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Study of scintillation properties of cerium-doped yttrium bromide

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Ce^{3+}-doped yttrium bromide scintillation crystals with the activator concentration (0.5, 1 and 2 mol. %) have been grown by Bridgman-Stockbarger method. The radioluminescence spectra of these materials include asymmetric band with the maximum at 422 nm. This band consists of two overlapping bands with the maxima at 418 and 456 nm. The scintillation pulse decay curves for the obtained material may me approximately described by two components with the decay constants 36 and 450 ns and the fraction of the faster component is 0.79. The dependence of the light yield of the studied material against Ce^{3+} concentration achieves maximum at 1 mol.% of Ce^{3+}, where the light yield is 43 % vs. NaI:Tl (approximately 17,000 photons per MeV).

Методом Бриджмена-Стокбаргера выращены сцинтилляционные монокристаллы на основе бромида иттрия, активированного добавками 0.5, 1 и 2 мол. % Ce^{3+}. Спектры радиолюминесценции этих материалов содержат асимметричный пик с максимумом при 422 нм, обусловленный перекрыванием двух пиков с максимумами при 418 и 456 нм. Кривая затухания сцинтилляционного импульса полученных монокристаллов может быть описана с использованием двух компонент — 36 и 460 нс, доля быстрой компоненты оценена, как 0.79. Зависимость светового выхода $YBr_3:Ce^{3+}$ от концентрации активатора проходит через максимум при 1 мол.% Ce^{3+}, максимальное значение световыхода равно 43 % по отношению к NaI:Tl (приблизительно 17000 фотонов/МэВ).

1. Introduction

Ce^{3+}-doped rare earth halides attract considerable attention of material scientists since beginning of the 21st century [1]. The discovery of new $LaCl_3:Ce^{3+}$ and $LaBr_3:Ce^{3+}$ bright scintillators promoted an intensive search for similar high-efficient compounds [2, 3]. Such investigations result in discovery of Ce^{3+}-doped gadolinium [4–6], praseodimium [7] and lutetium [8, 9] halides and several compounds demonstrated the scintillation characteristics exceeding those for such common scintillators as NaI:Tl or CsI:Tl. The doped iodides (excluding $LaI_3:Ce^{3+}$) possess higher light yield values comparing with the corresponding chlorides and bromides and sometimes this parameter approaches to 100,000 photons per MeV [5]. However, the routine synthesis of high-pure rare earth iodides is extremely difficult: it includes the direct synthesis and vacuum distillation of the obtained iodide [1]. Due to this reason, Ce^{3+}-doped rare earth chlorides and bromides may be of interest for material scientists, but properties of each new material can not be predicted and their practical studying is needed.

The purpose of this work is to study luminescence and scintillation properties of

Ce^{3+}-doped YBr_3 which properties were not studied yet.

2. Experimental

YBr_3 was obtained by dissolution of a weight of Y_2O_3 (99.99 %) in concentrated aqueous HBr of reagent quality taken with the excess of 5 %. Separately the amount of CeO_2 (99.9 %) providing concentration of Ce^{3+} in the final crystal equal to 0.5, 1 and 2 mol.% was dissolved in HBr under the heating:

$$2CeO_2\downarrow + 8HBr \rightarrow 2CeBr_3 + Br_2\uparrow + 4H_2O. \quad (1)$$

The solutions were mixed and the weight of ammonium bromide (99.9 %) corresponding to NH_4Br:YBr_3 molar ratio not less than 6 was added to the solution of rare earth bromides. Then this mixture was dried in air at 120–150°C, crushed and dried in vacuum ($p \leq 10$ Pa) at slow increase of temperature from 100 to 400°C with 8-h stop at 200°C. The obtained YBr_3:Ce^{3+} was placed in quartz ampoule of 18 mm diameter, melted and kept for a day in vacuum ($p \leq 10$ Pa). The crystals were grown by Bridgman-Stockbarger method; the temperature at the diaphragm was 905°C, temperature gradient was 6 °C/cm and the rate of the ampoule descent was 0.63 mm/h. The obtained ingot was cooled to the room temperature with the rate of 3°C/h. Then the ingot was cut and the detectors of 12 mm diameter and 2 mm height were prepared.

Radioluminescence spectra were recorded under ^{241}Am source excitation (γ, 59.6 keV) with the use of MDR-23 monochromator. The pulse-height spectra were obtained under ^{137}Cs (γ, 662 keV) and ^{241}Am irradiation and registered using PMT Hamamatsu R1307.

The scintillation pulse shapes of YBr_3:Ce^{3+} detectors were obtained by delayed-coincidence method [10]. Two 9142B (Electron Tubes Ltd.) photomultipliers were used for the detection scintillation photons both in "start" and in "stop" channels of the optical part of the set-up. Detectors were irradiated by gamma photons of a ^{152}Eu radionuclide source (γ, 41, 77.9, 122 keV). The photomultiplier in the"'start" channel was used to give the zero-time signal. It was placed in optical contact with the scintillator. A scintillation pulse was attenuated by a diaphragm to single photon mode and it was detected by the photomultiplier to generate delayed timing signal in the "stop" channel.

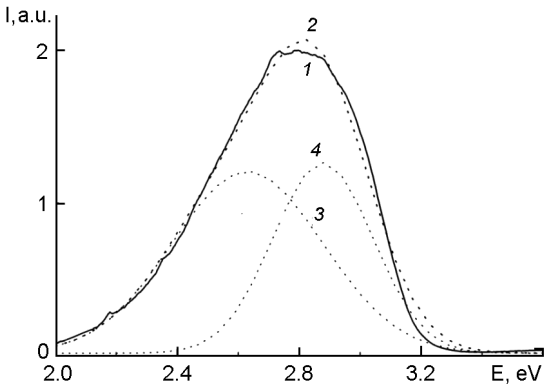

Fig. 1. The radioluminescence spectrum of YBr_3:1 mol.% Ce^{3+} at 298 K obtained under ^{241}Am irradiation (1) and its approximation (curve *2*). Lines *3* and *4* present components corresponding to $5d$–$4f$ transitions in Ce^{3+} ion.

3. Results and discussion

Since yttrium bromide crystals are referred to layered materials, the growth of perfect single crystals is very complicated. Although the growth and cooling routine was too continuous (300–400 h), it did not provide high quality of the grown crystal. Because of this reason some parameters (e.g., energy resolution) can not be measured.

Radioluminescence spectrum of Ce^{3+}-doped YBr_3 recorded at room temperature is presented in Fig. 1. In this spectrum there is only one asymmetric band with the maximum placed at 2.84 eV (422 nm). This band can be divided in components corresponding to transition from $5d$ level to 2 levels of ground state of Ce^{3+} — $^2F_{5/2}$ and $2F_{7/2}$ with maxima placed at 2.63 eV (456 nm) and 2.87 eV (418 nm).

To obtain information about composition of the scintillation pulse of YBr_3:Ce^{3+} material the curves of scintillation pulse decay were obtained (Fig. 2). They are described by two components for both materials according to the following equation:

$$I(t) = I_0 \cdot \left(A_1 \exp(t/\tau_1 + A_2 \exp(t/\tau_2)\right), \quad (2)$$

where I_0 and $I(t)$ are the initial and current intensities of the scintillation pulse, t is the time, A_1 and A_2 are the initial fractions of fast and slow components in the scintillation pulse, respectively, and τ_1 and τ_2 are the decay constants of fast and slow components.

The fast component of the scintillation pulse of YBr_3:Ce^{3+} is characterized by 36 ns decay constant and its fraction is 0.79. The

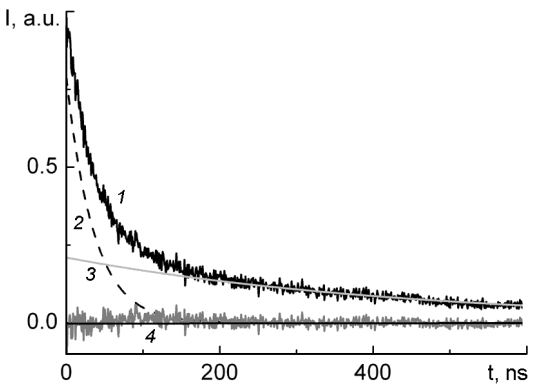

Fig. 2. The scintillation pulse decay curve of YBr_3:1 mol.% Ce^{3+} recorded under ^{152}Eu γ-excitation (*1*, black), the fast component (*2*, dashed, $A_1 = 0.79$, $\tau_1 = 36$ ns), the slow component (*3*, light grey, $A_2 = 0.21$, $\tau_2 = 640$ ns, deviation of calculated curve from the experimental one (*4*, grey).

decay constant of the slow component is 450 ns. So, we can conclude that YBr_3:Ce^{3+} is referred to fast scintillators.

The light yield of the obtained material is estimated on the basis of the pulse-height spectra recorded under ^{241}Am and ^{137}Cs excitation; the examples are presented in Fig. 3. As seen, the light yield of YBr_3:Ce^{3+} materials is essentially lower than that of NaI:Tl. It is of interest to trace the effect of Ce^{3+} concentration on the light yield of the obtained materials. Such dependences are presented in Fig. 4.

As it is known, different Ce^{3+}-activated rare earth-based halide scintillators are known to possess maximal light yield values in the activator concentration range from 0.1 to several mol.%. Therefore, it is enough to obtain 3–4 points in order to have imagination about the development of scintillation parameters with the activator concentration. In our case 3 points for YBr_3:Ce^{3+} allow to clear up this question. The light yield of Ce-doped yttrium bromide achieves maximum at concentration of Ce^{3+} near 1 mol.%. The maximal estimated value of the light yield is 43 % (~17,000 photons per MeV). In Fig. 4 we can see usual for activated material sections of the concentration dependence. Initial growth of the light yield is caused by increase of luminescence centers in the scintillator and, at concentrations exceeding 1 mol.% the light yield decreases owing to concentration quenching of the luminescence, which is proper just for activated scintillators. In the vicinities of

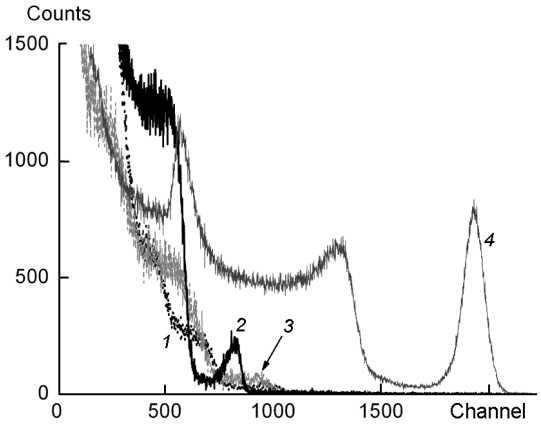

Fig. 3. The pulse height spectra of YBr_3:Ce^{3+} crystals containing 0.5 (*1*), 1 (*2*) and 2 (*3*) mol.% of activator in comparison with standard sample of NaI:Tl (*4*).

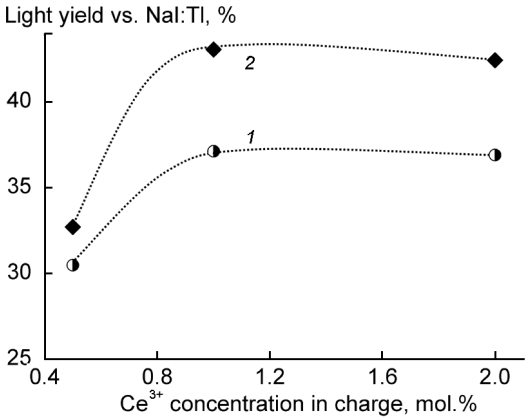

Fig. 4. The dependences of light yield of YBr_3:Ce^{3+} vs. Ce^{3+} concentration in the charge. Excitation sources are ^{241}Am (*1*) and ^{137}Cs (*2*).

1 mol.% of Ce^{3+} there is a plateau, where both effects are reciprocally compensated.

Concerning the light yield of Ce-doped yttrium halides it should be noted that the light yield of YCl_3:Ce^{3+} can be estimated as 4,500 photons/MeV [11] and this values for YI_3:Ce^{3+} is 98,600 photons/MeV [5]. So, the scintillation properties of YBr_3:Ce^{3+} are intermediate between those of the mentioned halides. Principally, the rise of the light yield of Ce-doped yttrium halides with the increase of anion radius is subjected to the common rule that the light yield increases with the decrease of the band gap of the scintillator, which decreases in "Cl–Br–I" sequence.

4. Conclusions

This work reported about growth YBr_3:Ce^{3+} crystals with different activator concentrations. The crystals demonstrated

typical layered structure. The radioluminescence spectra of the materials contain one asymmetric band formed by overlapping two peaks corresponding to $5d-4f$ transitions in cerium ion. The scintillation light decay curves are described by two components for all the materials. The decay parameters of $YBr_3:Ce^{3+}$ scintillators are estimated. The light yield for $YBr_3:Ce^{3+}$ crystals were determined. The concentration dependence passes through the maximum at 1 mol.% of Ce^{3+} and the running of the dependences corresponds to that for activated scintillation materials.

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Дослідження сцинтиляційних властивостей броміду ітрію, активованого церієм

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Методом Бріджмена-Стокбаргера вирощено сцинтиляційні монокристали на основі броміду ітрію, активованого добавками 0.5, 1 та 2 мол. % Ce^{3+}. Спектри радіолюмінесценції цих матеріалів містять асиметричний пік з максимумом при 422 нм, обумовлений перекриванням двох піків з максимумами при 418 и 456 нм. Крива загасання сцинтиляційного імпульсу одержаних монокристалів може бути описана з використанням двох компонент — 36 и 460 нс, частку швидкої компоненти оцінено, як 0.79. Залежність світловиходу $YBr_3:Ce^{3+}$ від концентрації активатора проходить через максимум при 1 мол.% Ce^{3+}, максимальне значення світловиходу дорівнює 43 % у відношенні до NaI:Tl (приблизно 17000 фотонів/МеВ).