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Scintillation properties of $CsBa_2Br_5:Eu^{2+}$

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ABSTRACT

In this study, the scintillation properties of Eu^{2+} activated $CsBa_2Br_5$ are reported. It is an analog of Eu^{2+} doped $CsBa_2I_5$ scintillator that exhibits excellent scintillation properties. Microcrystalline powder samples of this compound were synthesized by reaction in the molten state of cesium bromide, barium bromide and europium bromide. The concentration of an Eu was varied from 0% to 10%. The luminescence was studied under UV and X-ray excitation. The light output is strongly Eu^{2+} concentration dependent, reaching an estimated maximum of about 92,000 photons/MeV at 2% Eu under X-ray excitation. About 50% of the scintillation light decays in less than 1 μs. $CsBa_2Br_5:Eu^{2+}$ exhibits a complex concentration dependent emission centered around 435 nm.

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1. Introduction

In recent years, great efforts have been made to develop scintillators to detect gamma rays with improved efficiency and energy resolution. There are several known scintillators available; nevertheless, no one scintillator fulfills all the requirements that one needs in the ideal scintillator. Scintillator usefulness is an application dependent. In general, the ideal scintillator would be a dense, low-cost material, with high stopping power, fast decay time and excellent energy resolution and proportionality.

There has been considerable interest in alkaline earth halides activated with europium or cerium [1–4]. In particular, van Loef et al. [1] have shown that $LaBr_3$, when doped with Ce^{3+}, has a high light yield of 67,000 photons/MeV, with a decay time of 30 ns; and Cherepy et al. [2] have shown that $SrI_2:Eu^{2+}$ has a very high light yield of 90,000 photons/MeV with a decay time of 1200 ns. Despite outstanding scintillation properties, those materials present a significant challenge for practical applications. Both compounds are highly hygroscopic and need custom equipment for their crystal growth and handling. Recently, two new and bright halide-based scintillators, $CsBa_2I_5:Eu^{2+}$ [3] and BaBrI: Eu^{2+} [4], have been reported. The BaBrI has a light yield of $89{,}000 \pm 3000$ photons/MeV [5] and a decay time of 500 ns. The $CsBa_2I_5:Eu^{2+}$ has a light yield of $97{,}000 \pm 5000$ photons/MeV and a main decay time of 1500 ns.

In this study, we present the scintillation properties of Eu^{2+} activated $CsBa_2Br_5$, the bromide analog to $CsBa_2I_5$. The crystal structure of $CsBa_2Br_5$ is monoclinic and is isostructural to the $CsBa_2I_5$ structure. Scintillation properties for Ce^{3+} activated $CsBa_2Br_5$ have been reported [6], but not those of the Eu^{2+} activated $CsBa_2Br_5$.

2. Experimental

2.1. Synthesis

The powder samples were synthesized using the high-throughput facility presented in Ref. [7]. The samples were obtained by the melt solidification in an evacuated sealed quartz ampoule. Due to the hygroscopic nature of halides, all processing was performed in an argon-filled glove box, under dry conditions. The starting materials were $BaBr_2$ (Aldrich), CsBr (Aldrich) and $EuBr_2$ (Alfa Aesar). The $CsBa_2Br_5$:Eu samples were synthesized by the reaction of stoichiometric amounts of $BaBr_2$, CsBr and $EuBr_2$. The samples were evacuated at 150 °C and 10^{-6} Torr for 1 h to remove moisture, and then were sealed under vacuum. The sealed ampoules were placed in a tubular furnace and heated to 860 °C for about 48 h. The following mole percentages of $EuBr_2$ were chosen to dope $CsBa_2Br_5$ for the present study: 0.5%, 1%, 1.5%, 2%, 3%, 5%, 7% and 10%. At the end of the reaction, colorless solid products were obtained for each sample.

2.2. Characterization

The crystallinity and structure identification of each sample were determined by the powder X-ray diffraction. An in-house diffraction setup comprised of a Bruker Nonius FR591 rotating anode X-ray generator equipped with a copper target and a 50 kV and 60 mA electron beam was used. A more detailed description

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of this setup is supplied in Ref. [7]. All optical and X-ray measurements were performed on samples having comparable particle sizes in the range 5–20 μm and contained in cylindrical quartz cuvettes. A Nonius FR591water-cooled rotating copper-anode X-ray generator (50 kV, 60 mA, Bruker AXS Inc., Madison, WI) was used to excite the luminescence. A Spectra Pro-2150i spectrometer (Acton Research Corporation, Acton, MA) coupled to a thermoelectrically cooled PIXIS: 100 B charge coupled detector (CCD) (Princeton Instruments, Inc., Trenton, NJ) was used to measure the X-ray excited emission spectra (200–1000 nm). Room temperature pulsed X-ray spectra were measured on an in-house pulsed X-ray system, which produces 80 ps (fwhm) pulses of X-rays with a mean energy of 18 keV. Fluorescent photons from the sample were detected by a microchannel phototube with 35 ps (fwhm) response [8]. Photoluminescence excitation and emission spectra were obtained using an in-house-built optical spectrometer. The excitation spectral range 200–600 nm, while the emission spectral range 200–1000 nm.

3. Results and discussion

$CsBa_2Br_5$ forms a monoclinic structure [9,10] with space group $P2_1/c$ and cell parameters $a=9.987(3)$ Å, $b=8.6653(13)$ Å, $c=13.816(3)$ Å; $\beta=90.198(15)$. The structure is the $NH_4Pb_2Cl_5$ [11] type similar to that of the $CsBa_2I_5$ analog [9]. There are two crystallographically inequivalent sites for Ba: Ba1, which is coordinated by seven bromides, and Ba2, coordinated by eight bromides. It has a density of 4.48 g/cm^3. In $CsBa_2Br_5$, the activator, Eu^{2+}, is expected to occupy the divalent barium sites due to their similar ionic radii ($r(Ba^{2+})=1.38$ Å, $r(Eu^{2+})=1.20$ Å) [12] and an identical charge. The XRD pattern of all samples of the present study matched well with the XRD presented in the JCPDF 0045-0327 [13], indicating that the single phase material is produced.

3.1. X-ray excited emission spectra

The X-ray excited luminescence spectra of undoped and 0.5%–10% Eu activated $CsBa_2Br_5$, obtained at room temperature, are presented in Fig. 1. An undoped sample shows a very broad emission from 300 to 600 nm and exhibits an intrinsic luminescence similar to that found in alkali halides and alkaline earth halides [14,15]. All $CsBa_2Br_5$ samples activated with europium show high scintillation light yield compared to an undoped $CsBa_2Br_5$. The emission of $CsBa_2Br_5$:Eu^{2+} is a broad band emission from 380 to 520 nm, with maxima at 420 and 445 nm. The emission is not a characteristic of $5d$–$4f$ emission of Eu^{2+}. The presence of two emission bands could be tentatively assigned to the substitution of divalent europium on two barium sites in the $CsBa_2Br_5$ structure [10]. We observed that the emission centered near 445 nm becomes more dominant with respect to the 420 nm emission as an Eu concentration increases. It should be noted that an energy transfer involving self-trapped excitons and self-trapped holes is commonly observed in halide compounds [16,17] and could play a role in the observed emissions. The total light output of $CsBa_2Br_5$ is strongly Eu^{2+} concentration dependent and reaches a maximum at 2% Eu^{2+}. The highest light yield of 91,800 ph/MeV (four times that of the undoped compound) was observed for the 2% Eu doped $CsBa_2Br_5$ compound. Beyond this concentration, the light yield decreases as the Eu^{2+} concentration increases (Fig. 2). It should be noted that each data point in Fig. 2 is an average value of three samples synthesized, using the same synthesis procedure.

Fig. 3 shows the pulsed X-ray excited decay curves of undoped and Eu^{2+} activated $CsBa_2Br_5$. The decay curves of all samples are multi-exponential. The decay curves of an undoped $CsBa_2Br_5$

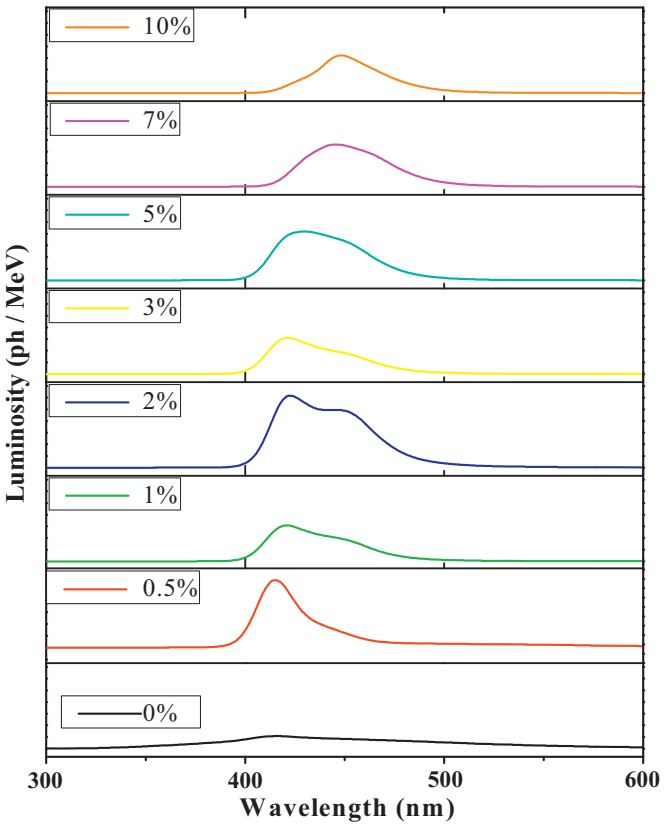

Fig. 1. X-ray excited emission spectra of undoped and an Eu doped $CsBa_2Br_5$. Inset figures indicate %Eu concentration.

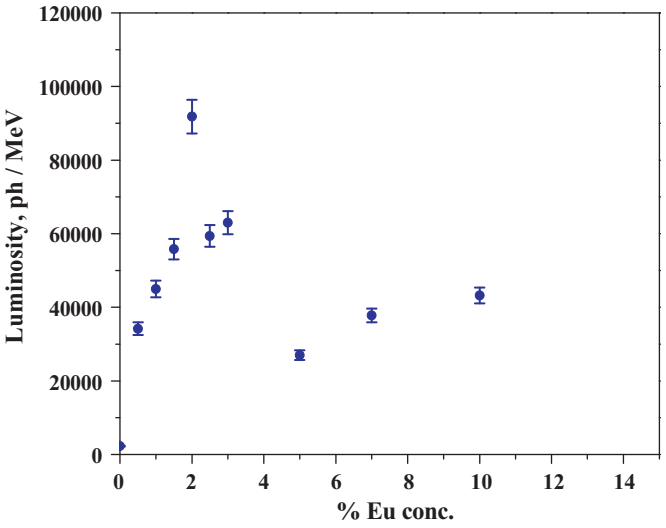

Fig. 2. Eu concentration dependence scintillation light yield of $CsBa_2Br_5$:Eu.

correspond to four single exponential components with decay times of 285 ns (11%), 754 ns (13%), 2228 ns (10%) and 5607 ns (17%). Upon an Eu^{2+} activation, the decay curves exhibit two main exponential components with decay times of 440 and 1240 ns (Table 1). The contributions to the total light output are in the range 6–21% and 39–67% for the first and second components, respectively. The contribution of a third, slower component is in the range 12–22%. The data presented in Fig. 4 suggest that the second component is mainly responsible for an increase in light output with an increase in an Eu concentration, and it levels off at