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Optical Properties of PbSe Qantum Dots Doped in Fluorophosphate Glasses

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PbSe quantum dots (QDs) were synthesed in fluorophosphate glass and their absorption and luminescence properties were investigated. The effect of the duration of the heat treatment on the spectral-luminescent properties was considered. The average diameter of the synthesized quantum dots has been calculated.

Keywords: Fluorophosphate glass, PbSe, Quantum dots.

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1. INTRODUCTION

At the moment, there is considerable interest in the creation of high-performance passive Q-switcher for range of transparency of fiber telecommunications networks. All technical solutions related to equipment fiber links require a simple and compact laser systems. A special place among occupy the solid-state lasers, operating in the Q-switching mode. These lasers can get nanosecond and picosecond pulses of light high power. Q-switching methods are quite diverse. One of these methods, widely used, is a Q-switched with a passive shutter (phototropic shutter bleachable filter, saturable absorber). Phototropic media can reversibly change the value of the absorption coefficient under the influence of powerful light beams. This is the basis for this method.

This method in combination with a sufficiently high radiation parameters, is easy to install in the valve cavity and does not require the use of additional sources of supply.

Nowadays more than one type of solid-state saturable absorbers for infrared laser range 1.3-1.5 microns (crystals with color centers, crystals and glasses doped with rare-earth or transition metal single-or multilayer epitaxial semiconductor saturable absorber (SESAM) are used. However such absorbers have significant disadvantages which include rapid aging (crystals with color centers), a large effective relaxation time and / or the need for focusing of intracavity to obtain the required levels of illumination (glass doped with erbium), or high cost associated with the complexity of the technology (SESAM). levels (glass doped with erbium), or high cost associated with the complexity of the technology (SESAM). Glasses containing quantum dots are a promising material for passive Q-switching and mode locking, since the position of the absorption peaks is determined by the size of the quantum dot, which gives the opportunity to "tune" spectral domain of optical nonlinearity which observed in the region of the first exciton absorption peak. Moreover, these glasses with quantum dots have advantages which compared with other materials for passive intracavity modulators and Q synchronizers modes due to a substantial gain in cost, because their manufacturing methods can use standard glass melting. The main requirement for materials of saturable absorbers is a narrow distribution of quantum dots (QDs) in size (ΔR / R ~ 10%, R – quantum dot size), resulting in a narrow first excitonic peak corresponding to the first exciton transition, and uniform distribution of the quantum dots in the amount of glass. It should be noted that the temperature-time regimes of formation of quantum dots in fluorophosphate glasses much softer than in silicate glasses, with their relative proximity to the glass transition temperatures (450-480°C for silicate and 425° C for fluorophosphate). This is due to different stroke dependence of viscosity on temperature for specified classes of glasses.

It should also be noted that the glass with PbSe quantum dots can be used in a broader spectral range than with PbS, due to differences in the values of the exciton Bohr radius (20 nm and 46 nm PbS for PbSe) and a bandgap (Eg PbSe = 0.29 eV Eg PbS = 0,41 eV at 300K).

Thus, to date, glass, studied in the work are quite promising systems prone to the formation of RbSe - quantum dots.

2. EXPERIMENTAL PROCEDURES

The samples of the fluorophosphate glasses of Na_2O-P_2O_5-Ga_2O_3-AlF_3-ZnO(Se)-PbF_2 with an equal concentration of the semiconductor phase PbSe were inverstigated. The synthesis was performed in closed glasscarbon crucible at the temperature of 950–1000°C under the argon atmosphere; the duration of the synthesis was 40 min. These conditions of the synthesis allowed receiving glasses with high transmission coefficient in 0.3–3 μm wavelength region. The glass melt

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was processed between two cold glass-carbon plates. The tempered glasses had a maximum thickness of 2 mm. For the synthesis of quantum dots samples were subjected to heat-treatment at 415°C for 20-120 min. The temperature of heat-treatment was indicated by DSC STA 449F1 Nietzsche. The absorption specter was recorded on Varian Cary 500 on Varian Cary 500 spectrophotometer in the range 300-3300 nm. Photoluminescence spectra were measured using the 980 nm excitation sources from a laser diodes. The RED-Wave-NIRX fiber optic spectrometers were used to recorded photoluminescence specter. All measurements were performed at room temperature.

3. RESULTS

The parent glass was transparent and their color was light-yellow. After heat-treatment at 415 ° for 40-120 min the color gradually changed. The grade of coloration (from light brown to black) of samples was depended from duration of the heat-treatment. Fig. 1 shows the absorption spectra of the glass heat-treated at room temperature. The clear first excitonic absorption peak in the near-infrared region for each of the samples was observed. Also the blue-shifted (their peak positions moved to the short wavelength side) compared to the location of the band-gap energy of the bulk material was demonstrated. In addition, with increasing heat-treatment times the peak positions moved to the long wavelength side (red-shift), indicating the strong quantum confinement effect in PbSe QDs.

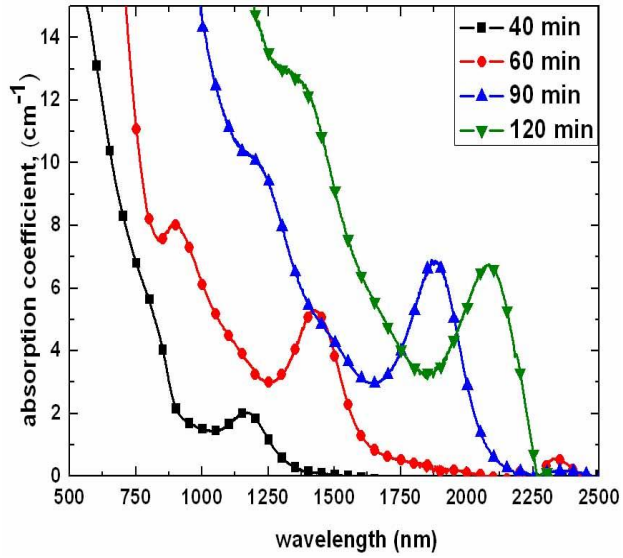

Fig. 1 – Absorption spectra of PbSe QDs in fluorophosphate glasses after heat-treatment during different duration at 415°C

Also photoluminescence was achieved in 1.1-1.6 μm wavelength region after heat-treatment for 20-60 min. (table 1). The photoluminescence was not found after heat-treatment for 90-120 min.

4. DISCUSSION

The average diameters of the QDs were computed using the following fitting formula [1] from the measured band-gap energies :

$$E_g(D) = E_g(\infty) + \frac{1}{0.0105 \cdot D^2 + 0.2655 \cdot D + 0.0667}. \quad (4.1)$$

where, D is diameter of PbSe QDs (in nm). $E_g(D)$ is the effective band-gap energy(in eV), calculated from the first exsitonic absorption peak. And $E_g(\infty)$ is the band-gap energy of the bulk PbSe semiconductor (0.29 eV). The sizes of PbSe QDs are presented in table 1.

Table 1 – Optical properties and sizes of PbSe QDs in fluorophosphate glasses. (D – calculated average diameter, λ_{abc} – absorption peak position, FWHM –full width at half maximum of absorption peak, λ_{PH} – peak wavelength of photoluminescence)

Heat-treatment time (min)	D(nm)	λ_{abc} (nm)	FWHM, cm^{-1}	λ_{PH},(nm)
40	4.1	1179	1136	1347
60	5.2	1429	1002	1592
90	7.8	1882	564	–
120	9.1	2082	518	–

As shown, average diameter of QDs increased with magnification duration of heat-treatment.
As shown in table 1, the FWHM (full width at half maximum) of absorption peak decreased with increased heat-treatment time. Probably it means, that the variance of Qds sizes decreased.

5. CONCLUSIONS

Lead selenide quantum dots were synthesized in fluorophosphate glasses, and their optical properties were investigated. QDs PbSe were precipitated through the thermal treatment at 415°C for 40-120 min. The position of the first exsitonic peak situated in 0.9-2.1 μm wavelength range and depended from duration treatment and The intensive photoluminescence was achieved in 1.1-1.6 μm region for samples, which treatment time was 40 - 60 min. The maximum diameter of synthesized QDs PbSe was 9.1 nm.

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