Characterization of tin selenides synthesized by high-energy milling

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Tin selenides $SnSe_X$ (x=1,2) were synthesized from tin and selenium powder precursors by high-energy milling in the planetary ball mill Pulverisette 6 (Fritsch, Germany). The orthorhombic tin selenide SnSe and the hexagonal tin diselenide $SnSe_2$ phases were formed after 4 min and 5 min of milling, respectively. Specific surface area of both selenides increased with increasing time of mechanochemical synthesis. The particle size distribution analysis demonstrated that the synthesized products contain agglomerated selenide particles consisting of numerous idiomorphic tin selenide crystals, measuring from 2 to more than 100 nm in diameter, which were also documented by TEM. UV-Vis spectrophotometry confirmed that tin selenide particles do not behave as quantum dots.

Key words: *tin selenide, semiconductor, milling, electron microscopy, optical properties*

Introduction

Metal selenides have attracted considerable attention due to their interesting properties and potential applications. Tin selenide (SnSe) and tin diselenide ($SnSe_2$) are interesting semiconductor compounds that are widely used as holographic recording systems, optical and optoelectronic materials in infrared electronic and memory switching devices and in photoelectrical cells. Different methods of the preparation of tin selenide and tin diselenide have been described in the literature. Semiconductors with narrow band gap have been synthesized by solvothermal route (Xie et al. 2000, Bernardes-Silva et al. 2005), electrodeposition (Subramanian et al. 1999) chemical vapor deposition (Boscher et al. 2008), sol-gel method (Reisfeld 2002), and mechanochemical synthesis (Shen and Blachnik 2003). Laboratory and industrial mills have been successfully employed to synthesize semiconducting metal sulphides (Baláž et al. 2002, Baláž 2008, Achimovičová et al. 2008a, Achimovičová et al. 2008b) and metal selenides (Ohtani and Motoki 1995, Achimovičová et al. 2009a, Achimovičová et al. 2009b). In general, the conventional (ceramic) methods of the preparation of metal selenides require high temperatures. Nevertheless, the reactions leading to the formation of selenides can be efficiently carried out already at ambient temperature in high-energy mills. The aim of this work was to prepare nanocrystalline SnSe and $SnSe_2$ by mechanochemical synthesis in a laboratory planetary mill, to study their crystalline structure, morphology, physico-chemical and optical properties.

Experimental

Mechanochemical synthesis of SnSe and $SnSe_2$ was performed by high-energy milling of tin (99.85 % Aldrich, Germany) and selenium powders (99.5 % Aldrich, Germany) in the planetary ball mill Pulverisette 6 (Fritsch, Germany) according to the following reactions:

$$Sn + Se \rightarrow SnSe \qquad \Delta H^0_{298} = -88.7\ kJ.mol^{-1} \qquad (1)$$

$$Sn + 2\ Se \rightarrow SnSe_2 \qquad \Delta H^0_{298} = -121\ \ kJ.mol^{-1} \qquad (2)$$

The reactions are thermodynamically possible because of the negative values of enthalpy change. 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 Sn – 3 g (reaction 1); 2.15 g (reaction 2), mass of Se – 2 g (reaction 1); 2.85 g (reaction 2), milling atmosphere – Ar, the rotation speed – 300 rpm, milling time – 4-10 min (reaction 1); 5-30 min (reaction 2).

X-ray diffraction measurements were carried out using a PHILIPS PW 1820 (Netherlands) diffractometer operating in the 2θ geometry using $Cu_{K\alpha 1}$ radiation. The specific surface area of the synthesized samples was determined by the low temperature nitrogen adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA), whereas the particle size distribution was measured by a Photon Cross Correlation Spectroscopy using a Nanophox particle size analyzer (Sympatec, Germany). The crystallinity and the morphology of tin selenide nanoparticles were studied using a transmission electron microscope JEM-2100 (Jeol

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Ltd., Japan). UV-Vis optical absorption spectra were taken using a HELIOS GAMMA spectrophotometer (Thermo Scientific, Great Britain).

Results and discussion

The selected X-ray diffraction patterns of mechanochemically synthesized tin selenide (Fig. 1) prepared according to the reaction (1) confirmed the presence of orthorhombic SnSe (JCPDS 32-1382). The mechanochemical synthesis of SnSe was almost completed after 10 min of milling with a conversion degree of 83 %. Small traces of un-reacted Sn were documented on the XRD patterns.

Mechanochemical synthesis of $SnSe_2$ according to the reaction (2) was almost completed after 30 min of milling with a conversion degree of 72 % (Fig. 2). The diffraction peaks were consistent with the hexagonal $SnSe_2$ phase (JCPDS 23-602). The intensities of the peaks corresponding to the un-reacted Sn and Se phases decreased with an increasing milling time. In addition to the hexagonal $SnSe_2$ phase the patterns also contained diffraction peak of (111) plane of orthorhombic SnSe, which overlaps the diffraction peak of (101) plane of $SnSe_2$. The weak reflections of planes (311) and (511) belong to SnSe.

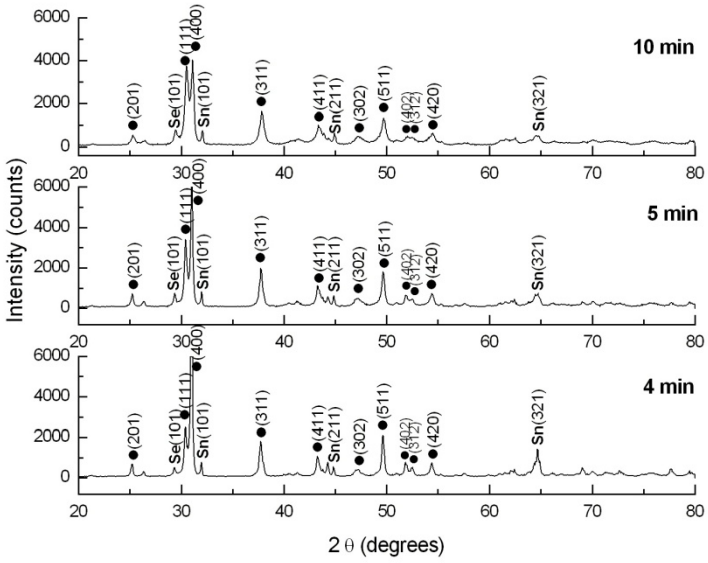

Fig. 1. X-ray diffraction patterns of mechanochemically synthesized tin selenide, ●SnSe.

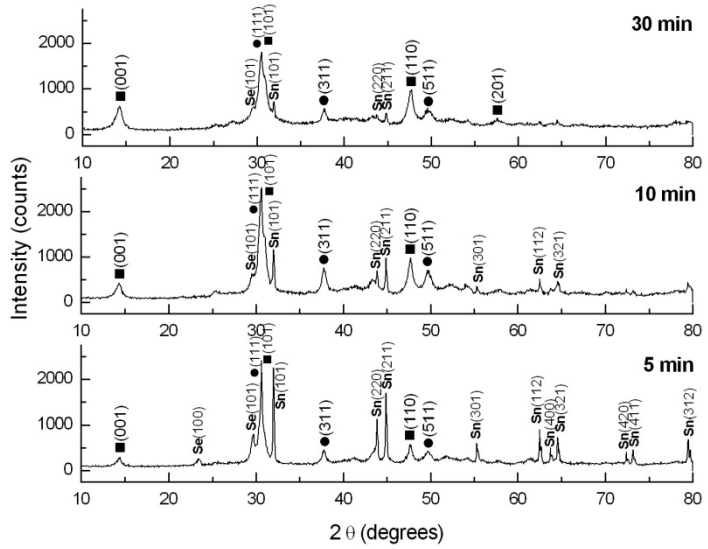

Fig. 2. X-ray diffraction patterns of mechanochemically synthesized tin selenide/tin diselenide, ●SnSe/■$SnSe_2$.

The values of specific surface area and the results of particle size distribution analysis of SnSe and $SnSe/SnSe_2$ are listed in Table 1. The specific surface area increased with the increasing time of

mechanochemical synthesis for both compounds. On the other hand, the particle size of the fraction x_{10} (10 % of synthesized particles) decreased for both compounds. The particle size distribution analysis demonstrated SnSe contained agglomerated particles ranging from 310 to 536 nm in size, and SnSe/$SnSe_2$ contained agglomerates ranging from 381 to 821 nm in size.

Tab. 1. Specific surface area and dispersity of mechanochemically synthesized SnSe and SnSe/$SnSe_2$ particles.

Sample	**Milling time** [min]	**Specific surface area** [$m^2.g^{-1}$]	**Particle size of x_{10} fraction** [nm]
SnSe	5	1.05	536
	7	2.20	489
	10	2.45	310
SnSe/$SnSe_2$	7	0.81	821
	10	1.31	555
	20	2.16	464
	30	2.24	381

TEM analysis of the mechanochemically synthesized SnSe sample confirmed the presence of thick clusters of un-reacted Sn or Se rich amorphous phase containing numerous up to 80 nm large idiomorphic SnSe crystals (Fig. 3). The measured lattice spacings from high-resolution TEM (HRTEM) image confirmed the presence of orthorhombic SnSe modification. The smallest crystals in this sample averaged in sizes between 2-8 nm. Many of these have shown the presence of low-angle tilt boundaries. The small crystals have a roundish shape, while the larger crystals appeared square-like. The orthorhombic SnSe phase seems to be quite abundant also in the mechanochemically synthesized SnSe/$SnSe_2$ sample, however in addition a considerable amount of hexagonal $SnSe_2$ crystallites could be observed (Fig. 4). Their sizes ranged from 3 nm up to more than 100 nm in diameter and show a plate-like morphology.

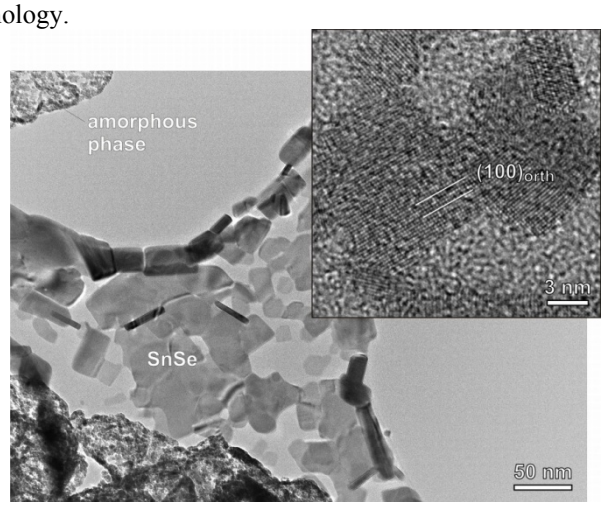

Fig. 3. TEM image of SnSe nanocrystals with an un-reacted amorphous phase. Time of mechanochemical synthesis: 10 min. The inset shows 8 nm large SnSe crystals with well resolved orthorhombic {400} lattice (d_{400}=0.285 nm).

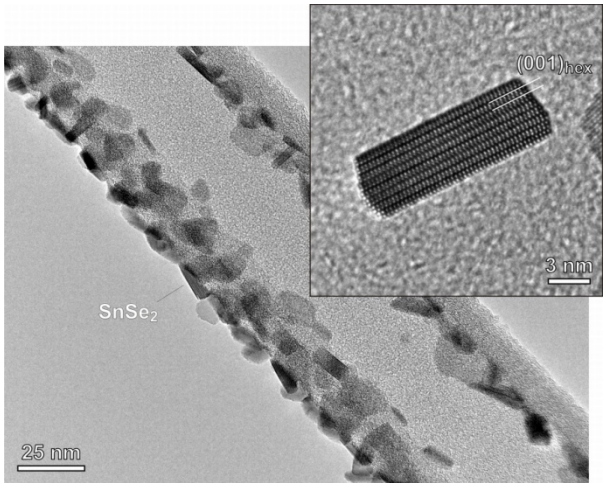

Fig. 4. TEM image of SnSe/$SnSe_2$ nanocrystals. Time of mechanochemical synthesis: 30 min. The inset shows an idiomorphic 15 nm large hexagonal $SnSe_2$ crystal with well resolved (002) and (101) lattice fringes (d_{002}=0.307 nm; d_{101}=0.291 nm).

Optical absorption spectra of mechanochemically synthesized selenides were recorded in the spectra range from 200 to 900 nm and are shown in Fig.5. The room temperature band gap energy of bulk (microcrystalline) SnSe is 0.95 eV (Pejova and Grozdanov 2007) and 1.27 eV for bulk $SnSe_2$ or $SnSe/SnSe_2$ (Bindu and Nair 2004). The spectra of mechanochemically synthesized SnSe and $SnSe/SnSe_2$ nanoparticles showed no absorption edge and its blue shift. It appeared from this that the mechanochemically synthesized tin selenides particles did not behave as quantum dots. Larger particles probably overwhelmed these potential quantum dots.

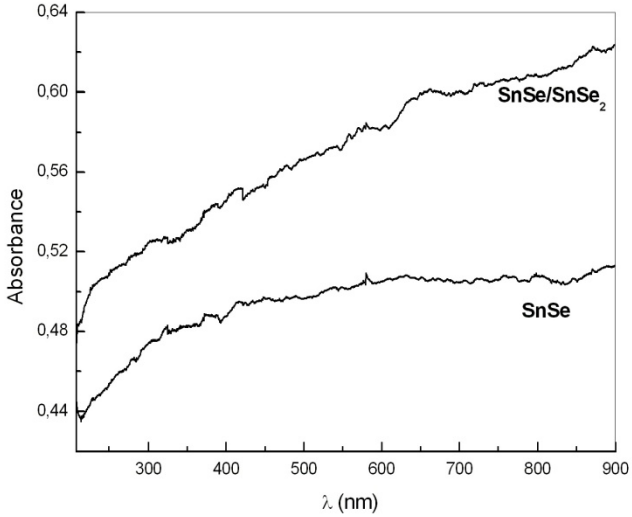

Fig. 5. UV-VIS optical absorption spectra of mechanochemically synthesized SnSe particles for 10 min and $SnSe/SnSe_2$ particles for 30 min.

Conclusion

Direct mechanochemical synthesis of tin selenide and tin selenide/tin diselenide composite from tin and selenium elements by high-energy milling is a very simple room temperature process with relatively short reaction time. X-ray diffraction and TEM analyses have shown that SnSe occurs in orthorhombic modification, whereas in the $SnSe/SnSe_2$ composite orthorhombic SnSe and hexagonal $SnSe_2$ coexist. Selenide crystals range from a few nanometers up to 100 nm in size, and they form agglomerated clusters. UV-Vis optical absorption spectrophotometry did not indicate a quantum confinement effect because the particle size of both synthesized compounds was larger than the excitonic Bohr radius of the bulk SnSe or $SnSe/SnSe_2$.

Acknowledgements: *The support through the project of the Slovak Grant Agency VEGA-2/0043/11, the project Slovak Research and Development Agency APVV-0189-10, the European Regional Development Fund - Operational Program "Research and Development" (nanoCEXmatI-26220120019 and nanoCEXmatII-26220120035), and German Academic Exchange Service (DAAD) is gratefully acknowledged.*

References

Achimovičová, M., Mockovčiaková, A., Dutková, E.: Optimalization of lead sulphide mechanochemical synthesis. *Chemical Papers 102, 864-866, 2008a.*

Achimovičová, M., Godočíková, E., Baláž, P., Kováč, J., Šatka, A.: Influence of soluble salt matrix on mechanochemical preparation of PbS nanoparticles. *Review on Advanced Materials Science 18, 216-220, 2008b.*

Achimovičová, M., Baláž, P., Dutková, E., Gock, E., Šepelák, V.: Mechanochemical synthesis of zinc selenide. *Journal of the Balkan Tribological Association 15, 79-85, 2009a.*

Achimovičová, M., Daneu, N., Rečnik, A., Ďurišin, J., Baláž, P., Fabián, M., Kováč, J., Šatka, A.: Characterization of mechanochemically synthesized lead selenide. *Chemical Papers 63, 562-567, 2009b.*

Baláž, P., Takacs, L., Ohtani, T., Mack, D.E., Boldižárová, E., Soika, V., Achimovičová, M.: Properties of a new nanosized tin sulphide phase obtained by mechanochemical route. *Journal of Alloys and Compounds 337, 76-82, 2002.*

Baláž, P.: Mechanochemistry in Nanoscience and Minerals Engineering. *Berlin Heidelberg: Springer, 2008.*

Bernardes-Silva, A.C., Mesquita, A.F., de Moura Neto, E., Porto, A.O., de Lima, G.M., Ardisson, J.D., Lameiras, F.S.: Tin selenide synthesized by a chemical route: the effect of the annealing conditions in the obthained phase. *Solid State Communications 135, 677-682, 2005.*

Bindu, K., Nair, P.K.: Semiconducting tin selenide films prepared by heating Se-Sn layers. *Semiconductor Science and Technology 19,1348-1353, 2004.*

Boscher, N.D., Carmalt, C.J., Palgrave, R.G., Parkin, I.P.: Atmospheric pressure chemical vapour deposition of SnSe and $SnSe_2$ thin films on glass. *Thin Solid Films 516, 4750-4757, 2008.*

Ohtani, T., Motoki, M.: Synthesis of binary copper chalcogenides by mechanical alloying. *Material Research Bulletin 30, 1495-1504,1995.*

Pejova, B., Grozdanov, I.: Chemical synthesis, structural and optical properties of quantum sized semiconducting tin (II) selenide in thin film form. *Thin Solid Films 515, 5203-5211, 2007.*

Reisfeld, R.: Nanosized semiconductor particles in glasses prepared by the sol-gel method: their optical properties and potential uses. *Journal of Alloys and Compounds 341, 56-61, 2002.*

Shen, J., Blachnik, R.: Mechanochemical syntheses of antimony selenide, tin selenides and two tin antimony selenides. *Thermochimica Acta 399, 245-246, 2003.*

Subramanian, B., Mahalingam, T., Sanjeeviraja, C., Jayachandran, M., Chockalingam, M.J.: Electrodeposition Sn, Se, SnSe and the material properties of SnSe films. *Thin Solid Films 357, 119-124, 1999.*

Xie, Y., Su, H., Li, B., Qian, Y.: A direct solvothermal route to nanocrystalline selenides at low temperature. *Material Research Bulletin 35, 459-464, 2000.*