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MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE LEAD SELENIDE

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Abstract

Mechanochemical synthesis of lead selenide PbSe nanoparticles has been performed by high-energy milling of lead and selenium powder in a planetary ball mill Pulverisette 6 (Fritsch, Germany) and in an industrial eccentric vibratory mill ESM 654 (Siebtechnik GmbH, Germany). Structural properties of the synthesized lead selenide were characterized by X-ray diffraction, which confirms crystalline nature of PbSe nanoparticles (JCPDS 6-354). The average size of PbSe crystallites of 37 nm was calculated from XRD data by Williamson-Hall method. The methods of particle size distribution analysis, specific surface area measurement, scanning electron microscopy and transmission electron microscopy were used for characterization of surface, mean particle size, and morphology of PbSe. An application of industrial mill verified a possibility of the synthesis of a narrow-band-gap semiconductor PbSe at ambient temperature and in a relatively short reaction time.

Introduction

Metal selenides are semiconducting materials with important optical and electrical properties which find applications in optoelectronics, telecommunication components, photovoltaics, thermoelectrics, infrared detectors and chemical sensors. PbSe is a binary IV-VI semiconductor with application as IR detectors and Pb^{2+} ion-selective sensors. PbSe nanocrystals have attracted great attention because of strong quantum confinement due to very large Bohr radius [1]. PbSe can be prepared by hydrothermal method [2], photochemical method [3], ultrasonic and γ-irradiation techniques [4], and high-temperature solution-phase synthesis [5]. Moreover, selenides of copper, silver, paladium, galium and zinc were prepared using the high-energy ball mills [6-8]. Baláž *et al* [9-10] reported synthesis of several semiconducting sulphides by high-energy milling [9-12]. Mechanochemical processing of sulphides has also been studied earlier by groups of McCormick and Takacs [13-18]. They have found that reactions, that require high temperature to perform, can be carried out at room temperature in a ball mill since during milling the reacting interfaces regenerate continually and reacting phases are separated from the product phases. Gock *et al* [19] developed mechanochemical synthesis of metal sulphides using an industrial eccentric vibratory mill and recently presented a system configuration for the manufacturing of nanoscale metal sulphides at a capacity of 100 kg/h. By avoiding SO_2 pollution, this innovative technology could replace pyrometallurgical processing in the field of material preparation. The aim of the present work was to study the mechanochemical synthesis of lead selenide at ambient temperature in a laboratory planetary mill and in an industrial eccentric vibratory mill.

Experimental

Mechanochemical synthesis of lead selenide PbSe from starting elements Pb (99%, 200 mesh, Ites, Slovakia) and Se (99.5%, Aldrich, Germany) was performed in a Pulverisette 6 (Fritsch, Germany) in an argon atmosphere at room temperature under the following conditions: a 250-ml tungsten carbide (WC) milling chamber; 50 WC balls of 10 mm diameter; mass of the starting mixture 5 g; rotational speed of the planet carrier 300 rpm; milling time 20 s - 15 min. The same process was performed in an industrial eccentric vibratory mill ESM 654 (Siebtechnik, Germany) in the argon atmosphere at room temperature under the following conditions: WC milling chamber; WC balls of 35 mm diameter with the total mass of 17 kg; mass of the starting mixture 100 g; rotational speed of the planet carrier 960 rpm; milling time 6-20 min.

The mechanochemical reaction between elemental lead and selenium is described as follows:

$$Pb + Se \rightarrow PbSe \qquad \Delta H^{0}_{298} = -100 kJ/mol \qquad (1)$$

The reaction (1) is thermodynamically possible because of negative value of enthalpy change.

The X-ray diffraction measurements were carried out using X´Pert diffractometer (Philips, Netherlands) working in the 2θ geometry with CuK_α radiation. The XRD lines were identified by comparing the measured patterns with JCPDS data cards. The size of synthesized PbSe crystallites was calculated using the Williamson-Hall analysis for deconvoluting the particle size broadening, β_{size}, and microstrain broadening, β_{strain} [20]. The corresponding integral breadths are linearly combined and the integral breadth of the total broadening β is given as follows:

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$$\beta = \frac{0.9\lambda}{D.\cos\theta} + 4\varepsilon \tan\theta \qquad (2)$$

where β is the integral breadth of the physically broadened profile, D is the volume weighted crystallite size, ε is the volume weighted average strain ($\Delta d/d$), λ is the X-ray wavelength, θ is the Bragg´s angle and d is the interplanar spacing.

Specific surface area was determined by the low temperature nitrogen adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA). Particle size distribution was measured by a laser diffraction system using a Nanophox 0139 P particle size analyzer (Sympatec, Germany).

The synthesized samples were also analyzed using a field-emission scanning electron microscope Leo 1550 (Germany) and transmission electron microscope JEOL 2100 (Japan).

For TEM/STEM studies the samples were immersed in an absolute ethanol or 2-propanol and ultrasonically de-agglomerated to separate the clusters into individual nanoparticles. The suspension containing nanocrystals of PbSe was deposited on carbon-coated copper grids and dried in air.

Results and Discussion

PbSe Mechanochemically Synthesized in Laboratory Mill

The selected X-ray diffraction patterns of the mechanochemically synthesized lead selenide prepared, according to the reaction (1), are shown in Fig.1 and confirm crystalline nature of PbSe. The peaks were identified based on JCPDS card 6-354 and correspond to clausthalite, PbSe. The average crystallite size of 37 nm was calculated from XRD data by Williamson-Hall method for mechanochemically synthesized PbSe (milling time: 10 min).

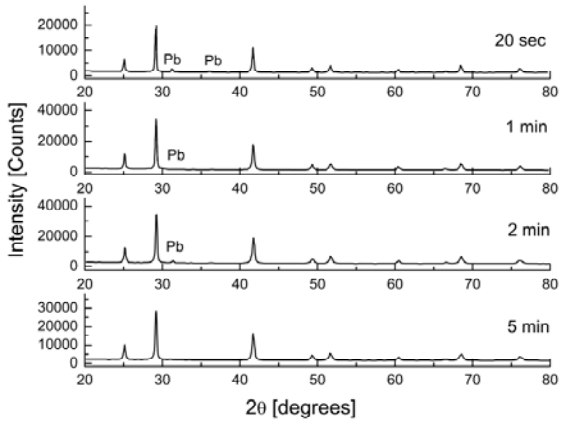

Figure 1. XRD patterns of lead selenide PbSe synthesized in the laboratory mill (milling time: 20 s - 5 min)

The values of specific surface area, mean particle size and conversion degree of the reactions are summarized in Table 1. The process of mechanochemical synthesis of PbSe is relatively fast and almost completed after 5 min. This is confirmed by a high degree of conversion, α = 87-94 % (Table 1). According to Tkáčová [21] the rate of reactions in mixtures of solids at an early stage of its progress is controlled by the number and area of contact spots created by homogenizing and by diffusion in solids. Specific surface area of mechanochemically synthesized PbSe increases with time of mechanochemical synthesis, and maximum value of 2.4 $m^2.g^{-1}$ has been reached for 12 min (Table 1). In the early stage of the mechanochemical synthesis (up to 2 min), the mean particle size of PbSe increases due to the creation of contact spots, high rate of diffusion, and growing layer of solid product. In the period of reaction (5-10 min), the mean particle size of PbSe achieves the lowest values, see Table 1. The prolonged time of synthesis results in an agglomeration effect of synthesized PbSe particles (Table 1).

Table 1. Specific surface area, S_A, mean particle size, D_M, and conversion degree of reaction, α, for PbSe synthesized in the laboratory mill for various times, t_M.

t_M	S_A [$m^2.g^{-1}$]	D_M [nm]	α [%]
20 s	0.2	687	87
1 min	0.8	1204	94
2 min	1.1	1632	90
5 min	1.8	12	94
10 min	2.2	17	94
12 min	2.4	52	-
15 min	2.0	72	-

Morphology of the synthesized PbSe was observed using SEM and TEM. SEM micrograph shows the formation of agglomerates of synthesized PbSe particles in the laboratory mill (Fig.2). It is clearly seen that the particles are agglomerated and have irregular shape and non-homogeneous size distribution.

Most of the PbSe nanocrystals were easily separated from the agglomerates after ultrasonic de-agglomeration. TEM micrograph revealed that synthesized PbSe nanocrystals are idiomorphic and the prevailing crystallographic form of the crystallites is cube (100) (Fig. 3(a)). Size of PbSe nanocrystals ranges from few nanometers up to 80 nm, with the average size being consistent with the value calculated from XRD data. The results of electron diffraction (ED) analysis of the lattice spacing of the PbSe nanocrystals (Fig. 3(b)) correspond to the reported XRD data for PbSe (JCPDS card 78-1903).

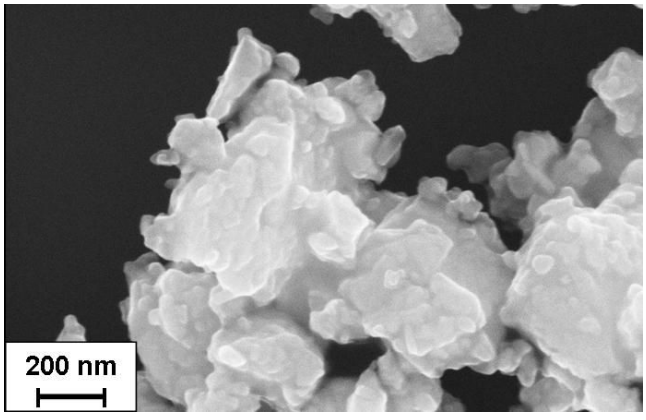

Figure 2. SEM image of lead selenide (PbSe) synthesized in the laboratory mill (milling time: 10 min)

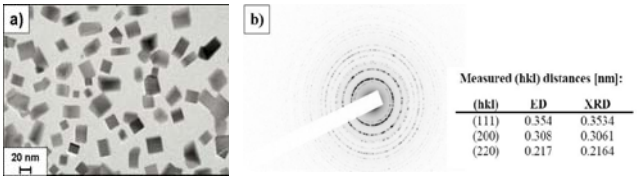

Figure 3. (a) TEM image of lead selenide PbSe synthesized in the laboratory mill (milling time: 5 min), (b) ED pattern of PbSe nanocrystals

PbSe Mechanochemically Synthesized in Industrial Mill

The X-ray diffraction patterns of the mechanochemically synthesized lead selenide prepared according to the reaction (1) in the industrial mill are shown in Fig.4. In this mill the process of mechanochemical synthesis is also fast and effective; the degree of conversion to PbSe is 97 % after 6 min of mechanochemical synthesis. Specific surface area of synthesized PbSe increases and the mean particle size decreases with time of mechanochemical synthesis (Table 2).

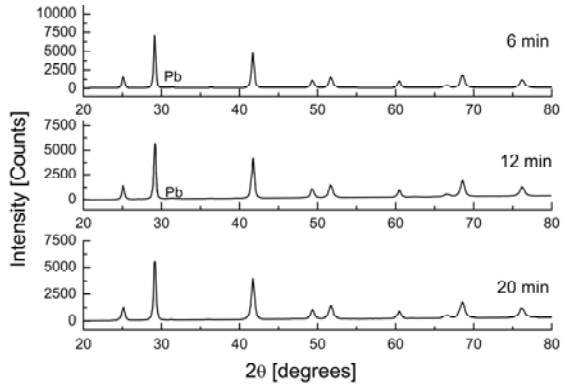

Figure 4. XRD patterns of Pb and Se precursors and lead selenide PbSe synthesized in the industrial mill (milling time: 6 - 20 min).

Table 2. Surface area, S_A, mean particle size, D_M, and conversion degree of reaction, α, for PbSe synthesized in the industrial mill for various times, t_M

t_M [min]	S_A [$m^2.g^{-1}$]	D_M [μm]	α [%]
6	0.4	14	97
20	0.8	8	98

STEM micrograph of mechanochemically synthesized PbSe in an industrial mill is shown in Fig.5. The smaller and bigger irregular nanoparticles situated in the clusters with the size from 0.2 to 1.0 μm are clearly distinguished.

TEM micrograph does not confirm that synthesized PbSe particles are idiomorphic, perfect stoichiometric cubes. This is in contrast to PbSe nanoparticles synthesized in the laboratory mill (Fig. 6(a)). In the industrial mill the stable aggregates develop that could not be destroyed ultrasonically. The values of the mean particle size of 14 μm and 8 μm also confirm this fact (Table 2).

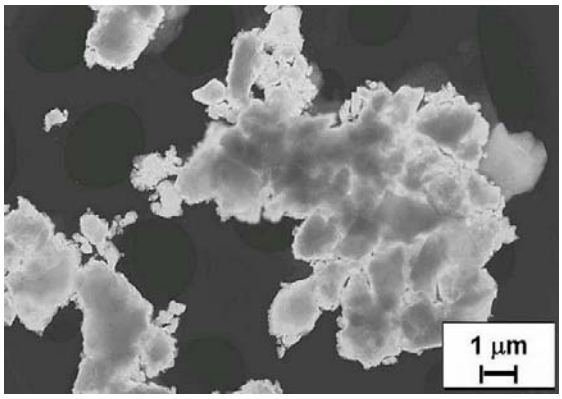

Figure 5. STEM image of lead selenide PbSe mechano-synthesized in the industrial mill (milling time: 20 min)

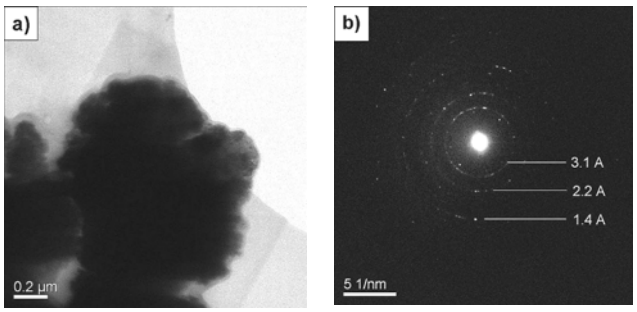

Figure 6. TEM image (a) and electron diffraction pattern (b) of PbSe mechanosynthesized in the industrial mill (milling time: 20 min)

Separation of aggregated particles becomes impossible because these particles are grown by chemical bonds [22-23]. The presence of Debye-Scherrer rings in the electron diffraction pattern provides evidence for the crystalline character of PbSe nanoparticles (Fig. 6(b)). The rings are almost continuous due to the fact that sample contains a fraction of very small particles. The bigger particles are visible in the electron diffraction pattern as discrete diffraction spots.

Conclusions

Lead selenide PbSe nanoparticles were synthesized by mechanochemical route from elemental Pb and Se. The mean particle size of the obtained particles (12-72 nm) is strongly dependent on the milling conditions. The crystalline nature and cube shape of the synthesized PbSe are well documented. Both, the laboratory as well as industrial mills show good applicability for this one-pot mechanochemical synthesis route.

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References

1. W.W. Yu, J.C. Falkner, B.S. Shih, V.L. Colvin, *Chem. Mater.,* 16 (2004) 3318.
2. B. Poudel, W.Z. Wang, D.Z. Wang, J.Y. Huang, Z.F. Ren, *J. Nanosci. Nanotechnol.*, 6 (2006) 1050.
3. J. Zhu, X. Liao, J. Wang, H.-Y. Chen, *Mater. Res. Bull.*, 36 (2001) 1169.
4. M. Chen, Y. Xie, J. Lu, Y. Zhu, Y. Qian, *J. Mater. Chem.*, 11 (2001) 518.
5. C.B. Murray, S. Sun, W. Gaschler, H. Doyle, T.A. Betley, C.R. Kagan, *J. Research & Devel.*, 1 (2001) 47.
6. T. Ohtani, K. Ikeda, Y. Hayashi, Y. Fukui, *Mater. Res. Bull.*, 42 (2007) 1930.
7. C.E.M. Campos, J.C. de Lima, T.A. Grandi, S.M. Souza, P.S. Pizani, *Solid State Commun.*, 142 (2007) 270.
8. J.C. de Lima, V.H.F. dos Santos, T.A. Grandi, *Nanostruct. Mater.*, 11 (1999) 51.
9. P. Baláž, E. Boldižárová, E. Godočíková, J. Briančin, *Mater. Lett.*, 57 (2003)1585.
10. E. Godočíková, P. Baláž, E. Gock, W.S. Choi, B.S. Kim, *Powder Technol.*, 164 (2006) 147.
11. M. Achimovičová, E. Godočíková, P. Baláž, J. Kováč, A. Šatka, *Rev. Adv. Mater. Sci.*, 18 (2008) 216.
12. P. Baláž, *Mechanochemistry in Nanoscience and Minerals Engineering*, Springer, Berlin Heidelberg (2008).
13. T. Tsuzuki, P.G. McCormick, *Appl. Phys.*, A65 (1997) 607.
14. T. Tsuzuki, P.G. McCormick, *Nanostruct. Mater.*, 12 (1999) 75.
15. P.G. McCormick, T. Tsuzuki, J.S. Robinson, J. Ding, *Adv. Mater.*, 13 (2001) 1008.
16. L. Takacs, M. Susol, *J. Solid State Chem.*, 121 (1996) 394.
17. L . Takacs, *Mater. Sci. Forum,* 513 (1998) 269.
18. L. Takacs, *Progr. Mater. Sci.*, 47 (2002) 355.
19. E. Gock, V. Vogt, P. Baláž, Proceedings of XXIV. *International Mineral Processing Congress*, Science Press, Beijing, (2008), p. 3246.
20. G.K. Williamson, W.H. Hall, *Acta Metall.*, 1 (1953) 22.
21. K. Tkáčová, *Mechanical Activation of Minerals*, Elsevier, Amsterdam (1989), p.155.
22. A.Z. Juhász, L. Opoczky, *Mechanical Activation of Minerals by Grinding: Pulverizing and Morphology of Particles*, Ellis Horwood, Chichester 1990.
23. P. Pourghahramani, E. Forssberg, *Int. J. Miner. Process*., 79 (2006) 106.