

Scintillation properties of single crystals of $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ solid solutions

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The influence of Eu content on scintillation properties of single crystals of $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ composition has been studied. The single crystals were grown using the directional crystallization (Bridgman method). The dependence of the scintillation parameters (light yield, energy resolution) of $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ single crystals on the Eu content reaches the optimum at $x = 0.01$. The absolute light yield of the $K(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{Cl}_5$ single crystal was estimated as 38000 photons per MeV.

Keywords: scintillator, chlorides, solid solutions, single crystals, absolute light yield, energy resolution.

Сцинтиляційні властивості монокристалів твердих розчинів $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$.
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Досліджено залежність сцинтиляційних параметрів монокристалів загального складу $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$, вирощених спрямованою кристалізацією за методом Бріджмена, від вмісту Європію. Залежність сцинтиляційних характеристик вказаних матеріалів (світловий вихід, енергетичне розділення) від вмісту Європію проходить через оптимум при $x = 0,01$. Абсолютний світловий вихід монокристалів $K(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{Cl}_5$ оцінено як 38 тис. фотонів/МеВ.

Исследованы зависимости сцинтилляционных параметров монокристаллов общего состава $K(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$, выращенных направленной кристаллизацией по методу Бриджмена, от содержания европия. Зависимость сцинтилляционных характеристик указанных материалов (световой выход, энергетическое разделение) от содержания европия проходит через оптимум при $x = 0,01$. Абсолютный световой выход монокристаллов $K(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{Cl}_5$ оценен как 38 тыс. фотонов/МеВ.

1. Introduction

Nowadays, chloride materials are among the most attractive for the development of new activated scintillators due to their higher chemical stability and lower hygro-

scopicity in comparison with other halides. It is well-known that the brightest halide scintillators today are solid solutions based on bromides ($\text{BaBr}:\text{Eu}^{2+}$ [1], $\text{LaBr}_3:\text{Ce}^{3+}$ [2]) or iodides ($\text{SrI}_2:\text{Eu}^{2+}$ [3], $\text{CaI}_2:\text{Eu}^{2+}$ [4], $\text{LuI}_3:\text{Ce}^{3+}$ [5]). Widely used commercial scin-

tillators are also iodide materials: NaI:Tl, CsI:Tl. From the viewpoint of scintillation efficiency, chloride materials occupy a rather modest position and $\text{LaCl}_3:\text{Ce}^{3+}$ should be mentioned as an example [6].

All the mentioned materials are quite hygroscopic; therefore, the developers of new halide scintillators pay their attention to matrices consisting of chemical compounds of alkali and alkaline earth metal halides, since the addition of alkali metal halide, as a rule, considerably decreases the material hygroscopicity and makes it possible to achieve the corresponding scintillation parameters [7].

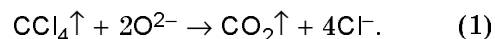
Our recent studies have led to the discovery of a new $\text{K}(\text{Sr}_{0.995}\text{Eu}_{0.005})_2\text{Cl}_5$ scintillator and a new method for pretreatment of the melt, which provides both purification and incorporation of the activator [8]. However, neither the determination of the dependence of the scintillation properties on the concentration of the activator nor the study of the absolute light yield of the material have been carried out. Therefore, this article presents the missing data.

2. Experimental

Reagents. Anhydrous extrapure KCl and SrCl_2 (4N, Merck) were used as reagents for the experiments without additional treatment. Extrapure Eu_2O_3 , (4N, "Shenzen Nexconn Pharmatechs") was used for the preparation of the dopant. To carry out carbohalogenation, CCl_4 of chemically pure grade ("Reakhim", Russia) and high-purity argon ("PASS", Ukraine) were used. The ratios of the initial components KCl: SrCl_2 : Eu_2O_3 (in mass %, respectively) for samples of the $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ composition were:

19.021:80.529:0.450	for	$x = 0.005$,
19.017:80.310:0.673	for	$x = 0.0075$,
19.012:80.089:0.899	for	$x = 0.01$,
19.004:79.649:1.347	for	$x = 0.015$ and
18.995:79.210:1.795	for	$x = 0.02$.

The charge was prepared by melting 60–70 g of a KCl: SrCl_2 : Eu_2O_3 mixture in a quartz ampoule under heating to 700 °C. The resulting melt contained suspended Eu_2O_3 and EuOCl which was formed due to the interaction between the liquid chloride melt and solid Eu_2O_3 [9]. The obtained suspension was carbohalogenated by the passing of argon through CCl_4 thermostated at 20 °C for 5 h. As a result of processing, a visually transparent melt without Eu oxo compounds was formed due to the quantitative removal of oxide ions (deoxidation):



The deoxidized melt was kept under vacuum of 4 Pa for 18 h, readily cooled and placed in a dry box where the boule was grinded. A weight of 12 g of the grinded mixture was placed in a quartz ampoule of 12 mm inner diameter with inner carbon sputter. The ampoule was evacuated and sealed.

The directional crystallization was performed in a two-zone tube furnace with the temperature difference of 80 °C between the zones. The temperature at the diaphragm was 625 °C. The ampoule was kept in the upper hot zone up until the interaction between the melt and the carbon sputter was finished (which was confirmed by the disappearance of gas bubbles); then the ampoule was lowered into the cold zone below the diaphragm at a speed of 3.2 mm/h. The directional crystallization procedure was finished within 48 h. Cooling to room temperature was carried out at a rate of 10 °C/h.

Measurements. Photoluminescence spectra were recorded using a combined spectrometer FLS 920 (Edinburgh Instruments) equipped with a xenon Xe 450W lamp for steady-state measurements and a hydrogen filled nF 900 nanosecond flashlamp.

The light yield and the energy resolution were determined from the pulse-height spectra by the comparison method [10]. The measurements were recorded using a pulse processing chain consisting of a photomultiplier R1307 PMT (Hamamatsu, Japan), a charge-sensitive preamplifier BUS 2-95 (Tensor, Russia), a custom shaping amplifier and a multichannel analyzer AMA-03F (Tensor, Russia). Each sample was connected to the photomultiplier input window using a Visilox V-788 silic on optical connection. The open parts of the detector and PMT photocathode were covered with three layers of Tetratex tape. ^{137}Cs (662 keV) served as a γ -ray source. All measurements were carried out under the same conditions using the shaping time of 8 μs and this value was chosen on the basis of data obtained in [8].

3. Results and discussion

As it was mentioned in [8], the directional crystallization of $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ melts results in the formation of a boule consisting of three zones: two opaque (the bottom and the top sections) and one transparent (the middle section). This is due to the features of KSr_2Cl_5 (or $\text{KCl}\cdot 2\text{SrCl}_2$) as an

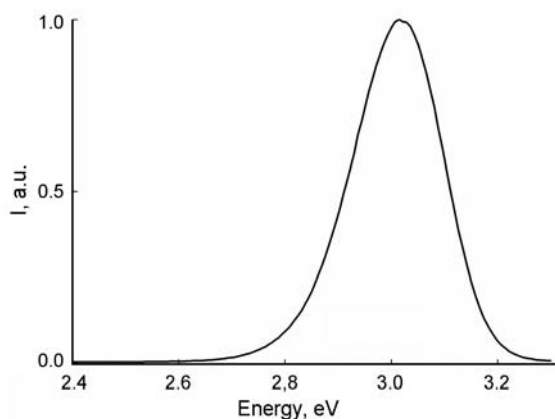


Fig. 1. Typical photoluminescence spectrum of a $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ single crystal (excitation at $E_{ex} = 3.8$ eV, $\lambda_{ex} = 322$ nm).

incongruent compound [11]. Therefore, the decomposition temperature on heating or the formation temperature on cooling (629 °C) are lower than the liquidus point for the $\text{KCl}-2\text{SrCl}_2$ mixture (645 °C). It means that cooling of the $\text{KCl} + (2 - 2x) \text{SrCl}_2 + 2x \text{EuCl}_2$ melt below 645 °C results in the formation of SrCl_2 or $\text{SrCl}_2:\text{Eu}^{2+}$ (in the presence of EuCl_2) crystals which serve as seeds for the crystallization of the following solid phases. This process leads to the formation of bottom opaque section of the boule. The following temperature decrease below 629 °C causes the crystallization of stable KSr_2Cl_5 or $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ which crystallizes from the melt enriched with KCl and the growing crystal forms the transparent section.

The crystallization of $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ results in increasing the KCl concentration in the melt and decreasing the melt temperature to the eutectic point where the mixture of residual phases is crystallized forming the top opaque section. Thus, directional crystallization does not allow a completely transparent boule to be obtained. Such a structure of the boule was observed for all the studied $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ compositions. The samples for the study of the scintillation parameters (height of 2 mm and diameter of 12 mm) were cut from the middle section of the grown boules.

Let us discuss the properties of the obtained scintillation crystals. The typical emission spectrum of $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ scintillation material is presented in Fig. 1. It includes a band with the maximum at 3.0 eV (418 nm) corresponding to the luminescence of halides doped with Eu^{2+} . The position of the emission maximum in Fig. 1 coincides

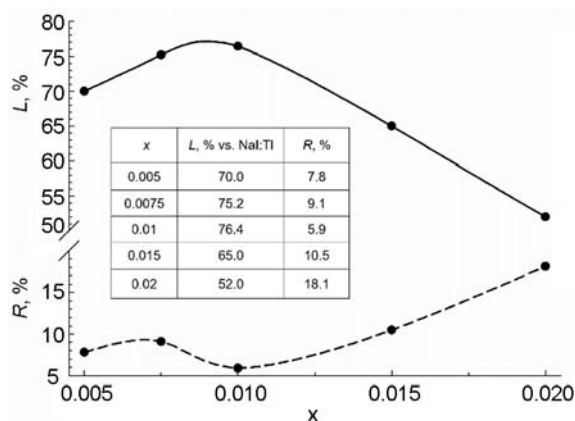


Fig. 2. The dependence of the relative light yield ($L, \%$) on the ratio NaI:Tl and the energy resolution ($R, \%$) for $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ scintillation materials vs the degree of Sr substitution with Eu , x .

with that in the X-ray luminescence spectrum [8], which proves that the obtained material is the scintillator and Eu^{2+} ions are the centers of emission. The analysis of the pulse height spectra of $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ materials makes it possible to build the concentration row for $\text{KSr}_2\text{Cl}_5:\text{Eu}^{2+}$ scintillators; the results of the light yield and energy resolution determination are shown in Fig. 2.

As it is seen from Fig. 2, both the concentration dependences pass through the optima placed at $x \approx 0.01$ that is caused by several reasons. Up to $x = 0.01$, an increase in the light yield is observed due to an increase in the concentration of emission centers in the sample. The following decrease in the luminosity can be explained not only by the concentration quenching but also by a decrease in the crystal lattice stability (although the appearance of inclusions is not visually observed) due to $\text{Eu}^{2+} \rightarrow \text{Sr}^{2+}$ substitution unless these ions are isomorphic. Their crystal radii are 0.131 and 0.132 nm [12], respectively, that corresponds to the Goldschmidt rule for perfectly isomorphic ions (<15 %). As for the electronegativities, they differ by 0.25 (0.95 for Sr and 1.2 for Eu [13]) which is significant (<0.2–0.4, the requirement of the Hume-Rothery rule).

The scintillation properties of the obtained $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ material are not worse than those of recently obtained Eu^{2+} -activated chloride scintillators. For instance, the relative light yield of 76.4 % in relation to NaI:Tl exceeds analogous values for $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Cl}_3$ (55 %) [14] and $\text{CsSr}_{0.95}\text{Eu}_{0.05}\text{Cl}_3$ (39 %) [15] and it is com-

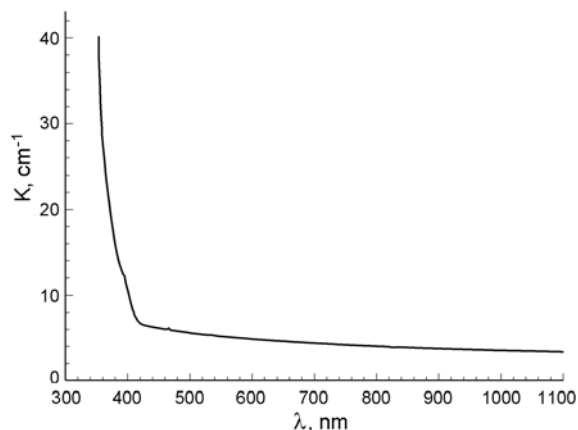


Fig. 3. The dependence of extinction coefficient (K , cm^{-1}) of the $\text{K}(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{Cl}_5$ scintillation material on the wavelength of the light.

parable with L value of $\text{RbCa}_{0.92}\text{Eu}_{0.08}\text{Br}_3$ (77 %) [14]. It should be added that the high efficiency of the new materials is achieved at much lower concentrations of the activator.

Naturally, it was of interest to determine the absolute light yield of the obtained material. It was estimated from the extinction coefficient of the obtained material, the corresponding dependence is shown in Fig. 3. These data gave the possibility to calculate the light collection coefficient as 0.52. The value of the absolute light yield was calculated according to the routine described in [16] and it was equal to 38000 photons per MeV.

In our opinion, the obtained material deserves a further study from the point of view of crystal growth. For example, an application of the Czochralsky method which is more suitable for the incongruent compounds may result in the obtaining of single crystals of larger volume possessing better scintillation properties.

4. Conclusion

A set of scintillation materials of a $\text{K}(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Cl}_5$ common composition was ob-

tained. This materials possess a good scintillation efficiency even at relatively small activator concentration ($x = 0 \div 0.02$).

The scintillation parameters of the obtained materials become optimal at $x = 0.01$ and the absolute light yield of $\text{K}(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{Cl}_5$ scintillator is 38000 photons per MeV.

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