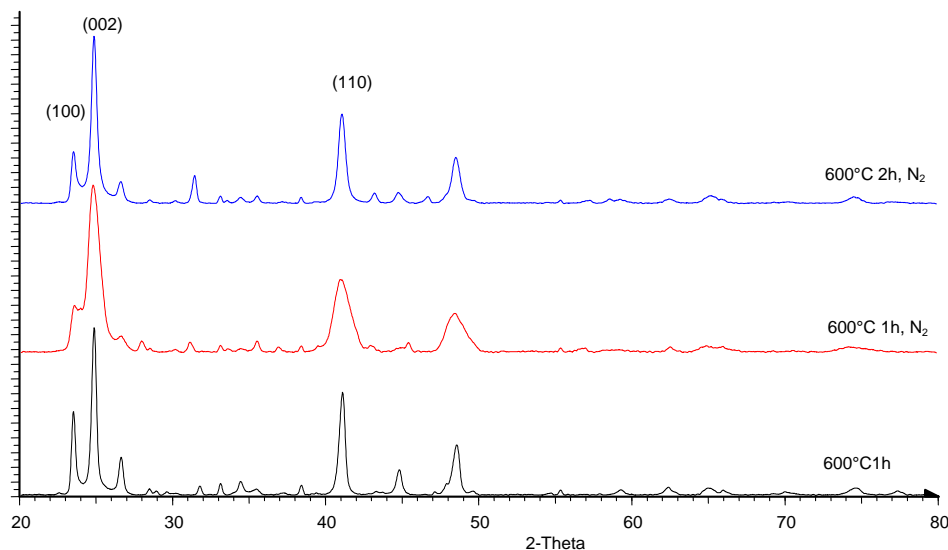


Fig. 4: X- ray diffraction patterns of CdSe_{0.6}Te_{0.4}, prepared by heating at 600 °C 1h on air (lowest) and heated at 600 °C 1h and 2h in N₂ atmosphere

It can be seen that nitrogen atmosphere affects the size of the CdSe_xTe_{1-x} nanoparticles at the same conditions. Nitrogen atmosphere reduces the size of the prepared particles, to the size of quantum dots in our case. The results obtained by calculations with Debye- Scherrer formula also indicate that prolonged heating times cause the growth of the prepared nanoparticles: particles prepared by heating on 600 °C 1h in N₂ atmosphere are substantially smaller (7.3 nm) than particles prepared on 600 °C 2h in N₂ atmosphere (16.5 nm). The average particle size of the products obtained after different temperature conditions is given in Table 1.

Table 1: Average particles size calculated with the Debye- Scherrer formula from the characteristic peaks for each material

preparation	product	particle size (nm)
Autoclave	1. CdSe (c)	$d_1= 13.2$
	2. CdSe (h)	$d_2= 35.0$
	3. CdTe	$d_3= 25.7$
500 air	$\text{CdSe}_{0.1}\text{Te}_{0.9}$	$d= 11.5$
600 air	$\text{CdSe}_{0.1}\text{Te}_{0.9}$	$d= 20.1$
500 1h air	$\text{CdSe}_{0.6}\text{Te}_{0.4}$	$d= 6.4$
500 2h air	$\text{CdSe}_{0.6}\text{Te}_{0.4}$	$d= 10.3$
600 1h air	$\text{CdSe}_{0.6}\text{Te}_{0.4}$	$d= 19.8$
600 1h N_2	$\text{CdSe}_{0.6}\text{Te}_{0.4}$	$d= 7.3$
600 2h N_2	$\text{CdSe}_{0.6}\text{Te}_{0.4}$	$d= 16.5$

Thermal analysis

The thermogravimetric curve, obtained by heating the as-prepared product in nitrogen flow (30 – 600 °C, 10 °C/min + 60 min isothermally), is shown in Fig. 5. The small mass loss between 30 and 120 °C ($\Delta m = 0.3\%$) can be attributed to traces of absorbed water. In the second step between 120 and 410 °C, the measured mass loss is 2.6%. It should be mentioned that XRD analyses of the products obtained by heating to 300 and 400 °C still show only the presence of binary chalcogenides, CdSe and CdTe. The fastest mass loss can be observed in the range between 410 and 530 °C ($\Delta m = 9.0\%$), followed by a mass loss of 1.8% up to 600 °C. In this temperature range, ternary cadmium chalcogenides start forming from the binary mixture. By isothermal heating for 1 h at 600 °C, further 1.7% of the initial mass was lost.

In a control experiment, the thermal behaviour of a mixture of commercially available CdSe and CdTe (both purchased by Aldrich) mixed in molar ratio 1:1 was also investigated by TG measurements and XRD analyses of intermediates and compared to particles synthesized by the solvothermal reaction. The mixture of binary chalcogenides requires higher temperature and longer reaction times to form pseudobinary chalcogenides $\text{CdSe}_x\text{Te}_{1-x}$ than solvothermal prepared binary particles. $\text{CdSe}_{0.1}\text{Te}_{0.9}$ particles start to form by heating at 600 °C for 2h, while $\text{CdSe}_{0.6}\text{Te}_{0.4}$ starts to form by heating at 700 °C for 2h and more. The particle sizes of $\text{CdSe}_x\text{Te}_{1-x}$ particles synthesized in this way are substantially bigger compared to products obtained from our solvothermally synthesized CdSe and CdTe nanoparticles. At 500 °C and 600 °C without isothermal heating, only the starting mixture of binary chalcogenides could be observed in this case. We believe that higher temperatures and prolonged times needed to form pseudobinary chalcogenides from commercially available bulk CdSe and CdTe are the result of bigger particle size compared to solvothermally synthesized nanoparticles.

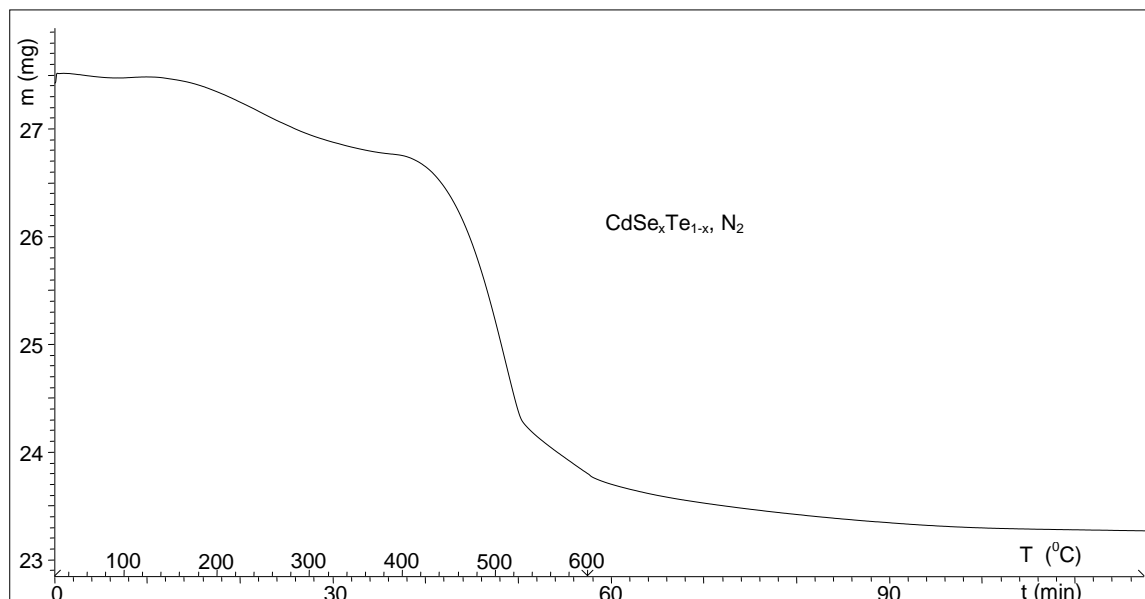


Fig. 5: Thermal behaviour of the as-prepared ternary cadmium chalcogenides

4. Conclusion

CdSe and CdTe nanoparticles have been successfully prepared via the solvothermal reaction from high purity elemental cadmium, selenium and tellurium in ethylenediamine in autoclave reactor. The as – prepared mixture of nanosized CdSe and CdTe was heated on air and in nitrogen atmosphere to form $\text{CdSe}_x\text{Te}_{1-x}$ with different compositions ratios ($x = 0.1$ and $x = 0.6$). The smallest prepared ternary chalcogenide particles were the size of quantum dots (6.4 nm). In a control experiment a mixture of commercially available CdSe and CdTe was also investigated. The heating temperature, time and atmosphere played a crucial role in controlling the nucleation and growth of ternary nanoparticles. Particles heated to 500 °C form ternary chalcogenides with a higher part of tellurium than selenium, $\text{CdSe}_{0.1}\text{Te}_{0.9}$. With prolonged time of heating ternary chalcogenides with the composition $\text{CdSe}_{0.6}\text{Te}_{0.4}$ were prepared. Using nitrogen atmosphere reduces the particle size of ternary chalcogenides compared to particles heated in air. Thermal analysis shows that pseudobinary $\text{CdSe}_x\text{Te}_{1-x}$ chalcogenides start to form at 440 °C using particles sintesized in autoclave, while the synthesis from a mixture of commercially available binary chalcogenides requires higher temperatures and prolonged time of heating, yielding products with bigger particle size.

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