Functional Materials 21, No.4 (2014)

Morphology of lead sulfide crystalline particles in size-limited state

O.S.Bezkrovnyi, Yu.V.Yermolayeva, O.M.Vovk, M.V.Dobrotvorskaya, M.A.Chayka, A.V.Tolmachev

Institute for Single Crystals, STS "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received September 16, 2014

Monocrystalline PbS particles of cubic structure ranging in size from 3 to 500 nm, were obtained. Influence of growth conditions on the final particles size and dispersion of lead sulfide nanocrystals, as well as effects of nanocrystals size on their shape have been studied. It was found that increasing of monocrystalline particles size more than 12 nm leads to transition of shape from spherical to cubic; that indicate predominance of surface energy influence on equilibrium geometry of nanocrystals.

Получены монокристаллические частицы PbS размерами 3–500 нм с кубической кристаллической структурой. Исследовано влияние условий роста на дисперсию, конечный размер нанокристаллов сульфида свинца. Установлено, что при уменьшении размеров монокристаллических частиц до 12 нм наблюдается переход от кубической формы к сферической, что свидетельствует о доминировании влияния поверхностной энергии на равновесную геометрию нанокристаллов.

Морфологія кристалічних частинок сульфіду свинцю у розмірно-обмеженому стані. *О.С.Безкровний, Ю.В.Єрмолаєва, О.М.Вовк, М.В.Добротворська, М.А.Чайка, О.В.Толмачов.*

Отримано монокристалічні частинки PbS розмірами 3–500 нм із кубічною кристалічною структурою. Досліджено вплив умов росту на дисперсію та кінцевий розмір нанокристалів сульфіду свинцю. Встановлено, що при зменшенні розмірів монокристалічних частинок до 12 нм спостерігається перехід від кубічної форми до сферичної, що свідчить про домінування впливу поверхневої енергії на рівноважну геометрію нанокристалів.

1. Introduction

One of the top innovative developing field in materials science is obtaining and testing of 2D and 3D consolidated materials using methods of directed self-assembly, where agglomerated semiconducting nanocrystals constitute basic structure-forming units [1–3]. Lead sulfide among great number of semiconductors attracts special attention due to strong size dependence of band gap. It opens broad prospects for its use in photovoltaic converters [2], photodetectors [4] infrared detectors [5], and electroluminescent and photoluminescent phosphors of IR emission [6, 7].

It is well known that an implementation of self-assembly of close-packing structures requires monosized spherical structural units of low agglomeration [8, 9].

The feature of the sulfides particles formation is low energy of metal-anion bond formation. This lead to the crystalline product formation in growth solution. Hence, varying growth conditions give rise to a possibility of obtaining the crystalline product with given morphology directly from a solution. This approach was implemented in the literature on the example of cadmium and zinc sulfides particles, which were obtained in plurality of morphological forms by crystallization from aqueous solutions [10–12].

However, a problem of PbS spherical particles formation remains poorly investigated. Comparing to cadmium and zinc sulfides lead sulfide has higher dissociation energy (337 kJ/mol for PbS, while 205 and 208 kJ/mol for ZnS and CdS, respectively) [13]. Because of this difference in metal-sulfur energy bond formation, growth rate of lead sulfide is significantly lower comparing to particles of ZnS and CdS. Thus, the formation of independent single crystalline PbS particles of cubic shape is possible [14]. It is reasonable to assume that it is necessary to increase growth rate for the formation of polycrystalline spheres. It can be achieved by increasing temperature of the growth medium. Similarly to ZnS and CdS, formation of great number of crystallization centers and their agglomeration into spheres to minimize surface energy takes place in the growth solution. It was shown [14] a possibility of PbS monocrystalline particles formation of different morphology including spheres by crystallization from organic salts melts. However, a disadvantage of this approach is the difficulty of controlling of particles size distribution in the final product.

An alternative approach in obtaining of crystalline spherical particles is the transition to nanoscales. Obviously, due to high curvature of surface of isolated nanoparticles there is large excess of surface energy, that may result distortion of crystal structure. It was shown in [15] that the difference in the lattice parameters may reach 17 % on the periphery comparing to the center of the nanoparticles. As a result of such distortion of the crystal lattice, it becomes possible to obtain spherical shaped isolated nanocrystals. This was observed on the example of 2–5 nm Y_2O_3 nanocrystals [16].

It is known that monodisperse isolated 2–3 nm nanocrystals of sulfides may be prepared by "explosive nucleation" method with sudden isolation of particles being formed [17–20]. However, despite a number of publications on sulfide nanocrystals obtaining and their properties testing, there are no special studies of size-limited conditions influence on morphology of nanocrystals. And the aim of the study presented is to investigate the influence of particle size of PbS on their morphology and determination of size limitations of existence of spherical shaped particles.

2. Experimental

PbS crystalline submicron particles have been obtained by precipitation method from aqueous solution. The synthesis was carried out by quick mixing of three solutions in 500 ml flask and further stirring at 25±0.05°C during 30 min in presence of gelatin (0.1 wt.%.) as stabilizing agent. In this method solution 1 (50 ml) contains 0.053 mol/l of $Pb(NO_3)_3$ and 0.22 mol/l of HNO_3, solution 2 (50 ml) contains 0.053 mol/l of thioacetamide and 0.22 mol/l of HNO_3, and solution 3 (100 ml) contains 0.22 mol/l of HNO_3. Aging time for each solution was 16 h prior using.

PbS nanocrystals synthesis is based on the procedure described in [21]. Variable synthesis parameters were: temperature and duration of the synthesis and reagents concentrations. The synthesis is carried out in nitrogen atmosphere to avoid oxidation. First, a stock solution of 0.16 g of S in 15 mL of oleyl amine (OLA) was heated until 80°C for 30 min under stirring and afterward cooled to room temperature. In a three-neck flask 0.56 g of $PbCl_2$ was mixed with 10 mL of OLA and heated until 150–225°C. After 30 min the solution of S (in a required molar ratio to $PbCl_2$) was injected into the three-neck flask. When desired growth time was reached, the reaction was quenched by pouring the growth solution into cold hexane. Excess of $PbCl_2$ and PbS agglomerates was then removed by centrifugation with following redispersion. The supernatant was precipitated by ethanol and redispersed in hexane. Latter two operations were repeated three times. The structure and morphology of nanoparticles were investigated by transmission electron microscopy (EM-125) and scanning electron microscopy (JSM-6390LV). Chemical composition was examined by X-ray photoelectron spectroscopy (XPS) with XPS-800 Kratos spectrometer.

3. Results and discussions

It is known that significant problem of sulfide nanocrystals obtaining is their oxidation giving sulfate anions [20, 21]. That's why chemical composition of the obtained nanocrystals was investigated. Fig. 1 shows the X-ray photoelectron spectrum of $4f$ level of lead ion. The spectrum contains two lines — 137.4 eV ($4f_{7/2}$) and 142 eV ($4f_{5/2}$)

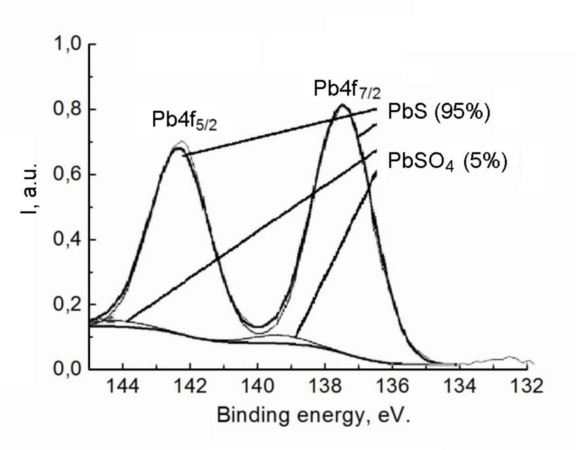

Fig. 1. Pb 4*f* X-ray photoelectron spectra of nanocrystals.

related to Pb^{2+} associated with sulfide anions S^{2-}. At the edge of these lines the weak lines at 139.4 eV and 144 eV are observed. They relate to Pb^{2+}, associated with sulfate anions SO_4^{2-}. Analysis of the area under the curve shows that content of the main substance in PbS nanocrystals is not less than 95 %. Content of $PbSO_4$ as the most likely product of sulfide oxidation does not exceed 5 %.

Typical image of different sizes (3–500 nm) of PbS crystals is shown on Fig. 2. It should be noted that the morphology of the PbS particles varies from spherical to cubic. Such changes are due to the influence of surface energy at the early stages on the particle growth. Consequently, the shape of <10 nm size crystalline particles is sphere (Fig. 2a). For large particles impact the surface energy becomes smaller and shape of the particles is determined by the growth rate of the planes. Planes that have a minimal growth rate are absorbed by planes with higher growth rate. That leaves only the planes with prime indices (100, 010, 001) and the particle acquires the cubic shape (Fig. 2b). That's why we investigated only nanometer scale particles in further to find a size range of spherical shape of PbS crystalline particles. Analysis

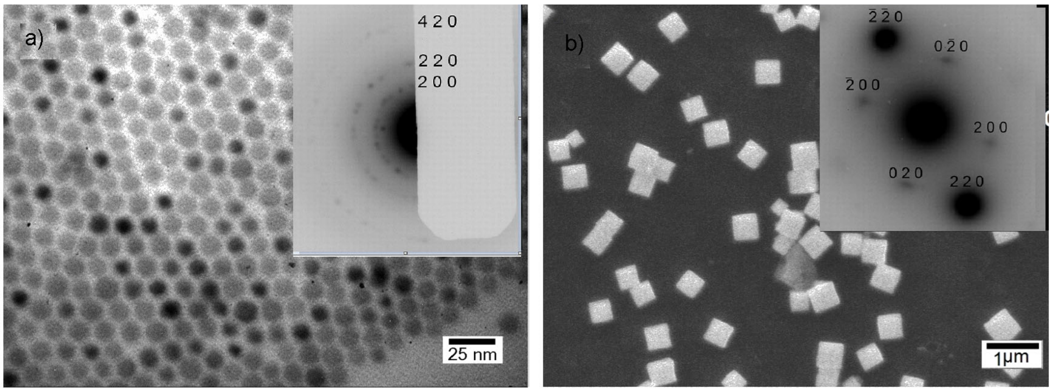

Fig. 2. Typical images and SAED pattern of nanosize (a) and submicron (b) crystals of PbS.

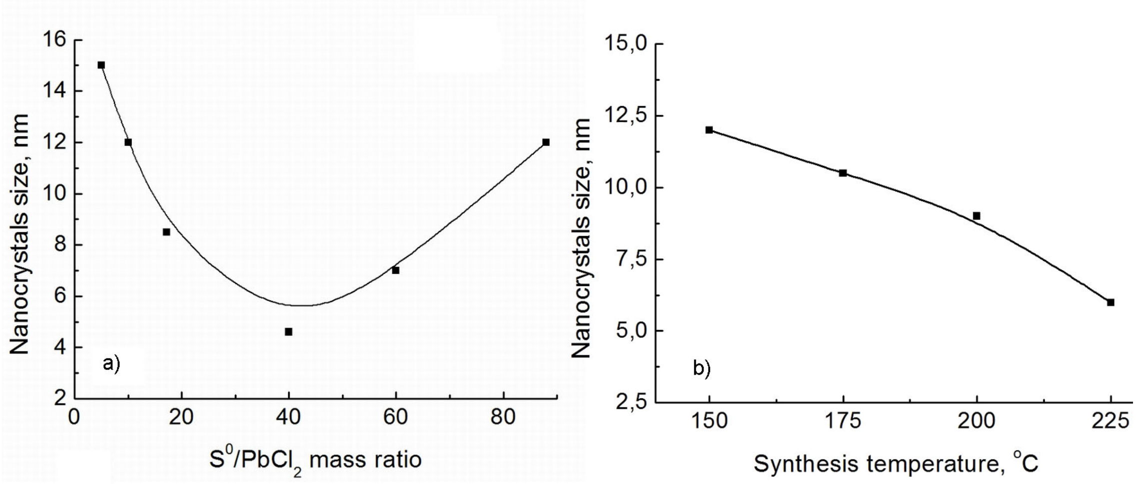

Fig. 3. Average diameter of PbS crystals depending on the $S/PbCl_2$ mass ratio (synthesis temperature 200°C) (a) and synthesis temperature ($S/PbCl_2$ mass ratio = 10/1) (b).

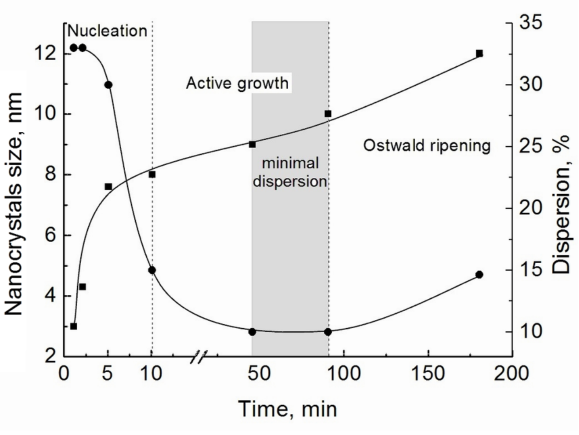

Fig. 4. Average diameter and size dispersion of PbS crystals depending on the synthesis time.

of electron diffraction of PbS particles displays that the obtained particles are monocrystalline with cubic structure (JCPDS No.05-0592).

It is known that size of nanocrystals formed during explosive nucleation is determined by the ratio of phase-forming ions in the reaction mixture. This affect to crystallization centers number in the growth solution. As it shown on Fig. 3 the minimum size of PbS nanocrystals is observed for weight ratio of $PbCl_2$:S = 1:40. Apparently, at this weight ratio of starting reactants the crystallization centers number is maximal. This leads to the minimum size of obtained PbS crystals. Deviations from the said ratio of starting reactants leads to increasing of PbS nanocrystals average size.

It should be noted that crystallization centers formation and crystal growth is diffusion-controlled process. As a result, the size of nanocrystals is being strongly influenced by synthesis temperature. It was found that increasing of the synthesis temperature leads to decreasing of nanocrystals size. The latter occurs due to increasing of number of nucleus, that in turn caused by increasing of probability of phase-forming ions collision (Fig. 3b). By taking into consideration the known fact of change of dispersed nanocrystals composition during the growth process we were investigated the time evolution of PbS nanocrystals size and their dispersion. Conditionally, growth of nanocrystals can be divided into three stages (Fig. 4). At the "nucleation" stage there is particle growth by secondary nucleation. It is due to high degree of supersaturation at this stage. As a result, there is a great dispersion of nanocrystals size observed. At the stage of "active growth" the supersaturation is lower and there is only growth of particles , which are already formed at the previous stage. This is followed by focusing of particles sizes. However, during further increasing of the growth time (at the Ostwald ripening stage) the larger nanocrystals occur as a result of dissolution of smaller ones. This is followed by defocusing of the particles size. Thus, we can distinguish the optimal time for nanocrystals formation with a minimal dispersion of size.

On the example of isolated nanocrystals of PbS we have shown the change in particles shape from spherical to cubic for nanocrystals bigger than 12 nm (see Fig. 5). A possible reason of this effect is deformation of the crystal structure of the particles. This may by the result of the excessive surface energy influence due to Laplace pressure $\Delta p = 2\sigma/r$, created by surface tension "σ". The value of which increases with decreasing of particle size "r". Apparently, in such circumstances, in order to minimize surface energy the formation of spherical shape nanocrystals takes place.

4. Conclusions

3–500 nm Monocrystalline PbS particles with cubic structure and content of the basic substance not less than 95 % were obtained. The influence of the synthesis conditions on PbS nanocrystals size and their dispersion have been investigated. The optimal synthesis conditions for obtaining

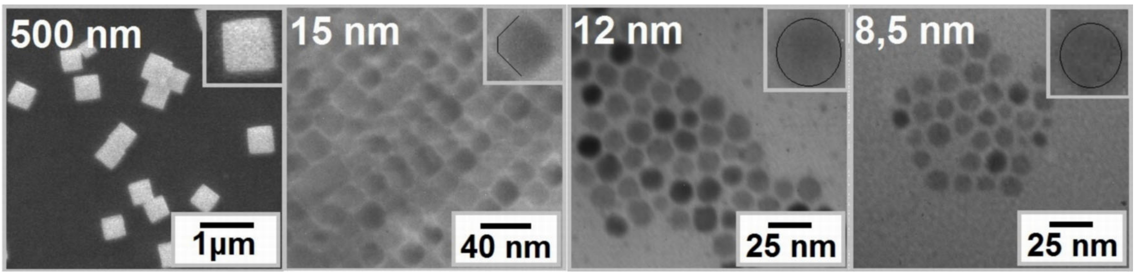

Fig. 5. Size evolution of PbS crystals morphology.

PbS nanocrystals with minimal dispersion in size (less than 10 %) were found. It was found, that increasing of the monocrystalline particles size more than 12 nm leads to transition of the nanocrystals shape from spherical to cubic. It indicates the dominance of the surface energy influence on the equilibrium geometry of the nanocrystals.

References

1. J.M.Luther, M.Law, Q.Song et al., *ACS.*, **2**, 271 (2008).
2. J.M.Luther, J.Gao, M.T.Lloyd et al., *Adv. Mater.*, **22**, 3704 (2010).
3. J.D.Klem, H.Shukla, S.Hinds et al., *Appl. Phys. Lett.*, **92**, 212105 (2008).
4. G.Konstantatos, E.H.Sargent, *Appl. Phys. Lett.*, **91**, 173505 (2007).
5. S.Miri, A.Rostami, M.Dolatyari et al., *E. Phys. St. Sol. A.*, **210**, 420 (2013).
6. G.Konstantatos, C.Huang, L.Levina et al., *Adv. Funct. Mater.*, **15**, 1865 (2005).
7. X.S.Zhao, E.H.Sargent, E.Kumacheva, *Range Adv. Mater.*, **16**, 926 (2004).
8. V.I.Roldugin, *Uspehi Himii*, **73**, 123 (2004).
9. Zhengwei Mao, Haolan Xu, Dayang Wang, *Adv. Funct. Mater.*, **20**, 1053 (2010).
10. R.Vacassy, S.M.Scholz, J.Dutta et al., *J. Am. Ceram. Soc.*, **81**, 2699 (1998).
11. B.Bodo, N.Talukdar, P.K.Kalita, *IJERA*, **2**, 1656 (2012).
12. W.Chao-Ming et al., *Chin. J. Struct. Chem.*, **27**, 445 (2008).
13. S.S.Batsanov, Strukturnaya Himiya. Faktyi i Zavisimosti, Dialog-MGU, Moscow (2000) [in Russian].
14. Z.Peng, Y.Jiang, Y.Song, C.Wang, H.Zhang, *Chem. Mater.*, **20**, 3153 (2008).
15. M.B Muradov, G.M.Eyvazova, Rashid Turan et al., *Nanotehnika*, **3**, 60 (2008).
16. R.Bazzi et al., *J. Luminescence.*, **102**, 445 (2003).
17. K.S.Babu, T.R.Kumar, P.Haridossa, C.Vijaya, *Talanta*, **66**, 160 (2005).
18. L.Cademartiri, E.Montanari, G.Calestani et al., *ACS*, **128**, 10337 **(2006).**
19. I.Moreels, K.Lambert, D.Smeets et al., *ACS NANO*, **3**, 3023 (2009).
20. L.Cademartiri, G.von Freymann, A.C.Arsenault et al., *Small*, **1**, 1 (2005).
21. N.Zhao, T.P.Osedach, Liang-Yi Chang et al., *ACS NANO*, **1** (2010).