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# Luminescent properties of glasses activated by $CsPbBr_3$ perovskite nanocrystals and europium ions

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**Abstract.** A series of borogermanate glasses with $CsPbBr_3$ perovskite nanocrystals and $Eu^{3+}$ ions is synthesized. At low concentrations of $Eu_2O_3$ in glass, $Eu^{3+}$ ions play the role of crystallization centers for the nucleation of perovskite nanocrystals. At high concentrations of $Eu_2O_3$ in glass, $CsPbBr_3$ nanocrystals nucleate only during additional heat treatment. The lifetime of $Eu^{3+}$ luminescence increases from 1.58 to 1.69 msec along with an increase in the $Eu_2O_3$ concentration. Along this, a slight distortion of the $Eu^{3+}$ environment occurs in the glass matrix, resulting in a slight redistribution of the characteristic luminescence bands.

**Keywords:** perovskite nanocrystals, borogermanate glasses, trivalent europium

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# Люминесцентные свойства стекол, активированных нанокристаллами перовскита $CsPbBr_3$ и ионами европия

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**Аннотация.** Синтезирована серия боргерманатных стекол с нанокристаллами перовскита $CsPbBr_3$ и добавкой ионов $Eu^{3+}$. С изменением концентрации ионов $Eu^{3+}$ наблюдается изменение люминесцентных свойств стекол в видимом диапазоне, при этом время жизни люминесценции $Eu^{3+}$ увеличивается с 1,58 до 1,69 мс.

**Ключевые слова:** нанокристалл перовскита, борогерманатное стекло, ионы европия

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## Introduction

Optical materials based on perovskite lead halide cesium nanocrystals are promising due to their unique optical, optoelectronic and photoelectric properties[1]. Due to the large absorption coefficient, high carrier mobility and emission efficiency, enabling perovskite to become ideal materials for combining with silicon photodetectors [2]. In addition, it has been widely used in initial solar cells, high-energy ray detection, light-emitting diode, lasers, and other fields in the span of an only few years. The rare-earth $Eu^{3+}$ ion-doped $CsPbX_3$ nanocrystals can achieve a higher photoluminescent quantum yield due to the energy transfer from excitons to $Eu^{3+}$ ions [3], thus improving the response of photodetectors. Herein, a series of borogermanate glasses co-doped with $CsPbBr_3$ perovskite nanocrystals and $Eu^{3+}$ ions was synthesized, and its luminescent properties were studied.

## Materials and Methods

The composition of the glasses under study was as follows: 4.97 ZnO – 4.83 $Na_2O$ – 4.3 PbO – 6.17 $Cs_2O$ – 19.94 $B_2O_3$ – 48.37 $GeO_2$ – 3.06 $K_2O$ – 5.19 Br – 1.66 $TiO_2$ – 0.98 $P_2O_5$ – x $Eu_2O_3$, where x = 0.5; 1; 2 wt.%. Glass synthesis was carried out in an air atmosphere at a temperature of 950 °C in closed glass crucibles. After synthesis, the glasses were inertially annealed at a temperature of 470 °C. In glass composition with 0.5 wt.% $Eu_2O_3$, the nucleation of $CsPbBr_3$ perovskite nanocrystals occurred spontaneously during the annealing process. In the remaining compositions, the nucleation of perovskite crystals occurred only after additional heat treatment at temperatures above glass transition temperature (470 °C). The glass absorption spectra were measured by a Lambda 650 spectrophotometer (Perkin Elmer) in the spectral range of 200–900 nm. For the luminescence and excitation spectra recording, as well as for the luminescence decay measurements the LS-55 spectrofluorimeter (Perkin Elmer) was used.

## Results and Discussion

Fig. 1 shows the absorption spectra of the glass samples under study. Since in glass with 0.5 wt.% $Eu_2O_3$ spontaneous precipitation of $CsPbBr_3$ nanocrystals occurred; a characteristic band corresponding to the absorption of semiconductor crystals is visible in the absorption spectrum in the region of 500 nm [4]. The intensity of the absorption band was only 1 $cm^{-1}$, which indicated a low concentration of the crystalline phase. This prevented confirmation of the nanocrystals' nucleation by X-ray diffraction. Absorption spectra of glass samples with 1 wt.% $Eu_2O_3$ and 2 wt.% $Eu_2O_3$ had a high scattering level and contained low-intensity absorption bands of $Eu^{3+}$ ions, corresponding to the transitions: 1 – $^7F_0 \rightarrow {}^5L_6$, 2 – $^7F_0 \rightarrow {}^5D_2$. In the region of 562 nm, a defect was observed in the spectra due to the measurement method and the low absorption intensity.

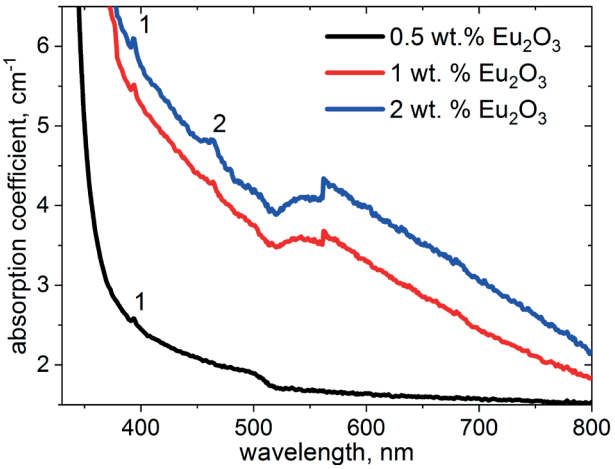


Fig. 1. Absorption spectra of the glasses under study

Fig. 2, *a* shows the luminescence spectra of glasses under study in the range of 375–730 nm under the excitation of 395 nm. For the glass with 0.5 wt.% $Eu_2O_3$ a narrow band with the maximum at 535 nm, corresponding to $CsPbBr_3$ perovskite nanocrystals, was observed [4]. Luminescence spectra of the glass with 1 wt.% $Eu_2O_3$ possessed two bands at 450 and 500 nm. The long-wavelength band also corresponded to the luminescence of perovskite nanocrystals, while the etymology of the short-wavelength band was not yet clear and required additional research. At this point, it can be assumed that broad blue luminescence may belong to $CsPbBr_3$ crystals of a very small subcritical size. In the region of 615 nm, both spectra also contained a $Eu^{3+}$ luminescence band corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition [5], but its intensity was 1000 and 100 times lower than the nanocrystals' luminescence intensity for compositions with 0.5 and 1 wt.% $Eu_2O_3$ respectively. Luminescence spectrum of glass with 2 wt.% $Eu_2O_3$ represented the bands of $Eu^{3+}$ ions, the designation of the main bands is shown in Fig. 2, *d*. However, in addition to them, the luminescence spectrum also contained low-intensity bands at 558, 537 nm, which can be attributed to the $^5D_1 \rightarrow {}^7F_3$ and $^4D_1 \rightarrow {}^7F_2$ transitions in $Eu^{3+}$ ions [6].

Excitation spectrum of the composition with 0.5 wt.% $Eu_2O_3$ exhibited a shape quite characteristic of semiconductor crystals. However, in the photoluminescence excitation spectrum of glass containing 1 wt.% $Eu_2O_3$ at wavelengths corresponding to the most intense absorption transitions in $Eu^{3+}$ ions (398 and 467 nm), dips were observed. It is worth noting that the excitation spectrum for luminescence with a maximum at 450 nm in the same sample was very different from that for nanocrystals, which once again confirmed the presence of another luminescent center in the material. Excitation spectrum of glass with 2 wt.% $Eu_2O_3$ consisted of characteristic bands of $Eu^{3+}$ ions; their correspondence to electronic transitions is indicated in Fig. 2, *d* [5].

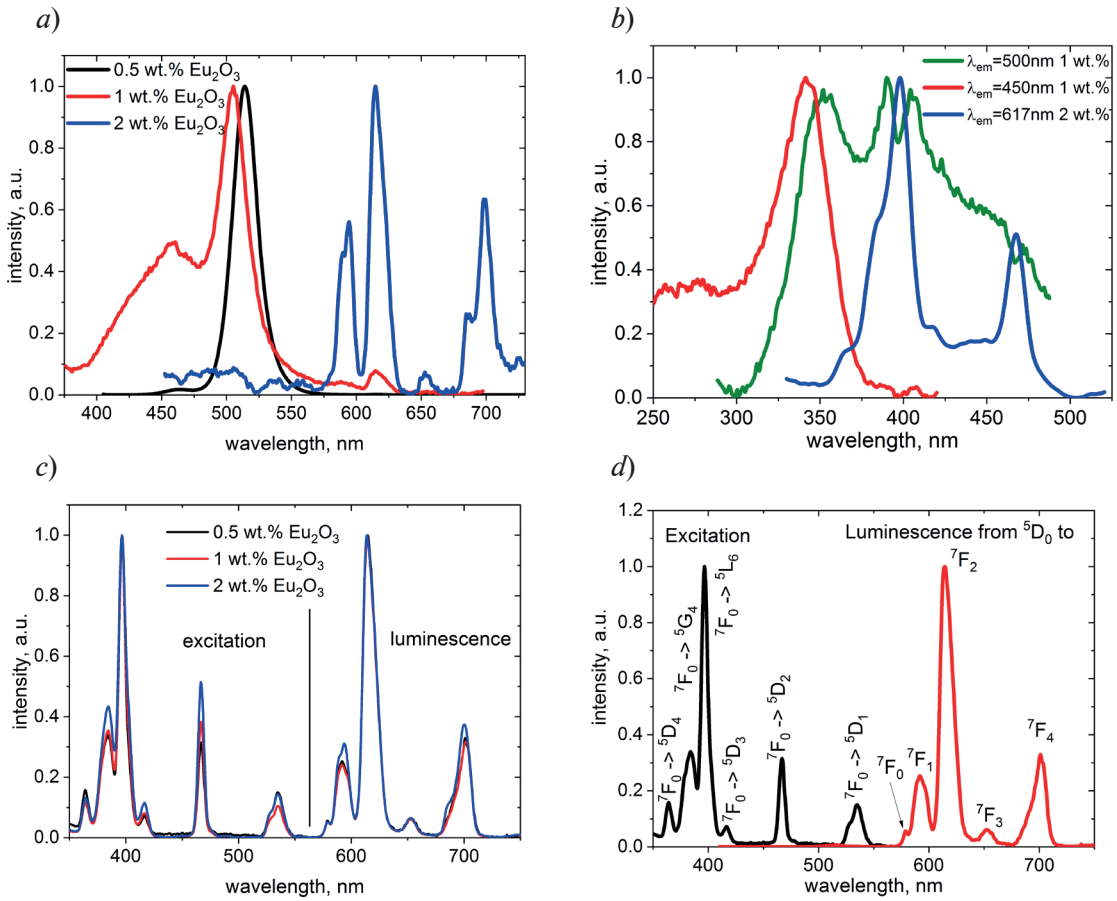


Fig. 2. Luminescence spectra of the glasses under study ($\lambda_{ex}$ = 395 nm) (*a*), photoexcitation spectra for different glass and different luminescence wavelengths (*b*), luminescence spectra of the glasses under study with the delay of 0.05 msec ($\lambda_{ex}$ = 395 nm) (*c*), luminescence and corresponding excitation spectra for glass with 0.5 wt.% $Eu_2O_3$, recorded with the delay of 0.05 msec (*d*)

In two of the three glass compositions, the nanocrystals' luminescence significantly exceeded the $Eu^{3+}$ luminescence, even though the intensity of the $CsPbBr_3$ exciton absorption band was minimal or absent altogether. The luminescence lifetime of $CsPbBr_3$ is limited to 30 ns [7], and the luminescence lifetime of europium ions in glasses can reach 2 ms [8]. The luminescence spectra of the material were recorded in the presence of a delay between the exciting pulse and signal detection of 0.05 ms (Fig. 2, *c*, *d*). This delay completely neutralized the influence of the $CsPbBr_3$ luminescence on the spectra, leaving only $Eu^{3+}$ bands. The luminescence intensity ratio (R) between intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions' bands measures the interaction strength between the host matrix and the dopant ions. The symmetry local site without inversion center around $Eu^{3+}$ ion leads to a higher value of R (R > 1), the opposite would lead to 1 > R > 0 [5]. The increase of the $Eu_2O_3$ content led to R decrease from 4.2 to 3.2, which indicated a slight change in the symmetry of the ligand field around $Eu^{3+}$ ions.

Using time-resolved luminescence spectroscopy, the luminescence lifetimes of $Eu^{3+}$ ions were obtained separately. Luminescence decay kinetics at 615 nm for glasses with 0.5 wt.% $Eu_2O_3$ and 1 wt.% $Eu_2O_3$ was approximated by a single exponential with decay times of 1.58 and 1.69 ± 0.02 ms, respectively. Luminescence decay kinetics at 615 nm in a composition with 2 wt.% $Eu_2O_3$ was approximated by two exponential components with lifetimes of 0.17 and 1.65 ms.

## Conclusion

As a result of the work, borogermanate glasses with $CsPbBr_3$ perovskite nanocrystals and different concentrations of $Eu_2O_3$ were synthesized. At low concentrations $Eu^{3+}$ ions played the role of crystallization centers for the nucleation of perovskite nanocrystals. At a high concentration of $Eu^{3+}$ ions, perovskite crystals nucleated only during additional heat treatment. The decay time of $Eu^{3+}$ luminescence increased along with an increase in the $Eu_2O_3$ content in glass. Along this, a slight distortion of the environment around $Eu^{3+}$ ions occurred.

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