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Synthesis of $Zn_{1-x}Cd_xS$ nanocrystals by electrolytic method

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The possibility of obtaining nanocrystals of the solid solution of zinc and cadmium sulfides by electrolytic method was investigated. Sodium thiosulfate solution in distilled water was used as an electrolyte. It was shown that the composition of the synthesized nanocrystals depends on the electrodes that served as sources of cadmium and zinc ions. X-ray diffraction method was used to determine the size of nanoparticles and type of the crystal structure. The size of the nanocrystals was calculated using Debye-Scherrer equation. It was found that the $Zn_{1-x}Cd_xS$ (x = 0, 0.07, 1) nanoparticles crystallize in the cubic sphalerite structure at room temperature of the electrolyte. The crystal lattice parameter of $Zn_{0.93}Cd_{0.07}S$ (a = 0.5432 nm) has an intermediate value between those of the cubic ZnS (a = 0.5402 nm) and CdS (a = 0.5887 nm). A good agreement between the obtained results and the literature values were established. The change of the unit cell parameters of the ZnS-CdS solid solution is described by the Vegard's law. Differential thermal analysis of the $Zn_{0.93}Cd_{0.07}S$ solid solution in the temperature range of 150-550 °C was performed for the first time. It was determined that the synthesized $Zn_{0.93}Cd_{0.07}S$ nanoparticles contain a large amount of adsorbed water at room temperature. With the subsequent heating of the evacuated ampoule with nanoparticle, thermal effects at 185°C, 335°C, and 475°C were established for the first time. The phase transition sphalerite-wurtzite after annealing of the solid solution at 550°C was observed. The thermal effects have been analyzed and compared with the available literature data.

Keywords: Zinc sulfide, Cadmium sulfide, ZnS-CdS solid solution, Nanocrystal size, X-ray diffraction, Differential thermal analysis.

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1. INTRODUCTION

Semiconductor compounds $A^{II}B^{VI}$ such as ZnS, CdS, CdSe, etc., are of considerable scientific and technological interest due to wide band gap. The synthesis of these compounds in the form of nanocrystals greatly extends the areas of their practical applications [1]. Various methods were proposed for obtaining nanocrystals such as magnetron sputtering, vacuum thermal spraying, molecular-beam epitaxy, plasmochemical, electrochemical synthesis, decomposition of chemical reagents, etc. [2-4], each with its advantages and disadvantages. The need for complex technological equipment stimulates the search for new methods of the synthesis of nanocrystals. The electrolytic method is one of the most economically efficient methods for obtaining nanoparticles, since the synthesis requires only metal electrodes and respective electrolyte [5].

The efficiency of solar cells significantly depends on the material of buffer layers, and the highest efficiency is achieved by using cadmium sulfide [6]. Zinc sulfide can also be used as a material for buffer layers of solar cells, electroluminescent devices, flat panel displays and lasers [7]. In particular, solid solutions of the ZnS-CdS system are promising materials for selective windows of thin-film solar cells due to wide transparency range [8, 9].

The objective of the work was to investigate obtaining nanocrystals of the solid solution of zinc and cadmium sulfides by electrolytic method and to determine the unit cell parameters of synthesized samples.

2. EXPERIMENTAL

The nanocrystals of zinc and cadmium sulfides as well as of the solid solution of the ZnS-CdS system were obtained by electrolytic method in a glass electrolyzer with zinc and cadmium electrodes. Sodium thiosulfate solution in distilled water with concentration varied within 39.3-74.3 g/l range was used as an electrolyte. The electrolysis process was held at room temperature of the electrolyte. The duration of the experiment was 3 hours, and the current density varied from $5.8 \cdot 10^{-3}$ to $2.3 \cdot 10^{-2}$ A/cm^2, with an adjustable DC power source. The reversal of the DC direction was applied every 30 minutes to ensure uniform use of electrode material. After electrolysis, the electrolyte was filtered using paper filter, and the resulting powder was washed five times with distilled water. The samples were air-dried at room temperature. In each experiment, the mass of zinc and cadmium electrodes and the mass of the resulting powder were determined.

X-ray diffraction (XRD) studies were performed on a DRON-4 diffractometer using CuK_α radiation, Bragg-Brentano geometry (θ-2θ scanning), at room temperature. Anode voltage and current were 41 kV and

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21 mA, respectively. The scan step was 0.05°, with the exposure time of 5 seconds.

Differential-thermal analysis (DTA) curves of investigated alloys were recorded using an H307-1 XY setup with chromel-alumel thermocouple. The rate of heating (cooling) of samples was 6-7°C/min. The temperature error of the setup did not exceed ± 3°C. DTA was performed both in air and in evacuated quartz ampoules (residual pressure ~1 Pa).

3. RESULTS AND DISCUSSION

Zinc and cadmium sulfides crystallize in two different structures, either cubic sphalerite type (T_d^2) or hexagonal wurtzite type (C^3_{6v}). Depending on the conditions, the color of ZnS varies from white to yellow-white, and CdS is golden yellow to yellow-red. In our case, white and red powders were obtained for ZnS and CdS, respectively. The white color of the nanocrystals of the ZnS-CdS solid solution indicates that its composition is closer to zinc sulfide than to cadmium sulfide.

X-ray diffraction patterns of the samples obtained over 3 hours with direct-current reversal every 30 min are presented in Fig. 1. The experimental patterns of the samples were processed by fitting each reflection with a Gaussian function which resulted in the following information: the angle position 2θ, full width at half-maximum height β (FWHM), the integral intensity of the reflection. Significant width of the reflections of the diffraction patterns shown in Fig. 1 indicates the small size of obtained nanocrystals.

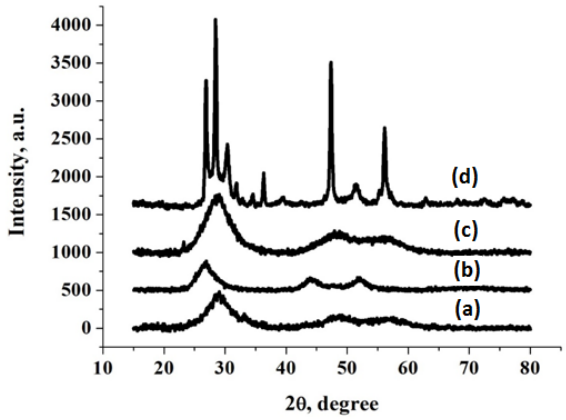

Fig. 1 – X-ray diffraction patterns of the samples obtained at room temperature of the electrolyte: *a* is ZnS nanocrystals (electrolyte temperature $t = 23$ °C, electrolyte concentration $c = 39.3$ g/l, current density $j = 2.3 \cdot 10^{-2}$ A/cm²), *b* is CdS nanocrystals ($t = 26$ °C, $c = 73.4$ g/l, $j = 1.0 \cdot 10^{-2}$ A/cm²), *c* is nanocrystals of a solid solution of the ZnS-CdS system ($t = 20$°C, $c = 39.3$ g/l, $j = 5.8 \cdot 10^{-3}$ A/cm²), *d* is the solid solution nanocrystals annealed in air at 550 °C

The size of the nanocrystals of the studied samples was determined using Debye-Scherrer equation [10]:

$$D = 0.89\lambda/(\beta \cdot \cos\theta), \quad (3.1)$$

where λ is the X-ray radiation wavelength; β is the FWHM of the reflection; θ is the reflection angle.

FWHM values were calculated by the equation:

$$\beta = (\beta^2_1 - \beta^2_2)^{1/2}, \quad (3.2)$$

where β_1, β_2 are the experimental and instrumental FWHM value of the reflection.

The instrumental FWHM component was determined by the analysis of the diffraction patterns of the reference powders of silicon and Al_2O_3 obtained under identical conditions.

The calculations of the nanoparticle sizes using Eq. (3.1) were averaged over the set of observed reflections. The structural parameters of nanocrystals were determined by the Wolf-Bragg equation:

$$2d \sin\theta = k\lambda, \quad (3.3)$$

where d is the interplanar distance, θ is the diffraction angle, λ is the X-ray wavelength.

The diffraction pattern of ZnS shown in Fig. 1(a) contains three broad reflections. The reflection planes with Miller indices calculated by Eq. (3.3) are: (111), $2\theta = 29.1°$; (220), $2\theta = 48.7°$; (311), $2\theta = 56.7°$. Obtained values correspond to the cubic structure of the sphalerite type. The dimensions of ZnS nanoparticles determined by Eq. (3.1) are 1.8 nm.

The structural parameters of CdS nanocrystals were determined from the data in Fig. 1(b) and Eqs. (3.1), (3.3). It was established that the planes with Miller indices (111), (220), (311) and (331) correspond to the 2θ angles 26.9°, 44.3°, 52.0°, 70.1°, respectively. Therefore, the synthesized CdS nanoparticles also crystallize in the cubic structure. The nanoparticle size determined by Eq. (3.3) is 3.2 nm. Obtained results agree well with the data of the authors of [14] on the study of CdS nanoparticles obtained by the electrolytic method at the electrolyte temperature 98 °C.

The analysis of the diffraction pattern in Fig. 1c shows that the solid solution of the ZnS-CdS system crystallizes in the cubic phase, and its reflections occupy intermediate angular positions between those of zinc sulfide and cadmium sulfide. The reflections with Miller indices (111), (220), (311) correspond to 2θ angles 28.8°, 48.7°, 56.0°, respectively, which are closer to the positions of ZnS reflections than CdS. The Debye-Scherrer equation estimates the nanoparticle size as 1.7 nm.

The X-ray diffraction pattern of the alloy of the ZnS-CdS solid solution after annealing in an electric oven in air at 550°C is presented in Fig. 1(d). The pattern contains considerably more reflections in comparison with those in Figs. 1(a)–(c). It was determined that the reflections at 2θ angles 26.9°; 28.5°; 30.4°; 39.4°; 47.4°; 51.4°; 55.3°; 56.1°; 57.2° correspond to the planes of the wurtzite structure with Miller indices (010), (002), (101), (102), (110), (103), (200), (112), (201), respectively.

Unit cell parameters are fundamental values for the identification of crystalline substances, the determination of the chemical bond distance, the study of phase transitions, solid solutions, and crystal defects. Several factors influence the accuracy of the determination of the crystallographic parameters of the sample, such as absorption by the sample material, X-ray refraction, divergence of the primary beam, dispersion, Lorentz factor and the polarization, temperature etc. Thus, the

use of single crystals is best to determine the crystallographic parameters. In the case of nanocrystalline samples, the problem is complicated by large width and low intensity of the reflections. In addition, there is no separation of the $K_{\alpha 1,2}$ doublet even in the region of large diffraction angles. Therefore, we used the extrapolation method to evaluate the unit cell parameters, since almost all systematic errors of X-ray measurements approach zero at the diffraction angle $\theta = 90°$. Nanocrystals of the samples with diffraction patterns shown in Fig. 1(a)–(c) crystallize in the sphalerite structure, therefore, using the Wolf-Bragg equation and the quadratic form for the cubic symmetry [12], the unit cell parameter can be calculated as:

$$1/d^2 = (h^2 + k^2 + l^2)/a^2, \qquad (3.4)$$

where a is the crystal lattice parameter; h, k, l are the Miller plane indices.

As an extrapolation function, we used the function proposed by Nelson and Riley [12]:

$$f(\theta) = 0.5(\cos^2\theta/\sin\theta + \cos^2\theta/\theta). \qquad (3.5)$$

The dependence of the unit cell parameter of CdS nanocrystals determined from different reflections on the value of the extrapolation function is shown in Fig. 2. The experimental points deviate from the linear dependence, therefore the extrapolation line was plotted by the least squares method. The calculated value of the unit cell parameter $a = 0.5887$ nm is consistent with the literature data for cadmium sulfide $a = 0.5835$ nm [10]. Similarly, the values for other samples were determined as $a = 0.5402$ nm for ZnS, $a = 0.5432$ nm for the ZnS-CdS solid solution. Thus, the crystal lattice period for the ZnS-CdS solid solution has an intermediate value between the crystallographic parameters of ZnS and CdS nanocrystals.

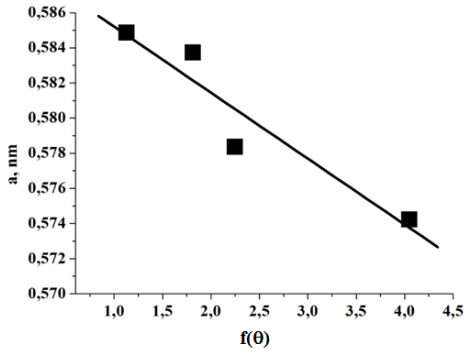

Fig. 2 – Graphical extrapolation for determining the crystal lattice parameter of cadmium sulfide nanocrystals

According to [8], a continuous solid solution series is formed in the ZnS-CdS system. In this case, according to Vegard's law [16], the parameter of the crystal lattice of alloys must vary in the linear function from zinc sulfide to cadmium sulfide, when the concentration of CdS changes. The dependence of the unit cell parameter of the solid solutions of the ZnS-CdS system on the molar content of CdS is calculated from Vegard's law: $a = 0.54$ nm (at the 0 mol.% CdS) and $a = 0.59$ nm (at the 1 mol.% CdS). The experimental values of the unit cell parameters of the cubic structure of the investigated samples were used in the calculation. Further calculations found that in our case the $Zn_{0.93}Cd_{0.07}S$ composition of the solid solution was obtained.

The authors of [13] investigated the structural and optical properties of the solid solutions of the ZnS-CdS system in the range of ZnS content from 21 to 89 mol. %. The solid solutions crystallized in the sphalerite structure. The monotonous dependence of the diffraction angles, interplanar distances, bandgap energy on the content of zinc sulfide was found. The values of the diffraction angle and the interplanar distance for the sample with ZnS content of 89 mol. % are close to the results obtained in our study.

The authors of [14] performed X-ray diffraction and optical studies of the $Zn_{1-x}Cd_xS$ solid solutions for x values of 0, 0.01, 0.04, 0.1, 0.2, 0.3, and 0.5. The nanocrystals with the cubic structure (sphalerite) were obtained. The linear dependence of the unit cell parameter which varied from 0.5406 nm to 0.5506 nm on the solid solution composition was established. The nanoparticle size for the sample with $x = 0.1$ as determined from XRD studies is 0.544 nm, which is slightly larger than for our sample $Zn_{0.93}Cd_{0.07}S$.

DTA curve of the $Zn_{0.93}Cd_{0.07}S$ solid solution in the temperature range of 150-550 °C is shown in Fig. 3. It was determined that the synthesized alloy at room temperature contains a large amount of adsorbed water (physical adsorption) that was removed by heating the material to 100 °C. After removing adsorbed water, the alloy was placed in an evacuated ampoule and reheated. The process of separating the bound water began at 185 °C. To prevent the explosion of the ampoule, it was depressurized, and the alloy was heated to 130 °C to remove the moisture. With the subsequent heating of the evacuated ampoule, minor thermal effects were observed at 335 °C and 475 °C.

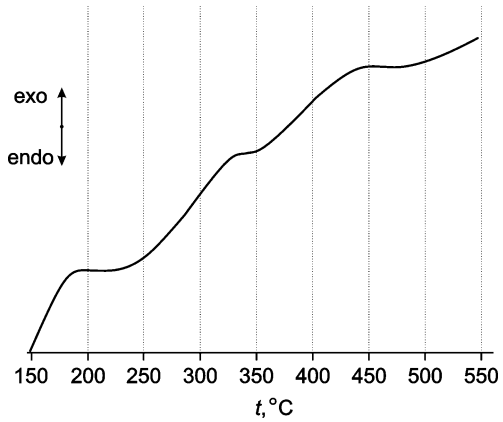

Fig. 3 – DTA thermogram of the $Zn_{0.93}Cd_{0.07}S$ alloy of the ZnS-CdS system

The nanoparticles of zinc, cadmium and mercury sulfides were investigated using differential scanning calorimetry, differential thermogravimetry and XRD methods in [15]. The nanoparticles were synthesized by chemical precipitation at 185 °C and crystallized in the sphalerite structure. Thermal effects for the ZnS sample were observed at about 250, 320 and 450 °C. The thermal effects for our solid solution $Zn_{0.93}Cd_{0.07}S$ were

observed at slightly different temperatures. The reason for this is likely the presence of impurities of wurtzite in the sphalerite phase, the completion of the phase transition sphalerite-wurtzite, and the oxidation of a small part of the material (XRD phase analysis shows the appearance of low-intensity reflections of zinc oxide). The absence of sharp thermal effects is due to the closeness of the enthalpy of formation of zinc sulfide for sphalerite and wurtzite, which is equal to 189.4 and 177.3 kJ/mol, respectively [16].

Physical properties of the $Zn_{1-x}Cd_xS$ solid solutions ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) obtained by the chemical method using $Zn(NO_3)_2$, $Cd(NO_3)_2$ and Na_2S solutions were investigated in [17]. The resulting nanoparticles of solid solutions were annealed in nitrogen atmosphere at a temperature that varied from 400 °C to 800 °C. X-ray structure and optical studies of photoluminescence and excitation spectra were performed. It was determined that obtained samples crystallize in the cubic structure, and the angle positions of the reflections vary from the values characteristic of CdS to those for ZnS. After thermal annealing at 400 °C the structure of the solid solutions does not change, whereas the phase transition sphalerite–wurtzite is observed with an increase of annealing temperature to 500 °C. Further increase of annealing temperature leads to the increase of the intensity of the reflections characteristic of the wurtzite structure. These data agree well with our results that the solid solution with the wurtzite cell structure was obtained after annealing at the temperature of 550 °C (Fig. 1d).

The diffraction patterns of zinc sulfide annealed in nitrogen atmosphere at 1000-1200°C for 15-17 hours were investigated in [18]. This temperature exceeds the phase transition temperature of sphalerite-wurtzite for the single-crystalline ZnS, therefore the samples crystallized in the hexagonal structure. The angle positions of reflections are close to our results (Fig. 1d) since the composition of our solid solution is close to zinc sulfide. In addition, the diffraction patterns contained weak reflections at 2θ angles 31.8°, 34.5°, 36.3° corresponding to the strongest zinc oxide reflections with Miller indices (010), (002), (101), respectively. The angle positions and the intensity ratio of the reflections correlate well with the results of XRD study of zinc oxide nanocrystals obtained by the electrolytic method which the authors investigated in [18, 19]. Low intensity of ZnO reflections is due to only slight surface oxidation of ZnS nanocrystals after their thermal annealing at 550 °C.

4. CONCLUSIONS

1. Electrolytic method of the synthesis of the nanocrystals of the ZnS-CdS system using zinc and cadmium electrodes and sodium thiosulfate solution at room temperature is proposed.

2. The solid solution of the ZnS-CdS system with CdS content of 7 mol. % was obtained. It was determined that the solid solution crystallizes in the sphalerite structure.

3. The crystal lattice period of the solid solution has an intermediate value between the periods of ZnS and CdS nanocrystals obtained by the same method.

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Синтез нанокристалів $Zn_{1-x}Cd_xS$ електролітичним методом

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Досліджено можливість отримання нанокристалів твердого розчину сульфідів цинку і кадмію електролітичним методом. Як електроліт використано розчин тіосульфату натрію в дистильованій воді. Показано, що склад синтезованих нанокристалів залежить від електродів, які слугували джерелами іонів кадмію і цинку. Розмір наночастинок та тип кристалічної структури визначено на основі даних дифракційного рентгенівського аналізу. Розмір нанокристалів розраховано за формулою Дебая-Шеррера. Встановлено, що за кімнатної температури електроліту наночастинки $Zn_{1-x}Cd_xS$ (x = 0; 0.07; 1) кристалізуються в кубічній структурі типу сфалерит. Розрахований параметр кристалічної гратки $Zn_{0,93}Cd_{0,07}S$ (a = 0.5432 нм) займає проміжне значення між величинами характерними для кубічних нанокристалів ZnS (a = 0.5402 нм) і CdS (a = 0.5887 нм) та узгоджується з опублікованими літературними даними. Зміни параметрів гратки сплавів твердого розчину ZnS-CdS описуються законом Вегарда. Вперше здійснено диференціальний термічний аналіз сплаву твердого розчину $Zn_{0,93}Cd_{0,07}S$ в температурному інтервалі 150-550°C. Встановлено, що синтезовані за кімнатної температури наночастинки складу $Zn_{0,93}Cd_{0,07}S$ містять значну кількість адсорбованої води. При подальшому нагріві вакуумованого зразка вперше встановлено теплові ефекти при 185 °C, 335 °C та 475 °C. При відпалі твердого розчину за температури 550°C спостерігається фазовий перехід сфалерит-вюрцит. Отримані теплові ефекти проаналізовано та порівняно з опублікованими літературними даними.

Ключові слова: Сульфід цинку, Сульфід кадмію, Твердий розчин ZnS-CdS, Розмір нанокристалів, Дифракційний рентгенівський аналіз, Диференціальний термічний аналіз.