TWO-PHOTON ABSORPTION OF CdS_xSe_{1-x} NANOCRYSTALS IN A GLASS MATRIX

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The method of a single light source has been used to determine the value of the two-photon absorption coefficient β of commercial glasses with CdS_xSe_{1-x} nanocrystalline inclusions at the lasing frequency of a ruby laser. The value of β for the system of nanocrystals in a glass matrix was found to become three orders of magnitude lower than that for bulk CdS_xSe_{1-x} single crystals. This phenomenon correlates by its order of magnitude with a reduction of the concentration of absorption centers. It has been shown that, as the energy of pump light quanta approaches the energy gap width in CdS_xSe_{1-x}, the value of β for such systems grows more slowly than that for CdS_xSe_{1-x} single crystals.

1. Introduction

The knowledge of the regularities, which are characteristic of the two-photon absorption of light by structures with a two-dimensional waveguide channel, has allowed one to develop photoelectric autocorrelators [1] and the converters that "transform" the width of the pulse generated by a femtosecond laser into the value of the current [2]. The main shortcoming of these devices is the dependence of their parameters on temperature. One can get rid of this disadvantage by designing the structures, where the channel is filled with quantum dots. Surely, the regularities of the influence of the size quantization of the current carrier motion on the two-photon absorption must be firstly elucidated. In this case, while studying the features of the two-photon absorption, nanocrystals of A^2B^6 semiconductors surrounded by a glass matrix serve as model objects. The coefficient of two-photon absorption $\beta_{\rm n}$ in such objects has been found (see Table 1) to depend on the average radius of nanocrystals $\bar{r}$ and the energy of pump light quanta $h\nu$ and to be considerably lower than the corresponding value of $\beta_{\rm m}$ in semiconducting single crystals with large dimensions (hereafter named as single crystals) with the same composition content [3]. This work aims at studying the influence of the composition content of CdS_xSe_{1-x} on a value of the two-photon absorption coefficient for nanocrystals and at comparing the results obtained with similar dependences for CdS_xSe_{1-x} single crystals.

2. Experimental Method and Specimens

The experimental specimens were fabricated of various commercial stained glasses. Their absorption spectra averaged over 3—4 specimens are shown in Fig. 1, and their parameters are quoted in Table 1. The relative error of estimating the absorption coefficient did not exceed ±5%, and the absolute error of determining the light quantum energy was lower than ±0.0003 eV. The composition content x of quantum dots (see Table 2) was determined by the Raman scattering method [4, 5] with an error of ±0.01. The approximation of the absorption spectra of KS-17 and KS-15 glasses by the root law allowed us to determine the optical width of the energy gap $E_{g\rm n}$ of nanocrystals in those matrices (see Table 2) with an error of ±0.0005 eV. The energy shift of the intrinsic absorption band edge caused by the size quantization of the current carrier motion is described by the equation [6–9]

$$E_{g\rm n} = E'_{g\rm n} + \frac{\hbar^2\pi^2}{2\bar{r}^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1,8q^2}{4\pi\varepsilon\varepsilon_0\bar{r}}, \qquad (1)$$

where $\bar{r}$ is the average radius of nanocrystals; m_e and m_h are the effective masses of an electron and a hole, respectively; ε is the relative dielectric permittivity; ε_0 is the dielectric permittivity of vacuum; q is the electron charge; and $\hbar$ is the Planck constant. The energy gap width of the nanocrystalline inclusions, $E'_{g\rm n} = E_{g\rm n} + P(dE_{g\rm n}/dP)$, was determined taking into account that the glass matrix squeezes nanocrystals. Here, $E_{g\rm n}$ is the energy gap width of nanocrystals in the absence of squeezing (it coincides with that of single crystals, $E_{g\rm m}$, with a similar composition content [10]; $dE_{g\rm n}/dP$ is the baric factor; and P is the pressure which was calculated following the formulas of work [11]. Substituting the known values of $E_{g\rm n}$ and $E_{g\rm m}$ into Eq. (1), we found the radius $\bar{r}$ (see Table 1). The calculation error for $\bar{r}$ did not exceed 0.05 nm.

Glasses KS-10 and OS-12 manifested the well-pronounced modulation of their absorption spectra caused by the size quantization of the current carrier motion. The formulas of work [11] allowed the absorption spectrum to be calculated (see Fig. 1) using the parameters $\bar{r}$ and E_{gm} for the fitting (see Table 2). The errors of the obtained values for $\bar{r}$ and E_{gm} did not exceed 0.05 nm and 0.0005 eV, respectively.

In order to determine β_n, we used the method of a single light source. A ruby laser which generated 20-ns emission pulses was used as a light source. The detailed description of such a technique can be found elsewhere (see, e.g., works [10, 12, 13]). A plane-parallel specimen 0.5 cm in thickness was illuminated normally with a linearly polarized light flux. The input, I_0, and output, I, intensities of this flux were detected by ELU-FT photo multipliers and registered by S8-12 oscillographs. The intensity I_0 was varied by means of a set of the calibrated neutral grey filters. In order to reduce the influence of systematic errors on the determination accuracy of β_n, several usual precautions were taken [12, 13]. First, a diaphragm was placed in the way of the laser-emitted beam before the stack of neutral grey filters; it cuts off the Gaussian-like beam at a level of 0.9. In such a way, we provided the formation of the light flux, whose form was close to cylindrical, and the distribution of

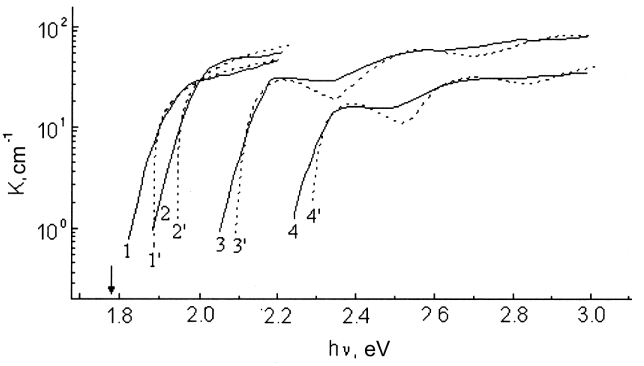

Fig. 1. Experimental (solid) and theoretical (dotted curves) absorption spectra of CdS_xSe_{1-x} nanocrystals in various glass matrices: KS-17 (*1* and *1′*), KS-15 (*2* and *2′*), KS-10 (*3* and *3′*), and OS-12 (*4* and *4′*). The arrow points at the energy of pump light quanta

T a b l e 1. Parameters of structures with nanocrystals

Glass brand	Quantum dot material	E_g, eV (300 °C)	$h\nu$**, eV	β, cm/GW	$\bar{r}$, nm	τ, ps	Source
Lab.	CdTe	1.500	1.165	3,6	3	50	[3]
Lab.	CdTe	1.500	1.165	10	10	50	[3]
Lab.	CdTe	1.500	1.165	25	20	50	[3]
Hoya 720	CdSeTe		1.165	0.188		75	[4]
RG-4		1.732	2.032	0.38		0.3	[5]
RG-8		1.832	2.032	0.53		0.3	[5]
Lab.	GaAs*	1.430	1.165	5.6	3.8	3×10^3	[6]
OG-590	$CdS_{0.50}Se_{0.50}$		1.569	23	3.0	30	[7]
RG-610	$CdS_{0.58}Se_{0.42}$		1.569, 1.033	22, 0.11	3.9	30	[7]
RG-630	$CdS_{0.66}Se_{0.34}$		1.569, 1.033	22, 3.1	3.7	30	[7]
RG-665	$CdS_{0.80}Se_{0.20}$		1.569, 1.033	32, 9.7	6.5	30	[7]
RG-695	$CdS_{0.92}Se_{0.08}$		1.569, 1.033	13, 8.4	4.3	30	[7]
RG-715	CdS		1.569, 1.033	34, 21	5.5	30	[7]
RG-830			1.033	26	5.3	30	[7]
RG-850			1.033	31	11.1	30	[7]

N o t e s: * — Nanoparticles in ethanol, ** — Energy of exciting quanta, Lab. means glasses with nanocrystals synthesized under laboratory conditions. For each glass specimen of the RG brand, the composition content, the average radius od nanocrystals, and the pump pulse duration are identical for both values of the pump photon energy

T a b l e 2. Parameters of CdS_xSe_{1-x} nanocrystals

Parameters	Glass brand			
	KS-17	KS-15	KS-10	OC-12
Composition content x	0.15	0.24	0.32	0.68
Optical energy gap width E_{gn}, eB	1.953	1.982	2.143	2.577
Average radius of a quantum dot $\bar{r}$, nm	4.0	3.7	2.9	3.0
Two-photon absorption coefficient of nanocrystals β_n, cm/GW	0.13	0.1	0.09	0.07
Two-photon absorption coefficient of single crystals* β_m, cm/GW	270	160	110	110
β_m/β_n	2200	1600	1300	1700

N o t e: * — The values of β_m were taken from Fig. 3, plotted on the basis of the data of work [10].

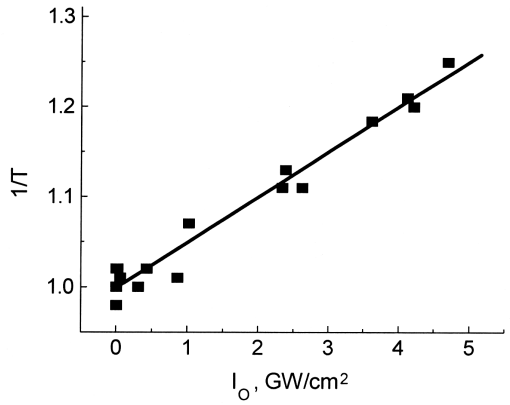

Fig. 2. Dependence of the inverse transmission $1/T$ on the intensity I_0 of the linearly polarized radiation incident normally upon a 0.5-cm plane-parallel glass plate with CdS_xSe_{1-x} nanocrystals inclusions

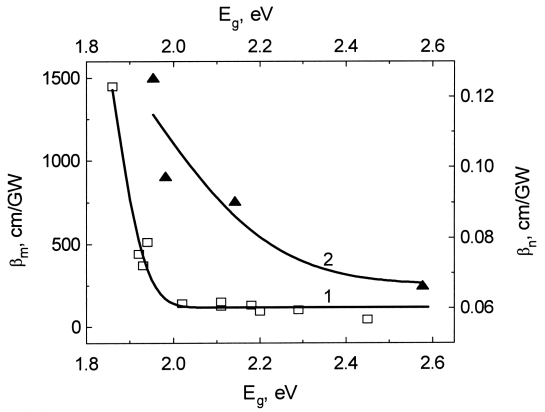

Fig. 3. Dependences of the two-photon absorption coefficient of CdS_xSe_{1-x} single crystals (β_m, curve *1*) and CdS_xSe_{1-x} nanocrystals (β_n, curve *2*) on the optical width of the energy gap E_g. The points display experimental data, and the solid curves approximate these data

radiation intensity over its cross-section was close to uniform. Secondly, the reflection of light from the back side of the crystal was taken into consideration. At last, the transmission T at the fixed light intensity was averaged over 10—15 pulses with identical distributions of the pulse intensity in time.

3. Results of Researches

For all the specimens under investigation, the dependence of the inverse transmission $T^{-1} = I_0/I$ on I_0 looked like that exhibited in Fig. 2 by points. For the approximation of this dependence, the relation [6–8]

$$\frac{1}{T} = \frac{I_0}{I} = \frac{\exp(Kd)}{(1-R)^2} + \frac{\beta_n[\exp(Kd)-1]}{K(1-R)} I_0 = A + BI_0, \tag{2}$$

was used, where K is the one-photon absorption coefficient, R the reflection coefficient, and d the specimen's thickness. Making use of the formula $K = d^{-1}\ln\left[A(1-R^2)\right]$ and the value of the constant A which was determined by the intersection point of the straight line and the ordinate axis (see Fig. 2), we found the value of K. Within the scope of experimental errors (± 0.05 cm^{-1}), the one-photon absorption coefficient turned out to be zero for all the specimens. Knowing the slope angle of the straight line (Fig. 2), we managed to determine the constant B, which allowed us to evaluate $\beta_n = [BK(1-R)]/[A(1-R)^2-1]$ with an error of $\pm 20\%$ (see Table 2).

CdS_xSe_{1-x} nanocrystals were synthesized in the form of hexagonal prisms chaotically oriented in the glass bulk. This enabled us to consider the propagation of a parallel linearly polarized flux of radiation in them as the propagation of two waves, with the vector of the electric field of each wave being either parallel or perpendicular to the optical axis of nanocrystals. The light attenuation in each of these fluxes is characterized by a specific coefficient of two-photon absorption, $\beta_\parallel$ or $\beta_\perp$, respectively. The resulting variation of the specimen's inverse transmission is proportional to the average value of the two-photon absorption coefficient $\beta_n = (\beta_\parallel + \beta_\perp)/2$. Therefore, the dependence of β_n on the optical width of the energy gap E_{gn} (Fig. 3, curve *2*; Table 2) should be compared with the dependence of the average value of the two-photon absorption coefficient of single crystals $\beta_m = (\beta_\parallel + \beta_\perp)/2$ on E_{gm} (Fig. 3, curve *1*; Table 2). As is seen from Fig. 3, these dependences manifest similar tendencies of the two-photon absorption coefficient to grow as the excitation quantum energy approaches the energy gap width. Their difference consists in the difference between the growth rates of β_n and β_m, as well as in the difference between the values of these coefficients (Table 2).

The reason for why the coefficient of two-photon absorption varies when we change over from the single crystal to the structure with nanocrystalline inclusions consists in the reduction of the concentration of absorbing centers. In the range of interband transitions, the coefficients of one-photon absorption are of the order of 10^5 cm^{-1} in CdS and in CdSe single crystals [14] and of several tens of cm^{-1} in glasses (Fig. 1). Provided that the values of the one-photon absorption cross-section

in nano- and single crystals are identical, the change over from single crystals to glasses with nanocrystalline inclusions is accompanied by the reduction of the concentration of absorbing centers by a factor of about 10^3. The coefficient of two-photon absorption undergoes the decrease by about the same factor (Table 2).

The difference between the growth rates of the two-photon absorption coefficient in single crystals and glasses with nanocrystalline inclusions is caused by the different nonparabolic characters of allowed energy bands in these materials.

4. Conclusions

The value of the two-photon absorption coefficient in glasses with CdS_xSe_{1-x} nanocrystalline inclusions has been found by approximately three orders of magnitude lower than that in CdS_xSe_{1-x} single crystals with the same composition content. This effect was explained by the lower concentration of absorption centers in the system of "nanocrystalline inclusions in a glass matrix" as compared to those in single crystals.

The coefficient of two-photon absorption in glasses with nanocrystals has been demonstrated to grow more slowly than that in single crystals as the energy of pump radiation quanta approaches the width of the energy gap. The probable reason of this phenomenon can be the difference between the levels of nonparabolicity of the allowed energy bands in single crystals and nanocrystals, which is caused by the influence of the near-surface layers and the spatial confinement of the current carrier motion in nanocrystals.

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ДВОФОТОННЕ ПОГЛИНАННЯ НАНОКРИСТАЛІВ CdS_xSe_{1-x} У СКЛЯНІЙ МАТРИЦІ

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Р е з ю м е

Методом одного джерела світла на частоті випромінювання рубінового лазера визначено величину коефіцієнта двофотонного поглинання β в промислових зразках скла, легованого нанокристалами CdS_xSe_{1-x}. Встановлено, що при переході від об'ємних монокристалів до нанокристалів у скляній матриці β зменшується на три порядки. За порядком величини цей результат узгоджується зі зменшенням концентрації центрів поглинання. Показано, що з наближенням енергії квантів світла накачки до ширини забороненої зони в таких системах коефіцієнт двофотонного поглинання зростає повільніше, ніж у монокристалах.