
Luminescent-kinetic parameters of CsPbCl₃ nanocrystals dispersed in wide-band perovskite-like matrices

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Abstract

CsPbCl₃ nanocrystals are obtained in perovskite-like CsBCl₃ (B=Sr, Ca, Mg) matrices doped with Pb ions (C_{Pb}=0.05 and 1 mol.%). The luminescent-kinetic parameters of the CsPbCl₃ nanocrystals dispersed in CsBCl₃ (B=Sr, Ca, Mg) matrices are studied under the pulsed UV and X-ray excitation. The conclusion about the formation of CsPbCl₃ nanocrystals is confirmed with the data of their luminescence decay kinetics and a short-wavelength shift of the exciton luminescence maximum, when compared to that of an excitonic luminescence in a bulk single CsPbCl₃ crystal. Under the pulsed X-ray excitation, re-absorption of core-valence luminescence of CsBCl₃ (B=Sr, Ca, Mg) matrices with the CsPbCl₃ nanocrystals is registered.

Keywords: nanocrystal, quantum size effect, luminescent-kinetic parameters, core-valence luminescence.

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1. Introduction

Investigation of luminescent-kinetic parameters of semiconducting CsPbCl₃-type nanocrystals (quantum dots) thermally created in CsCl-Pb, CsSrCl₃-Pb and RbPbCl₃-Cs single crystals is one of the promising ways to search for the materials attractive for fast scintillators [1-3].

CsPbCl₃ nanocrystals are characterized by an intense luminescence of free excitons with short decay times (tens of picoseconds) [4], which are one of the necessary conditions for their use as fast detectors of high-energy radiation.

Our investigations of luminescent-kinetic parameters, performed under the high-energy excitation, have shown that the semiconducting CsPbCl₃ nanocrystals, embedded in insulator matrices, are mainly excited due to the re-absorption of single lead centre luminescence

and the intrinsic matrix emission, with the slow component (10^{-6} ~ 10^{-3} s) dominating in the decay kinetics.

This gives rise to the slow component in the luminescence decay kinetics of CsPbCl₃ nanocrystals, undesirable for fast scintillators. Certain prospects open if the wide-band perovskite-like CsBCl₃ (B=Sr, Ca, Mg) matrices are used, exhibiting a core-valence luminescence (CVL) under the high-energy excitation ($E \geq 14$ eV). Since the CVL is characterized by a short decay time $\tau \approx (1.5 \pm 0.1)$ ns [5, 6], one can expect that due to re-absorption of the matrix CVL by the CsPbCl₃ nanocrystals, a luminescence can be excited in these nanocrystals with the main decay time $\tau \approx (1.5 \pm 0.1)$ ns, satisfying the conditions for the time characteristics of fast scintillators. In order to verify this assumption, we study in the present paper the luminescence

kinetic parameters of the CsBCl₃-Pb (B=Sr, Ca, Mg) crystals subjected to prolonged high-temperature annealing under the pulsed UV and X-ray excitation.

2. Experiment

The CsBCl₃-Pb (B=Sr, Ca, Mg) crystals were grown by the Stockbarger method in the two stages. At first the CsBCl₃ (B=Sr, Ca, Mg) crystal matrix, and then the CsBCl₃-Pb (B=Sr, Ca, Mg) crystal were grown. Concentration of the lead ions in the melt was 0.05 mole % (CsCaCl₃-Pb) or 1 mole % (CsSrCl₃-Pb, CsMgCl₃-Pb). The PbCl₂ material was repeatedly purified with a zone smelting technique (≈ 30 zones).

In order to form the CsPbCl₃ nanocrystals dispersed in the CsBCl₃ (B=Sr, Ca, Mg) matrix, the CsBCl₃-Pb (B=Sr, Ca, Mg) crystals were subjected to a prolonged (100 h) high-temperature ($T=200^\circ\text{C}$) annealing.

Luminescence kinetic characteristics of the crystals were measured under the pulsed UV and X-ray excitation. Duration of the exciting pulse τ was 1.0 and 1.5 ns, respectively, with the repetition frequency $f=100$ kHz. The luminescence spectra were recorded in the single photon counting regime, with the aid of set-up mounted on the basis of the MDR-2 monochromator. The actual luminescence decay times were determined with taking into account the exciting pulse shape and using the deconvolution procedure. According to [7], the iteration method used for the evaluation of one-exponent parameters of the decay time curve gives a satisfactory accuracy of approximation. Our experimental set-up permitted us to determine the time decay constants $\tau \geq 0.5$ ns.

The luminescence and luminescence excitation spectra under stationary excitation were measured with a deuterium lamp. The required range of the exciting light was allocated by DMR-4 monochromator. All the measurements were carried out at $T=77$ K.

3. Experimental results and discussion

The luminescence and the luminescence emission spectra of the CsBCl₃-Pb (B=Sr, Ca, Mg) crystals at a stationary excitation are given in Fig.1. Let us analyze the presented luminescence spectra. The relatively narrow band with the half-width $\Delta H=0.04$ eV and the maximums at $\lambda_{\text{max}}=414$, 416 and 412 nm (Fig.1 a, b, c; curves 1) in the CsSrCl₃-Pb, CsCaCl₃-Pb, CsMgCl₃-Pb crystals is similar to the free-

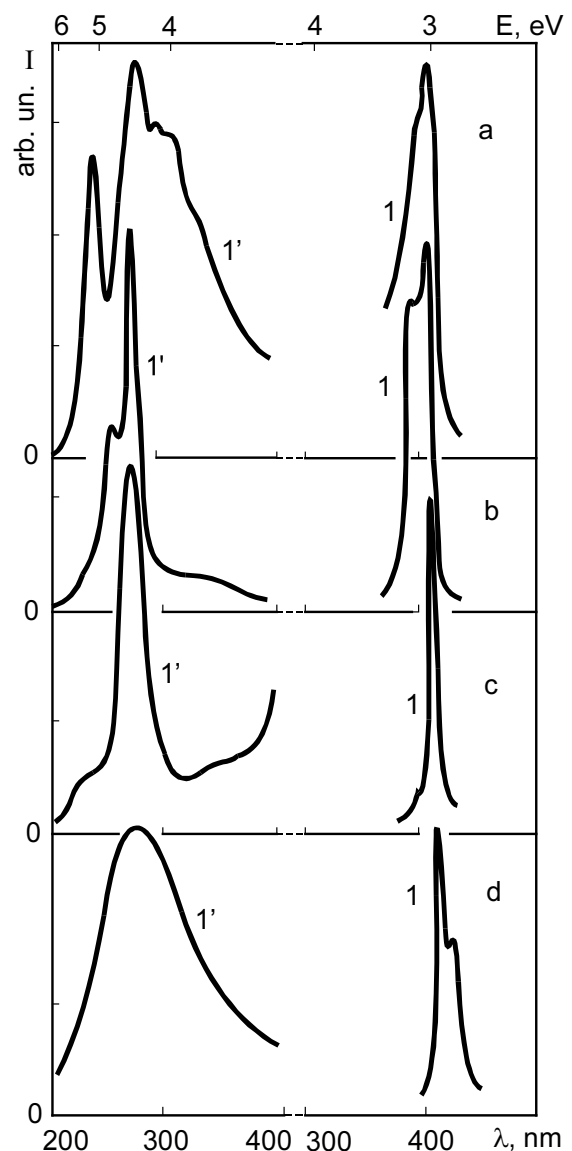


Fig.1. Luminescence spectra (curve 1) and excitation spectra (curve 1') of CsSrCl₃-Pb (a), CsCaCl₃-Pb (b), CsMgCl₃-Pb (c) crystals and CsPbCl₃ single crystal (d). $T=77$ K, $\lambda_{\text{ex}}=300$ nm.

exciton emission band of the CsPbCl₃ single crystal ($\lambda_{\max}=418$ nm, $\Delta H=0.025$ eV) (Fig.1 d, curves 1), the spectral position of which does not depend on the wavelength of the exciting light. Such a similarity of the spectral characteristics indicates that, during the high-temperature annealing in the CsSrCl₃-Pb, CsCaCl₃-Pb and CsMgCl₃-Pb crystals, the lead-containing aggregates of the CsPbCl₃ type dispersed in this matrix are formed.

Such a similarity of spectral characteristics of the mentioned luminescence bands indicates also that, during the high-temperature annealing in the CsSrCl₃-Pb, CsCaCl₃-Pb and CsMgCl₃-Pb crystals, the single lead centres are aggregating as nanocrystals of the CsPbCl₃ type embedded in the corresponding wide-band perovskite-like matrix.

An increase of the luminescence band half-width of CsPbCl₃ aggregates dispersed in the CsBCl₃ (B=Sr, Ca, Mg) matrices, when compared to that of the CsPbCl₃ single crystals, can be explained by a formation of CsPbCl₃ nanocrystals of different sizes, embedded in the CsBCl₃ (B=Sr, Ca, Mg) matrices.

The short-wave shift of the emission band maximum of CsPbCl₃ nanocrystals in the CsBCl₃ (B=Sr, Ca, Mg) matrices with respect to the position of the maximum of free exciton emission band in CsPbCl₃ single crystal by $\Delta E=60, 84$ and 45 meV, respectively, can be interpreted as a manifestation of quantum size effect. Using the relation between the magnitude of the short-wave shift and the average radius R_{QD} of the nanocrystal [8]

$$\Delta E = \frac{\hbar^2 \pi^2}{2\mu R_{QD}^2}, \quad (1)$$

where $\mu=0.65m_0$ [9, 10] is the reduced mass of exciton for the CsPbCl₃ single crystal (m_0 denoting the mass of a free electron), we determine the average radius of the CsPbCl₃ type nanocrystals dispersed in the CsBCl₃ (B=Sr, Ca, Mg) matrices ($R_{QD}\approx 2.8, 3.8$ and 4.0 nm in the CsSrCl₃, CsCaCl₃ and CsMgCl₃,

respectively).

The conclusion about the formation of CsPbCl₃ nanocrystals is confirmed by the data of their luminescence decay kinetics. The luminescence decay time for the CsPbCl₃ nanocrystals dispersed in CsBCl₃-Pb (B=Sr, Ca, Mg) crystals under the excitation in the matrix transparency region for CsSrCl₃, CsCaCl₃ and CsMgCl₃ ($\lambda_{ex} \geq 300$ nm) is described by the exponent with the decay time of $\tau=0.5$ ns. The same exponent describes the luminescence decay kinetics curves for CsPbCl₃ single crystal excited in the same spectral region. These data confirm clearly the formation of CsPbCl₃ nanocrystals in the CsBCl₃-Pb (B=Sr, Ca, Mg) crystals due to aggregation of single lead centres.

This fact was also confirmed for the CsSrCl₃-Pb crystal with making use of the time-resolved low-temperature spectroscopy ($T=77$ K) [2].

Along with the mentioned narrow bands, intense bands in the spectral ranges $\lambda=240\div 270$ nm and $\lambda=340\div 370$ nm exist in the X-ray luminescence of CsBCl₃-Pb (B=Sr, Ca, Mg) crystals at the pulsed X-ray excitation (Fig.2 a, b, c). According to [5,6], the luminescence bands in CsBCl₃ (B=Sr, Ca, Mg) crystals in the spectral range of $\lambda=240\div 270$ nm are attributed to the emissive core-valence transitions due to recombination of the core 5p-zone holes of Cs⁺ ions and the electrons of the nearest 3p-zone of Cl⁻ ions. As seen from Fig. 2, the nature of B = Sr, Ca, Mg ion affects negligibly the structure and spectral position of the CVL peculiar for the CsBCl₃ (B=Sr, Ca, Mg) matrices. It also manifests itself in the identity of luminescent-kinetic parameters for the core-valence luminescence of the mentioned crystals ($\tau=1.5\pm 0.1$ ns).

The wide band of X-ray luminescence in CsBCl₃ (B=Sr, Ca, Mg) crystals in the spectral range of $\lambda=340\div 370$ nm is attributed to the emission of single lead centres [11,12]. The

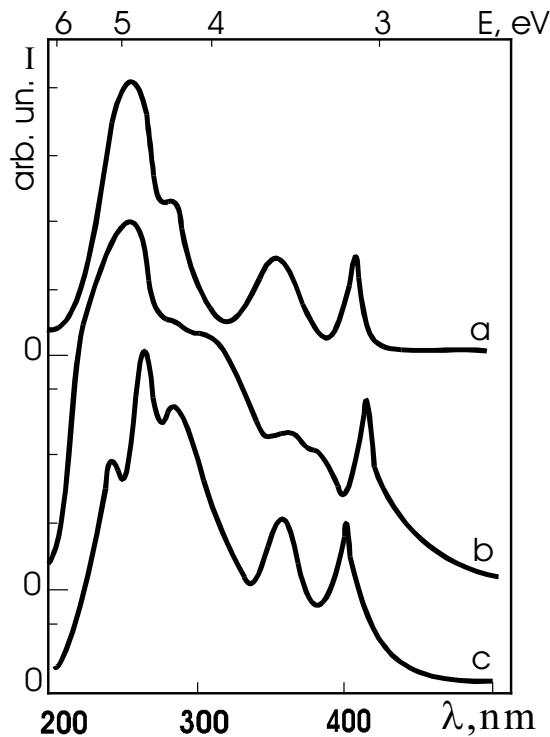


Fig.2. Luminescence spectra of CsSrCl₃-Pb (a), CsCaCl₃-Pb (b) and CsMgCl₃-Pb (c) crystals upon pulsed X-ray excitation. The detection time window is $\Delta\tau=100$ ns, $T=77$ K.

time parameters of this emission get into the microsecond range [2].

Decay kinetics of the narrow-band radiation of CsPbCl₃ nanocrystals embedded in the wide-zone CsBCl₃ (B=Sr, Ca, Mg) matrices is characterized by the decay time $\tau=(1.5\pm 0.1)$ ns. Coincidence of the luminescence kinetic parameters of CsPbCl₃ nanocrystals and those of the CVL in wide-band perovskite-like CsBCl₃ (B=Sr, Ca, Mg) matrices indicates that the luminescence of CsPbCl₃ nanocrystals is excited due to re-absorption of the CVL of CsBCl₃ (B= Sr, Ca, Mg) matrices excited by X-ray quanta. High probability of re-absorption of the CVL of CsBCl₃ (B=Sr, Ca, Mg) matrices by the CsPbCl₃ nanocrystals originates from spectral overlapping of the CVL characteristic for the CsBCl₃ (B=Sr, Ca, Mg) matrices and the excitation spectrum of the narrow-band luminescence in CsPbCl₃ single crystal (see Fig.2 a, b, c and Fig.1 a, b, c; curves 1').

A direct luminescence excitation of

CsPbCl₃ nanocrystals in the CsBCl₃-Pb (B=Sr, Ca, Mg) crystals by high-energy electron-hole pairs emerging in CsBCl₃ (B= Sr, Ca, Mg) crystals under X-ray irradiation is not likely, since the CsPbCl₃ nanocrystals are electrically neutral on the whole.

The results obtained in [2] show that the dominating excitation channel of the narrow-band luminescence in CsPbCl₃ nanocrystals in the band-to-band region of CsSrCl₃ matrix (at $E_{\text{excit}}\geq 14$ eV) is re-absorption of the CsSrCl₃ matrix CVL by Cs nanocrystals.

4. Conclusion

The luminescent-kinetic parameters for semiconducting CsPbCl₃-type nanocrystals (quantum dots) thermally created in CsBCl₃ (B=Sr, Ca, Mg) matrices are studied.

Studies of the kinetic parameters of CsPbCl₃ nanocrystals dispersed in wide-band perovskite-like matrices CsBCl₃ (B=Sr, Ca, Mg) have revealed that:

(1) The direct optical excitation of CsPbCl₃ nanocrystals in the transparency range of the mentioned matrices (at $\lambda_{\text{excit}}\geq 300$ nm) is accompanied by the intensive luminescence of CsPbCl₃ nanocrystals with the decay time of $\tau\approx 0.5$ ns;

(2) The excitation of CsBCl₃-Pb (B=Sr, Ca, Mg) crystals with the pulsed X-ray irradiation gives rise to luminescence of CsPbCl₃ nanocrystals with the decay time $\tau=(1.5\pm 0.1)$ ns. The latter value is explained by the fact that the luminescence of CsPbCl₃ nanocrystals is excited due to re-absorption of the CVL characteristic of CsBCl₃ (B=Sr, Ca, Mg) matrices.

The formation of CsPbCl₃ nanocrystals embedded in wide-band CsBCl₃ (B=Sr, Ca, Mg) matrices, possessing the luminescent decay time in the nanosecond range, opens a possibility for the development of fast detectors of high-energy radiation.

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