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# X-Ray excited and photoluminescence of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals embedded in borosilicate glass matrix

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## Abstract

The performed experimental studies of X-ray excited and photoluminescence, optical absorption and Raman scattering of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals, embedded in borosilicate glass matrix, have enabled the nanocrystal parameters (chemical composition, average radius, acceptor levels energy depth, electron-hole Coulomb interaction energy) is to be determined.

**Keywords:** nanocrystals, luminescence, quantum-size effect, acceptor levels

## Introduction

Luminescence of CdS<sub>1-x</sub>Se<sub>x</sub> mixed semiconductors have been thoroughly studied in the visible and near-infrared range [1, 2]. In the recent decade a special attention is paid to the studies of luminescence of these materials in nanocrystalline state [3–9]. CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals can be obtained by different techniques [7], especially by embedding into borosilicate glass matrix. Depending on the method of preparation, the characteristic size of nanocrystals can vary from several nanometers to hundreds of nanometers. Due to such three-dimensional spatial confinement, resulting in the energy band quantization, the nanocrystals, called quantum dots or quasi-zero-dimensional crystals, have become the model for the studies of quantum-size effects. Optical methods enable not only these effects to be experimentally observed, but also the basic parameters of the nanocrystals (average radius, chemical composition) are to be determined [8]. CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals, embedded in silicate glass matrix, are widely used as optical filters, their possible applications

as non-linear optical devices, waveguides, lasers are reported [7, 10].

The comparison of photoluminescence (PL) of nanocrystalline CdS<sub>1-x</sub>Se<sub>x</sub> with the bulk crystals of the same composition enabled the assignment of the observed bands [5]. It would be interesting to extend the PL studies to the nanocrystals of different composition, as well as to study X-ray excited luminescence. It is also important to exclude the luminescence of the glass matrix itself which can encumber the treatment of the observed spectra of the glass-embedded nanocrystals.

## Experimental

CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals, embedded into SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub>–ZnO–K<sub>2</sub>O–Na<sub>2</sub>O glass matrix, were obtained by conventional solid-state precipitation technique, similar to that, described in [11–13].

Raman spectra of the samples, enabling the chemical composition of the nanocrystals to be determined, were measured using a DFS-24 monochromator and a FEU-136 phototube, Ar<sup>+</sup>-

laser ( $\lambda=488.0$  nm) being used for excitation.

X-ray excited luminescence of the mixed nanocrystals was studied in the range 300–1000 nm. PL spectra were measured on a DFS-24 monochromator, Ar<sup>+</sup>-laser ( $\lambda=514.5$  nm) being used as the excitation source. X-ray luminescence (XL) was excited by an X-ray tube with molybdenum anticathode (40 kV, 20 mA) and detected by an MDR-23 monochromator.

Optical studies were performed at room temperature.

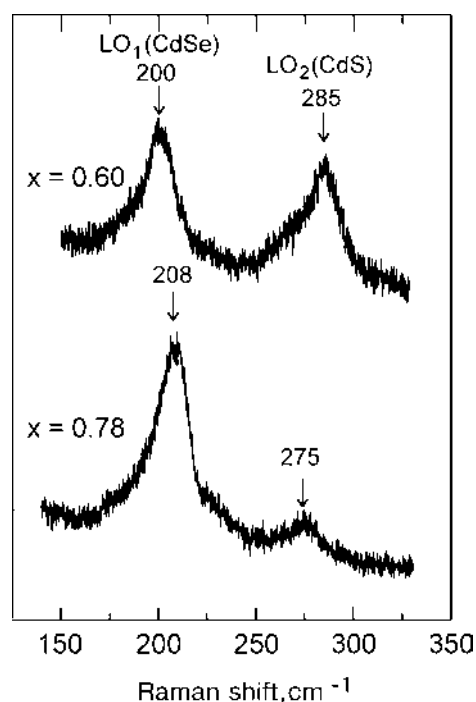
## Results and discussion

In order to determine the chemical composition of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals, embedded in the glass matrix, Raman scattering technique was used. Raman spectra of the investigated samples are shown in Fig. 1. Since the phonon spectra of CdS<sub>1-x</sub>Se<sub>x</sub> mixed crystals are characterized by a two-mode type of compositional transformation, the mixed crystal spectra contain bands, corresponding to both components of the solid solution, and, as it is shown in [14], from their spectral position the chemical composition of the nanocrystals can be determined. As it is seen from Fig. 1, in the investigated samples of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals in the glass matrix two distinct peaks of LO<sub>1</sub>(CdSe) and LO<sub>2</sub>(CdS) phonons are observed. Having compared their spectral position with the results of [14–16], we have determined the composition of the nanocrystals as  $x=0.60\pm 0.03$  (KS-10 sample) and  $x=0.78\pm 0.03$  (KS-13 sample).

The spectra of photo – and X – ray luminescence of the investigated samples are shown in Figs. 2 and 3, respectively. In the PL spectra of CdS<sub>0.4</sub>Se<sub>0.6</sub> nanocrystals two maxima at 1.86 and 2.13 eV with the halfwidths 0.39 and 0.12 eV are seen to be observed, while for CdS<sub>0.22</sub>Se<sub>0.78</sub> the maxima at 1.83 and 2.03 eV with the halfwidths 0.32 and 0.15 eV, respectively, are registered.

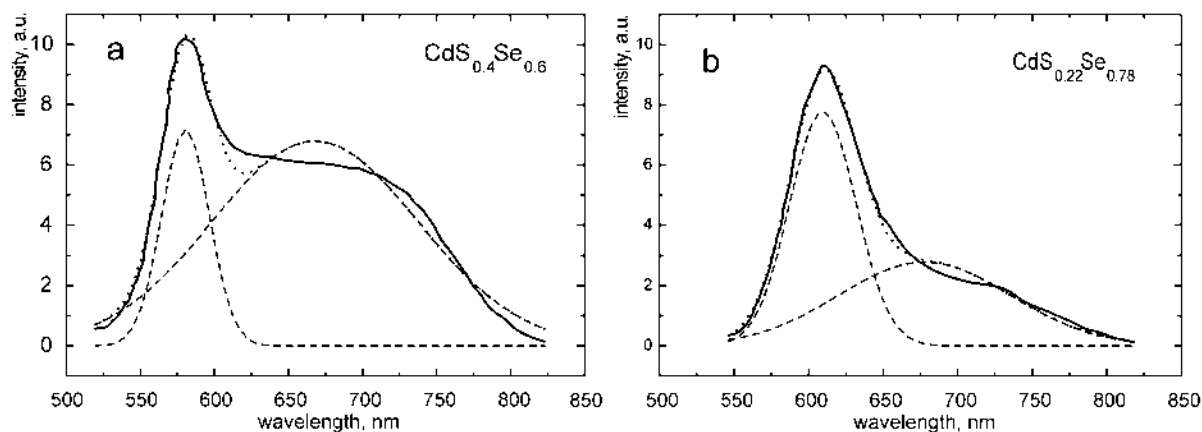
It should be noted that XL measurements of borosilicate glass matrix itself (Fig. 3,c) enabled

us to determine its contribution into the spectra, related to intrinsic and radiation-induced centres in the glass. Having subtracted the matrix contribution, we have obtained the spectra, shown in Fig.3(a,b), whose simulation by elementary Gaussian contours provided the energy position and halfwidth values of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystal XL bands. Thus, in the XL spectra the bands centered at 2.04 and 2.36 eV with halfwidths 0.35 and 0.54 eV, respectively (for CdS<sub>0.4</sub>Se<sub>0.6</sub>), and at 1.92 and 2.21 eV with halfwidths 0.30 and 0.38 eV, respectively (for CdS<sub>0.22</sub>Se<sub>0.78</sub>), have been detected.



**Fig. 1.** Raman spectra of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals embedded in borosilicate glass matrix.

For II-VI nanocrystals, embedded in a glass matrix, in PL spectra in most cases three impurity-defect bands with the maxima at  $h\nu_{ph1}$ ,  $h\nu_{ph2}$  i  $h\nu_{ph3}$  are observed. In our case under the excitation by Ar<sup>+</sup>-laser ( $\lambda=514.5$  nm) in the PL spectra only two maxima are observed, since the exciting light energy is not sufficient to excite the highest-energy band. It should be noted that the latter is revealed in the investigated samples at XL studies, centered at 2.36 eV (for  $x = 0.6$ ) and 2.03 eV (for  $x = 0.78$ ).



**Fig. 2.** Photoluminescence spectra of CdS<sub>0.4</sub>Se<sub>0.6</sub> (a) and CdS<sub>0.22</sub>Se<sub>0.78</sub> (b) nanocrystals embedded in borosilicate glass matrix: solid line – experiment, dotted line – approximation by superimposition of two Gaussian contours, each of which is shown by dashed lines.

In this case in the XL spectra two low-energy bands are not resolved due to lower resolution conditions.

The obtained luminescence spectra, compared with the results of optical absorption studies, where the quantum-size effects are revealed, provide the information on the energy parameters of the nanocrystals – acceptor levels energy depth and electron-hole Coulomb interaction energy. The highest-wavelength absorption band centered at  $h\nu_{01}$  is formed by valence electron transitions to the first quantum-size level, and the PL impurity band – due to radiative capture of a free electron from this level by an acceptor with the energy of  $E_A^i$  [8].

Then

$$E_A^i = h\nu_{01} - h\nu_{ph}^i - E_{01}^h, \quad (1)$$

where  $E_{01}^h$  is hole size-quantization energy, which, along with the electron size-quantization energy, is given by

$$E_{01}^{e,h} = 0.71\hbar^2\varphi_{01}^2 / 2m_{e,h}(\bar{r})^2, \quad (2)$$

$m_{e,h}$  being the electron (hole) effective mass,

$\varphi_{01}$  – the first root of the Bessel function,  $\bar{r}$  – the average radius of the nanocrystals, which in the case of strong size quantization is determined from the expression of the nanocrystal absorption coefficient

$$\alpha(h\nu) = A \sum_{ln} B_l \left( \mu r / \hbar^2 k_{ln}^2 \right) \left( 2\mu(h\nu - E_g) / \hbar^2 k_{ln}^2 \right)^{-3/2} P(r/\bar{r}), \quad (3)$$

$A$  being a constant,  $E_g$  – optical energy gap,  $\mu$  – reduced effective mass of charge-carriers,  $k_{ln} = \varphi_{ln}/r$ ,  $\varphi_{ln}$  – Bessel function roots,  $B_l$  – coefficients, proportional to transition probabilities, summation over  $l$  being carried out over all states of the valence band with the account of intracrystal and spin-orbit splitting.  $P(r/\bar{r})$  is a factor, taking into account the nanocrystal size dispersion and being described by the Lifshitz-Slyozov formula [8, 17].

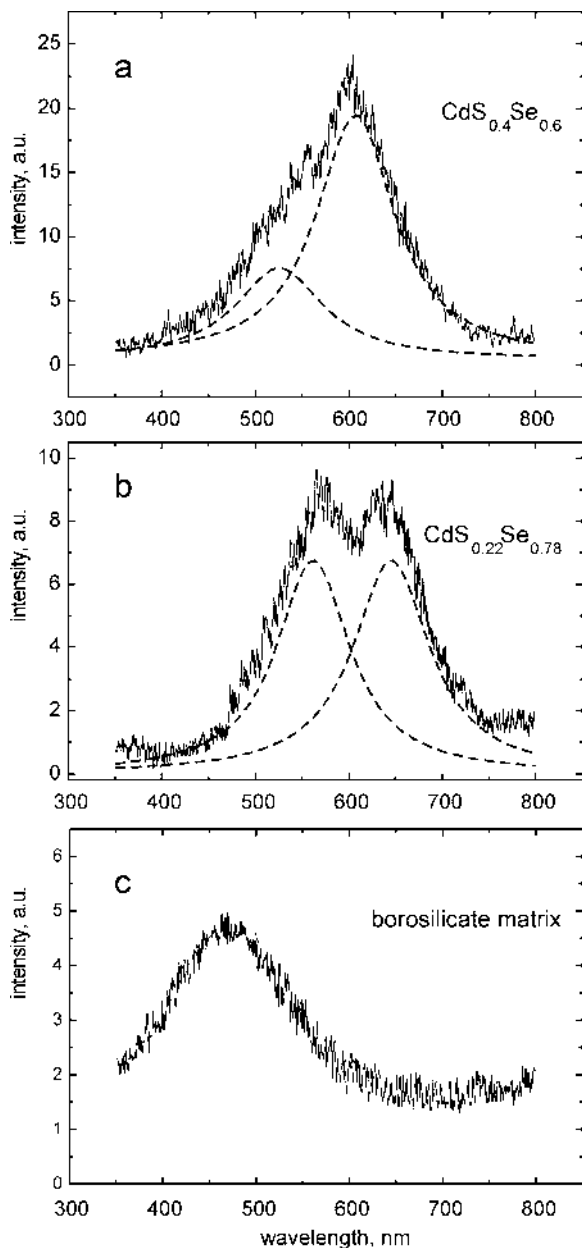
From the experimental absorption spectra of CdS<sub>1-x</sub>Se<sub>x</sub> nanocrystals, embedded in the glass matrix (Fig. 4), we have determined the average nanocrystal radii as 2.76 and 3.08 nm for  $x = 0.6$  and 0.78, respectively.

With the account of the obtained average nanocrystal radii values one can calculate the electron-hole Coulomb interaction energy

$$V = 1.786e^2 / \epsilon\bar{r}, \quad (4)$$

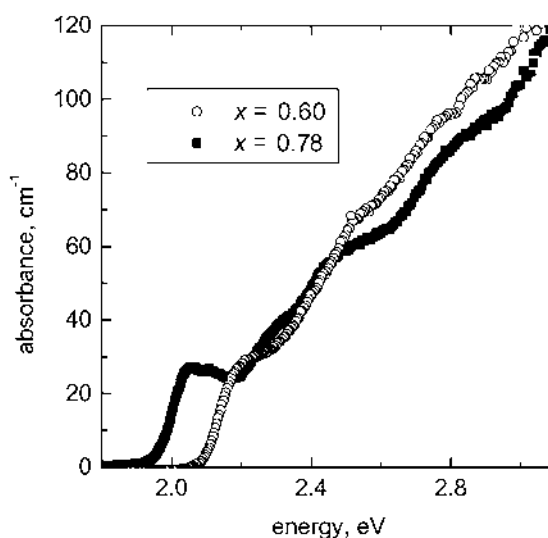
the dielectric permeability  $\varepsilon$  value for the mixed crystals being determined from the known values for the pure crystals (5.32 and 6.1 for CdS and CdSe, respectively [15, 16] ) as follows

$$\varepsilon = x\varepsilon_{\text{CdSe}} + (1-x)\varepsilon_{\text{CdS}} \quad (5)$$



**Fig. 3.** X-ray excited luminescence spectra of  $\text{CdS}_{0.4}\text{Se}_{0.6}$  (a) and  $\text{CdS}_{0.22}\text{Se}_{0.78}$  (b) nanocrystals, embedded in borosilicate glass matrix, and the borosilicate glass matrix itself (c). Solid line – experiment, dotted lines – Gaussian contours used for the simulation of the experimental spectra.

The electron-hole Coulomb interaction energy values  $V$ , calculated from Eq. (4), are 0.16 and 0.14 eV for  $\text{CdS}_{0.4}\text{Se}_{0.6}$  and  $\text{CdS}_{0.22}\text{Se}_{0.78}$  nanocrystals, respectively. Note that  $V$  value determines the energy difference between the first absorption maximum  $h\nu_{01}$  (Fig. 4) and the highest-energy luminescence band, corresponding to the direct recombination of the non-equilibrium charge-carriers (Fig. 3). From the analysis of the corresponding spectra the values  $V = 0.15$  eV ( $x=0.6$ ) and 0.14 eV ( $x=0.78$ ) are obtained, being in good agreement with those, calculated above.



**Fig. 4.** Optical absorption spectra of  $\text{CdS}_{1-x}\text{Se}_x$  nanocrystals, embedded in borosilicate glass matrix.

The acceptor level energy depth values, calculated from Eq. (1) with the account of hole effective mass values for CdS  $m_h^* = 0.53m_0$  [18] and for CdSe  $m_h^* = 0.44m_0$  [19], are 0.24 and 0.06 eV for  $\text{CdS}_{0.4}\text{Se}_{0.6}$ , and 0.14 and 0.05 eV for  $\text{CdS}_{0.22}\text{Se}_{0.78}$ , respectively.

## Conclusions

Optical properties of  $\text{CdS}_{1-x}\text{Se}_x$  nanocrystals, embedded in borosilicate glass matrix, were investigated. The chemical composition and average radius of the nanocrystals were obtained from Raman scattering and optical absorption spectra, respectively. The performed experi-

mental studies of X-ray excited and photoluminescence have enabled us to determine the acceptor levels energy depth and the electron-hole Coulomb interaction energy in the nanocrystals.

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