Fluorine Phosphate Glasses Doped with Cadmium Sulfide and Selenide Quantum Dots with High Quantum Efficiency at Room-temperature

E. V. Kolobkova[1,2], Zh. Lipatova[1], M. S. Kuznetsova[3] and N. Nikonorov[1]
[1]*Department of Optical Informatics Technologies and Materials, ITMO University, Saint-Petersburg, Russia*
[2]*St. Petersburg State Institute of Technology, Technical University, St. Petersburg, Russia*
[3]*Saint-Petersburg State University, St. Petersburg, Russia*

Keywords: Quantum Dots, Fluorine-phosphate Glass, Luminescence, Absolute Quantum Yield.

Abstract: The results of the study of the luminescent properties of the CdS(Se) quantum dots (QDs) with the mean size of 2-4 nm synthesized in the fluorine phosphate glass are discussed. The changes of the photoluminescence absolute quantum yield (PL AQY) magnitude of the CdS(Se) QDs with various mean sizes induced by the heat treatment are studied. It was found that the PL AQY of the CdSe QDs increases monotonically to a maximum and then fells down. PL AQY magnitudes for glasses doped with CdS QDs demonstrate weak dependence on the size. It was found that CdS(Se) QDs represents a series of excellent emitters in the 600-750 nm spectral region. PL AQY in the glasses can reach 50-65%, which is equal to the value in the colloidal nanocrystals and higher than it was reported earlier for the silicate glasses. The glass matrix protects the QDs from external influence and their optical properties remain unchanged for a long time.

1 INTRODUCTION

QDs are a type of nanomaterials with good fluorescent properties. The size-dependent emission is probably the most attractive property of semiconductor nanocrystals.

Among them, CdS and CdSe QDs are one of the most promising materials because QDs have bright luminescence in the visible range of the optical spectrum. For example, CdSe QDs have shown potential as superior biological labels (Han, M. *et al*., 2001, Bruchez, M. *et al*., 1998 and Chan, W. C. W., Nie, S. M., 1998), laser sources (Artemyev, M. *et al*., 2001, Klimov, V. I.*et al*., 2000) and tunnel diodes (Sundar, V. C. *et al*., 2000, Schlamp, M.C., Peng, X., Alivisatos,A.P., 1997).

Comparing with conventional fluorescent dyes CdS(Se) QDs have a wide continuously distributed excitation spectra, not only with symmetrical distributed narrow emission spectra, but also many other excellent properties such as adjustable color, excellent photochemical stability and high threshold of light bleaching (Qu, L., Peng, X. 2002).

However, colloidaly synthesized bare quantum dots, including CdSe(S) QDs, usually have surface defects, which diminish photoluminescence (PL) absolute quantum yield. The best PL AQY reported for the as-prepared nanocrystals at room temperature is around 20% in the wavelength range between 520 and 600 nm and is about a few percent or lower in the wavelength range above 600 nm and below 520 nm (Sundar, V. C. *et al*., 2000). In general, a low PL AQY is considered as a result of the surface states located in the bandgap of the nanocrystals, which act as trapping states for the photogenerated charges. These surface trapping states are originated from the dangling bonds of some of the surface atoms (Fu, H.; Zunger, A. 1997, Xu, K. M. *et al.,* 2010 and Kim J, M. *et al*., 2012). That`s why it is essential to control the QDs surfaces to reduce the surface defects by passivating the surface of QDs (Talapin, D.V. *et al.,* 2001). The core/shell structures solve optical problems, such as low PL AQY, and improve the stability of QDs. In (Talapin, D.V. *et al*., 2001) was shown that the room-temperature quantum efficiency of the band edge luminescence of CdSe QDs can be improved to 40-60% by surface

Kolobkova E., Lipatova Z., Kuznetsova M. and Nikonorov N.
Fluorine Phosphate Glasses Doped with Cadmium Sulfide and Selenide Quantum Dots with High Quantum Efficiency at Room-temperature.
DOI: 10.5220/0006266203280333
In *Proceedings of the 5th International Conference on Photonics, Optics and Laser Technology (PHOTOPTICS 2017)*, pages 328-333
ISBN: 978-989-758-223-3

passivation with inorganic (ZnS) or organic (alkylamines) shells. Annealing of the samples in different environments (oxygen, hydrogen, and air) seems to reduce the PL emission, due to the activation of non-radiative defect states.

Due to the failure of orange-red emitting materials in general, efforts in colloidal CdS/CdSe QDs formation were mainly concentrated on the wavelength region between 600 nm (orange) and 650 nm (red). Nevertheless, the stability and the reproducibility of the PL AQY are both not predictable. With some inorganic and organic surface passivation after the synthesis, the PL QY of the colloidal CdSe nanocrystals is boosted more than 50% in the range 520-600 nm, but the efficiency for the orange-red color window is still low. Especially for red (around 650 nm), the PL QY of the nanocrystals in solution was nearly zero (Qu, L., Peng, X. 2002).

Semiconductor nanoparticles CdS and CdSe dispersed in a silicate glass matrix are attracting much attention (Borreli, N. F. *et al.*, 1987, Su, Z., *et al.*, 1996 and Xu, K. *et al.,* 2010). The possibility of QDs formation in the optical material creates significant benefits for their application. Currently, optical transparent glasses doped with nanocrystals are of the great interest for the modern element base of photonics. These materials combine the best properties of nanocrystals and glasses (possibilities of pressing and molding, spattering, pulling optical fibers). In addition, the glass matrix protects the QDs from external influence. In the silicate glasses, the PL spectra consist of two bands: a less intense high-energy band, and a lower energy broader band. First band occurs at a wavelength 10-20 nm higher than the absorption edge and is due to direct electron-hole recombination. This peak shifts to the higher wavelength with increasing particle size. Second band is due to surface defects and occurs at 800-900 nm spectral region. PL AQY is less than 30% for CdS(Se) QDs in the silicate glasses and decreases as a size of QD increases (Borreli, N.F. et al., 1987).

In this study, we used a fluorine phosphate (FP) glass featuring with a number of advantages compared to conventional silicate glasses, including low temperature synthesis, possibility for a wide range adjustment of the formed quantum dots concentration, low temperature and time of heat treatment and higher spatial distribution homogeneity. Two-stage heat treatment afforded quantum dots with narrow size distribution. The CdS and CdSe QDs dispersed in a fluorine phosphate glasses are attracting much attention as nonlinear materials (Vaynberg, B. *et al.*, 1996 and Lipovskii, A.A. *et al.,* 1999), but information about luminescent properties is not available.

In this study, we represent the luminescent properties of a fluorine phosphate glass doped with CdS and CdSe QDs.

2 EXPERIMENTAL

In order to investigate the effect of the QDs sizes on the PL properties, the fluorine-phosphate (FP) glasses $0.25Na_2O$-$0.5P_2O_5$-$0.05ZnF_2$-$0.1Ga_2O_3$-$0.05AlF_3$-0.05NaF (mol. %) doped with CdS or CdSe were synthesized. The glass synthesis was conducted in an electric furnace at 1050ºC in the Ar-atmosphere using the closed glassy carbon crucibles. After quenching, the glasses were annealed at 320 C for 1 hour to release thermal stress, cut into pieces of 10.0 x 10.0 mm, and then were optically polished. Planar polished samples 0.4-1.0 mm thick were prepared for further investigation. The glass transition temperature measured with STA 449 F1 Jupiter (Netzsch) differential scanning calorimeter was found to be 390±3 C. Samples were heat treated using a muffle furnace (Nabertherm) with program temperature control to induce formation of CdS(Se) QDs at 410ºC. The optical density spectra of the studied FP glass samples were recorded using a double-beam spectrophotometer Lambda 650 (Perkin Elmer) in the 1.5-5 eV spectral region with 0.1 nm resolution. For registration of the emission spectra excited at λ =405 nm (3.06 eV) was used an EPP2000-UVN-SR (Stellar Net) fiber spectrometer. The luminescence was excited by semiconductor lasers (λ=405 nm). All measurements were performed at room temperature. Absolute quantum yield measurements were carried out inside the integrated sphere with Photonic Multichannel Analyzer (PMA-12, Hamamatsu) at room temperature. The measurement error for the absolute quantum yield (AQY) was ±1%.

3 RESULTS AND DISCUSSIONS

3.1 Glasses Doped with Cadmium Selenide Quantum Dots

The emission properties of semiconductor nanocrystals can be characterized by three fundamental parameters, which are the brightness, the emission color, and the stabilityof the emission.

A samples of the glass containing CdSe QDs were prepared by heat treatment of a $0.25Na_2O$-$0.5P_2O_5$-$0.05ZnF_2$-$0.1Ga_2O_3$-$0.02PbF_2$-$0.08AlF_3$ glass doped with 0.6 mol. % CdSe at T=410°C during 20-60 min.

Due to quantum size effects, the band gap of CdSe QDs increases from 2.2 eV to 3.0 eV, as the size of the nanocrystals decreases from 4.0 nm to 2.0 nm. The emission color of the PL of the nanocrystals shifts continuously from red (centered at 730 nm) to orange (centered at 630 nm) as size of QDs decrease (Fig1). QDs sizes were defined using data (Norris, D. J. and Bawendi M. G. 1996).

In the PL spectra, the broad band with a large Stokes shift is dominant, and the band-edge PL is negligibly weak. The emission spectrum of samples is dominated by "deep trap" emission, strongly red shifted from the band edge (Fig2).

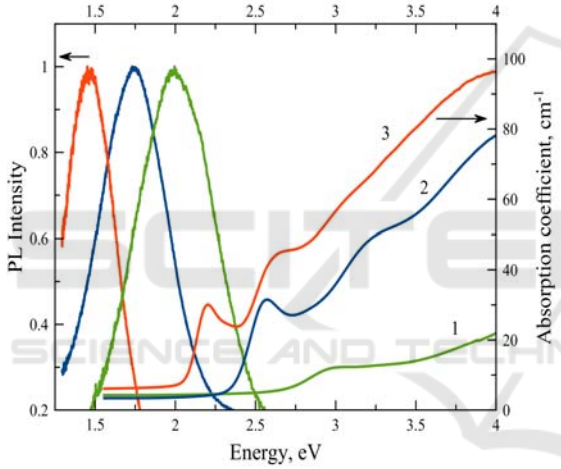

Figure 1: Absorption and luminescence spectra of the glass doped with CdSe QDs with a sizes 2.0 nm (1), 3.0 nm (2), 4.0 nm (3). The excitation energy is 3.06 eV.

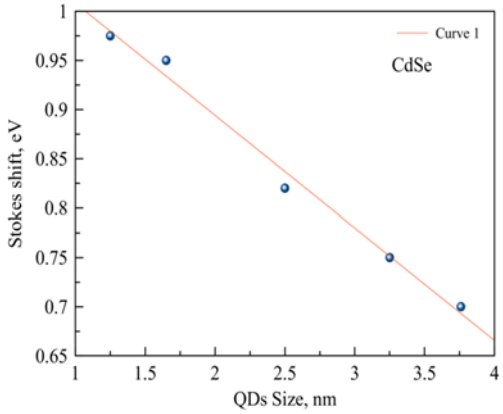

Figure 2: Dependence of the Stokes shift on the QDs size.

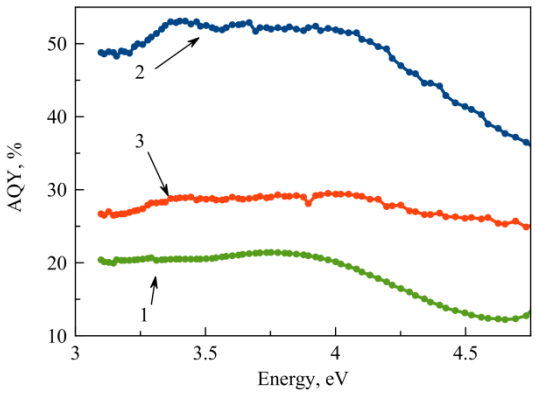

Figure 3: Dependence of the PL AQY for glasses doped with CdSe QDs with sizes 2.0 nm (1), 3.0 nm(2), 4.0 nm (3) on the excitation energy.

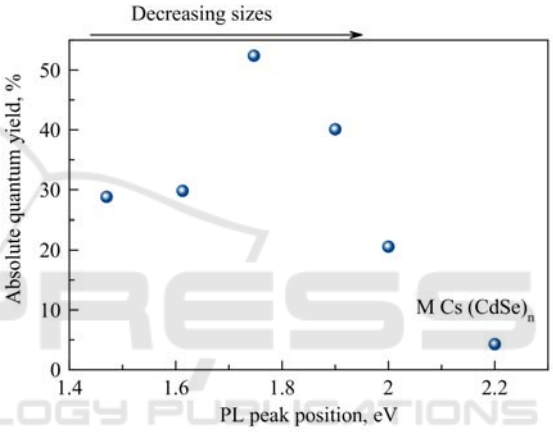

Figure 4: Dependence of the PL AQY on the CdSe QDs sizes.

Fig. 3 demonstrates dependence of the AQY magnitudes for glasses doped with CdSe QDs. The QDs concentration in the glasses 2 and 3 is equal (Fig.1), but AQY of the QD with size 3 nm is in two times higher. The emission color of the PL of the QDs with size 3 nm is red with λ_{max}=700 nm

The PL AQY magnitudes for glasses doped with CdSe QDs demonstrate nonlinear dependence on the size (Fig. 4).The PL AQY of the QDs increases monotonically to a maximum and then fells down to 30 % (Fig. 4). For convenience, the position with the maximum PL AQY is called the bright point as in (Qu, L., Peng, X. 2002). The bright point for CdSe QDs in FP glass is observed for QDs with size 3.0 nm.

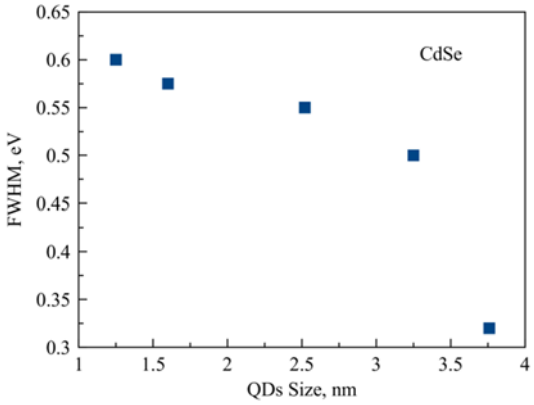

Figure 5: Dependence of the PL FWHM magnitudes for glasses doped with CdSe QDs with different sizes.

The typical full width at half-maximum (FWHM) of the PL peak of the CdSe QDs ensemble at room temperature in FP glass, around 600-300 meV, is noticeably broader than that observed for colloidal QDs (Qu, L., Peng, X. 2002). FWHM magnitudes decrease as QDs sizes increase (Fig 5).

The values of the PL AQY of the samples 1, 2 and 3 were measured several times during the year. The results of the measurements coincided, which confirmed the stability of luminescent characteristics.

3.2 Glasses Doped with Cadmium Sulfide Quantum Dots

As it was shown in (Lipatova, Zh.O., Kolobkova E.V., Aseev,V.A. 2015) heat treatment has a significant impact on properties of glasses doped with CdS QDs. Absorption peaks due to confined excitons are clearly observed in the higher-energy region compared with the band-gap energy of 2.5 eV in a CdS bulk crystal. These results evidently indicate the formation of CdS QDs. With increasing of the heat treatment duration, the exciton-absorption peak shifts to a lower-energy side. Based on a theory of the quantum size effect in spherical QDs (Martin J.L., Rivera R., Cruz S.A. 1998) the mean radii of prepared CdS QDs are estimated to be 2.3 and 3.5 nm. The observation of the clear absorption peaks indicates that the size-distribution width of the CdS QDs is rather small (Fig 6).

Fig. 6 clearly shows effect of the heat treatment on the absorption and emission spectra of FP glasses doped with CdS QDs with sizes 2.3 and 3.5 nm. In PL spectra, the broad PL band with a large Stokes shift (1.2 eV) is dominant, and the band-edge PL is negligibly weak. The emission spectrum of samples is dominated by "deep trap" emission, strongly red shifted from the band edge (Fig.6).

Fig. 7 demonstrates concentration and size dependence of the PL AQY magnitudes for glasses doped with CdS QDs.

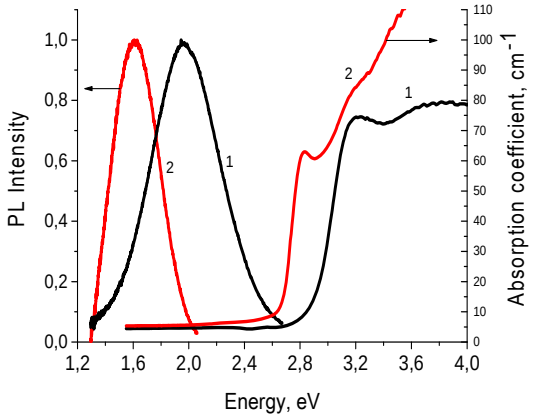

Figure 6: Absorption and luminescence spectra of the glasses doped with CdS QDs with a sizes 2.3 nm (1), 3.5 nm (2). The excitation energy is 3.06 eV.

Concentration of the QDs in the glass 3 is in two times higher than in glass 2. Comparison of the PL AQY of the two glasses doped with different QDs concentration (Fig. 7, curves 3 and 1) demonstrates PL concentration quenching as number of QDs increases above concentration threshold (Fig. 7).

The PL AQY magnitudes for glasses doped with CdS QDs with sizes 2.3 -3.5 nm demonstrate weak dependence on the size (Fig. 7). The PL AQY of the CdS QDs increases to 65 % for QDs with size 2.3 nm and then slowly fells down to 60 % for QDs with size 3.5 nm (Fig. 7). The values of the PL AQY of the samples 1, 2 and 3 were measured several times during the year. The results of the measurements coincided.

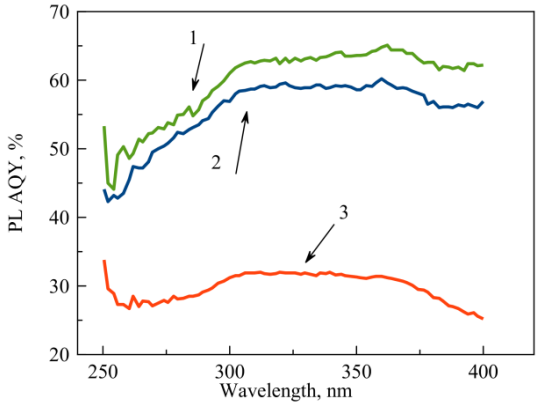

Figure 7: Dependence of PL AQY magnitudes for glasses doped with CdS QDs with sizes 2.3 nm (1), 3.5 nm (2) and 2.5 nm (3), respectively, on the excitation wavelength.

Absolute quantum yield allows estimating efficiency of converting UV light in the visible range that is why it is an important parameter for industrial applications of glasses doped with CdS(Se) QDs as luminescence down shifting material or phosphor.

4 CONCLUSIONS

The CdS(Se) nanocrystals synthesized in the fluorine phosphate glass represents a series of excellent emitters in the orange-red spectral region (600-750 nm) in terms of their PL AQY and the FWHM of the PL spectra, and they show the stability of the emission for a long time.

The photoluminescence quantum yield of CdSe QDs rises monotonically to a maximum value and then decreases gradually with QDs size increase. Such a maximum (a PL "bright point") is in 650-750 nm spectral range.

The PL AQY magnitudes for glasses doped with CdS QDs with sizes 2.3 -3.5 nm demonstrate weak dependence on the size.

We suggest that origin of these dependences is the difference in the interaction mechanisms between CdSe, CdS quantum dots and glass-network.

Experimental results suggest that the existence of the PL bright point is general phenomenon of CdSe QDs and likely is signature of an optimal surface structure reconstruction of the nanocrystals grown in a liquid (Qu, L., Peng, X. 2002) or in glass. Absolute quantum yield magnitude of luminescence glasses doped with CdS(Se) QDs can reach 50-65%, which is in two times higher than it was reported earlier in the silicate glasses. It opens up new prospects for using such materials as phosphors for white LEDs and down-convertors for solar cells.

ACKNOWLEDGEMENTS

Research was funded by Russian Science Foundation (Agreement #14-23-00136).

REFERENCES

Han, M. *et al.,* 2001. Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules. *Nat. Biotechnol.* 19. pp 631-635.

Bruchez, M. *et al.*, 1998. Semiconductor nanocrystals as fluorescent biological labels. *Science*. 281. pp 2013-2016.

Chan, W.C.W., Nie, S. M. 1998. Quantum dot bioconjugates for ultrasensitive nonisotopic detection. *Science,* 281, pp 2016-2018.

Artemyev, M. *et al.,*2001. Light trapped in a photonic dot: Microspheres act as a cavity for quantum dot emission. *Nano Lett*., 1. Pp 309-314.

Klimov, V. I. *et al.,* 2000. Optical Gain and Stimulated Emission in Nanocrystal.*Science*, 290,pp 314-317.

Sundar, V. C. et al.,2000, Full color emission from II-VI semiconductor quantum dot-polymer composites *Adv.Mater*. 12. Pp 1311-1312; Novel light emitting devices using cadmium selenide nanocrystals. *Abstracts of papers of the American chemical society*.220. ppU206-U206.

Schlamp, M.C., Peng, X., Alivisatos, A.P., 1997. Improved efficiencies in light emitting diodes made with CdSe(CdS) core/shell type nanocrystals and a semiconducting polymer. *J. Appl. Phys.* 82. Pp 5837–5842.

Qu, L., Peng, X. 2002. Control of Photoluminescence Properties of CdSe Nanocrystals in Growth. *J. Am. Chem. Soc*. 124(9).pp 249-255.

Fu, H.; Zunger, A. 1997. InP quantum dots: Electronic structure, surface effects, and the redshifted emission. *Phys. Rev. B: Condens. Matter*, 56, pp 1496-1508.

Talapin D.V., *et al.,*2001. Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-trioctylphosphine oxide-trioctylphospine mixture*, Nano Lett.* 14. pp 207–211.

Wang, X *et al.,*2003. Surface-Related Emission in Highly Luminescent CdSe Quantum Dots. *Nano Lett.,* 3(8) pp 1103-1106.

Borreli, N.F. et al.,1987. Quantum confinement effects of semiconducting microcrystallites in glass, *J. Appl. Phys.* 61.pp 5399–5409.

Su, Z.*et al*., 1996. Selenium molecules and their possible role in deep emission from glasses doped with selenide nanocrystals, *J. Appl. Phys.* 80.Pp 1054–105.

Vaynberg, B. *et al*., 1996. High optical nonlinearity of CdS_xSe_{1-x} microcrystals in fluorine-phosphate glass *Optics communications.* 132 (3-4). Pp 307-310.

Lipovskii, AA. *et al.,* 1999. Formation and growth of semiconductor nanocrystals in phosphate glass matrix. Journal of the European ceramic society.19 (6-7). Pp 865-869.

Xu, K.M. *et al*., 2010. Optical properties of CdSe quantum dots in silicate glasses. *J Non-Crystalline Solids.*356.Pp 2299–2301.

Martin, J.L., Rivera, R., Cruz, S.A. 1998. Confinement of excitons in spherical quantum dots. *J. Phys.: Condence Matter*. 10. Pp1349–1361.

Kim, J, M. *et al*., 2012. Photoluminescence enhancement in CdS quantum dots by thermal annealing. *Nanoscale Research Letters.* 7. Pp 482–489.

Lipatova, Zh.O., Kolobkova, E.V., Aseev,V.A. 2015. Kinetics and luminescence of cadmium sulfide quantum dots in fluorine-phosphate glasses, *Opt.*

Spectrosc. 119(I2), pp 229–233.

Norris, D. J. and Bawendi M. G. 1996. Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots. *Physical Rev. B.* 53, (24). pp 16338-16446.

Norris, D. J. and Bawendi, M. G. 1995. Structure in the lowest absorption feature of CdSe quantum dots. . Chem. Phys., 103(130). pp5260-5268.