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The Influence of Technological Modes on the Physical Properties of Cadmium Sulfide Nanocrystals Derived by the Electrolyte Method

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The effect of the sodium thiosulfate concentration and the electrolyte temperature on the process of obtaining cadmium sulfide nanocrystals by the electrolytic method using cadmium electrodes is investigated. X-ray diffraction studies were used to determine the nanocrystal sizes by the Debye-Scherrer formula and Williamson-Hall method. Comparison of the results of XRD studies with the results of Raman spectroscopy and differential thermal analysis is performed.

Keywords: Cadmium sulfide, XRD study, Size of nanoparticles, DTA, Raman scattering.

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1. INTRODUCTION

Cadmium sulfide (CdS) refers to semiconductor materials, which are considered as promising materials for manufacturing solar cells, in particular, as absorbing and buffer layers. Such layers are used in solar cells of new generation with a rather thin absorbing layer, the application of which is based on the use of nanotechnology advances [1].

To produce nanostructured CdS, various methods are used such as thermal spraying, magnetron spraying, chemical deposition, molecular beam epitaxy, pyrolysis, etc. CdS crystallizes in the thermodynamically stable hexagonal modification, a wurtzite structure, which is studied in sufficient detail. Information on the metastable cubic phase, a sphalerite structure, is limited. The data on the influence of the sizes of nanocrystals on their crystalline phase have appeared in recent years [2, 3].

The aim of this work was to investigate the effect of technological modes on the processes of obtaining CdS nanocrystals by the electrolytic method.

2. MATERIALS AND METHODS OF STUDY

CdS nanocrystals were prepared by the electrolytic method in a glass electrolyzer with cadmium electrodes. A sodium thiosulfate solution in distilled water, the concentration of which varied within (12.5-74.3) g/l was used as an electrolyte. The electrolysis process was performed at the electrolyte temperature, which varied from room to 100 °C. The duration of the experiment was 2 hours at a current density from $3.4 \cdot 10^{-3}$ to $1.0 \cdot 10^{-2}$ A/cm^2. The electrolyzer power supply was implemented from an adjustable regulated dc power supply. The reversal of the dc direction was carried out for uniform use of cadmium. The reversal time was 30 minutes.

After electrolysis, the electrolyte was filtered using a paper filter, and the obtained powder was washed five times with distilled water. The samples were dried in air at room temperature. The mass of cadmium electrodes and the mass of the obtained powder were determined in each experiment.

Ionometer I-130 M was used to determine the electrolyte pH, which, respectively, at the beginning and at the end of the process of producing nanoparticles was equal to 8.1 and 8.6. X-ray studies were performed on an X-ray diffractometer DRON-4 using CuK_α radiation at room temperature. The anode voltage and current were 41 kV and 21 mA, respectively. The scan step of the diffraction pattern is 0.05° and the exposure time is 5 s.

The recording of differential-thermal analysis (DTA) curves of the alloys is carried out using a chromel-alumel thermocouple. The heating (cooling) rate of the samples was 6-7 °C/min. The error of the temperatures of structural changes in the alloys did not exceed ± 5 K. DTA was performed in both air and evacuated (residual pressure ~1 Pa) quartz glass ampoules.

The Raman spectra were studied on a spectrometer Dilor at room temperature using laser radiation with a wavelength of 514.5 nm in the reflection geometry.

3. RESULTS AND DISCUSSION

CdS crystallizes in two different systems, namely, a cubic (T_d^2) – of the sphalerite type and a hexagonal (C^3_{6V}) – of the wurtzite type. Depending on the production conditions, its color may vary from golden-yellow to yellow-red. In our case, a red powder was obtained.

In Fig. 1 we illustrate the X-ray diffraction pattern of CdS nanocrystals obtained by the electrolytic method during 2 hours with current reversal in 30 min (electrolyte concentration 74.3 g/l, electrolyte temperature 98 °C, current density $1.0\ 10^{-2}$ A/cm^2). The diffraction pattern contains four broad reflexes with angular positions of 2θ: 26.75°; 44.19°; 52.45°; 71.33°. Using the well-known interplanar distances for both CdS modifications and the Wolf-Bragg formula, we calculated the angular position of X-ray reflexes. Comparing the calculation results with the experimental diffraction pattern, we concluded that when using the electrolytic method, a cubic modification of CdS was obtained, and the reflexes on the diffraction pattern have the following Miller indices: (111), (220), (311), (331), respectively.

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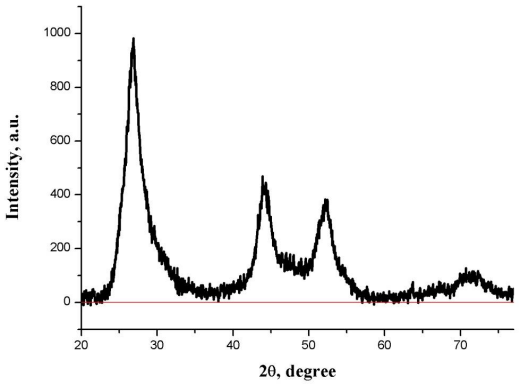

Fig. 1 – Diffraction pattern of CdS nanocrystals obtained at the electrolyte temperature of 98 °C (electrolyte concentration is equal to 74.3 g/l)

The large half-width of reflexes on the diffraction pattern indicates small crystal sizes. Similar results were obtained by the authors of [4] in the study of CdS obtained by the chemical method using $CdSO_4$, $Na_2S_2O_3$ and HEC solutions under ultraviolet irradiation at room temperature. To determine the particle sizes, the experimental diffraction pattern was processed describing each reflex by the Gaussian function, and, as a result, the following information was obtained: angular position 2θ, half-width (width at half height) β, integral intensity. The results obtained were applied to calculate the nanocrystal sizes using the Debye-Scherrer formula [5]:

$$D = 0.89\lambda/(\beta \cos\theta),$$

where λ is the X-ray radiation wavelength; β is the half-width of the reflex; θ is the diffraction angle.

The physical value of the half-width is calculated by the formula:

$$\beta = (\beta^2_1 - \beta^2_2)^{1/2},$$

where β_1 is the experimental value of the X-ray reflex half-width; β_2 is the instrumental value of the X-ray reflex half-width. The instrumental value of the X-ray reflex half-width was determined based on the analysis of the X-ray diffraction patterns of the reference silicon and Al_2O_3 powders obtained under the same conditions.

The calculations performed using the Debye-Scherrer formula showed that different results were obtained for different reflexes, and their mean values are about 3 nm. It should be noted that the calculations with and without taking into account the instrumental half-width lead to almost identical results. This result was predicted due to the fact that the experimental value of the half-width is much greater than the instrumental one.

The use of the Debye-Scherrer formula is based on the dependence of the X-ray reflex half-width on the particle size, and the half-width increases with decreasing size. Moreover, it is known that the half-width is influenced by mechanical stresses arising due to the crystal structure defects. In the case of nanoparticles, defects may appear since a significant portion of atoms is present on the surface; in addition, the contribution of surface atoms will increase with decreasing sizes. Therefore, we applied the Williamson-Hall method to determine the size and mechanical stresses acting in CdS nanocrystals [6]. In this case, the reflex half-width is described by the formula

$$\beta = 0.89\lambda/(D \cos\theta) + 4\varepsilon \mathrm{tg}\theta,$$

where λ is the X-ray radiation wavelength, ε is the relative elongation. In the last formula, the first term shows what contribution is made by the size effect to the half-width and the second one is caused by the contribution of mechanical stresses. We will write the last dependence in the following form:

$$\beta\cos\theta = 0.89\lambda/D + 4\varepsilon\sin\theta.$$

If this dependence is plotted in the coordinate system $4\sin\theta$, $\beta\cos\theta$, then we obtain a straight line, from which the nanocrystal size D and the relative elongation ε can be found. In Fig. 2 we illustrate the results of using the Williamson-Hall method for our sample. As seen, there is a deviation of the experimental points from a straight line. Therefore, the least squares method was applied to obtain reliable values of $0.89\lambda/D$ and relative elongation ε. As a result, the nanocrystal size $D = 8.6$ nm and the relative elongation $\varepsilon = 0.017$ were derived. As seen, the use of the Debye-Scherrer formula gives a smaller particle size than the Williamson-Hall method. The relative elongation is positive indicating that tensile stresses act in the nanocrystals.

Similar results were obtained by changing the electrolyte temperature, which varied within the range of 20-98 °C, indicating that the change in the electrolyte temperature does not influence the results of obtaining CdS nanocrystals for a given electrolyte concentration (74.3 g/l). Similar results were obtained in [6], where the authors investigated zinc oxide nanoparticles produced by chemical method using zinc acetate dihydrate, potassium hydroxide and methanol at a temperature of 52 °C. As a result of X-ray diffraction studies, the authors obtained the following nanoparticle sizes: 27 nm (using the Debye-Scherrer formula) and 35 nm (by the Williamson-Hall method). With decreasing concentration of sodium thiosulfate in the electrolyte to 12.5 g/l, the result of obtaining the product depends on the electrolyte temperature. With decreasing the latter from 96 °C to 19 °C, the obtained powder changes its color from red to yellow.

In Fig. 3 we present the diffraction patterns of the obtained samples at the temperatures of 96 °C (a) and 19 °C (b) (electrolyte concentration 12.6 g/l and current density $6.4 \cdot 10^{-3}$ A/cm^2). The diffraction patterns of CdS nanocrystals obtained at the electrolyte concentrations of 74.3 g/l (Fig. 1) and 12.6 g/l (Fig. 3a) are almost the

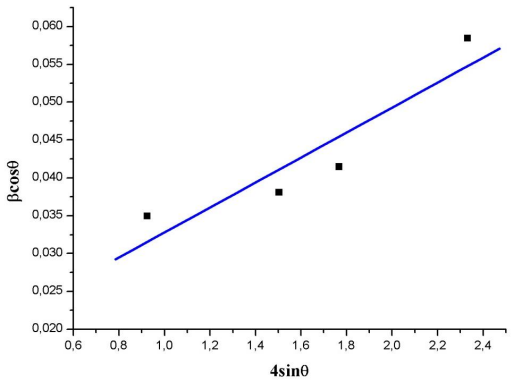

Fig. 2 – Results of the Williamson-Hall method for CdS nanocrystals (electrolyte concentration 74.3 g/l and electrolyte temperature 98 °C)

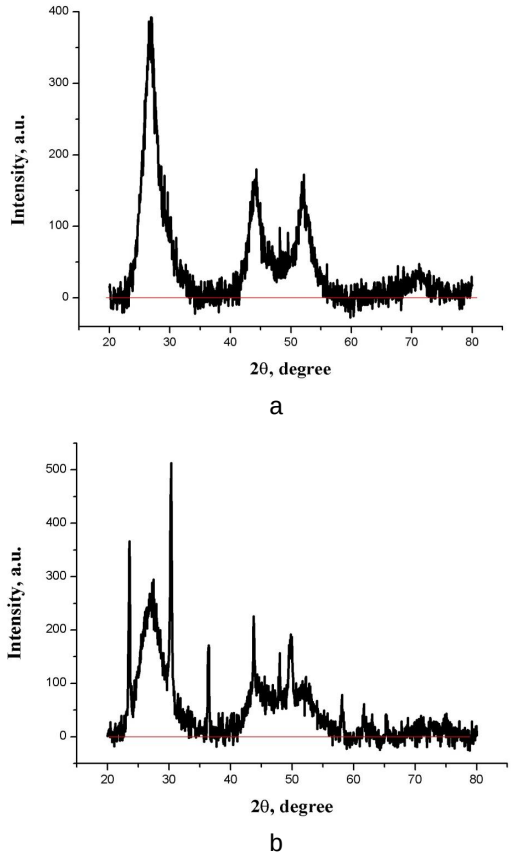

Fig. 3 – Diffraction pattern of CdS nanocrystals obtained at the electrolyte temperatures of 98 °C (a) and 19 °C (b)

same. The diffraction pattern of the sample produced at 19 °C (Fig. 3b) has a more complex character. It contains the wide bands typical for the cubic modification of CdS. Moreover, there are much narrower reflexes with the following angular positions: 23.7°, 30.2°, 36.4°, 43.9°, 47.9°, 58.2°. These reflexes are typical for $CdCO_3$, which was obtained by the authors of [7] when attempting to synthesize cadmium hydroxide by the electrolytic method. At that, a mixture of hydroxide and cadmium carbonate was obtained at the electrolyte temperature of 98 °C, and only $CdCO_3$ – at room temperature. The production of cadmium carbonate is caused by the presence of soluble carbon dioxide in water, which was used to prepare the electrolyte, and also the possibility of its ingress to the electrolyzer in the synthesis of nanocrystals. The nanoparticle sizes determined by the Debye-Scherrer formula are 1.9 nm for CdS and 56 nm for $CdCO_3$.

In Fig. 4 we illustrate the DTA thermograms of the sample obtained at a temperature of 96 °C (electrolyte concentration 12.6 g/l, current density $6.4 \cdot 10^{-3}$ A/cm^2). During the first heating of a non-vacuum-degassed alloy (see curve 1), a significant thermal effect is detected at a temperature of 100 °C caused by the water "removal" from a fine powder, which was adsorbed in it during the production process and subsequent drying of the powder. Curve 2 in Fig. 4 shows the completeness of this process. The third heating is carried out in a vacuum ampoule. Minor endo-effects were observed at the temperatures of ~ 402 °C and ~ 450 °C in the thermogram 3 in Fig. 4. The sphalerite-wurtzite phase transition probably corresponds to these effects as evidenced by the results of X-ray phase analysis. The authors of the review [8] discuss possible options for explaining the structure of CdS nanocrystals, whence it follows that the structure depends on the nanoparticle size. With a nanoparticle size greater than 9 nm, CdS crystallizes in the wurtzite structure, with sizes from 3 nm to 9 nm – in the structure of the "middle" lattice, and with sizes smaller than 3 nm – an amorphous phase is formed. In our case, the nanocrystal size determined by the Williamson-Hall method is equal to 8.6 nm. Therefore, probably, initially there occurs a transformation of the "middle" lattice to sphalerite, and then sphalerite transforms to wurtzite. Only reflexes typical for the hexagonal CdS are present in the diffraction pattern of this sample after annealing. The absence on the cooling curve 4 (Fig. 4) of thermal effects at specified temperatures indicates the irreversibility of the processes occurring in the alloy during its heating.

In Fig. 5 we illustrate the DTA thermograms of the sample obtained at a temperature of 19 °C (electrolyte concentration 12.6 g/l, current density $6.4 \cdot 10^{-3}$ A/cm^2). Interpretation of the curves 1 and 2 in Fig. 4 and Fig. 5 is close in its physical meaning. The thermogram 3 in Fig. 5 contains insignificant thermal effects at the temperatures of ~ 367 °C, ~ 438 °C and 495 °C. It should be noted that at a temperature of ~ 530 °C the ampoule with the studied sample exploded in the furnace implying the presence of a significant amount of the gas phase formed during heating. The following reaction of decomposition of cadmium carbonate can be one of the reasons for the gas phase formation:

$$CdCO_3 \rightarrow CdO + CO_2\uparrow.$$

In Fig. 6 we show the Raman spectrum of CdS nanocrystals obtained at the electrolyte temperature of 98 °C (electrolyte concentration 74.3 g/l and current density $1.0 \cdot 10^{-2}$ A/cm^2). The Raman spectrum is taken using an excitation with a wavelength of 514.5 nm at room temperature in the reflection geometry. As seen from Fig. 6, in the spectrum there are scattering bands with the frequency position of 302 cm^{-1}, 605 cm^{-1} and 906 cm^{-1}, the intensity of which monotonically decreases. These bands are due to scattering by LO phonons localized in the nanocrystals, respectively, of the first, second, and third orders. Their presence in the Raman spectrum is caused by the resonant nature of light scattering.

The authors of [11] studied the CdS nanoparticles obtained by the chemical method using $Cd(NO_3)_2$ $4H_2O$ and Na_2S $10H_2O$ solutions in methanol. Annealing of the prepared samples at the temperatures of 473, 573, 673, and 773 K was performed after synthesis. The obtained samples were investigated by the Raman method, and, as a result, it was established that changing sizes from 5 to 10 nm, the ratio of the scattering band intensities I_{2LO}/I_{1LO} for the cubic modification of CdS varies in the range of 0.2-0.5, and for the hexagonal modification this ratio is greater than 1. In our case, the ratio of these integral intensities is equal to 0.37 that confirms the fact of obtaining the cubic modification of CdS.

The scattering band of 302 cm^{-1} has a significant half-width (20 cm^{-1}), is asymmetrical and has a clearly expressed low-frequency shoulder. Such a shape may be due to the size effect, the presence of mechanical stresses, and the presence of the scattering band by surface optical phonons. The size effect leads to a shift of the scattering

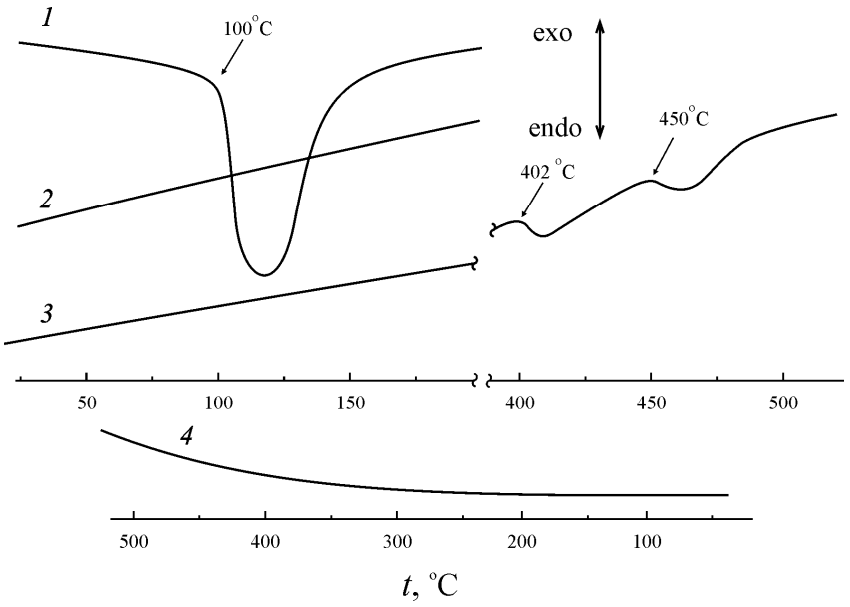

Fig. 4 – DTA heating (1-3) and cooling (4) curves of the sample obtained at a temperature of 96 °C: 1, 2 – unannealed sample and 3, 4 – vacuum-degassed sample

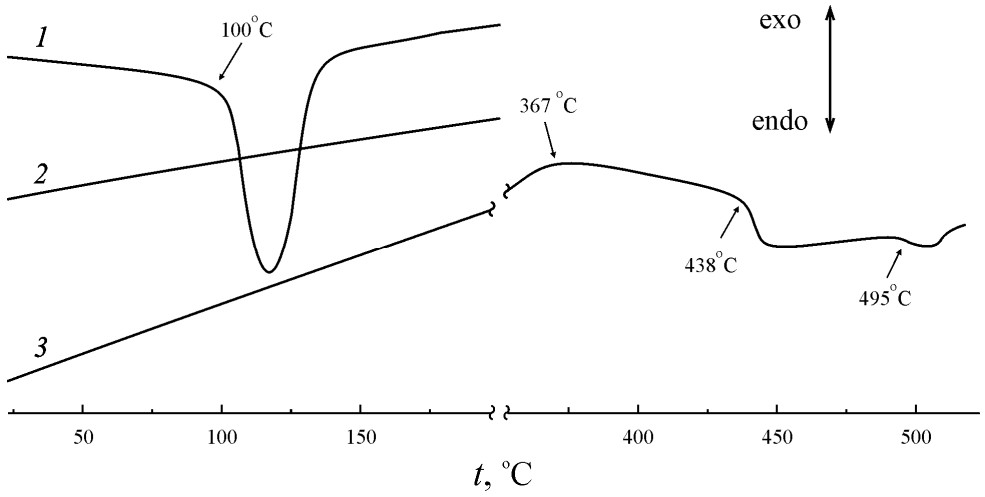

Fig. 5 – DTA heating (1-3) and cooling (4) curves of the sample obtained at a temperature of 19 °C: 1, 2 – unannealed sample and 3, 4 – vacuum-degassed sample

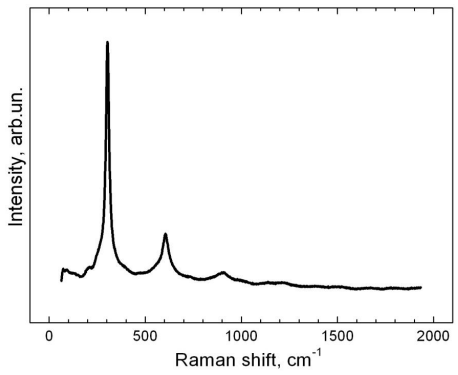

Fig. 6 – The Raman spectra of CdS nanocrystals ($\lambda = 514.5$ nm) obtained at the electrolyte temperature of 98 °C (electrolyte concentration 74.3 g/l)

band to the low-frequency range and an increase in the band half-width. The mechanical compression stresses lead to a shift of the band to the high-frequency side, the tensile stresses – to a shift to the low-frequency side. The scattering band by surface optical phonons is located between the TO and LO bands. As shown above, the tensile stresses act in the nanocrystals, the nanoparticle sizes are 8.6 nm, and, thus, as a result of all these factors, the frequency of the band 302 cm^{-1} is smaller and the half-width is larger than those for the single-crystal samples, which is equal to 305 cm^{-1} for CdS [12].

The authors of [13] investigated the nanoparticles obtained by chemical deposition using cadmium salt and sodium sulfide, which after deposition were maintained at a temperature of 150 °C for 4, 8 and 16 hours. X-ray studies showed that the obtained samples are CdS nanoparticles, which crystallize in the cubic system with a size of about 3 nm (the Debye-Scherrer formula). The use of the Williamson-Hall method showed that compressive stresses (the slope of the straight line is negative) act in the nanoparticles. The authors investigated the Raman spectra using excitation with a wavelength of 514 nm. The scattering band by LO phonons has a frequency po-

sition of 300 cm^{-1} and an asymmetry in the low-frequency side. Thermal annealing at a temperature of 150 °C does not significantly influence the Raman spectra. In our case, the scattering band by LO phonons, localized in the first-order nanocrystals, has the frequency top position of 302 cm^{-1} that is probably due to larger nanocrystal sizes (the Williamson-Hall method gives a size of 8.6 nm). The authors of [14] investigated the CdS quantum dots obtained on the Si substrate and calculated the dependence of the frequency position of the scattering band by LO phonons depending on their radius. These calculations give for the nanoparticles of 8.6 nm the frequency position of the scattering band by LO phonons of 303.5 cm^{-1} which slightly exceeds our value of 302 cm^{-1}. This is possible due to the action of mechanical tensile stresses as evidenced by the results of using the Williamson-Hall method and the contribution of scattering by surface optical phonons.

4. CONCLUSIONS

1. The possibility of obtaining CdS nanocrystals of the cubic modification of a size of ~8.6 nm by the electrolytic method using cadmium electrodes and sodium thiosulfate solution as an electrolyte at a temperature of the latter of 98 °C is established.

2. The nanocrystal sizes calculated by the Williamson-Hall method are greater than in the case of the Debye-Scherrer formula taking into account the instrumental half-width of the reflexes, in our case, 8.6 nm and 3.0 nm, respectively.

3. The study of the Raman spectra confirms the realization of the cubic modification of CdS.

4. It is established that CdS nanocrystals are obtained at the electrolyte concentration (sodium thiosulfate solution) of 74.3 g/l regardless of the electrolyte temperature; and at a concentration of 12.5 g/l depending on the electrolyte temperature, CdS or CdS-$CdCO_3$ crystals can be obtained.

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