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# Effect of femtosecond irradiation on the luminescence of CsPbI<sub>3</sub> perovskite crystals in borogermanate glass

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## ABSTRACT

The article demonstrates femtosecond-laser-induced crystallization of CsPbI<sub>3</sub> perovskite nanocrystals in borogermanate glass with no additional heat treatment. With an increase in the laser radiation power, the mean size of the precipitated crystals increases, which leads to the luminescence redshift from 660 up to 700 nm and its width decrease from 60 down to 35 nm. An increase in the mean size of CsPbI<sub>3</sub> nanocrystals is also accompanied by an increase in the size of the laser exposure modified region. The appearance of CsPbI<sub>3</sub> after irradiation with without additional heat treatment indicates the prospects for using this material for the repeated optical information recording.

## KEYWORDS

cesium lead iodide perovskite • borogermanate glass • femtosecond irradiation • laser-induced crystallization

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## Introduction

Cesium lead halide (CsPbX<sub>3</sub>) quantum dots (QDs) have attracted big attention because of their remarkable optical properties, such as size-dependent emission wavelengths, narrow emission spectra and high photoluminescence quantum yields [1–5]. They possess great potential applications in light-emitting diodes, lasers, solar cells and photodetectors. The propensity of lead-cesium halide nanocrystals to atmospheric air oxidation and low-temperature phase transitions led to the idea of their stabilization in a polymer [6–8] or glassy matrix [9–12]. Traditionally for glass-ceramics, isothermal heat treatment at temperatures exceeding glass transition temperature is a favorable way to realize controllable nucleation and volume nanocrystal growth in glass greed. This is the way when the optical properties of QDs can be guaranteed for a long-term period. On the other hand, femtosecond laser [13,14], due to its short pulse width and high peak power, can induce high transient temperature field, which is enough for the nuclei formation of QDs. Nonlinear absorption process happens while the fs laser interacts with the glass matrix, leading to the destruction of the glass network and the redistribution of atoms at the laser focal area, which is beneficial for ion migration to form nanocrystals and for the reduction in crystallization temperature. A promising application of laser crystallization of a glass matrix is the optical recording and storage of information with the spatial selectivity up to nanoscale [15–17]. However, in most studies [13,14], to obtain perovskite nanocrystals in a glass matrix after femtosecond irradiation, it is necessary to carry

out additional heat treatment, which makes this method unsuitable for single-stage information recording.

Here, the luminescent properties of CsPbI<sub>3</sub> nanocrystals, obtained by laser-induced crystallization in borogermanate glass, are demonstrated.

## Materials and Methods

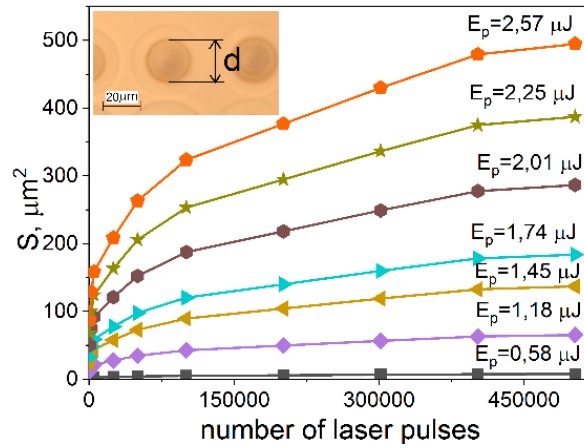
The initial glass matrix had the following composition: 6.67 ZnO-5.81 Na<sub>2</sub>O-31.3 B<sub>2</sub>O<sub>3</sub>-50.53 GeO<sub>2</sub> mol. %. The synthesis was carried out in air atmosphere at a temperature of 950 °C for 30 min using closed quartz crucibles [18,19]. For the subsequent nucleation of CsPbI<sub>3</sub> perovskite nanocrystals, CsCO<sub>3</sub>, PbO and KI were added to the batch composition. The luminescence spectra were studied with a Renishaw inVia Raman Microscope of 100–7000 cm<sup>-1</sup> working range at room temperature with the excitation wavelengths of 633 and 514 nm and 20× build-in lens. Laser-driven crystallization was obtained by ANTAUS femtosecond laser (AVESTA, operating wavelength of 1030 nm, pulse duration of 224 fs, pulse repetition rate of 50 and 100 kHz, pulse energy from 0.58 to 2.57 μJ, the pulse quantity in the irradiated region from 500 to 500,000). The laser beam was focused by the microscope objective lens with an N.A. of 0.4.

## Results and Discussion

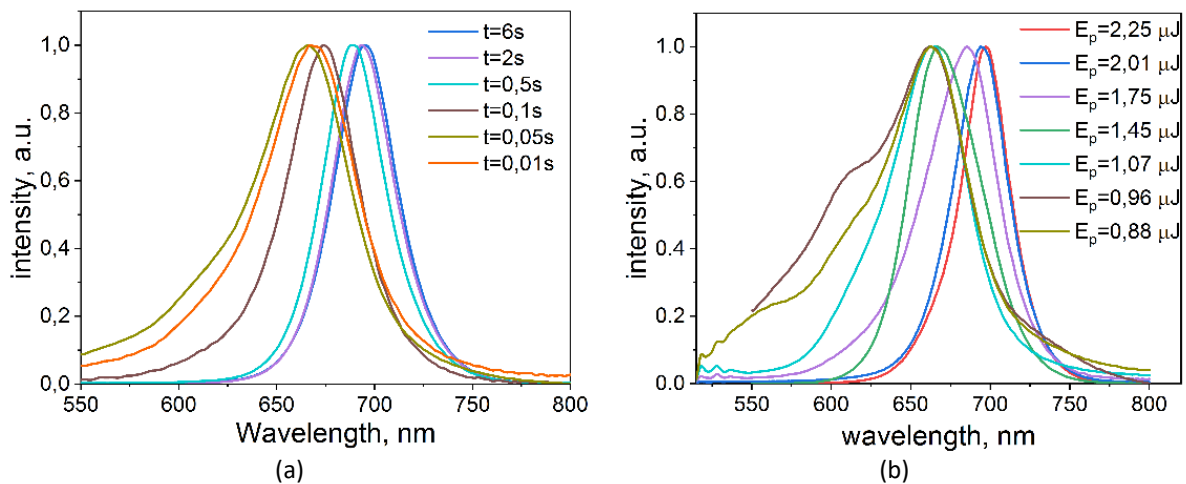
Insert in Fig. 1 shows photograph of the patterns obtained by femtosecond laser irradiation of glasses under study, whose ring-shaped prints are quite characteristic [20,21]. An optical breakdown zone is observed in the center of the ring: in the region of the laser beam waist, nonlinear multiphoton absorption occurred, due to which the local volume of glass was intensely heated, and thus expanded, creating stresses and leading to the destruction of the material [20]. The dark region, the size of which is designated as  $d$ , determines the temperature zone within which color centers were formed in the glass matrix due to the breaking of O-Ge-O bonds [22]. Due to the high contrast of this area with the neighboring one, using a Carl Zeiss microscope and built-in software, we determined the size  $d$ . Based on this size, we calculated the area of the modification zone  $S$  (Fig. 1), taking it to be ideally spherical as a first approximation. Further studies of the luminescent properties showed that CsPbI<sub>3</sub> nanocrystals were formed at the edges of this region. The largest light modified area indicated a change in the density and refractive index of the material without the formation of nanocrystals. Figure 1 shows the dependence of the modified area  $S$ , within which the nanocrystals were formed, on the number of pulses at different pulse energies  $E_p$ . When the number of pulses was less than 50,000, the modified area increased significantly; with a further increase in the number of pulses up to 500,000, the modified area increased only twofold. If we trace the dependence of the modified area on the pulse energy, it will be close to a linear function, in which the proportionality coefficient will depend on the exposure time (that is, the number of pulses).

The initial glass did not possess luminescence but contained all the components necessary for the formation of CsPbI<sub>3</sub> crystals. After femtosecond irradiation along the inner edge of the dark modified region, the size of which is shown in Fig. 1, red luminescence was detected. Figure 2 shows the luminescence spectra obtained after different laser exposure time (a) and with different pulse energy (b). Luminescence spectra were recorded under 514 nm laser excitation through the optical system of a microscope with a lens ×50. The luminescence maximum located in the region of 660–695 nm and the FWHM varied within 35–60 nm, which is typical for CsPbI<sub>3</sub> perovskite nanocrystals in glass [23,24]. As the pulse energy and their

number decreased, the luminescence spectrum shifted towards short wavelengths and widens. The luminescence intensity increased with increasing exposure time and pulse energy, however, since the optical design of the microscope is not intended for absolute measurement of intensity, but only relative, all spectra in Fig. 2 are shown normalized.



**Fig. 1.** The area of the modified region with nucleated CsPbI<sub>3</sub> QDs ( $S$ ) vs. number of fs laser pulses at different pulse energy  $E_p$ ; the insert: determining the size  $d$  of the modified area

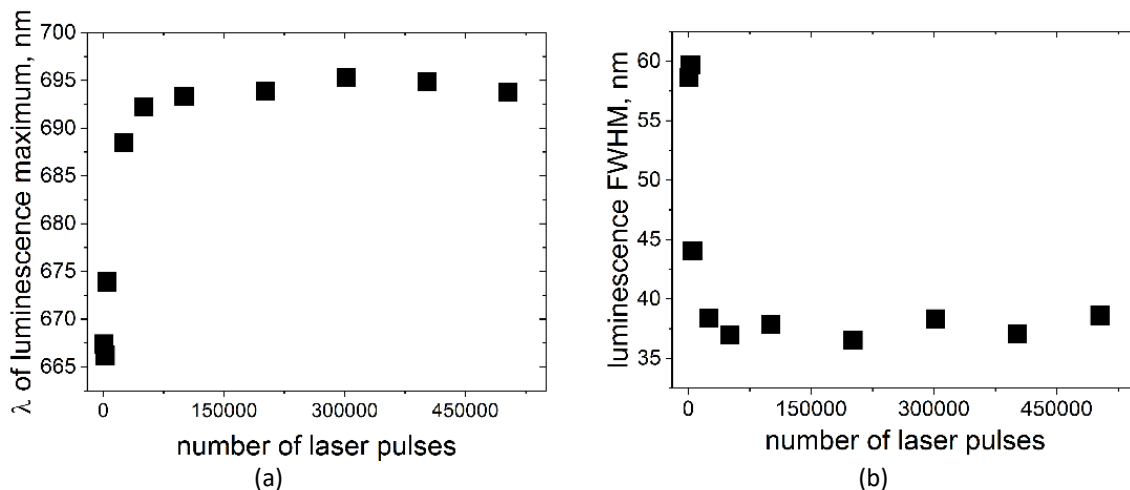


**Fig. 2.** Luminescence spectra of CsPbI<sub>3</sub> QDs in borogermanate glass obtained after fs laser exposure with different duration at  $E_p=2.57 \mu\text{J}$  (a), and at different pulse energy for duration of 10 s (b)

While using the maximum pulse energy (Fig. 2(a)), during the exposure time decrease from 10 to 0.01 seconds, the luminescence band maximum shifted from 695 to 666 nm, and the luminescence FWHM increased from 37 to 59 nm. Such transformations of the luminescence spectrum of semiconductor crystals indicate the presence of a size effect: with an increase in the mean size of QDs, the luminescence spectrum shifted to long wavelengths and vice versa [25–27]. The peculiarity of the crystal nucleation in glass meant that with a decrease in the mean size of crystals' ensemble, its size dispersion broadened, along with which the luminescence band width increased [25]. This means that with an increase in the laser exposure energy, the mean size of the crystals increased. For the shortest exposure time, the second luminescence band appeared near 610 nm. Figure 3 shows that the main changes in the luminescence spectrum occurred in the pulse number range up to 50,000, as in the case

of the modified area in Fig. 1. When the number of pulses was exceeded, the FWHM and the luminescence maximum location remained practically unchanged.

When the pulse energy changes (Fig. 2(b)), the transformation of the luminescence spectrum turned out to be more complicated. Quantitative changes (of location and FWHM) had the same range as in the first case. However, when small pulse energies were used, additional bands clearly appeared in the luminescence spectrum: at 610 and 560 nm. Their appearance may indicate that, in this case, the total radiation energy transferred to the material was insufficient for the formation of large crystals; therefore, instead of them, small crystals and clusters were formed in the glass structure, which can play a role of the nuclei of the crystalline phase [25–27] and can have luminescence in shorter wavelengths, but with bigger FWHM.



**Fig. 3.** Dependence of the maximum location (a) and FWHM (b) of CsPbI<sub>3</sub> QDs' luminescence on the number of fs laser pulses ( $E_p=2.57 \mu\text{J}$ )

An increase in laser exposure energy led to an increase in the size of the glass modified zone and the volume of the material, from which diffusion of cesium, lead, and iodine ions occurred for the subsequent formation of crystals during the cooling after laser exposure. It has been shown [28–30] that perovskite crystals precipitated only during the femtosecond laser exposure and the subsequent heat treatment of glass. This was since, during laser irradiation, perovskite crystals were formed in the glass matrix; however, a large number of defects in them led to nonradiative transfer of excitation and hence luminescence quenching. Subsequent heat treatment led to the relaxation of defects, the reduction of the nonradiative channel, and the appearance of luminescence of perovskite crystals. In our case, luminescence of perovskite CsPbI<sub>3</sub> nanocrystals was observed immediately after laser exposure, which is more promising for repeated recording and storage of information in glass using principles of local crystallization.

## Conclusions

Femtosecond-laser-induced crystallization of CsPbI<sub>3</sub> perovskite nanocrystals in borogermanate glass with no additional heat treatment was demonstrated. With an increase in the laser radiation energy, the mean size of the precipitated crystals increased, which led to the luminescence redshift from 660 up to 700 nm and FWHM decrease from 60 down to 35 nm. The absence of subsequent heat treatment to obtain the luminescence of crystals was promising for the development of materials for repeated optical recording of information.

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