Hydrostatic pressure effect on the optical spectra of glass-embedded $CdS_{1-x}Se_x$ nanocrystals

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Abstract. Effect of hydrostatic pressure on the optical absorption spectrra of $CdS_{1-x}Se_x$ nanocrystals embedded in borosilicate glass matrix, is studied. A pressure-induced blue shift of the optical absorption edge and confinement-related maxima is observed. Energy band gap pressure variation coefficients are determined, their compositional and size behaviour being discussed in view of possible structural difference within the nanocrystal ensemble.

1. Introduction

Size-dependent features in electronic structure of cadmium chalcogenide nanocrystals (quantum dots), revealed in their optical spectra, have made them an object of extensive scientific interest due to specific physical effects as well as to broad applications [1–3]. Size variation of CdSe nanocrystals (NCs) enables, for example, their luminescence to be tuned within practically the whole visible spectral range [2, 3]. Mixed $CdS_{1-x}Se_x$ NCs, grown in most cases by solid-state precipitation in glass matrices [4–6], offer additional oportunities for tuning due to variation of both the NC size and chemical composition.

Thorough studies of pressure effect on the optical properties were carried out for CdSe [7–12] and CdS [10, 13, 14] NCs, obtained by colloidal synthesis in organic polymers [7–13] as well as embedded in glass matrices [10, 14]. At higher pressures CdSe and CdS NCs undergo a phase transition from hexagonal to cubic phase [7–11, 13, 14]. Pressure effects for mixed $CdS_{1-x}Se_x$ NCs are much less investigated [10, 13, 15, 16], the studies were carried out only for a very limited set of compositions.

Here we report on the studies of $CdS_{1-x}Se_x$ NCs ($0.4 < x \leq 1$) embedded in a borosilicate glass matrix under hydrostatic pressure by optical absorption spectroscopy.

2. Experimental

$CdS_{1-x}Se_x$ quantum dots were grown in a borosilicate glass by solid-state precipitation technique generally similar to that of [4–6]. The chemical composition of the NCs was determined within $\Delta x = \pm 0.03$ from Raman spectroscopy [17]. The average NC size depended on the heat treatment temperature and duration and was determined from the absorption spectra. Plates with area of near 5×5 mm^2 and thickness down to 0.15 mm were prepared for optical measurements.

The spectra were measured at room temperature in a three-window optical pressure cell, benzene being used as a pressure medium. The pressure was varied from 0 to 0.4 GPa in increasing and decreasing mode. A LOMO MDR-2 monochromator with a FEU-106 phototube was used.

3. Results and discussion

Figure 1 presents the variation of optical absorption spectra of $CdS_{1-x}Se_x$ NCs of the same average radius (2.2–2.3 nm), but different chemical composition, under hydrostatic pressure. The pressure effect on the optical absorption spectra of CdSe NCs of different average size is shown in Figure 2. In the obtained absorption spectra once can clearly observe maxima, related to the charge-carrier confinement, whose spectral position depends on the NC size and composition.
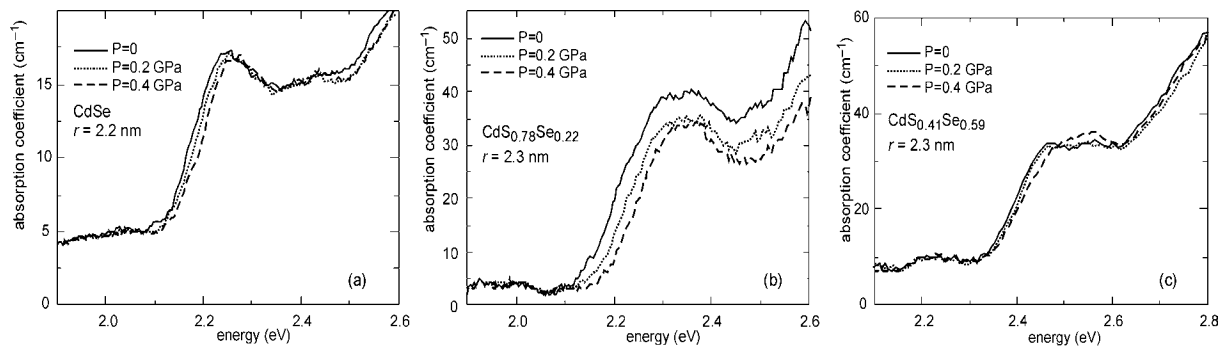

Figure 1. Effect of hydrostatic pressure on the optical absorption spectra of $CdS_{1-x}Se_x$ NCs embedded in a borosilicate glass.
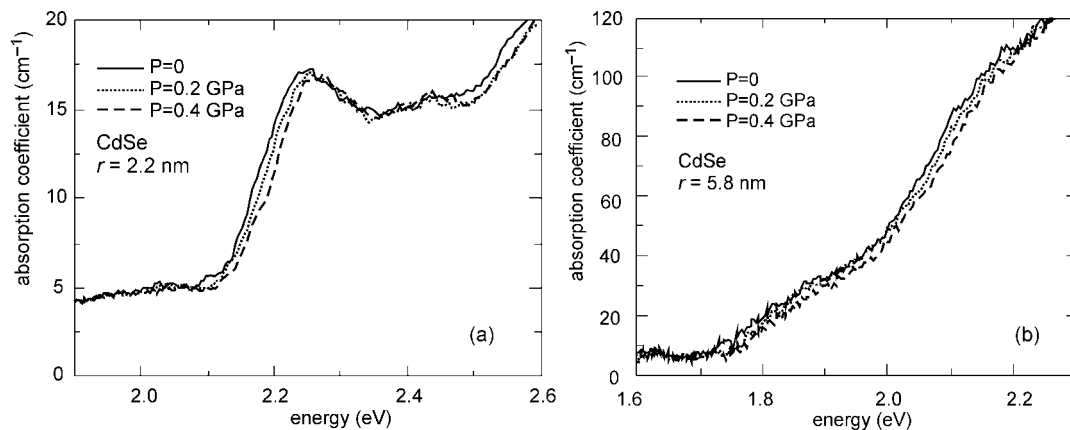

Figure 2. Optical absorption spectra of the glass-embedded CdSe NCs of different average size under hydrostatic pressure.

While scaling the absolute values of absorption coefficient α in the spectra, the value for the samples (borosilicate glass with the NCs embedded), not of the NCs themselves is meant. The actual α value for the NCs is by about two orders of magnitude higher, since the effective thickness of the NCs themselves is considerably smaller than the sample thickness, taking into account the concentration of the semiconductor phase in the samples which follows from the content of the relevant components in the initial mixture (below 1 %). An important point concerns the determination of the band gap value E_g in the NCs. Generally it is calculated from the experimental spectra by extrapolation of the $\alpha^2(h\nu)$ plot for allowed direct optical transitions. However, especially in disordered materials, when the density-of-states tails smear the absorption edge shape, often a substitutive parameter E_g^{α} is introduced, determined as the energy position of the fixed absorbance value α_f [18]. Usually for bulk materials α_f is taken at 10^2–10^3 cm^{-1}. In composites (semiconductor NCs in a dielectric medium), due to the above discussed difference in the absorption of the samples and the actual absorption of the NCs, the value $\alpha_f = 20$ cm^{-1} , corresponding to the steepest part of the edge, is often chosen for defining E_g^{α} [16].

For all the samples under study the hydrostatic pressure increase results in a blue shift of the absorption edge and the confinement-related maxima (Figures 1, 2), the corresponding data being summarized in Table 1.

Table 1. Parameters obtained from the optical studies of the glass-embedded $CdS_{1-x}Se_x$ NCs.

Composition	Average radius (nm)	Band gap pressure coefficient dE_g^{α}/dp (eV/GPa)
$CdS_{0.59}Se_{0.41}$	2.3	0.034
$CdS_{0.4}Se_{0.6}$	3.0	0.041
$CdS_{0.22}Se_{0.78}$	2.3	0.070
$CdS_{0.18}Se_{0.82}$	4.7	0.037
CdSe	2.2	0.045
CdSe	5.8	0.064

The measurements were performed at increasing and decreasing pressure and no hysteresis was observed in the investigated pressure range. This indicates that $CdS_{1-x}Se_x$ NCs are in direct contact with the glass matrix. It is consistent with the known fact that at normal conditions $CdS_{1-x}Se_x$ NCs in borosilicate glass already sustain hydrostatic pressure from the host matrix $\Delta p \approx 0.5$ GPa caused by the difference in thermal expansion coefficients of the NCs and the matrix [19]. Hence, for the correct determination of the average NC size from the absorption spectra one should introduce the glass matrix pressure-induced band gap increment $\Delta E_g^p = dE_g^{\alpha}/dp \cdot \Delta p$ into the expression for the energies of the confinement-related maxima known from the effective mass approximation [1]:

$$E_{(n_e,l_e),(n_h,l_h)} = E_b + \Delta E_g^p + \frac{\hbar^2}{2r^2}\left[\frac{\varphi_{n_e,l_e}^2}{m_e^*} + \frac{\varphi_{n_h,l_h}^2}{m_h^*}\right]. \qquad (1)$$

where E_b is the bulk energy gap for the same crystal composition, r is the NC radius, $\varphi_{n,l}$ are spherical Bessel function roots for the corresponding quantum numbers, m_e^* and m_h^* are the effective masses of electrons and holes, respectively. Since no data on the effective masses are available for $CdS_{1-x}Se_x$, the corresponding parameters can be estimated by interpolation using the known values of $m_e^* = 0.18m_0$ and $m_h^* = 0.53m_0$ for $x=0$ [20] and $m_e^* = (0.11–0.13)m_0$ and $m_h^* = (0.44–0.63)m_0$ for $x=1$ [21, 22] as well as the chemical composition values obtained from the Raman spectra [17]. The average NC radii, estimated from Eq. (1), are given in Table 1.

The obtained band gap pressure coefficient values are generally consistent with those reported earlier for $CdS_{1-x}Se_x$ NCs, ranging from 0.027 to 0.061 eV/GPa [7, 10, 12, 16]. No monotonous compositional trend could be observed for the NCs of the same average size (Figure 1). Neither can one claim unambiguously for the size dependence of the band gap pressure coefficient. While for CdSe the measured band gap pressure coefficient increases with the NC size, the situation is quite opposite for the mixed NCs with $x \approx 0.8$ (See Table 1). The observed spread of the measured band gap pressure coefficient values and the absence of its compositional and/or size dependence for $CdS_{1-x}Se_x$ NCs under study can be related with the possibility of coexistence of hexagonal and cubic nanoparticles in the ensemble of the glass-embedded NCs, which is quite probable for the case of the NC size below 1.5–2.5 nm even without additional external pressure [9, 10]. An efficient tool to distinguish between the pure hexagonal (wurtzite) and cubic (rocksalt) NC structure is Raman spectroscopy due to the absence of the first-order Raman spectrum for the rocksalt structure [13, 14]. However, in the case of coexistence of the two phases it can hardly be applied since the measured spectrum always contains the wurtzite-phase phonons. The Raman line intensities in NCs are subject to resonance effects and, hence, cannot be used for quantitative estimates. If the presence of NCs with zinc-blende cubic structure is assumed, it will be also difficult to confirm its coexistence with wurtzite since the LO phonon frequencies for the two phases are very close to each other [25], and in NCs for both of them the effects of phonon confinement and surface phonons on the Raman band frequencies

are larger than the difference between the phonon frequencies for the two phases [26]. Therefore, Raman spectroscopy cannot be applied to confirm the phase coexistence in this particular case.

4. Conclusions

The performed studies of influence of hydrostatic pressure on the optical absorption edge of $CdS_{1-x}Se_x$ ($0.4 < x \leq 1$) NCs embedded in a borosilicate glass matrix have shown a pressure-induced blue shift of the absorption edge and the confinement-related features. The identical character of the spectra obtained in the pressure increase and decrease mode as well as the absence of hysteresis confirm that in borosilicate glass $CdS_{1-x}Se_x$ NCs are in direct contact with the host matrix. The obtained band gap pressure coefficients dE_g/dP lie within 0.034 to 0.070 eV/GPa and do not show a distinct dependence on the NC composition or size. The obtained values agree well with those obtained earlier for colloidal and glass-embedded cadmium chalcogenide NCs [7, 10, 12, 16] as well as with the corresponding values for bulk CdS and CdSe [23, 24]. The absence of a pronounced compositional and size dependence of the band gap pressure coefficients for the glass-embedded $CdS_{1-x}Se_x$ NCs under investigation can be explained by possible coexistence of hexagonal and cubic NCs within the ensemble for the samples with the NC average size below 2.5 nm, inducing additional uncertainties into the average NC parameters.

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