

Study of de-aggregation of mechanochemically synthesized ZnSe nanoparticles by re-milling in the presence of ZnCl₂ solution

Marcela Achimovičová¹, Zdenka Bujňáková, Martin Fabián and Anna Zorkovská

Conventional mechanochemical synthesis of zinc selenide, ZnSe nanoparticles was performed in a planetary ball mill by high-energy milling of zinc (Zn) and selenium (Se) powders. Mechanochemically synthesized ZnSe was subsequently re-milled in circulation mill in ZnCl₂ solution in order to study de-aggregation, physical-chemical and optical properties of ZnSe nanoparticles. The mechanochemically synthesized and re-milled samples were characterized by X-ray diffraction analysis (XRD) that confirmed the presence of cubic and hexagonal ZnSe phases. Size of crystallites calculated from XRD patterns has decreased from 50 to 19 nm for cubic ZnSe phase and from 145 to 2.5 nm for hexagonal ZnSe phase after re-milling for 110 min in ZnCl₂ solution. Size, phase composition, morphology, and crystallinity of ZnSe nanoparticles were studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED). UV-Vis optical spectroscopy has provided an evidence of blue shift of the re-milled nanocrystalline ZnSe particles from the direct band gap of 2.67 eV characteristic of bulk ZnSe crystals. Colloidal stability of ZnSe nanoparticles dispersions was studied by ζ -potential measurements.

Key words: Zinc selenide, Mechanochemical synthesis, Re-milling, Nanoparticles

Introduction

Zinc selenide, ZnSe that belongs to group of II-VI binary semiconductors has appeared as perspective material for optoelectronic applications in light-emitting diodes, blue laser diodes, photo-detectors and full colour displays (Zhang et al., 2009; Kumar and Singh, 2009; Cao et al., 2011), tunable mid-IR laser sources (Fedorov et al., 2007) high speed optical devices, photovoltaic and laser screens (Archana et al., 2009). Nowadays, the preparation of ZnSe is usually focused on the synthesis of ZnSe nanoparticles from single molecular precursors with intrinsic optical and luminescent properties, respectively. All main ZnSe preparation routes require high or elevated temperatures for initiating and/or progress of the reactions for example pyrolysis of the organometallic precursors (Peng et al., 1997; Murray et al., 1993) and toxic H₂Se method (Wang and Herron, 1991; Jones, 1997). Later Li and co-workers (1999) have developed the solvothermal elemental reaction method of II-VI semiconductors nanocrystals preparation, and Wang and co-authors (1999) have used the low-temperature aqueous method of ZnSe preparation. Ball milling technique or so-called mechanochemical synthesis was also used for preparation of ZnSe (de Lima et al., 1999; Baltazar-Rodrigues et al., 2009; Gotor et al., 2013). This method has several advantages. Mechanochemical synthesis is simple, dry, time-convenient, one-step process under environmentally friendly and essentially waste-free conditions, which could be interesting for a subsequent semiconductor technology (Baláž et al., 2013). One disadvantage is only agglomeration of particles during milling or mechanochemical synthesis. In order to prevent the particles against agglomeration a presence of various liquids as water, polyvinylpyrrolidone, dodecane, cyclohexane, polymeric surfactants, and alcohols were used during milling (Williams and Phelan, 1985; Tangsathittalchi, 2002; Guérard, 2008; Yu et al., 2011; Bhattacharya et al., 2004; Haas et al., 2001; Baláž et al., 1988). In general, for electrostatic stabilization of colloidal particles the salts with monovalent (Cs, Rb, K, Na, Li) or divalent cations (Ba, Sr, Ca, Mg) are used. Different phases have different charge affinities, so that an electrical double layer forms at any interface and then electrostatic stabilization of colloids is based on the mutual repulsion of electrical charges of individual particles. ZnCl₂ is also the salt with the divalent cations and can be used for electrostatic stabilization of particles during milling.

Experimental

Mechanochemical synthesis of ZnSe was performed by high-energy milling of zinc (97 %, ITES, Slovakia) and selenium powders (99.5 %, Aldrich, Germany) in a planetary ball mill Pulverisette 6 (Fritsch, Germany) according to the reaction:

¹ Mgr. Marcela Achimovičová, PhD., Mgr. Zdenka Bujňáková, RNDr. Martin Fabián, PhD., RNDr. Anna Zorkovská, PhD., Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia, tel.: +421-55-7922606, achimovic@saske.sk, bujanakova@saske.sk, fabianm@saske.sk, zorkovska@saske.sk



The reaction is thermodynamically possible because of negative value of enthalpy change $\Delta H_{298}^0 = -159 \text{ kJ mol}^{-1}$. The following conditions were used for mechanochemical synthesis: loading of the mill – 50 balls of 10 mm diameter, material of milling chamber and balls – tungsten carbide, volume of milling chamber – 250 ml, mass of Zn – 2.26 g, mass of Se – 2.74 g, milling atmosphere – Ar, rotational speed of the mill planet carrier – 300 min^{-1} (5 Hz), milling time – 20 min.

Re-milling of mechanochemically synthesized ZnSe was performed in a circulation mill MiniCer (Netzsch, Germany) under following conditions: loading of the mill – 85 % balls of 0.6 mm diameter, material of milling chamber and balls – yttrium stabilized ZrO₂, volume of suspension – 300 ml, mass of sample – 2 g, milling atmosphere – 0.15 g.L^{-1} (10^{-3} M) ZnCl₂ solution, revolutions of the milling shaft – 3000 min^{-1} (50 Hz), milling time – 30, 60, 110 min.

X-ray diffraction measurements (XRD) were carried out using a D8 Advance diffractometer (Bruker, Germany) equipped with a θ/θ goniometer, CuK $_{\alpha}$ radiation (40 kV, 40 mA), a secondary graphite monochromator, and a scintillation detector. The diffraction data were collected over an angular range $20^{\circ} < 2\theta < 100^{\circ}$ with steps 0.025° and a counting time of 5 s.step^{-1} . The commercial Bruker processing tools have been used for the data treatment. Diffrac^{plus} Eva and the ICDD PDF 2 database have been used for the phase identification and the Diffrac^{plus} Topas software has been utilized for the Rietveld analysis.

Transmission electron microscopy (TEM) analysis was performed on a microscope Jeol JEM-2100 F. Prior to TEM investigation the powders were crushed in mortar, dispersed in ethanol and fixed on copper supported carbon films.

Nanophox Particle size distribution was measured by a photon cross correlation spectroscopy using a Nanophox particle size analyser (Sympatec, Germany). The values x_{50} represent particle mean diameter.

UV-Vis optical absorption spectra were taken using a Helios Gamma spectrophotometer (Thermo, Great Britain) in the range of 200-800 nm. Prior to UV-Vis measurements, samples were dispersed in absolute ethanol.

The surface charge of mechanochemically synthesized ZnSe particles and ZnSe nanoparticles after subsequent remilling in ZnCl₂ solution was determined by the laser-Doppler electrophoretic light scattering Zetasizer Nano-Z (Malvern, Great Britain) using a 4 mW He-Ne laser ($\lambda=632.8 \text{ nm}$). ζ -potential can be converted from measured electrophoretic mobility using the Smoluchowski's equation:

$$\zeta = \frac{\eta U_E}{\varepsilon} \quad (2)$$

where ζ is the zeta-potential, ε is the dielectric permittivity of the solution (equal to $\varepsilon_0 \varepsilon_r$, ε_0 is the permittivity of the vacuum and ε_r the relative permittivity of solution), U_E is the electrophoretic mobility of the dispersed particles and η is the viscosity of the dispersed phase. The ζ -potentials were calculated from the electrophoretic mobility using eq. (2), wherein the thickness of the electrical double layer is assumed to be smaller in comparison to the dispersed particle size. The Smoluchowski equation (without any other correction) as an approximation was used. 1 g of sample was dispersed in 1L of deionized water for the measurements. Then the each dispersion was subjected to sonification for 15 min. The pH of dispersions was 5.76. For each sample 3 measurements were averaged to determine the corresponding ζ -potential.

Results and discussion

The XRD patterns of mechanochemically synthesized ZnSe and re-milled ZnSe in the presence of ZnCl₂ solution are plotted in Figure 1. The results confirm that mechanochemically synthesized ZnSe contain 73 % of cubic (Stilleite, ICDD PDF 37-1463) and 16 % hexagonal (ICDD PDF 80-0008) ZnSe modifications (Tab. 1). Subsequent wet re-milling for 110 min brought about decreasing of the cubic phase and increasing of the hexagonal phase in ZnSe and the size of cubic and hexagonal crystallites has also markedly decreased. The agglomerates of ZnSe typically produced by dry milling were broken into the particles having the crystallites of 19 and 2.5 nm diameter after re-milling in ZnCl₂ solution. The amount of unreacted Zn has decreased to zero with re-milling in ZnCl₂ solution as well.

Tab. 1. Time of milling, t_M , the content of synthesized cubic ZnSe phase, C-phase, the content of synthesized hexagonal ZnSe phase, H-phase, cubic crystallite size, d_C , hexagonal crystallite size, d_H , and the contents of unreacted Zn and Se for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Sample	t_M [min]	C-phase [%]	d_C [nm]	H-phase [%]	d_H [nm]	unreacted Zn [%]	unreacted Se [%]
PM	20	73	50	16	145	6	5.5
PM/CM	20/110	61	19	31	2.5	0	8

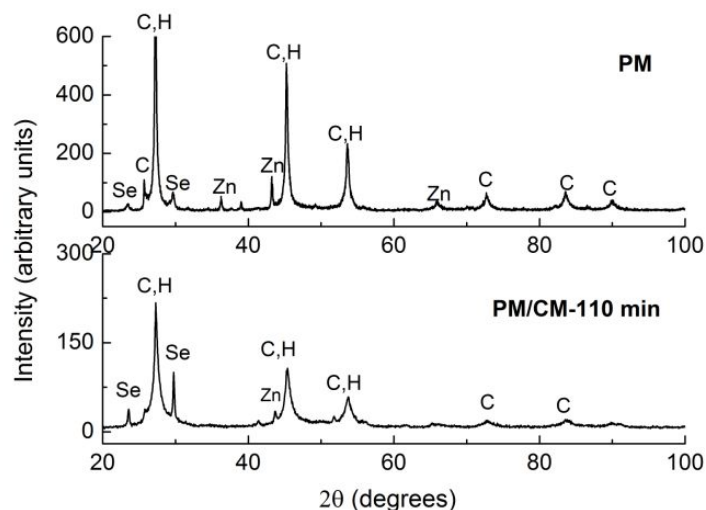


Fig. 1. X-ray diffraction patterns of mechanochemically synthesized ZnSe (PM) in planetary ball mill and re-milled ZnSe (PM/CM) in circulation mill for 110 min. C-cubic ZnSe, H-hexagonal ZnSe.

TEM analysis of mechanochemically synthesized ZnSe after 20 min of milling (sample PM, Tab. 1) has revealed that the sample contains two types of ZnSe grains: nanosized particles and larger up to about 1 μm large particles (Fig. 2a). Selected area electron diffraction (SAED) analysis has shown the nanosized particles have mostly cubic ZnSe modification, whereas the larger ZnSe particles mainly have comprised hexagonal modification of ZnSe. The favourable effect of wet re-milling on refinement of particles is clearly seen in Fig. 2b. Although in both cases the prepared particles were found in agglomerated state, those treated by wet re-milling (Fig. 2b) are characterized by smaller size (<50 nm) and have more homogenous distribution. The selected area electron diffraction pattern (SAED, Fig. 2b-inset) reflects the nanoscale character of prepared ZnSe sample.

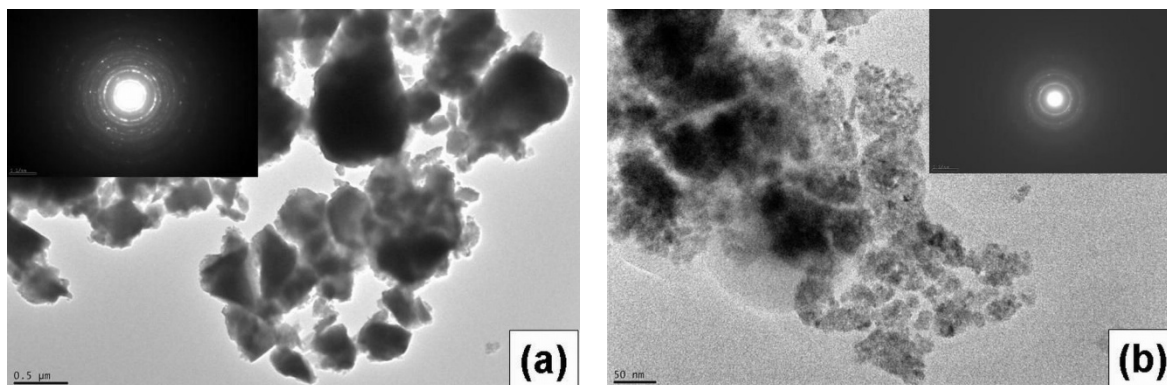


Fig. 2. (a) TEM image of the ZnSe mechanochemically synthesized after 20 min of milling (sample PM), (b) TEM image of the ZnSe mechanochemically synthesized after 110 min of wet re-milling in ZnCl_2 (sample PM/CM).

Figure 3 shows the particles of PM and PM/CM-30 min ZnSe samples have non-monomodal (polydisperse) density distribution. With increasing time of re-milling or circulation milling ZnSe particles assign monomodal density distribution and particle mean diameter values, x_{50} are decreasing (Tab. 2). Comparing PM-sample and sample re-milled in circulation mill in the presence of ZnCl_2 for 110 min particle mean diameter has decreased 4.3 times.

Tab. 2. The values of particle mean diameter and ζ -potential values for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Sample: re-milling time [min]	PM	PM/CM:30	PM/CM:60	PM/CM:110
Particle mean diameter, x_{50} [nm]	912	866	226	210
ζ -potential [mV]	-44.58	-2.41	+4.22	+3.69

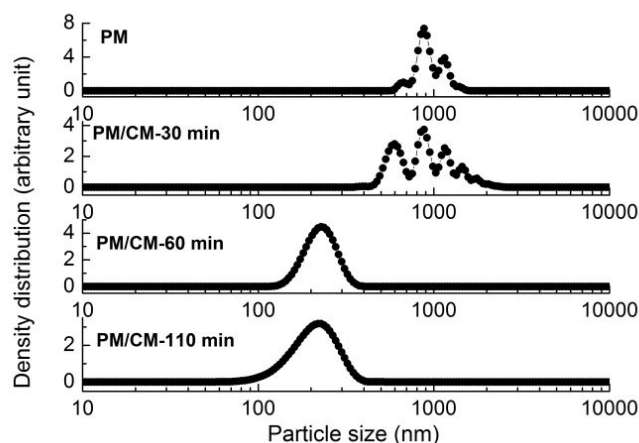


Fig.3. Density distribution curves of the mechanochemically synthesized ZnSe particles in planetary ball mill (PM) and ZnSe particles re-milled in circulation mill with ZnCl₂ (PM/CM).

UV-Vis optical absorption spectra for mechanochemically synthesized ZnSe in planetary ball mill and for ZnSe re-milled in circulation mill with ZnCl₂ solution are given in Figure 4 and they confirmed that samples re-milled with ZnCl₂ for 30 and 110 min contain nanoparticles. Their spectra assigned the blue shift from direct band gap energy of 2.67 eV characteristic for bulk ZnSe crystals (Wang and Du, 2006). The spectra illustrate the extended small absorption edges at about 252 nm and 260 nm that correspond to 4.93 and 4.77 eV. The spectrum of mechanochemically synthesized ZnSe in planetary ball mill has shown no absorption edge, and therefore, no blue shift from the direct band gap energy of bulk ZnSe crystals. This has evidenced, that particles mechanochemically synthesized in planetary ball mill are strongly aggregated.

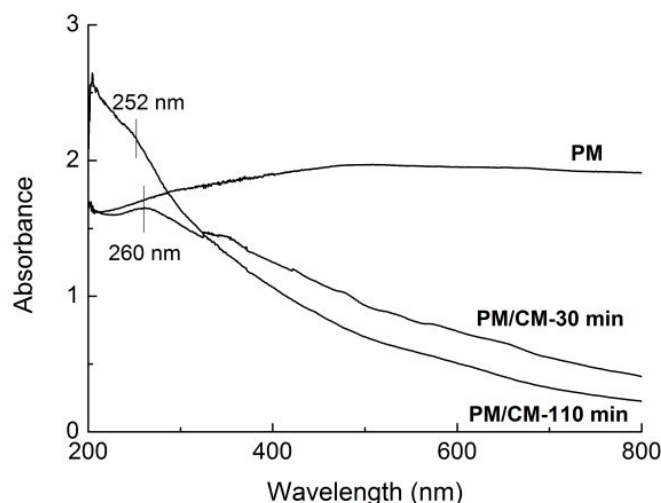


Fig.4. UV-Vis optical absorption spectra for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Generally, ζ -potential indicates the degree of repulsion between adjacent, similarly charged particles in the dispersion. A value of 30 mV (negative or positive) can be taken a general dividing line separating low-charged surfaces from highly-charged surfaces (Zetasizer Nano Series User Manual 2004). In our case ζ -potential of mechanochemically synthesized ZnSe particles and ZnSe particles re-milled with ZnCl₂ solution has changed from -44.58 to +3.69 mV. That means the divalent Zn²⁺ cations were adsorbed at the negatively charged mechanochemically synthesized ZnSe surface with increasing time of circulation milling (Tab. 2). The negative surface charge of ZnSe particles has decreased and changed to positive values in consequence of circulation milling in presence of ZnCl₂ solution. Probably attractive forces still prevail between the surfaces of ZnSe particles in 10⁻³ M ZnCl₂ solution at pH 5.76.

Conclusions

Comparative study of structural and physical properties of mechanochemically synthesized ZnSe and subsequently re-milled ZnSe in ZnCl₂ solution was performed. XRD analysis has confirmed that ZnSe contains cubic and hexagonal phases and after re-milling of mechanically synthesized ZnSe in ZnCl₂ solution in circulation mill the cubic crystallite size has decreased 2.6-times and the hexagonal crystallite size has decreased 58-times. TEM analysis has also demonstrated the favourable effect of wet re-milling on the refinement of ZnSe nanoparticles under 50 nm and their homogeneity. ZnSe particles have assigned monomodal density distribution with increasing time of re-milling and particle mean diameter value, x_{50} has decreased 4.3-times after 110 min of re-milling. UV-Vis optical absorption spectra of remilled ZnSe have assigned the blue shift from direct band gap energy of 2.67 eV characteristic for bulk ZnSe crystals. In consequence of re-milling in solution of Zn²⁺ cations ζ -potential of ZnSe has changed from -44.58 to +3.69 mV. However, total de-aggregation and stabilization of ZnSe nanoparticles has not been achieved.

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