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Growth and Spectroscopy of BaBrI Crystals Activated by Eu$^{2+}$ Ions

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Abstract. BaBrI crystals containing 0.01 to 8 mol. % of Eu$^{2+}$ activator have been obtained. The photo- and X-ray luminescence spectra correspond to Eu$^{2+}$ 5d – 4f characteristic transitions with a maximum at about 3 eV. The scintillation decay time is 400-500 ns (fast component) and 3700–5500 ns (slow component). It has been established that the decay time in BaBrI crystals depends on the activator concentration. In the absorption spectra of BaBrI: Eu$^{2+}$ crystals, a double peak is observed associated with 4f$^7$ – 4f$^6$5d$^1$ transitions in Eu$^{2+}$. On the edge of optical absorption, the band gap of 5.2 eV was estimated. We assume the resonant mechanism of energy transfer to the luminescence centers.

INTRODUCTION

Binary systems of fluoride crystals of alkaline-earth halides BaFCl and BaFBr doped with europium, in addition to their scintillation abilities, have wide application because of their ability to store part of the absorbed energy (X-ray phosphors) [1]. Recently discovered luminescent properties of BaBrI: Eu$^{2+}$, BaFI: Eu$^{2+}$ and CsBa$I_5$: Eu$^{2+}$ crystals are of interest due to the high light output [2]. While the scintillation properties of Eu-activated binary fluoride systems have been extensively studied, iodide binary systems remain relatively unexplored. In this paper, we present the results of a study of the luminescent and optical properties of BaBrI: Eu$^{2+}$ crystals.

Studies of the alkaline-earth halide systems activated by rare-earth ions are associated with a high light output of these crystals, a good energy resolution and a relatively fast decay time. At present, the highest light yield is observed in bromides and iodides activated by Eu and Ce [3]. The host-selection criteria for Eu$^{2+}$-activated scintillators include a high density, a high effective atomic number, and a relatively small width of the forbidden zone. Also, Eu$^{2+}$ ions must be incorporated into the lattice of the host in a controlled manner.

BaBrI crystals have a high density, estimated as 5.21 g/cm$^3$ [4] and a high effective atomic number of 51.75. Halide materials, especially chlorides, bromides, and iodides, have been found to have a small band gap, so BaBrI crystals are effectively activated by Eu$^{2+}$ ions. In activated crystals, a high light output of about 97.000 photons/MeV, a good energy resolution of 4–5%, and a relatively fast, compared to other Eu-activated alkaline earth halides, decay time of 400–500 ns [5] is achieved. The characteristics of BaBrI: Eu$^{2+}$ crystals allow to consider them as promising scintillation detectors.

The paper presents the results of the study of the basic optical properties and suggests a possible mechanism for the transfer of excitation energy from the crystal lattice to the luminescence centers in BaBrI: Eu$^{2+}$ crystals.
METHODOLOGY

Crystal growth

High-purity compounds BaBr$_2 \times 2$H$_2$O, BaI$_2 \times 2$H$_2$O, and EuBr$_3$ were used as starting materials for the growth of BaBrI: Eu$^{2+}$ crystals. For mixed BaBr$_2$/BaI$_2$ system, an analysis of thermogravimetric analysis (TG) and differential method scanning calorimetry (DSC) results was performed. According to TG, the compound loses water at temperatures: 50–100 °C, with a mass loss of 3.80%; at 120–160 °C, with a mass loss of 2.30%; at 160-210 °C with mass loss of 2.20%. According to DSC, the melting and crystallization points of the compound were estimated at 765.9 °C and 751.6 °C, respectively (Fig. 1).

![Thermogravimetric analysis (green line), differential method scanning calorimetry (red line).](image)

FIGURE 1. Thermogravimetric analysis (green line), differential method scanning calorimetry (red line).

The initial compounds of BaBr$_2$, BaI$_2$ were mixed in a molar ratio of 1: 1 [2]. The activator EuBr$_3$ was added to the mixture before drying. Compounds were placed in a quartz ampoule connected to a vacuum system. On each temperature shelf (located at 70, 140, 180) the raw material was kept for at least 4 hours. The heating rate was no more than 20–25 °C/h with constant evacuation. The presence of residual water was monitored with a vacuum gauge. At a temperature of 250–300 °C, intense release of gaseous iodine was detected.

After drying, the molten raw material was filtered through a quartz filter. To filter the melt of the initial compounds, an optimal design of quartz ampoules was developed (Fig. 2 (a)), consisting of two working volumes separated by a thin quartz tube. First volume was used preliminary for drying of the charge and a quartz filter is also installed in the volume (Fig. 2 (b)), after passing through which the molten raw material flows into the second volume of the ampoule. Quartz grit after high-temperature processing was used as filtering substance. After filtration, the second volume was removed with a gas burner with continuous evacuation for further growth of the single crystal in a multi-zone thermal installation using the Stockbarger-Bridgman method.

The temperature gradient was no more than 4 °C/cm. The crystal growth rate was 1 mm/h. After passing through the ampoule of the temperature gradient, the furnace was slowly cooled at a rate of 5–10 °C/h to prevent cracking and the accumulation of mechanical stress in the crystal. The obtained crystals are suitable for spectroscopic studies in the visible optical range.
Luminescence measurements

Because of the hygroscopicity of BaBrI: Eu$^{2+}$ crystals, samples were prepared for the study of optical characteristics in a dry box and placed in a desiccator with mineral oil to prevent contact with the atmosphere.

The photoluminescence spectra were measured on a Perkin-Elmer LS-55 spectrofluorometer. The excitation was carried out with a xenon lamp at a wavelength of 370 nm. For the signal recording, a photomultiplier was used, sensitive in the range from 200 to 900 nm. The width of the slit of the monochromator for excitation when measuring the luminescence spectra was 15 nm, the width of the slit of the monochromator recording the glow was 10 nm. The photoluminescence excitation spectra were measured at slit widths of 10 nm. The measurements were carried out at room temperature.

X-ray luminescence was excited by a 1.7BDM-100 X-ray tube. The voltage on the tube was 50 kV, current 0.5 mA. The luminescence was recorded with an MDR-2 monochromator with a diffraction grating of 1200 lines/mm and a Hamamatsu H6780-04 photomodule operating in the photon counting mode. The measurements were carried out at room temperature and at a temperature of 80 K using a cryostat.

The scintillation decay time was measured upon excitation with pulsed X-ray radiation. The excitation was carried out using a pulsed X-ray unit based on a modified MIRA-2D unit. The duration of the exciting pulse was 8–10 ns (width at half-height). Registration was carried out with an MDR-2 monochromator (1200 bars/mm grating), a Hamamatsu H6780-04 photomodule, and a Rigol DS1202CA oscilloscope at room temperature.

The absorption spectra were measured using a Perkin-Elmer Lambda 950 two-beam spectrophotometer in the spectral range from 200 to 2500 nm (6.2–0.5 eV).

The excitation spectra of BaBrI: Eu$^{2+}$ crystals in VUV were measured under excitation with a L9841 deuterium lamp, the recording was performed using a VMR-2 vacuum monochromator.
RESULTS AND DISCUSSION

BaBrI single crystals activated by Eu

According to the latest data, to obtain large-diameter SrI₂ crystals, the melt filtration method is used [3]. This procedure significantly improves the optical quality and scintillation characteristics of the crystals obtained. As a filtering substance, quartz grit was used, corresponding to quartz of high enrichment, having high absorption properties, it is able to bind oxide and hydroxide compounds on its surface. It is noted that the melt visually becomes more transparent and does not contain “flakes” – oxide and hydroxide compounds.

One of the drawbacks of the Bridgman-Stockbarger method is the undesirable formation of crystal nuclei and the formation of defects due to the interaction of the growing boundary crystal layer with the walls of the ampoule, but this can be avoided by maintaining a flat or slightly convex shape of the crystallization front during growth procedure [6,7]. Thus, the temperature zones of the furnace to control the shape and position of the crystallization front during growth can be calculated from the melting point or crystallization point of the material. In our case, the coefficient of the crystallization front is $\varnothing = 0.6$. Chang illustrates that for a flat crystallization front, which usually creates minimal thermal stresses, values of $\varnothing$ are required, close to 0.5, with a convex crystallization front, values of $\varnothing$ are greater than 0.5 [6].

The choice of a low gradient of 4 ° C/cm was based on the literature data [8,9] and experimental data obtained during this work. At a high temperature gradient, thermoelastic stresses arise in the crystallizing material, which are associated with the anisotropy of the thermal expansion coefficients, which promote cracking, which limits the size of single crystals. The disadvantage of a high gradient is also the volatilization of the components of the melt due to local overheating, which leads to significant (up to 10%) losses of raw materials and decomposition of the melt.

![Figure 3](image_url)

**FIGURE 3.** Monocrystals BaBrI: Eu²⁺.

In Fig. 3 (a), BaBrI: Eu²⁺ single crystal blocks with dimensions of 2×2×2 cm³ and 1.5×1.5×0.7 cm³ are depicted. Cracks are observed in the crystals due to insufficiently slow cooling. Figure 3 (b) depicts samples prepared for spectroscopy studies.

**Spectroscopy of BaBrI: Eu²⁺ crystals**

Figure 4 shows the normalized excitation and emission spectra of BaBrI-0.01 mol.% Eu²⁺ and BaBrI-5 mol.% Eu²⁺. For BaBrI: Eu²⁺, a wide excitation band is observed from 250 to 400 nm. The excitation spectrum consists of bands associated with $4f^7 - 4f^5 5d^1$ transitions in Eu²⁺ [10]. The most effective absorption occurs in the wide bands centered at 280 and 370 nm. The emission spectrum shows a peak at 415–422 nm. An overlap of the absorption spectrum and the emission spectrum in the region of 375–400 nm is observed. This overlap is due to self-absorption of Eu²⁺ 5d-4f radiation, as is observed in other Eu-activated crystals [11].
Emission spectra of BaBrI-0.01 mol.% Eu$^{2+}$ and BaBrI-5 mol.% Eu$^{2+}$ differ, an increase in emission intensity is observed with increasing activator concentration. A slight shift of the luminescence peaks is explained by the different BaBr$_2$ / BaI$_2$ ratio. Compounds with an excess of bromine have luminescence peaks with a higher energy than samples with an excess of iodine [4].

The X-ray luminescence spectra of BaBrI: Eu$^{2+}$ were measured at room temperature and at 80 K (Fig. 5).

The peaks are observed about 415–422 nm (2.9–3 eV), as in the photoluminescence spectra. The peak of exciton luminescence at 80 K is observed in the region of 310–330 nm, in crystals with small concentrations of the Eu$^{2+}$ activator (less than 0.1 mol.%). The intensity of X-ray luminescence at 80 K increases by a factor of 1.5. A decrease in intensity from 80 K to 300 K is associated with thermal quenching, when, during the lifetimes of excited states of the centers, nonradiative transitions occur within the luminescence centers themselves (intracenter quenching) or quenching is due to reabsorption of luminescence at the levels of quenching centers and re-trapping the resulting nonequilibrium charge carriers.

Table 1 shows the relative light outputs of BaBrI crystals with different concentrations of Eu$^{2+}$. The relative light output was estimated from the ratio of the areas of the X-ray luminescence spectra of a BaBrI: Eu$^{2+}$ crystal to a CaF$_2$: 0.3 mol.% Eu$^{2+}$ crystal with well known light output of 19,000 photons/MeV. Since the CaF$_2$: Eu$^{2+}$ crystal...
emits photons in the same spectral region as BaBrI: Eu\(^{2+}\) and the samples had the same volume of 10×10×3 mm\(^3\), there was no correction for the quantum efficiency.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Light output (photon / MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF(_2)-0.3 mol.% Eu(^{2+})</td>
<td>19000</td>
</tr>
<tr>
<td>BaBrI-0.01 mol.% Eu(^{2+})</td>
<td>21000</td>
</tr>
<tr>
<td>BaBrI-0.1 mol.% Eu(^{2+})</td>
<td>45000</td>
</tr>
<tr>
<td>BaBrI-3 mol.% Eu(^{2+})</td>
<td>52000</td>
</tr>
<tr>
<td>BaBrI-5 mol.% Eu(^{2+})</td>
<td>74000</td>
</tr>
<tr>
<td>BaBrI-8 mol.% Eu(^{2+})</td>
<td>84000</td>
</tr>
</tbody>
</table>

In the absorption spectrum of the BaBrI activated 0.05 mol.% europium, a double excitation peak is observed associated with 4f\(^7\) – 4f\(^6\)5d\(^1\) transitions in Eu\(^{2+}\) (Fig. 6). The double absorption peak is due to the splitting of the 5d state into two levels, \(e_g\) and \(t_{2g}\). The splitting occurs due to the influence of the electric field of the lattice.

Using the absorption spectrum, we estimated the band gap width \(E_g = 5.4\) eV from the edge of optical absorption. For BaBrI: Eu\(^{2+}\) crystals the experimentally calculated \(E_g\) is 5.58 eV [12].

Eu\(^{2+}\) activated crystals have a relatively fast decay time. In BaBrI crystals, the largest contribution, about 60–70%, is provided by the fast component 400–500 ns, and the slow component, 3700–5500 ns, provides about 30–40%. At low europium concentrations, the slow component makes a greater contribution. Figure 7 (a) shows the X-ray luminescence decay curves for crystals with different activator concentrations. Measurements of the decay time were also carried out upon photoexcitation by a nitrogen laser with 337 nm wavelength (Fig. 7 (b)). From the decay curves, it can be seen that only the fast component is present in BaBrI: Eu\(^{2+}\) crystals with relative high concentrations of europium. This is due to the fact that the luminescence center Eu\(^{2+}\) is excited directly. The decay time in BaBrI crystals depends on the concentration of the activator; the lower the mol.% of the activator in the crystal, the longer the scintillation becomes. With an increase in the concentration of ions Eu\(^{2+}\) more than 5 mol.% the slow component is absent, since the Eu\(^{2+}\) ions are located close to each other, which leads to rapid energy transfer to the center of the glow.
FIGURE 7. The decay time curves for BaBrI: Eu$^{2+}$ crystals: a) excitation with an x-ray tube; b) excitation with a nitrogen laser.

In some crystals, excitation in the exciton band produces a high yield of activator luminescence. This is the main evidence in favor of the exciton mechanism of energy transfer to the luminescence centers. In BaBrI: Eu$^{2+}$ crystals at low activator concentrations from 0.01 mol.% to 0.05 mol.%, an exciton luminescence band is observed in the region of 3.7 eV at a temperature of 80 K; above room temperature the exciton luminescence is not observed. Figure 8 shows the excitation spectra of low-concentration (0.01 mol.%) Eu$^{2+}$ and nominally pure BaBrI in VUV. In the region of exciton emission, there are several exciton excitation bands of 5 eV and 6.2 eV.

FIGURE 8. VUV excitation spectra of BaBrI crystals with low concentration (mol. 0.01%) of Eu$^{2+}$ and pure BaBrI crystals.

In the exciton emission spectra, a peak is observed in the region of 5 eV, lying in the region of the fundamental absorption edge, and a plateau with energy of 7 eV. In the emission spectrum of Eu$^{2+}$ ions, a doublet with energies of 4.1 and 4.2 eV was found, corresponding to the electron transition from the ground state 4f to the lowest state 5d. There is also a wide plateau in the region of interband transitions. Based on the excitation spectra, conclusions can be drawn about the possible mechanisms of energy transfer from hot charge carriers to europium ions. The presence of a plateau in the excitation spectrum of the emission of a europium ion indicates direct electron-hole capture and subsequent recombination. At the same time, the excitation band of the 4f – 5d europium ion, 280–370 nm, lies in the region of the emission band of the excitons 350 nm. Thus, resonance energy transfer from excitons to the europium ion is possible. The intensity of X-ray luminescence increases with the concentration of europium ions, which also justifies the resonant mechanism of energy transfer, since the distance between donor-acceptor pairs decreases with increasing concentration.
CONCLUSION

The method of preparation of the charge and optimal conditions for the growth of BaBrI: Eu$^{2+}$ crystals, selected on the basis of literature and experimental data, make it possible to obtain optical crystals that are transparent and suitable for spectrometric studies.

In this paper, the photo- and X-ray luminescence spectra are presented and analyzed. The photoluminescence and X-ray luminescence spectra confirm that europium is embedded in the BaBrI lattice in the bivalent state with characteristic 5d – 4f transitions with a maximum in the 2.9–3 eV range.

The absorption spectra of BaBrI: Eu$^{2+}$ have a double peak associated with 4f – 5d transitions. On the edge of optical absorption, the band gap was estimated as 5.2 eV. The estimated band gap agrees well with the theoretically calculated value of 5.34 eV.

The scintillation decay time is 400-500 ns for high concentrations of europium in the crystal (more than 5 mol.%). At lower activator concentrations, along with the fast component, there is a slow component with a contribution of 30–40% and a luminescence decay time of 3700–5500 ns. It is established that the decay time of scintillations depends on the concentration of the activator.

Energy transfer to the luminescence centers in BaBrI: Eu$^{2+}$ crystals presumably occurs through resonant energy transfer. (The article "Role of electron and hole centers in energy transfer in BaBrI crystals" [13], Shendrik et al., found that the fast energy transport from host to activator responsible for the scintillation of BaBrI-Eu proceeds by STE creation and resonance dipole-dipole transfer. At the same time, delayed energy transfer with participation of electron and hole centers formed by exciton decay takes place. Contribution of delayed energy transfer process decreases with increase of concentration of Eu$^{2+}$ ions due to diminution of distance between the dopant ions.).

ACKNOWLEDGMENTS

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