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Scintillation material on the basis of $Ba_xSr_{1-x}I_2$:Eu solid solutions

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Single crystals of solid solutions SrI_2:Eu, BaI_2:Eu and $Ba_xSr_{1-x}I_2$:Eu with concentration of EuI_2 equal to 0.5 mol.% were grown by Bridgman-Stockbarger method. Addition of BaI_2 to SrI_2:Eu is found to cause arising two emission bands in the luminescence spectrum. One of them with maximum ca 430 nm is usual for Eu-containing halides, another with maximum at wavelength in 550–580 nm range is characterized by the shift of maximum position at varying BaI_2 concentration. The latter band arising is explained by distortions of crystal lattice of solid solution as compared with that of BaI_2 or SrI_2 since Sr^{2+} and Eu^{2+} from the one hand and Ba^{2+} from the other one have appreciably different radii. As a result, the light yield for the obtained materials decreases and the energy resolution deteriorates.

Методом Бриджмена-Стокбаргера выращены монокристаллы SrI_2:Eu^{2+}, BaI_2:Eu и твердых растворов $Ba_xSr_{1-x}I_2$:Eu с концентрацией активатора 0,5 мол.%. Добавление в SrI_2:Eu йодида бария приводит к появлению двух пиков в спектре люминесценции. Первый из них характерен для европий-содержащих материалов (максимумы вблизи 430 нм), второй – с максимумом в области 550–580 нм, по мере повышения концентрации BaI_2 положение максимума смещается в длинноволновую область. Упомянутый пик появляется как следствие искажений кристаллической решетки твердого раствора из-за значительного различия ионных радиусов Sr^{2+} и Eu^{2+}, с одной стороны и Ba^{2+} с другой. Вследствие этого уменьшается световыход и ухудшается энергетическое разрешение полученных материалов.

One of the most pronounced present-day trends of the material science of scintillators is the intensive development of Ce^{3+} or Eu^{2+}-activated alkaline earth metal halides. For instance, authors of [1] studied scintillation properties of barium halides activated with addition of Ce^{3+} or Eu^{2+}. Following investigations [2] proved high enough scintillation efficiency of materials BaX_2:Eu (X — halide ion), which demonstrated light yield of about of 10,000 photon/MeV.

SrI_2:Eu^{2+} is very attractive for investigators owing to extremely high scintillation parameters; according to data of [2, 5] the material doped with 0.5 mol.% Eu^{2+} possesses light yield within 75–80 % in respect to NaI:Tl. Authors of [3] reported the light yield of SrI_2:Eu^{2+} to be 85,000 photon/MeV (at 0.5 mol.% Eu^{2+}) and 115,000 photon/MeV (at 6 mol.% Eu^{2+}).

Another direction of the development of new scintillation materials is the obtaining of materials on the basis anion-anionic solid solutions [6] that gives possibility to vary the technical characteristics of the scintillators changing a degree of anion-anion substitution. There is no common opinion about the effect of such a substitution on the

properties of scintillator, e.g., authors of [6] found that for $LaCl_3$–$LaBr_3$:Ce solid solutions the dependence of the light yield from a degree of Cl–Br substitution passes through maximum ca Cl:Br ratio 0.34:0.66 whereas data of [7] showed that for the said solid solutions the changing of the light yield going from pure $LaCl_3$:Ce to pure $LaBr_3$:Ce is monotonous. Similar data on ternary mixtures of alkaline earth metal halides with cation-cationic substitution are absent, although for the case of rare-earth halides the systems of such a kind are patented [8].

The purpose of the present work is to study the effect of Ba:Sr ratio in solid solutions of $Ba_xSr_{1-x}I_2$:0.5 mol.% Eu^{2+} ternary system on luminescent and scintillation characteristics of these materials. Binary SrI_2–BaI_2 system is characterized by limited solubility of the components in the solid state [9]. According to extrapolation from [9] the solubility of BaI_2 in SrI_2 should be of the order of some mass. % and the solubility of SrI_2 in BaI_2 may be 10 % or more.

Anhydrous BaI_2 and SrI_2 were prepared by interaction of the corresponding carbonates with iodine and hydrazine:

$$2MCO_3\downarrow + 2I_2\downarrow + N_2H_4\rightarrow \quad (1)$$
$$\rightarrow 2MI_2 + 2H_2O + 2CO_2\uparrow.$$

All the chemicals were of reagent quality, the carbonates were taken with 5 % excess to stoichiometric ratio to provide thorough purification of the formed alkaline earth iodides from heavy metals which under these conditions precipitates as carbonates or hydroxides. Filtered solutions of BaI_2 and SrI_2 were evaporated (the formed was evaporated up to formation of crystalline film on the solution surface and the latter was heated until the temperature of solution reached 138°C). $SrI_2 \cdot 6H_2O$ and $BaI_2 \cdot 2H_2O$ hydrates deposited after cooling were separated from the liquor and dried in vacuum with stepwise elevation of the temperature to 400°C.

EuI_2 was obtained by dissolution of Eu_2O_3 in aqueous HI (both chemicals were of reagent quality). Then NH_4I was added to EuI_3 solution in the ratio of 1 mole of NH_4I per 1 mole of EuI_3 and the obtained solution was dried and heated in vacuum to 400°C. When the temperature exceeded 200°C the thermal decomposition of EuI_3 to EuI_2 according to the following reaction:

$$2EuI_3 \xrightarrow{t} 2EuI_2 + I_2\uparrow, \quad (2)$$

was started. The process (2) was considered as finished after ending of iodine evaporation from the sintered powder.

The obtained anhydrous iodides were used for preparation of the charge for the growth of single crystals of SrI_2–BaI_2 system with concentrations of the former component equal to 2, 5, 10, 20, 90, 95 and 98 mol.%. Initial concentration of EuI_2 for all samples was 0.5 mol.%. The compositions of the solid solutions were chosen with the use of phase diagram of SrI_2–BaI_2 from the regions of formation of stable solid solutions [9].

The growth of Eu doped SrI_2–BaI_2 single crystals was performed by Bridgman-Stockbarger method. The temperature at diaphragm was chosen to be approximately equal to the melting point of the corresponding composition taken from the data of [9]. The temperature gradient in the growth zone was 5°C per cm and the rate of the lowering of growth ampoule was 1.3 mm/h. The grown crystals were cooled to room temperature the rate of temperature decrease was 3°C/h. Our experiments gave us possibility to obtain only following single crystals: BaI_2:0.5 mol.% Eu^{2+}, SrI_2:0.5 mol.% Eu^{2+} and some solid solutions $Ba_xSr_{1-x}I_2$:0.5 mol.% Eu^{2+} with the predominance of SrI_2.

Scintillation properties of the obtained materials were used for the following studied in the form of scintillation detectors of diameter of 12 mm and height of 2 mm. Source ^{137}Cs (γ-rays, 662 keV) was used for the excitation of scintillations, the measurements of light yield were performed using PMT Hamamatsu R1307, at the registration time equal to 10 μs. The radioluminescence spectra were obtained using ^{241}Am source, MDR-23 monochromator was used for the spectra registration.

The radioluminescence spectra of the solid solutions include 2 emission bands — the first narrow band is placed at 435 nm and the second relatively broad band is characterized by maximum shifting from 550 to 580 nm with the increase of Ba^{2+} concentration in the solid solution (Fig. 1). The band at 435 nm corresponds to luminescence of Eu^{2+} ($5d \rightarrow 4f$ transition), and reasons of arising other band require elucidation. For this purpose let us analyze the radioluminescence spectra of "pure" SrI_2 or BaI_2 activated with Eu^{2+} as they are presented in [3]. The luminescence spectrum of SrI_2:0.5 mol.% Eu^{2+} contains only a band

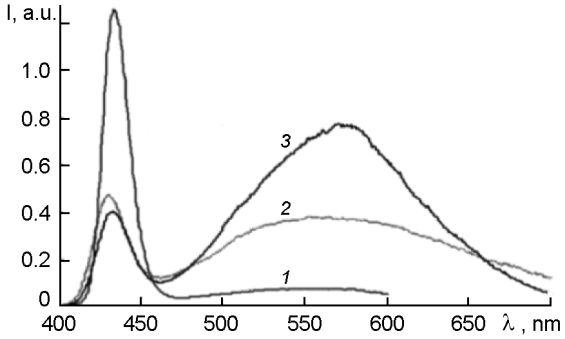

Fig. 1. Radioluminescence spectra of scintillation materials on basis of $Ba_xSr_{1-x}I_2$:0.5 mol.% Eu solid solutions with concentration of BaI_2 equal to 2 (*1*), 5 (*2*) and 10 (*3*) mol.% (the source of γ-rays is ^{241}Am).

near 435 nm, whereas in the case of BaI_2:0.5 mol.% Eu^{2+} two bands at 420 nm (that is proper to Eu^{2+} luminescence) and 550–580 nm that resembles the spectra obtained in the present work. Authors of [3] additionally performed zone refining for the purification of the charge, this leads to decrease of the arbitrary intensity of the long-wave band with the simultaneous considerable decreasing light yield. The long-wave bands were referred to a recombination transition caused by admixtures, which were not identified.

In our opinion, the reason of the long-wave band existence may be due to distortions of crystal lattice at the formation of solid solutions of substitution. It is well-known [9] that in SrI_2–BaI_2 system increasing concentration of both component in the solid solution on the basis of another one leads to instability of the formed solution and, finally, to its decomposition.

The typical pulse height spectrum of $Ba_xSr_{1-x}I_2$:0.5 mol.% Eu^{2+} solid solutions at small BaI_2 concentrations is presented in Fig. 2. As is seen from this Figure the light yield of $Sr_{0.98}Ba_{0.02}$:Eu solid solution as 34 % in respect to NaI:Tl and energetic resolution is equal to 27 %. The dependences of the light yield (L) and energetic resolution (R) of SrI_2:Eu, BaI_2:Eu and $Ba_xSr_{1-x}I_2$:Eu solid solutions is depicted in Fig. 3. The addition of barium to the material on the basis of SrI_2 causes fall of light yield, seemingly, because of appreciable distortions of crystal lattice, it is observed simultaneous worsening energetic resolution (R value increases).

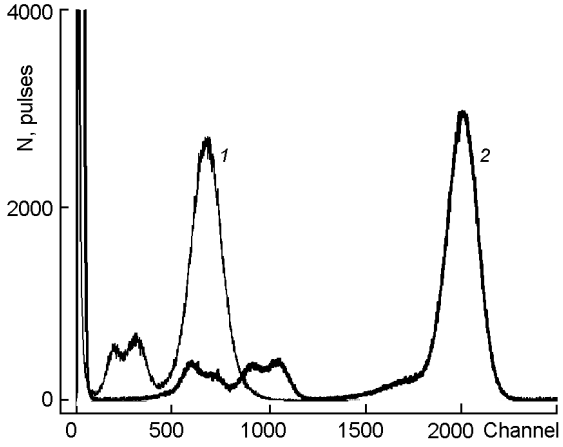

Fig. 2. Pulse height spectra of $Sr_{0.98}Ba_{0.02}$:0.5 mol.% Eu (*1*) and NaI:Tl (*2*) the source of γ-rays is ^{241}Am.

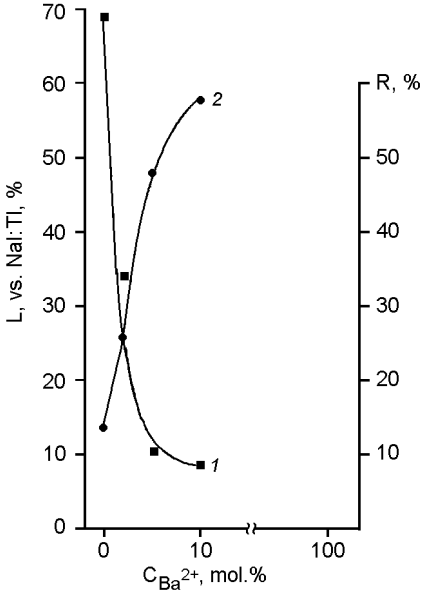

Fig. 3. Dependences of light yield, L, (*1*) and energetic resolution, R, (*2*) of SrI_2–BaI_2:Eu (0.5 mol.%) solid solutions from BaI_2 concentration (the source of γ-rays is ^{241}Am).

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Сцинтиляційний матеріал на основі твердих розчинів $Ba_xSr_{1-x}I_2$:Eu

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Методом Бріджмена-Стокбаргера вирощено монокристали SrI_2:Eu, BaI_2:Eu та твердих розчинів $Ba_xSr_{1-x}I_2$:Eu з концентрацією активатора 0,5 мол.%. Додавання до SrI_2:Eu йодиду барію веде до появи двох піків у спектрі люмінесценції. Перший з них є притаманним для європій-вмісних матеріалів (максимуми поблизу 430 нм), другий з максимумом в області 550–580 нм, при підвищенні концентрації BaI_2 положення максимуму зміщується у довгохвильову область. Згаданий пік з'являється як наслідок спотворень кристалічної гратки твердого розчину з огляду на значну відмінність іонних радіусів Sr^{2+} та Eu^{2+}, з одного боку і Ba^{2+}, з іншого. В наслідок цього зміньшується енергетичне розділення одержаних матеріалів.