

## Article

# Highly Luminescent Rb-Doped Cs<sub>4</sub>PbBr<sub>6</sub> Nanocrystals in Borogermanate Glass

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**Abstract:** For the first time, the synthesis, luminescent and structural properties of stable perovskite-type (Cs<sub>1-x</sub>Rb<sub>x</sub>)<sub>4</sub>PbBr<sub>6</sub> (R = Cs, Rb) nanocrystals are shown. In the absence of rubidium, Cs<sub>4</sub>PbBr<sub>6</sub> and CsPbBr<sub>3</sub> perovskite crystals precipitate in the ZnO–Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub> glass matrix. With ascending rubidium content, the precipitation of (Cs,Rb)<sub>4</sub>PbBr<sub>6</sub> nanocrystals is replaced by the Rb<sub>4</sub>PbBr<sub>6</sub> nanocrystals nucleation. Nucleated nanocrystals exhibit an intense green luminescence. With an increase of the rubidium content, the luminescence maximum shifts to the blue region, the luminescence quantum yield increases from 28 to 51%, and the average decay time increases from 2 to 8 ns. Several assumptions have been made about the nature of the green luminescence of perovskite-like Cs<sub>4</sub>PbBr<sub>6</sub> and (Cs,Rb)<sub>4</sub>PbBr<sub>6</sub> crystals in glasses. It is concluded that the most probable cause is the impurity inclusions of CsPbBr<sub>3</sub> and (Cs,Rb)PbBr<sub>3</sub> crystals.

**Keywords:** perovskite quantum dots; cesium lead bromide perovskite; Rb-doping; Cs<sub>4</sub>PbBr<sub>6</sub> quantum dots; borogermanate glass



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## 1. Introduction

About 25% of the world's electricity demand is used for lighting [1]. White light-emitting diodes, which are much more efficient than incandescent and fluorescent lamps, are becoming more and more popular in order to reduce lighting energy costs. Using semiconductor quantum dots in light sources, it is possible to achieve a good spectral overlap between the sensitivity of the eye and the emission spectrum. Light emission can also be adjusted to the desired hue [2].

By varying the halogen ions in perovskite CsPbHal<sub>3</sub> nanocrystals, the luminescence color of the material can be changed over the entire visible region. Since CsPbHal<sub>3</sub> crystals can be created both with one type of halogen ion, and with two at the same time, the luminescence peak wavelength can be tuned with a very small spectral step by varying the ratio of the corresponding halogens. By now, many works have shown the possibility of obtaining mixed chlorine-bromine [3] and bromine-iodine [4,5] perovskite crystals, both in solutions and in glass matrices. In addition, due to their relatively low energy of formation and high resistance to defects, they can be easily synthesized with simple procedures at much lower temperatures [6].

However, in addition to the halogen-ion replacement in perovskite crystals, the replacement of the alkali ion is also possible. Many studies have shown both complete and partial replacement of cesium ions by rubidium and potassium ions in colloidal perovskite nanocrystals of CsPbCl<sub>3</sub> [7,8], CsPbBr<sub>2</sub>Cl [9], CsPbBr<sub>3</sub> [10–12], and CsPbBrI<sub>2</sub> [13]. There

are much fewer similar works on the preparation of perovskite nanocrystals with mixed alkali ions in glass, since the alkali ions in the glass structure play the role of the grid modifiers and do not tend to enter the crystalline phase so actively. However, the preparation of Pb-crystals of perovskites  $\text{CsPbBr}_3$  [14] and K-doped crystals of  $\text{CsPbI}_3$  [15] and  $\text{CsPbBr}_3$  [12] in zinc-borosilicate glass was shown. When a cesium ion is replaced by any smaller alkali ion, a short-wavelength shift of the luminescence maximum occurs from 5 nm [15] up to 50 nm [14]. Structurally, the occurrence of Rb and K ions in  $\text{CsPbBr}_3$  crystals is usually proved by reflection shifts in the diffraction pattern towards large angles relative to the reflections' position of pure  $\text{CsPbBr}_3$ . However, all studies show a shift of diffraction reflections by tenths of a degree with almost complete replacement of cesium ions by other alkalis, which raises doubts that the substitution of alkali ions can have such a strong effect on the luminescence location of nanocrystals.

Much controversy considers the fact that crystals of the  $\text{A}_4\text{PbX}_6$  type have luminescence in the visible region. The first works on growing and studying the optical properties of perovskite and perovskite-like single crystals were published by Nikl et al. [16–19]. They showed that the electronic structure of  $\text{Cs}_4\text{PbBr}_6$  was similar to the electronic structure of  $\text{PbBr}_2$  crystals. The exciton absorption bands in  $\text{PbBr}_2$  crystals were due to the  $^1s_0 \rightarrow ^3p_1$  transition of the cationic Frenkel exciton [16] in  $\text{Pb}^{2+}$  ions [20]. The exciton absorption edge occurred at 310–330 nm, and the maximum exciton luminescence occurred at 360–380 nm. This is a spin-forbidden transition, which can be partially allowed due to spin-orbit interaction. According to Schmitt [21], when potassium ions in the  $\text{KBr}:\text{Pb}^{2+}$  crystalline matrix were replaced by rubidium ions, the luminescence lifetime of lead ions slightly increased, and the maximum luminescence band shifted to the red region. According to Nickl et al. [18,22], the lifetime of the main  $\text{Pb}^{2+}$  luminescence band in the region of 360 nm was about several milliseconds. A similar luminescence lifetime was found in  $\text{Cs}_4\text{PbCl}_6$  crystals [23], which was correlated with the luminescence of isolated  $\text{Pb}^{2+}$ -emitting centers. The luminescence in  $\text{CsPbCl}_3$  crystals can be explained under the assumption of Wannier–Mott exciton creation in the  $\text{Pb}^{2+}$  sublattice, possessing a lifetime on the order of several nanoseconds [24] and subject to a strong quantum size effect [25].

Starting from 1995, various authors [26–29] have shown that when  $\text{CsCl}:\text{Pb}^{2+}$  crystals were grown,  $\text{CsPbCl}_3$  aggregates spontaneously appeared in them, which had intense narrow-band luminescence with short lifetimes. When works on  $\text{Cs}_4\text{PbBr}_6$  crystals with green luminescence appeared in the literature, debates about the nature of this luminescence began [30–33]. Saidaminov et al. [31] reported the preparation of a highly luminescent phosphor and claimed that the high-luminescence quantum yield (QY) originated from  $\text{PbBr}_6^{4-}$  octahedra in  $\text{Cs}_4\text{PbBr}_6$ . However, in perovskite, octahedra are corner-sharing, and both 6s and 6p states of Pb participate in the construction of conduction and valence bands. In  $\text{Cs}_4\text{PbBr}_6$ , the octahedra are isolated from each other, causing a discontinuity of the electronic structure and an ultra-large  $E_g$  [34]. It was shown [35] that in the absorption spectra of single crystals or crystalline films of  $\text{Cs}_4\text{PbBr}_6$ , in addition to the absorption bands in the near UV region, a low-intensity absorption band at about 500 nm was observed, which corresponded to the absorption of  $\text{CsPbBr}_3$ .

It is assumed [36] that the structure of  $\text{Rb}_4\text{PbBr}_6$  crystals will coincide with that of  $\text{Cs}_4\text{PbBr}_6$ , and their absorption bands will also locate in the near UV spectral range with the corresponding luminescence in the blue region corresponding to Frenkel excitons in  $\text{Pb}^{2+}$  ions. However, single crystals or crystalline films of this composition have not been reported so far. Only the preparation of  $\text{Rb}_4\text{PbBr}_6$  crystals in the form of a shell on  $\text{CsPbBr}_3$  crystals has been shown [6], while  $\text{Rb}_4\text{PbBr}_6$  crystals did not exhibit any characteristic spectral properties, only increasing the luminescence stability of  $\text{CsPbBr}_3$  crystals.

Thus, this work shows the precipitation of  $(\text{Cs,Rb})_4\text{PbBr}_6$  nanocrystals in a borogermanate matrix glass upon equimolecular substitution of rubidium ions for cesium ions, and the effect of this substitution on the luminescent and structural properties of nanocrystals.

## 2. Materials and Methods

### 2.1. Material Synthesis

For the study, a series of borogermanate glasses with a composition of: 23.59 B<sub>2</sub>O<sub>3</sub>–38.09 GeO<sub>2</sub>–6.41 Na<sub>2</sub>O–5.03 ZnO–1.38 P<sub>2</sub>O<sub>5</sub>–2.85 TiO<sub>2</sub>–4.99 K<sub>2</sub>O–5.41 × (1 – x) Cs<sub>2</sub>O–(5.41 × x) Rb<sub>2</sub>O–2.26 PbO–9.98 Br mol.%, where x = 0; 0.25; 0.5; 0.75 (x is calculated from the batch composition) was chosen. Glass was synthesized in an air atmosphere at a temperature of 950 °C for 30 min. Perovskite nanocrystals were precipitated in the glass matrix during fine annealing from 450 °C.

The studies of glass chemical composition were performed by X-ray fluorescence spectroscopy (XRF) using an X-ray fluorescence spectrometer ARL PERFORM'X by Thermo Scientific with Rh tube, 4.2 kW/60kV generator, FPC and Sc detectors (detectable chemical elements: from oxygen to uranium). The study was performed at ambient temperature in the vacuum atmosphere. The chemical composition was averaged over a sample area of 20 mm<sup>2</sup>.

### 2.2. Spectral Characterisation

UV-Vis-NIR absorption spectra were recorded using a Lambda 650 two-beam spectrophotometer (Perkin Elmer, Waltham, MA, USA) in the 300–900 nm range, with a step of 1 nm and an integration time of 1 s. Plane samples 0.2 mm thick, polished on both sides, were used for the measurements.

Photoexcitation and photoluminescence spectra were obtained by spectrofluorometer LS-55 (Perkin Elmer) in the 200–900 nm region with 1 nm step.

Absolute quantum yield was measured on an Absolute PL Quantum Yield Measurement System C9920-02G, -03G (Hamamatsu, Hamamatsu City, Japan), consisting of PMA-12 Photonic multichannel analyzer with a InGaAs sensor (200–950 nm range with 2 nm resolution), A10104-01 Integrating sphere unit, Monochromatic light source L9799-01 with a 150 W Xenon light source, and remote-controlled monochromator (250–950 nm range, bandwidth from 2 to 5 nm).

Photoluminescence decay curves were measured at emission peak for each sample by the time-correlated, single-photon counting (TCSPC) technique with a confocal microscope NTEGRA Spectra, equipped with a 473 nm diode laser (40 ps pulse width, 20 MHz repetition rate) as an excitation source and a photomultiplier tube (PMT) as a detector. Excitation light was focused on a sample surface by 10x objective (NA = 0.28) with average power density 0.3 W/cm<sup>2</sup>.

### 2.3. Structural Characterisation

X-ray diffraction patterns were obtained using a Rigaku Ultima IV X-ray diffractometer (Japan) at room temperature. The radiation from a copper anode with  $\lambda$  (CuK $\alpha$ ) = 1.5418 Å was used with the filter for a CuK $\beta$  radiation. The X-ray diffraction patterns were taken in the 2 $\theta$ / $\theta$  angle range from 18° to 36° in the Bragg–Brentano geometry with the scanning speed of 0.25°/min. In the experiment, the voltage across the tube was 40 kV, the current was 40 mA, and the output power was 1.6 kW. The diffraction reflections were interpreted using the ICDD PDF-2 diffraction database. For the calculation of the X-ray diffraction patterns, the positions of the diffraction peaks were determined, and the relative integral intensity was calculated.

## 3. Results

### 3.1. XRF Studies

In the process of glass synthesis, its real chemical composition begins to differ from the chemical composition of the batch. Because of this, the XRF analysis was carried out, the results of which are presented in Table 1. Since boron is too light of an element for the XRF method, we assumed that its weight content in the glass composition remained the same as in the batch. Based on this assumption, the glass composition obtained by XRF measurements was recalculated and shown in Table 1. The actual ratio of the content of

rubidium/cesium ions in the series of glasses under study was as follows: 0/1; 0.1/0.9; 0.3/0.7; 0.5/0.5.

**Table 1.** The calculated batch composition and the glass compositions according to XRF results (mol. %).

| Components                    | Composition #2 |         | Composition #3 |         | Composition #4 |         |
|-------------------------------|----------------|---------|----------------|---------|----------------|---------|
|                               | Batch          | XRF     | Batch          | XRF     | Batch          | XRF     |
| Na <sub>2</sub> O             | 6.65           | 3.67    | 6.65           | 3.33    | 6.65           | 5.11    |
| Cs <sub>2</sub> O             | 5.59           | 11.12   | 3.74           | 6.9     | 1.87           | 3.58    |
| Rb <sub>2</sub> O             | 1.86           | 1.52    | 3.71           | 2.8     | 5.57           | 4.18    |
| ZnO                           | 5.21           | 3.27    | 5.21           | 4.31    | 5.21           | 3.65    |
| B <sub>2</sub> O <sub>3</sub> | 24.46          | 27.75   | 24.46          | 26.84   | 24.46          | 25.45   |
| GeO <sub>2</sub>              | 39.48          | 39.75   | 39.48          | 41.75   | 39.48          | 43.31   |
| TiO <sub>2</sub>              | 1.77           | 0.85    | 1.77           | 1.59    | 1.77           | 2.6     |
| PbO                           | 1.92           | 3.94    | 1.92           | 4.25    | 1.92           | 3.57    |
| K <sub>2</sub> O              | 3.96           | 1.77    | 3.96           | 1.99    | 3.96           | 2.58    |
| Br                            | 7.92           | 4.71    | 7.92           | 4.21    | 7.92           | 3.85    |
| P <sub>2</sub> O <sub>5</sub> | 1.18           | 1.66    | 1.18           | 2.02    | 1.18           | 2.12    |
| Cs/Rb ratio                   | 0.75/0.25      | 0.9/0.1 | 0.5/0.5        | 0.3/0.7 | 0.25/0.75      | 0.5/0.5 |

The volatility of halogens leads to a strong decrease in their concentration in the glass composition despite the low-synthesis temperature. However, the remaining amount was enough for the formation of perovskite nanocrystals in such a concentration that the glass possessed high-intensity luminescence, which is presented below.

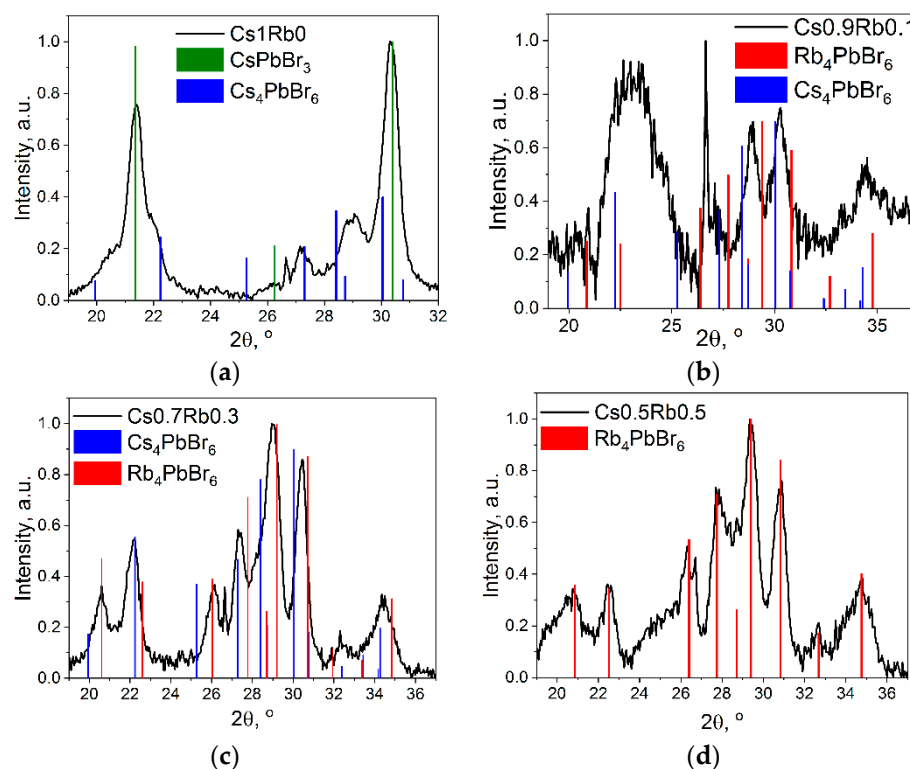
### 3.2. Structural Properties

The dimensionality degree of the perovskite materials is determined by the connections of the octahedral units. In Cs<sub>4</sub>PbBr<sub>6</sub> crystals, the [PbX<sub>6</sub>]<sup>4−</sup> octahedral units are completely isolated, which make these crystals a so-called “0D perovskite”; however, in a strict approximation, these crystals do not have the perovskite structure. The CsPbBr<sub>3</sub> crystal is the case of a three-dimensional perovskite with complete corner sharing octahedra. The cations are situated in the voids created by the octahedral fragments. The spatial arrangement of the lead-halide octahedra is largely influenced by the size of the A cation and the A:B:X stoichiometry [37].

In Composition 1, the nucleation of CsPbBr<sub>3</sub> (cubic  $\overline{Pm}3m$  space group,  $a = b = c = 5.95 \text{ \AA}$  [38]) and Cs<sub>4</sub>PbBr<sub>6</sub> (trigonal, R-3c,  $a = 13.7216 \text{ \AA}$ ,  $b = 13.7219 \text{ \AA}$ ,  $c = 17.3153 \text{ \AA}$  [39]) was obtained (Figure 1a). The Cs<sup>+</sup> cations in Cs<sub>4</sub>PbX<sub>6</sub> have split into two distinct sites [39]. The structure consists of alternating [PbX<sub>6</sub>]<sup>4−</sup> octahedra and Cs<sup>+</sup>(2) trigonal prisms that share one trigonal face to form infinite [CsPbX<sub>6</sub>]<sub>n</sub><sup>3−</sup> chains perpendicular to the c axis. These chains are joined together through six Cs<sup>+</sup>(1) cations, forming edge-sharing distorted decahedra that are corrugated chains extending along the [001] direction [37].

The coexistence of both compounds has been reported before, in bulk and thin films, as well as in nanometer-sized aggregates dispersed in a crystal lattice. CsPbBr<sub>3</sub> NCs embedded in the Cs<sub>4</sub>PbBr<sub>6</sub> matrix with high PLQY and stability can be synthesized due to good lattice matching [40,41]. Because of this, it is also rather difficult to prove the production of a core/shell CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> system, since the crystalline phases are more likely to mix, forming a continuous solid solution [40]. However, in [42,43], it is argued that the Cs<sub>4</sub>PbBr<sub>6</sub> layer passivates and stabilizes the CsPbBr<sub>3</sub> particles.

It is noted in [44,45] that the CsPbX<sub>3</sub> impurity phase is likely unavoidable in melt-grown Cs<sub>4</sub>PbX<sub>6</sub> because of incongruent melting in its phase diagram. However, the reverse situation (inclusions of Cs<sub>4</sub>PbBr<sub>6</sub> in CsPbBr<sub>3</sub> crystals) occurs much less frequently and in those cases when the content of cesium in the composition is several times higher than the content of lead [46].



**Figure 1.** XRD patterns of glass composition № 1 (a), № 2 (b), № 3 (c), № 4 (d), vertical lines indicate the positions of reflections for CsPbBr<sub>3</sub> (card № 01-072-7931), Cs<sub>4</sub>PbBr<sub>6</sub> (cif № 1538416), Rb<sub>4</sub>PbBr<sub>6</sub> (cif № 1539639).

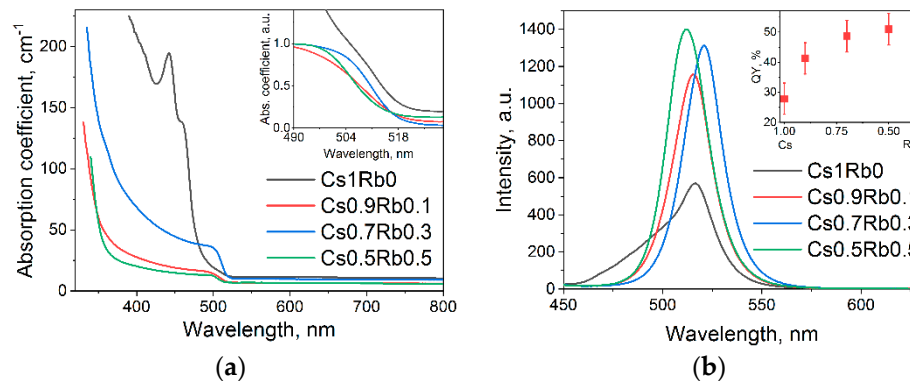
Compositions 2 and 3 contain a crystalline phase whose diffraction maxima occupy exactly an intermediate position between the peaks of pure Cs<sub>4</sub>PbBr<sub>6</sub> and Rb<sub>4</sub>PbBr<sub>6</sub> crystals (Figure 1b,c), while in Composition 2, the reflections are closer to Cs<sub>4</sub>PbBr<sub>6</sub>, and in Composition 3, they are closer to Rb<sub>4</sub>PbBr<sub>6</sub>. Thus, due to the compression/stretching of the crystal lattice, due to the introduction of alkali ions of smaller or larger diameters, respectively, this led to a subsequent change in the lattice parameters. The introduction of rubidium ions into pure cesium crystals shifts the diffraction maxima towards higher angles, due to the lattice contraction with a smaller, alkali metal ion [6] by an average of 0.26° [47].

There is no unequivocal information on the formation of crystals of the A<sub>4</sub>PbX<sub>6</sub> type upon substitution of an alkali ion. However, there is information about the possibility of the nucleation of crystals of the Cs<sub>4</sub>PbX<sub>6</sub> type, where X = Br, I [48]. In [10,13], partial substitution of Cs for Rb ions in crystals of the APbBr<sub>3</sub> type is shown. At the same time, the diffraction patterns in Figure 2b,c do not contain reflections corresponding to CsPbBr<sub>3</sub> crystals.

In Composition 4, the Rb<sub>4</sub>PbBr<sub>6</sub> phase (trigonal  $\bar{R}3c$  space group,  $a = 13.4$  Å,  $b = 13.4$  Å,  $c = 16.56$  Å) prevails (Figure 1d). The position of the diffraction peaks of these crystals was determined purely theoretically, based on DFT calculations by Körbel et al. [36], since Rb<sub>4</sub>PbBr<sub>6</sub> single crystals have not yet been obtained. Wang and others [6] show the preparation of a CsPbBr<sub>3</sub>/Rb<sub>4</sub>PbBr<sub>6</sub> system of the core/shell type. Confirmation of the crystals' chemical composition and type was provided based on XRD data; however, the authors themselves admitted that they could not fully prove that the resulting structures really consist of a core/shell, and not of mixed crystalline inclusions. The glass diffraction pattern also lacks peaks corresponding to RbPbBr<sub>3</sub> crystals. RbPbBr<sub>3</sub> was predicted, and the location of diffraction peaks was calculated by Körbel in [36], but there is no evidence that such crystals could be obtained experimentally in the form of a single crystal, microcrystalline powders, or nanocrystals in an amorphous matrix.



The average size of nanocrystals in the series of Compositions 2–4 is the largest for Composition 2; therefore, the location of its luminescence band falls out of the tendency to shift to the short-wavelength region with an increase in the rubidium content, which will be shown below.



**Figure 2.** (a) Absorption spectra of the perovskite glass with different Cs/Rb ratio; the insert shows normalized spectra near the absorption edge at 510 nm. (b) Photoluminescence spectra of these glass under excitation of 390 nm. The inset: concentration dependence of QY.

### 3.3. Spectral Properties

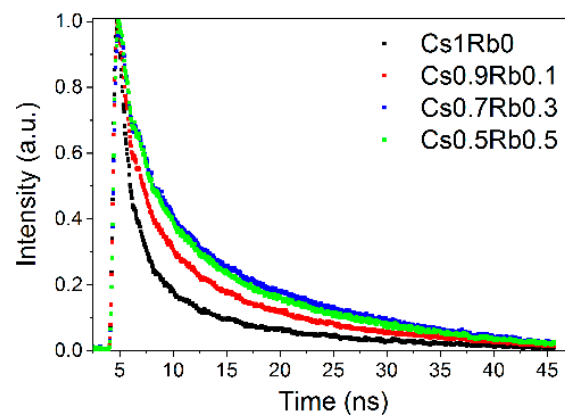
Figure 2a demonstrates absorption spectra of the obtained glass with different rubidium/caesium ions concentrations ratio. The spectra demonstrate exciton absorption in the direct gap semiconductor crystal near 520 nm [4,5,7]. According to XRD data, all samples contain a crystalline phase of the  $A_4\text{PbBr}_6$  type, which is characterized by a large band gap and a corresponding arrangement of absorption bands at wavelengths of 317 nm or less. However, in our case, the concentration of the crystalline phase did not allow us to resolve absorption bands in the near UV region for most glasses, except for Composition 1. Perhaps, this confirms that there are  $\text{Cs}_4\text{PbBr}_6$  absorption bands. This also affected on the luminescence spectra of this composition, providing two close-locating bands (Figure 2b). The insert in Figure 2a illustrates the change of the absorption edge location depending on the Cs/Rb ratio. The main trend is that the edge shifts towards short wavelengths while rubidium concentration increases. The luminescence peak location shows the same behavior when shifting for 10 nm from Compositions 2 to 4. The inset in Figure 1b presents the results of absolute quantum yield (QY) measurements, and its value increases up to 51% with the ascending  $\text{Rb}^+$  ions concentration.

The luminescence decay curves (Figure 3) were obtained at wavelengths corresponding to the maximum of the emission band upon excitation at a wavelength of 473 nm. The measured curves were fitted with a bi-exponential decay function. The parameters of fitted curves are presented in Table 2, in which the short-lived component ( $\tau_1$ ) is related to the energy transfer to trap states, and the long-lived component ( $\tau_2$ ) associates to the exciton recombination transitions. For some applications of glasses doped with perovskite nanocrystals, for example, scintillators, where the lifetime of emission plays an important role but is not measured directly, one of the key characteristics is the average lifetime. The average fluorescence lifetimes were calculated with the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (1)$$

where  $A_i$  is the amplitude of component  $i$ , and  $\tau_i$  is the lifetime of component  $i$ . The duration of both components, as well as the average lifetime, grows with increasing rubidium content up to 0.3, and presents small changes with further increase. The order of the obtained lifetimes coincides with that of pure  $\text{CsPbX}_3$  [7,42] and mixed  $\text{CsPbBr}_3/\text{Rb}_4\text{PbBr}_6$  [6] nanocrystals. For  $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$  hybrid- or hetero-structures, the lifetime is several

tens of nanoseconds [49,50]. The luminescence of lead ion impurities in alkali halide crystals is on the order of several milliseconds [37].



**Figure 3.** Fluorescence decay kinetics of perovskite glass with different Cs/Rb ratio.

**Table 2.** Fluorescence lifetimes of perovskite nanocrystals in the studied glass-ceramics.  $\tau_i$ —lifetime of  $i$  fluorescence component,  $\tau_{avg}$ —average fluorescence lifetime, excitation wavelength  $\lambda_{ex} = 473$  nm.

| Sample     | $A_1$ | $\tau_1$ (ns) | $A_2$ | $\tau_2$ (ns) | $\tau_{avg}$ (ns) |
|------------|-------|---------------|-------|---------------|-------------------|
| Cs1Rb0     | 34    | 1.25          | 0.45  | 9.32          | 1.97              |
| Cs0.9Rb0.1 | 11.82 | 1.60          | 0.66  | 11.22         | 4.31              |
| Cs0.7Rb0.3 | 5.44  | 2.01          | 0.74  | 14.30         | 8.05              |
| Cs0.5Rb0.5 | 5.51  | 2.03          | 0.74  | 13.14         | 7.20              |

An increase in the luminescence lifetime upon the addition of rubidium ions to nanocrystals can be associated with two main reasons. The first is the presence of defects in perovskite nanocrystals. Numerous works on the synthesis of perovskite nanocrystals have shown [4,5,7,12] that obtained  $ABX_3$  crystals have a defective structure. The incorporation of rubidium ions could relax structural defects or, as suggested in [7], create a protective passivation layer on the surface, reducing the defectiveness of the surface layers of nanocrystals. This would lead to a decrease in the contribution of the short-lived component in the emission lifetime due to a reduction in the nonradiative channel for excitation transfer to crystal defects. The second reason is the presence of two types of crystals in Cs1Rb0 glass: emissive and non-emissive. According to XRD, the concentration of both types of crystals is of the same order, so the nonradiative relaxation channel from emissive crystals to non-emissive ones has a large contribution, and the luminescence lifetime for Cs1Rb0 glass is the shortest. When rubidium was added to the glass, only one kind of crystals was nucleated, which were emissive, and the channel of non-radiative energy transfer to non-emissive crystals ceased to contribute to the luminescence lifetime. Therefore, when comparing Cs1Rb0 and Cs0.9Rb0.1 glass, the lifetime increased twice.

#### 4. Discussion

The nature of the green luminescence in the samples under study is not obvious.  $APbX_3$  perovskite structure is characterized by corner-sharing  $[PbX_6]^{4-}$  octahedra with the  $A^+$  cations filling the voids created by four neighboring  $PbX_6^{4-}$  octahedra. In the  $A_4PbX_6$  structure ( $A = Rb^+, Cs^+$ ), the  $PbX_6^{4-}$  octahedra are completely decoupled in all dimensions and the optical properties of such crystals closely resemble those of individual  $[PbX_6]^{4-}$  clusters that have been observed experimentally in halide salts doped with  $Pb^{2+}$  ions [32]. For  $Cs_4PbBr_6$  crystals, weak luminescence was obtained in the region of 375–380 nm upon irradiation in the excitation bands at 250 and 310 nm [19]. However, there is still no clear idea whether  $Cs_4PbBr_6$  crystals exhibit luminescence in the green region or not. At the

moment, there are two main opinions on this issue. It was shown in [30,33,49] that since CsPbBr<sub>3</sub> NCs can have very high-PL quantum yields (PLQYs), up to 95%, only a very small fraction of them can be enough to result in a green, CsPbBr<sub>3</sub>-like emission, even if apparently no trace of CsPbBr<sub>3</sub> can be found by X-ray diffraction analysis [30]. Based on this, Cs<sub>4</sub>PbBr<sub>6</sub> crystals do not exhibit luminescence in the visible region. On the other hand, the authors of [46,51,52] showed by different methods the complete absence of the CsPbBr<sub>3</sub> phase, but the presence of intense luminescence in the green region. Based on these cases, Wang and co-authors [53] even proposed a classification of Cs<sub>4</sub>PbBr<sub>6</sub> crystals into three types, according to the supposed nature of their luminescence (or its absence): P-Cs<sub>4</sub>PbBr<sub>6</sub> (pure nonemissive), D-Cs<sub>4</sub>PbBr<sub>6</sub> (defective emissive), H-Cs<sub>4</sub>PbBr<sub>6</sub> (hybrid with CsPbBr<sub>3</sub> emissive).

The main difference between emissive crystals in such a system was the presence of impurities or defects. If the absence of CsPbBr<sub>3</sub> in the system is confirmed by other methods, but luminescence is present, then radiative transitions are carried out using defects in Cs<sub>4</sub>PbBr<sub>6</sub>, such as Br vacancies, self-trapped excitons and others. The first characteristic feature of defect luminescence is the absence of the quantum size effect on it [39]. Thus, it is possible to check the reliability of this theory by synthesizing crystals with different sizes. However, in later studies in glasses, it was shown that the luminescence of Cs<sub>4</sub>PbBr<sub>6</sub> crystals shifts with a change in their synthesis regimes (which directly affects the average size of the crystals), and no CsPbBr<sub>3</sub> crystals were found in the matrix. The second characteristic feature of the defect-based luminescence is the lifetime of the order of one hundred nanoseconds [43,45], while the luminescence of cubic perovskite crystals has a lifetime of the order of several nanoseconds [40,42].

Thus, we can assume two possible sources of green emission.

The first assumption: We do have impurity crystals of the APbBr<sub>3</sub> type, their number is very small, so they were not detected by XRD, but their luminescence is large, so we still notice it despite the small number and size. Rubidium ions are evenly distributed in the glass; therefore, they are incorporated into the structure both of Cs<sub>4</sub>PbBr<sub>6</sub>, which is why we see shifts in diffraction peaks, and of CsPbBr<sub>3</sub>, which is why the shift in the luminescence band occurred. This theory is confirmed by the size effect and short luminescence lifetimes. The increase in lifetime is explained by the following: the introduction of Cs<sub>4</sub>PbBr<sub>6</sub> nanoparticles attached on CsPbBr<sub>3</sub> NCs could improve emission lifetime by decreasing the non-radiative energy transfer to the trap states, via controlling the trap density [30].

The second assumption: Optical properties of Cs<sub>4</sub>PbBr<sub>6</sub> raised from the 6s<sup>2</sup> Pb<sup>2+</sup> cations electronic outer shell [39]. In [45], two UV-emission bands were found in Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals attributed to different optical transitions related to Pb<sup>2+</sup> ions that are occupying Cs<sup>+</sup> sites. The high-energy band is attributed to the allowed <sup>3</sup>P<sub>1</sub> → <sup>1</sup>S<sub>0</sub> optical transition of the Pb<sup>2+</sup> ion and the low-energy band is a consequence of the charge transfer state (D-state) emission of the Pb<sup>2+</sup> ion in the host lattice [19]. For these bands, the short component, τ<sub>1</sub> of 0.04–0.15 μs, originates from the <sup>3</sup>P<sub>1</sub> → <sup>3</sup>P<sub>0</sub> transition as a non-radiative recombination, and the long-lifetime component, τ<sub>2</sub> of 1.10–1.41 μs, originates from the <sup>3</sup>P<sub>1</sub> → <sup>1</sup>S<sub>0</sub> transition as a radiative recombination [47]. The self-trapped excitons appearing in the structure can create additional low-energy levels in the bandgap of Pb<sup>2+</sup> ions, from which radiative transitions can occur, including those in the green region. In this case, the green luminescence may have a defect nature, and its shift to the blue region with an increase in the rubidium concentration may occur, since the created defect can be associated with an alkali ion. For example, these are radiative transitions related to Pb<sup>2+</sup> ions that are occupying partly Rb<sup>+</sup>, partly Cs<sup>+</sup> sites. Because the energy level of the defect increases, the time of non-radiative relaxation to it decreases, which leads to a decrease in the contribution of τ<sub>1</sub> in the luminescence lifetime. However, this assumption does not look plausible because of the obtained luminescence decay time, which for radiative transitions from trap states should be of the order of 0.05 μs or more. In our case, the lifetime is units of nanoseconds, which confirms the validity of the first assumption.



## 5. Conclusions

The paper shows the spectral and structural properties of perovskite-type  $(\text{Cs}_{1-x}\text{Rb}_x)_4\text{PbBr}_6$  ( $R = \text{Cs}, \text{Rb}$ ) nanocrystals in  $\text{ZnO-Na}_2\text{O-B}_2\text{O}_3\text{-GeO}_2$  glass. In the absence of rubidium,  $\text{Cs}_4\text{PbBr}_6$  and  $\text{CsPbBr}_3$  perovskite crystals precipitated in the borogermanate matrix. With ascending rubidium content, the precipitation of  $(\text{Cs,Rb})_4\text{PbBr}_6$  nanocrystals were replaced by the  $\text{Rb}_4\text{PbBr}_6$  nanocrystals nucleation. Nucleated nanocrystals exhibited intense green luminescence. With an increase of the rubidium content from  $\text{Cs}_{0.9}\text{Rb}_{0.1}$  to  $\text{Cs}_{0.5}\text{Rb}_{0.5}$ , the luminescence maximum shifted to the blue region from 521 to 511 nm, the luminescence quantum yield increased from 28 to 51%, and the average decay time increased from 2 to 8 ns. The nature of the green luminescence of perovskite-like  $(\text{Cs,Rb})_4\text{PbBr}_6$  and  $\text{Cs}_4\text{PbBr}_6$  crystals in glasses is proposed based on two assumptions: hybrid- and defect-based theories. The authors are inclined to the first assumption and the presence of perovskite  $(\text{Cs,Rb})\text{PbBr}_3$  and  $\text{RbPbBr}_3$  crystals in the glass as well.

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