

Growing of Alkaline Earth Halide Scintillation Crystals and Their Optical Properties

A. A. Shalaev^{a, *}, A. I. Rusakov^a, R. Yu. Shendrik^a, A. K. Subanakov^b,
Yu. V. Sokol'nikova^a, and A. S. Myasnikova^a

^a Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia

^b Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Ulan-Ude, Russia

*e-mail: alshal@mail.ru

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Abstract—The features of using the Bridgman method for growing alkaline earth halides crystals BaBrI, BaClI, and SrBrI are discussed. The results of the study of scintillation characteristics of grown crystals activated by europium ions are presented. The actual content of europium in crystals is determined and the values of the luminescence yield and decay time are estimated. X-ray luminescence and absorption spectra of the obtained crystals are given.

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INTRODUCTION

During the last decade, along with the improvement of traditional fluoride and oxide scintillation systems [1], researchers have been actively searching for effective halide matrices with high light yield and resolution [2]. To date, of all the inorganic scintillators of this class manufactured industrially, lanthanum bromide activated by cerium has demonstrated the best characteristics. Lanthanum based scintillators produced by Saint-Gobain have a high light yield (63 photons/keV), high energy resolution (2.9%, at 662 keV) and a short luminescence decay time (about 16 ns). At present, the main drawback of these scintillators is their high cost.

With this in mind, it is relevant to mention the prospect of systems with different combinations of alkaline earth iodides as lattice-forming elements activated by rare-earth ions [3]. The most effective activators are bivalent europium, trivalent cerium, and praseodymium. Express assessment of the main scintillation characteristics of a number of binary and ternary halogen systems in the form of fine-crystalline powders was carried out at the National Lawrence laboratory in Berkeley (United States) with the aim to determine the most promising variants of compounds for further development of single-crystal scintillation detectors [4]. Compounds BaBrI : 8% Eu, SrClI : 5% Eu, CsBa₂I₅ : 4% Eu showed a high light yield, but monocrystalline samples of these compounds with optimal size for spectral studies were not obtained [3].

A significant disadvantage of this class of scintillators is their hygroscopicity. This property complicates

the process of preparing the raw materials, because the charge for growing crystals requires thorough multi-stage drying. In addition, certain technological procedures are needed for the processing of the obtained crystals before their use. This problem can be solved by sealing hygroscopic crystals in special housings, such as those used for classic scintillation detectors NaI(Tl).

Furthermore, these crystals are characterized by anisotropic thermal expansion [5], which causes their cracking during growth and subsequent cooling. Therefore, the choice of parameters such as temperature gradient, growth rate, and annealing modes of the obtained crystal require special attention.

This paper presents a method of growing alkaline earth halides crystals activated by europium ions and considers their basic scintillation properties.

EXPERIMENTAL METHOD AND DISCUSSION OF RESULTS

BaBrI, BaClI, and SrBrI crystals have an orthorhombic crystal structure of PbCl₂ type [6]. The europium ions in these compounds substitute the barium and strontium ions, respectively. These compounds melt congruently at a stoichiometric component ratio of 1 : 1 (BaBr₂–BaI₂, BaCl₂–BaI₂, and SrBr₂–SrI₂). The high hygroscopicity of the initial mixture requires ensuring the growth without contact of the crystal with the external environment. In addition, in order to avoid violation of stoichiometry over the melt, an atmosphere containing volatile components of the crystallized substance must be created. Therefore, the

most convenient method of crystallization in this case is the Bridgman method in which the charge is in a sealed quartz ampule during the whole growing process.

The compounds of alkaline earth halides are known for their high hygroscopicity in the air, so the drying of raw materials before growing the crystal requires special attention. The levels of hydration and possible dehydration temperatures and also melting and crystallization temperatures of charge compositions were determined by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The charge was analyzed using a STA 449 CJupiter synchronous thermal analyzer (NETZSCH), which allows fixing the DSC and TG curves. Such analysis makes it possible to study phase transitions and obtain information about the thermal behavior of the sample (Fig. 1). The results for compound BaBrI are shown in Fig. 1a. The mass loss in the temperature range of 50–240°C is 9.3%, which corresponds to the three peaks on the DSC curve. Before melting there is a small peak at a temperature of 683°C. Melting of the charge begins at a temperature of 747°C and ends at a temperature of 776°C. DSC curve of the cooling also exhibits a minor peak at a temperature of 775°C before crystallization which begins at 744°C and ends at 755°C. Figure 1b presents curves for BaClI. TG reveals a mass loss of 10.04% in the temperature range from room to 220°C. The DSC heating curve shows that the melting begins at 807.5°C; according to the cooling curve, the crystallization begins at 789.1°C. The curves for SrBrI are presented in Fig. 1c. According to the TG data, the compound loses water in the temperature ranges of 110–150 and 160–220°C with the total weight loss of 19.52%. According to the DSC heating and cooling curves, the melting point of this compound is 507.6°C and the crystallization temperature is 472.7°C.

The obtained DSC and TG data were used as a basis for choosing the drying modes of raw materials and establishing the melting and crystallization temperatures of the studied compounds.

Anhydrous compound of extra-pure grade manufactured by LANKhIT (Moscow) were used as initial compounds for preparing the charge. However, preliminary multistage drying of the initial reaction mixtures does not ensure complete removal of oxygen-containing impurities, which can serve as spontaneous crystallization centers resulting in numerous defects, which in turn can contribute to the cracking of the crystal. Therefore, the next step in the preparation of the charge was the filtration of the melt through a filter made of quartz grit with a granule size of an order of 400–450 μm. After high-temperature annealing, the grits actively adsorb oxygen- and hydrogen-containing impurities on its surface. After the filtration procedure, even visually there is an increase in the transpar-

ency of the melt and the absence of flakes caused by oxide and hydroxide inclusions.

To filter the melt of the initial compounds, a quartz system was designed which consisted of two work volumes separated by a thin quartz tube. The upper volume is used for preliminary drying of the charge. It has a quartz filter, passing through which the molten raw material flows into the lower volume of the system. After filtration, the lower volume was sealed off from the quartz system and placed in a setup for crystal growth. The procedure of drying the mixture and filtration of the melt before sealing off the lower ampule is carried out at a constant evacuation. The crystals were grown from the melt by the vertical Bridgeman method in vacuumed quartz ampules with a diameter of 10–30 mm. To optimize the process of crystal formation, several forms of ampules with different configuration of the bow were tested. The setup for crystal growth has twenty heating modules and is equipped with sixteen thermocouples, which allow simulating a temperature gradient with a complex profile. The setup is controlled with a PC and special software.

One of the most time-consuming steps of obtaining crystals of this type is the selection of the optimal growth mode. After crystallization of the melt, the resulting single crystal can be deformed due to the difference in the thermal expansion coefficients of the substance and the ampule walls. As a result, dislocations, blocks, and other defects can occur in the ingot, which lead to cracking of the crystal. Therefore, “soft” growth parameters with small temperature gradients (no more than 4°C/cm) and a speed of about 1 mm/h were selected. After passing the work zone of the temperature gradient, the ampule was cooled at a rate of 5–10°C/h to prevent cracking and stress accumulation in the crystal.

Due to the hygroscopicity of halide materials, special methods should be used to protect crystal samples from air exposure. After removing from the ampule, the crystal was immediately placed in a plastic container filled with Vaseline oil. Extraction and processing of the crystal took place in a dry glove box. For spectral studies, either single-crystal plates with a diameter of 10–15 mm and a thickness of 2–3 mm or cubic samples of 10 × 10 mm were cut.

The structure of the grown single crystals was studied by powder and single-crystal x-ray diffraction methods on a D8 ADVANCE X-8 APEX diffractometer (Bruker AXS). X-ray phase analysis was used to determine the composition and control the stoichiometry of the resulting compound. For BaClI single crystals, the crystallographic parameters were determined for the first time and the results of these studies were presented in [7].

BaBrI and SrBrI crystals were activated by europium using compound EuBr₃, and EuCl₃ for BaClI crystals. Due to the similarity of the ionic radii and the ion charges, europium ions replace barium ions in

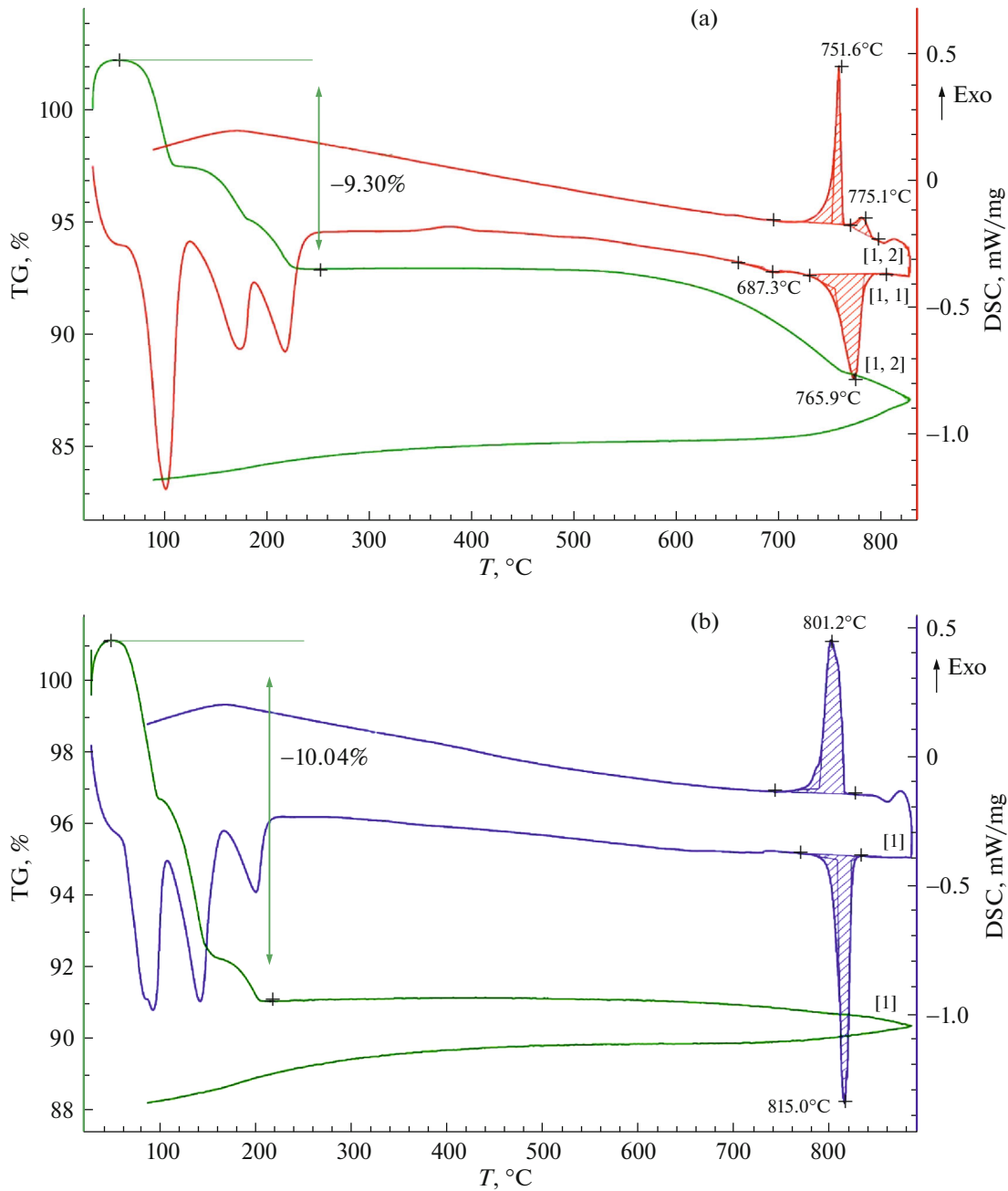


Fig. 1. Differential scanning calorimetry and thermogravimetry curves: (a) BaBrI, (b) BaClI, and (c) SrBrI.

BaClI and BaBrI, and strontium in SrBrI. To estimate the content of Eu impurity in the BaBrI crystal lattice, several samples with Eu concentrations corresponding to 0.01%, 0.05%, 0.1%, 5%, and 7% were analyzed. The analyte content was determined by the method of inductively coupled plasma mass spectrometry (ICP-MS) from a solution obtained after dissolving the crystal and separating barium as the main interfering element. Measurements were carried out on an Element 2 (Finnigan MAT, Germany) high-resolution mass spectrometer. In addition, two crystals were

also analyzed by the method of X-ray fluorescence that does not require preliminary chemical sample preparation.

The results showed a lower europium content compared to the introduced additives. At the same time, an increase in the intensity of Eu signal in solutions was observed with an increase in the concentration of the introduced additives. Two principally different methods gave close values of the Eu content: 3.1% (ICP-MS) and 2.1% (XRF) for a sample with a 7% Eu

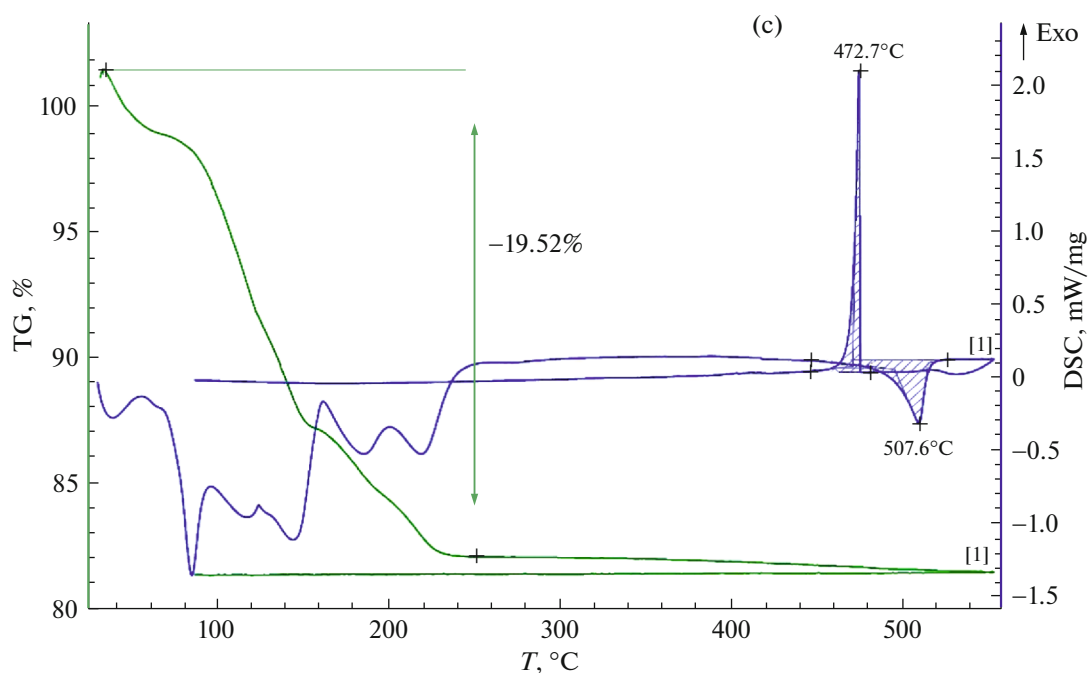


Fig. 1. (Contd.)

addition, and 0.003% (ICP-MS) and $< 0.01\%$ (XRF) for a sample with 0.05% Eu addition.

The lower Eu concentration compared to the calculated value may be due to losses during the crystal growth. One can expect that for BaClI and SrBrI crystals the difference in the measured and calculated concentrations of Eu will be similar.

However, despite the lower actual concentrations of Eu compared to the amount, which was initially added to the charge, the studied crystals show a high yield of luminescence (Table 1).

The X-ray luminescence spectra of the grown crystals were analyzed using an 10-L-01 X-ray tube at a voltage of 50 kV and a current of 1 mA. The luminescence was recorded by a MDR-2 monochromator equipped with a 1200 lines/mm diffraction grating and a Hamamatsu H6780-04 photomultiplier operating in the photon counting mode.

The X-ray luminescence spectra of the studied crystals (Fig. 2) exhibit broad bands with maximum in the range from 415 to 418 nm depending on the crystal type (Table 1). The intensity of the band depends on

the Eu concentration in the sample. The position of the peak in the luminescence spectrum also indicates that europium enters into the crystal lattice in the bivalent state with characteristic for this state $5d-4f$ transitions [6, 8]. The bivalent europium replaces the barium or strontium ions. The crystal-type dependent change in the position of the Eu^{2+} spectrum maximum is due to the change in the environment, i.e., in the distance between the cation (Ba or Sr) and anions (Br, I, Cl). Using X-ray fluorescence spectra we evaluated the light yield of the grown crystals compared with the widely used scintillator $\text{CaF}_2 : \text{Eu}$ (21 500 photons/MeV). For this purpose, samples of the same size were made. The integral intensity of the X-ray luminescence of the studied crystals was compared with the integral luminescence intensity of a $\text{CaF}_2 : \text{Eu}$ sample with a known light yield. Since the luminescence of all the studied samples is in the same spectral region, no spectral sensitivity adjustment was required.

The absorption spectra of the studied crystals were obtained using a Lambda 950 spectrophotometer.

Table 1. Main scintillation properties of grown crystals

Crystal	Light yield (photons/meV)	Luminescence maximum, nm	Decay time, ns	Band gap E_g , eV [7, 8]
BaBrI : 5% Eu	74000	415	400	5.6
BaClI : 5% Eu	25000	421	450	6.3
SrBrI : 0.1% Eu	15000	418	320	6.0

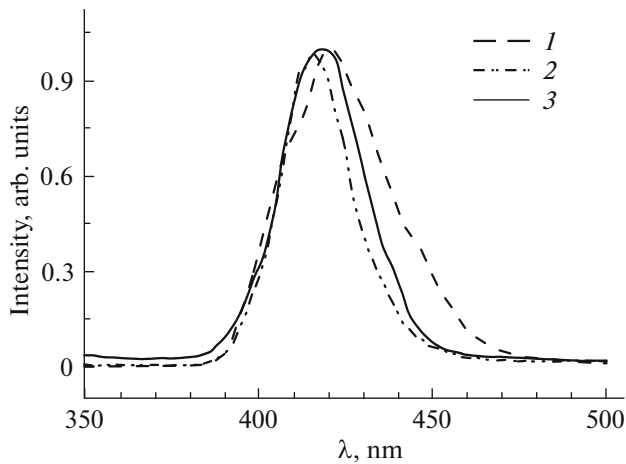


Fig. 2. Normalized spectra of x-ray fluorescence of crystals at room temperature: (1) BaCl₂:0.1 mol % Eu, (2) BaBrI:0.1 mol % Eu, and (3) SrBrI:0.1 mol % Eu.

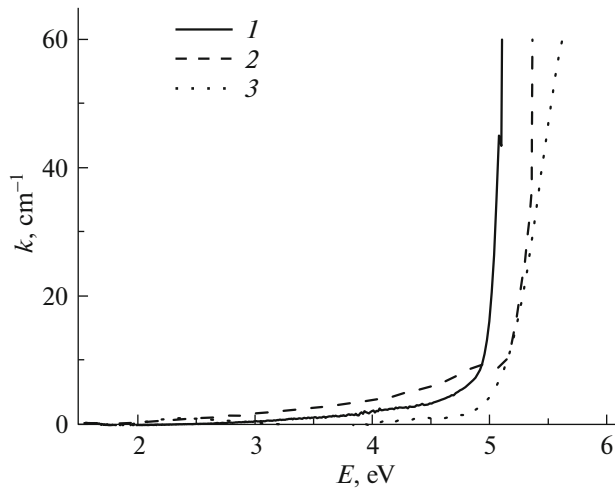


Fig. 3. Absorption spectra of nominally pure crystals: (1) BaBrI, (2) SrBrI, and (3) BaCl₂.

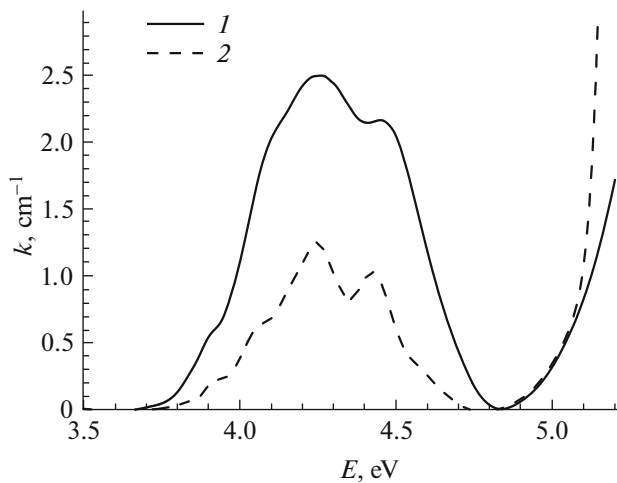


Fig. 4. Absorption spectra of BaCl₂ crystals: (1) 0.1 mol % Eu and (2) BaBrI:0.05 mol % Eu.

The absorption spectrum of unactivated crystals exhibit no peaks (Fig. 3). The edge of the fundamental absorption is in the region of 5.5–6 eV, which corresponds to the determined earlier [7, 9] value of the band gap in the studied crystals. After activation by europium, the absorption spectra of the crystals exhibit a double peak in the region of 4.0–4.5 eV. These peaks are associated with the $4f^7-5d14f^6$ transitions in europium ions. The width of the band gap in the crystals was estimated by the optical absorption edge (Table 1). It should be noted that the spectra and Table 1 show the concentrations of europium introduced into the charge before growing crystals. As shown earlier, the actual europium content in the grown crystals is lower.

CONCLUSIONS

In this work the Bridgman method was used for growing crystals of alkaline earth halides BaBrI, BaCl₂, and SrBrI. Due to the high hygroscopicity of the compounds, the preparation of the charge for crystal growth requires significant attention. In this regard, the charge was analyzed by thermogravimetric analysis and differential scanning calorimetry. The obtained data were used to select the drying modes of the initial mixtures and to establish the melting and crystallization temperatures of the studied compounds. In order to remove oxygen-containing impurities that can serve as centers of spontaneous crystallization, the melt was filtered through a quartz filter. This procedure helps to increase the optical quality of the grown crystals. The actual concentration of europium entered into BaBrI crystals was estimated by the ICP-MS and XRF methods. The obtained results show a lower europium content in the crystals compared with the input concentrations in the charge. Despite this fact, the grown crystals are characterized by a high quantum yield of luminescence and there is a clear correlation between the concentration of europium introduced into the charge and the intensity of the luminescence. Additional research is required to study the factors affecting the entry of rare-earth impurities into the crystal structure during its growth. The identification of these patterns can contribute to the development of new technologies aimed at obtaining a higher scintillation efficiency of alkaline earth halide crystals.

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