

## PREPARATION AND CHARACTERIZATION OF TERNARY CADMIUM CHALCOGENIDES

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Ternary cadmium chalcogenides were prepared using different methods: hydrothermal, microwave, and sonochemical synthesis in ethylenediamine (en) and different en/water solutions, as well as by direct reactions of elemental precursors and binary cadmium chalcogenides. The obtained ternary nanoparticles CdSe<sub>x</sub>Te<sub>1-x</sub> ( $x = 0.1$  and  $x = 0.6$ ) were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The formation and transformation of ternary phases was studied by thermal analysis (TGA). The as-prepared chalcogenides were nanosized with different shapes and crystallite sizes between 6 and 35 nm, depending on the preparation method.

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### 1. Introduction

Semiconductor materials such as CdSe, CdTe, and CdSe<sub>x</sub>Te<sub>1-x</sub> are the bases of modern electronic devices. Miniaturizations of electronic functional elements to nanolevel face physical limitations regarding the resolution of lithographic processes, and significant changes in electronic, magnetic, optical, and other characteristic properties when compared to bulk materials [1]. It is already known that semiconducting tellurides have found applications as sensors or laser materials, optical filters, solar cells, and in many other devices [2, 3]. The high photosensitivity [4] and near optimum band gap [5] of 1.45 eV make CdTe an excellent *n*-type window material in the hetero-junction solar cells CdS/CdTe with efficiencies over 16% [6, 7]. The pseudobinary compounds CdSe<sub>x</sub>Te<sub>1-x</sub> are also a group of promising materials, which have received considerable attention due to its applications in the production of solar cells, semiconductor-metal Schottky barrier cells [5], solar coatings on buildings in warm climates [8], etc. It has been reported that electronic and optical properties of CdSe<sub>x</sub>Te<sub>1-x</sub> can be tuned between 1.3 and 1.7 eV by changing the value of *x*, leading to a decrease in the band gap energy by increasing the Te content [9].

Until now, most investigations have focused on the synthesis, size control, compositions, and structures of binary metal chalcogenides. It is well known that the method of synthesis plays a crucial role in shaping the prepared nanoparticles, and that the state of its surface determines the properties of nanoparticle. Murray et al. reported a high – temperature organometallic route for the synthesis of CdSe nanoparticles based on the high – temperature nucleation and growth of nanoparticles from

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organometallic precursors [10]. Such prepared semiconductor nanoparticles were in different shapes like nanodots, nanorods, and tetrapods, depending on the precursors and surfactants the authors used [11, 12]. Wang et al. also synthesized a variety of MSe ( $M = \text{Zn, Cd}$ ) nanorods in ethylenediamine [13]. Other authors used different methods for preparing semiconductor nanoparticles (CdSe) like single – source precursors, micellar methods, catalytic – growth approach, and template methods. Solvothermal methods include the crystallizing of substances from high-temperature solutions of suitable precursors, which are added into a solvent, capable of regulating crystal growth, at different ratios. The mixture is then placed in an autoclave reactor and maintained at elevated temperatures and pressures to form nanoparticles. By using this method, nanosized cadmium chalcogenides of various morphologies were synthesized [14–19].

This paper presents the preparation and characterization of the nanosized ternary chalcogenides  $\text{CdSe}_x\text{Te}_{1-x}$  ( $x = 0.1$  and  $x = 0.6$ ). Ternary chalcogenides were prepared from elemental Cd, Se, and Te using the solvent ethylenediamine (en) using the solvothermal method in the autoclave reactor, microwave synthesis, and by the sonochemical method in the Suslick cell.  $\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles of different compositions were also synthesized by the direct reactions of high-purity elemental cadmium, selenium, and tellurium, as well as from CdSe and CdTe, heated in air or within a  $\text{N}_2$  atmosphere. This method for the preparation of binary or ternary semiconductor nanoparticles without solvent has been, to the best of our knowledge, not reported as yet.

## 2. Experimental

$\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles of different compositions were synthesized by the direct 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. 0.4593 g (= 4 mmol) of cadmium, 0.1616 g (= 2 mmol) of selenium and 0.2625 g (= 2 mmol) of tellurium were thoroughly mixed together and small amounts of the mixture heated up to 600 or 700 °C in a *Mettler Toledo TGA 851<sup>e</sup>* system, by applying a heating rate of 10K/min, in static air and within a nitrogen atmosphere (100 ml/min), followed by isothermal heating for one or two hours.

CdSe (99.99%, electronic grade, 10  $\mu\text{m}$ ) and CdTe (99.99%, metals basis, < 250  $\mu\text{m}$ ) produced by Aldrich, mixed at a ratio of 1:1, were also heated as described above, and the as-obtained products were compared to particles prepared by the direct reactions of elemental precursors.

Solvothermal reactions were carried out within a Parr mixing autoclave reactor (PARR 5500 Series Compact Reactor), whilst the microwave reactions were performed in a CEM Discover SP Microwave oven, and the sonochemical synthesis was carried out using a Sonics & Materials VCX 750 sonicator with a direct immersion Ti horn. Elemental feedstock solutions were prepared from 0.4593 g (= 4 mmol) of cadmium, 0.1616 g (= 2 mmol) of selenium and 0.2625 g (= 2 mmol) of tellurium added to 100 ml of different diamines: 1,2 ethylenediamine (p.a. 99%, Sigma Aldrich), 1,4 diaminobutane (99%) and 1,8 diaminoctane (98%) purchased from Acros Organics. Elemental feedstock solutions prepared in 100 ml of ethylenediamine (en) and different en/water solutions were maintained within the autoclave reactor for 20 h at 200 °C with stirring during the heating period and then allowed to cool to room temperature. During the microwave procedure, 6 to 8 ml of prepared elemental feedstock solutions in en, 1,4 diaminobutane, 1,8 diaminoctane and en/water solutions at different volume ratios, were heated at 200 °C for 15 and 30 min within the microwave oven at 200 W. In the sonochemical procedure, 15 ml of the prepared elemental feedstock solutions in en were sonicated in the Suslick cell for 15, 30 and 60 min at 70% amplitude of 750W. All reaction conditions and times for each of the preparation reactions had been predefined during exploratory research experiments.

In all cases, black precipitates were obtained, centrifuged for 5 min at 7000 rpm and washed with distilled water to pH = 7, and then with absolute ethanol. 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 500, 600 and 700 °C for one and two hours in air and in nitrogen with a flow of 100 ml/min.

The products were characterized using an AXS-Bruker/Siemens model D5005 X-ray powder diffractometer (XRD) equipped with a CuK $\alpha$  radiation source and a graphite monochromator ( $\lambda=1.54178$  Å). Thermal analyses (TGA/SDTA) were performed on a on a *Mettler Toledo TGA 851<sup>e</sup>* system in static air, and within a nitrogen atmosphere (100 ml/min), both with a heating rate of 10K/min. The morphologies and sizes of the products were observed by transmission electron microscopy (TEM). The thermionic electron-source TEM (JEOL 2100) was operated at 200 kV. For the TEM investigation the nanoparticles were deposited on a copper-grid-supported perforated transparent carbon foil.

### 3. Results and discussion

The solvothermal reaction of Cd metal powder with elemental Se and Te was used to produce CdSe<sub>x</sub>Te<sub>1-x</sub> nanoparticles. Solvent and reaction temperatures played a crucial role in controlling the nucleation and growth of binary CdE (E= Se, Te) and ternary CdSe<sub>x</sub>Te<sub>1-x</sub> ( $x = 0.1$  and  $x = 0.6$ ) nanoparticles within the autoclave reactor. The X- ray powder diffraction patterns in Fig. 1 show that the products obtained by the sovothermal reaction in en were binary chalcogenides of nanometer scale: cubic and hexagonal crystalline modifications of CdSe, as well as CdTe and some unreacted cadmium. The crystallite size of the nanoparticles ( $d_x$ ) was estimated from the full – width at half – maximum ( $\beta$ ) using Scherrer's formula:

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

Here,  $\lambda$  is the wavelength of the X – ray radiation and  $\theta$  is the angle of diffraction.

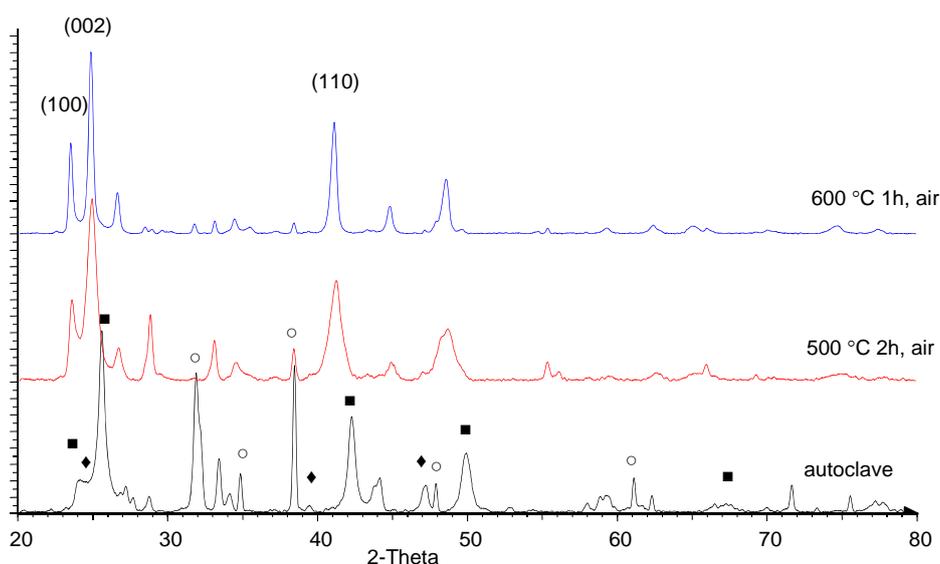


Fig. 1: X- ray diffraction patterns of CdSe and CdTe prepared within the autoclave reactor and CdSe<sub>0.6</sub>Te<sub>0.4</sub> prepared by isothermal heating of as – prepared particles (o = Cd, ♦ = CdTe, ■ = CdSe).

By heating the as - prepared mixture in air (500 °C followed by 2 h isothermal heating or 600 °C followed by 1 h isothermal heating), the ternary compound  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  was obtained. The patterns correspond to (100), (002) and (110) peaks of hexagonal  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ . As reported previously,  $\text{CdSe}_x\text{Te}_{1-x}$  with different compositions ratios ( $x = 0.1$  and  $x = 0.6$ ) can be produced by using other regimes of heating [20].

$\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles from an elemental feedstock solution in en/water mixtures at different volume ratios (1:1 and 1:3) were also prepared within the autoclave reactor, using the same reaction conditions as mentioned above. In both cases, the products were mixtures of binary CdSe and ternary chalcogenides  $\text{CdSe}_x\text{Te}_{1-x}$  with different composition ratios ( $x = 0.1$  and  $x = 0.6$ ) in nanometer scale. All the prepared nanoparticles were smaller than 20 nm in diameter.

Solvothermally prepared binary chalcogenides were the results of the following reactions:



E corresponds to the corresponding chalcogene element ( $\text{E} = \text{Se}, \text{Te}$ ) and en is ethylenediamine. Other authors also reported that they produced binary nanocrystalline chalcogenides products by solvothermal reaction  $\text{CdE}$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) with different nanoparticles morphology [13 - 19]. By heating the solvothermally-prepared mixture of binary chalcogenides up to 500 °C and higher temperatures in air or nitrogen flow, ternary chalcogenides were prepared by the reaction:



By heating the prepared mixtures of elementary particles up to 600 °C and more in air, ternary chalcogenides were formed by the reaction:

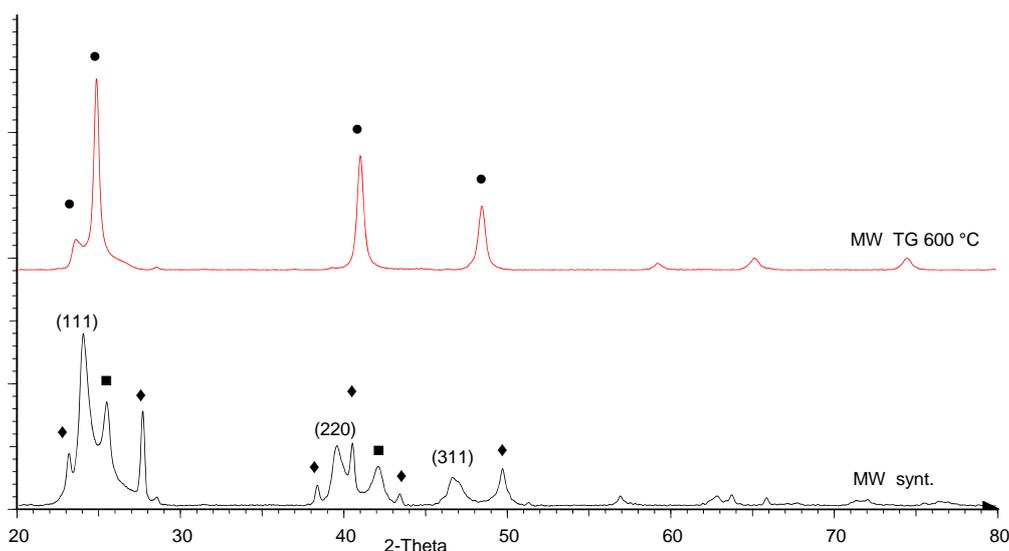


Fig. 2: X-ray powder diffraction patterns of the ternary compound  $\text{CdSe}_{0.1}\text{Te}_{0.9}$ , prepared by 30 min microwave synthesis at 200 °C and 200 W, and  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  produced by heating to 600 °C (● =  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ , ◆ = Te, ■ = CdSe).

Fig. 2 shows the X-ray powder diffraction patterns of the ternary compound  $\text{CdSe}_{0.1}\text{Te}_{0.9}$ , prepared by 30 min microwave synthesis (200 °C, 200 W) from prepared mixtures of the elementary feed solutions in an en/water mixture (volume ratio en :  $\text{H}_2\text{O}$  = 1 : 4). 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 heating of this product to 600 °C in air causes transformation of the product from cubic  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  to hexagonal  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ , also of nanometer scale. The calculated particle size by the Scherrer formula, calculated using the average of the (220) and (311) peaks, was 14.5 nm for  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  and 20.4 nm for  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  prepared by heating the initial product up to 600 °C. It should be mentioned that by using higher diamines with a longer C - chain (1,4 diaminobutane and 1,8 diaminooctane) during the microwave synthesis, only weak peaks of binary chalcogenides were observed next to the elemental precursors, so it can be concluded that using higher diamines offers no advantage compared to en.

The sonochemical procedure was carried out in a 27 ml Suslick Cell, where 15 ml of the prepared elemental feedstock solution in en and different en/water solutions were sonicated by Ti – horn at 70% of 750W for 15, 30, and 60 min. After 15 min of sonication, some products of binary and ternary chalcogenides were found and also unreacted elemental Cd, Se and Te. X-ray powder diffraction patterns also showed some amino (- $\text{NH}_4$ ) and cyano (-CN) groups produced by the sonication of en. When prolonging the time of sonication to 30 and 60 min., the products were the same, only the diffraction peaks were broader, indicating products with smaller crystallite sizes. By sonicating the elemental feedstock solutions with different en/water volume ratios, it could be observed that the products were a mixture of binary and ternary chalcogenides. The elemental feedstock solutions in en/water mixtures (volume ratio = 1:2) were also sonicated for 30 min., yielding mostly cubic CdSe with a particle size of 10.2 nm. Products prepared by sonication of the elemental feedstock solution in en and different en/water mixtures were not heated, due to health risk reasons concerning the cyano- groups.

$\text{CdSe}_x\text{Te}_{1-x}$  was produced from the direct reactions of high purity elemental cadmium, selenium and tellurium mixture heated up to 600 or 700 °C. Whilst heating up to 600 °C, some  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  was formed in the presence of CdSe and CdTe. When prolonging the heating time to two hours at 600 °C, only  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  and CdSe were produced. By heating up to 700 °C, the formation of  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  with a particle size of 20.1 nm was observed, in the presence of some CdSe. With prolonged heating times (1h and 2h at 700 °C), only  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  with particle sizes of 20.4 and 23.4 nm was formed, see Fig. 3.

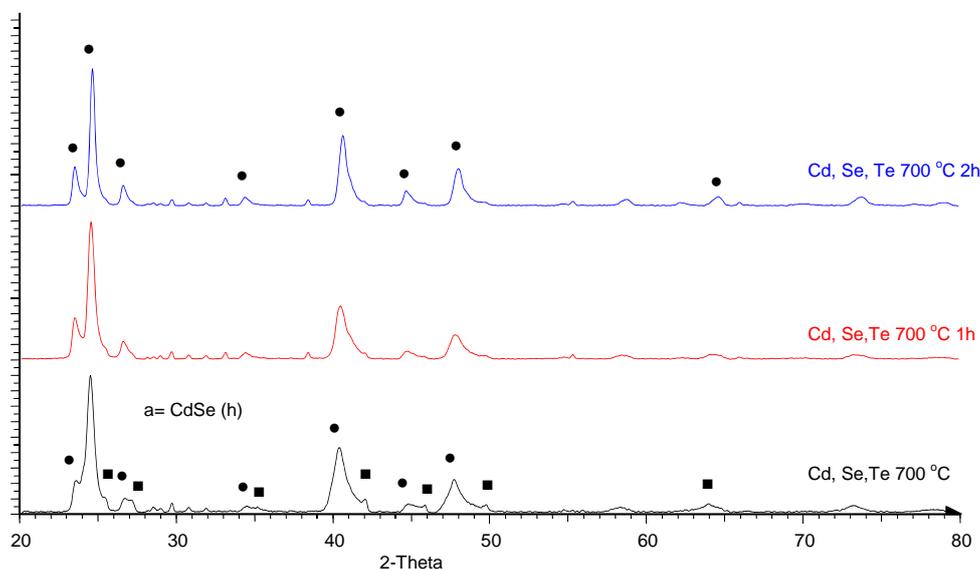


Fig. 3: X-ray diffraction patterns of  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  prepared by the heating of a mixture of elemental Cd, Se and Te (● =  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ , ■ = CdSe).

The calculated particle sizes of the as-prepared  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  were close to the particle sizes of those products prepared from a mixture of commercially-available CdSe and CdTe, mixed at a molar ratio 1:1 and heated up to 700 °C for two hours (24.8 nm), carried out within a control experiment. The mixture of binary chalcogenides required higher temperatures and longer reaction times to form pseudobinary chalcogenides  $\text{CdSe}_x\text{Te}_{1-x}$  than elementary particles. Products, obtained by heating the solvothermally prepared CdSe/CdTe mixture, had the same composition ( $\text{CdSe}_{0.6}\text{Te}_{0.4}$ ) and smaller particle sizes when compared with products obtained by heating elemental and binary precursors. The calculated particle sizes were: 6.4 nm for the product obtained by heating for one hour at 500 °C, 10.3 nm for the product obtained by heating for two hours at 500 °C and at 19.8 nm one hour at 600 °C. It can be concluded that higher temperatures and prolonged times needed to form pseudobinary chalcogenides from commercially available bulk CdSe and CdTe were the result of bigger particle sizes compared with solvothermally synthesized nanoparticles.

All the particle sizes were calculated, using the Scherrer formula, from the averages of three strongest peaks: CdSe (23.8°, 25.4°, 41.9°),  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  (23.9°, 39.7°, 46.8°),  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  (23.3°, 24.7°, 40.9°). Particle sizes calculated by the Scherrer formula are close to the particle size determined from TEM images. The ternary compound  $\text{CdSe}_x\text{Te}_{1-x}$ , obtained by heating the solvothermally prepared CdSe/CdTe mixture at 500 °C to 600 °C for different time periods in air and  $\text{N}_2$  atmosphere was mostly  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ .

All the obtained particles were in nanometer scale and smaller than 30 nm, as can be seen in Table 1. Table 1 also presents products and particle sizes obtained by sonication of elemental Cd, Se, Te in en and different en/water mixtures. The products obtained by sonochemical reaction were mostly CdSe and, in some cases, traces of  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ . Due to limitations regarding the X-ray powder data base, only two stoichiometric ternary chalcogenides,  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  and  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ , could be detected, whilst all the other synthesized ternary chalcogenides with a different Se : Te ratio are listed below using the general formula  $\text{CdSe}_x\text{Te}_{1-x}$ .

Products of the microwave synthesis and their particle sizes are presented in Table 2. These particles were prepared from elemental Cd, Se, and Te in en or en/water solutions by 15 or 30 min of microwave synthesis at 200 W and 200 °C. The products were mostly CdSe and  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  of nanometer scale, and smaller than 20 nm. Particles prepared by the heating of elementary Cd, Se, Te or binary CdSe and CdTe in air, are also presented in Table 2. Chalcogenides prepared from elemental

particles started to form ternary chalcogenides at temperatures of 650 °C and above, yielding mostly  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ . Mixtures of commercially available CdSe and CdTe start to form ternary chalcogenides with particle sizes of 20 – 30 nm by heating to 600 - 700 °C for 2 hours.

Table 1. Particle sizes of solvothermally and sonochemically prepared CdSe<sub>x</sub>Te<sub>1-x</sub> particles.

Reactant ratio (autoclave)	Preparat ion	Heated	Products	Particle size [nm]	Reactant ratio (sonicated)	Preparation	Heated	Products	Particle size [nm]
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	500 °C air	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 11.5	Cd:Se:Te= 4:2:2 mmol, en	70%, 750W, 15 min	/	CdSe <sub>x</sub> Te <sub>1-x</sub>	d= 26.5
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	600 °C air	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 20.1	Cd:Se:Te= 4:2:2 mmol, en	70%, 750W, 30 min	/	CdSe <sub>x</sub> Te <sub>1-x</sub>	d= 27.0
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	500 °C 1h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 6.4	Cd:Se:Te= 4:2:2 mmol, en	70%, 750W, 60 min	/	CdSe <sub>x</sub> Te <sub>1-x</sub>	d= 24.8
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	500 °C 2h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 10.3	Cd:Se:Te = 4:2:2 mmol, en: H <sub>2</sub> O= 1:1	70%, 750W, 60 min	/	CdSe	d= 8.0
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	600 °C 1h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 19.8	Cd:Se:Te = 4:2:2 mmol, en: H <sub>2</sub> O = 1:2	70%, 750W, 60 min	/	CdSe	d= 9.3
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	600 °C 1h N <sub>2</sub>	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 7.3	Cd:Se:Te = 4:2:2 mmol, en: H <sub>2</sub> O = 1:2	70%, 750W, 30 min	/	CdSe	d= 10.2
Cd:Se:Te= 4:2:2 mmol, en	20 h, 200°C	600 °C 2h N <sub>2</sub>	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 16.5	Cd:Se:Te = 4:2:2 mmol, en: H <sub>2</sub> O = 1:3	70%, 750W, 60 min	/	CdSe	d= 12.4
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O = 1:1	20 h, 200°C	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 19.2	Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O = 1:3	70%, 750W, 30 min	/	CdSe	d= 15.6
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O = 1:3	20 h, 200°C	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 15.9	Cd:Se:Te = 4:2:2 mmol, en: H <sub>2</sub> O = 2:1	70%, 750W, 60 min	/	CdSe	d= 13.8
			CdSe <sub>x</sub> Te <sub>1-x</sub>	d= 12.0	Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O = 2:1	70%, 750W, 30 min	/	CdSe <sub>x</sub> Te <sub>1-x</sub> CdSe	d <sub>1</sub> = 29.1 d <sub>2</sub> = 21.0

Table 2: Particle sizes of nanoparticles prepared by microwave synthesis and by heating of elementary and binary mixtures.

Reactant ratio (microwave)	Preparation	Heated	Products	Particle size [nm]	Reactant ratio (elementary)	Preparation	Heated	Products	Particle size [nm]
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 1:5	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 23.2	Cd:Se:Te= 4:2:2 mmol	/	500 °C air	CdSe <sub>0.6</sub> Te <sub>0.4</sub> CdSe	d <sub>1</sub> = 22.2 d <sub>2</sub> = 29.8
Cd:Se:Te= 1:0,6:0,4 mmol, en	200W, 200 °C, 30 min	/	CdSe	d= 20.3	Cd:Se:Te= 4:2:2 mmol	/	500 °C 1h air	CdSe	d= 34.4
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 1:4	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub> CdSe	d <sub>1</sub> = 14.5 d <sub>2</sub> = 19.8	Cd:Se:Te= 4:2:2 mmol	/	650 °C air	CdSe	d= 33.0
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 1:4	200W, 200 °C, 30 min	600 °C air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 20.4	Cd:Se:Te= 4:2:2 mmol	/	700 °C air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 20,1
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 5:1	200W, 200 °C, 15 min	500 °C 1h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 12.2	Cd:Se:Te= 4:2:2 mmol	/	700 °C 1h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 20.4
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 5:1	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 16.0	Cd:Se:Te= 4:2:2 mmol	/	700 °C 2h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 23.4
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 4:1	200W, 200 °C, 15 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 15.7					
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 4:1	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 16.3	<b>Reactant ratio (binary)</b>	<b>Preparation</b>	<b>Heated</b>	<b>Products</b>	<b>Particle size [nm]</b>
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 3:1	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 16.7	CdSe:CdTe= 1:1mmol	/	300 °C (0 – 2h) air	CdSe, CdTe	/
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 3:1	200W, 200 °C, 15 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 17.3	CdSe:CdTe= 1:1mmol	/	500 °C (0 – 2h) air	CdSe, CdTe	/
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 2:1	200W, 200 °C, 30 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 17.5	CdSe:CdTe= 1:1mmol	/	600 °C (0 – 1h) air	CdSe, CdTe	/
Cd:Se:Te= 4:2:2 mmol, en: H <sub>2</sub> O= 2:1	200W, 200 °C, 15 min	/	CdSe <sub>0.1</sub> Te <sub>0.9</sub>	d= 16.9	CdSe:CdTe= 1:1mmol	/	600 °C 2h air	CdSe <sub>x</sub> Te <sub>1-x</sub>	d= 34.8
					CdSe:CdTe= 1:1mmol	/	700 °C 2h air	CdSe <sub>0.6</sub> Te <sub>0.4</sub>	d= 24.8

Fig. 4a shows the TG curves, measured in ambient air, for  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  samples, prepared by solvothermal reaction and by the microwave synthesis, both from elementary precursors. For the sample synthesized by microwave synthesis, the initial weight loss between 30 and 200 °C ( $\Delta m \approx 0.4\%$ ) can be attributed to the loss of adsorbed solvent. By further heating, two significant weight losses could be observed: between 200 and 420 °C, 3.8% of the initial weight was lost whilst from 420 to 550 °C, another 3% was lost. These results are thought to be due to the loss of elemental Te at elevated temperatures. Above 550 °C, a steady weight loss was observed due to the sublimation of  $\text{CdSe}_{0.4}\text{Te}_{0.6}$ . The sample prepared by solvothermal reaction showed a slow weight loss ( $\Delta m = 3\%$ ) from 30 to 410 °C, followed by a quick loss between 410 and 505 °C ( $\Delta m \approx 5\%$ ). The thermal behavior above 550 °C was identically to that of the sample prepared by microwave synthesis.

The TG curves for the preparation of  $\text{CdSe}_{0.6}\text{Te}_{0.4}$  by heating mixtures of elementary precursors and mixtures of binary chalcogenides, are shown in Fig. 4b. The weight loss of the binary mixture ( $\text{CdS} : \text{CdTe} = 1 : 1$ ) up to 700 °C was negligible ( $\Delta m < 0.2\%$ ), whilst after 2h of isothermal heating the measured weight loss was 2%. When heating elemental precursors ( $\text{Cd} : \text{Se} : \text{Te} = 2 : 1 : 1$ ), a weight loss of 3.1% was observed between 500 and 650 °C. The explanation for this difference could again be the loss of elemental Te in this area, which also explains the deficit of Te in the product ( $\text{Se} : \text{Te} = 0.6 : 0.4$ , despite using a molar ratio of  $\text{Se} : \text{Te} = 1 : 1$  during the synthesis). In the isothermal part, both samples showed very identical behavior with weight losses of  $\approx 2.3\%$  after 2h at 700 °C.

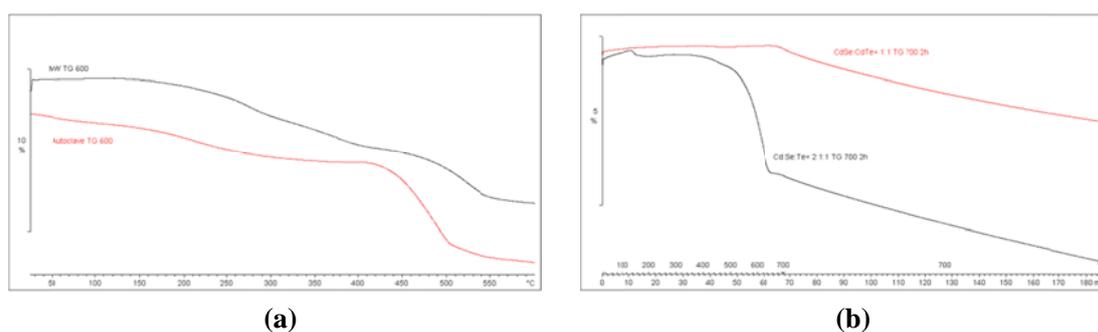
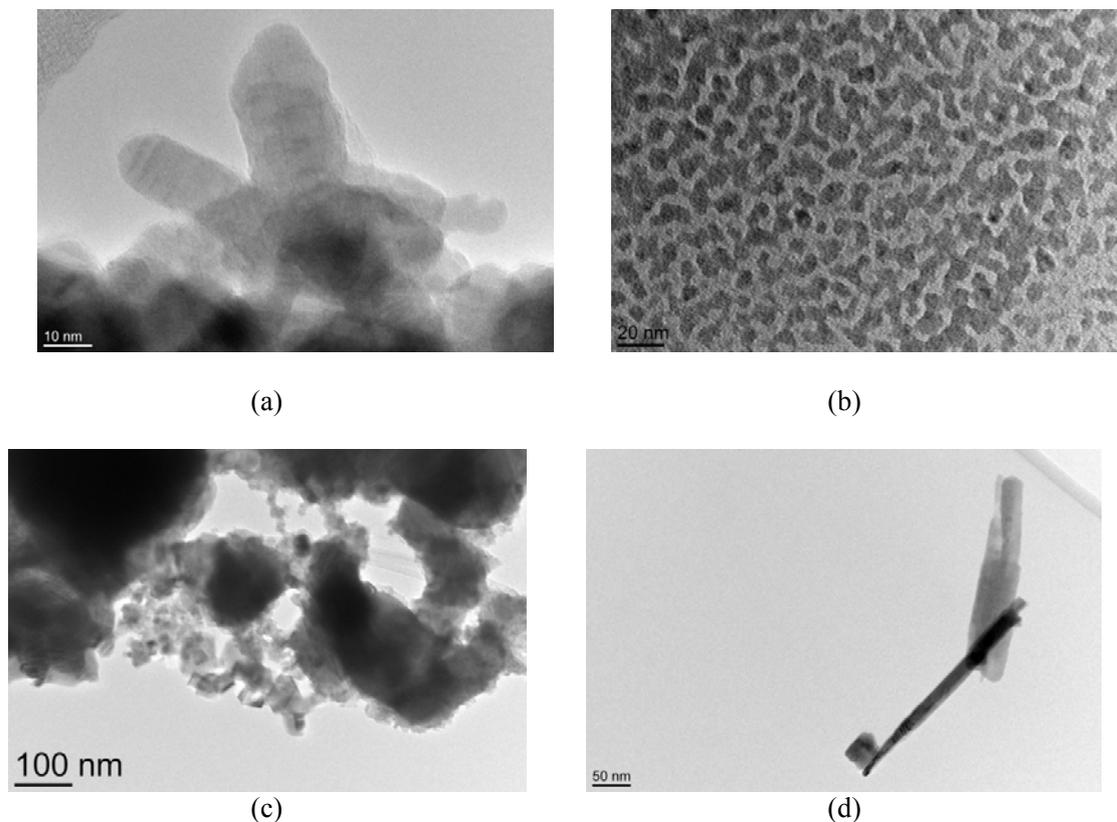


Fig. 4: Thermograms of prepared  $\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles: (a) prepared solvothermally and prepared by 30 min microwave synthesis (MW), both heated up to 600 °C (b) elementary and binary compounds heated up to 700 °C followed by 2 h isothermal heating.

Fig. 5 shows TEM images of  $\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles by different procedures of preparation. Image (a) represents  $\text{CdSe}_x\text{Te}_{1-x}$  nanoparticles ( $x = 0.1$  and  $x = 0.6$ ) prepared solvothermally in the autoclave using an 1:1 en : water solution, maintained for 20 h at 200 °C. Particle sizes determined by Scherrer formula were 19.2 nm for  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  and 13.9 nm for  $\text{CdSe}_{0.6}\text{Te}_{0.4}$ . The calculated particle sizes were close to the particle sizes observed on TEM images for all further cases. It can also be seen that all the particles were well-crystallized and that the  $\text{CdSe}_{0.1}\text{Te}_{0.9}$  particles were in tetrapod-like molecular structures, as already reported for some CdTe nanoparticles [12].



*Fig. 5: TEM images of  $CdSe_xTe_{1-x}$  nanoparticles prepared by different methods: (a) autoclave product ( $en/water = 1:1$ ), (b) autoclave product ( $en$ ) heated to 600 °C, (c) autoclave product ( $en$ ) heated to 600 °C for 1 h, (d) microwave product ( $en$ ) 30 min.*

Image **(b)** displays the product, prepared by heating of binary chalcogenides, prepared solvothermally in  $en$  to 600 °C, to form the ternary chalcogenide  $CdSe_{0.1}Te_{0.9}$ . The nanoparticles size calculated by the Scherrer formula is 20.1 nm. A prolonged time of heating at 600 °C for one hour caused transformation to the ternary chalcogenides  $CdSe_{0.6}Te_{0.4}$ , as shown within image **(c)**. The TEM image of the ternary compound  $CdSe_{0.1}Te_{0.9}$ , prepared by 30 min. of microwave synthesis at 200 °C and 200 W in  $en$ , is shown in image **(d)**. The microwave-prepared particles of ternary chalcogenides  $CdSe_xTe_{1-x}$  formed a nanorod-like product that is totally different in shape compared to particles prepared in the autoclave reactor or by the direct reaction of the elemental mixture heated up to 600 or 700 °C.

#### 4. Conclusion

In summary,  $CdSe_{0.6}Te_{0.4}$  and  $CdSe_{0.1}Te_{0.9}$  nanoparticles were successfully synthesized by a direct reactions from elemental precursors, as well as by microwave synthesis. The as – synthesized nanoparticles were well-crystallized having hexagonal and cubic structures, and particle sizes within the range 6 – 35 nm. The methods used are simple and appear to be suitable for the production of larger amounts of ternary  $CdSe_xTe_{1-x}$  chalcogenides.

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