Structure and scintillation of Eu^{2+} -activated calcium bromide iodide

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Abstract

We report the structure and scintillation properties of Eu^{2+} -activated calcium bromide iodide. $\text{CaBr}_{0.7}\text{I}_{1.3}$ was the only composition that could be synthesized in the $\text{CaBr}_2\text{-CaI}_2$ system. The compound has an effective atomic number of 47 and crystallizes in a trigonal crystal system with the R-3 space group and a density of 3.93 g/cc. The structure is layered and contains Ca in an octahedral environment with the Br/I anions jointly occupying a single site. Eu^{2+} -activated samples show an intense narrow emission, characteristic of the $5d\text{-}4f$ transition of Eu^{2+} , when excited with UV or X-rays. The sample with 0.5% Eu shows a light output of 63,000 ph/MeV at 662 keV with 96% of the light emitted with a monoexponential decay time of 1,332 ns. An energy resolution of 10.4% full width at half maximum (FWHM) has been achieved for 662 keV gamma rays at room temperature.

Keywords: scintillator, solid solutions, CaI_2 , europium, calcium bromide iodide.

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1. Introduction

Inorganic scintillators play an important role in the detection of ionizing radiation with applications in national security, medical imaging and high energy physics. Two binary alkaline earth scintillator crystals were reported as early as the 1960's, $\text{CaI}_2\text{:Eu}$ [1] and $\text{SrI}_2\text{:Eu}$ [2]. In recent years, there has been renewed interest in the development of scintillators with improved performance. This led to new reports on scintillation of the Eu^{2+} -activated alkaline earth binary halides: CaI_2 [3], CaBr_2 [4], SrI_2 [5], BaI_2 [5-7], BaBr_2 [7] and BaCl_2 [7, 8].

An unexpected result was obtained by mixing the Ba halides. The mixed halides BaFI [9], BaBrI [10], BaClI [11] and BaBrCl [11] showed a clear improvement in the scintillation properties compared with the binary halides. Solid solutions offer the possibility to tailor properties by incrementally varying the composition. A few alkaline earth mixed halide systems have been studied and shown to exhibit a variety of structures, depending on the constituent species. We have previously shown that solid solutions in the $\text{BaBr}_2\text{-BaI}_2$ system form over the entire composition range and crystallize in the orthorhombic, anion-ordered PbCl_2 structure-type [12]. The $\text{SrBr}_2\text{-SrI}_2$ system is more complicated and contains solid solutions with different structures, depending on the Br/I ratio [11, 13]. $\text{CaI}_2\text{:Eu}$ and $\text{CaBr}_2\text{:Eu}$ are known to be bright scintillators with luminosities as high as 110,000 [3] and 39,000 [4] ph/MeV, respectively. Solid solutions of CaBr_2 and CaI_2 , however, have not been reported. CaBr_2 crystallizes in an orthorhombic crystal system with the Pnmm space group. The structure is an orthorhombic distortion of the tetragonal rutile CaF_2 structure. CaI_2 , on the other hand, crystallizes in a trigonal crystal system in the P-3m1 space group. The structure is layered similar to CdI_2 , with weak van der Waals bonding between the iodide layers. In this paper, we report the structure of $\text{CaBr}_{0.7}\text{I}_{1.3}$, the only composition that could be synthesized in the $\text{CaBr}_2\text{-CaI}_2$ system. Phase separation was observed for all other compositions. The luminescence and scintillation properties of Eu^{2+} activated samples are also presented.

2. Experimental procedure

Synthesis

High-purity reactants in the form of beads (10 mesh) were obtained from Sigma-Aldrich and used without additional purification. The reactants and products are sensitive to moisture and were handled in an Ar-filled glovebox maintained below 0.1 ppm of O_2 and H_2O . The synthesis of samples was achieved by mixing appropriate ratios of CaBr_2 (purity 99.98%), CaI_2 (purity 99.999%) and $\text{EuBr}_2/\text{EuI}_2$ (purity 99.99%) in sealed quartz ampoules. The ampoules were heated to 800°C , a temperature that is above the melting temperature of each of the reactants. The ampoules were positioned off the vertical, held at 800°C for 4 hours, then quenched to room

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4 temperature. Small, clear crystals (dimensions 1-5 mm) were obtained. The Eu concentration in
5 the reactants was varied from 0 to 5 mol%. The Eu concentrations in the text are nominal
6 compositions that were added to the melt.
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8 9 Characterization

10 Structure

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14 Structure determination was carried out by single crystal XRD on a Bruker SMART-
15 CCD platform diffractometer using MoK α radiation. The crystal (dimensions 0.15x0.1x0.04
16 mm³) was mounted on a glass fiber and was transferred to the diffractometer. The SMART
17 program [14] was used to determine the unit cell parameters and data collection (15 sec / frame,
18 0.3 deg. /frame for a sphere of diffraction data). The data were collected at 150K using an
19 Oxford nitrogen gas cryostream system. The raw frame data were processed using the SAINT
20 program [15]. The empirical absorption correction was applied based on psi-scan. Subsequent
21 calculations were carried out using the SHELXTL program [16]. Additional information about
22 the data collection are presented in Table 1.
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27 Phase identification was performed by powder X-ray diffraction (XRD) with a Bruker
28 Nonius FR591 rotating anode X-ray generator equipped with a Cu target at a 50 kV and 60 mA
29 electron beam.
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32 Scintillation properties

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35 The high-throughput facility described in [17] was used for characterization of the
36 samples. For luminescence measurements, samples of crystalline particles of size ranging from
37 0.5 to 2 mm were packed in gas tight quartz ampoules with an inner diameter of 4 mm and length
38 of 15 mm.
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41 X-ray excited luminescence was obtained using the rotating anode described above as
42 excitation source and a SpectraPro-2150i spectrometer (Acton Research Corp., Acton, MA)
43 coupled to a PIXIS:100B charge-coupled detector (Princeton Instruments, Inc., Trenton, NJ) to
44 record the spectral response [18].
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47 Photoluminescence excitation and emission spectra were obtained using an in-house-built
48 optical spectrometer. A Xe-broad-spectrum lamp was the excitation source used to excite the
49 samples between 200 and 600 nm. The emission was measured from 250 to 1000 nm using the
50 same set-up that was described for the X-ray excited luminescence.
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54 The time response of the X-ray excited luminescence was measured using a custom-made
55 pulsed X-ray system consisting of an ultrafast laser (200 fs pulses at 165 kHz), a light-excited X-
56 ray tube, a Hamamatsu R3809U-50 microchannel PMT and an Ortec 9308 picosecond time
57 analyzer. The impulse response of the system is 100 ps FWHM [18].
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The luminosities were estimated from the pulsed X-ray decay measurements by summing all detected photons. Relative luminosity of each sample was obtained by comparison to a CsBa₂I₅:Eu single crystal with known luminosity (100,000 photons/MeV) [19], measured under identical conditions. Error bars correspond to statistical variations obtained in the measurements.

The pulse height gamma-ray spectrum was measured by a Hamamatsu R6231-100 photomultiplier tube (PMT) under ¹³⁷Cs 662 keV γ -ray excitation. The PMT was connected to a Canberra 2005 preamplifier, an Ortec 672 spectroscopic amplifier and an Ortec EASY-MCA-8K multichannel analyzer. As-synthesized samples were optically couples to the PMT with a Viscasil 600,000 (GE) and covered with layers to UV light reflective PTFE tape. The light output was estimated by comparison of the photopeak position with the response of a 5x5x5 mm³ NaI:Tl single crystal from Amcrys measured under identical conditions. The energy resolution, defined as the FWHM of the 662 keV full absorption peaks, was also calculated.

3. Results and discussion

Crystal structure description

CaBr_{0.7}I_{1.3} was the only composition that could be obtained in pure form while investigating the CaBr_xI_{2-x} system over the composition range 0 < x < 2. Attempts to synthesize other compositions were unsuccessful and yielded the starting reactants. The samples were obtained as clear crystals with dimensions of 1-5 mm as shown in Fig. 1(a). CaBr_{0.7}I_{1.3} (CSD no. 425579) crystallizes in the trigonal space group R-3 (number 148) with unit cell parameters a = 4.3588(9) Å, c = 20.022(9) Å and density calculated to be 3.929 g/cc. A schematic of the structure is shown in Fig. 1(b) with the atomic positions tabulated in Table 2. Similar to CaI₂, the structure is layered. The lattice contains a single cation site and a single anion site jointly occupied by the bromide/iodide ions (Table 2). The Br⁻/I⁻ anions are arranged in a cubic close-packed arrangement (stacking sequence ...ABCABC...), with the Ca²⁺ cations occupying all the octahedral holes between alternate layers of close-packed anions. Thus, half of the available octahedral holes are occupied.

The structure can also be visualized as being built from Ca(Br,I)₆ octahedra. Each octahedron shares edges with six adjacent identical units within each layer. The Ca(Br,I)₆ octahedra are slightly distorted, with a Ca-Br/I distance of 3.0168 (8) Å and bond angles deviating by at most 2.5° from the ideal value of 90°. The Ca-X bond distance is intermediate to that in CaBr₂ (2.8749 and 2.8963 Å) [20] and CaI₂ (3.1243 Å) [21]. Bromide/iodide ions in adjacent layers are separated by a distance of 4.18 Å with the distance between the 2 adjacent layers being 3.35 Å. Due to weak Van der Waals bonding between the layers, the crystal cleaves easily in a direction perpendicular to the c-axis.

Since there is a single cation site present, the activator Eu would substitute Ca in the lattice, putting the lattice in tension as the ionic radius of Ca²⁺ (1 Å) is much less than that of

Eu²⁺ (1.17 Å) for the octahedral coordination [22]. In this study, we have synthesized samples with up to 5% Eu without detecting any impurity phases in the powder X-ray diffraction.

Photoluminescence

Fig. 2 shows the room temperature photoluminescence spectra for undoped and Eu-doped CaBr_{0.7}I_{1.3}. Fig. 2(a) shows the excitation and emission spectra for the undoped sample. Upon excitation below 240 nm, the sample shows a broad emission between 350 and 650 nm. The emission appears to be a superposition of several peaks. The excitation spectrum shows a small maximum below 230 nm as well as a feature at 255 nm. Due to limitations in measuring excitation wavelengths below 220 nm in our system, we are unable to obtain the excitation maximum. Excitation at 255 nm yields an emission centered at 400 nm with weak features at 480 nm and 640 nm. The excitation band at 255 nm might be due to a trace of Eu²⁺ contamination.

Addition of Eu results in the appearance of a intense blue emission that is attributed to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu²⁺, as shown in Figs. 2(b)&(c). The sample containing 0.1% Eu shows a single emission band centered 460 nm, as expected due to the single cation site in the lattice. The FWHM of the emission is 1,600 cm⁻¹. The Stokes shift was calculated for the sample with the lowest Eu concentration. The difference between the lowest excitation energy (~425 nm) and emission maximum (460 nm) yielded a Stokes shift of 1,790 cm⁻¹. The FWHM and Stokes shift of the emission are in the range of the Eu²⁺ emission in CaBr₂ and CaI₂ [23, 24]. Increase in the Eu concentration results in a progressive red shift of the emission maximum, with the emission of the sample containing 5% Eu centered at 470 nm. The position of the emission maximum is in between the values of 433 nm and 467 nm reported for the related Eu²⁺ activated halides CaBr₂ and CaI₂, respectively [23].

The excitation spectrum for each sample shows two distinct bands, centered at 260 nm and 350 nm. There is a significant overlap between the emission spectrum for the undoped sample and the excitation of the Eu²⁺ activated samples. Excitation via either band yields the Eu²⁺ emission. The intensity of the 260 nm excitation band is higher than the 350 nm band. The relative intensity of the 350 nm band decreases on increasing the Eu concentration. The divalent europium ion in CaBr_{0.7}I_{1.3} occupies the Ca²⁺ site, which is surrounded by six bromide/iodide ions in an octahedral arrangement. The crystal field splits the degenerate Eu²⁺ 5d excited state into a lower energy triplet (t_{2g}) and higher energy doublet (e_g) [25]. Thus, the excitation band centered at 260 nm represents excitation of an electron from the 4f ground state to the higher energy e_g excited states and the band at 350 nm, excitation to the lower energy t_{2g} excited state. For all concentrations, we observe a slight overlap between the excitation and emission spectra, indicating the possibility of self absorption.

X-ray excited luminescence

Fig. 3 shows the room temperature X-ray excited emission spectra for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different amounts of Eu. The undoped sample shows a broad emission between 350 and 650 nm. The emission is identical to that obtained upon optical excitation at 225 nm (Fig. 2(a)). Thus, the host related emitting centers can be excited either by the X-rays (higher energy) or UV light (lower energy) at room temperature. A broad emission with a maximum at 430 nm has been reported for undoped CaI_2 crystals upon excitation with UV and X-rays [26]. The origin of the band is unclear and is attributed to impurities or defects.

Addition of 0.1% Eu results in the appearance of the Eu^{2+} emission at 461 nm, in addition to the host-related emission at lower energies. Further addition of Eu results in an increase in the intensity of the Eu^{2+} emission and the disappearance of the low energy host emissions. Thus, the absorbed energy is efficiently transferred to the dopant europium ions. We also observe a slight narrowing of the emission and a minor red shift in the peak position. Shown in Table 3 are the emission maxima for samples with different Eu concentrations. The emission maximum increases from 461 nm for the 0.1% Eu doped sample to 474 nm for 5% Eu doping. This shift and narrowing of the emission is attributed to the self absorption that is expected due to the overlap between the excitation and emission bands (Fig. 2(b)).

Room temperature X-ray excited luminescence decay curves are presented in Fig. 4 with the major decay fractions listed in Table 3. Each curve is normalized to 1 at zero time for ease of comparison. The decay curves are close to mono-exponential with a small constant fraction (representing light that is slower than 15 μs). For the undoped sample, the majority of the light (85%) decays in 1,260 ns. The origin of the relatively fast decay of luminescence in the undoped sample is unclear. Similar observations have been made for undoped and Eu-doped CaI_2 . Undoped calcium iodide has been found to exhibit a decay lifetime (550 ns) that is faster than the Eu^{2+} -activated crystals (790 ns) [1]. The origin of the fast decay in undoped CaI_2 is still not understood. Upon Eu addition, we observe a slight increase in the decay times. There is a progressive increase on further increasing the Eu concentration, as shown in the inset in Fig. 4 and Table 3. This is possibly due to greater self absorption on increasing the Eu concentration.

The luminosities were estimated from the pulsed X-ray decay measurements by summing all detected photons. The relative luminosity of each sample was obtained by comparison to a $\text{CsBa}_2\text{I}_5\text{:Eu}$ single crystal with a luminosity of 100,000 ph/MeV, measured under identical conditions. Error bars correspond to statistical variations obtained in the measurements. Shown in Fig. 5 and Table 3 are the relative luminosities versus Eu concentration for the samples. The undoped sample is estimated to have a luminosity of 45,000 ph/MeV. The highest luminosity obtained is 83,500 ph/MeV, for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing 1% Eu. Further increase in the Eu concentration results in a slight decrease in the luminosities due to concentration quenching.

Presented in Fig. 6 is the pulse height spectrum on a $0.5 \times 1.5 \times 2 \text{ mm}^3$ $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}(0.5\%)$ crystal exposed to a ^{137}Cs radioactive source measured using a spectroscopic amplifier with a shaping time of 10 microseconds. Also shown in the spectrum for a $5 \times 5 \times 5 \text{ mm}^3$ NaI:Tl crystal

(Amcryst) measured under identical conditions. Light output was estimated by comparison of the photopeak position with the response of the NaI:Tl crystal that has a light output between 43,000 and 45,000 ph/MeV [27, 28] and accounting for the PMT quantum efficiency provided by the manufacturer. The light output of $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}(0.5\%)$ was estimated to be 63,000 ph/MeV, in good agreement to that obtained by X-ray excitation (Table 3). The energy resolution, defined as the FWHM of the 662 keV full absorption peak, was calculated to be 10.4%. The light output obtained is between the values reported for $\text{CaI}_2\text{:Eu}$ [1, 3] and $\text{CaBr}_2\text{:Eu}$ [4]. It can be inferred that contrary to what was observed for the Ba mixed halides, there is no improvement from the brightest compound, $\text{CaI}_2\text{:Eu}$ (Table 4). A summary of the structure and scintillation properties of the three calcium halide scintillators is presented in Table 4.

4. Conclusions

We have presented the structure and scintillation properties of $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}$. The compound crystallizes in a trigonal layered structure. Upon optical and X-ray excitation, the Eu^{2+} activated samples show a bright blue emission. The position of the emission maximum varies from 461 to 474 nm and the decay lifetime between 1,321 and 1,630 ns, depending on the Eu concentration. Light yield of 63,000 ph/MeV was obtained for $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}(0.5\%)$ with 96% of the light decaying at 1,332 ns. Some self absorption and re-emission is evident from the increase in the peak wavelength and decay time on increasing the Eu^{2+} concentration. The layered structure might make the growth of large-sized crystals challenging, but the compound is a very bright scintillator and can be used for applications that do not require single-crystals.

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Figure captions

Fig. 1: (a) Photograph of a small crystal and (b) schematic of the structure of $\text{CaBr}_{0.7}\text{I}_{1.3}$.

Fig. 2: Room temperature photoluminescence spectra for $\text{CaBr}_{0.7}\text{I}_{1.3}$ (a) Excitation and emission curves for undoped sample, (b) 2D contour excitation versus emission maps for sample containing 1% Eu and (c) Excitation and emission spectra for samples containing different Eu concentration that are normalized to the excitation/emission maxima.

Fig. 3: Room temperature X-ray excited emission spectra for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations.

Fig. 4: Room temperature X-ray excited decay curves for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations. Each curve is normalized to 1 at zero time. The inset shows the changes in decay time constant with Eu^{2+} concentration.

Fig. 5: Estimated luminosities for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations.

Fig. 6: Pulse height spectrum for $\text{CaBr}_{0.7}\text{I}_{1.3}:\text{Eu}(0.5\%)$ measured under ^{137}Cs (662 keV) excitation. A NaI:Tl crystal is used as the reference.

Tables

Table 1: Crystallographic data and refinement parameters for $\text{CaBr}_{0.7}\text{I}_{1.3}$ (CSD no. 425579)

Empirical formula	$\text{CaBr}_{0.7}\text{I}_{1.3}$
Formula weight	261.14 g mol^{-1}
Effective atomic number	47
Wavelength	$\text{Mo K}\alpha\ (\lambda = 0.71773\text{ \AA})$
Crystal system, space group	Trigonal, $R\text{-}3$ (No. 148)
Unit cell dimensions	$a = 4.3588\ (9)\text{ \AA}, c = 20.022\ (9)\text{ \AA}$
Cell volume	$329.43\ (17)\text{ \AA}^3$
Z, Calculated density	3, 3.949 g cm^{-3}
Absorption coefficient, μ (Mo K α)	16.69 mm^{-1}
θ range for data collection	$3.1 - 28.2^\circ$
Reflections collected/unique	170 reflections with $I > 2\ \sigma(I) / R_{\text{int}} = 0.046$
GOF on F^2	1.339
Final R indices [$I > 4\sigma(I)$]	$R_1^{\text{a}}=0.0654, wR_1^{\text{b}}=0.1893$
R indices (all data)	$R_1^{\text{a}}=0.0686, wR_1^{\text{b}}=0.1925$

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table 2: Atomic coordinates of $\text{CaBr}_{0.7}\text{I}_{1.3}$

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occupancy
Ca	0	0	0	0.0198 (15)	1
Br	0.6667	0.3333	0.0807 (5)	0.0280 (9)	0.35 (8)
I	0.6667	0.3333	0.0807 (5)	0.0280 (9)	0.65 (8)

Table 3: Emission peak wavelength and decay components for $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:xEu}^{2+}$ obtained upon X-ray excitation

Eu concentration (%)	Emission peak wavelength (nm)	Major decay fraction	Luminosity (ph/MeV)
0	455	1,260 ns (85%)	46,000
0.1	461	1,321 ns (94%)	69,000
0.25	462	1,328 ns (95%)	62,500
0.5	465	1,332 ns (96%)	64,000
1.0	468	1,352 ns (96%)	83,500
2.0	470	1,390 ns (95%)	79,000
5.0	474	1,630 ns (91%)	72,000

Table 4: Comparison of structure and scintillation properties of Eu^{2+} activated CaBr_2 , $\text{CaBr}_{0.7}\text{I}_{1.3}$ and CaI_2

	$\text{CaBr}_2\text{:Eu}$	$\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}$	$\text{CaI}_2\text{:Eu}$
Crystal system	Orthorhombic	Trigonal	Trigonal
Space group	Pnnm	R-3	P-3m1
Emission peak (nm)	448	468	470
Decay lifetime (ns)	2,512	1,350	790
Luminosity (ph/MeV)	39,000 ^a	83,000 ^b	86,000 [1] ^a ; 110,000 [3] ^a
Eu conc., reference	8%, [4]	1%, this study	NA, [1]; 0.5%, [3]

^a 662 KeV gamma ray excitation

^b X-ray excitation

Figures

Fig. 1: (a) Photograph of a small crystal and (b) schematic of the structure of $\text{CaBr}_{0.7}\text{I}_{1.3}$.

Fig. 2: Room temperature photoluminescence spectra for $\text{CaBr}_{0.7}\text{I}_{1.3}$ (a) Excitation and emission curves for undoped sample, (b) 2D contour excitation versus emission maps for sample containing 1% Eu and (c) Excitation and emission spectra for samples containing different Eu concentration that are normalized to the excitation/emission maxima.

Fig. 3: Room temperature X-ray excited emission spectra for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations.

Fig. 4: Room temperature X-ray excited decay curves for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations. Each curve is normalized to 1 at zero time. The inset shows the changes in decay time constant with Eu^{2+} concentration.

Fig. 5: Estimated luminosities for $\text{CaBr}_{0.7}\text{I}_{1.3}$ containing different Eu concentrations.

Fig. 6: Pulse height spectrum for $\text{CaBr}_{0.7}\text{I}_{1.3}\text{:Eu}(0.5\%)$ measured under ^{137}Cs (662 keV) excitation. A NaI:Tl crystal is used as the reference.