Spectral luminescence parameters of CsPbCl$_3$ nanocrystals dispersed in perovskite-like matrix

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Abstract
Luminescence spectral and kinetic characteristics of CsPbCl$_3$ nanocrystals, dispersed in perovskite-like CsSrCl$_3$ matrix, have been studied under excitation by synchrotron radiation in the UV–visible spectral region (4 to 20 eV). Various time components in the decay kinetics of CsPbCl$_3$ nanocrystals appear due to direct excitation of nanocrystals or reabsorption of the luminescence of other emitting centres. Shortening of the luminescence decay time of the CsPbCl$_3$ nanocrystals with respect to that observed for a CsPbCl$_3$ single crystal has been explained as evidence of quantum-size effect.

1. Introduction

Some years ago, a new type of luminescence microcrystals showing clear quantum-size effect was discovered: small semiconducting CsPbCl$_3$-like aggregates thermally created in CsCl:Pb and PbCl$_2$:Cs crystals and dispersed in CsCl or PbCl$_2$ crystal lattices [1–3].

High-temperature treatment of a CsCl:Pb crystal leads to the motion of anion and cation (v_c^-) vacancies that results in the structural redistribution of the coordination number of single Pb^{2+}–v$_c^-$ emitting centres from eightfold to sixfold. Such reconstruction leads to the creation of a CsPbCl$_3$ cluster like a CsPbCl$_3$ molecule. A similar thermal treatment of a PbCl$_2$:Cs crystal leads to the structural redistribution of anion coordinational neighbourhood of a Pb^{2+} cation from ninefold to sixfold, which is accompanied by diffusion of a Cs$^+$ cation in a PbCl$_2$:Cs crystal that results in the creation of a CsPbCl$_3$ molecular centre.

A tendency of CsPbCl$_3$ molecular centres to aggregate leads to the creation of nanocrystals and afterwards a CsPbCl$_3$-like microcrystals, dispersed in a CsCl and PbCl$_2$ matrix, respectively.

Owing to a very fast and intense luminescence of free excitons of CsPbCl$_3$ nanocrystals, which is even faster compared to single crystals due to quantum confinement effect, these systems may find applications, for example, in fast scintillators.

However, not all single Pb^{2+}–v$_c^-$ centres in a CsCl:Pb crystal aggregate; therefore, CsPbCl$_3$ nanocrystals and single Pb^{2+}–v$_c^-$ centres coexist. It was shown in [4] that emission of single

Pb^{2+}–v_c^- centres in a CsCl matrix is reabsorbed by $CsPbCl_3$ nanocrystals. This fact leads to prolongation of the intrinsic luminescence decay time of the latter.

A similar situation is realized in $PbCl_2$:Cs crystals where luminescence of self-trapped excitons (STE) of a $PbCl_2$ matrix is reabsorbed by nanocrystals and $CsPbCl_3$ microcrystals, which also leads to prolongation of their luminescence decay time [5].

The presence of the slow decay component in the luminescence of $CsPbCl_3$ nanocrystals, which were thermally created in CsCl or $PbCl_2$ crystals, as well as the low efficiency of energy transfer from the matrices to $CsPbCl_3$ nanocrystals can limit possible applications of these systems.

Searching for more 'effective' matrices for $CsPbCl_3$ nanocrystals we observed that $CsPbCl_3$ nanocrystals dispersed in a $CsSrCl_3$ perovskite-like matrix. The matrix choice is caused by the expectation of a more simple mechanism of microcrystals creation in view of the similar perovskite structure of matrix and microcrystal elementary cells.

The study of luminescence characteristics of the $CsPbCl_3$ microcrystals, dispersed in a $CsSrCl_3$ matrix, under excitation by synchrotron radiation is necessary for the clarification of the mechanism of exciting radiation transformation into intrinsic electronic excitations of the matrix as well as of the $CsPbCl_3$ microcrystals. From a practical point of view, these investigations allow us to determine the perspectives for the application of these materials for the registration and visualization of high-energy radiation.

2. Experiment

A $CsSrCl_3$:Pb single crystal containing 0.5 mol.% of $CsPbCl_3$ was grown by the Stockbarger method. To produce $CsPbCl_3$ nanocrystals dispersed in a $CsSrCl_3$ matrix, a $CsSrCl_3$:Pb crystal was annealed for 20–100 hours at 180–200 °C. Such high-temperature treatment leads to thermal activation of the motion of anion and cation vacancies. As a result, in a $CsSrCl_3$ matrix some clusters like a $CsPbCl_3$ molecule are created, aggregating in the form of nanocrystals of fixed sizes.

The experiments were carried out at SUPERLUMI station in HASYLAB (Hamburg, Germany). The crystal was excited by the synchrotron radiation passed through a normal incidence 2m-vacuum monochromator (the spectral width of the entrance slit was about 0.2 nm). The luminescence of the crystal located on a crystal holder of a helium cryostat was detected by a photomultiplier through a secondary monochromator B&M. The luminescence decay kinetics was studied under pulse synchrotron excitation (the pulse duration $\approx$0.1 ns and repetition period 480 ns). A time-correlated single photon counting method with time-to-amplitude conversion was used. Instrumental response to the exciting pulse has FWHM of 0.4 ns. Luminescence decay times were determined by accounting for the exciting pulse duration by using the deconvolution procedure. Time-resolved emission and excitation spectra were recorded within a time window (length Δt) delayed with respect to synchrotron radiation pulses (delayed δt). In the present experiment the delay is $\delta t_1 = 1.5$ ns and the length is $\Delta t_1 = 5$ ns for a short time window (called a fast component) and for a long time window (called a slow component) the delay is $\delta t_1 = 150$ ns and the length is $\Delta t_1 = 50$ ns. The experimental set-up is described in [6] in more detail.

3. Results and discussion

3.1. Luminescence spectra of a CsSrCl₃:Pb crystal

Luminescence spectra (LS) of the annealed $CsSrCl_3$:Pb crystal excited at 10 K in the transparency region of a $CsSrCl_3$ matrix ($\lambda_{exc} = 320$ or 250 nm) are shown in figure 1(a)
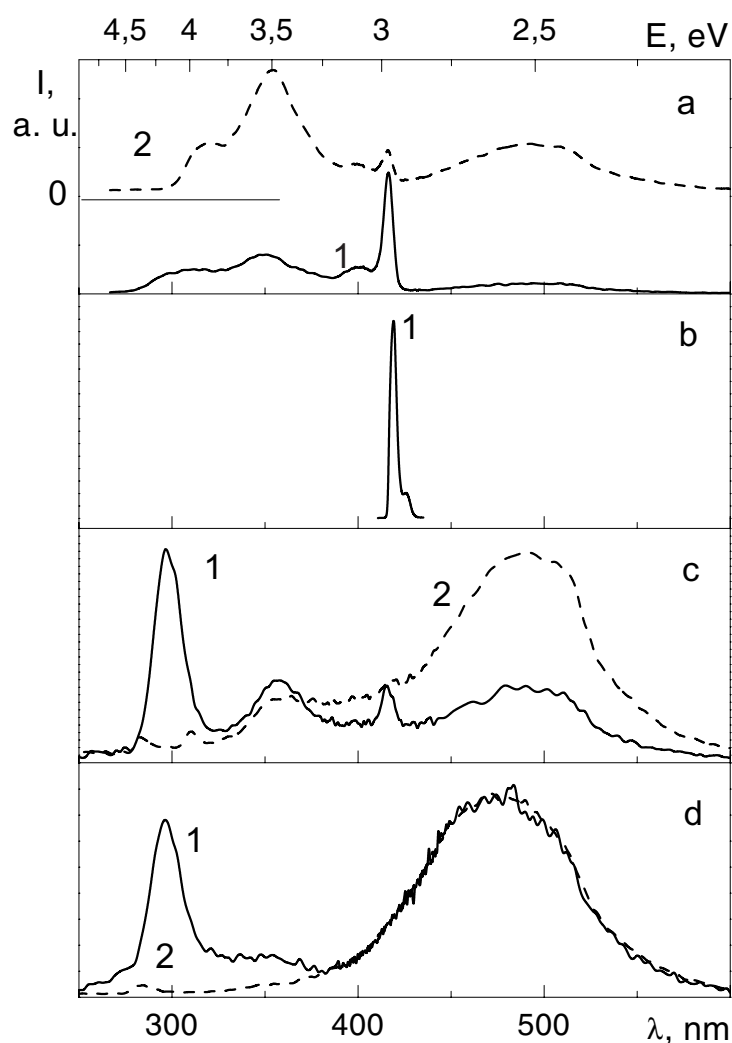
Figure 1. Luminescence spectra of fast (curves 1) and slow (curves 2) decay components of CsSrCl₃–Pb crystal ($C_{Pb} = 0.5$ mol.%) luminescence, measured under $\lambda_{exc} = 320$ or 250 nm (a); $\lambda_{exc} = 170$ nm (c) and $\lambda_{exc} = 120$ nm (d) excitation. Luminescence spectrum of fast decay component of CsPbCl₃ single crystal under 242 nm excitation (b). $T = 10$ K.

(curves 1, 2). Spectral location of wide non-elementary bands at $\lambda_{max} = 300$–310 and 330–360 nm can be ascribed to the emission of different lead centres, as was found in KCaCl₃:Pb, RbCaCl₃:Pb, CsCaCl₃:Pb and SrCl₃:Pb crystals [7, 8]. This coincidence of luminescence spectra can be explained by the similar structure of matrices and lead centres in the crystals mentioned. Thus, conditions creation of Pb²⁺ centres in CsSrCl₃:0.5 mol.% CsPbCl₃ are realized during crystal growth.

Narrow band (halfwidth FWHM = 0.03 eV) peaking at $\lambda_{em} = 416$ nm is similar to the free exciton emission band of a CsPbCl₃ single crystal ($\lambda_{em} = 419.6$ nm; FWHM = 0.025 eV) observed under the same excitation (figure 1(b)). Such similarity of the spectral characteristics points to the fact that the above-mentioned thermal treatment results in the

formation of $CsPbCl_3$ nanocrystals dispersed in a $CsSrCl_3$ matrix. Owing to the possible occurrence of a quantum-size effect the high-energy shift of the free exciton emission band of $CsPbCl_3$ nanocrystals, dispersed in a $CsSrCl_3$ matrix (about 26 meV), is observed with respect to the location of the free exciton emission band in the $CsPbCl_3$ single crystal. Besides the quantum-size effect, nanocrystals are influenced by a hydrostatic compression effect. But the value of local strain made by the $CsSrCl_3$ matrix on $CsPbCl_3$ nanocrystals is small, because the lattice constant of $CsSrCl_3$ matrix is practically equal to the $CsPbCl_3$ crystal in the cubic phase ($a_{CsSrCl_3} = 5.606$ A; $a_{CsSrCl_3} = 5.605$ A [9]). Due to this fact, the influence from the side of the $CsSrCl_3$ matrix on $CsPbCl_3$ nanocrystals is minimal.

Assuming a spherical shape of the nanocrystals, their size can be determined from the relation

$$\Delta E = \hbar^2 \pi^2 / 2\mu R_{QD}^2$$

between the value of the high-energy shift ΔE of their emission band and a nanocrystal radius R_{QD} [10]. Here $R_{QD} = 0.65\ m_0$ is the reduced exciton mass in a $CsPbCl_3$ single crystal; m_0 is the free electron mass [11, 12]. The average size of the $CsPbCl_3$ nanocrystals dispersed in a $CsSrCl_3$ matrix is estimated to be about 5 nm. As the radius of the free exciton of $CsPbCl_3$ single crystal is equal to 1 nm, we can speak of the quantum confinement of the exciton ($R_{QD} < 10r_{ex}$) [1].

The wide band at 490 nm is interpreted as radiative decay of self-trapped excitons (STE) of the $CsSrCl_3$ matrix [13]. A relatively poor intensity of the fast decay component of STE emission (see figure 1(a), curve 1) is explained by the fact that a greater part of STE emission goes out of the boundaries of the time gate used for registration of the fast component.

Excitation of the $CsSrCl_3$:Pb crystal in the range of the exciton peak of the $CsSrCl_3$ matrix ($\lambda_{exc} = 170$ nm) (the exciton reflection peak is located at $\lambda = 162$ nm, $T = 293$ K [14]) leads to partial redistribution of lead centres and STE of $CsSrCl_3$ matrix emission intensity (figure 1(c), curves 1, 2).

In the LS of a $CsSrCl_3$:Pb crystal excited in fundamental absorption region of the $CsSrCl_3$ matrix (7.3 eV $\leqslant E_{exc} \leqslant 10.3$ eV) the emission bands of single Pb^{2+} centres and STE of the $CsSrCl_3$ matrix dominate (figure 1(d), curves 1, 2)($\lambda_{exc} = 120$ nm).

Thus, the LS of the $CsSrCl_3$:Pb crystal contains emission bands of Pb^{2+} single centres, complex lead centres, $CsPbCl_3$-like nanocrystals and also STE of the $CsSrCl_3$ matrix.

We expect that clusterization of $CsPbCl_3$ molecules will occur effectively taking into account the similar perovskite structure of the $CsSrCl_3$ matrix and $CsPbCl_3$ cluster. However, different melting temperatures of the $CsSrCl_3$ matrix and $CsPbCl_3$ crystal do not favour $CsPbCl_3$ nanocrystals creation during the clusterization of $CsSrCl_3$. Moreover, the absence of charge-compensating vacancy (in the case of $CsSrCl_3$ activation with $CsPbCl_3$) makes the clusterization process of single and complex lead centres in the form of $CsPbCl_3$-like nanocrystals more complicated.

Unlike a single crystal of $CsPbCl_3$ where the 419.6 nm luminescence is observed only for a short time window, the 416 nm narrow-band emission of investigated crystals can be detected in both short and long time windows.

3.2. Excitation spectra of CsSrCl$_3$:Pb crystal

The excitation spectra for different types of $CsSrCl_3$:Pb crystal luminescence, all measured in the spectral range $E_{exc} \leqslant 10$ eV, are shown in figure 2(a)–(d).

The shape of the excitation spectrum of 300 nm luminescence of $CsPbCl_3$ nanocrystals (figure 2(a), curve 1) is similar to the characteristic of single emitting centres. One can
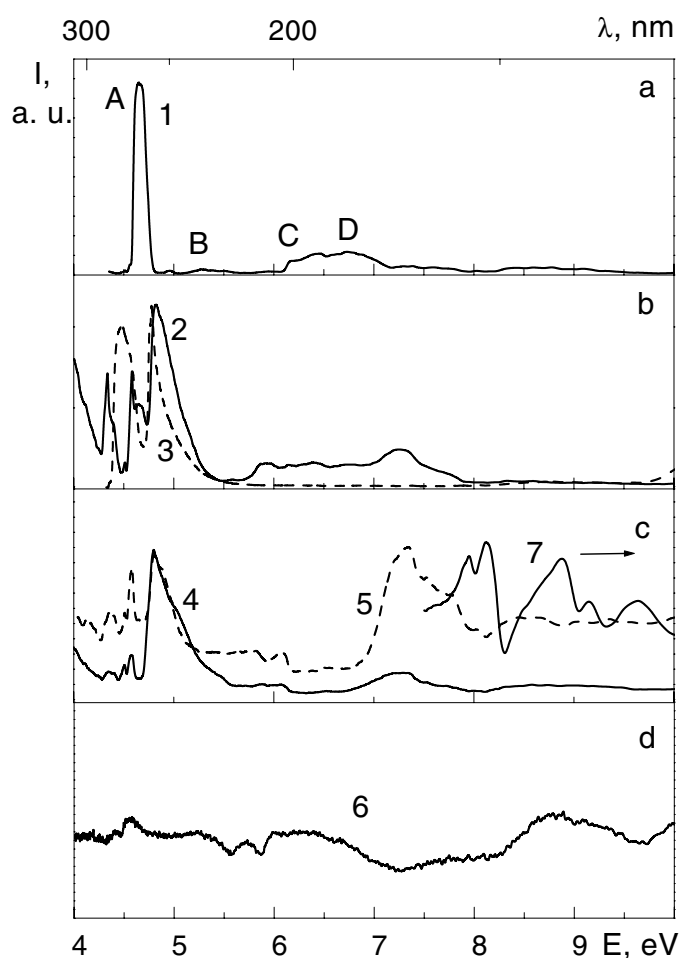
Figure 2. Excitation spectra of (a) the fast decay component of the 300 nm emission of single Pb^{2+} centres in CsSrCl3 (curve 1); (b) the fast (curve 2) decay component of the 360 nm emission of complex Pb^{2+} centres in CsSrCl3 and fast (curve 3) decay component of 330 nm emission of PbCl2 crystal; (c) the fast (curve 4) and slow (curve 5) decay components of the 416 nm emission of the CsSrCl3:Pb (C_{Pb} = 0.5 mol.%) crystal; and (d) the free exciton 419.6 nm emission of a CsPbCl3 single crystal (curve 6). Reflection spectrum of CsSrCl3 matrix (curve 7). T = 10 K.

see a band characteristic for A-band of absorption peaking at 270 nm and also B-, C- and D-absorption bands that correlate with respective bands in alkali halide crystals [15]. Under excitation in A- and C-absorption bands of these centres, decay kinetics curves practically coincide and contain a fast decay component with $\tau_f \approx$ 20–30 ns characteristic of decay kinetics of single lead centres.

Analysis of the excitation spectrum of the 360 nm luminescence band (figure 2(b), curve 2) allows us to ascribe it to the emission of complex lead centres or, probably, to the emission of PbCl2 microphase.

Certain structural similarities of the excitation spectrum of 360 nm luminescence band (curve 2) to that characteristic of 330 nm intrinsic luminescence of PbCl2 crystal (curve 3)

suggests that the structure of the complex lead centres is similar to the $PbCl_2$-molecule structure, i.e. single lead centres possibly aggregate in the form of the $PbCl_2$ microphase.

Creation of the $PbCl_2$ microphase in the $CsSrCl_3$:Pb crystal, unlike the case of $CsPbCl_3$, is accompanied by matrix defect creation because the $CsSrCl_3$ matrix does not contain structural elements characteristic of the $PbCl_2$ crystal.

Therefore, some difference in the spectral location of emission bands of complex lead centres in $CsSrCl_3$:Pb ($\lambda_{max} = 360$ nm) and STE band of intrinsic luminescence of $PbCl_2$ crystal ($\lambda_{max} = 330$ nm) can be explained by the sensitivity of the spectral location of the STE emitting transition in the $PbCl_2$ microphase to the structural defect presence [16, 17].

The excitation spectrum of $CsPbCl_3$ nanocrystal luminescence (figure 2(c), curves 4, 5) differs greatly from the excitation spectrum of the $CsPbCl_3$ single crystal (figure 2(d), curve 6). It reproduces the main features of the excitation spectrum of $PbCl_2$ microphase luminescence. This fact indicates the possible reabsorption of $PbCl_2$ microphase emission by $CsPbCl_3$ nanocrystals.

Some difference in the excitation spectrum of the slow component of $CsPbCl_3$ nanocrystals emission in 7–8 eV spectral range is caused by a partial passing of 416 nm STE emission of the $CsSrCl_3$ matrix that is effectively excited in the 7–8 eV energy range.

In the band-to-band transitions region of a $CsSrCl_3$ crystal ($8 < E_{exc} < 14$ eV), direct optical excitation of $CsPbCl_3$ nanocrystals or direct recombination with matrix electron–hole pairs is insignificant (figure 3(a), curve 1).

Therefore, luminescence of $CsPbCl_3$ nanocrystals in the energy range $E_{exc} > 14$ eV is excited by (1) high-energy electron–hole pairs of a $CsSrCl_3$ matrix created after absorption of excitation quanta with $E_{exc} > 14$ eV, (2) reabsorption of core-valence luminescence (CVL) of a $CsSrCl_3$ matrix and of emission of complex lead centres (figure 3(c), curve 4 and figure 3(d), curve 5). The high effectiveness of the $CsPbCl_3$ single crystal intrinsic luminescence excitation by photo quanta with $E_{exc} > 14$ eV is evidence of the first channel.

We studied the ratio of intensities of fast (figure 3(d), curve 6) and slow (curve 7) components of $CsPbCl_3$ nanocrystals luminescence as a function of excited radiation energy ($E_{exc} > 12$ eV (curve 8)) in order to establish the main channel of nanocrystals luminescence excitation. The I_{fast}/I_{slow} curve is qualitatively similar to that characteristic of the excitation spectrum of the $CsSrCl_3$ matrix CVL (curve 9). Therefore, reabsorption of the $CsSrCl_3$ matrix CVL by $CsPbCl_3$ nanocrystals is the main channel of $CsPbCl_3$ nanocrystals excitation in the energy range $E_{exc} > 14$ eV.

Conclusions on the mechanism of $CsPbCl_3$ nanocrystals emission made on the basis of excitation spectra of single Pb^{2+} centres and $CsPbCl_3$ nanocrystals are confirmed by the measurements of luminescence decay times of nanocrystals.

3.3. Luminescence decay kinetics of the CsSrCl₃:Pb crystal

The luminescence decay curve of the $CsPbCl_3$ nanocrystals, dispersed in the $CsSrCl_3$ matrix (curve 1), obtained under excitation in the transparency region of $CsSrCl_3$ matrix are shown in figure 4 ($E_{exc} = 3.83$ eV). This curve can be approximated by two exponents with decay times $\tau_{f1} = 0.40$ ns, $\tau_{f2} = 12.1$ ns ($\tau_{f1} = 0.48$ ns, $\tau_{f2} = 7.0$ ns for $CsPbCl_3$ single crystal). The smaller value of τ_{f1} obtained for $CsPbCl_3$ nanocrystals as compared with that characteristic of a $CsPbCl_3$ single crystal can be explained as an occurrence of the quantum-size effect.

Under excitation in the $E_{exc} > 4.5$ eV energy range, the real decay kinetics of the $CsPbCl_3$ nanocrystals emission cannot be seen clearly as it possesses the features of the decay kinetics of 360 nm complex lead centres emission and 490 nm intrinsic emission of the $CsSrCl_3$ matrix. However, under excitation in the mentioned energy range, decay
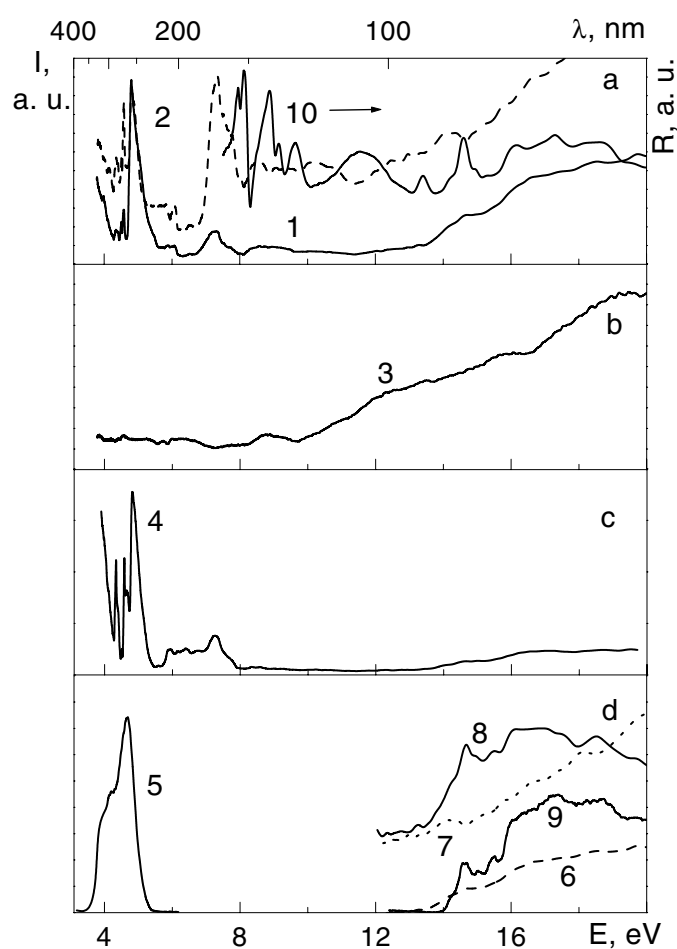
Figure 3. Excitation spectra of (a) the fast (curve 1) and slow (curve 2) decay components of the 416 nm emission of the CsSrCl$_3$:Pb (C_{Pb} = 0.5 mol.%) crystal; (b) the free exciton 419.6 nm emission of a CsPbCl$_3$ single crystal (curve 3); (c) the fast (curve 4) decay component of the 360 nm emission of complex Pb^{2+} centres in CsSrCl$_3$; and (d) the fast (curve 6) and slow (curve 7) decay components of the 416 nm emission of the CsSrCl$_3$:Pb crystal and the ratio I_{fast}/I_{slow} of these curves (curve 8). Excitation spectrum of CVL (curve 9) and CVL (curve 5) of the CsSrCl$_3$ matrix. Reflection spectrum of the CsSrCl$_3$ matrix (curve 10). T = 10 K.

kinetics has a fast component $\tau_f \approx 0.6$ ns (figure 4, curve 2) which coincides with a fast component of complex lead centres emission (curve 3). It must be pointed out that luminescence decay kinetics of the intrinsic luminescence band of the PbCl$_2$ crystal with λ_{max} = 330 nm is also characterized by a fast component with decay time $\tau_f \approx 0.6$ ns [18]. The presence of a slow component $\tau_s > 10\,\mu$s is explained by the contribution of STE emission of the CsSrCl$_3$ matrix whose emission spectrum partially hits in the nanocrystals emission region.

Thus, the fast luminescence decay of CsPbCl$_3$ nanocrystals with $\tau_f = 0.4$ ns is observed only under direct optical excitation of CsPbCl$_3$ nanocrystals in the transparency region of the CsSrCl$_3$ matrix.
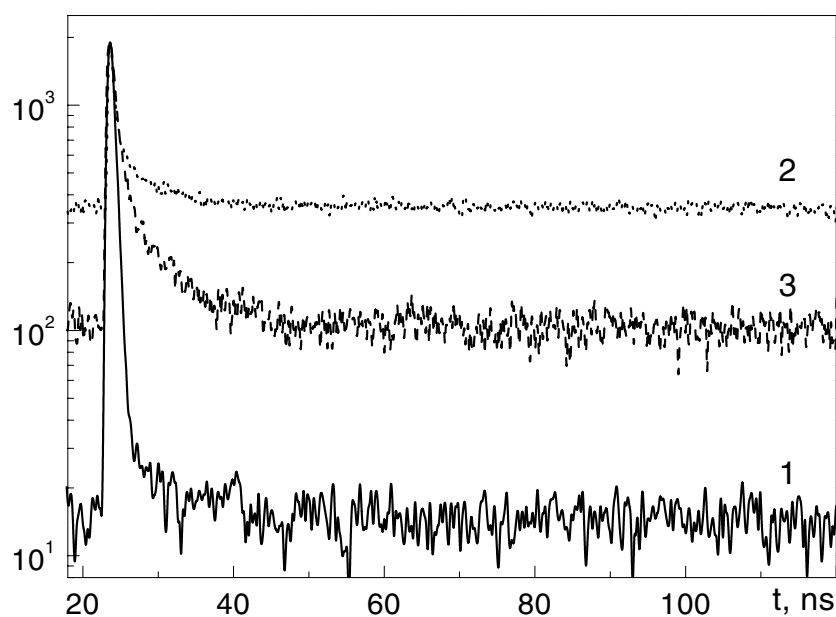
Figure 4. Decay curves obtained for the luminescence: of the $CsPbCl_3$ nanocrystals dispersed in $CsSrCl_3$ matrix (curve 1) under excitation $E_{exc} = 3.82$ eV; nanocrystals dispersed in a $CsSrCl_3$ matrix (curve 2) and of complex lead centres in $CsSrCl_3$ matrix (curve 3) under excitation in the exciton absorption region of the $CsSrCl_3$ matrix $E_{exc} = 7.2$ eV. $T = 10$ K.

Decay kinetics of $CsPbCl_3$ nanocrystals emission excited in the fundamental absorption region of the $CsSrCl_3$ matrix is characterized by fast ($\tau_f = 0.6$ ns) and slow ($\tau_s \approx 10\,\mu s$) components.

4. Conclusions

1. Prolonged (20 h) annealing of a $CsSrCl_3$:Pb (0.5 mol.% of Pb) single crystal at 200 °C leads to the aggregatization of single lead centres with further creation of complex lead centres and $CsPbCl_3$ nanocrystals dispersed in a $CsSrCl_3$ crystal matrix.

2. High-energy shift of the free exciton emission band of $CsPbCl_3$ nanocrystals (about 26 meV) and the shortening of its decay time (down to 0.40 ns) as compared with that characteristic of a $CsPbCl_3$ single crystal (0.48 ns) can be caused by the possible occurrence of quantum-size effect.

3. Along with direct optical excitation, $CsPbCl_3$ nanocrystals luminescence is also excited due to reabsorption of 360 nm complex lead centres emission and 265 nm core-valence luminescence of the $CsSrCl_3$ matrix. Owing to this fact, the peculiarities of luminescence decay kinetics are determined by decay parameters of complex lead centres ($\tau_f \approx 0.6$ ns) and core-valence luminescence ($\tau_f = 1.5$ ns). Furthermore, the appearance of a slow decay component is explained by slight overlapping of the $CsSrCl_3$ matrix STE and $CsPbCl_3$ nanocrystal emission bands.

4. The presence of the slow decay component in the luminescence of $CsPbCl_3$ nanocrystals as well as the small efficiency of energy transfer from the $CsSrCl_3$ matrix to $CsPbCl_3$ nanocrystals would limit possible applications of the $CsSrCl_3$:Pb system as a fast scintillator.

Acknowledgments

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