Broadband emission in the near-infrared range in glasses doped with PbS quantum dots and Er^{3+} ions

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Abstract—This work presents borosilicate glasses co-doped with PbS quantum dots and Er^{3+} ions for broadband NIR luminescence. The heat-treatment increased the absorbance of glass in the visible range and shits absorption edge towards longer wavelengths. Glass co-doped with PbS/Er^{3+} after heat treatment at 490°C showed broadband luminescence in 1-1.6 µm range under pumping at the wavelength of 980 nm. In the case of pumping at the wavelength of 808 nm, the obtained band was lower due to non-radiative processes and, finally, lower intensity of Er^{3+} ions luminescence.

Over the years, the near-infrared (NIR) range has been widely used due to applications in fiber-optic telecommunications, medicine, and gas sensing. Emission in this spectral range can be achieved using glasses singly doped and co-doped with lanthanides ions (Er^{3+}, Tm^{3+}, Ho^{3+}), pumped by commercially available laser diodes (808 nm, 980 nm) [1]. There are also solutions based on amorphous and glass-ceramics materials doped with transition metal ions and bismuth, aimed at applications in the 1.3 µm band [2−3]. However, all the active dopants mentioned are characterized by a strictly defined emission band that cannot be tuned over a wide spectral range. A solution to this problem is using nanocomposites doped with quantum dots (QDs), which exhibit a tunable luminescence spectrum depending on the size of the quantum dots in the glass matrix. PbS and PbSe quantum dots exhibit a tunable luminescence spectrum ranging from 1.0 µm to even 2.5 µm, depending on the size of the photonic structures formed in the glass [4]. Over the years, numerous solutions have been proposed for glasses doped with quantum dots and rare-earth ions for the visible (VIS) spectral range [5−7]. However, there is still a lack of co-doped systems combining QDs and RE, which are characterized by broadband near-infrared emission due to the superposition of emission bands from RE ions and quantum dots. Studies can be found in the literature on the influence of lanthanide ions doping on the luminescence spectrum shift of PbS quantum dots [8−9]. Regarding broadband luminescence in the near-infrared range, glasses co-doped with PbS and Tm^{3+} can be found in the literature [10−11]. It is also worth noting the possibility of fabricating fibers doped with PbS and PbSe quantum dots for application in fiber amplifiers [12−13].

This letter presents borosilicate glass doped with PbS quantum dots and Er^{3+} ions for applications in broadband radiation sources and fiber amplifiers.

Borosilicate glass samples doped with zinc sulfide, lead oxide, and Er^{3+} ions had the following molar composition: $30.95SiO_2$-$29B_2O_3$-$25Na_2O$-10ZnO-3BaO-1ZnS-1PbO $0.05Er_2O_3$. ZnS and PbO in the glass matrix act as nucleators for PbS quantum dots during further heat treatment [14]. Glass samples were prepared by standard melting and quenching method. The homogeneous set was melted in a silica crucible for 30 minutes at 1100 °C. Molten glass was poured into a stainless steel plate and then annealed at 400°C for 3 hours. After slowly cooling to room temperature, glass samples were polished to get appropriate optical properties with a thickness of 3.4 mm. The glasses were then annealed in a tube furnace to obtain PbS quantum dots in the glass matrix. The annealing process was carried out at a temperature of 490 °C for 10 hours. Absorbance spectra of glass samples were measured using the Stellarnet Blue-Wave spectrometer in a range of 300 nm to 1000 nm. The luminescence properties of fabricated glasses were measured with Acton 2300i monochromator under 808 nm, 940 nm, and 980 nm laser diode excitation.

First, the glass samples' absorbance spectra (Fig. 1) were examined before and after heat treatment. An absorption band corresponding to the Er^{3+}:$^4I_{15/2}\rightarrow{}^4H_{11/2}$ transition was observed in both investigated cases. The sample annealed at 490°C for 10 hours exhibited increased absorption in the visible range, suggesting the nucleation of PbS quantum dots. The increasing absorption in the visible range and the redshift of the absorption edge is a well-known phenomenon in glasses doped with PbS quantum dots and is strictly related to their presence and increasing size within the glass matrix [12].

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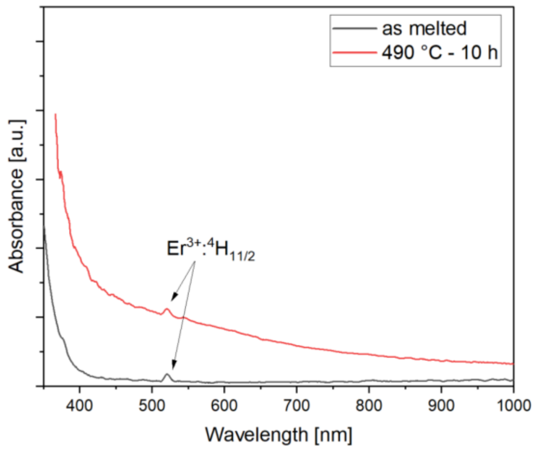

Fig. 1. Absorbance spectra of glass samples doped with QDs and 0.05 mol% Er_2O_3 before heat treatment and after.

Figure 2 presents the luminescence spectra of glasses before the heat treatment and after heat treatment at the temperature of 490 °C for 10 h under excitation at the wavelength of 980 nm. The melted sample is characterized by luminescence of 1.53 μm corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. After heat treatment, the glass emission band at 1.32 μm appears related to the luminescence of PbS quantum dots. In this case, the observed spectrum can be described as a superposition of luminescence bands from PbS quantum dots and Er^{3+} ions. In this case obtained, 3 dB and 10 dB bands were equal to 218 nm and 512 nm, respectively. The presented result is promising in the case of applications in fiber amplifiers operating in II and III telecommunication windows pumped by commercially available semiconductor lasers.

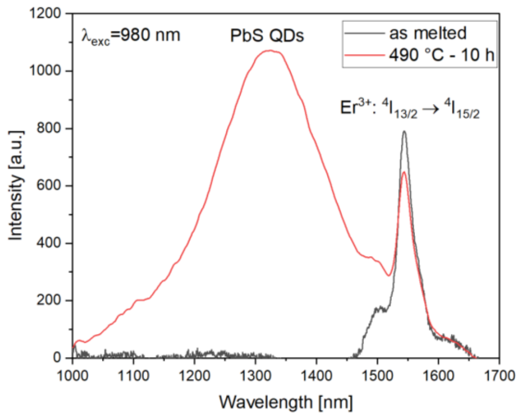

Fig. 2. Luminescence spectra of glasses before and after heat treatment under excitation at the wavelength of 980 nm.

In the following step, luminescence properties were investigated under pumping at the wavelength of 808 nm. In the analyzed case (Fig. 3), a lower emission intensity was obtained in the 1.53 μm band corresponding to the erbium transition. This may be related to the lower absorption coefficient of Er^{3+} ions at the wavelength of 808 nm compared to 980 nm [15]. Hence, the lower absorption in this band results in reduced luminescence intensity. As a melted sample, no luminescence was observed in the 1.3 μm band due to the lack of PbS quantum dots in the glass matrix.

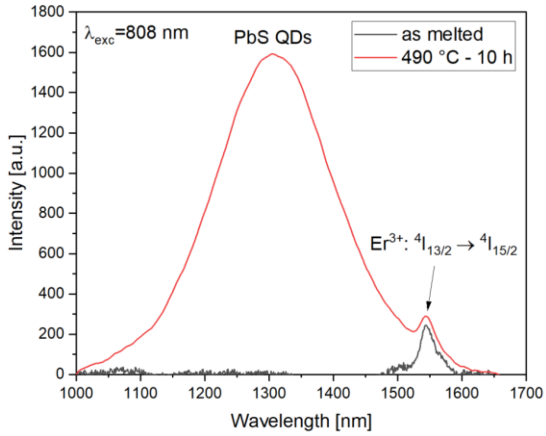

Fig 3. Luminescence spectra of glasses before and after heat treatment under excitation at the wavelength of 808 nm.

Under pumping, heat-treated glass at the wavelength of 808 nm obtained 3 dB and 10 dB bands were equal to 220 nm and 490 nm, respectively. The mentioned 10 dB bandwidth, in this case, is lower than that achieved at the 980 nm pumping wavelength due to the lower intensity in the 1.53 μm band corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions. The wavelength of the pump emission does not affect the emission wavelength of the quantum dots, which remained at 1306 nm in both cases. The emission wavelength of the quantum dots is strictly related to their size within the glass matrix, allowing tunable luminescence depending on application requirements. The presented results provide an alternative to glasses doped with praseodymium, nickel, chromium, and bismuth ions for applications in fiber amplifiers operating in the 1.3 μm band.

Based on the presented results of absorbance and luminescence spectra of borosilicate glasses co-doped with PbS/Er^{3+}, it can be concluded that the condition for obtaining a 1.3 μm luminescence band is the proper heat treatment of glass to obtain PbS quantum dots in the glass matrix. Moreover, the presented solution is highly attractive for applications in fiber amplifiers operating in the second and third telecommunication windows, due to emission bands at 1300 and 1535 nm. Comparing both pumping variants (980 nm and 808 nm), better results were obtained for the 980 nm pump laser wavelength. This is due to the lower value of the absorption coefficient of Er^{3+} ions at the wavelength of 808 nm compared to 980 nm. In the presented results, the wavelength of the pumping radiation does not affect the emission wavelength of PbS quantum dots. In summary, the presented borosilicate glasses doped with PbS/Er^{3+} may have potential applications in fiber optics, particularly in telecommunication fiber amplifiers and broadband amplified spontaneous emission (ASE) sources operating in the 1.0−1.6 μm band.

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