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Thermoluminescence peculiarities of $CdS_{1-x}Se_x$–doped borosilicate glasses

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Thermally stimulated luminescence of the X-ray irradiated CdSSe-doped borosilicate glases have been studied. The two well defined temperarure maxima discovered for total thermoluminescence intensity, as well as the thermoluminescence dependence on the nanocrystal size and X-ray dose are discussed.

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1. Introduction

Ensembles of semiconductor nanocrystals (NCs) placed in various matrices, due to their unique physical properties, possess variety of applications from optoelectronics and photonics [1–3] to several biological (medical) treatments [4, 5] and dosimetry applications [6, 7]. Recall that a decisive role in all applications of NCs plays the spatial confinement effect which is realized pronouncedly for the NCs sizes smaller than the exciton Bohr radius in the bulk semiconductor. For example, for CdS and CdSe semiconductors belonging to the $A_{II}B_{VI}$ group, the exciton Bohr radius is 2.4 nm and 5.4 nm, respectively [8]. Such a peculiarity leads to discrete energy states in the conduction and valence bands and to the size-tunable optical transitions in visible and near-infrared wavelength region - one of the prominent properties of these nanoscale objects. Important consequence of the spatial confinement is also the elevated ratio of the number of surface to volume atoms for a separate NC. In bulk crystals this ratio is very small, much less than unity, whereas in small NCs it increases strongly approaching unity. NCs can be synthesized using various chemical and physical methods. In particular, the semiconductor NCs can be grown successfully in glass matrices, for example, in borosilicate glasses [9]. Such robust systems are convenient to study the luminescence phenomena in low–dimensional structures, in particular, the thermoluminescence effect. Thermally stimulated luminescence (TSL) studies provide additional information regarding radiative recombination centers in the semiconductor NCs and at their interfaces with the host matrix as well. Besides, last but not least, the TSL studies are the basis for applications in dosimetry [10, 11]. To our knowledge, only few experimental studies of TSL into glass-embedded $A_{II}B_{VI}$ compounds and especially in pseudobinary AB_xC_{1-x} NCs alloys examined here were reported so far [12-16].

2. Experimental procedure

Samples of the doped borosilicate glass were prepared by means of a conventional melt–quenching technique [9,17]. The batch (SiO_2 −50%, B_2O_3 −25%, Al_2O_3 −10%, Na_2O−12%, K_2O − 2%, Sb_2O_3 − 1%, + 2 wt.% of CdO, 1 wt.% of Se, and 1.5 wt.% of S) was melted at temperature of 1300° C for one hour in Al_2O_3 crucibles. After the rapid melt–quenching process to the room temperature the doped glass ingot was additionally annealed within a few hours in the gradient temperature furnace with temperature ranging from 400°C to 750°C. The whole ingot changes its

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color from colorless out of furnace to dark red at its high temperature end. During the heat treatment process above a diffusion of the dopant ions leads to a formation of semiconductor NCs within the glass network matrix with different average sizes in the along of the glass ingot.For further research, the obtained ingot was cut into the pieces according to their color. Samples of various colors differ from each other in an average diameter (size) d of created NCs. This fact is confirmed by the standard investigations such as the optical absorption measurements performed in the relevant photon energy range and the transmission electron microscopy (TEM) studies as well. These routine studies show that during the heat treatment process a diffusion of the dopant ions within the given above glass network matrix leads to a formation of semiconductor CdSSe NCs. The composition of $CdS_{1-x}Se_x$ NCs was determined from the Raman scattering spectra measured at room temperature. To study the TSL, the samples were pre-irradiated using a cooper anticathode tube (50 kV, 20 mA). The integral intensity of TSL in sensitivity region (300 nm - 800 nm) was measured in the photon counting regime in the temperature interval 300 K - 775 K at the constant rate of sample heating equal to 1 K/s. The TSL spectra were recorded within 1 hour after the X-ray irradiation. This is due to the fact that the irradiated samples show an intense spontaneous after-irradiation which decays exponentially with time. This circumstance is illustrated in Fig.1, where the decay curves for the $CdS_{0.35}Se_{0.65}$ sample with average size in 3.8 nm (hereinafter referred to as the main sample) at various irradiation doses are shown.

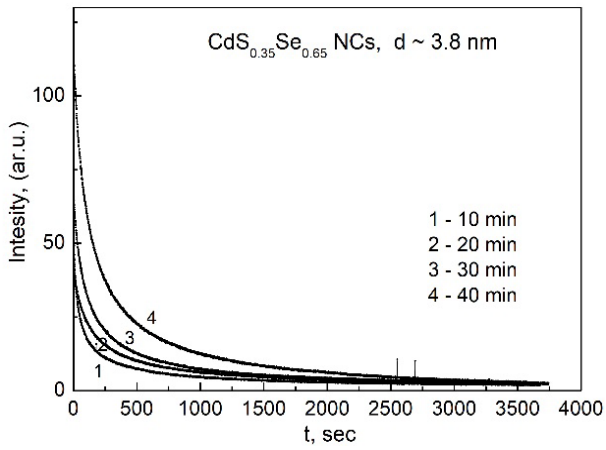

Fig. 1. Decay of the X-ray radiation-induced emission for borocilicate glass embeded CdSSe nanocrystals with average diameter 3.8 nm.

3. Results and discussion

In this Section we report on the X-ray irradiation impact on the optical absorption and thermoluminescence of the CdSSe–doped glass samples prepared as described above. The optical-absorption measurements were carried out at room temperature on an AvaSpec- 2048 spectrometer in the photon energy range from 1.5 eV to 3 eV and for the $CdS_{0.35}Se_{0.65}$ composition sample the results are shown in Fig.2. The respective TEM image shown in the inset in Fig.2 indicates the presence of highly crystalline NCs with an average size about 3.8 nm. It is seen that NCs have almost spherical shape which apparently points out to their zinc-blend structure [9]. The studied sample was irradiated with X-ray for different times of 10, 20, 30, 40 and 60 minutes and the corresponding absorption spectra are shown in Fig.2. It should be noted here that the main properties of the optical absorption and TSL for the obtained set of samples (from the ingot) with average sizes ranging from 3 nm to 10 nm (within the limits of confinement conditions) are qualitatively the same - the structure of the spectra, and their characteristics under irradiation. For non-irradiated sample, the absorption spectrum, which is shown in Fig.2 by the solid curve, exhibits the pronounced excitonic peak indicating

the quantum confinement effect. The absorption peak position agrees well with the data presented in the work [18] for the given composition and size of CdSSe NCs. Dashed curves in Fig.2 refer to the irradiated samples. It is seen that the X-ray irradiation results in a gradual transformation of the optical absorption spectra. The confinement-related excitonic peaks are smeared out the stronger the longer is the irradiation time. The absorption edge does not show any significant shift towards higher energies, at least within the limits of the applied radiation doses. A degradation of the absorption peaks seen in Fig.2 is due to the irradiation-induced high frequency ionization of the NCs leading to the charge carrier transfer between the NCs and the host matrix. Similar transformations of the optical absorption spectra were reported, e.g., in Ref.[15, 19] for the X–ray irradiated $CdS_{1-x}Se_x$–doped borosilicate glasses. In Fig.3 (on the left side) are shown the TSL glow curves for the sample characterizing by the absorption spectra given in Fig.2.

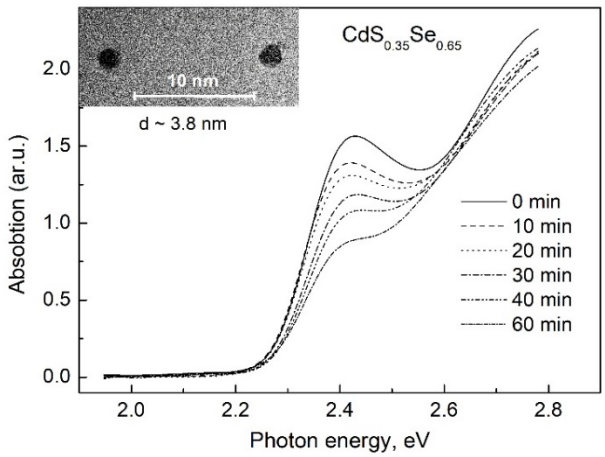

Fig. 2. Optical absorbtionspectra for X-irradiated CdSSe sample.

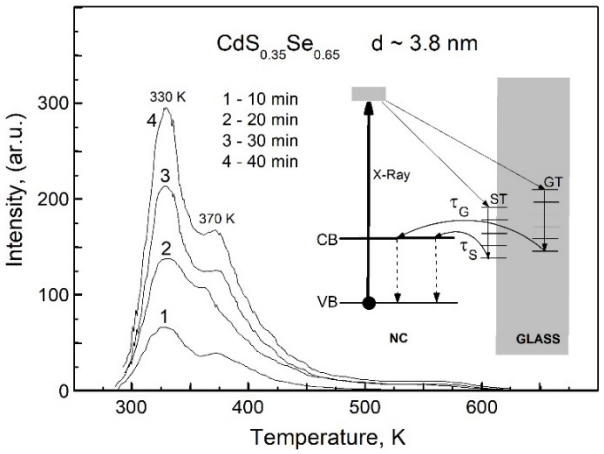

Fig. 3. Glow curves for the main sample at different duration of irradiation (left) and schematic representation of two channel model (right), see text.

The heating rump rate is equal to 1K/s and the curves refer to the four different irradiation durations. It is seen that the thermoluminescence is the more efficient the longer is the radiation duration. The two resolved peaks are rather clearly visible in each of the glow curves. The first low temperature peak is situated at 330 K and the second peak is located at 370 K. Note that the TSL curves reported in papers [13, 14] are also accompanied by

some swellings at the high temperature side. Presence of the two rather pronounced peaks on the glow curve points out apparently to a participation of at least the two different sources of the TSL. We propose here a simple two channel model, which is schematically shown in Fig.3. We suppose that the one source is due to the surface states (the ST states) localized at the NC-glass boundary. The second source is assumed to be related to the traps in the glass matrix (the GT states). Similar localized states were considered, e.g., in Ref.[20] to explain the laser–induced darkening in semiconductor–doped glasses and in Ref.[13] at the studies of absorption spectra of CdSe–doped aluminoborosilicate glasses. As noted above, the model, which we suggest here, is schematically presented on the right side of Fig.3. The X–ray ionizes the NCs transferring the confined electrons into the glass (thick arrow) and the holes remain in the NCs. Extra electrons in the glass matrix relax to the ST and GT localized states (thin arrows). Then electrons are thermally activated from both the GT and ST states with different activation times τ_S and τ_G (rounded arrows), respectively, and recombine with the remaining holes (dashed arrows). One can assume that the model above is sensitive to the glass composition and the NC sizes. In this regard note that for $CdS_{1-x}Se_x$ glasses of various compositions and the NC's sizes, significantly different positions of the low temperature TSL peaks are reported in the literature. For example, in the paper [13] the measured position of the thermoluminescence peak for CdS–doped glass corresponds to 470K at the rump rate of 4 K/s. At the same time for $CdS_{0.2}Se_{0.8}$–doped glasses the peak location about 360 K at the rump rate of 0.4 K/s is reported in Ref.[14]. An observable dependence of the thermoluminescence intensity on the NCs size is also reported, e.g., in Ref.[14,21]. For the here studied CdSSe–doped glass, in Fig.4 we present the values of the TSL intensity for the four samples with different average sizes of the embedded NCs. Fig.4 shows a pronounced decrease of the thermoluminescence intensity with an increase of the NC sizes.

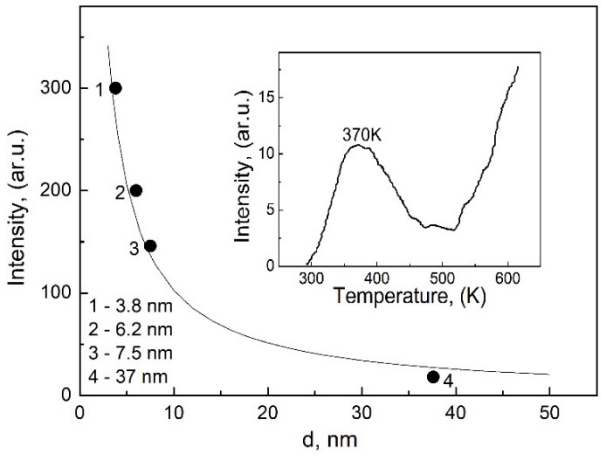

Fig. 4. Main panel: NC size dependence of TSL intensity. Inset:glow curve for the sample with largest NCs, see text.

As is shown by the solid curve in Fig.4, the TSL decay follows nearly the hyperbolic dependence on the NC sizes. Within the framework of the model considered here, such a result can be associated with a decrease in the role of surface states in the electron localization. Recall that for the separate NC, the ratio of the number of surface to volume atoms is approximately inversely proportional to the NC's size. An increase in the number of electrons permanently trapped in the glass matrix can be here also important. Inset in Fig. 4 snows the glow curve for the glass sample containing the largest NCs, which have already non-spherical but cylinrical shape and the size around 76 nm x 21 nm. The respective TEM imagies are presented in Fig.5.

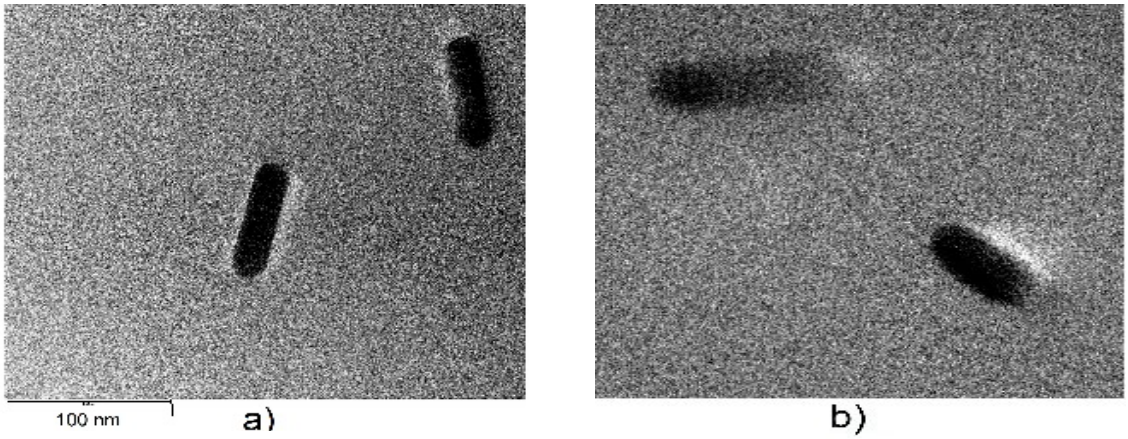

Fig. 5. TEM images of saples with bulk-like CdSSe nanocrystals.

These bulk-like NCs are, apparently, beyond the confinement regime. The sample containing such large NCs is cut out in the dark red end of the glass ingot. In Fig.5 a) is seen that the NCs have cylindrical form of the hexagonal symmetry with length about 76 nm and rouded end, wich are well seen in Fig.5 b). Note that for these NCs, the volume is approximately equivalent to the sphere volume with a diameter of about 37 nm, see main panel in Fig.4. For such a sample the TSL glow curve is shown in the inset in Fig.4. The irradiation dose is equivalent to the maximum one in Fig.3. Comparing the obtained result with those in Fig.3 one can conclude that for the case of large NCs, the TSL intensity is about more than one order of magnitude lower than for the main sample with the NCs size about 3.8 nm. Besides, the TSL intensity in this case shows only one peak without any pronounced structure, as is seen in the inset in Fig.4. Fig.6 shows a dependence of the TSL peak intensity on a duration of the irradiation for the main sample from Fig.3.

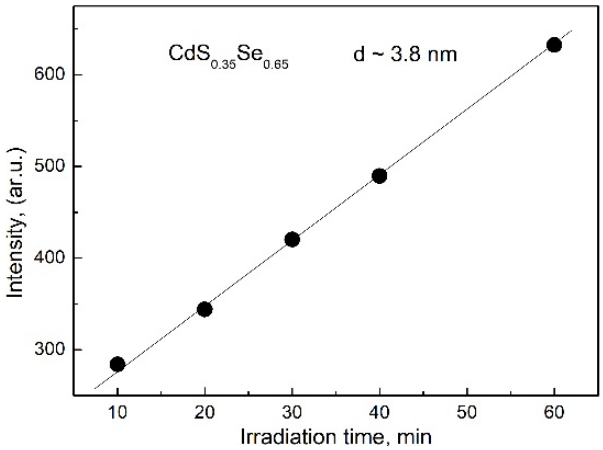

Fig. 6. Intensity of TSL in dependence on X-ray irradiation time.

It is seen that this dependence is very close to the linear one. It is obvious that such a dependence is convenient for the dosimetry to determine the absorbed dose of radiation. At high doses when the traps are saturated, the dose dependence deviates from linear. In our case, we suppose, the applied radiation doses are far from the saturation regime.

5. Conclusion

The thermoluminescence of $CdS_{0.35}Se_{0.65}$–doped borosilicate glasses prepared by means of a conventional melt–quenching technique has been investigated after their exposure with X–rays. The measured thermoluminescence is the more intense the smaller is the average size of the embedded nanocrystals. The glow curves of the total thermoluminescence show the two well resolved peaks, which can be related with the states localized on the nanocrystal–glass surface and the electron traps in the glass matrix as well. Thermoluminescence intensity shows linear dependence on the irradiation time. This circumstance indicates the possibility of using the CdSSe-doped glasses for radiation dosimetry.

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