ISSN 1027-5495. Functional Materials, 29, No.4 (2022), p. 481-487.
doi:https://doi.org/10.15407/fm29.04.481

Comparison of luminescent properties of halide perovskite nanocrystals in solutions and polymer films

T.V.Skrypnyk, I.I.Bespalova, I.I.Grankina, O.G.Viagin, S.L.Yefimova, A.V.Sorokin

Institute for Scintillation Materials, National Academy of Sciences of Ukraine, 60 Nauky Ave., 61072 Kharkiv, Ukraine

Received September 5, 2022

Halide perovskite nanocrystals of different anion compositions were synthesized using the ligand-assisted reprecipitation method. It has been shown, that toluene is a more suitable solvent compared to chloroform from the point of view of better nanocrystal stability. Chloride perovskites reveal shorter lifetimes but weaker luminescence compared to bromide ones. Embedding perovskite nanocrystals into poly(methyl methacrylate) films leads to a significant shortening the lifetimes of the nanocrystals and much longer stability of the samples. That makes them promising for the creation of fast scintillation materials.

Keywords: perovskite, nanocrystals, polymer films, luminescence, lifetime, exiton.

Порівняння люмінесцентних властивостей галогенідних перовскітних нанокристалів у розчинах і полімерних плівках. *Т.В.Скрипник, І.І.Беспалова, І.І.Гранкіна, О.Г.Вягін, С.Л.Єфімова, О.В.Сорокін*

Галогенідні перовскітні нанокристали різного аніонного складу були синтезовані методом переосадження з підтримкою лігандів. Було показано, що толуол є більш прийнятним розчинником порівняно з хлороформом з точки зору кращої стабільності нанокристалів. Хлоридні перовскіти мають коротший час життя, але слабшу люмінесценцію порівняно з бромідними. Введення нанокристалів перовскіту в плівки полі(метилметакрилату) приводить до значного скорочення часу життя нанокристалів і значно більшої стабільності зразків. Це робить галогенідні перовскітні нанокристали перспективними для розробки швидких сцинтиляційних матеріалів.

1.Introduction

Halide perovskites in the form of nanometer-sized colloidal crystals or nanocrystals (NCs) have attracted the attention due to their unique optical versatility, high photoluminescence quantum yields, and accessible synthesis [1]. Perovskite NCs predominantly have a ionic lattice, and their optical and electronic properties are highly tolerant to structural defects and surface states [1, 2]. New colloidal methods for the synthesis of halide nanocrystals of perovskite, as well as interesting characteristics of this new type of material, have attracted the attention of many researchers [1–8]. Halide perovskite nanocrystals of the general formula $CsPbX_3$ (where X is Cl, Br, or I) can be obtained both in the form of powders and in the form of transparent colloidal solutions [1–8]. Due to the quantum-confnement effect, such nanocrystals have a fast nanosecond luminescence of free excitons, the quantum yield of which can reach 90 % [1–8]. Another feature of such nanocrystals is that the replacement of anions in the $Cl^-/Br^-/I^-$ series changes the band gap, resulting in a successive shift of the edges of the absorption spectra and lumines-

cence maxima from the blue to the red region [1–8]. This allows one to vary their optical properties in a wide spectral range.

The unique properties of $CsPbX_3$ nanocrystals, as well as their high effective atomic number (Z_{eff} = 62–66), allow us to consider them as scintillation materials [9–14]. Thus, it was shown that colloidal solutions of $CsPbBr_3$ nanocrystals have intense X-ray luminescence and show a linear dependence of the scintillation response in the voltage of 20–60 kV range on an X-ray tube [9]. It was also shown that when irradiated with low-energy X-ray quanta (10 keV), the yield of thin-film luminescence (0.1 mm) of $CsPbBr_3$ nanocrystals can reach 54 % of the yield of CsI:Tl crystal [9]. In addition to X-ray sensors, also perovskite-based scintillators for gamma and alpha detection were proposed [9–14].

One of the current requirements in scintillators physics is the timing resolution in the 10 ps range; this requires scintillators with a high light yield, a short rise time, and a decay time, as well as the ultrafast scintillation mechanisms to produce prompt photons as a result of transient phenomena and/or quantum confinement [15]. In this connection, various nanoscale scintillators have been actively studied [16]. Among them, the nanosized halide perovskite crystals can be a material that can meet all requirements.

In this work, both stationary and time-resolved optical properties of halide perovskite nanocrystals of various compositions in solutions and PMMA are studied in order to reveal their prospects as fast scintillation materials.

2. Experimental

The following starting materials were used for the synthesis of $CsPbX_3$ nanocrystals (NCs): lead (II) bromide ($PbBr_2$, 99.99 %), lead (II) chloride ($PbCl_2$, 99.99 %), lead (II) iodide (PbI_2, 99.99 %), cesium bromide (CsBr, 99.99 %), cesium chloride (CsCl, 99.99 %), cesium iodide (CsI, 99.99 %), oleic acid (90 %), *n*-octylamine (99 %) from "Sigma-Aldrish"; anhydrous toluene from "CARLO ERBA Reagents"; chloroform and dimethylformamide (DMF) from "Makrochem".

The ligand-assisted reprecipitation (LARP) technique was used to obtain colloidal solutions of $CsPbX_3$ nanocrystals. According to the described method [17], 0.1 mmol of cesium halide CsX and 0.2 mmol of lead halide PbX_2 (X = Cl or Br) were dissolved in 5 ml of DMF (which was previously additionally dried) using ultrasonic treatment; then 20 μl of *n*-octylamine and 0.5 ml of oleic acid were added to the mixture of metal halides. In this way, a transparent, colorless initial mixture of precursors was obtained. It should be noted that the stability of the initial mixture of the precursors decreases in the series Br>Cl>I.

To obtain a colloidal solution of perovskite nanocrystals, 100 μl of the initial mixture of the precursors was added to 10 ml of toluene or chloroform with intensive stirring at room temperature (20–25°C). The bright color of the obtained colloidal solution was observed. In a such way, colloidal solutions of $CsPbBr_3$, $CsPbBrCl_2$ and $CsPbCl_3$ were obtained.

Here we developed a method for obtaining poly(methyl methacrylate) (PMMA) films containing $CsPbX_3$ NCs for applications in scintillation technology. To form films on a glass substrate, a PMMA granule weighing 0.02 g was dissolved in 0.5 ml of chloroform, after which 1 ml of a toluene colloidal solution of perovskite nanocrystals was added, intensively mixed, and the mixture was applied to the corresponding precleaned substrate. The resulting film on the substrate was dried at room temperature and kept in an oven at a temperature of 60°C for 12 hours. In this way, transparent films on glass substrates were obtained. The mass fraction of perovskite nanocrystals is 2 wt % in all the film samples obtained. Film samples obtained in this way are stable for more than two months.

Luminescence spectra were registered using a monochromator MDR-23 (LOMO, USSR) supplied with a PMT R9110 (Hamamatsu, Japan). A diode laser with λ_{em} = 405 nm was used as an exciting light source. Measurements of absorption spectra were performed using a two-beam spectrophotometer SPECORD 200 (Analytik Jena, Germany). To obtain absorption spectra of the thin solid samples, we used a fluorescent microscope operating in the transmitted light mode with a 10X/0.50NA objective and equipped with a spectrophotometer USB4000 (Ocean Optics, USA). Luminescence decay curves were measured using a picosecond spectrofluorimeter Fluotime 200 (PicoQuant, Germany) using a picosecond laser module with a wavelength of 379 nm. The instrument response function was 100 ps. TEM images of the particles were obtained at Sumy State University using a transmission electron microscope PEM-125 (Selmi, Ukraine) operating at 90 kV.

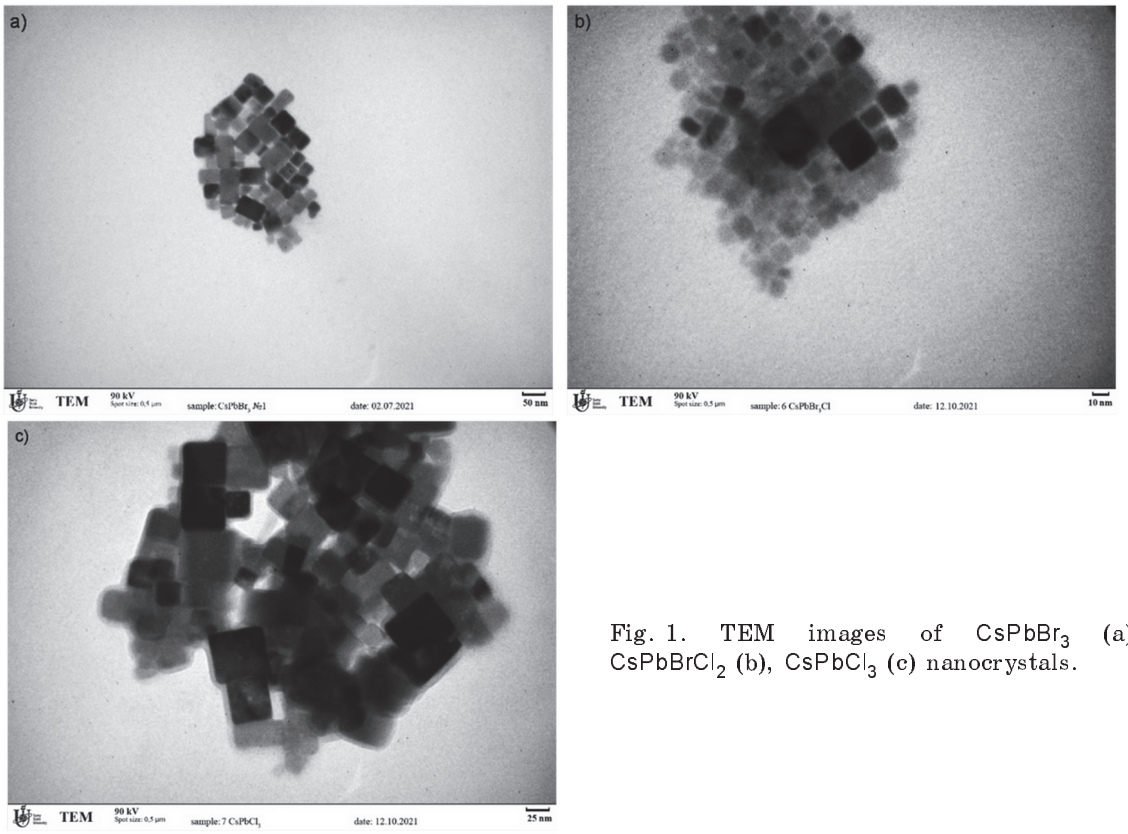


Fig. 1. TEM images of $CsPbBr_3$ (a), $CsPbBrCl_2$ (b), $CsPbCl_3$ (c) nanocrystals.

3. Results and discussion

According to TEM data, $CsPbBr_3$ NCs have a size of 35–45 nm (Fig. 1a), $CsPbBrCl_2$ NCs — 10–20 nm (Fig. 1b), $CsPbCl_3$ NCs — 25–50 nm (Fig. 1c).

To determine the optical characteristics of colloidal solutions of LHP NCs, we started with the most common bromide perovskites $CsPbBr_3$ [1–8]. The bromide NCs were synthesized in such solvents as toluene and chloroform. The optical spectra of $CsPbBr_3$ NCs in toluene (Fig. 2a) are typical for halide perovskites [1–8] and show an exciton band (λ_{max} = 495 nm) at the low-energy edge of the absorption band and a narrow luminescence band (λ_{max} = 512.5 nm, $\Delta\nu_{FWHM}$ = 675 cm^{-1}) with a small Stokes shift (690 cm^{-1}).

The luminescence decay curve (Fig. 2b) is non-single-exponential and can be approximated by three exponents corresponding to τ_1 ~ 10 ns (74 %), τ_2 ~ 48 ns (24 %) and τ_3 ~ 350 ns (2 %), which give an average lifetime τav ~ 27 ns (averaging over amplitudes). A significant deviation from the single-exponential law can be associated with the size distribution of NCs, as well as the influence of local inhomogeneities of the environment. Although the main contribution (in terms of amplitude) is given by the shortest component, the presence of a long component, although with a low contribution, leads to a lengthening of the luminescence decay time to 1.5 μs (Fig. 2b), which is undesirable for applications requiring short lifetimes. One of the explanations for the presence of the long component is delayed luminescence due to the capture of charge carriers by shallow traps [18–21].

It was found that the stability of the obtained NCs significantly depends on the purity of the initial components used. The use of higher quality components and optimization of the conditions for obtaining NCs made it possible to largely overcome the problem of their instability in toluene (Fig. 3a). From Fig. 3a, it can be seen that within 14 days after the preparation of the solutions, the luminescence band of bromide NCs in toluene did not shift, although its intensity gradually decreased. The latter can be associated with the aggregation of NCs and their gradual precipitation.

Unlike colloidal solutions in toluene, the solutions in chloroform, unfortunately, turned out to be unstable even after optimizing the conditions for perovskite NCs preparation and using high-quality precursors (Fig. 3b). This may be due to other

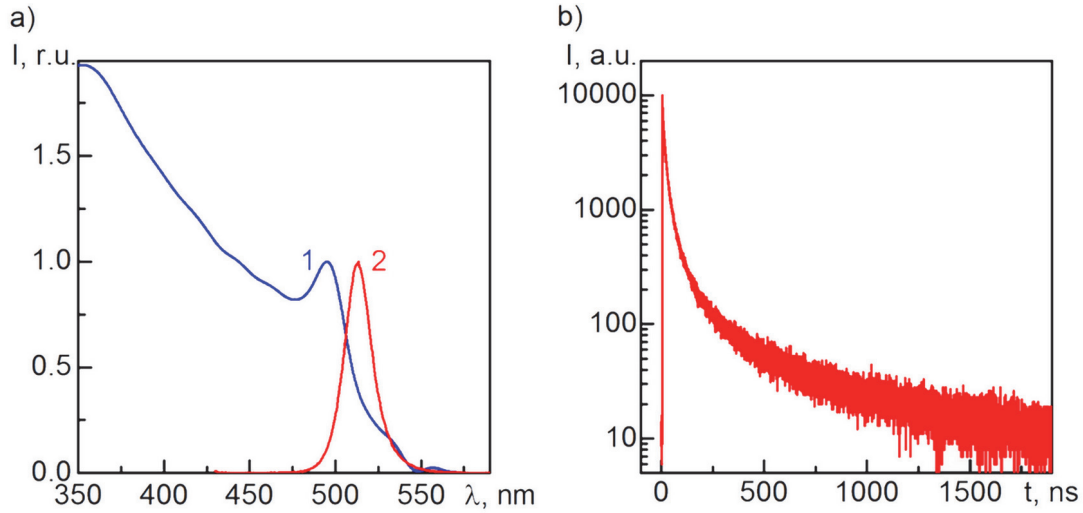


Fig. 2. a) Absorption (1) and luminescence (2, λ_{exc} = 405 nm) spectra and b) luminescence (λ_{exc} = 379 nm) decay curve of $CsPbBr_3$ nanocrystals in toluene. Spectra in panel (a) are normalized to the maximum of excitonic band for clarity.

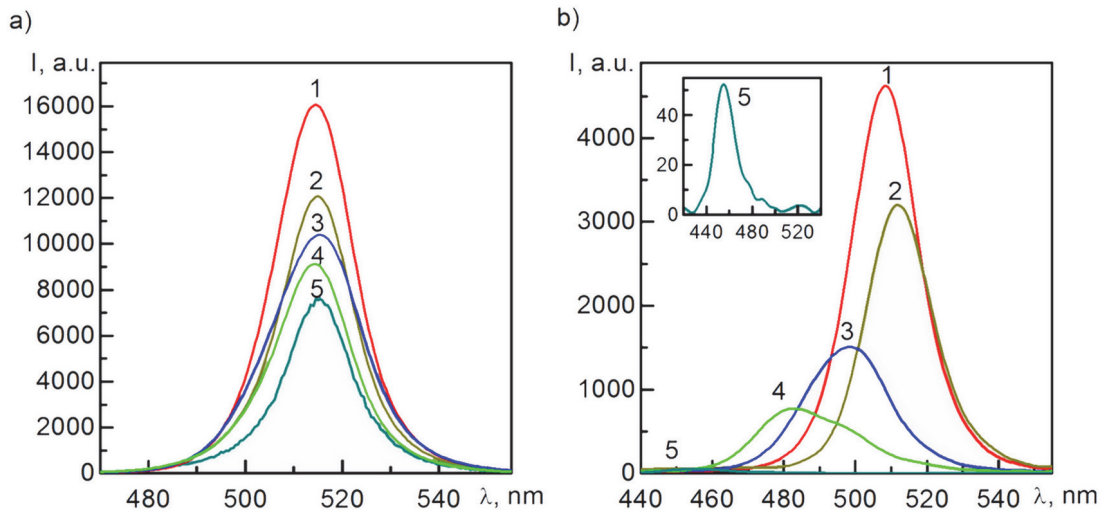
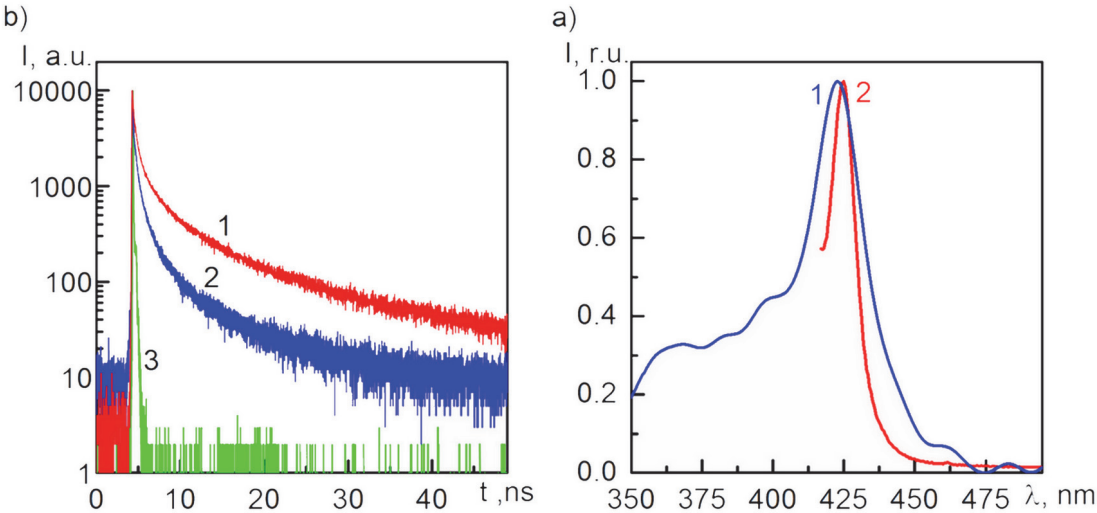


Fig. 3. Luminescence spectra (λ_{exc} = 405 nm) of $CsPbBr_3$ nanocrystals in toluene (a) and chloroform (b) depending on the time after preparation: *1* — measured immediately after preparation, *2* — measured after 1 day, *3* — measured after 5 days, *4* — measured after 7 days, 5 — measured after 14 days. The inset in panel (b) shows spectrum 5 on a larger scale.

conditions of the interaction of the solvents and nanocrystals of this composition. Unlike toluene, for the chloroform solutions, we observed not only a gradual shift of the luminescence band but also a significant monotonous decrease in its intensity within 14 days after the preparation of the samples. For a fresh NCs solution in chloroform (Fig. 3b), the maximum of the luminescence band was observed at λ_{max} = 508 nm (i.e. at shorter wavelength compared to luminescence for toluene solutions, Fig. 3a), after 14 days it shifted to λ_{max} = 455 nm (Fig. 3b, on the insert). At the same time, the width of the band increased slightly: from $\Delta\nu_{FWHM}$ = 860 cm^{-1} for the fresh solution to $\Delta\nu_{FWHM}$ = 1000 cm^{-1} for the solution after 14 days. This can be associated with the evolution of NCs during their gradual dissolution and reduction in size [4]. Thus, it can be concluded that chloroform is not suitable for the storage of the NCs and can be used only in limited cases, when nanocrystals prepared in chloroform will be immediately transferred to another medium, for example, to a polymer film.

The next step was to study the possibility of synthesizing perovskite NCs with various anionic compositions, namely $CsPbBrCl_2$ and $CsPbCl_3$ (Fig. 4).



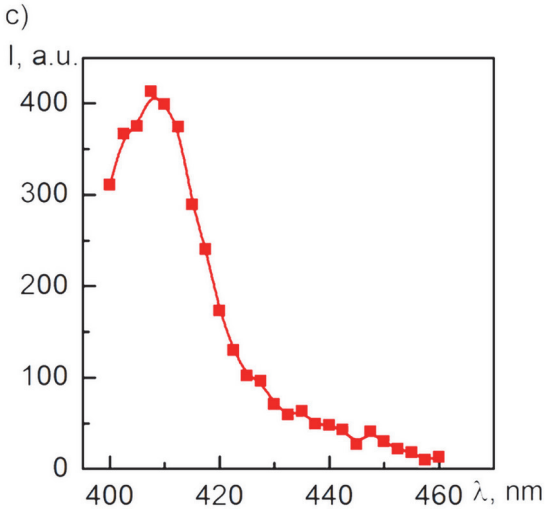


Fig. 4. a) Absorption and luminescence (λ_{exc} = 405 nm) spectra of $CsPbBrCl_2$ nanocrystals in toluene (the spectra are normalized to the maximum of excitonic band for clarity); b) luminescence (λ_{exc} = 379 nm) decay curves of solutions of $CsPbBrCl_2$ (*1*) and $CsPbBr_3$ (*2*) nanocrystals in toluene, curve 3 — IRF; c) time-resolved luminescence (λ_{exc} = 379 nm) spectrum of $CsPbBr_3$ nanocrystals in toluene.

As expected, the absorption and luminescence spectra of $CsPbBrCl_2$ NCs (Fig. 4a) are significantly shifted to the blue region of the spectrum relative to $CsPbBr_3$ NCs (Fig. 2a). At the same time, for $CsPbBrCl_2$ NCs, both the absorption band (λ_{max} = 423 nm) and the luminescence band (λ_{max} = 425 nm) are lower in intensity (not shown), than the corresponding bands of bromide NCs with the same content of nanocrystals in the solution. It is known that the luminescence quantum yield for chloride NCs is much lower compared to bromide ones, which makes the latter more "popular" [1–8]. At the same time, the Stokes shift for $CsPbBrCl_2$ NCs (130 cm^{-1}) is much smaller compared to bromide NCs, which indicates a much smaller influence of the solvate shell on the relaxation of exciton excitations [4]. In some sense, the spectra of $CsPbBrCl_2$ NCs (Fig. 4a) are similar to the spectra of $CsPbBr_3$ NCs formed in chloroform 14 days after preparation (Figs. 3b), but they are more stable (because these NCs are formed in toluene) and their luminescence is more intense. Another similar feature is the much shorter average luminescence lifetime of $CsPbBrCl_2$ NC $\tau_{average}$ ~ 1.1 ns (Fig. 4b). This makes chloride NCs promising for applications requiring short lifetimes, despite "weaker" optical characteristics [15, 22, 23].

Purely chloride NCs, namely $CsPbCl_3$, have spectra shifted even more to the blue region and, unfortunately, cannot be excited by a laser with a wavelength of 405 nm due to overlapping the spectra of laser emission and NCs luminescence. However, it was possible to register their luminescence spectrum using the time-resolved luminescence recording technique (TRES) and a picosecond fluorimeter with a laser excitation wavelength of 379 nm (Fig. 4c). Thus, the maximum of the luminescence band turned out to be λ_{max} = 408 nm. And the decay time of the luminescence of $CsPbCl_3$ NCs ($\tau_{average}$ ~ 0.27 ns) is even

shorter compared to $CsPbBrCl_2$ NCs (Fig. 4b). But the luminescence intensity is also lower, according to the data obtained from the luminescence decay curves. Thus, the chloride NCs exhibit short lifetimes with lower luminescence intensity and may also be promising for the creation of fast scintillators.

The spectra of bromide NCs incorporated into a PMMA polymer film (Fig. 5) are similar to the spectra for toluene solutions, but there are some differences: for the luminescence band (λ_{max} = 504 nm), the Stokes shift is smaller (320 cm^{-1}), but the width is much larger ($\Delta\nu_{FWHM}$ = 960 cm^{-1}). Such changes can be explained by the effect of the polymer environment on exciton excitations in NCs and some quenching of luminescence.

A positive point is the much bigger stability of perovskite NCs in polymer films. In general, the experiments proved that by optimizing the conditions for obtaining polymer films containing perovskite nanocrystals, it is possible to achieve at least a two-month stability of the prepared samples.

The most important result of the incorporation of $CsPbBr_3$ NCs into polymer films is a significant shortening in the luminescence decay times (Fig. 6a). Thus, for bromide NCs, approximation by three components showed the following results: τ_1 ~ 350 ps (86 %), τ_2 ~ 1.95 ns (13 %), and τ_3 ~ 16 ns (1 %) with an average value of $\tau_{average}$ ~ 670 ps (averaging by amplitudes). It should be noted that with such short decay times, it is necessary to take into account the instrumental function (IRF) of the device and carry out deconvolution. Thus, we obtained an average lifetime of fewer than 1 ns with a short tail that decays completely before 200 ns, which is promising for scintillation applications. This shortening is mostly due to the quenching of luminescence in the polymer medium (according to preliminary estimates, the quantum yield of luminescence becomes less than 10 %). But further, the quantum yield can be increased due to the use of the effect of plasmon enhancement of luminescence [24–30].

As well as for the solutions in toluene (Fig. 4), $CsPbBrCl_2$, and $CsPbCl_3$ nanocrystals in the polymer film show less intense luminescence bands, which are blue-shifted corresponding to bromide NCs, with maxima λ_{lum} = 416 nm and 408 nm, respectively (Fig. 6b). Similarly to the solution case, their luminescence decay curves are shorter compared to $CsPbBr_3$ (Fig. 6a) giving very short average lifetimes as τ_{av} ~ 230 ps for $CsPbBrCl_2$ and τ_{av} ~ 100 ps for $CsPbCl_3$. Thus, the assumption regarding their possible application in the development of fast scintillators was confirmed.

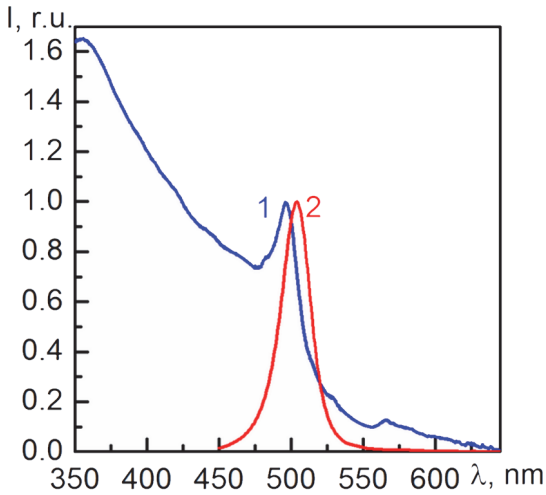


Fig. 5. Absorption (*1*) and luminescence (*2*, λ_{exc} = 405 nm) spectra of $CsPbBr_3$ nanocrystals in a PMMA film. The spectra are normalized to the maximum of excitonic band for clarity.

4. Conclusions

Inorganic halide perovskite nanocrystals of the $CsPbX_3$ type, where the anions X are Br, Cl, or their mix, were obtained in toluene and chloroform. It was found that the stability of the obtained nanocrystals in chloroform is much less compared to toluene. Depending on the anion composition of perovskite nanocrystals, the colloid solution with lifetimes from 30 ns to less than 1 ns can be obtained. The chloride nanocrystals exhibit the shortest lifetimes and lowest luminescence intensity. The technique of embedding of perovskite nanocrystals into PMMA polymer films has been worked out, and the conditions for the stability of nanocrystals in these films for two months or more have been determined. It was shown that the lifetime for all nanocrystals embedded into polymer films is much less compared to those in toluene. Depending on the perovskite anion composition, the optimal parameters of perovskite nanocrystal-based materials can be chosen taking into account their short lifetime, intense luminescence, and maximum spectral position. The polymer films containing halide perovskite nanocrystals can be considered as promising for the creation of fast-yielding scintillation materials.

Acknowledgments. The authors thank the Ukrainian Army for the opportunity to pre-

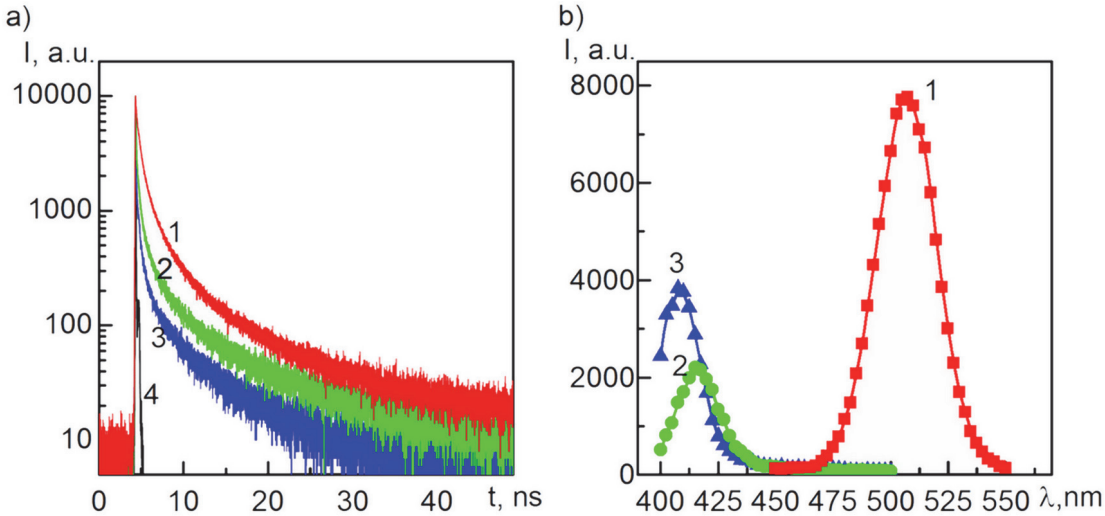


Fig. 6. a) Luminescence decay curves (λ_{exc} = 379 nm) of $CsPbBr_3$ (*1*), $CsPbBrCl_2$ (*2*) and CsPbCl3 (*3*) nanocrystals in a PMMA film, curve 4 — IRF; b) time-resolved luminescence spectra (λ_{exc} = 379 nm) of $CsPbBr_3$ (*1*), $CsPbBrCl_2$ (*2*) and $CsPbBr_3$ (*3*) nanocrystals in a PMMA film.

pare the work for publishing. A.Sorokin expresses sincere gratitude to Dr.Franziska Fennel from the University of Rostock for the invaluable help.

References

1. Q.A.Akkerman, G. Raino, M.V.Kovalenko et al., *Nat. Mater.*, **17**, 394 (2018).
2. A.Dey, J.Ye, A.De et al., *ACS Nano*, **15**, 10775 (2021).
3. M.V.Kovalenko, L.Protesescu, M.I.Bodnarchuk, *Science*, **358**, 745 (2017).
4. J.Shamsi, A.S.Urban, M.Imran et al., *Chem. Rev.*, **119**, 3296 (2019).
5. Perovskite Quantum Dots, ed. by Y.Zhou, Y.Wang, Springer Singapore, Singapore (2020).
6. A.L.Efros, L.E.Brus, *ACS Nano*, **15**, 6192 (2021).
7. N.Wang, W.Liu, Q.Zhang, *Small Methods*, **2**, 1700380 (2018).
8. Z.Song, J.Zhao, Q.Liu, *Inorg. Chem. Front.*, **6**, 2969 (2019).
9. Q.Chen, J.Wu, X.Ou et al., *Nature*, **561**, 88 (2018).
10. Q.Xu, J.Wang, W.Shao et al., *Nanoscale*, **12**, 9727 (2020).
11. S.Chhangani, M.Kumar, R.M.Sahani et al., *Mater. Today Proc.*, **48**, 1028 (2022).
12. L.Lu, M.Sun, T.Wu et al., *Nanoscale Adv.*, **4**, 680 (2022).
13. L.Clinckemalie, D.Valli, M.B.J.Roeffaers et al., *ACS Energy Lett.*, **6**, 1290 (2021).
14. Z.Zhang, H.Dierks, N.Lamers et al., *ACS Appl. Nano Mater.*, **5**, 881 (2022).
15. C.Dujardin, E.Auffray, E.Bourret-Courchesne et al., *IEEE Trans. Nucl. Sci.*, **65**, 1977 (2018).
16. P.Lecoq, C.Morel, J.O.Prior et al., *Phys. Med. Biol.*, **65**, 21RM01 (2020).
17. X.Du, G.Wu, J.Cheng et al., *RSC Adv.*, **7**, 10391 (2017).
18. M.A.Becker, C.Bernasconi, M.I Bodnarchuk et al., *ACS Nano*, **14**, 14939 (2020).
19. V.S.Chirvony, S.Gonzalez-Carrero, I.Suarez et al., *J. Phys. Chem. C*, **121**, 13381 (2017).
20. Y.Wang, M.Zhi, Y.Chan, *J. Phys. Chem. C*, **121**, 28498 (2017).
21. S.J.W.Vonk, M.B.Fridriksson, S.O.M.Hinterding et al., *J. Phys. Chem. C*, **124**, 8047 (2020).
22. S.K.Gupta, Y.Mao, *Front. Optoelectron.*, **13**, 156 (2020).
23. R.M.Turtos, S.Gundacker, S.Omelkov et al., *Npj 2D Mater. Appl.*, **3**, 37 (2019).
24. P.Chen, Z.Xiong, X.Wu et al., *J. Phys. Chem. Lett.*, **8**, 3961 (2017).
25. D.Afanasyev, N.Ibrayev, N.Nuraje, *Front. Mater.*, **7**, 600424 (2021).
26. K.Gu, H.Peng, S.Hua et al., *Nanomaterials*, **9**, 770 (2019).
27. Y.Wu, Q.Han, M.Wang et al., *Opt. Express*, **29**, 36988 (2021).
28. C.-M.Yang, F.-C.Chen, *Nanomaterials*, **11**, 993 (2021).
29. S.Zhang, Y.Liang, Q.Jing et al., *Sci. Rep.*, **7**, 14695 (2017).
30. W.Zhao, Z.Wen, Q.Xu et al., *Nanophotonics*, **10**, 2257 (2021).