



## BaBrI:Eu<sup>2+</sup>, a new bright scintillator

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### ABSTRACT

The scintillation properties of BaBrI:Eu<sup>2+</sup> are reported. Crystals were produced by the vertical Bridgman technique in a sealed quartz ampoule. Excellent scintillation properties were measured. A light yield of  $81,000 \pm 3000$  photons per MeV (ph/MeV) of absorbed gamma-ray energy was measured. An energy resolution (FWHM over peak position) of  $4.8 \pm 0.5\%$  was observed for the 662 keV full absorption peak. Pulsed X-ray luminescence measurements show two exponential decay components of 297 and 482 ns with a contribution to the total light output of 23% and 77%, respectively. Under X-ray and UV excitation, the emission corresponds to a broadband center at 413 nm. These initial values make BaBrI:Eu<sup>2+</sup> one of the brightest and the fastest known Eu<sup>2+</sup>-doped scintillators.

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### 1. Introduction

Very few known scintillators have good energy resolution, which is essential for spectroscopic applications such as isotopic identification of nuclear materials. High luminosity and relatively high speed (less than 1  $\mu$ s) are also highly desirable for these applications. Only 18 compounds are reported with an energy resolution of less than 6% [1]. Among those, only SrI<sub>2</sub> is activated by Eu<sup>2+</sup>. While activation with Eu<sup>2+</sup> yields scintillation light that is slower than that produced from Ce<sup>3+</sup> activation, it is still fast enough for many applications such as those related to national security. In this paper we present the scintillation properties of BaBrI:Eu<sup>2+</sup>. Barium-mixed halides activated by Eu<sup>2+</sup> have been extensively studied as X-ray phosphors [2–4] but have not been investigated as scintillators.

### 2. Experimental methods

The crystals were grown from the melt by the vertical Bridgman technique in an evacuated sealed quartz ampoule. The temperature gradient was about 30 °C/cm and the growth rate 1 mm/h. The starting materials were BaBr<sub>2</sub>, BaI<sub>2</sub>, EuBr<sub>2</sub> and EuI<sub>2</sub>. The nominal melt composition had 8% Eu. A photograph of the obtained crystal is shown in Fig. 1. Upon removal from the ampoule, the crystal was found to be clear, with the yellow coloration confined to the crystal/ampoule interface and

attributed to iodine segregation. It was also found to have several large grains. Clear small single-crystal pieces were used for the measurements. The structure of the crystal was determined by X-ray diffraction. The crystal is orthorhombic with Eu fully substituted on the Ba sites. The structure is of the PbCl<sub>2</sub>-type [5]. The density, calculated from the structure, is 5.18 g/cm<sup>3</sup> and was measured to be  $5.3 \pm 0.2$  g/cm<sup>3</sup>. It is interesting to note that the crystal is much less hygroscopic than SrI<sub>2</sub>:Eu as judged qualitatively from handling the crystals in the laboratory.

Pulse height spectra were recorded under gamma-ray excitation (<sup>137</sup>Cs) with a Hamamatsu R6231-100 photomultiplier tube (PMT) connected to an Ortec 113 preamplifier, an Ortec 672 spectroscopic amplifier and an Ortec EASY-MCA-8K multichannel analyzer. The PMT high voltage was fixed at 650 V. Samples were optically coupled onto the window of the PMT with Viscasil 600000 from General Electric and covered with layers of ultraviolet-reflecting tape (PFTE tape). All the measurements were done on samples with size ranging from 0.1 to 1 mm<sup>3</sup>.

A Nonius FR591 water-cooled rotating copper-anode X-ray generator (50 kV, 60 mA) (Bruker AXS Inc., Madison, WI) is used to



Fig. 1. 1 cm in diameter BaBrI:Eu<sup>2+</sup> shown as-grown in a sealed quartz ampoule.

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measure the X-ray excited luminescence. A SpectraPro-2150i spectrometer (Acton Research Corp., Acton, MA) coupled to a thermoelectrically cooled PIXIS:100B charge-coupled detector (CCD) (Princeton Instruments, Inc., Trenton, NJ) was used to measure the X-ray excited emission spectra.

The X-ray excited decay curves were recorded on a custom-made pulsed X-ray set-up. The system consists of an ultra-fast laser, a light-excited X-ray tube, a Hamamatsu R3809U-50 microchannel PMT and an Ortec 9308 picosecond time analyzer [6,7]. The impulse response of the system is 100 ps FWHM.

The photoluminescence excitation and emission spectra were collected at room temperature on a Horiba Fluorolog 3 fluorescence spectrometer.

### 3. Results

Fig. 2 shows pulse height spectra for BaBr:Eu<sup>2+</sup> and NaI:Tl (St. Gobain) under <sup>137</sup>Cs irradiation and amplifier shaping time of 10 μs. To determine the photopeak position and the energy resolution of crystals, part of the photopeak was fitted by Gaussian curves. For BaBr:Eu<sup>2+</sup> the photopeak is accompanied by satellite peaks at lower energy due to escape of the characteristics K<sub>α</sub>, K<sub>β</sub> X-rays of Ba. The light output of BBI was estimated by comparing the response of NaI:Tl to the one of BaBr:Eu<sup>2+</sup>. From the fitting, a light output of 81,000 ± 3000 photons per MeV was estimated for BaBr:Eu<sup>2+</sup>, corresponding to 1.9 times the light output of NaI:Tl commonly reported between 43,000 and 45,000 ph/MeV [8,9]. Table 1 gives estimated light outputs as a function of the shaping time. An energy resolution (FWHM over peak position) of 4.8 ± 0.5% was measured for the 662 keV full absorption peak.

The X-ray induced emission spectrum of BaBr:Eu<sup>2+</sup> at room temperature is shown in Fig. 3. The spectral shapes are not

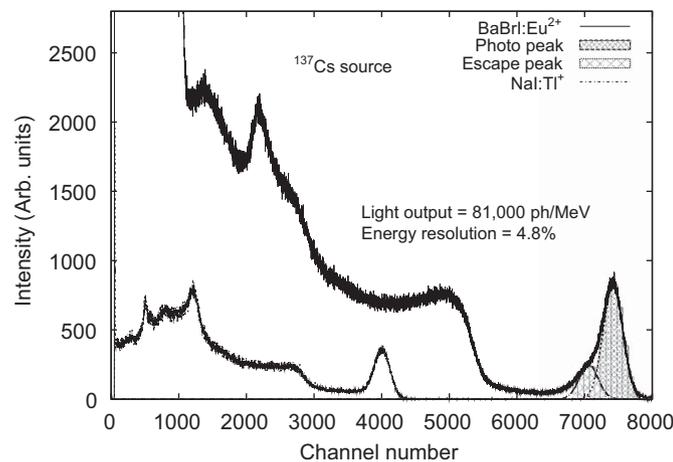


Fig. 2. Pulse height spectra of BaBr:Eu<sup>2+</sup> and NaI:Tl measured under <sup>137</sup>Cs gamma-ray excitation.

Table 1

Light yield derived from pulse height spectra of BaBr:Eu<sup>2+</sup> under 662 keV gamma ray excitation for various shaping times. The energy resolution was recorded with a shaping time of 10 μs at the 662 keV photopeak.

Estimated light yield (10 <sup>3</sup> ph/MeV)				Energy resolution (%)
0.5 μs	3 μs	6 μs	10 μs	
61 ± 2	81 ± 3	81 ± 3	81 ± 3	4.8

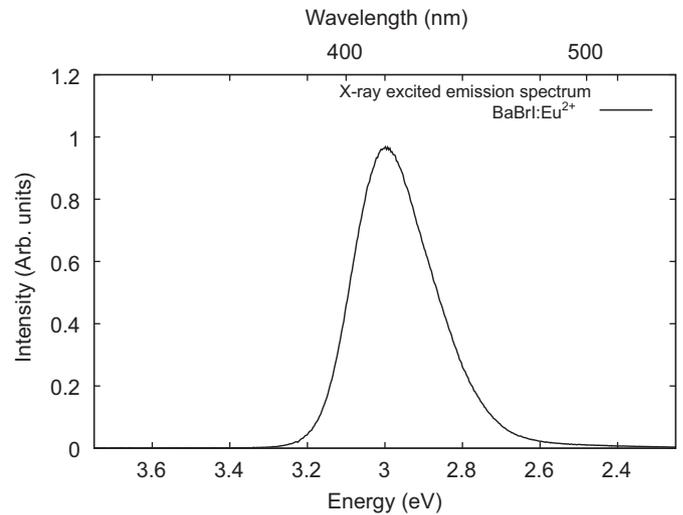


Fig. 3. Normalized X-ray excited emission spectrum of BaBr:Eu<sup>2+</sup> at room temperature.

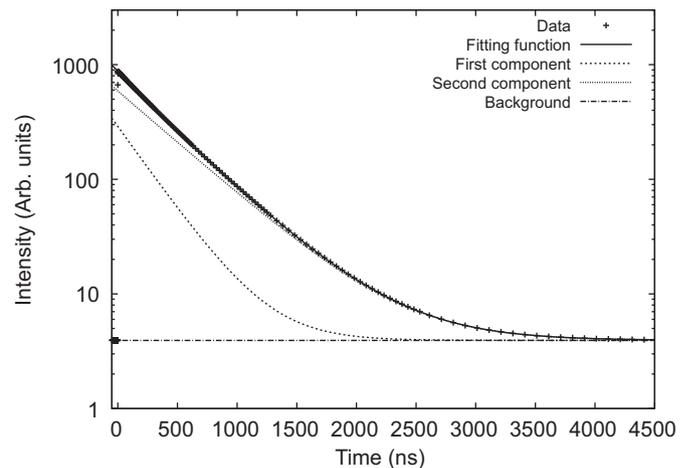


Fig. 4. Pulsed X-ray decay curve of BaBr:Eu<sup>2+</sup> at room temperature.

Table 2

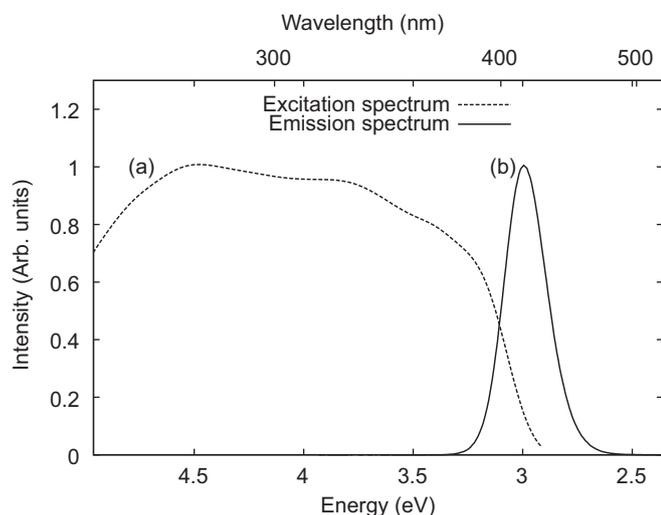
Decay times of X-ray excited luminescence.

Decay time (ns)	Fraction of light (%)
297	23
482	77

corrected for the grating efficiency and the photo detector quantum efficiency. The spectrum presents one broadband emission from 3.4 to 2.6 eV with a maximum at 3 eV. The emission is characteristic of a divalent europium 5d–4f transition.

Fig. 4 shows the X-ray excited decay curve of BaBr:Eu<sup>2+</sup>. The decay curve corresponds to two single exponential components with a lifetime of 296 ± 1 and 480 ± 5 ns, and a contribution to the total light output of 23% and 77%, respectively (Table 2). The rise time is less than 1 ns.

Fig. 5 shows the Eu<sup>2+</sup> emission spectrum measured under 4.1 eV optical excitation. The emission is similar to the divalent europium 5d–4f broadband observed under X-ray excitation. The excitation spectrum monitoring the 3 eV emission (Fig. 5) shows a



**Fig. 5.** Normalized excitation (a) and emission (b) spectra of BaBr:Eu<sup>2+</sup> at room temperature.

broadband from 5 to 3 eV with a maximum around 4.5 eV. The overlap between the excitation and emission spectra indicates that the scintillator might undergo self-absorption as observed in other Eu-doped compounds [10].

#### 4. Conclusion

We present the scintillation characterization of BaBr:Eu<sup>2+</sup> grown by the Bridgman technique in a sealed evacuated quartz ampoule. These first results show that the crystal is activated efficiently with Eu<sup>2+</sup> and yields excellent scintillation properties. The light output is estimated to be 81,000 photons per MeV with a scintillation pulse mainly decaying within 500 ns. Its energy resolution is 4.8% at 662 keV. The density, calculated from the structure, is 5.18 g/cm<sup>3</sup> and was measured to be 5.3 g/cm<sup>3</sup>. These initial results are very promising considering that the crystal quality can still be improved and optimized. The density and scintillation decay time are superior to those of SrI<sub>2</sub>:Eu<sup>2+</sup> [1] and the crystal is also less hygroscopic.

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