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# Scintillation properties of $ACa_{1-y}Eu_yX_3$ (A = K, Rb, Cs, X = Cl, Br) crystals

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The presented paper describes a series of new $Eu^{2+}$-activated scintillators of $Ca_{1-y}Eu_yX_2$, $ACa_{1-y}Eu_yX_3$, (A=K, Rb, Cs; X=Cl, Br, $0 \le y \le 0.08$). All the single crystals were grown using the Bridgman-Stockbarger method and their operational characteristics were compared including affinity for atmospheric moisture and scintillation properties (light yield, energetic resolution and decay constant of scintillation light). The maximal values of light yield of $ACa_{0.92}Eu_{0.08}X_3$ materials in the sequence A = K, Rb, Cs were observed for Rb-containing crystals: 38500 photons per MeV for $RbCa_{0.92}Eu_{0.08}Cl_3$ and 54000 photons per MeV for $RbCa_{0.92}Eu_{0.08}Br_3$. The distribution coefficients of $Eu^{2+}$ in all the studied crystals are very close to unity that can be explained by perfect isomorphism of $Eu^{2+}$ and $Ca^{2+}$ cations.

**Keywords**: scintillation materials, Bridgman-Stockbarger method, calcium halides.

Исследованы свойства новых сцинтилляционных материалов $Ca_{1-y}Eu_yX_2$, $ACa_{1-y}Eu_yX_3$, (A=K, Rb, Cs; X=Cl, Br, $0 \le y \le 0{,}08$), выращенных методом Бриджмена-Стокбаргера. Изучены эксплуатационные (чувствительность к действию атмосферной влаги) и сцинтилляционные (световой выход, энергетическое разрешение, кинетические параметры затухания сцинтилляционного импульса) характеристики. Максимальный световой выход в материалах $ACa_{0,92}Eu_{0,08}X_3$ в последовательности щелочных металлов A = K, Rb, Cs наблюдается для рубидий-содержащих кристаллов: 38500 фотонов/МэВ для $RbCa_{0,92}Eu_{0,08}Cl_3$ и 54000 фотонов/МэВ для $RbCa_{0,92}Eu_{0,08}Br_3$. Коэффициенты вхождения европия (II) во все изученные кристаллы близки к единице, что может быть объяснено изоморфизмом катионов $Eu^{2+}$ и $Ca^{2+}$.

**Сцинтиляційні властивості кристалів $ACa_{1-y}Eu_yX_3$ (A = F2K, Rb, Cs, X = Cl, Br).** *О.Ю.Гриппа, Н.В.Реброва, Т.Е.Горбачова, В.Л.Чергинець.*

Досліджено властивості нових сцинтиляційних матеріалів $Ca_{1-y}Eu_yX_2$, $ACa_{1-y}Eu_yX_3$, (A= K, Rb, Cs; X = Cl, Br, $0 \le y \le 0{,}08$), вирощених методом Бріджмена-Стокбаргера. Вивчено експлуатаційні (чутливість до дії атмосферної вологи) і сцинтиляційні (світловий вихід, енергетичне розділення і кінетичні параметри загасання сцинтиляційного імпульсу) характеристики. Максимальний світловий вихід у матеріалах $ACa_{0,92}Eu_{0,08}X_3$ у послідовності лужних металів A = K, Rb, Cs спостерігається для рубідій-вмісних кристалів: 38500 фотонів/МеВ для $RbCa_{0,92}Eu_{0,08}Cl_3$ і 54000 фотонів/МеВ для $RbCa_{0,92}Eu_{0,08}Br_3$. Коефіцієнти входження європію (II) у всі досліджені кристали є близькими до одиниці, що може бути пояснене ізоморфізмом катіонів $Eu^{2+}$ і $Ca^{2+}$.

## 1. Introduction

Halide scintillators for X- and γ-rays have attracted much attention for medical and security applications. It could be related to their high light yield and good energy resolution in comparison to other compounds. The highest performance scintillators are $SrI_2:Eu^{2+}$ and $CaI_2:Eu^{2+}$, which exhibit light yield *ca.* 120,000 ph/MeV with an energy resolution of 3 % and 110,000 ph/MeV with an energy resolution of 5.2 %, respectively [1, 2]. Both halides are highly hygroscopic. The layered structure of $CaI_2:Eu^{2+}$ leads to mechanical instability and causes difficultias during the growing of a single crystal and further treatment with the crystal. Though it is possible to receive $SrI_2:Eu^{2+}$ crystal of a large size [3, 4] and high quality, it demands high level of purification of the starting materials, which increases the costs of the production. As a result, the last decade ternary alkali and alkaline earth halides with following formulas: $AM_2X_5$, $AMX_3$, $A_2MX_4$ and $A_4MX_6$ (A = K, Rb, Cs; M = Ca, Sr, Ba; X = Cl, Br, I) have been studied intensively and a lot of effective scintillating materials among them have been found [5–17].

We previously reported scintillation properties of $KCaBr_3:Eu^{2+}$, $RbCaBr_3:Eu^{2+}$, $RbCaCl_3:Eu^{2+}$ and $CsCaBr_3:Eu^{2+}$ [18–20]. The crystal of $CsCaBr_3:Eu^{2+}$ shows 28,000 ph/MeV [18], while Eu-doped $KCaBr_3$, $RbCaBr_3$ and $RbCaCl_3$ bulk crystals exhibit 10 %, 77 % and 55 % of relative light yield to that of $NaI:Tl^+$, respectively [18–20]. However, Eu-doped $KCaCl_3$ have not been investigated yet.

The aim of the study was to extend our previous research on mixed calcium halides with new data and to summarize all the results. A new crystal of $KCa_{1-y}Eu_yCl_3$ composition has been grown and its scintillating properties were investigated. The properties of $ACa_{1-y}Eu_yX_3$ (A = K, Rb, Cs; X = Cl, Br) and $CaX_2$ (X = Cl, Br) materials were compared and the value of absolute light yield for $RbCa_{1-y}Eu_yX_3$ (X = Cl, Br) crystals has been estimated.

## 2. Experimental

Different stoichiometric mixtures of $Ca_{1-y}Eu_yX_2$ and $ACa_{1-y}Eu_yX_3$ (A=K, Rb, Cs; X = Cl, Br, $0 \le y \le 0.08$) were prepared. AX, $CaX_2$ and $EuX_2$ were used as starting materials. $CaX_2$ and $EuX_2$ were obtained from $CaCO_3$ (3N) and $Eu_2O_3$ (5N). A powder of $CaCO_3$ ($Eu_2O_3$) was dissolved in the corresponding commercial acid (36 % HCl extra pure or 48 % HBr of reagent grade) with formation of $CaX_2$ ($EuX_3$). The solution was evaporated until crystallization started. The wet $CaX_2 \cdot H_2O$ ($EuX_3 \cdot H_2O$) were dehydrated in the presence of corresponding $NH_4X$. $EuX_2$ (X=Cl, Br) was obtained from $EuX_3$ by heating in a vacuum at 850°C for 24 h.

Single crystals of $Ca_{1-y}Eu_yX_2$ and $ACa_{1-y}Eu_yX_3$ (A = K, Rb, Cs; X = Cl, Br) were grown in evacuated quarts tubes using the Bridgman-Stockbarger technique. The bottom of the growth ampoule had a conical shape in order to stimulate crystal nucleation. The ampoule was placed in a furnace and heated to a temperature of 50°C above the melting point of crystals and kept at this temperature for 24 h to achieve good mixing of all the components. During the growth process, the sealed quartz tube was moved downward from the hot to the cold zone of the furnace with a rate of 1–3 mm/h. The temperature gradient was 5°C/cm, the cooling speed was 5–7°C. The grown boules were 40–70 mm long and 12 mm in diameter. They were cut to cylinders ∅12×2 $mm^2$, polished and mounted in aluminum containers. The hygroscopic nature of the halides makes them difficult to handle, as dry condition mast be maintained.

The hygroscopicity of the crystals was estimated by measuring the change in weight of the samples exposed to ambient atmosphere for 50 min with a temperature of 23°C and relative humidity of 40±2 %. The sample with dimensions of ∅12×2 $mm^2$ were cut from the grown boules. The surfaces of the samples were unpolished.

Scintillation decay curves were recorded using ∅12×2 $mm^2$ crystals mounted in aluminum housing. The packed specimens were placed directly on a PMT (Hamamatsu R6231-01) photocathode without optical grease. Scintillation pulses were excited using radiation from $^{137}Cs$ gamma source and recorded using Rigol DS6064 digital oscilloscope. For each specimen several hundred waveforms with energies corresponding to the photopeak were recorded and then averaged. This averaged waveform was considered as the scintillation decay curve of the studied crystal.

The light yield and the energy resolution were measured by a pulse method described in detail in [22]. Housed scintillators were coupled to a R1307 Hamamatsu PMT entrance window using silicon optical compound Visilox V-788. Open parts of the de-

Table 1. Congruently melting compounds in the $AX–CaX_2$ systems (A = K, Rb, Cs, X = Cl, Br).

| System | Ternary compound | Structure | Space group | Melting point, °C | Reference |
|---|---|---|---|---|---|
| $KBr–CaBr_2$ | $KCaBr_3$ | Orthorhombic | *Pnma* | 639 | [23] |
| $RbBr–CaBr_2$ | $RbCaBr_3$ | Orthorhombic | *Pnma* | 742 | [23] |
| $CsBr–CaBr_2$ | $CsCaBr_3$ | Cubic | *Pm3m* | 823 | [23] |
| $KCl–CaCl_2$ | $KCaCl_3$ | Orthorhombic | *Pnma* | 741 | [24] |
| $RbCl–CaCl_2$ | $RbCaCl_3$ | Orthorhombic | *Pnma* | 855 | [25] |
| $CsCl–CaCl_2$ | $CsCaCl_3$ | Cubic | *Pm–3m* | 910 | [26] |

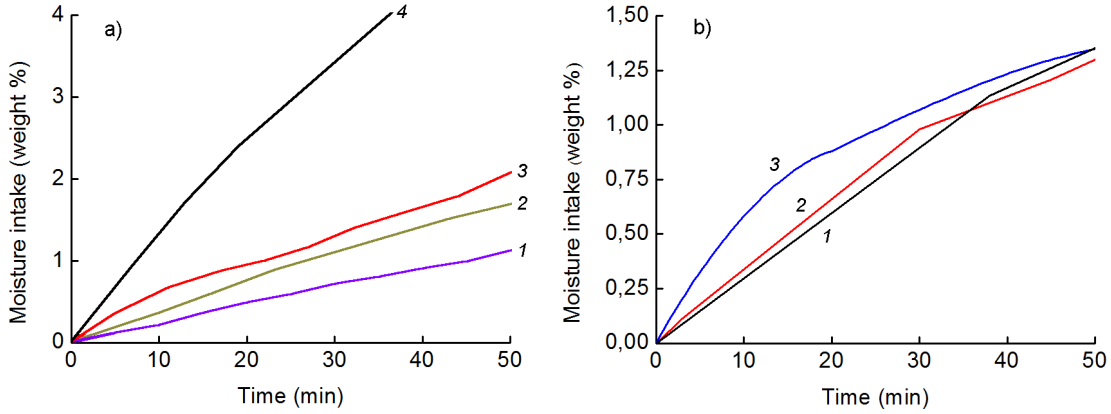


Fig. 1. Hygroscopic nature of (a) — $CsCa_{0.95}Eu_{0.05}Br_3$ (*1*), $RbCa_{0.95}Eu_{0.05}Br_3:Eu^{2+}$ (*2*), $Ca_{0.95}Eu_{0.05}Br_2$ (*3*) and $Ca_{0.95}Eu_{0.05}I_2:Eu^{2+}$ (*4*) (b) — $KCa_{0.95}Eu_{0.05}Cl_3:Eu^{2+}$ (*1*), $RbCa_{0.95}Eu_{0.05}Cl_3:Eu^{2+}$ (*2*) and $CaCl_2$ (*3*) crystals under temperature of 23°C and relative humidity of 40±2 %.

tectors and PMT photocathode were covered by three layers of Tetratex tape. As a gamma-ray source $^{137}Cs$ (662 keV) was used. The PMT output was connected to a charge-sensitive preamplifier BUS 2-95 (Tenzor, Russia), custom shaping amplifier and a multichannel analyzer AMA-03F (Tenzor, Russia). Relative light yields were determined by comparing the peak position of our crystals to those of a NaI:Tl crystal with the same size and shape. The instrumental error of the light yield and the *R* determinations does not exceed 5 %.

The europium content in the single crystals was determined by complexonometric titration with standard EDTA solution using xylenol orange as indicator [23].

### 3. Results and discussion

The data on phase diagrams of the binary systems $AX–CaX_2$ (A=K, Rb, Cs, X=Cl, Br) published [24–27] show that only one congruent compound of $ACaX_3$ composition exists in the said systems. The crystal structure information and melting point for each such compound are shown in Table 1. Congruent melting makes $ACaX_3$ suitable for single crystal growth by Bridgman-Stockbarger method. All the ternary halides of $ACaX_3$ can be easy activated with $Eu^{2+}$, which preferentially substitutes the $Ca^{2+}$ sites.

The single crystals described in the present work were grown 12 mm in diameter and 50–70 mm in length. Calcium chloride exhibits a phase transition from tetragonal to orthorhombic structure at 235°C [28], as a result its single crystals crack and completely destroy during the cooling. In the case of $CaBr_2$ the phase transition occurs at 553°C, which allows obtaining single crystals suitable for composing a scintillation detector. Shifting from binary to ternary halides $ACaX_3$ (A=K, Rb, Cs, X=Cl, Br) leads to structural stability. The exception is $KCa_{0.995}Eu_{0.005}Br_3$, it had crumbled into powder over a week due to phase transitions.

The moisture absorption by the grown crystals were measured at room temperature and a relative humidity of 40±2 %. Their corresponding relative moisture uptakes as a function of time are shown in Fig. 1a and b. The specimen of $Ca_{1-y}Eu_yBr_2$ is significantly resistant to atmospheric moisture in comparison to $CaI_2:Eu^{2+}$. There is no essential

Table 2. Scintillation decay times of $Ca_{1-y}Eu_yBr_2$, $ACa_{1-y}Eu_yX_3$ (A=K, Rb, Cs, X=Cl, Br) crystal with different concentrations of $Eu^{2+}$

| Composition | Scintillation decay time, μs | | |
|---|---|---|---|
| | $y$ = 0.03 | $y$ = 0.05 | $y$ = 0.08 |
| $Ca_{1-y}Eu_yBr_2$ | 1.645 | 2.511 | NA |
| $RbCa_{1-y}Eu_yBr_3$ | 2.70 | 3.14 | 3.56 |
| $CsCa_{1-y}Eu_yBr_3$ | NA | 0.134, 5.27, 28 | 0.145, 6.097 |
| $KCa_{1-y}Eu_yCl_3$ | 1.7 | 2.44 | 2.59 |
| $RbCa_{1-y}Eu_yCl_3$ | 1.74 | 2.48 | 2.73 |

change in moisture sensitivity with introducing RbX into $CaX_2$ (X = Cl, Br) lattice, while the ternary halides of $CsCa_{1-y}Eu_yX_3$ are less moisture sensitive than $CaX_2$ (X=Cl, Br).

For the single crystals of $CaBr_2$, $CsCaBr_3$, $RbCaBr_3$ and $RbCaCl_3$ the distribution coefficients of $Eu^{2+}$ were determined; they were found to be 1.00±0.03, 1.07±+0.17, 0.98±+0.04 and 0.99±+0.08, correspondingly. The obtained distribution coefficients are very close to unity and therefore one can conclude that the studied systems show complete isomorphism, though the difference in the ionic radii of $Eu^{2+}$ and $Ca^{2+}$ is 15 %, which is boundary value by Goldschmidt [29].

Scintillation decay curves show (Fig. 2) that ternary calcium halides described in the work are slow scintillators. Decay times increase with the increasing concentration of europium and their values are between 0.137 and 6.1 μs, which are in good correspondence with the lifetime of the $Eu^{2+}$ center (~ 1–10 μs) [30]. The increasing of decay times with europium concentration could be the result of self-absorption of $Eu^{2+}$, the same behavior is observed in other $Eu^{2+}$-activated halides [5, 6, 10, 11]. Table 2 presents the scintillation decay time of $CaBr_2$:$Eu^{2+}$ and $ACa_{1-y}Eu_yX_3$ (A=K, Rb, Cs, X=Cl, Br) crystals with different $Eu^{2+}$ concentration. In $RbCa_{1-y}Eu_yBr_3$ the increasing concentration of $Eu^{2+}$ from 3 to 8 mol. % leads to increasing of decay constants from 2.70 μs to 3.56 μs. In the chloride analogue the same increasing of the dopant leads to increasing of time constants from 1.74 to 2.73 μs. It should be noted that similar tendency can be seen for time constants with the increasing of temperature: 0.806 (77 K) → 1.635 μs (293 K) [19]. For the crystals of $Ca_{1-y}Eu_yBr_2$ the increasing of activator concentration from 3 to 5 mol. % increases decay time from 1.65 to 2.51 μs [31]. The

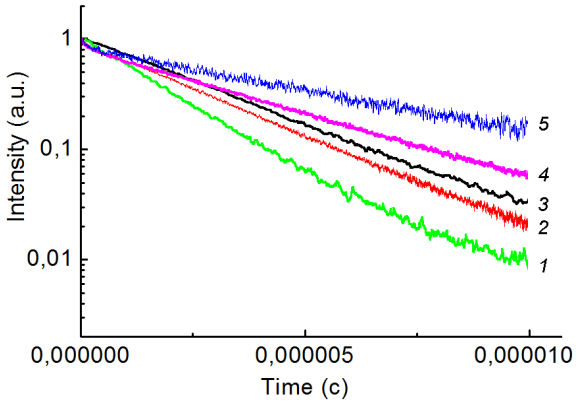


Fig. 2. Normalized scintillation time profiles of $KCa_{0.95}Eu_{0.05}Cl_3$ (*1*), $Ca_{0.95}Eu_{0.05}Br_2$ (*2*), $RbCa_{0.95}Eu_{0.05}Cl_3$ (*3*), $RbCa_{0.95}Eu_{0.05}Br_3$ (*4*) and $CsCa_{0.95}Eu_{0.05}Br_3$ (*5*).

pulse decay curve of $CsCa_{0.95}Eu_{0.05}Br_3$ could be described with three exponents and the decay constants are 0.134 μs, 5.27 μs and 28 μs. The contributions of each to the total light yield are 0.43 %, 89.82 % and 9.75 %, respectively. In the case of $CsCa_{0.92}Eu_{0.08}Br_3$ the decay time values increase to 0.145 μs and 6.09 μs for the first and the second component, respectively. The third component is impossible to measure correctly with the method used in the work.

For all the obtained in the work samples light yield and energy resolution were measured. For better comparison of scintillating efficiency a shaping time of 12 μs was chosen. Light yield measurements were performed at room temperature under excitation by $^{137}Cs$ source.

Pulse height spectra of the crystals are presented in Fig. 3. They correspond to the maximal values of light yield. Table 3 recapitulates the scintillation properties of $Ca_{1-y}Eu_yBr_2$ and $ACa_{1-y}Eu_yX_3$ (A=K, Rb, Cs, X = Cl, Br). The maximal light yield for the

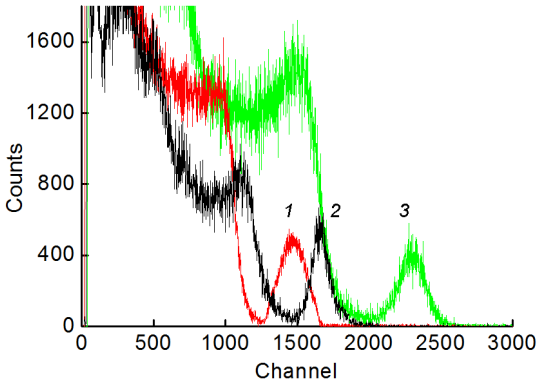


Fig. 3. Pulse height spectra of 8 mol.% $Eu^{2+}$-doped $KCaCl_3$ (*1*), $CaBr_2$ (*2*) and $RbCaBr_3$ (*3*).

Table 3. Scintillation properties of $Eu^{2+}$-doped of the $AX–CaX_2$ (A = K, Rb, Cs, X= Cl, Br) crystals

| Material | Light yield, ph/MeV | Energy resolution at 662 keV, % |
|---|---|---|
| $Ca_{0.92}Eu_{0.08}Br_2$ | 39,000 | 9.1 |
| $KCa_{0.995}Eu_{0.005}Br_3$ | 7,000 | 14 |
| $RbCa_{0.92}Eu_{0.08}Br_3$ | 54,000 | 8.2 |
| $CsCa_{0.92}Eu_{0.08}Br_3$ | 24,000 | 9.3 |
| $KCa_{0.92}Eu_{0.08}Cl_3$ | 34,000 | 13.6 |
| $RbCa_{0.92}Eu_{0.08}Cl_3$ | 38,500 | 12 |
| $CsCa_{0.9}Eu_{0.1}Cl_3$ [5] | 18,000 | 8.9 |

solid solutions of $Ca_{1-y}Eu_yBr_2$ and $ACa_{1-y}Eu_yX_3$ was achieved at $y = 0.08$ of $Eu^{2+}$. With the increase of activator concentration to $y = 0.09$ the quality of the $Ca_{1-y}Eu_yBr_2$ and $CsCa_{1-y}Eu_yBr_3$ crystals became yellow and the deterioration of the scintillating parameters took place. The crystals doped with $y = 0.1$ of $Eu^{2+}$ have orange-yellow color and there is no photopeak in their pulse height spectra due to the concentration quenching.

To summarize the scintillating properties of $ACa_{0.92}Eu_{0.08}X_3$ (X=Cl, Br; A= K, Rb, Cs) in Fig. 4 the dependence of the maximal light yield vs. the ionic radius of the alkali metal is presented. In the raw of $K \rightarrow Rb \rightarrow Cs$ the highest values of light yield were observed at rubidium-containing compounds. Thus, $RbCa_{0.92}Eu_{0.08}Br_3$ shows light yield of 54,000 ph/MeV and $RbCa_{0.92}Eu_{0.08}Cl_3$ shows light yield of 38,500 ph/MeV.

Shifting from $Eu^{2+}$-doped binary halides of calcium to ternary matrices leads to an improvement of certain properties, i.e. the single crystals of $CsCa_{1-y}Eu_yBr_3$<F255 are

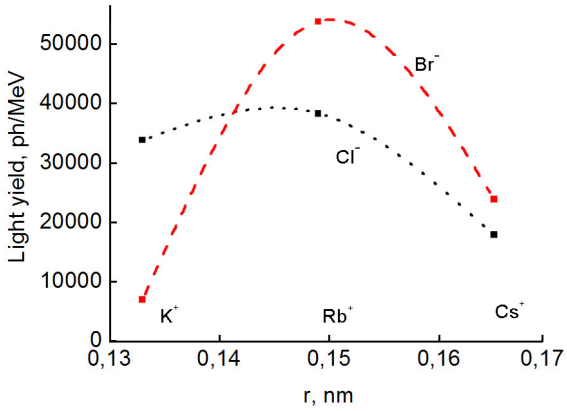


Fig. 4. The dependences of the maximal light yield of $ACa_{0.92}Eu_{0.08}X_3$ (A=K, Rb, Cs, X=Cl, Br) crystals vs. the ionic radius of the alkali metal.

less moisture sensitive in comparison with $Ca_{1-y}Eu_yBr_2$, while the crystals of $RbCa_{1-y}Eu_yBr_3$ exhibit higher light yield. The single crystals of $RbCa_{1-y}Eu_yBr_3$, $CsCa_{1-y}Eu_yBr_3$ and $RbCa_{1-y}Eu_yCl_3$ compositions retain their scintillating properties for at least two years.

It has been concluded that crystals of $Ca_{1-y}Eu_yCl_2$ and $KCa_{1-y}Eu_yBr_3$ may hardly find practical application as scintillators because of structural instability caused by structural transitions in a cooling process. In the case of $CsCa_{1-y}Eu_yBr_3$ it is possible to grow crystals of large sizes suitable for practical use. We managed to grow the single crystal of $CsCa_{0.95}Eu_{0.05}Br_3$ with the size of ∅45×100 $mm^2$.

## *4. Conclusions*

A series of new $Eu^{2+}$-activated scintillators of $Ca_{1-y}Eu_yX_2$, $ACa_{1-y}Eu_yX_3$, (A=K, Rb, Cs; X=Cl, Br, $0 \le y \le 0.08$) compositions is investigated. Their single crystals were grown by the vertical Bridgman-Stockbarger method. The distribution coefficients of activator in the crystals are very close to unity which indicates the complete isomorphism of $Eu^{2+}$ and $Ca^{2+}$ in the studied systems. It has been found that in the single crystals of the ternary $Eu^{2+}$-activated halides $ABX_3$ (A=K, Rb, Cs; X=Cl, Br) the maximum values of light yield are observed in Rb-containing materials. The light yields are 54,000 ph/MeV for $RbCa_{0.92}Eu_{0.08}Br_3$, 38,500 ph/MeV for $RbCa_{0.92}Eu_{0.08}Cl_3$ and 34,000 ph/MeV for $KCa_{0.92}Eu_{0.08}Cl_3$.

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