

## Growth and Study of Scintillation Properties of BaBrI Crystals Activated by Samarium Ions

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**Abstract**—BaBrI crystals activated by Sm<sup>2+</sup> ions were synthesized by the Bridgman method. The Sm content in the samples was analyzed by the method of mass spectrometry with inductively coupled plasma. The results of the study of the optical and scintillation characteristics of the synthetic crystals, such as photoluminescence, X-ray luminescence, and absorption spectra, are reported. The light yield of the luminescence of the studied samples was estimated.

**Keywords:** crystal growth, alkaline-earth halides, samarium, luminescence, rare-earth ions, defects

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### INTRODUCTION

Alkaline-earth halide crystals activated by rare-earth ions are promising scintillation materials [1]. They are characterized by a relatively small band gap (4–6 eV), which contributes to the efficient formation of electron–hole pairs for each absorbed photon of ionizing radiation [2]. Thereby, the systems with various combinations of alkaline-earth iodides as lattice-forming elements have high light output values and good energy resolution [3]. Most often, divalent europium, as well as trivalent cerium and praseodymium with luminescence bands in the ultraviolet and visible spectral regions (350–600 nm) are the activators for such scintillators [4].

Until recently, divalent samarium was not considered as an activator for scintillation crystals.

It was shown in [5] that the activation of SrI<sub>2</sub> crystals by S<sup>2+</sup> ions leads to 5*d*–4*f* luminescence with a maximum of luminescence at a wavelength of 753 nm under X-ray and UV excitations. The lifetime of the excited 5*d* state of Sm<sup>2+</sup> is 1.25 μs. When a crystal is heated, the luminescence decay time increases due to the self-absorption process. In this case, the photons emitted by Sm<sup>2+</sup> can be reabsorbed by other Sm<sup>2+</sup> ions. Such absorption of radiation may be multiply increasing the decay time of the luminescence and the light output of the scintillator. At the same time, it was noted in [5] that self-absorption of luminescence in SrI<sub>2</sub> crystals activated by Sm<sup>2+</sup> is weaker than in similar-sized SrI<sub>2</sub> crystals activated by Eu<sup>2+</sup> with the same concentrations.

To date, almost all commercial scintillators are designed to detect luminescence by photomultiplier

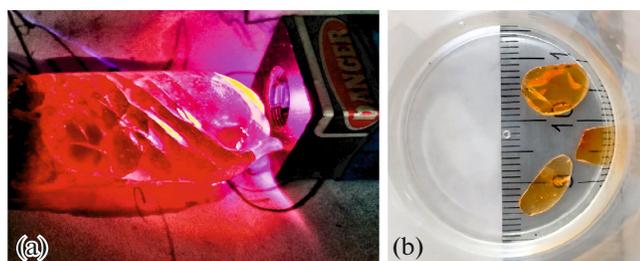
tubes (PMTs) with a maximum sensitivity in the range of 400–440 nm. To register the luminescence of crystals activated by samarium, photodetectors operating in the visible and infrared regions are required. These can be semiconductor avalanche photodiodes with a maximum sensitivity in the region of 600–800 nm, which have much higher quantum efficiency (80–90%) than the traditional PMTs (up to 35%) [6]. Usage of them will ultimately contribute to the development of a new class of effective scintillation materials with the long-wavelength radiation in the red or near infrared range.

In [7–9], we considered aspects of growth of BaBrI, BaClI, and SrBrI crystals and reported the optical and scintillation properties of these crystals activated by europium and cerium ions. Analysis of the luminescence spectra measured under X-ray excitation allowed us to assume the probable mechanisms of energy transfer.

This work highlights some of the features of growing BaBrI : Sm<sup>2+</sup> crystals. The results of study of the optical properties of the crystals obtained are reported for the first time.

### METHODOLOGY OF EXPERIMENTS

BaBrI : Sm<sup>2+</sup> crystals (Fig. 1a) were synthesized from the melt by the vertical Bridgman method in a multizone thermal installation in vacuumized quartz ampoules. The description of the procedure of growing BaBrI crystals and the preceding preparatory work is given in detail in [10]. The initial BaBr<sub>2</sub>–BaI<sub>2</sub> compounds were mixed in equal molar proportions 1 : 1. SmI<sub>2</sub> was introduced as an activator directly into the



**Fig. 1.** (a) BaBrI : 1% Sm<sup>2+</sup> crystal irradiated with a laser with a wavelength of  $\lambda = 405$  nm; (b) samples of the BaBrI : 1% Sm<sup>2+</sup> crystal prepared for spectral studies.

mixture prior to drying. The calculated concentrations of the introduced samarium additives correspond to 0.1, 1, 5, and 10% of the analyte. Crystalline iodine (1 mol %) was added to the mixture for more efficient removal of water, since it forms a reaction atmosphere in an ampoule and helps to remove water from the compounds upon melting [11].

The temperature gradient during the growth of BaBrI : Sm<sup>2+</sup> crystals did not exceed 4°C/cm. The low gradient helps to avoid thermoelastic stresses that stimulate the defect formation in the crystal. After crystallization of the melt, the ampoule was cooled at a rate of 5–10°C/h in order to prevent cracking and the accumulation of stresses in the crystal.

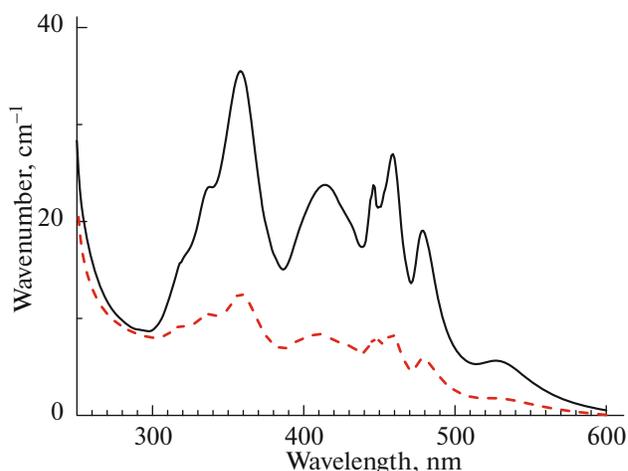
Due to the hygroscopic nature of the halogen materials, the extraction and processing of crystals was carried out in a dry glove box. Single-crystal plates with a diameter of 10–15 mm and a thickness of 2–3 mm were cut out for spectral studies (Fig. 1b).

The degree of incorporation of Sm impurity into the structure of BaBrI crystals was estimated by mass spectroscopy with inductively coupled plasma (ICP-MS). The solutions obtained by dissolving the crystals with further separation of barium as the main matrix component were analyzed on an Element 2 high-resolution mass spectrometer (Finnigan MAT, Germany). To plot the calibration dependence, we used a standard solution of CLMS-1 (Spex, United States). Rhodium was added as an internal standard; its concentration in the studied solutions was 2 ng/mL.

The measurements showed the lower Sm concentrations in the studied samples in comparison with the

**Table 1.** Concentrations of Sm in BaBrI crystals

Introduced into the charge, %	Registered in the crystals by ICP-MS, %
0.1	0.00001
1	0.0084
5	0.034
10	0.095



**Fig. 2.** Absorption spectra of BaBrI : 1% Sm<sup>2+</sup> (solid line) and BaBrI : 5% Sm<sup>2+</sup> (dashed line) crystals.

calculated values of the additives introduced into them (Table 1). However, with increasing concentration of admixtures, an increase in the Sm signal intensity was observed, which may indicate exhaustion of analyte during crystal growth.

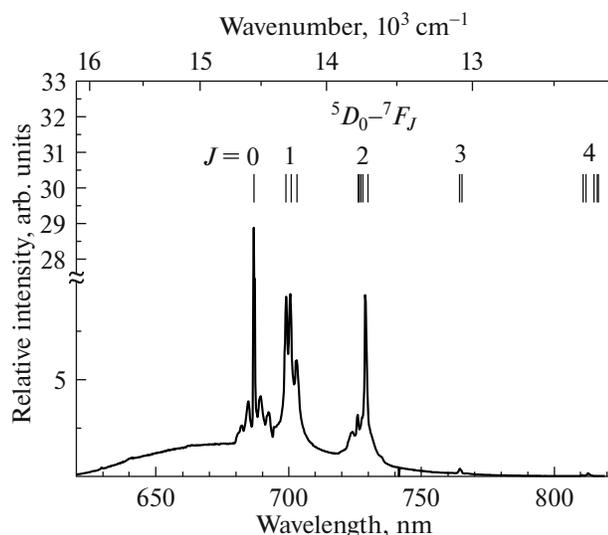
The correctness of ICP-MS analyses was evaluated for the sample with the highest concentration of Sm impurity by comparison with the data obtained by the X-ray fluorescence analysis with total external reflection of the exciting beam (XRPA), which were 0.1% analyte.

Measurements of all characteristics in the crystals were carried out in accordance with the marking of the calculated values of samarium admixtures; therefore, hereinafter, the samples studied are designated according to the concentrations of impurities introduced into the mixture and not actually entering the crystal.

The absorption, photoluminescence, and X-ray luminescence spectra of the grown crystals were analyzed. The absorption spectra of BaBrI : Sm<sup>2+</sup> crystals were measured at room temperature on a Lambda 950 spectrophotometer (Perkin Elmer). The X-ray luminescence and photoluminescence spectra were recorded using a system consisting of an MDR-2 monochromator (grating 600 lines/mm) and a Hamamatsu 6780-04 photomodule. Photoluminescence was excited by a semiconductor laser with a wavelength of 405 nm; X-ray luminescence was produced by an X-ray tube at 50 kV and 0.1 mA.

## DISCUSSION OF RESULTS

The synthetic BaBrI–Sm<sup>2+</sup> crystals have a golden red color (Fig. 1b). This is due to absorption of light in the visible region of the spectrum. The absorption spectra of BaBrI : 1% Sm<sup>2+</sup> and BaBrI : 5% Sm<sup>2+</sup> crystals are shown in Fig. 2. There are five split intense

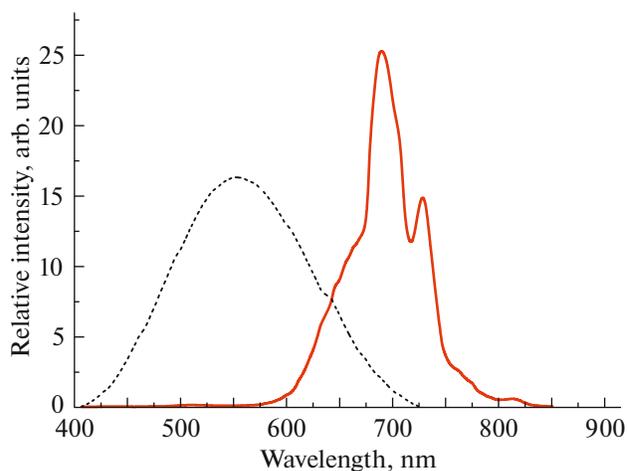


**Fig. 3.** Luminescence spectrum of BaBrI : 1% Sm<sup>2+</sup> crystals obtained at room temperature upon excitation by a laser with a wavelength of 405 nm. The vertical lines show 4f–4f transitions from <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>J</sub> ( $J = 0, 1, 2, 3, \text{ and } 4$ ) in the BaBr<sub>2</sub> crystal [13].

absorption bands in the region from 300 to 600 nm, which correspond to 4f–5d transitions in Sm<sup>2+</sup> ions with a low symmetry environment [12–14].

Excitation by light with wavelengths of the absorption peaks results in intense luminescence. Its spectrum is shown in Fig. 3. The photoluminescence spectrum contains a wide band due to the 5d–4f transitions in the Sm<sup>2+</sup> ion and structured bands corresponding to the <sup>5</sup>D<sub>0</sub> transitions of the 4f shell to the levels of the main <sup>7</sup>F<sub>J</sub> multiplet ( $J = 0, 1, 2, 3, \text{ and } 4$ ). The intense band at 740 nm corresponding to the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub> transition indicates the low-symmetry environment of the divalent samarium ion in this crystal as well. Divalent samarium is isoelectronic to the trivalent europium ion; therefore, it can be concluded that the environment of the ion is symmetric from the splitting of the luminescence bands corresponding to the splitting of the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>J</sub> transitions [15]. Based on the analysis of the luminescence spectrum, we can conclude that the symmetry group of the Sm<sup>2+</sup> ion in this crystal is  $D_{3h}$ , which corresponds to the symmetry group of Ba<sup>2+</sup> ions that isovalently replace divalent samarium in this crystal [7, 16].

Luminescence of Sm<sup>2+</sup> ions is excited by X-ray radiation as well. Figure 4 shows comparison of X-ray luminescence of BaBrI : 5% Sm<sup>2+</sup> and CsI : Tl crystals. Samples for measurements were identical in thickness and surface area. The integrated X-ray luminescence intensity of both crystals is almost equivalent. Thus, the light yield of BaBrI : 5% Sm<sup>2+</sup> crystals is close to that of CsI : Tl crystal in magnitude, which is ~45 pho-



**Fig. 4.** Luminescence spectrum of a BaBrI : 5% Sm<sup>2+</sup> crystal (red solid curve) upon X-ray excitation in comparison with a CsI : Tl crystal (black dashed curve).

tons per keV. An increase in the Sm<sup>2+</sup> concentration in BaBrI crystals results in an increase in the luminescence light yield, as in the case of an increase in the concentration of other activators in BaBrI crystals [9, 17]. Thus, we can assume that BaBrI crystals activated by Sm<sup>2+</sup> may be a promising X-ray luminophore or scintillator with a luminescence band in the red spectral region.

## CONCLUSIONS

In this paper, we have discussed the features of the Bridgman method of synthesis of BaBrI crystals activated by Sm<sup>2+</sup> ions. Using the ICP-MS method, the real concentration of samarium incorporated in the grown crystals was estimated. The results showed a lower level of samarium concentration in crystals compared with the activator concentrations introduced into the charge. Despite this fact, a high light yield of luminescence is observed in synthetic crystals and there is a clear correlation between the samarium concentration introduced into the charge and the luminescence intensity. It has been established that samarium enters the crystal in a divalent state. Photo- and X-ray excitation of crystals results in strong luminescence in the region of 740 nm with a light output comparable to that of a such traditional scintillator as CsI : Tl. As luminescence in the red region of such crystals may be registered using semiconductor avalanche LEDs with a higher quantum efficiency compared to traditional PMTs, it can be expected that BaBrI crystals activated by Sm<sup>2+</sup> ions may be a promising matrix for creating high-performance scintillation detectors of a new class.

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## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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