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Preparation of Nanocrystalline Lead Sulfide Powder with Controlled Particles Size

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Abstract—Lead sulfide nanopowders have been prepared from aqueous solutions of lead acetate and sodium sulfide in the presence of sodium ethylenediaminetetraacetate or citrate. From microscopy and X-ray diffraction data purity and size of the formed nanoparticles are determined by the reagents concentrations, presence and nature of the complexing ligand, and the ratio of lead ions concentration to that of the ligand. PbS nanoparticles of the predefined size ranged from 5 to 55 nm can be prepared by controlled hydrochemical precipitation.

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The interest to nanocrystalline state of the matter originates from often observed unique set of its physical and chemical properties. Much attention is paid to the synthesis of semiconductor nanoparticles to be applied to modern microelectronic devices. Significant part of research on the synthetic methods has been directed to the preparation of nanoparticles with controlled size and shape [1, 2].

The interest to lead sulfide is not only due to its semiconductor properties (narrow forbidden band of 0.41 eV and large exciton size of 18–24 nm) but also to variety of its particles morphology depending on the preparation conditions.

Nanocrystalline lead sulfide can be potentially utilized in electroluminescent devices, IR photodetectors, solar cells, near-IR communication devices, and switches [3–6]. Nanotubular, dendritic, star-, and flower-shaped PbS nanoparticles have been prepared [7–11]. Modern methods of lead sulfide synthesis include spontaneous self-organization of PbS nanoparticles to yield nanotubes [7], hydro- and solvothermal synthesis [11], homogeneous hydrolysis in the presence of surfactants [12], electrodeposition of nanofilms [13], solution precipitation under microwave heating [14], microwave-assisted thermal decomposition of precursors, for example, lead diethyldithiocarbamate $Pb(C_2H_5)_2(NCS_2)_2$ [15], and ultrasonic treatment of nanopowder precipitating from the solution [16]. However, the effects of conditions of semiconductor nanocrystals growth on their quantum properties have not been ultimately defined.

The most widely used method of nanocrystalline PbS preparation is the chemical precipitation from aqueous solutions (so-called *one-pot* synthesis) [17–21]. This method is based on the reaction of lead salt with sodium sulfide or thiourea, sometimes [11] elemental sulfur is used. The special feature of the method is strong dependence of the formed nanoparticles size on the nature and concentrations of the reagents as well as on the reaction medium and temperature [17–22]. To the very best of our knowledge, systematic studies of PbS particles size and their phase composition as a function of hydrothermal precipitation conditions has been lacking so far.

In order to fill in the gap, in this work we studied the influence of synthesis conditions (initial regents concentrations, nature and concentration of the added chelating ligand, and synthesis duration) on the size and purity of the prepared lead sulfide nanoparticles.

The conditions of PbS preparation and the resulting nanoparticles sizes are collected in the table.

From X-ray diffraction data, all prepared PbS powders possessed cubic lattice of the *B*1 type, the

Precipitation conditions and properties of PbS nanoparticles

Reagents concentrations in the reaction mixture[a], mol/L				t, h[b]	$\langle D \rangle$, nm	Lattice period a_{B1}, nm
$Pb(CH_3COO)_2$	Na_2S	Na_3Cit	Na_2EDTA			
0.025	0.025	0	0	0	20–27[c]	0.5933(4)
0.005	0.005	0	0.005	0	24±3	0.5933(1)
0.0125	0.0125	0	0.0125	0	30±3	0.5933(1)
0.050	0.050	0	0.050	0	35±3	0.59337
0.050	0.050	0	0.0125	0	8±1[c]	0.5934(3)
0.050	0.050	0	0.0250	0	10±1	0.5941(3)
0.050	0.050	0	0.0333	0	14±2	0.5936(1)
0.050	0.050	0	0.0375	0	20±3	0.5934(1)
0.050	0.050	0	0.050	0	35±3	0.59337
0.050	0.050	0	0.075	0	50±5[c]	0.59335
0.050	0.050	0	0.050	0	35±3	0.59337
0.050	0.050	0	0.050	120	55±6	0.59335
0.050	0.050	0	0.050	260	55±6	0.59357
0.050	0.050	0	0.050	460	55±6	0.59326
0.050	0.050	0	0.050	770	55±6	0.59340
0.00125	0.00125	0.00125	0	0	No precipitate	–
0.00125	0.00125	0.00125	0	1440	No precipitate	–
0.0025	0.0025	0.0025	0	0	4.5–5.0[c]	0.5949(7)
0.005	0.005	0.005	0	0	4.5–5.0	0.594(3)
0.005	0.005	0.005	0	70	7–8	0.593(2)
0.0125	0.0125	0.0125	0	0	4.5–5.0	0.594(3)
0.025	0.025	0.025	0	0	4.5–5.0	0.5926(3)
0.050	0.050	0.050	0	0	7–8	0.591(1)
0.100	0.100	0.100	0	0	7–8	0.590(1)
0.025	0.025	0.025	0	0	4.5–5.0	0.5926(3)
0.025	0.025	0.025	0	70	5 ± 1	0.592(2)
0.025	0.025	0.025	0	240	5 ± 1	0.592(3)
0.025	0.025	0.025	0	360	5 ± 1	0.594(3)
0.025	0.025	0.025	0	500	5 ± 1	0.594(1)
0.025	0.025	0.025	0	720	5 ± 1	0.593(3)

[a] Precipitation time was of 5 min in all the experiments. [b] Duration of PbS incubation in the mother liquor. [c] The precipitate contained admixture phases.

lattice period a_{B1} being of 0.5902–0.5949 nm that was consistent with the results reported elsewhere [21, 23–25]. It was demonstrated that the nanostructured PbS films could have the $D0_3$ cubic structure; however, PbS particles were of the $B1$ type irrespectively of the particle size [23, 26, 27].

The X-ray diffraction pattern of PbS prepared via $Pb(AcO)_2$ reaction with Na_2S (0.025 mol/L of each) in the absence of chelating ligand is shown in Fig. 1. According to the results, the specimen contained about 54% of the side product ($PbSO_4$). The average PbS particle size was of $<D>$ = 20–27 nm; it could not be precisely determined due to the presence of admixtures. Thus, without any chelating ligand pure PbS could not be prepared.

X-ray diffraction patterns of PbS particles prepared in the mixtures with equal concentrations of $Pb(AcO)_2$, Na_2S, and disodium salt of ethylenediaminetetraacetic acid Na_2EDTA are shown in Fig. 2. At the reagents concentration of 0.005 mol/L each, average size of the prepared PbS nanoparticles was of 24 nm. The increase in the components concentrations to 0.0125 and 0.050 mol/L led to the larger precipitating particles, of 30 and 35 nm on the average, respectively (see table). Within the accuracy of the X-ray diffraction experiment the admixtures were absent in the prepared samples.

Microscopy pictures of the nanocrystalline PbS powder with the average particles size of 24 nm are shown in Fig. 3. This sample was prepared by precipitation from solution containing $Pb(AcO)_2$, Na_2S, and Na_2EDTA (0.005 mol/L each). The sample consisted of microscopic (6–10 μm) aggregates (Fig. 3a). At higher magnification (Fig. 3b) smaller aggregates (about 1 μm) were revealed. At the highest magnification (100000×) it was evident that the aggregates were formed of the 30–50 nm nanoparticles (Fig. 3c). Thus, the microscopy (visible nanoparticles size) and X-ray diffraction (coherent diffraction area size) data demonstrated that the PbS powders consisted of highly aggregated nanoparticles, the aggregation occurring apparently due to hydrophobicity of the particles surface.

The influence of Na_2EDTA concentration on phase composition and particles size of PbS product was studied at equal concentrations of $Pb(AcO)_2$ and Na_2S (0.050 mol/L each), Na_2EDTA concentration ranging from 0.0125 to 0.075 mol/L. X-ray diffraction pattern of the product prepared at 0.0125 mol/L of Na_2EDTA contained diffraction reflections of lead sulfate admixture (Fig. 4), the admixture content was about

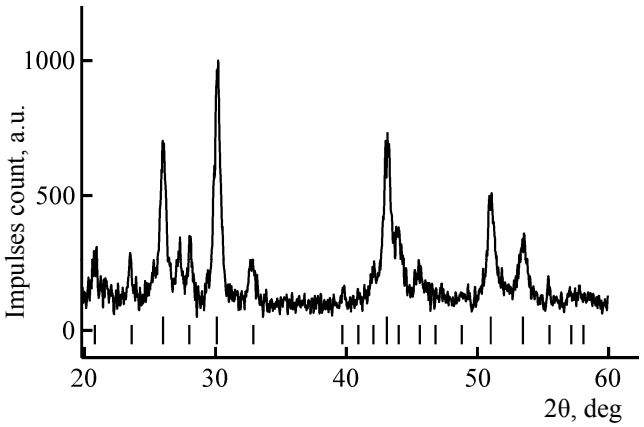

Fig. 1. X-ray diffraction pattern of PbS nanopowder prepared in the absence of chelating ligand, $Pb(OAc)_2$ and Na_2S concentrations in the reaction mixture being of 0.025 mol/L each. Long and short strokes point at PbS and $PbSO_4$ reflections, respectively.

15 wt %. $PbSO_4$ was evidently formed due to too low concentration of the chelating ligand. The admixture phases of $PbSO_4$ (10 wt %) and S (8 wt %) were found in the precipitate prepared at the highest Na_2EDTA concentration, 0.075 mol/L. In the latter case, white suspension was formed along with black PbS precipitate, and the reaction mixture was thus light-brown. The pure PbS powder, free of admixtures, could only be prepared when the $[Pb^{2+}] : [S^{2-}] : [Na_2EDTA]$ ratio was changed from 1 : 1 : 1 to 1 : 1 : 0.5. Besides, PbS nanopowder precipitation was accompanied with the formation of PbS film covering the glass surface of the beaker.

With increasing Na_2EDTA concentration in the reaction mixture from 0.0125 to 0.075 mol/L, the size of precipitated nanoparticles grew from 8 to 50 nm (Fig. 5a). Additional experiments showed that incubation of the prepared PbS nanoparticles in the mother liquor affected their size. In particular, 35 nm particles were initially formed at $Pb(AcO)_2$, Na_2S, and Na_2EDTA concentrations of 0.050 mol/L each. After 120 h incubation in the mother liquor, PbS particles size grew up to 55 nm (Fig. 5a); however, further incubation during 600–700 h did not change the particles size.

Using sodium citrate Na_3Cit as complexing ligand gave somewhat different results. At $Pb(AcO)_2$, Na_2S, and Na_3Cit concentrations of 0.00125 mol/L each lead sulfide precipitate was not formed at all. After mixing the reagents, the solution remained black and non-transparent within at least 170 h. Evidently, the formed PbS nanoparticles existed as stable suspension. The dispersion color intensity decreased within 240 h after

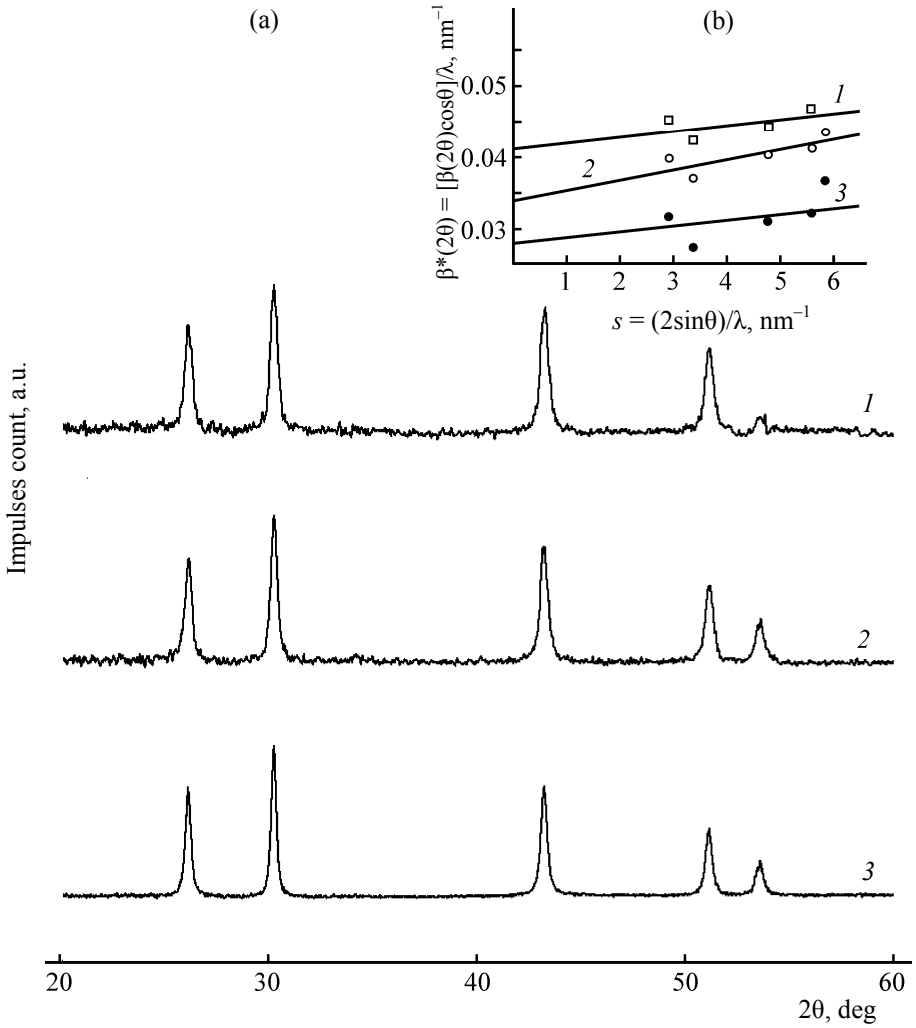

Fig. 2. X-ray diffraction patterns of PbS nanopowder (a) and specific broadening β*(2θ) of the reflections as function of the scattering vector *s* (b). Equal concentrations of $Pb(OAc)_2$, Na_2S, and Na_2EDTA of 0.005 (*1*), 0.0125 (*2*), and 0.050 mol/L (*3*); average particles size <*D*> of 24 (*1*), 30 (*2*), and 35 nm (*3*).

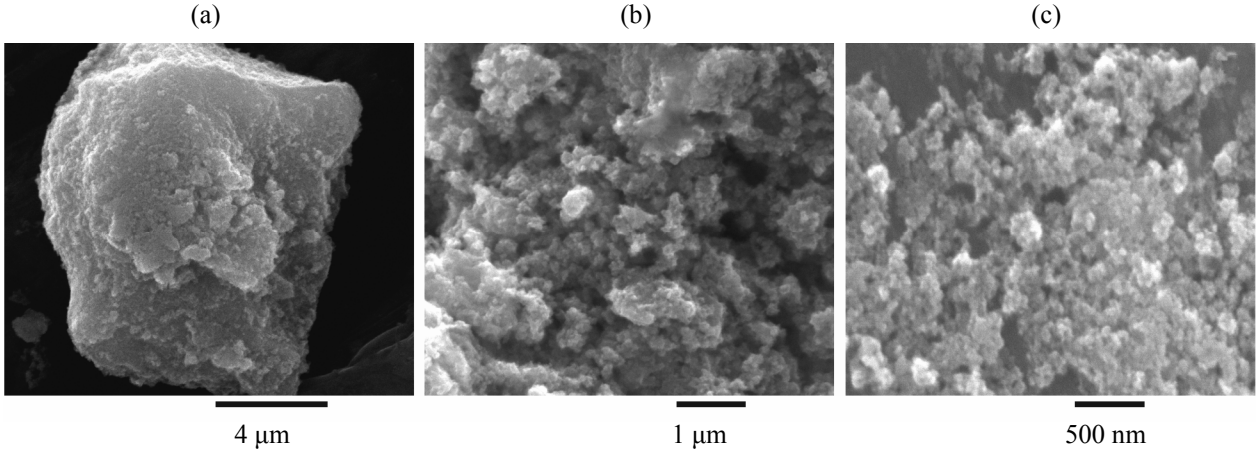

Fig. 3. Microstructure of PbS nanopowder prepared at equal concentrations of $Pb(AcO)_2$, Na_2S, and Na_2EDTA of 0.005 mol/L; magnification: 20000× (a), 30000× (b), and 100000× (c).

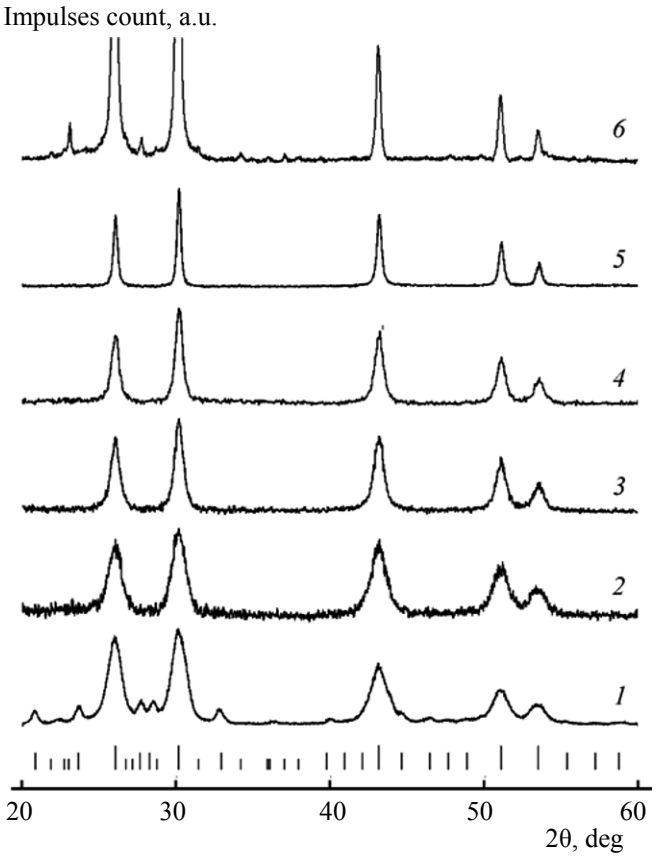

Fig. 4. X-ray diffraction patterns of PbS nanocrystalline powders prepared at concentrations of $Pb(AcO)_2$ and Na_2S of 0.050 mol/L each and at Na_2EDTA concentration of 0.0125–0.075 mol/L. Long, medium, and short strokes point at reflections of PbS, $PbSO_4$, and S, respectively. (*1*) [Na_2EDTA] = 0.0125 mol/L, <*D*> = 8 nm; (*2*) [Na_2EDTA] = 0.025 mol/L, <*D*> = 10 nm; (*3*) [Na_2EDTA] = 0.033 mol/L, <*D*> = 14 nm; (*4*) [Na_2EDTA] = 0.0375 mol/L, <*D*> 20 nm; (*5*) [Na_2EDTA] = 0.05 mol/L, <*D*> = 35 nm; (*6*) [Na_2EDTA] = 0.075 mol/L, <*D*> 50 nm.

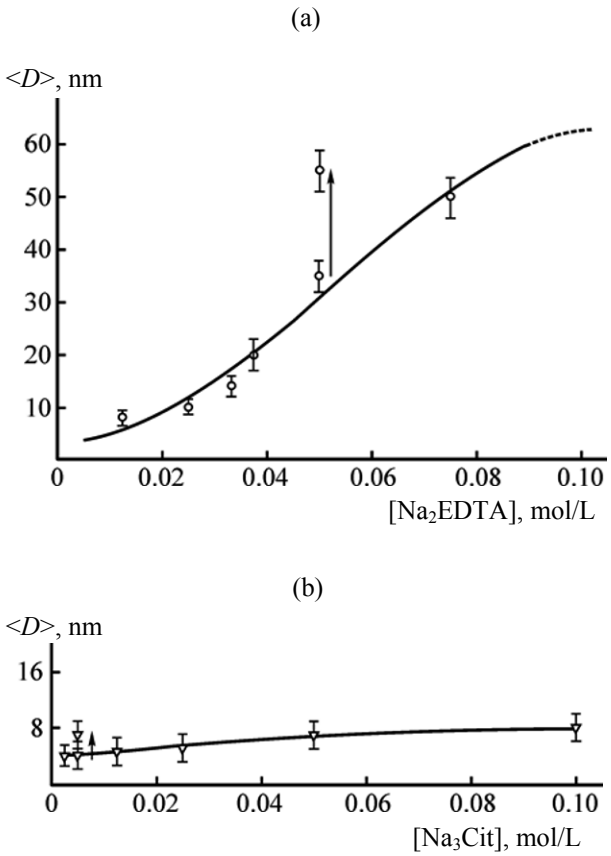

Fig. 5. Effect of the chelating ligand initial concentration on the size of PbS nanoparticles <*D*>. (a) PbS precipitated in the presence of Na_2EDTA at $Pb(OAc)_2$ and Na_2S concentrations of 0.050 mol/L each; the arrow shows the particles increase after 120 h incubation in the mother liquor; (b) PbS precipitated in the presence of Na_3Cit at equal concentrations of $Pb(OAc)_2$, Na_2S, and Na_3Cit; the arrow shows the particles increase after 70 h incubation in the mother liquor.

the mixing, and after 1440 h (60 days) the mother liquor turned light yellow. Even after such prolonged incubation the particles precipitation was not visually observed; therefore, gradual dissolution (probably, accompanied with oxidation) of PbS nanoparticles should have accounted for the mother liquor discoloration.

PbS precipitated in the presence of citrate at $Pb(AcO)_2$, Na_2S, and Na_3Cit equal concentrations of 0.0025 to 0.100 mol/L each. At 0.0025 mol/L of the components, the admixture of lead sulfate phase was found in the nanopowder. The admixture content could not be detected because the only reflection assigned to $PbSO_4$ was observed in the X-ray diffraction pattern, at $2\theta \approx 22.5°$; however, it was broad and diffuse. The precipitates formed at higher reagents concentrations did not contain any admixture phases. The X-ray diffraction patterns of the products prepared in the presence of citrate contained very broad reflections (Fig. 6). The particles size estimated from the lines broadening was of 4–5 to 7–8 nm (see table) and was slightly increasing with Na_3Cit concentration (Fig. 5b).

At was noted above, at $Pb(AcO)_2$, Na_2S, and Na_3Cit concentrations of 0.00125 mol/L each, the formed PbS nanoparticles did not precipitate, but rather dissolved after prolonged mixture incubation. In view of that it was interesting to check the stability of the precipitates formed in the more concentrated systems. In particular, PbS precipitate formed at $Pb(AcO)_2$, Na_2S, and Na_3Cit concentrations of 0.005 mol/L each was incubated in the mother liquor during 70 h. The precipitate was not

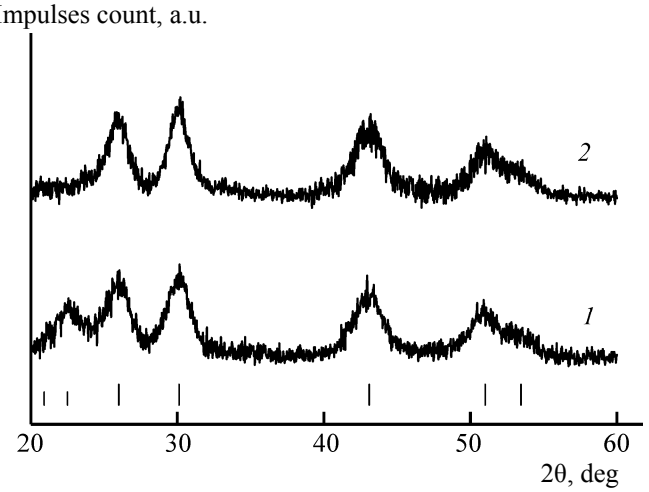

Fig. 6. X-ray diffraction pattern of nanocrystalline PbS powders prepared from mixtures of $Pb(OAc)_2$, Na_2S, and Na_3Cit solutions; concentrations of all components 0.0025 mol/L (*1*) and 0.025 mol/L (*2*). The pattern (*1*) contains reflections due to $PbSO_4$ admixture. Long and short strokes show reflections of PbS and $PbSO_4$, respectively. $\langle D \rangle \approx$ 5 nm.

dissolved, but the particle size increased to 7–8 nm. Similar experiment carried out at the reagents concentrations of 0.025 mol/L each did not reveal any particle size change after 720 h incubation (see table).

The formation of admixture oxygen-containing phases in the absence of the complexing ligand or at its low concentration was due to interaction of the ions with water hydrating lead ions and/or with dissolved oxygen, giving $PbSO_3$, $PbSO_4$, $(PbOH)_2S$, $PbO{\cdot}PbSO_4$, etc. The comparison of the ions concentration and the solubility constants of the possible oxygen-containing phases showed that the formation of the latter was indeed possible at low concentration of Na_2EDTA or Na_3Cit, thus supporting the experimental observations.

The precipitation from aqueous solutions turned out to be equilibrium process suitable for preparation of PbS nanoparticles almost free of the deformational distortions in crystal lattice. Indeed, the analysis of the diffraction lines broadening showed that the microstrain in the synthesized powders was very low (less than 0.13%, within the experimental accuracy).

To conclude, the precipitation in the absence of any complexing ligand did not produce lead sulfide powders free of the admixture phases. The introduction of Na_2EDTA allowed preparation of PbS particles of the 8 to 55 nm average size. Using Na_3Cit, average particle sizes of 5 to 10 nm could be achieved. The precipitates PbS nanoparticles free of admixtures were obtained at equal initial concentrations of $Pb(AcO)_2$ and Na_2S in the range between 0.005 and 0.100 mol/L when the initial concentration of complexing ligand differed from that of lead acetate no more than 2 times.

The average size of so prepared PbS particles depended on lead acetate, sodium sulfide, and the complexing ligand concentrations as well as on the nature of the ligand. The variation of those parameters allowed controlling the particles size in the range of 5 to 55 nm at 298 K. Nanoparticles smaller than 12 nm could not be prepared in the presence of Na_2EDTA. In order to prepare PbS nanoparticles smaller than 10 nm, the use of Na_3Cit was found to be preferential; whereas Na_2EDTA should be applied to produce PbS nanoparticles of about 50 nm size.

EXPERIMENTAL

Stable PbS nanoparticles were prepared by precipitation from aqueous solutions of lead acetate $Pb(AcO)_2$ and sodium sulfide Na_2S. The reaction mixtures were obtained by dilution and mixing of the stock solutions of $Pb(AcO)_2$, Na_2S, and Na_3Cit or Na_2EDTA. Nanoparticles synthesis was carried out at 298 K and pH 5.5–6.5; the pH value was checked with pH/Conductivity/TDS Tester HI 98130 ionomer (Hanna Instruments).

Initial concentrations of $Pb(AcO)_2$ and Na_2S in the reaction mixtures were varied between 0.00125 and 0.100 mol/L, the complexing ligands concentrations were 0–0.100 mol/L (Na_3Cit) and 0–0.075 mol/L (Na_2EDTA) (see table). Equimolar ratio of $Pb(AcO)_2$ and Na_2S was used in all preparations. The reaction mixture volume was always the same, 200 mL.

The reagents solutions were mixed as follows. The complexing ligand solution was added to the solution of lead acetate, the total volume was brought to 100 mL, and then it was mixed with 100 mL of Na_2S solution. In the additional experiments it was shown that the order of complexing ligand addition to the reagents solution did not affect the particle size; however, in some cases it could lead to formation of the admixture phases. Lead sulfide was formed almost immediately after the reagents mixing, and the reaction mixture turned black; then the particles precipitated within several minutes, and the solution became clear. Usually the synthesis time was kept at 5 min that allowed quantitative precipitation of PbS.

Immediately after the precipitation PbS was washed with distilled water via decanting, filtered off, and

dried in air at 323 K. In some experiments the formed PbS particles were incubated in the mother liquor solution during certain period of time (see table).

Lead sulfide was formed according to the following scheme.

$$Pb(AcO)_2 + Na_2S \rightarrow PbS\downarrow + 2\ NaOAc.$$

Note that the above reaction, being the major pathway, is usually accompanied with various hydrolysis processes [21]. The conditions of lead sulfide and hydroxide formation accounting for the hydrolysis and hydroxo complexes formation were discussed in [28, 29].

Elemental composition of the nanopowders was analyzed by energy dispersion analysis using JEOL-JSMLA 6390 electron microscope equipped with JED 2300 analyzer.

Phase composition and average size of the prepared particles were characterized by X-ray diffraction [1, 23, 30]. The measurements were run with Shimadzu XRD-7000 diffractometer applying the Bragg-Brentano method (Cu$K_{\alpha 1,2}$ radiation, $2\theta = 18°–60°$ with $\Delta(2\theta) = 0.03°$ step and exposition of 10 s per point). The diffraction patterns were processed using X'Pert Plus software package [31]. Diffraction reflections were fitted with pseudo-Voigt function. The reflection signal broadening was defined as $\beta(2\theta) = [(FWHM_{exp})^2 - (FWHM_R)^2]^{1/2}$ with $FWHM_{exp}$ being full width of the signal at half-height and $FWHM_R$ being the diffractometer instrumental broadening function. The $FWHM_R(2\theta) = (u\tan^2\theta + v\tan\theta + w)^{1/2}$ of the used diffractometer was determined in the additional run of the reference sample (cubic LaB_6, NIST Standard Reference Powder 660a); the function parameters were as follows: $u = 0.00616$, $v = –0.00457$, and $w = 0.00778$.

The average particle size $\langle D \rangle$ (or, more correct, the average size of the coherent diffraction area) and the microstrain developed in the samples were estimated from the diffraction lines broadening, plotting the specific broadening $\beta^*(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$ as a function of the scattering vector $s = (2\sin\theta)/\lambda$. The average particle size $\langle D \rangle$ was then determined from $\beta^*(2\theta)$ extrapolation to $s = 0$; in other words, $\langle D \rangle = 1/\beta^*(2\theta) = \lambda/[\cos\theta\beta(2\theta)]$ at $\theta = 0$, as $\beta(2\theta)|_{\theta=0}$ is by definition equal to $\beta_s(2\theta)$ due to small particles size ("size" broadening). The microstrain value ε was deduced from the slope of the $\beta^*(s)$ linear plot, $\varepsilon = \{[\beta^*(2\theta)]/2s\} \equiv [(\tan\varphi)/2]$.

Phase composition of the prepared PbS powders was determined from X-ray diffraction data using Match!©Crystal Impact software package [32]. Microstructure of the powders was studied by scanning electron microscopy (JEOL-JSM LA 6390).

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