Scintillation properties of Eu^{2+}-doped SrCl$_2$ and CsSrCl$_3$ single crystals

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Eu^{2+}-doped CsSrCl$_3$ scintillation crystals with activator concentration 0.5, 1 and 5 mol. % and SrCl$_2$:Eu^{2+} material doped with 1 mol. % of the activator have been grown by Bridgman-Stockbarger method. The radioluminescence spectra of CsSrCl$_3$:Eu^{2+} materials include a narrow band with the maximum which position is shifted from 437 to 448 nm with Eu^{2+} concentration increase and the spectrum for SrCl$_2$:Eu^{2+} contains a band with the maximum at 414 nm. The light yield of CsSrCl$_3$:Eu^{2+} material achieves maximal value at 5 mol. % of Eu^{2+} and it is equal to 39 % in respect to NaI:Tl (ca 16,000 photons per MeV) and energetic resolution R is 11.5 %, whereas for SrCl$_2$:1 mol. % of Eu^{2+} the light yield consists 30 % (ca 12,000 photons per MeV) and $R = 9.2$ %. The scintillation pulse decay curves for CsSrCl$_3$:Eu^{2+} is described by two components with the decay constants 420 ns and 2.8 µs and the fraction of the faster component is 0.3.

Сцинтилляционные монокристаллы CsSrCl$_3$, активированные добавками Eu^{2+} 0,5, 1 и 5 мол. %, и SrCl$_2$:1 мол. % Eu^{2+} выращены из расплава методом Бриджмена-Стокбаргера. Спектры радиолюминесценции CsSrCl$_3$:Eu^{2+} имеют единичный узкий пик с максимумом, положение которого смещается от 437 до 448 нм в зависимости от концентрации активатора, в случае материала SrCl$_2$:Eu^{2+} максимум наблюдается при 414 нм. Световыход CsSrCl$_3$:Eu^{2+} достигает максимального значения при 5 мол. % Eu^{2+} и составляет 39 % относительно NaI:Tl (около 16000 фотонов/МэВ) при энергетическом разрешении $R = 11,5$ %, для SrCl$_2$:1 мол. % Eu^{2+} световыход равен 30 % (около 12000 фотонов/МэВ) и $R = 9,2$ %. Кривая затухания сцинтилляционного импульса для CsSrCl$_3$:Eu^{2+} может быть описана двумя компонентами с константами затухания 420 нс и 2,8 мкс и долей более быстрого компонента 0,3.

1. Introduction

Modern trends in development of Eu^{2+}-activated alkali and alkaline earth halide scintillators consist in a shift of the emphasize from the doped single substances on complex halide compounds containing one- and two-charged metal cations. For instance, scintillation properties of such materials as CsBa$_2$I$_5$:Eu^{2+}, CsSrI$_3$:Eu^{2+} and CsEuI$_3$ have been recently reported [1, 2]. The reason why only iodide compounds become the object of such great attention consists in generally accepted opinion that they possess the narrowest band gaps in comparison with compounds formed by other halide ions. Nevertheless, some difficulties of obtaining iodide materials are caused by lower

stability of iodide compounds as formed by the "'softest" base (according to "hard and soft acids and bases" concept [3] the strength of bonding in pairs formed by alkali, alkaline earth and rare-earth cations and halide ions decreases with the increase of anion radius in $F \rightarrow Cl \rightarrow Br \rightarrow I$ sequence). Ditto, the individual iodides are less stable than corresponding bromides and chlorides, and the action of residual water and oxygen in the growth atmosphere can lead to appreciable pollution of the grown single crystals by oxygen traces. These admixtures worsen the scintillation parameters of the obtained materials because of interaction with the activator cation (Eu^{2+}), which was shown in [4] to be very strong Lux acid.

Therefore, the complex of chloride and bromide compounds based on alkali and alkaline earth metal salts deserve to be studied as prospective scintillation materials.

The purpose of the present work is investigation of luminescence and scintillation properties of the compound formed by cesium and strontium chlorides. According to the phase diagram of $CsCl–SrCl_2$ system [5], in the said system only one stable compound, $CsSrCl_3$ is formed. The melting point of this compound is 842°C that allows to perform the crystal growth without appreciable difficulties. For a comparison we performed parallel investigation of $SrCl_2:Eu^{2+}$ material.

2. Experimental

$SrCl_2$ was synthesized by dissolution of a weight of $SrCO_3$ of 99.99 % purity in extra pure hydrochloric acid taken with the excess of 5 %. Then the weight of NH_4Cl corresponding to $NH_4Cl:SrCO_3$ molar ratio equal to 0.5 was added to the formed solution of $SrCl_2$. The obtained mixed solution was evaporated, placed in quartz ampoule with the diameter of 60 mm and 300 mm height and heated in vacuum (ca 10 Pa) up to 400°C with 4-hours stop at 200°C which was necessary to removal of chemically bonded water. Ammonium chloride sublimates from the charge in 200–350°C temperature range that prevents pyrohydrolysis of the obtained anhydrous chloride.

The charge of $CsSrCl_3$ was synthesized by such a way. A weight of $SrCO_3$ (99.99 %) was dissolved in extra pure hydrochloric acid with the formation of $SrCl_2$ solution. Then the weight of $CsCl$ corresponding to $CsCl:SrCO_3$ molar ratio equal to 1 was added to the solution of $SrCl_2$ and NH_4Cl as

it was described in the previous paragraph. The obtained mixed solution was evaporated to formation of the mixture of crystals. This mixture was placed in quartz ampoule with the diameter of 60 mm and 500 mm height and heated in vacuum up to 400°C. The following heating was performed in the flow of argon saturated by CCl_4 vapor. The mixture was melted and kept at 870–900°C in $Ar+CCl_4$ atmosphere for 4 h. upon to the absence of wetting the ampoule walls by the melt which serves as an indicator of complete removal of oxide ion admixtures (down to 10^{-4} mol·kg^{-1}). The principal reaction taking place at the purification can be presented by the following scheme:

$$2SrO + CCl_4 \uparrow \rightarrow 2SrCl_2 + CO_2 \uparrow \quad (1)$$

taking into account that oxide ions O^{2-} in the melt are distributed between Cs^+ and Sr^{2+} cations and the following equilibrium

$$Cs_2O + Sr^{2+} \rightleftarrows SrO + 2Cs^+ \quad (2)$$

under the treatment conditions is practically completely shifted to the right.

Eu^{2+} was added in the form EuI_2 as the most stable halide of europium (II). The routine of EuI_2 synthesis is presented in detail in [5].

In the frame of this work pure $CsSrCl_3$ and the samples containing 0.5, 1 and 5 mol.% of Eu^{2+} were grown (the attempt to obtain the sample doped with 10 mol.% of Eu^{2+} failed because of breaking down of the formed solid solution). To make this the growth charge was placed in quartz ampoule of 18 mm diameter, melted and kept for a day at 870°C in vacuum (ca 10 Pa). The crystals were grown by Bridgman-Stockbarger method; the temperature at the diaphragm was 842°C for pure $CsSrCl_3$ and 840°C for the doped crystals, whereas for pure and Eu^{2+}-doped $SrCl_2$ it was 874°C. The temperature gradient in the growth zone was 10°C/cm and the rate of the ampoule descent was 2.6–2.8 mm/h. The obtained ingot was cooled to the room temperature with the rate of 10°C/h. Then the ingot was cut and the detectors of 12 mm diameter and 2 mm height were prepared. It should be noted that in the case of $CsSrCl_3$ the final ingot included brown-and-red precipitate in the bottom section because of the formation and precipitation of EuO under the experimental conditions. This was caused by the existence of oxygen-containing admixtures in EuI_2 which, in the con-
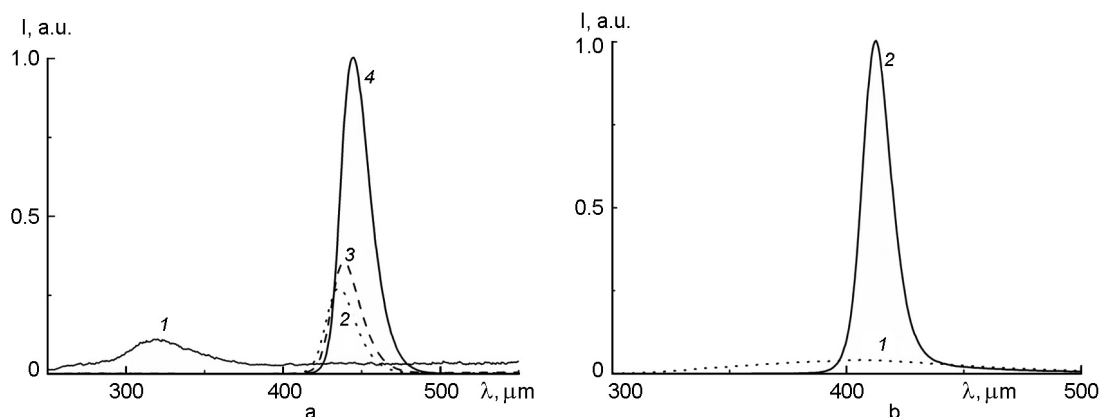
Fig. 1. The radioluminescence spectra obtained under ^{241}Am excitation at RT: a) pure $CsSrCl_3$ (*1*) and $CsSrCl_3$ doped with 0.5 (*2*), 1 (*3*) and 5 mol.% of Eu^{2+} (*4*); b) pure $SrCl_2$ (*1*) and $SrCl_2$ doped with 1 mol.% of Eu^{2+} (*2*).

trast with the chloride matrixes could not be purified under hard conditions.

The radioluminescence spectra (^{241}Am γ-irradiation) of the obtained materials were recorded using MDR-23 monochromator. The pulse-height spectra were obtained under ^{137}Cs (γ, 662 keV) and ^{241}Am irradiation and registered by PMT Hamamatsu R1307.

The scintillation pulse shape of $CsSrCl_3$:Eu^{2+} detector was obtained using the delayed-coincidence method (Bollinger and Thomas, 1961). Two 9142B (Electron Tubes Ltd.) photomultipliers were used for the detection of scintillation photons both in "start" and in "'stop" channels of the optical part of the set-up. The detectors were irradiated by gamma photons of ^{152}Eu radionuclide source (γ, 41, 77.9, 122 keV). The photomultiplier in the "start" channel was used to give zero-time signal. It was placed in optical contact with the scintillator. A scintillation pulse was attenuated by a diaphragm to single photon mode and then detected by the photomultiplier to generate delayed timing signal in the "stop" channel.

3. Results and discussion

Radioluminescence spectra of the materials based on $CsSrCl_3$ and $SrCl_2$ are presented in Fig. 1a and Fig. 1b, respectively. As seen the spectra for the pure chloride matrixes are quite different. The emission spectrum of $CsSrCl_3$ includes a relatively narrow band (290−360 nm) with the maximum at 321 nm, whereas the radioluminescence spectrum of pure $SrCl_2$ contains wide band (300−500 nm) of low intensity which, similarly to results of [6] may be attributed to

the presence of cation admixtures (Ba^{2+} and Ca^{2+}).

An addition of Eu^{2+} to the said matrixes results in disappearance of these bands. All the Eu^{2+}-doped crystals contain only one narrow band which can be ascribed to $5d−4f$ transition in Eu^{2+} ion. In the case of $CsSrCl_3$ the position of the band maximum is shifted from 437 to 448 nm when Eu^{2+} concentration increases from 0.5 to 5 mol.% (thereat FWHM value reduces from 23 to 21 nm). As for $SrCl_2$:Eu^{2+} material, the maximum of the emission band is placed at 414 nm that is in a good agreement with the results of [7]. Authors of [7] note also that an increase of Eu^{2+} concentration causes the shift of the said maximum from 410 to 416 nm (FWHM is 14 nm) that principally corresponds to similar effect observed in $CsSrCl_3$:Eu^{2+} system. An increase of the activator concentration in $CsSrCl_3$ matrix leads to subsequent increase of the integral intensity of the emission band, and increase of Eu^{2+} concentration from 0.5 to 5 mol.% (i.e. in 10 times) causes increase of this parameter by factor of 4.

The results of the light yield determination show that the increase of the activator

Table. Relative light yield (*LY*, in respect to NaI:Tl) and energetic resolution (*R*) of some Eu^{2+}-doped $CsSrCl_3$ crystals

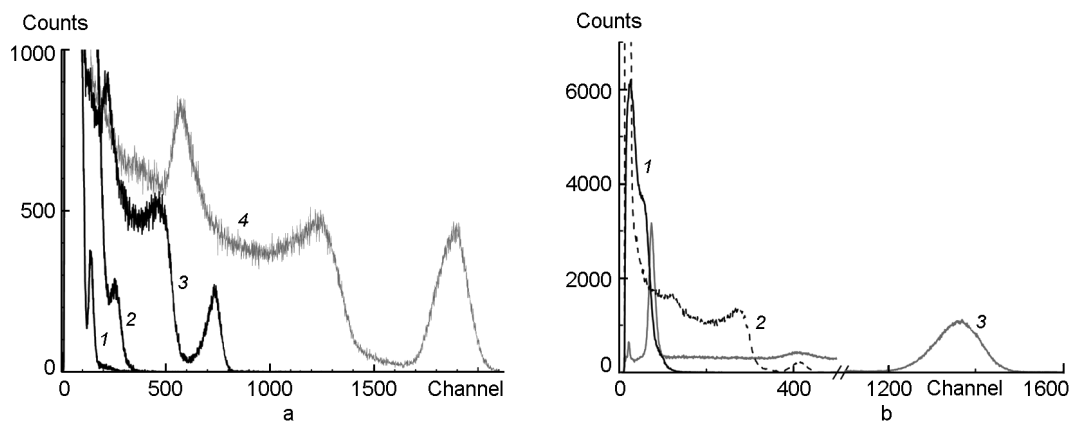| Detector	LY (γ–^{137}Cs)	R, %
$CsSrCl_3$:0.5 % Eu^{2+}	8.3	18.4
$CsSrCl_3$:1.0 % Eu^{2+}	13.5	
$CsSrCl_3$:5.0 % Eu^{2+}	38.9	11.5
$CrCl_2$:1.0 % Eu^{2+}	30.3	9.2

Fig. 2. Pulse height spectra obtained under ^{137}Cs excitation: a) CsSrCl$_3$ doped with 0.5 (*1*), 1 (*2*) and 5 mol.% of Eu^{2+} (*3*); b) pure SrCl$_2$ (*1*) and SrCl$_2$ doped with 1 mol.% of Eu^{2+} (*2*); in comparison with standard NaI:Tl sample (a*4* and b*3*).

concentration in CsSrCl$_3$ leads to the increase of the light yield that can be seen from the pulse-height spectra (Fig. 2a). The maximal value of the light yield is observed for the sample doped with 5 mol.% of Eu^{2+} and it is approximately equal to 39 per cent (ca 16 000 photons per MeV) as compared with NaI:Tl (Table).

As for SrCl$_2$:Eu^{2+} scintillator, its light yield is estimated to be near 30 % as compared with NaI:Tl. So, both materials are bright enough scintillators and complex matrix doped with considerable amount of Eu^{2+} is somewhat brighter than doped strontium chloride. As for SrCl$_2$:Eu^{2+} material, it should be noted that the concentration of Eu^{2+} ca 1 % corresponds to the plateau section [7] where the maximal values of LY is observed and the exceeding of this concentration leads to the decrease of the scintillation parameters owing to concentration quenching of the luminescence.

The best energy resolution for the doped CsSrCl$_3$ samples is observed for the material doped with 5 mol.% of Eu^{2+} (11.5 %) whereas for doped SrCl$_2$ material this parameter is equal to 9.2 %.

The scintillation pulse decay curve for CsSrCl$_3$:Eu^{2+} material doped with 5 mol. % of the activator is presented in Fig. 3. As seen it may be approximated using two components with decay constants 420 ns and 2.8 µs. The fraction of the faster component is 0.3 and that of the slower one is 0.7. In the case of SrCl$_2$ there is only one component with the decay constant which is estimated as 2 µs [7]. This means that both scintillators are rather slow.
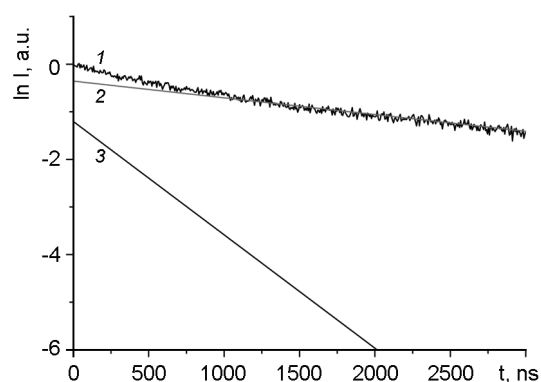

Fig. 3. The scintillation pulse decay for CsSrCl$_3$ material doped with 5 mol. % of Eu^{2+}: total pulse (*1*) and fractions of component with the decay constants equal to 2.8 is (*2*) and 420 ns (*3*).

4. Conclusions

So, in this work CsSrCl$_3$ scintillation crystals doped with 0.5, 1 and 5 mol. % of Eu^{2+} and SrCl$_2$:1 mol. % of Eu^{2+} have been grown by Bridgman-Stockbarger method. In the case of the binary matrix the precipitation of a part of Eu^{2+} in the form of EuO takes place. The radioluminescence spectra of CsSrCl$_3$:Eu^{2+} include a bands with the maxima placed in the region from 437 to 448 nm, their position is dependent on Eu^{2+} concentration increase and the spectrum for SrCl$_2$:Eu^{2+} contains a band with the maximum at 414 nm. The maximal LY of CsSrCl$_3$:Eu^{2+} is observed at 5 mol. % of Eu^{2+} (39 % in respect to NaI:Tl) and R is 11.5 %, whereas for SrCl$_2$:1 mol. % of Eu^{2+} LY is 30 % and $R = 9.2$ %. The scintillation pulse decay curves for CsSrCl$_3$:Eu^{2+} is described by two components with the decay

constants 420 ns and 2.8 µs and the fraction of the faster component is 0.3.

References

1. E.D.Bourret-Courchesne, G.Bizarri, R.Borade et al., *Nucl. Instr. Methods Phys. Res..A*, **612**, 138 (2009).
2. K.Yang, M.Zhuravleva, C.L.Melcher, *Phys. Stat. Solidi, Rapid Res. Lett.*, **5**, 43 (2011).
3. R.G.Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).
4. V.L.Cherginets, T.P.Rebrova, Yu.N.Datsko et al., *J. Chem. Eng. Data*, **55**, 5696 (2010).
5. G.A.Bukhalova, V.M.Burlakova, *Zh. Neorg. Khim.*, **11**, 2812 (1966).
6. O.M.Berdichevskii, M.S.Pidzyrailo, G.B.Stryganiuk, Z.A.Khapko, *J. Phys. Stud*, **8**, 376 (2004).
7. J.Moon, S.Kim, H.Kim et al., in: Abstr. Int. Conf. Inorg. Scintillators and Their Ind. Application, Alushta, Ukraine (2005), p.52.

Сцинтиляційні властивості монокристалів SrCl$_2$ і CsSrCl$_3$, активованих добавками Eu^{2+}

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Сцинтиляційні монокристали CsSrCl$_3$, активовані добавками Eu^{2+} 0,5, 1 і 5 мол. %, і SrCl$_2$: 1 мол. % Eu^{2+} вирощено з розплаву методом Бріджмена-Стокбаргера. Спектри радіолюмінесценції CsSrCl$_3$:Eu^{2+} мають одиничний вузький пік з максимумом, положення якого зміщується від 437 до 448 нм у залежності від концентрації активатора, у випадку матеріалу SrCl$_2$:Eu^{2+} максимум спостерігається при 414 нм. Світловихід CsSrCl$_3$:Eu^{2+} досягає максимального значення при 5 мол. % Eu^{2+} і складає 39 % відносно NaI:Tl (близько 16000 фотонів/МеВ) при енергетичному розділенні $R = 11,5$ %, для SrCl$_2$:1 мол. % Eu^{2+} світловихід дорівнює 30 % (близько 12000 фотонів/МеВ) і $R = 9,2$ %. Крива загасання сцинтиляційного імпульсу для CsSrCl$_3$:Eu^{2+} може бути описана двома компонентами з константами загасання 420 нс і 2,8 мкс і часткою швидшого компонента 0,3.