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INFLUENCE OF SOLUBLE SALT MATRIX ON MECHANOCHEMICAL PREPARATION OF PbS NANOPARTICLES

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Abstract. The synthesis of PbS nanocrystalline semiconductor particles was performed in a laboratory mill without and with an addition of a soluble salt (sodium acetate or sodium chloride). The salt matrix was removed by washing with de-ionized water and methanol. X-ray analysis, specific surface area measurement, particle size distribution analysis, UV-VIS spectroscopy and scanning electron microscopy were used for a characterization of microstructure and surface properties of synthesized PbS particles (JCPDS 5-592). Based on this comparative study it can be established, that by the addition of sodium acetate and as well as sodium chloride the specific surface area and the mean particle size of PbS are influenced.

1. INTRODUCTION

Recently, it has been reported that nanostructured materials can be synthesized by mechanochemically induced solid-state displacement reactions [1-7]. This method of synthesis is performed in milling devices – mills and the milling is a key operation for nanostructured materials preparation. Most of unique properties of nanoparticles depend not only on their nanodimension but also on dispersity. During dry milling the adhesive forces grow with decreasing particle size and cyclic stressing leads to recombination of newly created particles into unstable aggregates, or even into stable agglomerates, as a result of various reasons, e.g. partial fusion of the surfaces of particles [8].

Tsuzuki and McCormick [5,7,9] prepared agglomeration-free nanopowders of various sulphides dispersed within a soluble salt matrix by mechanochemical processing. The salt matrix is selectively removable by washing with water and moreover this new synthesis method has significant potential for large scale production due to high efficiency and low cost process. Lead sulphide is an important semiconductor due to its optical and electronic properties and it is used as an advanced material in many fields such as IR detectors and Pb^{2+} ion-selective sensors. One of the goals in semiconductor science is to control the morphology of nanoparticles [10].

The aim of this study was to compare physicochemical properties of PbS nanoparticles synthesized by simple mechanochemical route with and without soluble organic (CH_3COONa) and inorganic (NaCl) salt matrix, respectively.

2. EXPERIMENTAL

Mechanochemical synthesis of PbS nanoparticles without soluble salt matrix was performed in a planetary mill Pulverisette 6 (Fritsch, Germany)

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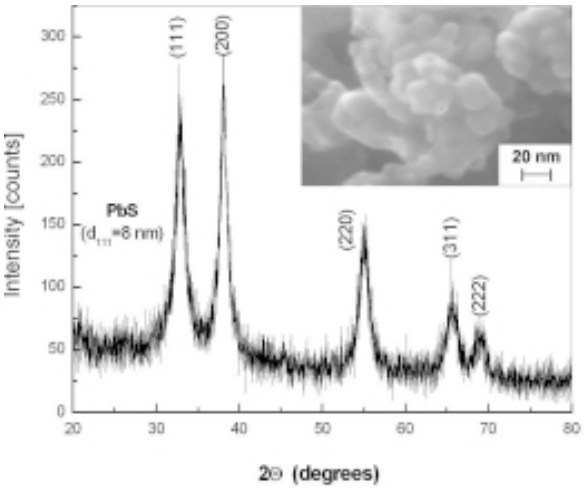

Fig. 1. X-ray diffraction pattern and SEM microphotograph of mechanochemically synthesized PbS nanoparticles without salt matrix. Time of mechanochemical synthesis, t_M=5 min.

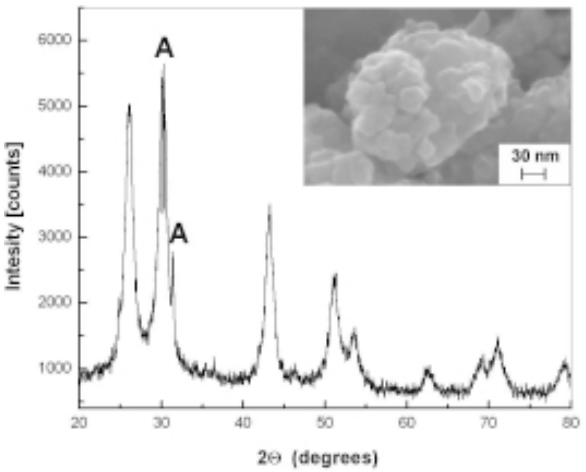

Fig. 2. X-ray diffraction pattern and SEM microphotograph of mechanochemically synthesized PbS nanoparticles with CH_3COONa addition (A-CH_3COONa). Time of mechanochemical synthesis, t_M=5 min.

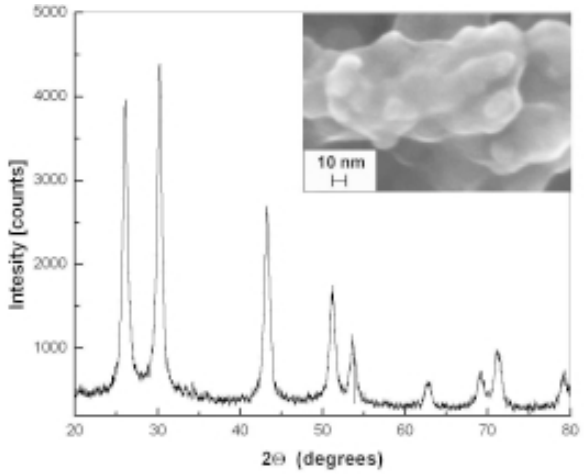

Fig. 3. X-ray diffraction pattern and SEM microphotograph of mechanochemically synthesized PbS nanoparticles with NaCl addition. Time of mechanochemical synthesis, t_M =5 min.

according to the reaction (1). The following milling conditions were used: loading of the mill with 50 balls of 10 mm diameter; material of milling chamber and balls: tungsten carbide; rotation speed of the planet carrier: 400 rpm; milling time in argon atmosphere: 1-20 min.

$$(CH_3COO)_2 Pb.3H_2O + Na_2S.9H_2O \rightarrow PbS + 2CH_3COONa + 12H_2O, \quad (1)$$

$$(CH_3COO)_2 Pb.3H_2O + Na_2S.9H_2O + CH_3COONa \rightarrow PbS + 3CH_3COONa + 12H_2O, \quad (2)$$

$$(CH_3COO)_2 Pb.3H_2O + Na_2S.9H_2O + NaCl \rightarrow PbS + 2CH_3COONa + NaCl + 12H_2O. \quad (3)$$

The application of organic and inorganic salt matrix, respectively was performed according to reactions (2) and (3). The weight and the molar ratio between the reactants were selected empirically in the initial powder mixture. After the completion of reactions (1) - (3) PbS nanoparticles have been washed by water and methanol, decanted and dried.

X-ray diffraction measurements were carried out by using a diffractometer DRON 2.0 (Russia) with goniometer GUR 5 and FeK_α radiation, and a diffractometer Philips PW 1050 (Germany) working in the 2θ regime with CuK_α radiation. The scanning electron micrographs of investigated samples were obtained on a scanning electron microscope LEO 1550 (Germany). The specific surface area was determined by nitrogen sorption method at liquid nitrogen temperature, using a Gemini 2360 ap-

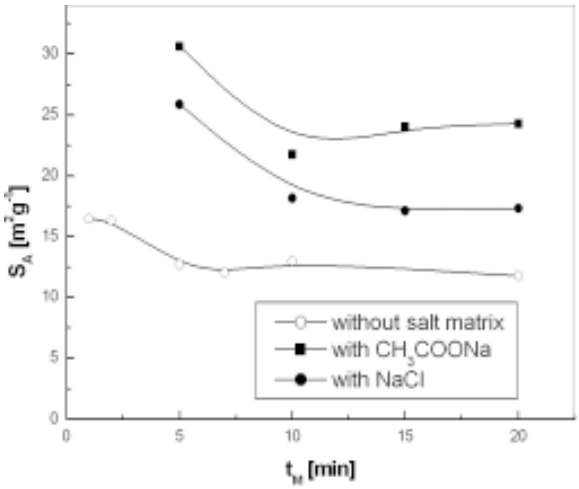

Fig. 4. Specific surface area, S_A of synthesized PbS with and without soluble salt matrix vs. time of mechanochemical synthesis, t_M.

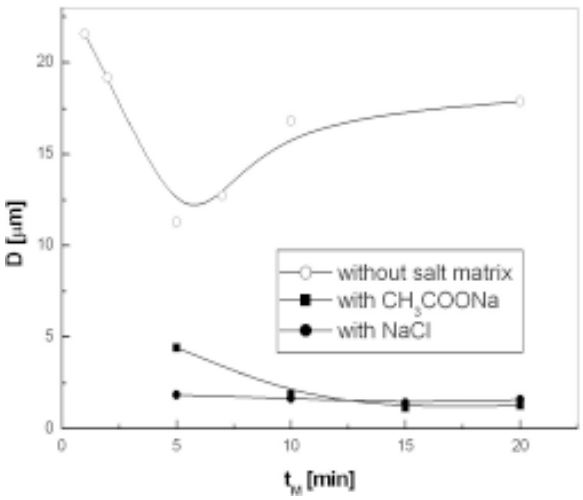

Fig. 5. Dependence of mean nanoparticle size of PbS, *D* vs. time of mechanochemical synthesis, t_M.

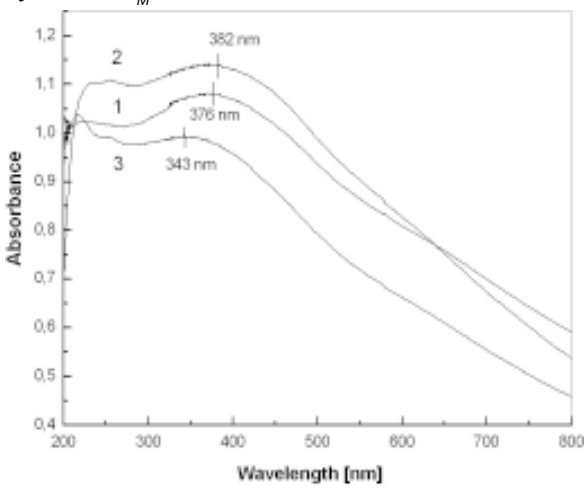

Fig. 6. UV-VIS optical absorption spectra of mechanochemically synthesized PbS nanoparticles, 1 - without salt matrix, 2 - with CH_3COONa, 3 – with NaCl.

paratus (Micromeritics, USA). The particle size distribution was measured by He-Ne laser beam scattering (λ = 0,6328 mm) on a particle size analyzer HELOS (Sympatec GmbH, Germany) with wet dispergation unit SUCCEL 12LA. UV-VIS optical absorption spectra were measured on the spectrophotometer HEλIOS GAMMA (Great Britain) in the range 200-800 nm in silica glass cell by dispergation of PbS particles in absolute ethanol.

3. RESULTS AND DISCUSSION

3.1. Mechanochemically synthesized PbS nanoparticles without salt matrix

X-ray diffraction pattern of PbS nanoparticles prepared by mechanochemical reaction (1) is given in Fig. 1. We clearly see the diffraction peaks corresponding to (111), (200), (220), (311), (222) planes of lead sulphide PbS phase (JCPDS 5-592). No other products were confirmed in this mechanochemically synthesized product. Calculated particle size of crystallites according to Scherrer´s formula [11] is 8 nm. Inset of SEM microphotograph shows the agglomerates of obtained PbS nanoparticles. The surface analysis reveals non-homogeneous distribution of nanoparticles that form the irregular particles.

3.2. Mechanochemically synthesized PbS with organic and inorganic salt matrix

It is obvious from X-ray diffraction patterns (Figs. 2 and 3), that PbS was prepared by mechanochemical synthesis according to reactions (2)-(3). The diffraction peaks conform to various planes of lead sulphide (JCPDS-5-592) and also non-reacted sodium acetate (JCPDS-28-1029). SEM analysis of PbS prepared with CH_3COONa salt matrix confirmed more homogeneous distribution of PbS nanoparticles with indication of cubic morphology, although still agglomerated particles (Fig. 2). SEM

analysis of PbS prepared with NaCl salt matrix illustrates the agglomerate of PbS nanoparticles with dimensions 10-20 nm (Fig. 3).

3.3. Evaluation of salt matrix effect on physico-chemical properties of mechanochemically synthesized PbS

Specific surface area measurement and particle size distribution are the most commonly used methods for analysis of dispersion system of nanoparticles prepared by mechanochemical synthesis. Fig. 4 shows the dependence of specific surface area, S_A of mechanochemically synthesized PbS with and without addition of CH_3COONa and NaCl, respectively, on the time of mechanochemical synthesis, t_M. The obtained values of specific surface area were 2–2.4 times higher during 5-20 min of mechanochemical synthesis with addition of CH_3COONa. The effect of NaCl addition is slightly less pronounced. The value of specific surface area for the sample with time of mechanochemical synthesis, t_M = 5 min increased twice and for the sample with time of mechanochemical synthesis, t_M = 20 min increased 1.5-times. However, the effect of agglomeration was not overcome due to interparticles sticking during mechanochemical synthesis.

On the basis of analysis of PbS particle size distribution the mean size of particles value, *D* was calculated. Fig. 5 shows that addition of sodium ace-tate or sodium chloride favourably affects mechanochemical synthesis of PbS nanoparticles from the viewpoint of PbS particles preparation with smaller size. The value, *D* of PbS particles decreased 2.5-14 times during mechanochemical synthesis with addition of CH_3COONa and 6-11 times during mechanochemical synthesis with addition of NaCl.

UV-VIS optical absorption spectra of mechanochemically synthesized PbS nanoparticles with and without salt matrix are shown in Fig .6. The spectra illustrate soft extended absorption edge (~376 nm) of PbS nanoparticles synthesized without salt matrix, which corresponds to 3.28 eV. Also the UV-VIS absorption edge is about 382 nm for PbS synthesized with the addition of CH_3COONa, which corresponds to 3.23 eV and 343 nm for PbS synthesized with NaCl addition, which corresponds to 3.62 eV. These UV-VIS spectra assign the blue shift from the direct band gap 0.41 eV of bulk PbS crystals [12]. This is an indication of quantum confinement, because the mean size of the PbS nanoparticles is smaller than the excitonic Bohr radius of the bulk PbS (ca. 18 nm) [13].

4. CONCLUSION

In this study lead sulphide, PbS was synthesized by one-stage solid phase reaction – mechanochemical synthesis in the planetary ball mill. The addition of soluble salt matrix (CH_3COONa or NaCl) improved the specific surface area and the homogeneity of particle size distribution of synthesized PbS. According to El-Shall [14] organic or inorganic chemical additives can influence milling due to the modification of the milling regime or to influence interactions between particles and balls and mill wall, and among particles themselves (due to the changes in frictional characteristics). We can probably apply this statement for PbS mechanochemical synthesis with CH_3COONa or NaCl addition. UV-VIS spectra confirmed that prepared PbS particles were nanodimensional. In future experiments we consider to prepare agglomeration-free PbS nanoparticles with the cubic morphology dispersed in soluble salt matrix by the choice of suitable experimental conditions such as mechanochemical synthesis conditions (milling time, milling atmosphere, size of milling balls), stoichiometry of reactants and concentration of added salt matrix.

ACKNOWLEDGEMENT

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