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Fabrication and Properties of Nanostructured ZnO and ZnS

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The possibility of obtaining zinc oxide and sulfide nanocrystals by electrolytic method using sodium thiosulfate solution as the electrolyte is given. Received samples were examined by methods of X-ray diffraction analysis and absorption spectrometry. The size of nanoparticles is defined by Williamson-Hall and Debye-Scherrer methods. Found that the nanocrystals data of substances are in tension, which affect the value of the broadening of x-ray peaks.

Keywords: Zinc oxide, Zinc sulfide, Nanoparticles, X-ray diffraction analysis, Size determination.

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1. INTRODUCTION

In recent years, semiconductor low-dimensional structures, such as quantum wells, quantum wires and quantum dots are of considerable interest in connection with their unusual, in comparison with the bulk materials, optical, magnetic, and electrical properties [1].

An interest in wide-band-gap semiconductor compounds of the A^2B^6 group, such as CdS, ZnS, ZnTe, ZnO, has significantly increased after the transition to nanotechnology [2]. These materials attract the increased attention of researches due to their unique electrical and optical properties. This is associated with the possibility of production on their basis of a number of high-efficient devices of micro-, opto-, and acoustoelectronics.

Zinc sulfide ZnS, which at room temperature has a large band gap of $E_g = 3.68$ eV, is a promising material for fabrication of emitting diodes and lasers operating in the blue-green spectral region, photodetectors.

Zinc oxide ZnO with the band gap of $E_g = 3.36$ eV is one of the promising metal oxides for the production on the basis of a nanoscale material of new devices in order to use them in optoelectronic engineering, microelectronics, processes of conversion of solar energy into chemical energy, as catalysts, etc. Nanocrystals of the ZnO-ZnS system are considered promising for fabrication of optoelectronic devices of the ultraviolet range [3, 4].

Recently, the various methods including hydrothermal methods, microemulsion methods, sol-gel methods, use of microwave radiation, sonochemical methods, chemical deposition methods, etc. [5] are used for the synthesis of semiconductor nanoparticles. It is clear that each method has advantages and drawbacks. The electrolytic method does not require for implementation complex equipment and utilization of scarce reagents [6].

The aim of the present work is the investigation of the physical properties of ZnS nanoparticles obtained by the electrolytic method.

2. EXPERIMENTAL

Nanostructured zinc sulfide was obtained by the electrolytic method [7] in a glass electrolyzer with zinc electrodes of the following sizes: diameter is 8 mm; height is 200 mm. Solution of sodium thiosulfate in deionized water with the concentration of 12.5 g/l was used as the electrolyte. The electrolysis process was performed at an electrolyte temperature, which varied from the room one to 100 °C. The duration of the experiment was 2 hours at the current density of $1.21 \cdot 10^{-2}$ A/cm^2. The electrolyzer power was from adjustable regulated DC power supply. Reverse of the DC direction was carried out for the uniform use of zinc electrodes. The reversal time was 30 min.

After completion of the electrolysis, the electrolyte was filtered using a paper filter; the obtained powder was washed five times by deionized water. The samples were dried in air at room temperature. The X-ray structural analysis was conducted on an X-ray diffractometer DRON-4 using CuK$_\alpha$-radiation at room temperature. The anode voltage and current were, respectively, equal to 41 kV and 21 mA. The scan step of the diffraction pattern was 0.05° and the exposure time – 5 s. Measurements of the electrolyte transmission spectra after completion of the process were performed on the spectrophotometer Carry-50 at room temperature.

3. RESULTS AND DISCUSSION

Zinc sulfide is crystallized in two different systems: cubic (T_d^2) – sphalerite and hexagonal (C_{6V}^3) – wurtzite [8]. Depending on the production conditions, the color of zinc sulfide can be changed from white to yellow-white. In our case, the powder of white color was obtained.

In Fig. 1 we illustrate the X-ray diffraction patterns of the samples obtained by the electrolytic method during 2 hours with reverse of the DC direction in 30 min. The electrolyte temperature was equal to 25 °C (a) in the first experiment and 98 °C (b) in the second one. For the X-ray structural analysis, the experimental diffraction patterns were divided into stripes described by the Gauss function. Thus, the following information about the parameters of reflexes was obtained: the value of the angle 2θ, half-width β (width at half height of the reflex), and integral intensity.

Based on the acquired information for the diffraction pattern (Fig. 1b) and calculation using the Wulf-Bragg formula

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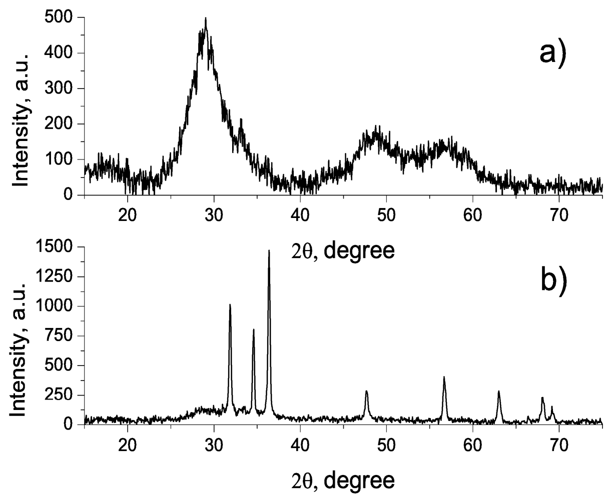

Fig. 1 – X-ray diffraction patterns of the samples obtained at the electrolyte temperature of 25 °C (a) and 98 °C (b)

$$d \sin\theta = k\lambda , \quad (1)$$

it was established that the obtained reflexes are typical for the zinc oxide (see Table 1).

These results correlate well with the data obtained in [7] in the study of zinc oxide nanoparticles produced by the electrolytic method. Moreover, there are low-intensity bands, which are similar to the bands of the diffraction pattern shown in Fig. 1a.

As seen from the diffraction pattern (Fig. 1a), there are three wide reflexes which indicate small sizes of the obtained particles. The similar diffraction patterns were obtained in [9] for zinc sulfide nanoparticles produced by the chemical method using $ZnCl_2$ and Na_2S, which are typical for the cubic modification of ZnS. Based on the acquired information and calculation by the Wulf-Bragg formula, it was established that the obtained reflexes are from the planes (see Table 2). This corresponds to the cubic structure of the sphalerite type.

Thus, zinc sulfide nanocrystals obtained at the electrolyte temperature of 25 °C are of the cubic structure and those obtained at the temperature of 98 °C are the mixture of zinc oxide and sulfide.

The sizes D of the obtained samples of zinc oxide and sulfide are determined by the X-ray structural analysis based on the Debye-Scherrer formula [10]

$$D = \frac{k\lambda}{\beta \cos(\theta)} . \quad (2)$$

Here k is the coefficient, whose value depends on the particle shape ($k = 0.89$ for an ellipsoid); λ is the X-ray radiation wavelength; β is the half-width (width at half height of the X-ray reflex), 2θ is the angular position of the X-ray reflex.

Table 1 – Reflexes of the samples (ZnO) obtained at 98 °C

plane	(100)	(002)	(101)	(102)	(110)	(103)	(200)	(112)	(201)
2θ	31.6°	34.6°	36.4°	47.7°	56.7°	63.0°	66.6°	68.1°	69.3°

Table 2 – Reflexes of the samples (ZnS) obtained at 25 °C

plane	(111)	(220)	(311)
2θ	29.30°	48.98°	58.36°

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

$$\beta = \sqrt{\beta_1^2 + \beta_2^2} , \quad (3)$$

where β_1 is the experimental value of the half-width of the X-ray reflex and β_2 is the instrumental value of the half-width of the X-ray reflex.

The instrumental value β_2 of the half-width of X-ray reflexes was determined based on the analysis of the X-ray diffraction patterns of the standard powders of monocrystalline silicon and Al_2O_3, which were obtained at the same conditions and comparison of the obtained results with the reference ones. The performed calculations of the sizes of nanocrystallites have shown that for different reflexes the obtained results had different values, and their averaged values are equal to 33 nm for zinc oxide (Fig. 1b) and 1.2 nm for zinc sulfide (Fig. 1a).

It was assumed that surface and structural defects of the nanocrystals, which lead to the appearance of mechanical stresses, have also impact on the values of the reflex half-width β in addition to the size effect.

The mechanical stress ε is described by the formula

$$\varepsilon = \frac{\beta}{4 \operatorname{tg}\theta} , \quad (4)$$

where ε is the relative deformation and β is the physical value of the reflex half-width.

As a result, the following dependence for the physical value of the reflex half-width in the case of both factors will be true:

$$\beta = \frac{k\lambda}{D \cos\theta} + 4\varepsilon \operatorname{tg}\theta . \quad (5)$$

The Williamson-Hall method [11] is grounded on the equality (4) and allows to separate two factors, which influence the value of the reflex half-width. To this end, it is enough to write the relation (4) in the form of

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \quad (6)$$

and consider the latter dependence in the coordinate system ($4\sin\theta$; $\beta\cos\theta$). Obviously, for this choice of the coordinate system, relation (5) is a linear function. Thus, the values of D and ε can be determined in the presence of reliable experimental data obtained from the analysis of the X-ray profiles of the samples. In particular, one can use the least squares method [12].

In Fig. 2 we illustrate the results of the Williamson-Hall method use for the zinc oxide (Fig. 1b) obtained by the electrolytic method at the electrolyte temperature of 98 °C. As seen, the scattering of experimental points with respect to some straight line takes place. As a result of calculations by the least squares method, the following values were obtained: $D = 72$ nm, $\varepsilon = 0.96 \cdot 10^{-3}$. The angular coefficient of the straight line is positive that indicates the action of tensile stresses in the sample.

A similar procedure for using the Williamson-Hall method was performed for the zinc sulfide obtained at the electrolyte temperature of 25 °C and its results are presented in Fig. 3. The following sizes of nanoparticles were obtained: $D = 2.1$ nm, $\varepsilon = 0.026$. The angular coef-

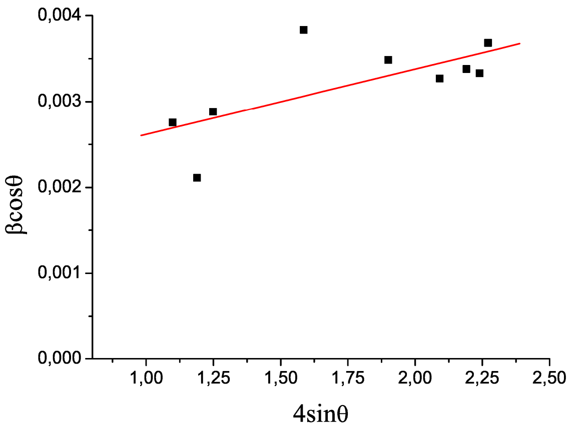

Fig. 2 – The use of the Williamson-Hall method for the determination of the contributions of the size effect and mechanical stresses for zinc oxide

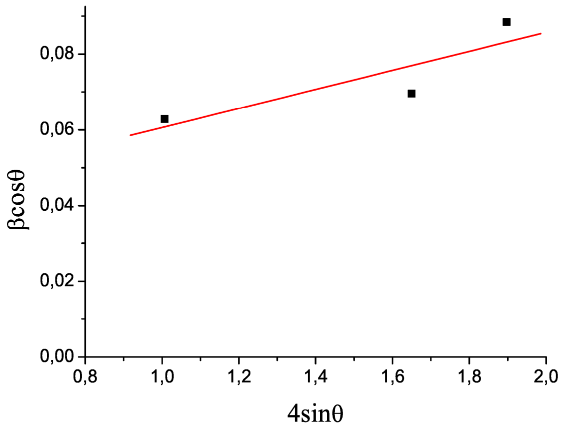

Fig. 3 – The use of the Williamson-Hall method for the determination of the contributions of the size effect and mechanical stresses for zinc sulfide

ficient of the straight line is positive that implies the action in the sample of tensile stresses, whose values of the relative elongation are larger than for zinc oxide as shown above.

The authors of [13] have studied by the Williamson-Hall method the CdS samples obtained by the chemical deposition technique using cadmium and sodium sulfide salts. The compressive stresses (the angular coefficient of the straight line is negative) acted in the samples. The values of $D = 35$ nm and $\varepsilon = 1.31 \cdot 10^{-3}$ [11] were obtained when studying the zinc oxide produced by the chemical deposition method using $Zn(CH_3COO)_2 \cdot 2H_2O$ and KOH solutions in methanol at the temperature of 52 °C. In this case, tensile stresses (the angular coefficient of the straight line is positive) acted in the nanoparticles.

The absorption spectra were studied after completing the process of the sample fabrication at the electrolyte temperature of 25 °C. The studies were carried out on the spectrophotometer Carry-50 at room temperature. Light absorption near the absorption edge is described by the following dependence:

$$\alpha \cdot h\nu = \left(h\nu - E_g\right)^n , \qquad (6)$$

where h is the Plank constant, ν is the radiation frequency, α is the constant, E_g is the band gap. The value of the power exponent n depends on the nature of the optical transitions: $n = 1/2$ for direct allowed transitions; $n = 3/2$ for direct forbidden transitions; $n = 2$ for indirect allowed transitions; $n = 3$ for indirect forbidden transitions. Therefore, for the determination of the behavior of the optical transitions, one needs to calculate and plot the dependences of $(\alpha \cdot h\nu)^n$ on the photon energy $h\nu$. In the case of obtaining a linear region, they conclude about the nature of the optical transitions by the value of the power exponent n.

Zinc sulfide and oxide belong to the direct gap semiconductors and, thus, calculation of the dependence of $(\alpha \cdot h\nu)^2$ on the photon energy $h\nu$ was performed for the analysis of the absorption spectra. As seen from Fig. 4, on the latter dependence it is possible to separate only one straight region, which gives the band gap of 3.71 eV. The last value correlates well the band gap of cubic crystals of zinc sulfide at room temperature 3.72 eV [13].

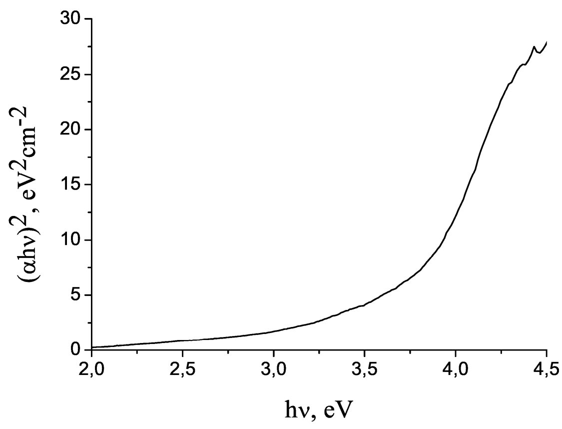

Fig. 4 – Dependence of $(\alpha \cdot h\nu)^2$ on the photon energy $h\nu$

4. CONCLUSIONS

1. The possibility of production of ZnS and ZnO nanoparticles by the electrolytic method at the electrolyte temperatures of 25 °C and 98 °C, respectively, is shown.

2. The X-ray structural analysis of the manufactured samples indicated that ZnS nanoparticles of the cubic structure were obtained at the electrolyte temperature of 25 °C and ZnS and ZnO mixture – at 98 °C.

3. The sizes and acting mechanical stresses in nanocrystallites were estimated using the Debye-Scherrer and Williamson-Hall methods for the analysis of the profile of X-ray peaks.

4. The band gap of ZnS nanoparticles at room temperature ($E_g = 3.71$ eV) was determined from the transmission spectra.

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