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VARIATION OF $\text{CdS}_{1-x}\text{Se}_x$ NANOCRYSTAL PARAMETERS UNDER HYDROSTATIC PRESSURE

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The effect of hydrostatic pressure on the optical absorption spectra of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals embedded in borosilicate glass matrix is studied. The energy gap pressure coefficients and compressibility values for $\text{CdS}_{0.4}\text{Se}_{0.6}$ (average size 2.76 nm) and $\text{CdS}_{0.22}\text{Se}_{0.78}$ (3.08 nm) samples are obtained. The effect of the glass matrix pressure upon the nanocrystals is discussed.

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1. Introduction

$\text{CdS}_{1-x}\text{Se}_x$ nanocrystals (quantum dots) are of extensive scientific interest in view of wide possible applications as well as due to quantum-size effects arising from the spatial confinement of charge carriers [1–4]. A special attention is paid to the hydrostatic pressure effect on the optical properties of the nanocrystals, whose investigations enable the nanocrystal parameter behaviour versus pressure to be traced. Such studies were carried out for CdSe [5–10] and CdS [8, 11–14] quantum dots, both capped [5–11] and embedded in borosilicate [8, 12] and germania [13, 14] glass matrices. The performed experiments enabled not only the values of pressure variation coefficients for energy parameters to be determined, but also the phase transitions in nanocrystals from hexagonal to cubic phase to be reached, the transition pressure values being estimated from the Raman measurements [5–9, 11–14]. Much less investigated are pressure effects for mixed $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals [8, 11, 15].

Here we report the influence of hydrostatic pressure on $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals embedded in borosilicate glass matrix studied by optical absorption spectroscopy.

2. Experimental

$\text{CdS}_{1-x}\text{Se}_x$ quantum dots were embedded in a matrix of $\text{SiO}_2\text{--B}_2\text{O}_3\text{--ZnO--K}_2\text{O--Na}_2\text{O}$ glass by conventional solid-state precipitation technique generally similar to that described in [4]. About $5\times 5\text{ mm}^2$ plates with the thickness down to 0.13 mm were prepared for optical measurements.

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

Low-temperature absorption measurements at normal pressure were carried out on a LOMO MDR-23 monochromator with a UTREX cryostat.

3. Results and discussion

The optical absorption spectra of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in the glass matrix at different hydrostatic pressure and temperature values are shown in Figs. 1, 2. The composition of the nanocrystals was determined from the Raman measurements of the LO phonon frequencies, corresponding to

the CdS- and CdSe-sublattices of the two-mode solid solutions [16], by comparing them with the known Raman results for $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in a broad compositional range [17–19]. The features in the absorption spectra, related to the quantum-size effects (charge-carrier confinement) (See Fig. 2), enabled us to determine, according to [20], the mean radius of the nanocrystals as 2.76 nm ($x=0.6$) and 3.08 nm ($x=0.78$).

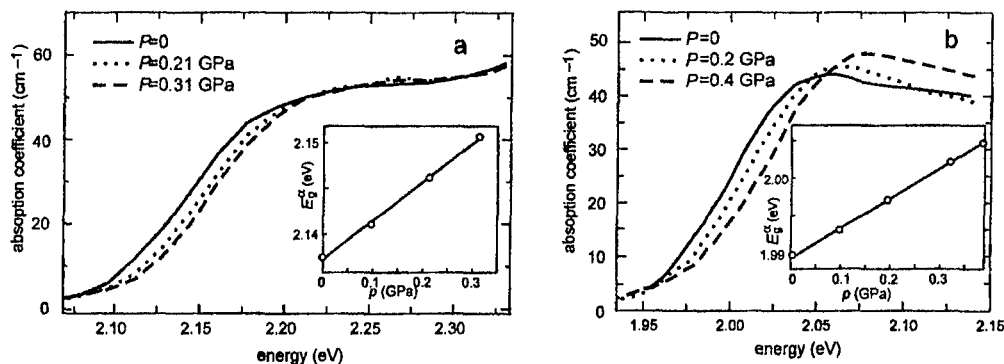


Fig. 1. Hydrostatic pressure effect on the optical absorption spectra of $\text{CdS}_{0.4}\text{Se}_{0.6}$ (a) and $\text{CdS}_{0.22}\text{Se}_{0.78}$ (b) nanocrystals in borosilicate glass matrix. The inserts show the dependences of the energy gap E_g^α on the pressure value.

It should be noted that while scaling in Figs. 1, 2 the absolute values of absorption coefficient α , we mean the absorbance of the samples (borosilicate glass with the quantum dots embedded), not of the quantum dots themselves. The actual absorbance of the microcrystals should be much higher, since the effective thickness of the quantum dots themselves is considerably smaller than the sample thickness, taking into account the concentration of $\text{CdS}_{1-x}\text{Se}_x$ in the samples which follows from the content of the relevant components in the initial mixture (about 1 %). Hence, the actual absorption coefficient of the nanocrystals is by about two orders of magnitude higher than that of the composite, displayed at the vertical axes.

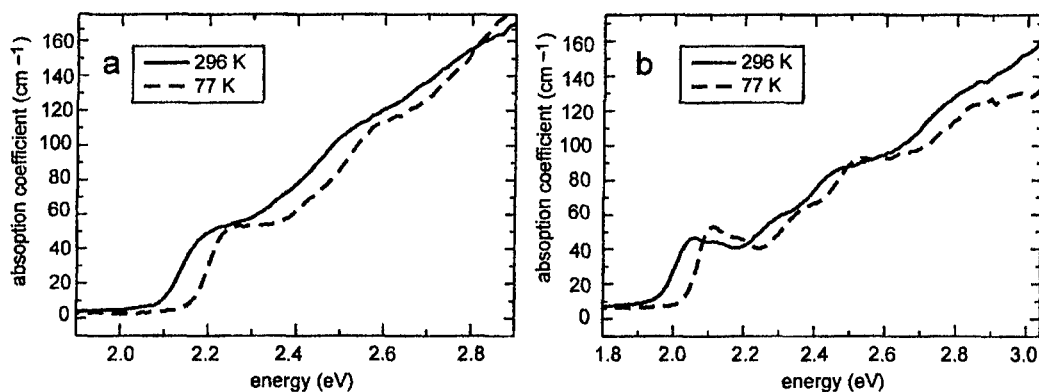


Fig. 2. Optical absorption spectra of $\text{CdS}_{0.4}\text{Se}_{0.6}$ (a) and $\text{CdS}_{0.22}\text{Se}_{0.78}$ (b) nanocrystals in borosilicate glass matrix at 77 and 296 K.

One more point that should be taken into account, concerns the determination of the band gap value E_g in the nanocrystals. 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 may smear the shape of the absorption edge, while studying the edge variation under different factors often a substitutive parameter E_g^α is introduced, being determined as the energy position of the fixed absorbance value α_f [21, 22]. Usually for bulk materials α_f is taken of the order of 10^2 – 10^3 cm^{-1} . In our case, due to the above discussed difference in the absorbance of the samples and the actual absorbance of the nanocrystals, we have chosen for defining E_g^α the value $\alpha_f = 25$ cm^{-1} , what corresponds to the middle of the edge part of the spectra.

The increase of pressure is observed to result in a blue shift of the optical absorption edge of the nanocrystals. This is illustrated by Fig. 1 where only the edge part of the spectra is shown. In the investigated pressure range the absorption edge shift is linear (as seen from the insert in Fig. 1) and equals to 0.041 eV/GPa for CdS_{0.4}Se_{0.6} and 0.039 eV/GPa for CdS_{0.22}Se_{0.78} samples. These results are consistent with the band gap pressure coefficients dE_g/dp for CdS_{1-x}Se_x nanocrystals measured by other authors [5, 8, 10, 14] which vary from 0.027 to 0.061 eV/GPa, depending on the nanocrystal size, composition and host media. It should be noted that dE_g/dp values for the bulk crystals also fall into this interval, ranging from 0.033 [23] to 0.058 [24] eV/GPa for CdS and from 0.037–0.040 [23, 24] to 0.058 [25] eV/GPa for CdSe.

The measurements were performed at increasing and decreasing pressure, no hysteresis being observed in the investigated pressure range. This indicates that CdS_{1-x}Se_x nanocrystals are in direct contact with the glass matrix. It should be noted that at normal conditions CdS_{1-x}Se_x quantum dots in borosilicate glass already sustain hydrostatic pressure from the host matrix caused by the specific features of their preparation [26, 27]. While being cooled from the synthesis temperature to the room temperature the quantum dots are compressed by the matrix since the value of thermal expansion coefficient for the latter ($A_g = 1.02 \times 10^{-5} \text{ K}^{-1}$) considerably exceeds those for II–VI semiconductors. Then the hydrostatic pressure of the glass matrix Δp upon the nanocrystals is given by [27]

$$\Delta p = \frac{(A_g - A_{\parallel})\Delta T + 2(A_g - A_{\perp})\Delta T}{2S_{11} + 2S_{12} + 4S_{13} + S_{33}}, \quad (1)$$

where A_g is thermal expansion coefficient for the glass, $A_{\parallel}$ and $A_{\perp}$ – thermal expansion coefficients for CdS_{1-x}Se_x, $\Delta T = T_s - T_m$ – the variation of temperature from the synthesis temperature T_s to the measurement temperature T_m , S_{ij} ($i, j=1, 2, 3$) – elastic constants of CdS_{1-x}Se_x lattice. Note that Eq. (1) is applicable when the pressure is supposed to be independent of the nanocrystal size and the nanocrystals are large enough to preserve hexagonal crystal structure, what in the case of CdS_{1-x}Se_x quantum dots is valid in case their mean radius exceeding 1.5–2.5 nm [1, 7, 8]. In this case the values for bulk semiconductor materials can be applied, for the case of the mixed CdS_{1-x}Se_x crystals they can be obtained by interpolation of the corresponding values for pure CdS and CdSe which are listed in Table 1.

Table 1. Relevant parameters of bulk CdS and CdSe crystals.

Parameter	CdS	CdSe	Reference
dE_g/dp , eV/GPa	0.033	0.037	[23]
	0.058	0.040	[24]
		0.058	[25]
$A_{\parallel}$, K ⁻¹	2.6×10^{-6}	2.9×10^{-6}	[27]
$A_{\perp}$, K ⁻¹	4.6×10^{-6}	4.9×10^{-6}	[27]
S_{11} , N ⁻¹ ·m ²	2.069×10^{-11}	2.338×10^{-11}	[28]
S_{12} , N ⁻¹ ·m ²	-0.999×10^{-11}	-1.122×10^{-11}	[28]
S_{13} , N ⁻¹ ·m ²	-0.581×10^{-11}	-0.572×10^{-11}	[28]
S_{33} , N ⁻¹ ·m ²	1.697×10^{-11}	1.735×10^{-11}	[28]
dE_g/dT , eV/K	-4.4×10^{-4}	-4.6×10^{-4}	[29]
	-3.8×10^{-4}		[30]
	-5.5×10^{-4}		[31]

Using the quoted parameters for the bulk crystals and Eq. (1), the hydrostatic pressure of the borosilicate glass matrix upon CdS_{1-x}Se_x nanocrystals for the range of compositions under investigation was calculated as $\Delta p \approx 0.55 \text{ GPa}$ [27].

Since the borosilicate matrix pressure Δp upon CdS_{1-x}Se_x quantum dots depends on the sample temperature, its temperature variation could be estimated from the optical absorption edge measurements at different temperatures. Fig. 2 shows the relevant spectra at ambient atmospheric pressure at 77 and 296 K. As seen from the figure, cooling of the samples results in the absorption edge shift by 0.07 eV for both nanocrystal compositions; note that the features related to the quantum-size effects also shift in energy by the same value. It should be noted that both above mentioned methods of

estimating the absorption edge shift – by $\alpha^2(h\nu)$ plot extrapolation and by using a substitutive parameter E_g^α , corresponding to $\alpha_f = 25 \text{ cm}^{-1}$, gave the same value of the temperature-induced absorption edge shift.

Since the temperature shift of the absorption edge for $\text{CdS}_{1-x}\text{Se}_x$ quantum dots in the glass matrix results from the combination of the proper temperature-related edge shift and the edge shift due to the temperature-related increase of the pressure of the host matrix, both of them shifting the edge to the higher energies, it could be expected, in case the above assumption of applicability of the bulk parameters for the nanocrystals being valid, that the corresponding calculations would enable us to separate the contributions of these two effects into the temperature shift of the absorption edge. However, the experimental results have shown the absorption edge shift in $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in borosilicate glass matrix at the temperature decrease from 296 to 77 K (0.07 eV) to be smaller than that estimated using the interpolated values for the bulk crystals (0.09–0.12 eV) even without the account of the host matrix pressure variation. Hence, the values of the relevant parameters (dE_g/dT , dE_g/dP) for the bulk crystals cannot be applied for quantitative estimation of temperature and pressure effects of semiconductor nanocrystals, since in the latter confinement-related changes in electron-phonon coupling may occur as well as surface-(interface-) related effects can be revealed much stronger due to much higher surface-to-volume ratio what is manifested as the decrease of phonon frequencies in Raman spectra of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals [18, 19].

The energy gap temperature variation at constant pressure can be described as [32]

$$\left(\frac{dE_g}{dT}\right)_p = \left(\frac{dE_g}{dT}\right)_v - \frac{3A}{\beta} \left(\frac{dE_g}{dp}\right)_T, \quad (2)$$

where A is the volume thermal expansion coefficient and β is compressibility. The first term in this expression corresponds to the contribution of electron-phonon coupling into the energy gap variation, and the second one – to the gap variation due to the crystal volume change. The performed experiments enabled us to obtain compressibility values $1.73 \times 10^{-11} \text{ Pa}^{-1}$ and $1.8 \times 10^{-11} \text{ Pa}^{-1}$ for $\text{CdS}_{0.4}\text{Se}_{0.6}$ and $\text{CdS}_{0.22}\text{Se}_{0.78}$ nanocrystals, respectively. Hence, from Eq. (2) the contribution of the electron-phonon coupling was about $4 \times 10^{-4} \text{ eV/K}$ for both samples while the gap variation due to the nanocrystal volume size was about $8.5 \times 10^{-5} \text{ eV/K}$.

We have studied the effect of hydrostatic pressure on the optical absorption spectra for the sample of $\text{CdS}_{0.4}\text{Se}_{0.6}$ nanocrystals in the borosilicate glass matrix subjected to annealing at 925 K during 6 h, which was performed in order to increase the nanocrystal size in the matrix. The measurements have shown the pressure variation of the optical gap to decrease ($dE_g/dP = 0.03 \text{ eV/GPa}$) with respect to the initial value. Hence, while describing the effects of external factors on $\text{CdS}_{1-x}\text{Se}_x$ quantum dots in glass matrices, the correct account of the nanocrystal size and composition should be carried out instead of using the relevant parameters for the bulk crystals.

4. Conclusions

The performed optical studies of influence of hydrostatic pressure effect on the absorption edge of $\text{CdS}_{1-x}\text{Se}_x$ quantum dots has enabled us to obtain the energy gap pressure coefficients $dE_g/dP = 0.041 \text{ eV/GPa}$ for $\text{CdS}_{0.4}\text{Se}_{0.6}$ ($r = 2.76 \text{ nm}$) and 0.039 eV/GPa for $\text{CdS}_{0.22}\text{Se}_{0.78}$ ($r = 3.08 \text{ nm}$) samples which agree well with the corresponding values for bulk and nanocrystalline CdS and CdSe.

The investigation of hydrostatic pressure and temperature effect on the optical spectra of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in borosilicate glass matrix has shown that the correct description of the observed effects requires the dependence of the corresponding parameters on the nanocrystal size and composition to be taken into account.

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