Synthesis, Luminescent and Structural Properties of the Cd$_{1-x}$Cu$_x$S and Cd$_{1-x}$Zn$_x$S Nanocrystals

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This paper describes the *in-situ* synthesis in polymer films of the nanocrystals (NCs) of the ternary semiconductors Cd$_{1-x}$Cu$_x$S and Cd$_{1-x}$Zn$_x$S as well as the results of investigations of their structure and optical properties. It has been established that, in case of Cd$_{1-x}$Cu$_x$S in a large range of Cu to Cd ratios, the hexagonal structure is dominating in NCs synthesized, while in case of Cd$_{1-x}$Zn$_x$S the dominating crystalline structure of NCs corresponds to cubic structure of CdS. However in both cases formation of separate phases of either CdS and CuS or CdS and ZnS has not been revealed, confirming formation of ternary semiconductor compounds. It has been revealed an opposite effect of increasing concentrations of Cu and Zn cations in ternary compounds on intensity of an impurity photoluminescence, for the former this intensity decreases, but for latter it increases. The possible reasons for these phenomena are discussed.

Keywords: Nanocrystals, Thin nanocomposite polymer films, Ternary semiconductor compounds Cd$_{1-x}$Cu$_x$S and Cd$_{1-x}$Zn$_x$S, *In-situ* sol-gel synthesis, XRD, UV-vis spectroscopy, Photoluminescence.

1. INTRODUCTION

Nanocrystals (NCs) of the wide-gap semiconductors A^{2}B^6 are widely used due to their high luminescence quantum yield in different areas of optical- and nanoelectronics for creating of light-emitting devices, night vision devices with high resolution, solar batteries, as fluorescent markers for medical diagnosis and so on. Nowaday challenge is development of the technologies for formation of nanostructures directly in polymer matrices that are characterized by high efficiency, stability of luminescence, and extended color gamut of radiation. This might provide perspectives for such nanostructures in creating a new generation of highly efficient, low-energy light emitting devices. One of the important task is obtaining and investigation of semiconductor NCs doped with various impurities; that has both the theoretical and practical values in order to establish the mechanism of impurity implementation into NCs and to find effective ways to control the spectral distribution of radiation. It should be noted, that scientific publications contain contradictory information about the mechanism of introducing the impurities into NCs. Some authors claim that any impurity are pushed out from NCs, while in other studies it is stated that some impurities do penetrate into NCs. Thus, it has been found that Magnesium impurity easily penetrates into NCs CdS and ZnSe, while these can not be introduced into CdSe NCs [1]. Influence of Zn dopants on structural and optical properties of CdS NCs have been investigated in [2-6].

Most studies claim that in CdS NCs and in NCs of ternary compounds based on CdS, the surface defects (without specifying their nature) serve as the radiative recombination centres. Therefore, the comprehension of the nature of local centres causing a radiating recombination in NCs is an important scientific problem that should be studied.

In our previous work [7], the optical and structural characteristics of the defective NCs CdS doped with impurities of Cu and Zn in the range from 1% to 10% have been studied; and it has been found that Cu impurities passivate the surface radiative centres and that lead to a sharp decrease in the intensity of bands corresponding photoluminescence (PL); on the contrary, Zinc impurities create additional centres of radiative recombination in NCs CdS that results in a substantial increase in PL intensity.

This paper summarizes the results of investigations of optical, luminescent, structural-defective properties of semiconductor NCs synthesized in polymer matrices based on CdS with a high content of Cu and Zn, corresponding to the formation of ternary compounds Cd$_{1-x}$Cu$_x$S and Cd$_{1-x}$Zn$_x$S (x = 0-1).

2. EXPERIMENTAL

The polymer films with the embedded semiconductor NCs were prepared in several stages. Initially, a solution of the peroxide reactive copolymer (PRC, see formula below), polyethylene glycol (PEG-200, see formula below) and a mixture of Cadmium acetate (CdAc$_2$) with either Zinc acetate (ZnAc$_2$) or with Copper acetate (CuAc$_2$) in dimethylformamide was prepared at various ratios of CdAc$_2$: MAc$_2$ from 3 : 1 to 1 : 4.56. For comparison, NCs of binary semiconductors CdS, CuS and ZnS were prepared under similar conditions.

In the first stage, thin polymer films containing Cd^{2+} and/or another metal cations (either Zn^{2+} or Cu^{2+}) were deposited by spin-coatings on the glass plates, afterwards in the second stage these films were subjected to annealing and crosslinking at T = 393 K for 2 hours. It was found that under these conditions a high degree of cross-linking of the polymer films was
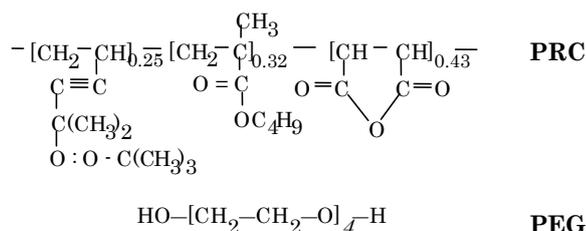
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Fig. 1. – Chemical structure of the polymers used for obtaining the thin nanocomposite films with embedded semiconductor NCs

achieved owing to both types of reactions, namely i) interaction of hydroxyl groups of PEG-200 with the anhydride functionalities PRC and ii) a sequence of radical reactions, involving decomposition of the PRC peroxide functionalities, Hydrogen abstract from polymer backbones and recombination of the macroradicals formed. As a result, the content of the gel fraction in the cross-linked polymer films reached 96 % and higher. In the third stage, NCs of ternary semiconductor compounds were formed inside the polymer films during their exposure to gaseous hydrogen sulphide (H_2S) for 6 hours at 60 °C. In all cases the theoretical content of NCs in the polymer films was kept to be 20 %. An average thickness of the final nanocomposite films thus obtained was about 20 nm.

Short description and coding of the samples of nanocomposite films with embedded NCs $Cd_{1-x}M_xS$

Table 1 – Coding of the samples of nanocomposite films with embedded NCs $Cd_{1-x}M_xS$

NCs of $Cd_{1-x}Cu_xS$		NCs of $Cd_{1-x}Zn_xS$	
x	code	x	code
0.00	Cd100	0.00	Cd100
0.25	Cu25	0.25	Zn25
0.33	Cu33		
0.50	Cu50	0.50	Zn50
0.60	Cu60		
0.75	Cu75	0.75	Zn75
0.82	Cu82		
1.00	Cu100	1.00	Zn100

Absorption spectra in the visible region of thin polymer films with embedded NCs were recorded on a Shimandzu UV 3600 spectrophotometer. The spectra were analysed after their mathematical processing, providing selection using the mathematic apparatus of the OriginLab program, providing selection of a smoothing function, numerical differentiation and decomposition of a complex spectrum into their components by approximation curves with a normal Gaussian distribution.

X-ray diffraction (XRD) data of nanocomposite films were collected at ambient temperature on a Philips X'Pert-MPD x-ray diffractometer ($CuK_{\alpha 1}$, $\lambda = 0.15418$ nm) using sample chamber with a Bragg-Brentano para-focusing optics configuration.

Spectra of photoluminescence (PL) was measured on an automated setup, consisting of the modulation light source (helium-cadmium laser LH-70, 325.0 nm, output 10 mW), monochromator MDR-23 photodetector device, amplifier and control PC.

3. RESULTS AND DISCUSSION

3.1 Nanocrystals of $Cd_{1-x}Cu_xS$

Absorption spectra

As a primary visual indicator, confirming the synthesis of NCs of the semiconductor compounds $Cd_{1-x}Cu_xS$ in a polymer film, served the appearance of a certain coloration, which depended on the NCs composition and varied from bright yellow for $x = 0$ to gray-green for $x = 1$. It should be noted that the polymer film itself, as well as films with Cd^{2+} ions, were colourless; and the addition of Cu^{2+} ions imparted the films a barely noticeable blue tone.

It could be concluded from analysis of the optical absorption spectra shown in Fig. 2a and the data published [7] that even at the Cu content lower than that for Cd in the system (e.g. at $x = 0.33$ and higher), the CuS compound behave as a 'host' while Cd ions were included as a 'guest'. Earlier [7] we found that at Cu content ≤ 10 %, the 'host' was CdS, and the 'guest' was Cu ions located mainly at the surface of NCs. The appearance of a sufficiently intense absorption in the region of 700-900 nm (Fig. 2a), whereas for CdS this region is practically transparent, was a good evidence on dominant CuS structure in NCs. In this case, doping of CuS with Cd ions resulted in a shift in the absorption maximum to a long-wavelength region from $\lambda_{max} = 854$ nm for pure CuS to $\lambda_{max} = 862$ nm for the ternary compound with the Cd content of 67 %. At the same time, the absorption in the region of 450 nm, characteristic for CdS NCs, disappeared.

Another important conclusion following from the analysis of absorption spectra was that ternary semiconductors of the type $A_{1-x}B_xS$ were formed in such systems, while separate phases of AS and BS compounds were not formed, since these spectra were characterized by the presence of only one absorption maximum, being close to the maximum absorption of the 'host' compound.

One of the main important parameters used to characterize and analyse the properties of semiconductors is the energy gap (band gap E_g). The optical band gap can be calculated from the optical absorption spectra using the Tauc's method [10]. The graphical representation of the Tauc's plot, shown in the inset in Fig. 2a, allowed to determine the value of the E_g, equalling 2.53 eV and 2.56 eV for NCs of CuS and $Cd_{0.5}Cu_{0.5}S$ respectively. Thus, despite a huge difference in the compositions, there was observed only a slight shift in the energy gap for these NCs. Interestingly, when doping Cu^{2+} ions ($x \leq 0.1$) into CdS NCs, the optical band gap remained practically unchanged [7]. The values of $E_g = 2.53$ eV for the CdS compounds obtained (see the inset in Fig. 2b) were higher than $E_g = 2.42$ eV for this compound in the macrocrystalline state, that indicated the formation of CdS compound in polymer films in the form of nanocrystals.

X-ray diffraction analysis

Effect of Cu Content on the crystalline structure of $Cd_{1-x}Cu_xS$ NCs was investigated by X-ray diffraction. X-ray diffraction pattern of $Cd_{1-x}Cu_xS$ NCs are shown in Fig. 3. All diffraction peaks were approximated by Gauss function.

Samples Cd100 and Cu33 were found to have cubic structure with the lattice constants $a = 5.830$ Å and $a = 5.789$ Å respectively. Samples Cu82 and Cu100 had hexagonal structure with the lattice constants $a = 3.788$ Å, $c = 16.33$ Å. The structure of the samples Cu60 and Cu75 with intermediate Cu contents ($x = 0.60$-0.75) could be rather characterized as mixed, although both diffraction peaks associated with cubic and hexagonal phases were not well pronounced. In our previous work [7], we didn't observed any changes in the lattice constants of NCs with a low Cu content ($x \le 0,1$), but in this study, for Cu content $x \ge 0,1$ a reduction of the lattice constants was observed, that followed from their comparison of the sample Cu33 ($x = 0.33$) with the sample Cd100 ($x = 0$).

The average sizes of $Cd_{1-x}Cu_xS$ NCs were estimated from the most intensive (111) XRD peak for the cubic structure and (006) XRD peak for the hexagonal structure using the Debye- Sherrer equation; and it was found that, despite of a high difference in contents of Cd and Cu in NCs, their sizes did not vary too much and lay in the range of 2.5-4.7 nm. The relative lattice deformations in NCs were estimated applying Hall formula. Only for the cubic lattice in plane (311) a decrease in the lattice deformation occurred gradually with increasing Cu content, whereas for other planes, e.g. (111), (220) for the cubic lattice and (006), (110) for the hexagonal lattice, no significant changes in the lattice deformation were found.

Photoluminescence spectra

PL spectra of $Cd_{1-x}Cu_xS$ NCs ($x = 0.00$-1.00) at $T = 300$ K is shown in Fig. 4. PL spectra consisted of two areas: the intrinsic exciton band E (420-500 nm) and two impurity-bound exciton bands D_1 and D_2 (500 ÷ 650 nm). As shown in [7, 11], the impurity PL bands of CdS NCs, both undoped and Cu-doped or Zn-doped at their low contents, were caused by radia tive recombination of nonequilibrium charge on the NC surface defects. Similar PL bands were described in [12], summarizing the investigations of the Cu-doped CdS NCs. However, the nature of radiative recombination centres in NCs of CdS and the ternary compounds based on it has still not been ascertained.

Previously it was speculated that luminescence occurs through the surface defects which have unestablished nature [3], through the centres V_{Cd}-V_S [13], through V_{Cd} acceptor centres [14-16]. The results obtained in this work evidenced that the impurity PL of the $Cd_{1-x}Cu_xS$ NCs (bands D_1 and D_2) was not associated with V_{Cd}. Indeed, as can be seen in Fig. 4, the impurity bands D_1 and D_2 existed in spectra of CdS NCs ($x = 0$) as well as in spectra of CuS NCs ($x = 1$), though the latter contained no atoms of Cd. In our opinion the impurity PL of NC $Cd_{1-x}Cu_xS$ associated with recombination centres formed by the interstitial atoms of Sulphur. It should be noted, that a similar interpretation was proposed in [17, 18] to explain the increase in the intensity of "green" luminescence of CdS monocrystal. In our case, formation of intrinsic defects by interstitial Sulphur atoms could be anticipated because the final stage in synthesis of NCs was exposure of the polymer films with metal cautions to gaseous hydrogen

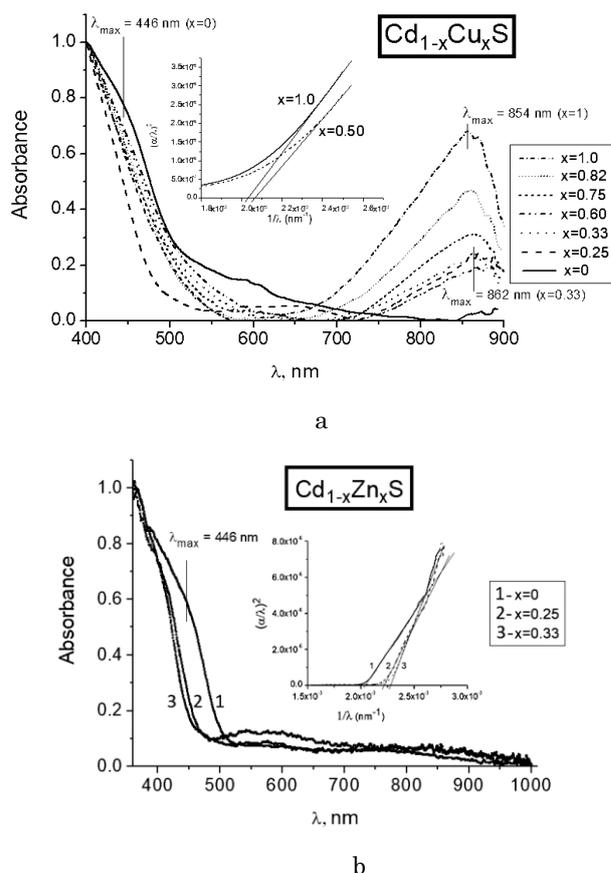sulphide; therefore some excess of Sulphur atoms in the structure of $Cd_{1-x}Cu_xS$ NCs looks quite reasonable.

a

b

Fig. 2 – Absorption spectra of polymer films with embedded NCs of $Cd_{1-x}Cu_xS$ (a) and $Cd_{1-x}Zn_xS$ (b). Tauc's plots in coordinates $(\alpha/\lambda)^2$ vs. $1/\lambda$ are shown in insets

Noteworthy features connected with the positions of the impurity PL bands. If for NCs with cubic structure ($x = 0 - 0.33$), where CdS was a 'host' while Cu atoms were a 'guests', the spectral position of both bands D_1 and D_2 remained practically unchanged; for NCs with hexagonal structure ($x = 1$-0.75), where CuS – 'host' and Cd – 'guest', on the contrary, the spectral position of both maxima of the bands D_1 and D_2 were shifted towards a long wave region. Indeed, a decrease in the Cu content in NCs from 1.0 to 0.75 brought about the shift for D_1 – from 552 nm to 560 nm and for D_2 – from 578 nm to 593 nm.

Within the framework of the proposed model of radiative recombination in the $Cd_{1-x}Cu_xS$ NCs, according to which the impurity PL is the result of capture of nonequilibrium charge carriers (electrons) by local centres, formed by interstitial Sulphur ions, the reason for a sharp quenching of the impurity PL bands caused by Cu-doping of CdS NCs [7] becomes obvious.

In the process of forming the undoped CdS NCs, Sulphur coming from the gas phase can create a large number of interstitial ions; and in this case the intensity of the impurity PL was high enough. At the same time, during formation of the Cu-doped NCs of CdS, the Sulphur ions reacted with Copper creating CuS molecules, incorporated into NC structure, consequently the concentration of interstitial Sulphur ions decreased
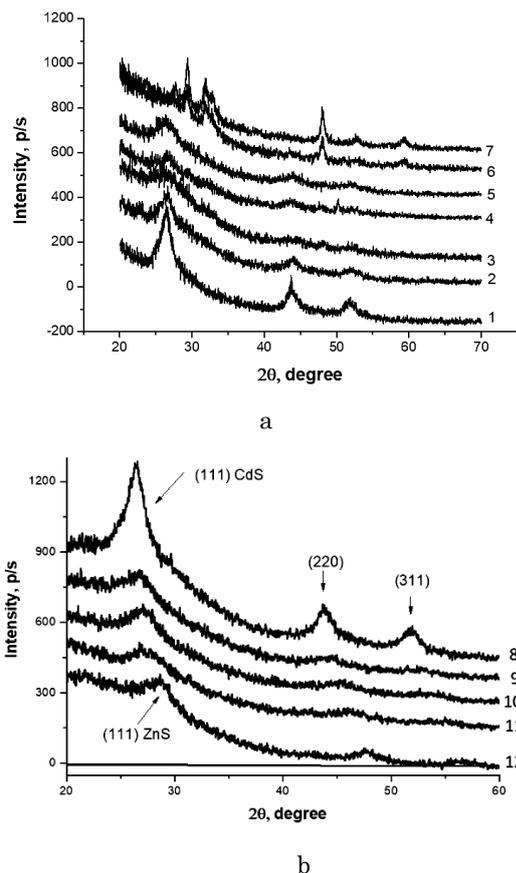
a

b

Fig. 3 – XRD patterns of NCs of $Cd_{1-x}Cu_xS$ (a) and $Cd_{1-x}Zn_xS$ (b) with different compositions. The pattern number corresponds to the following samples listed in Table 1: 1 – Cd100; 2 – Cu33; 3 – Cu50; 4 – Cu60; 5 – Cu75; 6 – Cu82; 7 – Cu100; 8 – Cd100; 9 – Zn25; 10 – Zn50; 11 – Zn75; 12 – Zn100
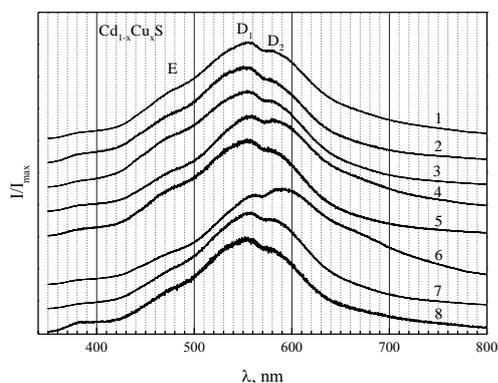

Fig. 4 – PL spectra of $Cd_{1-x}Cu_xS$ NCs at $T = 300$ K. The line number corresponds to the following samples listed in Table 1: 1 – Cd100; 2 – Cu25; 3 – Cu33; 4 – Cu50; 5 – Cu60; 6 – Cu75; 7 – Cu82; 8 – Cu100

sharply, that brought about a decrease in the intensity of the impurity PL. At sufficiently high concentrations of Copper impurities a crystalline phase of a ternary $Cd_{1-x}Cu_xS$ compound was generated.

3.2 Nanocrystals of Cd1-xZnxS

Absorption spectra

Evidence of the formation of ternary semiconductor

compounds $Cd_{1-x}Zn_xS$ in a polymer film was its yellow coloration. The degree of coloration depends on the composition of the ternary compound and varies from bright yellow at $x = 0$ to colourless at $x = 1$. The fundamental absorption edge of the obtained compounds shifted to a blue region (Fig. 2b) and, accordingly, the E_g was regularly increased (Inset in Fig. 2b). It seems that at least in the region of $0.25 \leq x \leq 0.33$ the dominant structure in the NCs remained the structure of CdS, into which Zn^{2+} ions are embedded; that leads to assumption that CdS was a 'host' while Zn was a 'guest' in these ternary compounds.

X-ray diffraction analysis

Precise analysis of XRD spectra for $Cd_{1-x}Zn_xS$ NCs with Zn content changing from $x = 0$ to $x = 1$ was performed (Fig. 3b). All the spectra confirmed the cubic crystalline structure, since the diffraction peaks related to the (111), (220), and (311) planes were clearly recognizable. The exact positions of diffraction peaks for these planes depended on the Zn content in NCs and gradually shifted from $2\theta = 26.5°$, 43.9°, 51.9° (respectively for the plans of (111), (220), (311) characteristic for cubic structure of CdS) up to $2\theta = 28.57°$, 47.63°, 56.49° (respectively for the plans of (111), (220), (311) characteristic for cubic structure of ZnS) with changing x from 0 to 1. It seems, that both inclusion of Zn atoms into host CdS structure as well as Cd atoms into host ZnS structure could have occur quite easily because it did not require a reorganization of the crystalline structure drastically as in the case of $Cd_{1-x}Cu_xS$ NCs. The average sizes of $Cd_{1-x}Zn_xS$ NCs were estimated from the most intensive (111) XRD peak using the Debye-Sherrer equation; and it was found that, despite of a high difference in the contents of Cd and Zn in NCs, their sizes did not vary too much and lay in the range of 2.5-3.3 nm. The relative lattice deformation in NCs were estimated applying Hall formula. Interestingly, the lowest value of the relative lattice deformation was observed for the sample with Zn content $x = 0.75$, which coincided with the Zn content providing the lowest NC size.

Photoluminescence spectra

PL spectra of the $Cd_{1-x}Zn_xS$ NCs depending on the contents of Cd and Zn ($x = 0$-1.0) are shown in Fig. 5.

With increasing Zn content in the Cd1-xZnxS NCs all the PL bands shifted towards a short-wave region, that indicated widening of a gap between the quantized energy levels. It is noteworthy, that this shift depended on the x value unevenly. It is noteworthy, that this shift depended on the x value unevenly. Thus, if comparing sample Zn75 and sample Zn100 the shift in position of the peak D_2 was 10 nm, whereas if comparing other pairs of samples Zn50-Zn75, Zn25-Zn50, this shift was much lower, only 4 and 2 nm respectively; and if comparing samples Cd100 and Zn25 the shifts of both bands D_1 and D_2 occurred slightly towards a long-wavelength region.

Further more detailed investigations should be performed to comprehend the reasons for a shift in position of the bands D_1, D_2 in PL spectra of NC $Cd_{1-x}Zn_xS$ and $Cd_{1-x}Cu_xS$, as well as to explain the difference in the ratios of intensities of these bands as it can be seen in Figs. 4 and 5.

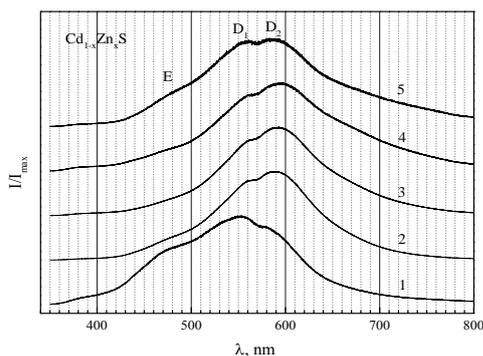**Fig. 5** – PL spectrum of $Cd_{1-x}Zn_xS$ NCs at $T = 300$ K. The line number corresponds to the following samples listed in Table 1: 1 – Cd100; 2 – Zn25; 3 – Zn50; 4 – Zn75; 5 – Zn100
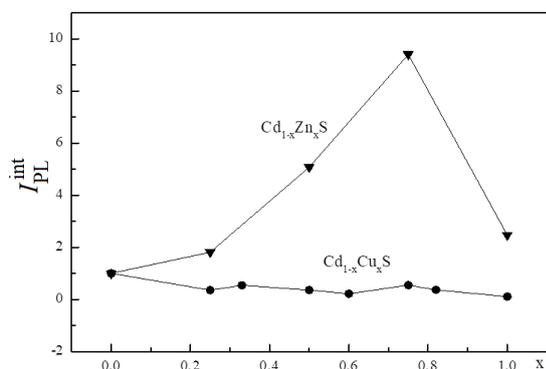

Fig. 6 – The effect of nanocrystal composition of semiconductors $Cd_{1-x}Cu_xS$ and $Cd_{1-x}Zn_xS$ on the intensity of their integrated PL

4. CONCLUSIONS

Nanocrystals of the ternary semiconductors $Cd_{1-x}Cu_xS$ and $Cd_{1-x}Zn_xS$ were synthesized in polymer films applying the *in-situ* sol-gel method developed. It was revealed that in case of $Cd_{1-x}Cu_xS$, the hexagonal structure dominated in NCs in a large range of Cu-Cd ratios; whereas in case of $Cd_{1-x}Zn_xS$, the dominating

crystalline structure of NCs corresponded to the cubic structure of CdS.

The PL spectra of NCs of semiconductors $Cd_{1-x}Cu_xS$ and $Cd_{1-x}Zn_xS$ consisted of two impurity bands and the exciton band which was much weaker by the intensity than previous ones. Analysing the PL spectra of NCs of the ternary compounds $Cd_{1-x}Cu_xS$ and $Cd_{1-x}Zn_xS$, we found that their PL intensity depended on their composition in different ways. As aforementioned for $Cd_{1-x}Cu_xS$ NCs, a decline of the impurity PL intensity was observed with increasing Cu content; and the reason for this was a decrease in concentration of the Sulphur interstitial centres, responsible for the PL bands D_1 and D_2.

On the contrary, for $Cd_{1-x}Zn_xS$ NCs, an increasing Zn content in the NCs resulted in an increase in the intensity of the impurity PL (Fig. 6). Probably, an increase of Zn content in $Cd_{1-x}Zn_xS$ compounds brought about an increase in concentration of the Sulphur interstitial centres by 'knocking out' the S atoms from a regular lattice node into an interstice. This mechanism probably took place at a low content of the Zn impurities in the CdS NCs [7]; whereas, for NCs of ternary compounds $Cd_{1-x}Zn_xS$ the dependence of the integrated PL intensity on the x value (Fig. 5) completely correlated with the corresponding dependence of the relative lattice deformation on the Zn content in NCs. Indeed, the minimum deformation observed for the sample Zn75 that coincided with the maximum value of PL intensity. Growth of the lattice deformation in other samples of $Cd_{1-x}Zn_xS$ NCs was accompanied by dropping the PL intensity.

Thus, it can be stated that the PL intensity of the $Cd_{1-x}Zn_xS$ NCs fairly depends on the deformation level of their lattices; the smaller the lattice deformation, the higher the PL intensity.

Синтез, люмінесцентні та структурні властивості нанокристалів $Cd_{1-x}Cu_xS$ і $Cd_{1-x}Zn_xS$

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У роботі описується синтез *in-situ* в полімерних плівках нанокристалів (НК) потрійних напівпровідників $Cd_{1-x}Cu_xS$ і $Cd_{1-x}Zn_xS$, а також результати досліджень їх структури і оптичних властивостей. Встановлено, що у разі $Cd_{1-x}Cu_xS$ у широкому діапазоні співвідношень Cu-Cd у синтезованих НК домінує гексагональна структура, тоді як у разі $Cd_{1-x}Zn_xS$ домінуюча кристалічна структура НК відповідає кубічній структурі CdS. Разом з тим, в обох випадках утворення окремих фаз CdS і CuS або CdS і ZnS не було знайдено, що підтверджує утворення потрійних напівпровідникових сполук. Було виявлено протилежний вплив збільшення концентрації катіонів Cu і Zn в потрійних сполуках на інтенсивність домішкової фотолюмінесценції, якщо для перших ця інтенсивність зменшується, то для останніх вона зростає. Обговорюються можливі причини цих явищ.

Ключові слова: Нанокристали, Тонкі нанокомпозитні полімерні плівки, Потрійні напівпровідникові сполуки $Cd_{1-x}Cu_xS$ і $Cd_{1-x}Zn_xS$, *In-situ* зол-гель синтез, Рентгенівська дифрактометрія, Ультрафіолетова спектроскопія, Фотолюмінесценція.

Синтез, люминесцентные и структурные свойства нанокристаллов $Cd_{1-x}Cu_xS$ и $Cd_{1-x}Zn_xS$

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В работе описывается синтез *in-situ* в полимерных пленках нанокристаллов (НК) тройных полупроводников $Cd_{1-x}Cu_xS$ и $Cd_{1-x}Zn_xS$, а также результаты исследований их структуры и оптических свойств. Установлено, что в случае $Cd_{1-x}Cu_xS$ в большом диапазоне отношений Cu-Cd в синтезированных НК доминирует гексагональная структура, тогда как в случае $Cd_{1-x}Zn_xS$ доминирующая кристаллическая структура НК соответствует кубической структуре CdS. Тем не менее, в обоих случаях образование отдельных фаз CdS и CuS или CdS и ZnS не было найдено, что подтверждает образование тройных полупроводниковых соединений. Было выявлено противоположное влияние увеличения концентрации катионов Cu и Zn в тройных соединениях на интенсивность примесной фотолюминесценции, если для первых эта интенсивность уменьшается, то для последних она возрастает. Обсуждаются возможные причины этих явлений.

Ключевые слова: Нанокристаллы, Тонкие нанокомпозитные полимерные пленки, Тройные полупроводниковые соединения $Cd_{1-x}Cu_xS$ и $Cd_{1-x}Zn_xS$, *In-situ* золь-гель-синтез, Рентгеновская дифрактометрия, Ультрафиолетовая спектроскопия, Фотолюминесценция

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