

Production and properties of $\text{CsSrBr}_3:\text{Eu}^{2+}$ scintillator

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CsSrBr_3 scintillation crystals doped with Eu^{2+} (0.5, 1 and 5 mol. %) have been grown by Bridgman-Stockbarger method. The radioluminescence spectra of $\text{CsSrBr}_3:\text{Eu}^{2+}$ materials include a narrow band with the maximum which position is shifted from 435 to 442 nm with increase of Eu^{2+} concentration in the growth melt. The light yield of $\text{CsSrBr}_3:\text{Eu}^{2+}$ material achieves maximal value at 5 mol. % of Eu^{2+} and it is equal to 35 % relative to NaI:Tl and the best energetic resolution is 9 %.

Монокристаллы сцинтиллятора на основе CsSrBr_3 , активированного добавками Eu^{2+} (0,5, 1 и 5 мол. %), выращены методом Бриджмена-Стокбаргера. В спектрах радиолуминесценции полученных материалов наблюдается узкая эмиссионная полоса, положение максимума которой смещается от 435 до 442 нм при увеличении концентрации Eu^{2+} в твердом растворе. Световыход материала $\text{CsSrBr}_3:\text{Eu}^{2+}$ достигает максимального значения при концентрации Eu^{2+} в ростовом расплаве 5 мол. % и составляет 35 % относительно NaI:Tl , наилучшее энергетическое разрешение равно 9 %.

1. Introduction

Scintillation materials based on Eu^{2+} -activated compounds of alkali and alkaline earth metal halides are now among the most popular objects for investigations in the material science of scintillators. Such compounds as $\text{CsBa}_2\text{I}_5:\text{Eu}^{2+}$, $\text{CsSrI}_3:\text{Eu}^{2+}$ which demonstrate quite high light yield (97,000 and ca 40000 photons per MeV [1, 2]) are now considered as attractive materials for the practical use. Besides the iodide compounds, there are several communications concerned with obtaining and investigations of other halides of $\text{CsSrX}_3:\text{Eu}^{2+}$ family, whereas the compounds based on Cs and Ba chlorides and bromides are unstable. The analysis of $\text{CsCl}-\text{BaCl}_2$ diagram (http://www.crct.polymtl.ca/fact/phase_diagram.php?file=BaCl2-CsCl.jpg&dir=FTsalt) show that CsBaCl_3 compound is incongruent; Cs_2BaCl_4 is a congruent compound but

at temperatures lower than 245°C it breaks down to CsCl and BaCl_2 . Therefore, although the scintillation properties of $\text{Cs}_2\text{BaCl}_4:\text{Eu}^{2+}$ were examined in [3], it is unclear, what compound they belonged to (since the studied powder actually consisted of several different phases). The similar situation is observed in $\text{CsBr}-\text{BaBr}_2$ system.

There are, at least, two communications devoted to $\text{CsSrX}_3:\text{Eu}^{2+}$ ($X=\text{Cl}, \text{Br}$) materials. We reported the dependence of scintillation properties of $\text{CsSrCl}_3:\text{Eu}^{2+}$ single crystals doped with 0.5, 1 and 5 mol. % of the activator [4]. The mentioned above paper [3] contains the "estimated" light yield value of fusion cake with nominal composition $\text{CsSrBr}_3:3$ mol.% of Eu^{2+} which is 40,000 photons per MeV.

The aim of the present work is investigation of luminescence and scintillation properties of $\text{CsSrBr}_3:\text{Eu}^{2+}$ single crystals doped

with different amounts of Eu^{2+} to obtain more information about this material. According to the phase diagram of CsBr-SrBr_2 system [5], there is the only one stable compound, CsSrBr_3 with the melting point of 759°C , therefore, the growth of the single crystals will be comparatively easy.

2. Experimental

The raw of CsSrBr_3 was synthesized in such a way. A weight of SrCO_3 (99.99 %) was dissolved in HBr of reagent grade with the formation of SrBr_2 solution. Then the weight of cesium bromide (99.9 %) providing $\text{CsBr}:\text{SrBr}_2$ molar ratio equal to 1 was added to the solution of SrBr_2 . Ammonium bromide of reagent grade taken in proportion of 0.5 mole per 1 mole of SrBr_2 was added to the solution for avoiding pyrohydrolysis processes at the raw heating. The obtained mixed solution was evaporated to formation of the mixture of crystals. This mixture was placed in a quartz ampoule with the inner diameter of 60 mm and 500 mm height and heated in vacuum up to 500°C .

Eu^{2+} was added to the obtained CsSrBr_3 in the form EuI_2 , which was synthesized according to routine presented in [6].

In the present study pure CsSrBr_3 single crystals and the samples containing 0.5, 1 and 5 mol.% of Eu^{2+} were grown. For this purpose the raw obtained as described above had been placed in a quartz ampoule of 18 mm diameter, melted and kept for a day at 800°C in vacuum (ca 10 Pa). The crystals growth was performed by Bridgman-Stockbarger method; the temperature at the diaphragm was 760°C for pure CsSrBr_3 and 750°C for the doped crystals. The temperature gradient in the growth zone was $10^\circ\text{C}/\text{cm}$ and the rate of the ampoule descent was 2.6–2.8 mm/h. The obtained single crystal was cooled to the room temperature with the rate of $10^\circ\text{C}/\text{h}$. Then the ingot was cut and the detectors of 12 mm diameter and 2 mm height were composed.

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

3. Results and discussion

The radioluminescence spectra of the pure CsSrBr_3 and $\text{CsSrBr}_3:\text{Eu}^{2+}$ materials are presented in Fig. 1. The emission spectrum of CsSrBr_3 includes a wide band of low in-

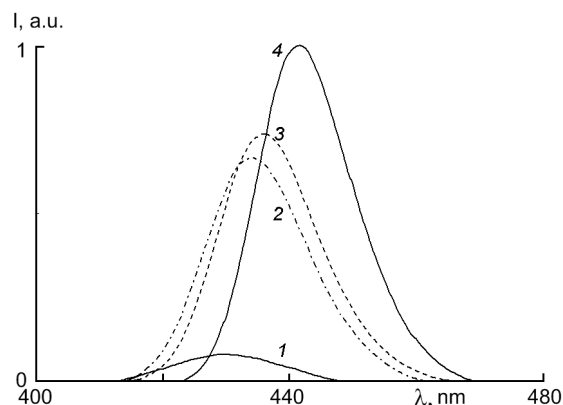


Fig. 1. Radioluminescence spectra of pure CsSrBr_3 (1) and CsSrBr_3 doped with 0.5 mol.% (2), 1 mol.% (3) and 5 mol.% of Eu^{2+} (4).

tensity which may be attributed to the presence of admixtures.

All Eu^{2+} -doped crystals contain only one narrow band which can be ascribed to $5d-4f$ transition in Eu^{2+} ion. Position of the band maximum is shifted from 435 to 442 nm together with the increase of Eu^{2+} concentration from 0.5 to 5 mol. % (FWHM values are within 18–19 nm range). The similar shift takes place in the case of the other Eu -activated compounds based on alkali and alkaline earth halides, e.g., CsSrCl_3 [4] or SrCl_2 [7]. In the latter work this effect is explained by strengthening of crystal field owing to substitution of Sr^{2+} ion with smaller Eu^{2+} (the crystal ion radii are equal to 0.132 and 0.131 nm, respectively). The increase of the activator concentration in this case does not result in appreciable change of the emission band width. The present data qualitatively agrees with our data concerning $\text{CsSrCl}_3:\text{Eu}^{2+}$ materials [4]. However, the changes of position of the emission band maximum and FWHM in bromide scintillator are less than in the case of chloride ones. The increase of the activator concentration in CsSrBr_3 matrix leads to subsequent increase of the integral intensity of the emission band.

The measurements of the light yield (LY) of $\text{CsSrBr}_3:\text{Eu}^{2+}$ materials show that the increase of the activator concentration in CsSrCl_3 leads to the sequential increase of the LY that can be seen from the pulse-height spectra obtained under γ - ^{137}Cs excitation (Fig. 2). The standard NaI:Tl sample demonstrated the follow parameters: the channel number for the photo peak is 2316 and the energetic resolution is 6.3 %.

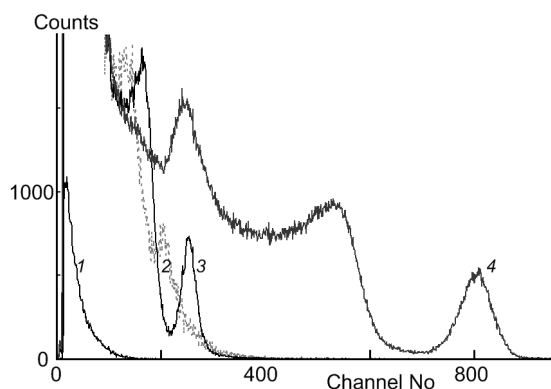


Fig. 2. Pulse height spectra obtained under γ - ^{137}Cs excitation for pure CsSrBr_3 and CsSrBr_3 doped with 0.5 (2), 1 (3) and 5 mol.% of Eu^{2+} (4).

As seen, the pure material CsSrBr_3 is not referred to scintillators. The maximal value of the LY is observed for the sample doped with 5 mol.% of Eu^{2+} and it is approximately equal to 35 % as compared with NaI:Tl (Table). It should be noted that $\text{SrBr}_2:\text{Eu}^{2+}$ material obtained earlier possesses the LY value ca 23 % as compared with NaI:Tl and the energy resolution near 33 %.

So, in contrast to chloride analogs where the scintillation properties of $\text{CsSrCl}_3:\text{Eu}^{2+}$ and $\text{SrCl}_2:\text{Eu}^{2+}$ are comparable, in the case of bromides the complex material possesses essentially better characteristics than $\text{SrBr}_2:\text{Eu}^{2+}$.

4. Conclusion

CsSrBr_3 scintillation crystals doped with 0.5, 1 and 5 mol. % of Eu^{2+} have been

Table 1. Relative light yield (LY , %, in respect to NaI:Tl) and energetic resolution (R , %) of some Eu^{2+} -doped CsSrBr_3 crystals

Detector	LY (γ - ^{137}Cs)	R
$\text{CsSrBr}_3:0.5 \text{ \% Eu}^{2+}$	8.8	–
$\text{CsSrBr}_3:1 \text{ \% Eu}^{2+}$	11.0	13.1
$\text{CsSrBr}_3:5 \text{ \% Eu}^{2+}$	34.9	8.8

grown by Bridgman-Stockbarger method. The radioluminescence spectra of $\text{CsSrBr}_3:\text{Eu}^{2+}$ include bands with the maxima placed in the region from 435 to 442 nm, their position is dependent on Eu^{2+} concentration. The maximal LY of $\text{CsSrBr}_3:\text{Eu}^{2+}$ is observed at 5 mol. % of Eu^{2+} (35 % in respect to NaI:Tl) and R is 9 %.

References

1. E.D.Bourret-Courchesne, G.Bizarri, R.Borade et al., *Nucl. Instr. Meth. Phys. Res., A*, **612**, 138 (2009).
2. K.Yang, M.Zhuravleva, C.L.Melcher, *Phys. Stat. Solidi, Rapid Res. Lett.*, **5**, 43 (2011).
3. E.D.Bourret-Courchesne, G.Bizarri, R.Borade et al., *J. Cryst. Growth*, DOI:10.1016/j.jcrysgro.2012.01.014 (2012).
4. V.L.Cherginets, A.Yu.Grippa, T.P.Rebrova et al., *Functional Materials*, **19**, 187 (2012).
5. R.Riccardi, C.Sinistri, C.V.Campari et al., *Z. Naturforsch.*, **25a**, 781 (1970).
6. V.L.Cherginets, T.P.Rebrova, Yu.N.Datsko et al., *J. Chem. Eng. Data*, **55**, 5696 (2010).
7. J.Moon, S.Kim, H.Kim et al., in: Proc. Int. Conf. Inorg. Scintillators and Their Ind. Application, Alushta, Ukraine (2005).

Одержання і властивості сцинтилятора $\text{CsSrBr}_3:\text{Eu}^{2+}$

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Сцинтиляційні монокристали на основі CsSrBr_3 , активованого добавками Eu^{2+} (0,5, 1 та 5 мол. %), вирощено методом Бриджмена-Стокбаргера. У спектрах радіюлюмінесценції одержаних матеріалів спостерігається вузька емісійна смуга, положення максимуму якої зміщується від 435 до 442 нм при зростанні концентрації Eu^{2+} у твердому розчині. Світловихід матеріалу $\text{CsSrBr}_3:\text{Eu}^{2+}$ досягає максимального значення при концентрації Eu^{2+} у ростовому розплаві 5 мол. % і складає 35 % відносно NaI:Tl , найкраще енергетичне розділення дорівнює 9 %.