

Scintillation properties of europium doped RbCaCl₃ crystals

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The scintillation properties of RbCa_{1-x}Eu_xCl₃ ($x = 0.005, 0.03, 0.05, 0.08$) single crystals grown from the charge obtained by the solution routine using the Bridgman-Stockbarger method are reported. The luminescence spectra of RbCa_{1-x}Eu_xCl₃ crystals show a single band with a maximum which position shifts from 437 to 443 nm with increase of mole fraction of Eu²⁺ from 0.005 to 0.08. The decay of the scintillation pulse can be described using single component and the decay time rises towards concentration of Eu²⁺ in crystals. The relative light yield achieves 55 per cent vs. NaI:Tl for RbCa_{0.92}Eu_{0.08}Cl₃ sample.

Keywords: rubidium chloride, calcium chloride, europium, scintillator, luminescence.

Изучены сцинтилляционные свойства монокристаллов RbCa_{1-x}Eu_xCl₃ ($x = 0,005, 0,03, 0,05, 0,08$), выращенных методом Бриджмена-Стокбаргера из шихты, полученной раствором способом. Спектры люминесценции кристаллов RbCa_{1-x}Eu_xCl₃ включают полосу с максимумом, положение которого смещается от 437 до 443 нм при увеличении молярной доли Eu²⁺ в шихте от 0,005 до 0,08. Кривые затухания сцинтилляционного импульса для всех исследованных образцов являются одноэкспоненциальными, при этом время затухания возрастает с увеличением концентрации Eu²⁺ в образцах. Относительный световой выход достигает максимального значения 55 % относительно NaI:Tl для образца состава RbCa_{0,92}Eu_{0,08}Cl₃.

Сцинтиляційні властивості монокристалів RbCaCl₃, активованих європієм. *Н.В.Реброва, О.Ю.Гриппа, А.С.Пушак, Т.Є.Горбачова, В.Ю.Педаш, В.Л.Чергинець, В.О.Тарасов.*

Досліджено сцинтиляційні властивості монокристалів RbCa_{1-x}Eu_xCl₃ ($x = 0,005, 0,03, 0,05, 0,08$) вирощених методом Бриджмена-Стокбаргера з шихти, одержаної розчинним способом. Спектри люмінесценції кристалів RbCa_{1-x}Eu_xCl₃ включають смугу з максимумом, положення якого зміщується від 437 до 443 нм при зростанні молярної частки Eu²⁺ у шихті від 0,005 до 0,08. Криві загасання сцинтиляційного імпульсу для всіх досліджених зразків є одноекспоненційними, при цьому час загасання зростає в міру підвищення концентрації Eu²⁺ у зразках. Відносний світловий вихід досягає максимального значення 55 % відносно NaI:Tl для зразка складу RbCa_{0,92}Eu_{0,08}Cl₃.

1. Introduction

The latest researches in material science of scintillators are mainly devoted to development of Eu²⁺-activated matrixes based on

cesium and alkaline earth halides with the common formula CsMX₃ (M = Ca, Sr; X = Cl, Br, or I). The scintillators of common CsMX₃:Eu²⁺ (M=Ca, Sr; X=Cl, Br, or I) composition [1–4] with perovskite-type struc-

ture have been extensively studied because of their good scintillation properties that makes them available for the detection of gamma-rays. Thus, $\text{CsSr}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$ exhibits high scintillation light yield of 65,000 ph/MeV (photons per a MeV) with the energy resolution of 5.9 % at 662 keV and scintillation decay time of 3.3 μs [1]. The scintillation light yield of $\text{CsSr}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ is 33,400 ph/MeV with energy resolution of 11.5 %, while in the case of $\text{CsSr}_{0.95}\text{Eu}_{0.05}\text{Br}_3$ the light yield is 31,300 ph/MeV with energy resolution of 9 % [2]. The decay times at room temperature (*rt*) are 2.7 μs and 2.5 μs , respectively [2].

The light yield of $\text{CsCa}_{0.97}\text{Eu}_{0.03}\text{Cl}_3$ was reported in [3] to be 38,500 ph/MeV with the energy resolution of 8 % at 662 keV and scintillation decay times of 0.66 μs (15 %) and 1.72 μs (85 %). The reported light yields were 18,000 ph/MeV for $\text{CsCa}_{0.9}\text{Eu}_{0.1}\text{Cl}_3$ [3] and 23,000 ph/MeV for $\text{CsCa}_{0.95}\text{Eu}_{0.05}\text{Br}_3$ [4]. The energy resolutions are 8.9 % and 9.9 %, respectively. The scintillation decay time of $\text{CsCa}_{0.9}\text{Eu}_{0.1}\text{Cl}_3$ is fitted with double-exponential decay components with lifetimes of 2.51 μs (17 %) and 5.05 μs (83 %) [3]. The decay time profile of $\text{CsCa}_{0.95}\text{Eu}_{0.05}\text{Br}_3$ is complex and corresponds to three-exponential components with lifetimes of 0.134 μs (0.43 %), 5.27 μs (89.82 %) and 28 μs (9.75 %) [4].

The corresponding rubidium compounds have been paid less attention. One of the reasons of this consists in the fact that rubidium contains 28.75 mol. % of ^{87}Rb isotope which is β -irradiator with half-decay time of $4.8 \cdot 10^{10}$ years [5]. On the other hand, comparing with the mixed cesium halides the rubidium analogs are not so prone to phase transitions in sub-solidus region and, in particular, RbCaCl_3 compound possesses lower melting point comparing with CsCaCl_3 (855°C vs. 908–910°C) [6]. Previously the interest in them arose from core-valence luminescence and related fast scintillation. The photoluminescent properties of RbCaCl_3 activated with Yb^{2+} , Eu^{2+} , Cu^+ , Mn^{2+} , Ce^{3+} were well-described [7–9] and the scintillator $\text{RbCaCl}_3:\text{Cs}^+$ were reported [10]. However, the scintillation properties of RbCaCl_3 activated by Eu^{2+} have not been studied yet. The present work describes the effect of the Eu^{2+} concentration on the scintillation properties of $\text{RbCaCl}_3:\text{Eu}^{2+}$ single crystals.

2. Experimental

CaCl_2 was obtained by dissolution of CaCO_3 powder (5N) in 36 mas. % HCl (extra pure). This solution was evaporated to dry state and mixed with NH_4Cl . The mixture was dehydrated slowly in a dynamic vacuum and the temperature was raised until the NH_4Cl sublimated. Before the crystal growth RbCl (3N) was dried at 200°C in a dynamic vacuum. The dry CaCl_2 was mixed in a glow box with RbCl and EuCl_2 . EuCl_2 was preliminary obtained from EuCl_3 by heating in vacuum (*ca.* 5–10 Pa) at 850°C for 24 h. The routine of EuCl_3 synthesis was similar to that of CaCl_2 and Eu_2O_3 (5N) was used as a starting material. For the crystal growth charge of four compositions of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ ($x=0.005, 0.03, 0.05$ and 0.08) was prepared.

Single crystal of common $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ ($x = 0.005 \div 0.08$) composition were grown in evacuated and sealed quartz ampoules by the vertical Bridgman-Stockbarger technique. The ampoule was placed in a furnace and heated to 900°C and kept at this temperature for 24 h to provide the homogenization of the melt. The temperature gradient in the growth region was 5°C/cm, the downward motion of the ampoule was 2 mm/h and the temperature on the diaphragm was equal to the melting point of RbCaCl_3 compound, 855°C [6]. The obtained single crystal was cooled to the *rt* with the rate of 5°C/h. The grown boules of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ were removed from the ampoules in a dry atmosphere, cut to $\varnothing 12 \times 2$ mm cylinders, polished and mounted in aluminum housing.

The excitation and emission spectra of the crystals were recorded using LUMINA spectrofluorimeter (Thermo Scientific, USA) with a spectral resolution of 2.5 nm. The X-ray spectra were recorded by spectrophotometer KSVU-23 using X-ray source REIS-I with tube voltage up to 35 kV.

Scintillation decay curves of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ materials were recorded using $\varnothing 12 \times 2$ mm² 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

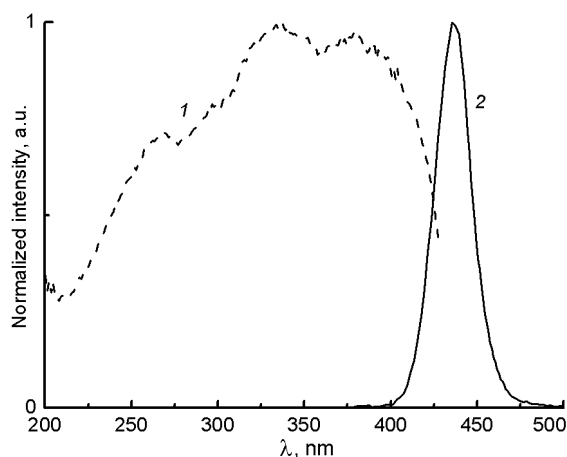


Fig. 1. Normalized excitation (1) and emission (2) spectra of $\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ (*rt*).

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 [11]. Housed scintillators were coupled to a R1307 Hamamatsu PMT entrance window using silicon optical compound Visilox V-788. Open parts of the detectors 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 (Tensor, Russia), custom shaping amplifier and a multichannel analyzer AMA-03F (Tensor, 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 measurements were done under the same conditions. The energy resolution (R) was determined from the full width at half maximum (FWHM) of the 662 keV peak. The instrumental error of the light yield and the R determinations does not exceed 5 %.

3. Results and discussion

The normalized photoluminescence excitation and emission spectra of $\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ at *rt* are presented in Fig. 1. The emission spectra are characterized by bands with maximum placed at 433 nm and the width of emission band (FWHM) values 22 nm. The excitation spectra of $\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ were measured at 440 nm emissions. The shape of the photoluminescence excitation spectrum for $\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ is typical for Eu^{2+} -doped halide scintillators and include a broad band between 200 nm and 420 nm. The excitation spectra are at-

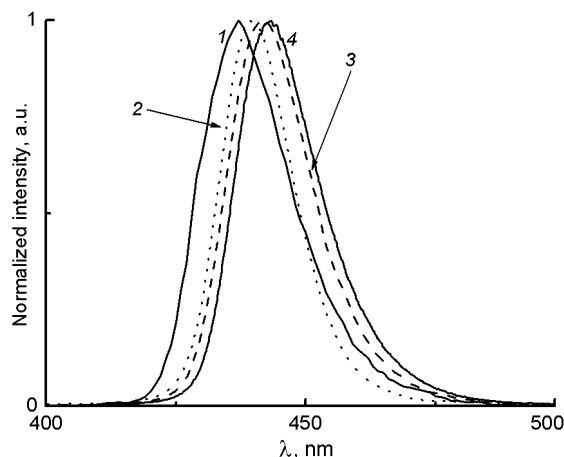


Fig. 2. X-Ray excited luminescence spectra of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$: 1 — $x = 0.005$, 2 — $x = 0.003$, 3 — $x = 0.05$, 4 — $x = 0.08$ (*rt*).

tributed to the host absorption and the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F)5d^1$ transitions of Eu^{2+} ion. Three pronounced bands with maxima placed at 269, 337 and 380 nm give the evidence that the crystal lattice of the compound is low-symmetric; according to the data of [12] RbCaCl_3 has orthorhombic lattice which transforms sequentially to tetragonal and cubic ones at the temperature elevation.

There is an overlapping between the excitation and emission spectra, which could be described by self-absorption of the Eu^{2+} . The light emitted by one Eu^{2+} ion could be absorbed and re-emitted by another. Such overlaps were observed in other halides compounds [1–4, 13–15]. The photoluminescence data recorded on the $\text{RbCaCl}_3:5\% \text{Eu}^{2+}$ single crystal are in good correspondence with the spectrum of $\text{RbCaCl}_3:\text{Eu}^{2+}$ powder [8].

The X-ray excited luminescence spectra of single crystals of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ compositions are presented in Fig. 2. They contain one narrow band corresponding to $5d-4f$ transition in Eu^{2+} ion. The maximum position shifts from 437 to 443 nm towards the increase of Eu^{2+} concentration and FWHM values are in 18–20 nm range. Such a shift also takes for other Eu^{2+} -activated compounds based on alkali and alkaline earth halides [4, 13]. All the emission spectra are not symmetric.

Fig. 3 shows the normalized *rt* decay curves for $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ samples ($x = 0.03, 0.05$ and 0.08). The decay curves are fitted by a single-exponential decay function. The decay time is 1.74 μs for $\text{RbCa}_{0.97}\text{Eu}_{0.03}\text{Cl}_3$, 2.48 μs for $\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ and 2.73 μs

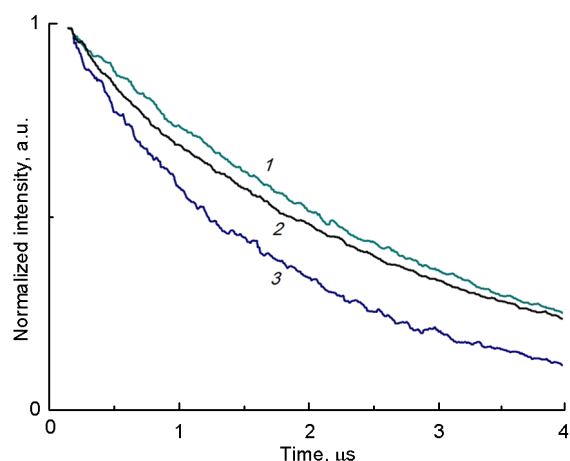


Fig. 3. Normalized scintillation time profiles of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$: 1 — $x = 0.003$, 2 — $x = 0.05$, 3 — $x = 0.08$ (rt).

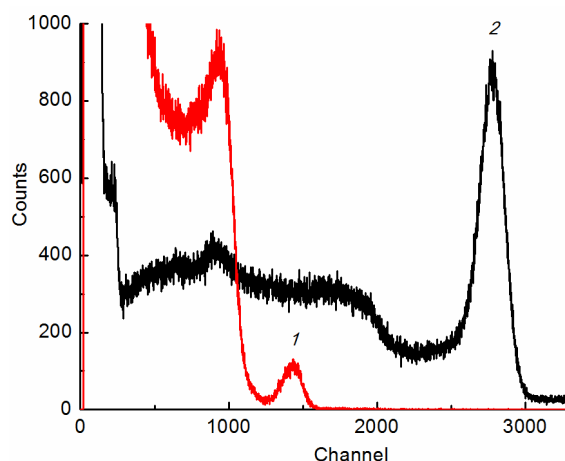


Fig. 4. Pulse height spectra of $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$ (1) and NaI:Tl (2) measured under ^{137}Cs gamma-ray excitation (rt).

Table 1 Some functional parameters of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ scintillators

Composition	Radioluminescence, nm	Light yield, %	Energy resolution at 662 keV, %	Scintillation decay, μs
$\text{RbCa}_{0.995}\text{Eu}_{0.005}\text{Cl}_3$	437	8	—	NA
$\text{RbCa}_{0.97}\text{Eu}_{0.03}\text{Cl}_3$	439	28	—	1.74
$\text{RbCa}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$	441	40.1	12.4	2.48
$\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$	443	55	12	2.73

for $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$. These values are in a good agreement with the lifetime of the Eu^{2+} center ($\sim 1\text{--}10\ \mu\text{s}$) [16]. The scintillation decay time of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ crystals increases with Eu^{2+} concentration, which is also observed in other halides [4, 13] and can be explained by self-absorption of Eu^{2+} .

The pulse height spectra are presented in Fig. 4. Table summarizes scintillation parameters of $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$.

As the concentration of Eu^{2+} in $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ increases, the number of luminescence centers and the light yield increases. The maximal value of the relative light yield (55 per cent comparing with NaI:Tl standard) and the energy resolution (12 %) at γ -irradiation, 662 keV is observed for the sample of $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$ composition.

4. Conclusions

In this study $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ ($x = 0.005, 0.03, 0.05, 0.08$) scintillation crystals have been grown by the Bridgman method. The X-ray luminescence spectra contain one narrow band corresponding to $5d\text{--}4f$ transition in Eu^{2+} ion; its maximum shifts from 437 to 443 nm towards Eu^{2+} concentration in the charge. Both the emission and excita-

tion spectra are proper to Eu^{2+} -doped halide scintillation materials.

The scintillation pulse decay curves for $\text{RbCa}_{1-x}\text{Eu}_x\text{Cl}_3$ materials are described by one component and the decay time increases from 1.74 to 2.73 μs at increase of x from 0.03 to 0.08.

The sample of $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$ composition possesses the maximal value of the relative light yield (55 % vs. NaI:Tl) and the best energy resolution (12 %) at 662 keV γ -irradiation.

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