PACS 78.66.H.

Model of optical transitions in A_2B_6 wurtzite type quantum dots

Kunets V.P.

Institute of Semiconductor Physics, NAS of Ukraine, 45, prospect Nauki, 03028 Kyiv, Ukraine, phone 265 62 82

Abstract. Model of optical transitions in A_2B_6 wurtzite type quantum dots is proposed. It is based on the effective mass approximation and the quantum confinement effects, the valence band degeneracy in Γ point of the Brillouin zone and the effective mass anisotropy of the holes are also taken into account. A good agreement between the theoretically calculated and experimentally measured absorption spectra of CdSe and $Zn_xCd_{1-x}S$ wurtzite nanocrystals embedded into a borosilicate glass matrix is achieved in the framework of the model. It is also concluded that the effective mass approximation is yet enough justified for the nanocrystals with the average radius being lowered to ~2.0 nm.

Keywords: absorption, quantum dot, quantum confinement.

1. Introduction

Optical properties of A_2B_6 semiconductor quantum dots are strongly depended on their sizes due to the quantum confinement effects [1-3]. The absorption edge of the «large» dots ($r > a_B$, where r is the dot radius and a_B is the Bohr exciton one) is quite similar to that of the bulk crystal. The exciton peaks can be distinctly observed at low temperatures [1] being gradually disappeared with the size decrease. In the spectra of the «small» dots ($r < a_B$) the typical quantum-sized oscillations concerned with the optical transitions between the discrete quantum confinement levels are usually observed [2,3].

The simplest model to describe both the optical transitions and the absorption edge was proposed in [4] for the first time but only partial agreement with the experiment was achieved in [2] afterwards because of neglecting the valence band degeneracy in the Γ point of the Brillouin zone and the effective mass anisotropy of the holes in the hexagonal dots. The spin-orbit interaction was theoretically studied in [5] for CdSe dots where the energy spectrum was calculated in the quasi-cubical approach and the corresponding probabilities were estimated. However, a respective absorption spectrum was not derived theoretically. Some aspects of the problem were also discussed in [6] where, effectively, a semiphenomenological model was proposed and the effective mass anisotropy of the holes was taken into account when calculating such spectra.

In this paper, next step in developing the model is fulfilled, and the modified formula for $K(\hbar\omega)$ is proposed. Then the comparison with the experiment for CdSe and $Zn_xCd_{1-x}S$ wurtzite nanocrystals embedded into a borosilicate glass matrix is presented.

2. Model of optical transitions and energy spectrum of A_2B_6 wurtzite type quantum dots

The energy spectrum $E(\vec{k})$ of the bulk crystals in the Brillouin zone is determined by the wave vector $\vec{k} \sim 1/N_i$, where N_i is a number of atoms in the crystal. As N_i considerably exceeds the number of atoms in the unit cell the $E(\vec{k})$ dependence is considered as the quasi-continuous one (Fig. 1a). The conduction band of A_2B_6 wurtzite bulk crystals is isotropic [7]. Therefore, effective masses of electrons in parallel and perpendicular directions towards C axis of the
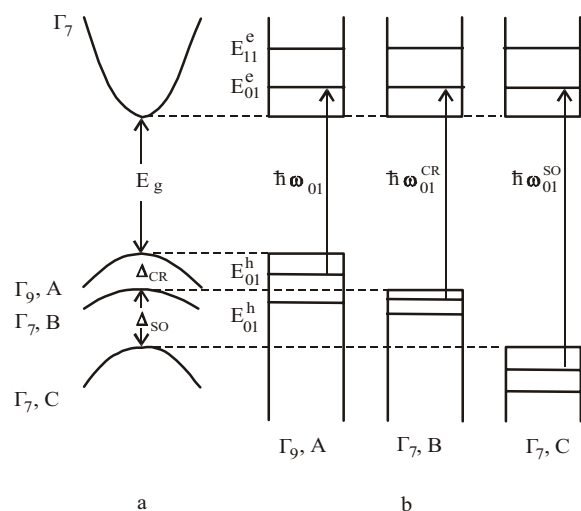

Fig. 1. The scheme of valence band splittings in bulk crystals (a) and corresponding optical transitions in a quantum dot (b).

crystal are identical, $m_e^{\parallel} = m_e^{\perp}$. These are listed in Table 1 for CdS, CdSe and ZnS. At the same time, their valence bands are splitted to three subbands: $\Gamma_9\,(A)$, $\Gamma_7\,(B)$ and $\Gamma_7\,(C)$ in Γ point of the Brillouin zone due to the crystalline field and spin-orbit interaction. Corresponding splittings are $\Delta_{CR} = 0.027$ eV, $\Delta_{SO} = 0.065$ eV for CdS; $\Delta_{CR} = 0.041$ eV, $\Delta_{SO} = 0.420$ eV for CdSe; and $\Delta_{CR} = 0.055$ eV, $\Delta_{SO} = 0.092$ eV for hexagonal ZnS [7], respectively. Each of the valence subbands is anisotropic and characterized by different effective masses $m_h^{\parallel}, m_h^{\perp}$ of the holes.

The energy spectrum of the quantum dots is essentially different from the bulk spectrum (Fig. 1b). The momentum of the confined carrier depends on the sphere radius and gets the discrete values defined by $\varphi_{\ell n}$ roots of the Bessel functions and $r\,(k_{\ell n} = \varphi_{\ell n}/r)$ in the model of spherical quantum dot. Therefore, the energy spectrum also becomes discrete in the strongly confined regime ($\bar{r} < a_B$). Moreover, the distances between the nearest quantum confinement levels considerably exceeds their natural half widths. The levels positions are determined in such model as follows [4]:

$$E_{\ell n}^{e,h} = \frac{\hbar^2 \varphi_{\ell n}^2}{2m_{e,h}r^2}, \qquad (1)$$

where l and n are the orbital and main quantum numbers.

The wurtzite structure of A₂B₆ quantum dots embedded into the borosilicate glass matrix is not varied when the size decreases almost down to 1.5 nm [11] as it follows from the X-ray diffraction and TEM data [11-13]. On the other hand, the Bohr exciton radii in the bulk CdS and CdSe are 3.0 and 5.6 nm, respectively. Therefore, one can conclude that the carriers motion in the hexagonal periodic potential and in the strong confinement regime takes place in CdS, for example, at the average radii 1.5 nm $< \bar{r} <$ 3.0 nm. For CdSe quantum dots the same size interval is larger to some extent, namely, 1.5 nm $< \bar{r} <$ 5.6 nm.

The deviations from the cubic symmetry in the lattice structure of the hexagonal dots (cubic symmetry was used for energy structure calculations of both the bulk crystals and the quantum dots for the first time) should also violate the spherical symmetry of the isoenergetic surfaces of the valence states near the $\vec{k} = 0$ point of the Brillouin zone and

their splittings caused by spin-orbit interaction and a rather small addition to the crystal field stemmed from the atoms situated in the second coordination sphere. Such features will cause the essential differences in the energy spectra of the carriers under confinement in comparison with the bulk and the cubic quantum dots. As it follows from the formula (1), the effective mass anisotropy of the holes should lead to the essential differences of their energies $E_{\ell n}^{h}$ in the different directions as regards to C axis. It should additionally split the quantum confinement levels of the holes.

Fig. 2 shows the size dependences of the confinement energies calculated by the formula (1) for the different components of the effective masses: $m_e = m_{e\perp} = m_{e\parallel}$, $m_h = m_{h\perp}$ and $m_h = m_{h\parallel}$. It is clearly observed that the decrease of the quantum dot radius drasticaly shifts the levels. Moreover, these shifts are considerably dependent on effective masses of carriers. The larger is the mass the smaller is the shift. Besides, the degeneracies of the holes' confinement energies are distinctly observed at some values of r for the different valence subbands.

To calculate both the energy spectrum of the hexagonal quantum dots and the absorption edge of the whole structure with a great number of size-dispersed nanocrystals chaoticaly oriented in the space, the following model is proposed. It is supposed that:

(a) both the effective mass approximation and the parabolic dispersive law $E\,(\vec{k})$ are valid for the dots with $\bar{r} > 1.5 \div 2.0$ nm;

(b) carrier motions are independently quantized in the conduction band and in each of the valence subbands, $\Gamma_9\,(A)$, $\Gamma_7\,(B)$ and $\Gamma_7\,(C)$ (Fig. 1b);

(c) the crystalline field and spin-orbit splittings in the dots are supposed to be the same as in the bulk;

(d) tunneling effects for carriers crossing the dot surface are assumed to be insignificant at least for the lowest energy states in the well, and carrier wavefunctions does not significantly depend on the value of the potential barrier.

The effective mass anisotropy of the holes, the Coulomb interaction between electrons and holes, the chaotic orientation of the nanocrystals in the space confirmed by TEM [11], and the stationary size distribution described by the Lifshitz-Slezov theory [14] are also taken into account.

Table 1. Effective masses of electrons and holes in CdS, CdSe and ZnS hexagonal bulk crystals.

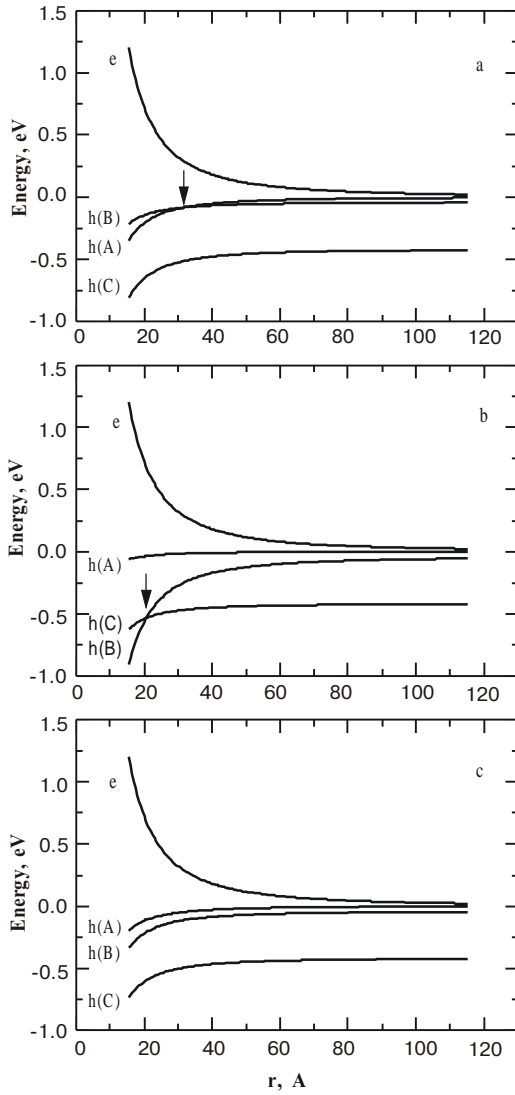| Semiconductor	Conduction band, Γ_7	Γ_9 (B) valence band		Γ_7 (B) valence band		Γ_7 (C) valence band	
	$m_{e\perp}, m_{e\parallel}$	$m_{h\perp}$	$m_{h\parallel}$	$m_{h\perp}$	m_h	$m_{h\perp}$	m_h
CdSe	0.13±0.03 [7]	0.45±0.09 [8] 0.42*[10]	2.5 [8], [9]	0.9±0.2 [8] 0.94*[10]	0.18*[10]	0.40*[10]	0.77*[10]
CdS	0.205±0.01 [7]	0.7±0.1 [8] 0.56*[10]	~5.0 [8] 2.5*[10]	1.2*[10]	0.24*[10]	0.43*[10]	0.77*[10]
ZnS	0.28±0.01 [8]	0.51±0.05 [8]	~1.4 [10]	1.1*	0.32*[10]	0.55*[10]	0.85*[10]

Theoretical data are marked by asterisks.

3. Absorption spectra of the structures with CdSSe and ZnCdS nanocrystals

The absorption edge of a single nanocrystal with the radius r_i is formed by the optical transitions between the well separated quantum confinement levels if $r_i \leq a_B$ and should consist of a number of narrow lines. If the photon energy exceeds the bandgaps ($E_g + \Delta_{CR}$ or $E_g + \Delta_{CR} + \Delta_{SO}$) the optical transitions with the participation of light and heavy holes in $\vec{E} \perp C$ and $\vec{E} \parallel C$ polarizations are occured due to chaotic nanocrystal orientations in space. The photon energy absorbed by the nanocrystal with the radius r_i is given by the expression

$$\hbar \omega_{\ell n}^{ij} = E_g^j + E_{\ell n}^{e,h} - \frac{e^2}{\varepsilon r_i} \qquad (3)$$

where $j = 1, 2, 3$ for the transitions with the participation of A, B and C valence states with the corresponded band gaps $E_g^1 = E_{g0}$, $E_g^2 = E_{g0} + \Delta_{CR}$ and $E_g^3 = E_{g0} + \Delta_{CR} + \Delta_{SO}$ (Fig. 1), E_{g0} is the bulk band gap energy, e is the charge of the carrier. The last term in (3) describes Coulomb interaction between the electron and hole. In this case the absorption coefficient of a single nanocrystal with the radius r_i can be written by analogy to [4] as follows:

$$K_i(\hbar \omega) = A \sum_{j=1}^{3} \sum_{\ell n} (2l+1) \delta \left(\hbar \omega - E_g^j - E_{\ell n}^{e,h} - \frac{e^2}{\varepsilon r_i} \right), \qquad (4)$$

where ω is the frequency of the incident light.

The size dispersion of nanocrystals which is described by Lifshitz-Slezov function $P(u = r / \bar{r})$ leads to the wide energy «bands» formed by the different nanocrystals and, as a consequence, to respective absorption bands. In this case the absorption coefficient of the whole structure with the size dispersed nanocrystals can be obtained in the following form:

$$K(\hbar \omega) = A \sum_{j=1}^{3} \sum_{\ell n} B_{\ell n} \left(\frac{\mu_j \bar{r}^2}{\hbar^2 \varphi_{\ell n}^2} \right) \times$$

$$\times \left(\frac{2 \mu \bar{r}^2 \left(\hbar \omega - E_g^j \right)}{\hbar^2 \varphi_{\ell n}^2} \right)^{-3/2} P \left(\frac{1}{\sqrt{\xi_{\ell n}}} \right), \qquad (5)$$

where $\xi_{\ell n} = 2 \mu_j r^2 \left(\hbar \omega - E_g^j \right) / \hbar^2 \varphi_{\ell n}^2$; B_{ln} are the coefficients propotional to the optical transition probabilities in respect with the selection rules [5]; μ_j are the corresponded reduced effective masses $\left(\frac{1}{\mu_j} = \frac{1}{m_{oe}} + \frac{1}{m_{oh}^j} \right)$, $m_{oe} = m_{e\perp} = m_{e\parallel}$), and m_{oh}^j values are calculated using the formula (2).

The calculation of the absorption spectrum is based on the fact that the certain photon energy is absorbed by nanocrystals with the certain radius r_i only, i.e. resonantly with participation of the levels $E_{\ell n}^e$ and $E_{\ell n}^h$ correspond-

Fig. 2. The lowest quantum confinement levels of electrons (e) and holes (h) in A, B and C valence subbands as the function of size in CdSe quantum dots for different effective mass components: $m_h = m_{h\perp}$ (a), $m_h = m_{h\parallel}$ (b) and $m_h = m_{oh}$ (c). Size at which the degeneracy of the holes energy can be observed is depicted by arrows.

The effective mass anisotropy is included in the model using the so-called «optical» effective mass as follows:

$$\frac{1}{m_{ok}} = \frac{1}{3} \left(\frac{\varepsilon_\perp}{\varepsilon_\parallel} \frac{1}{m_{\parallel h}} + \frac{2}{m_{\perp h}} \right) \qquad (2)$$

where $\varepsilon_{\perp, \parallel}$ are the static dielectric constants in the different directions towards C axis of the dot. In fact, the isotropic energy surfaces is used in this case, and each of the valence band is considered as the spherical one with the dispersive law $E(\vec{k})$ described only by a single effective mass. The degeneracy of the hole energy disappears in this case (Fig. 2c).

ing to $\hbar\omega_i$ (Fig. 1b, formula (3)). Due to the absence of any interaction between the well separated nanocrystals in the sample, the calculation of the spectrum for a single nanocrystal is done as the first step using the energy structure described by the formula (3). Then the absorption spectrum of the structure as a whole is obtained being summing from all of the nanocrystals with different sizes.

The absorption edge of the glasses with CdSe ($\bar{r} = 21\text{Å}$) and ZnCdS ($\bar{r} = 21\text{Å}$) nanocrystals are shown in Fig. 3 by dots. The average radii listed above were obtained, in part, by the low angle X-ray diffraction methods [5, 15]. The spectra $K(\hbar\omega)$ calculated using the formula (5) are also pictured by thin lines. The crystalline field and spin-orbit splittings of the mixed nanocrystals were determined as the line interpolation between CdS and CdSe or between ZnS and CdS (Table 1). From Fig. 3 one can conclude a good agreement between the calculated and experimentaly measured spectra. As the fitting parameters $\bar{r}$ and E_g values were used. These are well agreed with the ones obtained by X-ray methods (Table 2). However, E_g values obtained by the same way for CdSe nanocrystals are slightly different from the bulk ones due to the hydrostatic pressure effects [16]. A good agreement with the experiment shows that the model proposed adequately reflects the real picture of the optical transitions in such structures.

As it follows from the simple estimations, the mass anisotropy induced splittings can take values of about several dozens of millielectronvolts (Fig.4) that is already comparable with the crystalline field splitting in the bulk. For example, $\dfrac{\Delta\mu}{\mu}$ value caused by the mass anisotropy of the holes in CdS can consist of about 10%. Thus, for the transitions in CdS nanocrystals with $r \approx 2.3$ nm with participation of the lowest energy levels ($\ell = 0$, $n = 1$) the estimated value is about 0.056 eV, i.e. it is approximately equal to the Coulomb energy ($\sim e^2/\varepsilon r$) and to the pressure induced band gap shifts [16]. The splittings of A exciton lines ($n = 2$) observed in the transmission spectra of the bulk CdS and CdSe crystals at 1.6 K [8] consist only of about several tenths of electronvolts. Note, that the broadening of the absorption bands caused by the size dispersion considerably exceeds these values. Thus, such splittings should only additionally broaden the absorption bands. At sizes lower than 1.5 nm the picture should be also complicated by the presence of

the cubic phase nanocrystals that seems to be observed for ZnCdS nanocrystals (Fig. 3) where some differences between the calculated and experimental curves are nevertheless observed.

In conclusion, the model proposed allows to describe adequately the absorption spectra of A_2B_6 wurtzite type nanocrystals with the average radii in the range of $\sim 1.5 \div 2.0$ nm $\leq \bar{r} \leq a_B$ and to conclude that the effective mass approximation is yet valid for such nanocrystals. The everage radii of nanocrystals, band gap energies, confinement energies,
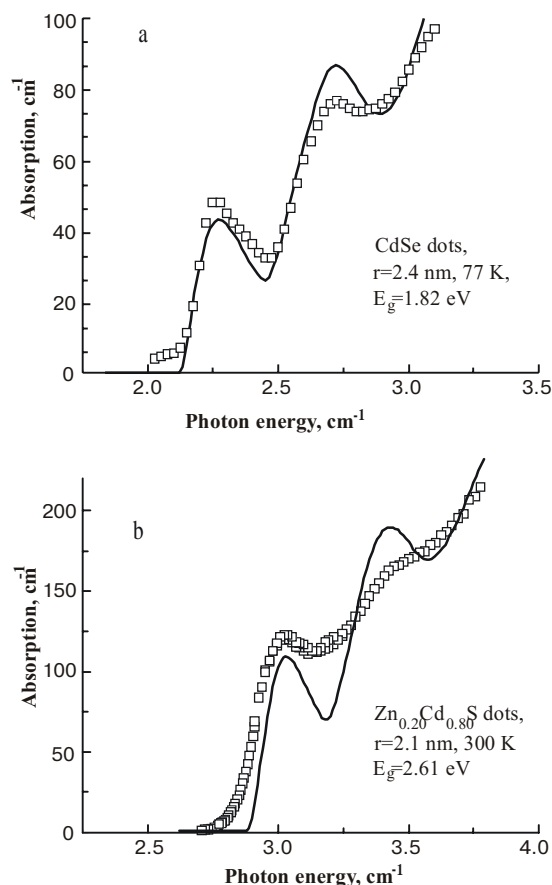

Fig. 3. Absorption spectra of CdSe [5] and ZnCdS quantum dots. Solid curves are experimental data, thin curves are the theoretical ones.

Table 2. Parameters of CdSe and ZnCdS quantum dots.

Quantum dots	$\bar{r}$, nm	$\bar{r}$, nm Ref. data	E_g, eV	Contributions to the absorption spectra from the different valence subbands[2]		
				$\Gamma_9(A)$	$\Gamma_7(B)$	$\Gamma_7(C)$
CdSe	2.40[2]	2.60 [5]	1.82[1,2] (77 K)	0.70	0.10	0.20
$Zn_{0.20}Cd_{0.80}S$	2.50[2]	-	2.61[1,2] (300 K)	0.60	0.15	0.25

1) Data obtained with account of the matrix pressure effect [16].

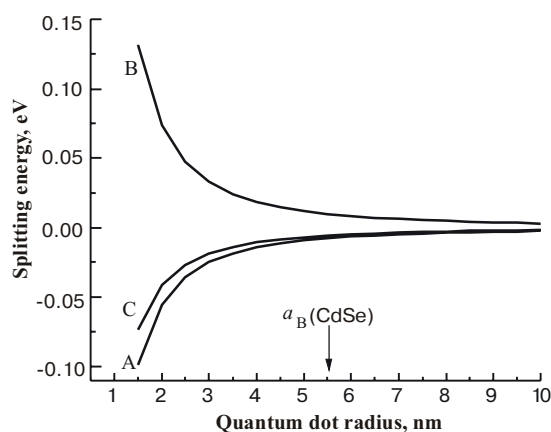2) Data obtained as fitting parameters.

Fig. 4. Splitting energy induced by the mass anisotropy of the holes as a function of a dot radius. The Bohr exciton radius for CdSe is shown by an arrow.

Coulomb energies, etc., can be estimated as the fitting parameters when calculating the absorption spectra.

The author wish to express his deep gratitude for fruitful discussions to Prof. Lisitsa M. P. and Dr. Kulish N.R. as well as for the technical assistance to Malysh N.I. and Kunets Vas.P.

References

1. A.I. Ekimov, Al.L. Efros, A.A. Onushchenko. Quantum size effect in semiconductor microcrystals. Solid State Communications.- 1985.-**56**, N 11.-P. 921-924.
2. N.R. Kulish, V.P. Kunets, M.P. Lisitsa. Absorption spectra of semiconductor microcrystals in quantum confinement conditions // Ukr. Phys. J.-1990.-**35**, N12.-P.1817-1821.
3. U. Woggon, S.V. Gaponenko. Excitons in quantum dots.- Phys. St. Sol. (b)- 1995.- **189**.- P. 285-343.
4. Al. L. Efros, A. L. Efros. Band-to-band absorption of the light in semiconductor ball // FTP.-1982.- **16**, N7.- P.1209-1214.
5. A.I. Ekimov, F. Hache, M.C. Schanne-Klein et al. Absorption and intensity-dependent photoluminescence measurements on CdSe quantum dots: assignment of the first electronic transitions. Opt. Soc. Am.-1993.- **10**, N 1. P. 100-107.
6. V.P. Kunets. Absorption adge spectroscopy of A$_2$B$_6$ small quantum dots // DAN of Ukraine.-1999.-N9.-P. 86-91.
7. P.I. Baranski, V.P. Klochkov, I. V. Potykevich. Semiconductor electronics.-Kiev: Naukova Dumka.-1975.
8. Physics and chemistry of II-VI compounds. Edited by S.A. Medvedev.-Moscow, Mir.-1970.
9. V.I. Gavrilenko, A.M. Grehov, D.V. Korbutyak, V.G. Litovchenko. Optical properties of semiconductors. Handbook, Kiev-Naukova Dumka.-1987.
10. M. Cardona. Band parameters of semiconductors with zincblende, wurtzite and germanium structure// J. Phys. Chem. Solids.-1963.-**24**, N 12.- P. 1543-1555.
11. J.J. Ramsden. Electron diffraction anomalies in small CdS clasters. J.Cryst.Growth.-1987.- **82**, N3.-P.569-572.
12. B. Champagnon, B. Andrianasolo, A. Ramos, M. Gandais, M. Allais, J.-P. Benoit. Size of Cd(S,Se) quantum dots in glasses: Correlation between measurements by high-resolution transmission electron microscopy, small-angle x-ray scattering, and low-frequency inelastic Raman scattering // J. Appl. Phys.-1993.- **73**, N 6.- P. 2775-2780.
13. A.P. Alivisatos. Semiconductor Nanocrystals // MRS Bulletin.- 1995 (August).-P. 23-32.
14. I.M. Lifshits, V.V. Slezov. About the kinetic of the diffusive desolve of the oversaturated solid solutions // ZETP.-1958.-**35**, N2.-P. 479-492.
15. V.A. Zulkov, D.V. Kovalev, S.G. Kotov, et al. Decay of photoluminescence kinetics in passive keys based on KS glasses // J. Appl. Spectr. (Belarus).-1988.-**49**, N 6.-P. 919-924.
16. V.P. Kunets. Influence of hydrostatic pressure on the optical properties of CdSSe nanocrystals // Ukr. Phys. J.-1998.-**43**, N1. P. 64–69.