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Wavelength-tunable absorption and luminescence of SiO_2–Al_2O_3–ZnO–Na_2O–K_2O–NaF glasses with PbS quantum dots

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Lead sulfide quantum dots (QDs) with average diameter of 3.0–6.5 nm were grown in novel SiO_2–Al_2O_3–ZnO–Na_2O–K_2O–NaF glasses highly-doped with PbO and elemental sulfur by means of single-stage heat-treatment at temperatures slightly lower the vitrification point. Introduction of two alkaline components to the glass system allows us to perform the synthesis without control of sulfur evaporation, while stabilization of PbS crystal nuclei was provided by addition of NaF. Optical absorption and photoluminescence of these PbS-QD-doped glasses were studied in dependence on treatment temperature (480–520 °C) and duration (5–130 h). The growth rate of QDs was substantially enhanced with the increase of treatment temperature. The position of 1S–1S excitonic absorption peak was tuned from 0.75 to 1.6 μm, accompanied by management of peak absorption within 7–45 cm^{-1} range. Intense Gaussian-shaped photoluminescence associated with radiative exciton recombination from 1S–1S state was observed in 1.1–1.6 μm spectral range.

1. Introduction

Glasses doped with lead sulfide (PbS) quantum dots (QDs) attract attention as appropriate materials for passive *Q*-switching and mode-locking of near-IR solid-state lasers [1–3]. They are characterized with high bleaching contrast [4,5], fast ps recovery time [6,7], low saturation intensity [8,9] and appropriate laser damage threshold [10]. PbS-QD-doped glasses offer simple technological process of synthesis, chemical stability and the possibility to create all-solid and compact devices. As a result, they were successfully used as saturable absorbers in both flashlamp- [11,12] and diode-pumped [13–15] lasers. The distinctive feature of PbS compound is high excitonic Bohr radius $a_B \sim 20$ nm [16] that allows one to achieve strong quantum confinement of excitons for crystals with diameter lower than 10 nm [17]. Moreover, under such conditions the energy spectrum of excitions depends substantially on the nanocrystal diameter. This leads to associated shift of absorption bands in extremely wide spectral range of 1–2 μm [18,19].

The typical method of synthesis of PbS-QD-doped glasses is the heat-treatment of as-cast glass [18–20] (recently, Ag^+ ion diffusion was utilized to assist this process [21]). The appropriate choice of treatment schedule (that means one- or two-stage treatment, temperature and duration) allows one to change the average diameter of PbS nanocrystals and, hence, to determine the position of excitonic absorption peaks. PbS QDs in glasses are characterized with intense and broad luminescence associated with radiative exciton recombination [22]. Clearly, spectral position of luminescence bands also depends on the QD diameter and can be tuned by appropriate heat-treatment mode. Thus, PbS-QD-doped glasses are attractive for realization of in-fiber light amplification [23,24]. As a result, investigation of relation between heat-treatment conditions and optical properties of glasses containing PbS nanosized crystals is of practical importance for photonics applications.

In the present paper, we perform a detailed experimental study of optical absorption and photoluminescence of novel alumina-alkali-silicate glasses doped with PbS QDs. For this, the influence of temperature (480–520 °C) and duration (5–130 h) of one-stage heat-treatment on the spectroscopic properties was investigated. It was accompanied by determination of material parameters like spectral position and peak absorption of main 1S–1S excitonic absorption band, average diameter of PbS nanocrystals, full-width at half-maximum (FWHM) of absorption and luminescence bands, and Stokes shift between their maxima. It was found that introduction of two alkaline components (Na_2O and K_2O) to the glass system results in increased stability of the synthesis that can be performed without control of sulfur evaporation. Moreover, it leads to good optical quality of glasses even under high-temperature treatment (with optical losses lower than

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0.02 cm^{-1}). Appropriate concentration of dopants (PbO and S) allows us to obtain highest peak absorption coefficients even reported for 1S–1S excitonic absorption band (more than 40 cm^{-1}).

2. Experimental

The initial glass was prepared in the SiO_2–Al_2O_3–ZnO–Na_2O–K_2O system. The raw materials were weighed and homogenized in 100 cm^3 corundum crucible. The PbO oxide (2.6 mol%) and elemental sulfur (9.8 mol% that is nearly 2.5 times higher than in our previous paper [25]) were utilized as dopants. Sodium fluoride (NaF, 7.5 mol%) was added in order to stabilize the PbS crystal nuclei and to prevent their dissolution in the melt. The synthesis was performed at $\sim 1400 \pm 50$ °C for 2 h in the gas furnace. No attempts were made in order to prevent the sulfur evaporation. The melt was cast to the steel surface and then annealed at $\sim$400 °C for 2 h in the muffle furnace in air. Then the glass boule was cooled down to room temperature. The initial glass was transparent with dark yellow-brown color and X-ray amorphous. It contains no cracks, regions of non-uniform coloration, signs of opalescence and air bubbles.

The growth of PbS QDs was provided by heat-treatment of initial glass at temperatures slightly lower the vitrification point $T_g \sim 520$ °C. The samples were treated at 480 °C for 20–130 h, at 490 °C for 15–75 h, at 500 °C for 10–55 h, at 510 °C for 10–50 h or at 520 °C for 5–45 h. It allows us to investigate the influence of treatment temperature and duration on the optical properties of glasses. For all these samples, PbS was the sole precipitated crystalline phase (as determined from X-ray diffraction analysis, the procedure was identical to one described in Ref. [25]). The treatment was performed in 50 cm^3 corundum crucibles and the samples were buried with alumina powder. The heat-treated samples were dark-brown or black.

For study of spectroscopic properties, thin (0.2–1 mm) polished plates were cut from the glass boules. Absorption spectra were recorded with a CARY Varian 5000 spectrophotometer. The luminescence was excited by focused radiation of InGaAs 980 nm laser

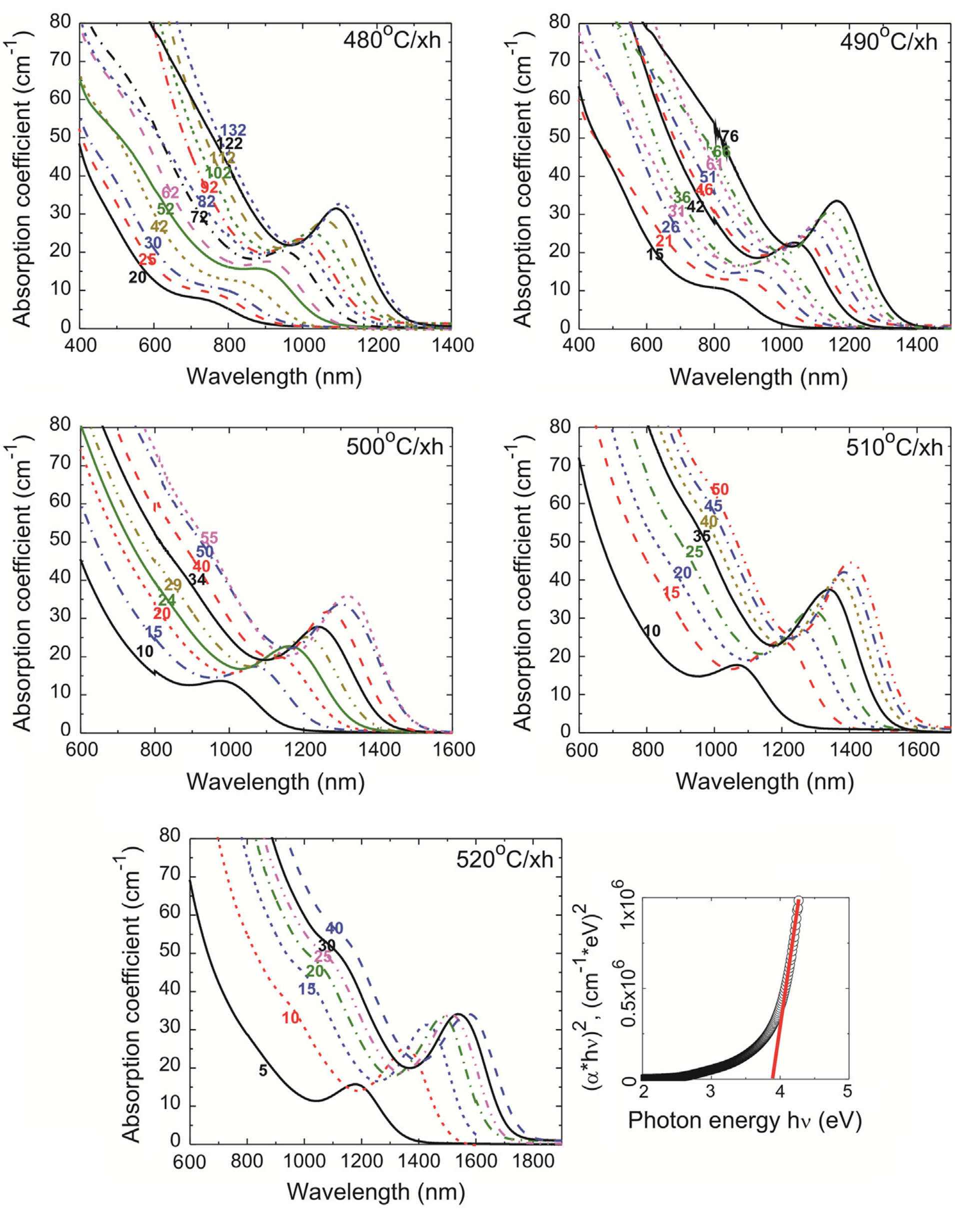

Fig. 1. Optical absorption spectra of PbS-QD-doped glasses for various heat-treatment temperatures (480–510 °C); the numbers on graphs indicate the duration of treatment in hours (h); inset represents estimation of UV absorption edge for as-cast glass.