Obtaining and scintillation properties of crystals based on Eu^{2+} doped $Ba(Br_{0.9}Cl_{0.1})_2$ solid solution

V.L.Cherginets[1], Yu.N.Datsko[1], A.Yu.Grippa[1], T.V.Ponomarenko[1], N.V.Rebrova[1], T.P.Rebrova[1], T.E.Gorbacheva[1], A.V.Lopin[2], O.G.Trubaeva[1], V.Yu.Pedash[1]

[1] Institute for Scintillation Materials, STC "Institute for Single Crystals ", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

[2] Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Scintillation crystals based on $BaBr_2$–$BaCl_2$ solid solution corresponding to minimal melting point in the phase diagram doped with Eu^{2+} (from 0.3 to 3 mol. %) were grown by Bridgman-Stockbarger method. The X-ray luminescence spectra of pure matrix of $Ba(Br_{0.9}Cl_{0.1})_2$ composition includes wide emission band with the maximum which position is placed near 410 nm. The emission spectra of the Eu^{2+}-activated materials contain narrow bands with the maxima at 411–413 nm. The absolute light yield of $Ba(Br_{0.9}Cl_{0.1})_2$:Eu^{2+} material doped with 3 mol. % of the activator is ca. 32600 photons per MeV and the best energetic resolution is 9.5 %. The decay curve for the studied materials is described by one component with the time constant of 70 ns. Distribution coefficient of Eu^{2+} in the studied matrix is estimated as $k = 0.72\pm0.05$. All the obtained parameters are close to those of $BaBr_2$:Eu^{2+} single crystals obtained under similar conditions.

Keywords: Scintillation crystals, uminescence, solid solution.

Сцинтилляционные монокристаллы на основе активированного европием твердого раствора $BaBr_2$–$BaCl_2$ с составом, соответствующим минимальной температуре плавления на фазовой диаграмме, выращены методом Бриджмена-Стокбаргера. Получен концентрационный ряд, в котором содержание Eu^{2+} варьировалось от 0.3 до 3 мол. %. Спектр рентгенолюминесценции чистой матрицы $Ba(Br_{0.9}Cl_{0.1})_2$ имеет широкую эмиссионную полосу с максимумом при 410 нм. Эмиссионные спектры кристаллов, активированных добавками Eu^{2+}, включают узкую полосу с максимумом в пределах 411–413 нм. Абсолютный световыход материала $Ba(Br_{0.9}Cl_{0.1})_2$:Eu^{2+} с 3 мол. % оценен как 32600 фотонов/МэВ при энергетическом разрешении 9.5 %. Кривые затухания сцинтилляционного импульса для изученных материалов описываются одним компонентом с константой затухания около 700 нс. Коэффициент вхождения Eu^{2+} в изучаемую матрицу равен 0.72 ± 0.05. Все полученные параметры близки к таковым для монокристалла $BaBr_2$:Eu^{2+}, полученного в подобных условиях.

Одержання і сцинтиляційні властивості кристалів на основі твердого розчину Ba(Br$_{0.9}$Cl$_{0.1}$)$_2$, активованого європієм. *В.Л.Чергинець, Ю.М.Дацько, О.Ю.Гриппа, Т.В.Пономаренко, Н.В.Реброва, Т.П.Реброва, Т.Є.Горбачова, О.В.Лопін, О.Г.Трубаєва, В.Ю.Педаш.*

Сцинтиляційні монокристали на основі активованого європієм твердого розчину BaBr$_2$–BaCl$_2$ зі складом, що відповідає мінімальній температурі топлення на фазовій діаграмі, вирощено методом Бріджмена-Стокбаргера. Одержано концентраційний ряд, в якому вміст Eu^{2+} варіювався від 0.3 до 3 мол. %. Спектр рентгенолюмінесценції чистої матриці Ba(Br$_{0.9}$Cl$_{0.1}$)$_2$ має широку емісійну смугу з максимумом при 410 нм. Емісійні спектри кристалів, активованих добавками Eu^{2+}, включають вузьку смугу з максимумом у межах 411–413 нм. Абсолютний світловихід матеріалу Ba(Br$_{0.9}$Cl$_{0.1}$)$_2$:Eu^{2+} з 3 мол. % оцінений як 32600 фотонів/МеВ при енергетичному розділенні 9.5 %. Криві загасання сцинтиляційного імпульсу для вивчених матеріалів описуються одним компонентом з константою загасання близько 700 нс. Коефіцієнт входження Eu^{2+} у матрицю, що досліджено дорівнює 0.72±0.05. Всі одержані параметри є близькими до відповідних характеристик монокристала BaBr$_2$:Eu^{2+}, одержаного в подібних умовах.

1. Introduction

Nowadays scintillation materials based on Eu^{2+}-activated complex compounds or solid solutions of alkali and alkaline earth metal halides attract attention of investigators working in material science of scintillators. This is caused by relatively high functional parameters of these materials exceeding those of widely used NaI:Tl single crystals. For instance, such materials as CsBa$_2$I$_5$:Eu^{2+}, CsBa$_2$I$_5$:Eu^{2+} and Eu^{2+}-doped solid solution of BaBr$_2$–BaI$_2$ system (0.5:0.5) demonstrate high absolute light yield approaching 100,000 photons per MeV together with excellent energy resolution *ca.* 3 per cent [1–3]. Such interest to the iodine-containing compounds is explained by the common opinion that these materials possess narrower band gap comparing with bromide and chloride compounds. Nevertheless, the latter halides are characterized by higher resistance to influence of oxygen-containing atmosphere components and lower hygroscopicity than the iodide compounds.

Our recent investigation of bromide and chloride scintillators of CsSrX$_3$:Eu^{2+} shows that their scintillation parameters are comparable with those of the common used scintillators, therefore, the similar materials also should be prospective for the practical use [4, 5].

The present work is devoted to study of scintillation properties of the material belonging to BaBr$_2$–BaCl$_2$ solid solution system. The phase diagram of the said BaBr$_2$–BaCl$_2$ system is referred to the systems with persistent row of solid solutions possessing minimal melting point of 841°C at content of BaCl$_2$ equal to 10 mol. % [6]. As is known, the crystallization processes of BaBr$_2$–BaCl$_2$ solid solutions possessing compositions deviating from the most low-melting one results in obtaining crystal with different ratios of the constituent anions along the growth axis. In this case the grown Eu^{2+}-doped sample should be characterized by additional non-uniformity of the dopant distribution. Choosing Ba(Br$_{0.9}$Cl$_{0.1}$)$_2$ gross-composition we avoid the non-uniformity of the anion distribution. However, the second non-uniformity connected with the entering of Eu^{2+} in the crystal remains and, so, it can be studied.

2. Experimental

Both components of the solid solution, BaBr$_2$ and BaCl$_2$ were obtained by dissolution of BaCO$_3$ (mass fraction of the main component is 0.9999) in 55 per cent hydrobromic or 37 per cent hydrochloric acid, respectively, both acids were of "chemically pure" grade. Some excess of barium carbonate was added to the obtained solution that provided the precipitation of heavy and lighter alkaline-earth metal cation from the obtained solution. After filtration the said solution was acidified to pH within 3–4 and evaporated to the formation of wet crystalline powder. The latter was dried in vacuum (*ca.* 5–10 Pa) at stepwise temperature elevation from room temperature (*rt*) to 200°C.

EuBr$_2$ was used for the doping of the obtained crystals. It was obtained by dissolution of Eu$_2$O$_3$ (mass fraction of the main component is 0.99999) in the hydrobromic acid taken with 2 per cent excess that resulted in obtaining aqueous solution of EuBr$_3$. Then ammonium bromide (mass fraction of the main component is 0.9999) was added to the formed solution and its amount corresponded to mole ratio of NH$_4$Br

to $EuBr_3$ equal to 4. This solution was evaporated dry and placed in quartz ampoule. The next stage of the process was the obtaining of $EuBr_2$ by thermal decomposition of $EuBr_3$:

$$2EuBr_3 \xrightarrow{t \sim 400^{\circ}C, \; vacuum} 2EuBr_2 + Br_2\uparrow. \quad (1)$$
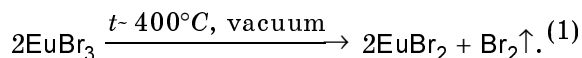
To make this, the ampoule with $EuBr_3$ + NH_4Br mixture was heated to 500°C in vacuum (*ca.* 5 Pa) with stepwise temperature elevation. The sublimation of ammonium bromide was observed at 250–300°C and HBr formed owing to the dissociation process provided additional deoxidization of $EuBr_3$. The elimination of bromide started at temperatures above 300°C and the complete decomposition according to Eq. (1) was achieved at 500°C.

Then obtained $EuBr_2$ was melted at 683°C and cooled to *rt*.

To prepare charge of $Ba(Br_{0.9}Cl_{0.1})_2$ matrix $BaBr_2$ and $BaCl_2$ powders were mixed in mass ratio 92.8:7.2, respectively. Preparation of charge for growth of activated materials was performed by mixing matrix with $EuBr_2$ and the mass fractions of the latter were: 0.0032 (0.3 mol. % of Eu^{2+}), 0.0108 (1 mol. % of Eu^{2+}) and 0.0324 (3 mol. % of Eu^{2+}).

The single crystals were grown by Bridgman-Stockbarger method; the temperature at the diaphragm was 840°C both for the pure halide matrix and for the doped crystals. 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 single crystal 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.

Estimation of the distribution coefficient of Eu^{2+} in $Ba(Br_{0.9}Cl_{0.1})_2$ matrix was performed on the basis of complexonometric determination of Eu content in the grown samples.

The X-ray luminescence spectra were recorded using a setup consisted of X-ray emitter (PEIC-I) and receiving block including monochromator (MDR-23), PMT (PMT-100), amplifier, analog-digital converter and PC. The pulse-height spectra were obtained under ^{137}Cs (γ, 662 keV) irradiation and registered using PMT Hamamatsu R1307.

The kinetics of scintillation light decay was studied as follows. The studied sample was placed directly on the photocathode of
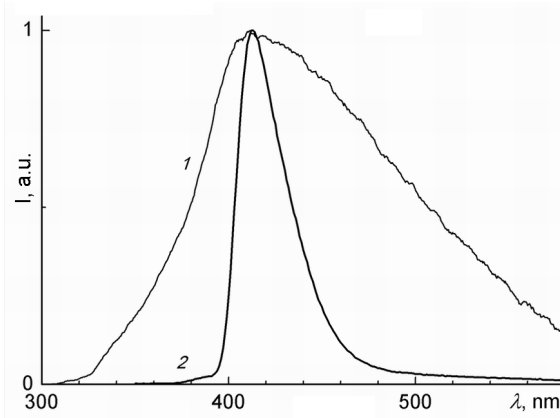

Fig. 1. Normalized X-ray luminescence spectra of single crystals of $Ba(Br_{0.9}Cl_{0.1})_2$ (*1*) and $Ba(Br_{0.9}Cl_{0.1})_2$:1 mol. % Eu^{2+} (*2*) compositions, room temperature.

PMT XP 9822QB without optical contact. The other surfaces of the sample were coated with 3 layers of TETRATEC film. The measurements of the pulse shape were performed using the natural background irradiation without additional γ-ray sources for several hours. The events of enough for the registration intensity by LeCroy Wave-Surfer 422 oscilloscope took place some times per a minute. The total pulse was considered as the scintillation light of the studied crystal.

3. Results and discussion

Examples of X-ray luminescence spectra of $Ba(Br_{0.9}Cl_{0.1})_2$ matrix and $Ba(Br_{0.9}Cl_{0.1})_2$:Eu^{2+} single crystal are presented in Fig. 1. The emission spectrum of the undoped solid solution includes a wide asymmetric band (Fig. 1, curve *1*) which is proper to $BaBr_2$–$BaCl_2$ solid solutions which compositions differ from one studied in this work [7]. The maximum of this band is placed near 410 nm that is in the excellent agreement with the results of [7] and authors of [8] ascribe this band to recombination either of pair consisting of F and V_k. The second possible reason according to [8] is the contamination of the matrix by traces of Eu^{2+}. However, the latter is hardly possible since addition to such matrix of 0.1 mol. % of Eu^{2+} causes considerable reduction of the matrix band intensity and shift of the band maximum to 390 nm and simultaneously the small band with the maximum at 610 nm proper to Eu^{3+} luminescence appears. This permits to make an assumption that the existence of these bands is caused by other admixtures.

Indeed, Eu^{3+} ion cannot exist in a high-temperature halide melt (as it has been mentioned above the minimal melting point in $BaCl_2$–$BaBr_2$ system is 841°C) containing bromide or iodide ions. However, the presence of oxygen and oxide-ion traces in the melt and surrounding atmosphere favours running the following process:

$$2Eu^{2+} + 2O^{2-} + \tfrac{1}{2}O^2\uparrow \rightarrow Eu_2O_3\downarrow \qquad (2)$$
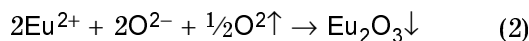
and the existence of trivalent europium in the precipitated solid oxide phase is undoubted. Eu^{2+} has been found in [9] to be inclined to formation of insoluble oxides due to interaction with oxygen-containing admixtures in halide melts. Just luminescence of small Eu_2O_3 results in arising additional emission band (610 nm) [7]. So, the band observed in the undoped matrix could be connected with the presence of oxygen-containing admixtures in the mixed halide melt, and, hence, in the final crystal.

The addition of larger amount Eu^{2+} (0.3 mol. % and more) results is complete suppression of the matrix band and narrow band (FWHM = 0.025 eV), proper for other crystals based on Eu^{2+}-doped alkaline earth halides arises, which is caused by $4f^6 5d^1$–$4f^7$ in Eu^{2+} ion (Fig. 1, curve *2*). This band is characterized by a maximum at 412 nm and its position is practically independent of Eu^{2+} concentration. It should be noted, however, that the integral intensity of the emission of the sample doped with Eu^{2+} is considerably smaller than that of pure matrix and it sequentially increases with the rise of Eu^{2+} concentration in the samples.

An example of excitation and luminescence spectrum of Eu^{2+}-doped $Ba(Br_{0.9}Cl_{0.1})_2$ sample is presented in Fig. 2. The emission spectrum was recorded with an excitation of 360 nm and it shows a band with maximum at 405 nm (FWHM = 0.025 eV). The Eu^{2+} emission can be excited via abroad band between 250 and 380 nm. For the sample containing 1 mol. % Eu^{2+}, the excitation intensity is highest at 275 nm and it sequentially decreases at lower energies. As is seen there is overlapping between the excitation and emission spectra for samples containing high Eu^{2+} concentrations.

The measurements of the light yield (*LY*) and energy resolution (*R*) of pure and Eu^{2+}-doped $Ba(Br_{0.9}Cl_{0.1})_2$ crystals show that in the Eu^{2+} concentration sequence (mol. %) $0 \rightarrow 0.3 \rightarrow 1 \rightarrow 3$ the relative *LY* (fraction with respect to NaI:Tl) is 0.18 (*R* = 11 %) $\rightarrow$ 0.14 (*R* = 10) $\rightarrow$ 0.27 (*R* = 11 %) $\rightarrow$ 0.31 (*R* = 9.5 %). That is,

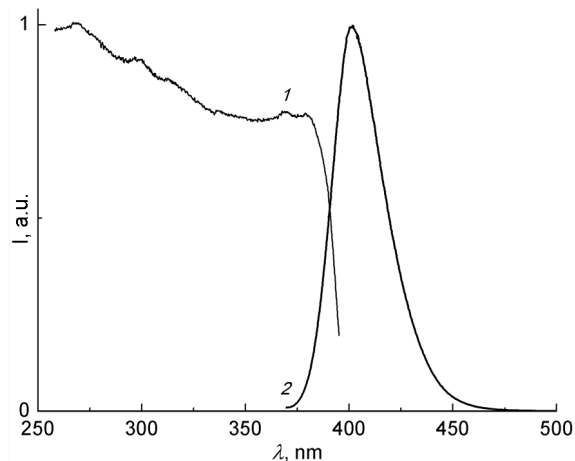Fig. 2. Normalized excitation (*1*) and luminescence (*2*) spectra of $Ba(Br_{0.9}Cl_{0.1})_2$:1 mol. % Eu^{2+} single crystals, room temperature.

the luminosity passes through the minimum at low Eu^{2+} concentrations that can be explained in details using the above-considered data of [7]. The shape of the emission spectrum of the matrix can be caused by the presence of O^{2-} ions in melt (BaO admixtures). Small amounts of Eu^{2+} act as scavengers removing both Eu^{2+} and O^{2-} from the melt and, hence from the final crystals.

From the above-presented concentration row it can be seen that at Eu^{2+} concentrations exceeding 1 mol. % approaches to a plateau of luminosity. For the sample containing 3 mol. % of Eu^{2+} (8 mm diameter and 2 mm height, light collection coefficient is 0.21) the absolute light yield was estimated according to routine described in [10] to be 32,600 photons per MeV. For grown under the same conditions $BaBr_2$:1 mol. % Eu^{2+} scintillator the relative *LY* is 0.32 (*R* = 10 %).

The decay curves of scintillation light for the obtained Eu^{2+}-doped materials can be described using single component with the decay times lying in 660–700 ns range and the decay time decreases with increasing Eu^{2+} concentration in the crystal.

As for distribution coefficient of Eu^{2+} in $Ba(Br_{0.9}Cl_{0.1})_2$ matrix, its estimation for samples which charge contains more than 1 mol.% $EuBr_2$ yields value $k = 0.72\pm0.05$, whereas for pure $BaBr_2$ this constant is equal to 0.73. So, small addition of chloride into bromide does not lead to appreciable changes in Eu^{2+} distribution between liquid and solid phase and does not effect scintillation properties of the corresponding Eu^{2+}-doped scintillators.

4. Conclusions

Scintillation crystals of undoped and Eu^{2+}-doped crystals based on $Ba(Br_{0.9}Cl_{0.1})_2$ matrix based were grown by Bridgman-Stockbarger method and were studied by traditional methods. The X-ray luminescence spectra of the pure matrix includes wide emission band with the maximum at 410 nm. The emission spectra of the Eu^{2+}-activated materials contain narrow bands with the maxima at 411–413 nm. The absolute light yield of $Ba(Br_{0.9}Cl_{0.1})_2$:3 mol. % Eu^{2+} is ca. 32600 photons per MeV and the best energetic resolution is 9.5 %. The decay curve for the Eu^{2+}-doped materials is described by one component with the time constant of 700 ns. Distribution coefficient of Eu^{2+} in the studied matrix is estimated as $k = 0.72\pm0.05$. All the obtained parameters are close to those of $BaBr_2$:Eu^{2+} single crystals obtained under similar conditions.

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