Scintillation properties of Eu^{2+} -doped KBa_2I_5 and K_2BaI_4

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Abstract

We report two new ternary metal halide scintillators, KBa_2I_5 and K_2BaI_4 , activated with divalent europium. Single crystal X-ray diffraction measurements confirmed that KBa_2I_5 has a monoclinic structure ($P2_1/c$) and that K_2BaI_4 has a rhombohedral structure ($R3c$). Differential scanning calorimetry showed singular melting and crystallization points, making these compounds viable candidates for melt growth. We grew 13 mm diameter single crystals of $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ in evacuated quartz ampoules via the vertical Bridgman technique. The optimal Eu^{2+} concentration was 4% for KBa_2I_5 and 7% for K_2BaI_4 . The X-ray excited emissions at 444 nm for $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ 4% and 448 nm for $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ 7% arise from the 5d-4f radiative transition in Eu^{2+} . $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ 4% has a light yield of 90,000 photons/MeV, with an energy resolution of 2.4% and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ 7% has a light yield of 63,000 ph/MeV, with an energy resolution of 2.9% at 662 keV. Both crystals have an excellent proportional response to a wide range of gamma-ray energies.

Index Terms

Scintillator, metal halide, Gamma-ray detection.

Highlights

- New Eu^{2+} doped scintillators KBa_2I_5 and K_2BaI_4
- $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ 7% have light yields above 60,000 ph/MeV and energy resolution lower than 3.0% at 662 keV.
- $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ exhibit excellent proportional response to a wide range of gamma-ray energies.

1. Introduction

Scintillators are used in a wide variety of applications as radiation sensors. As a result, such materials are developed with a specific set of properties that will satisfy the requirement for each application. For medical imaging applications scintillators with a high light yield are preferred [1]. This will improve the spatial resolution and produce a higher quality image, thus enabling new technology for earlier diagnosis of disease. Scintillators used in gamma-ray spectroscopy for national security applications require both high light output and excellent energy resolution. This provides unambiguous identification of radioactive sources and discrimination of potential threat sources from non-threat sources, especially in the presence of background radiation [2]. Regardless of the application, cost of the radiation detector is a major factor for consideration of widespread utilization, and for this reason alone $\text{NaI}:\text{Tl}^{+}$ is the most commonly used scintillator [2]. It has a modest light yield of ~38,000 ph/MeV and a relatively poor energy resolution approaching 7% at 662 keV [3], but it is much less expensive than semiconductor radiation detectors and most other available scintillators, mainly due to precursor availability and ease of growth.

In recent years, great efforts have been made to discover and develop new metal halide scintillators, mainly due to their potentially high scintillation light yield of 80,000+ ph/MeV and energy resolution approaching the ideal ~2% at 662 keV. Crystals such as $\text{SrI}_2:\text{Eu}$ [4], $\text{CsBa}_2\text{I}_5:\text{Eu}$ [5], $\text{BaBrI}:\text{Eu}$ [6] and $\text{LaBr}_3:\text{Ce},\text{Sr}$ [7] have the potential to replace $\text{NaI}:\text{Tl}$ in some applications [8]. We have recently reported a promising scintillator, Eu^{2+} -doped KSr_2I_5 , with exceptional scintillation properties including a light yield of 94,000 ph/MeV with an energy resolution of 2.4% at 662 keV [9]. The objective of the present work is to demonstrate scintillation performance of two new Eu^{2+} -doped scintillators, K_2BaI_4 and KBa_2I_5 , grown via the vertical Bridgman method. Compared to the Sr-containing counterpart, these Ba-containing compounds are expected to have higher density, which is advantageous for efficient detection of gamma-ray radiation. In addition, Ba-containing scintillators are known to be less deliquescent [10-12], which makes them a more practical choice for detector device integration. Similar to KSr_2I_5 , both K_2BaI_4 and KBa_2I_5 can be activated with the Eu^{2+} luminescence centers via partial replacement of Ba atoms in the crystal lattice. KBa_2I_5 has a monoclinic crystal structure, with a density of 4.52 g/cm³ [13]. Although neither the KI-BaI₂ phase diagram nor the crystallographic information for K_2BaI_4 are available in the literature, our initial growth experiments suggest that both compounds melt congruently. In this work we present the structural analysis and scintillation properties of Eu^{2+} -doped KBa_2I_5 and K_2BaI_4 .

2. Experimental

The optimum europium concentration was investigated by synthesizing 4 g polycrystalline samples of $\text{K}_2\text{Ba}_{1-x}\text{Eu}_x\text{I}_4$ and $\text{KBa}_2(1-y)\text{Eu}_y\text{I}_5$ with $5 \leq x \leq 10$ and $2.5 \leq y \leq 6$ in a single-zone clamshell furnace. The 99.99% pure anhydrous KI, BaI₂ and EuI₂ raw materials from Sigma-Aldrich were mixed and loaded into quartz ampoules in a glove box with an atmosphere containing < 0.1 ppm of water and oxygen. The loaded ampoules were dried at 200 °C and sealed under a vacuum of 10⁻⁶ torr. The temperature was slowly raised to 740 °C, which is 29 °C above the melting point of BaI₂, the component with the highest melting point. This temperature was held for 7 h and then slowly decreased to room temperature over a period of 7 h. The ampoule was then inverted and the procedure above was repeated to encourage complete mixing of all constituents. The

resulting solidified material was polycrystalline, but 4 mm³ to 8 mm³ single crystal specimens could be identified and were selected for evaluation. These specimens, with Eu concentrations ranging from 2.5 to 10 %, allowed us estimate the optimal Eu concentration for maximum light yield. Once this was done, 13 mm diameter crystals of KBa₂I₅:Eu²⁺ and K₂BaI₄:Eu²⁺ were grown using a two-zone transparent vertical Bridgman furnace, using a solidification rate of 1 mm/h and cooling a rate of 10 °C/h. It should be recognized that additional factors such self absorption and a segregation coefficient different from unity could slightly shift the optimal Eu concentration for larger crystals grown under different conditions.

Crystallographic studies utilized ~ 0.001 mm³ crystal fragments isolated from boules grown in this study and suspended in paratone oil and each mounted on a plastic loop attached to copper pin/goniometer. Single-crystal diffraction data were collected at 250K using a Rigaku XtaLAB PRO diffractometer with MoK α radiation (λ = 0.71073 Å) equipped with a Dectris Pilatus 200K detector and an Oxford N-HeliX cryocooler. Peak indexing and integration was done using d*trek in the CrystalClear package [14]. A numerical absorption correction was applied using ABCOR [15]. The SIR-2011 in WinGX and SHELXL-2013 software packages were used for data processing and structure solution and refinement [16]. Crystal structure projections were made with VESTA [17]. Monoclinic structures like KBa₂I₅, where the beta angle is close to 90, can mimic orthorhombic structures, and in this case, addition of the twin model 1 0 0, 0 -1 0, 0 0 -1, with unequal fractions of the two domains lowers the R1 agreement factor by nearly one half.

The melting and crystallization temperatures were determined through differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) using a Setaram Labsys Evo TG-DSC. The measurement was carried out on a ~50 mg specimen at a ramp rate 5 K/min, under a flow of ultra-high purity argon gas.

Moisture sorption profiles were recorded using a Dynamic Vapor Sorption technique on a DVS Intrinsic by Particulate Systems. The measurements were carried out under identical conditions: spherical samples with a surface area ~28 ± 2 mm², 25 °C, 40 % relative humidity, 60 minutes exposure time [11].

The radioluminescence (RL) emission spectra were recorded at room temperature under continuous 30 keV X-ray irradiation. The steady state photoluminescence (PL) spectra and the PL decay time (lifetime) were measured at room temperature with a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer. The PL lifetime was measured using the time correlated single photon counting technique. A Horiba Jobin Yvon NanoLed with an emission wavelength of 370 nm and a pulse width of ~1 ns was used as an excitation source. The emission monochromator was set to 444 nm and 448 nm for KBa₂I₅:Eu²⁺ and K₂BaI₄:Eu²⁺ respectively in order to monitor the Eu²⁺ emission intensity.

For accurate light yield and scintillation decay time measurements, the specimens were protected from moisture by immersing them in an oil-filled quartz cell. The scintillation decay time was measured with the time-correlated single photon counting technique with excitation by a ¹³⁷Cs gamma-ray source [18]. The cell was coupled to a Hamamatsu 3177-50 photomultiplier tube (PMT) and to a Hamamatsu R6231-100 PMT for measuring the absolute light yield and energy resolution (ER), respectively, where energy resolution is defined as $R = \Delta E(\text{FWHM})/E$, of a photopeak of energy E [19]. A hemispherical dome of Spectralon was used as a reflector. An amplifier shaping time of 10 μs was used to integrate the exponentially decaying scintillation pulse.

3. Results and Discussion

3.1. Crystal structure

KBa₂I₅ is a new compound with the TIPb₂Cl₅ structure-type, which is known for at least 13 different compositions already reported in the Inorganic Crystal Structure Database. The TIPb₂Cl₅ structure-type is fairly densely packed despite having ions with large coordination numbers. All polyhedra share corners, edges and faces, with no open channels. There are two types of BX_n polyhedra, a BX₈ distorted square antiprism and a BX₇ distorted monocapped trigonal prism. The AX₈ is the largest polyhedron and is also a distorted square antiprism. In the case of KBa₂I₅ the polyhedral volumes are 60.07 (Ba1I₇), 83.33 (Ba2I₈), and 90.25 (KI₈) Å³, which suggests that Eu doping would likely prefer the Ba1 site given its significantly smaller relatively ionic size of Eu to that of Ba; structure drawing in Fig. 1. Given the poor fidelity to determine the Eu over Ba using x-rays, the Eu content was not refined. Tables 1 and 2 summarize the structural parameters and refinement details.

K₂BaI₄ is a new compound with the Yb₃As₄ structure-type, which is known for two different compositions already reported in the Inorganic Crystal Structure Database. A wider compositional range for the chlorides, A₂MCl₄, A = K, Rb, Cs, M = Eu, Sr, Ba, Pb, has been reported in the thesis by Flick (1990) [20]. Crystal structures for few of these compounds have been reported in detail, and that may be related to the presence of incommensurate modulations. Phase studies of binaries, K-I nor Ba-I, have not reported an A₃I₄ phase, so apparently K₂BaI₄ phase is stabilized by the ternary composition. The structure is rhombohedral (noncentrosymmetric), and its single (K,Ba)I₈ polyhedron can be described as a distorted square antiprism with a mean bond length of 3.66 Å; see structure drawing in Fig. 2. The refinement strategy adopted was to preserve the K:Ba ratio of 2, but let the occupancy of the A-site vary. The resulting occupancy is slightly in excess of 1 and is close to being charge balanced. The K and Ba ions are assumed to be randomly distributed on the metal site. Tables 1 and 3 summarize the structural parameters and refinement details.

Table 1. Crystal structure data and single-crystal X-ray diffraction refinement results for KBa₂I₅ and (K_{2.07(3)}Ba_{1.05(3)})I₄.

Formula	KBa ₂ I ₅	(K _{2.07(3)} Ba _{1.05(3)})I ₄
fw (g)	948.28	4973.34
T (K)	250	250
Crystal system	monoclinic	Rhombohedral
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3 <i>c</i>
<i>a</i> (Å)	10.2922(11)	14.937(9)
<i>b</i> (Å)	9.1713(9)	14.937(9)
<i>c</i> (Å)	14.6853(15)	9.165(6)
α (°)	90	90
β (°)	90.025(3)	90
γ (°)	90.	120.
<i>V</i> (Å ³)	1386.2(2)	1771(17)

Table 2. Fractional atomic coordinates and equivalent isotropic atomic displacement parameters for KBa₂I₅ (space group $P2_1/c$)*at 250K.

Atom	<i>x</i>	<i>y</i>	<i>Z</i>	<i>U</i> _{eq} (Å ²)
K	-0.0005(3)	0.9723(3)	-0.1789(2)	0.0118(6)
Ba1	0.24795(14)	0.57674(9)	0.00739(6)	0.0267(2)
Ba2**	0.49980(18)	0.97050(17)	-0.17803(12)	0.0394(6)
I1	0.54283(14)	0.66696(17)	0.09578(11)	0.0368(3)
I2	-0.04304(14)	0.67043(18)	0.09647(12)	0.0415(4)
I3	0.2619(2)	0.96188(13)	0.00157(8)	0.0507(4)
I4	0.2642(2)	0.33147(13)	0.18482(9)	0.0501(4)
I5	0.25549(18)	0.69491(11)	-0.22081(7)	0.0336(3)

* All atoms are in general positions.

** Site occupancy refined to 0.851(8) Ba + 0.149(8) K, giving the formula K_{1.15}Ba_{1.85}I₅.

Fig 1. Crystal structure of KBa₂I₅ at 250K showing the KI₈, Ba1I₇ and Ba2I₈ polyhedra. Anisotropic atomic displacement ellipsoids are plotted at 99% probability.

Table 3. Fractional atomic coordinates and equivalent isotropic atomic displacement parameters for (K_{2.07}Ba_{1.05})I₄ (space group $R3c$) at 250K.

Atom	Site	Symmetry	<i>x</i>	<i>y</i>	<i>Z</i>	<i>U</i> _{eq} (Å ²)
A*	18 <i>b</i>	1	0.6240(2)	0.1247(2)	0.0787(4)	0.0405(5)
I1	6 <i>a</i>	3	0	0	0.1313(3)	0.0428(8)
I2	18 <i>b</i>	1	0.2123(1)	0.2849(1)	0.1172(2)	0.040(1)

* refined occupancy = 0.69(1)K + 0.35(1)Ba

Fig. 2. Crystal structure of K_2BaI_4 at 250K showing the $(\text{K,Ba})\text{I}_8$ polyhedron. Anisotropic atomic displacement ellipsoids are plotted at 99% probability.

3.2. Melting point determination and moisture absorption

Differential scanning calorimetry curves are shown in Fig 3a-b. $\text{KBa}_2\text{I}_5\text{:Eu}$ 4% has a melting point of 569°C and a crystallization point of 554°C (Fig 1a). $\text{K}_2\text{BaI}_4\text{:Eu}$ 7% has a melting point of 579°C and a crystallization point of 550°C (Fig 1b). The difference between the melting and the crystallization peaks indicates that $\text{K}_2\text{BaI}_4\text{:Eu}$ 7% has a larger degree of supercooling (29°C) compared to $\text{KBa}_2\text{I}_5\text{:Eu}$ 4% (15°C). This information is needed in order to design a thermal profile that would allow us to grow the crystals with a stable solid-liquid interface. It is also important to note that no phase transitions were found in the specimens measured.

The Dynamic Vapor Sorption technique was used to determine the moisture absorption of single crystals of $\text{KBa}_2\text{I}_5\text{:Eu}$ 4% and $\text{K}_2\text{BaI}_4\text{:Eu}$ 7% as shown in Fig. 4. For comparison purposes the moisture absorption of two well-known scintillators, $\text{LaBr}_3\text{:Ce}$ 5% and NaI:Tl , were measured under identical conditions. Both Ba-containing crystals have relatively low moisture uptake, comparable to the absorption rate of NaI:Tl that shows approximately 2% weight gain over 60 minutes at 40% humidity.

Fig 3. (a) Differential scanning calorimetry curve, $\text{KBa}_2\text{I}_5\text{:Eu}$ has a melting point of 569°C and a crystallization point of 554°C . (b) $\text{K}_2\text{BaI}_4\text{:Eu}$ has a melting point of 579°C and a crystallization point of 550°C .

Fig 4. Moisture absorption rate of $\text{LaBr}_3\text{:Ce}$, $\text{K}_2\text{Ba}_4\text{:Eu}$ 5%, NaI:Tl and $\text{KBa}_2\text{I}_5\text{:Eu}$ 4%. The moisture sorption profiles were plotted by determining the percent weight change as a function of time.

3.3. Europium optimization and crystal growth

The optimum activator concentration in a scintillator often involves a tradeoff between efficient charge carrier migration to the activator sites which is aided by high activator concentration and minimization of self-absorption which is aided by low activator concentration. The measured scintillation light yield versus Eu concentration for rapidly screened samples is shown in Fig 5. The maximum light yield was found to be at 4% and 7% Eu^{2+} molar concentration for KBa_2I_5 and K_2Ba_4 respectively. It is worth noting that the optimum europium concentration that yielded the maximum light yield, may not be the concentration used for detector applications. Eu^{2+} activated crystals are known for having self-absorption effects [21, 22]. This affects the performance of the crystals as they increase in size [23]; therefore a lower concentration of europium will be considered for crystals 1 inch or larger.

Two 13 mm diameter single crystals were grown using a two-zone transparent furnace. We were able to extract a $5 \times 8 \times 13 \text{ mm}^3$ and a $5 \times 5 \times 7 \text{ mm}^3$ samples from the grown boules of $\text{KBa}_2\text{I}_5\text{:Eu}$ 4% and $\text{K}_2\text{Ba}_4\text{:Eu}$ 7%, respectively. As seen in Fig. 6a-b, $\text{K}_2\text{Ba}_4\text{:Eu}$ 7% displayed better transparency than $\text{KBa}_2\text{I}_5\text{:Eu}$ 4%, but both crystals are far from ideal. In general, the crystal growth of Ba-containing scintillators is challenging, mainly due to cracking and non-uniformity. This has slowed the development and widespread application of scintillation crystals such as $\text{CsBa}_3\text{:Eu}$, $\text{CsBa}_2\text{I}_5\text{:Eu}$ and BaBrI:Eu [6, 24-26].

Fig. 5. Light output as a function of Eu^{2+} concentration in KBa_2I_5 and K_2Ba_4 .

Fig 6. (a) A $5 \times 8 \times 13 \text{ mm}^3$ crystal of $\text{KBa}_2\text{I}_5\text{:Eu}$ 4%, (b) a $5 \times 5 \times 7 \text{ mm}^3$ crystal of $\text{K}_2\text{Ba}_4\text{:Eu}$ 7%.

3.4. Optical and Scintillation properties

X-ray excited radioluminescence (RL) spectra of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% are shown in Fig. 7a. $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% has a single emission peak at 444 nm while $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% has an emission centered at 448 nm, with a slight broadening on the longer wavelength side of the band. This small asymmetry in $\text{K}_2\text{BaI}_4:\text{Eu}$ is under further investigation, but it may reflect the different ligand structure surrounding the Eu site as compared to KBa_2I_5 , thus causing the emission to be slightly broader.

Photoluminescence (PL) excitation and emission of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% are shown in Fig. 7b. The PL excitation spectrum of each compound exhibits a broad region of poorly resolved bands from ~270 nm to ~420 nm resulting from the complex manifold of energy levels in Eu^{2+} . On the other hand, the PL emission spectrum of each compound consisted of a single well defined peak centered at 444 nm for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and 448 nm for $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%, thus confirming that the only radiative transition is from the lowest energy 5d excited state. Similar to the RL emission, the PL emission of $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% is slightly broadened, thus suggesting that the cause lies in the local environment of the Eu^{2+} site rather than defects or distortions in the matrix. For both PL emission measurements, an excitation of 400 nm was used. The photoluminescence decay time is shown in Fig. 7c, the Eu^{2+} center was directly excited by a 370 nm NanoLED pulser; the tracked emissions were 444 nm for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and 448 nm for $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%, i.e. the peak emission wavelengths. The lifetime of the Eu^{2+} 5d₁ excited state was 840 ns and 700 ns for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%, respectively. The baseline difference between the two samples is due to different count rates arising from different sample sizes and sample positioning in the excitation light path. The baseline is taken into account when fitting the data in order to extract the excited state lifetime. The observed PL decay is typical for Eu^{2+} 5d to 4f transitions, and a single exponential decay function provides a good fit to the data.

In section 3.1 we discussed that the KBa_2I_5 ($P2_1/c$ - monoclinic) structure has two Ba sites, Ba1 (BaI_7 - 60.07 Å³) and Ba2 (BaI_8 - 83.33 Å³) and these results suggested that Eu ions would prefer the Ba1 site given the smaller ionic size of Eu compared to Ba. In addition the narrow peaks in the PL and RL spectra suggest that Eu^{2+} primarily occupies only one of the Ba sites, although it is not possible to say with certainty which site is occupied.

The results obtained from the radioluminescence and photoluminescence measurements are commonly seen in europium doped scintillators due to the 5d-4f radiative transition in Eu^{2+} [27-30]. No evidence of emission from perturbed Eu was observed.

Fig 7. (a) Radioluminescence emission spectra of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% (peak maximum at 444 nm) and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% (peak maximum at 448 nm), (b) the PL excitation of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% spectrum comprises multiple unresolved overlapping bands from 280 nm to 433 nm measured by monitoring the 444 and 448 nm emissions respectively. Both crystals exhibit a sharp PL emission band with peak maximum around 444 and 448 nm, using any excitation wavelength in the range of 300–410 nm. (c) The Eu^{2+} lifetime of 840 ns and 700 ns were measured for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% (370 nm was used as the excitation wavelength).

The measured scintillation light yield and energy resolution of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% are summarized in Table 4. The light yield of a $2 \times 2 \times 1 \text{ mm}^3$ sample of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% was 90,000 ph/MeV with 2.4% energy resolution at 661.7 keV as shown in Fig. 8a. For a similar size sample of $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%, a light yield of 63,000 ph/MeV and an energy resolution of 2.9% were measured (Fig 9a).

The pulse height spectra were also recorded at lower energies, using ^{57}Co (122 keV) and ^{241}Am (59.5 keV) sealed sources. At 122 keV the energy resolution was 5.4% for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and 6.9% for $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%. The energy resolution at 59.5 keV was 7.6% and 8.7% respectively. Larger specimens of both crystals were measured using a ^{137}Cs source. In spite of the lack of transparency of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and using a larger $5 \times 8 \times 13 \text{ mm}^3$ specimen (shown in Fig 6a), we were able to measure an energy resolution of 2.7%. For $\text{K}_2\text{BaI}_4:\text{Eu}$ 7%, we used a $5 \times 5 \times 7 \text{ mm}^3$ specimen (shown in Fig 6b) and we measured an energy resolution of 3.0%, shown in Fig 8b and 9b respectively. These results are very promising for national security applications, where scintillators are required to have excellent energy resolution to provide unambiguous identification of radioactive sources and discrimination of potential threat sources from non-threat sources.

The light yield and energy resolution obtained for $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ are comparable to $\text{SrI}_2:\text{Eu}^{2+}$ and $\text{CsBa}_2\text{I}_5:\text{Eu}^{2+}$, all having light yields above 90,000 ph/MeV and energy resolution lower than 3.0% [31, 32]. $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ has a much lower light yield, but nevertheless an excellent energy resolution was measured.

For the scintillation light yield non-proportionality measurements, a set of γ -ray sources was used to obtain various γ -ray excitation energies. The relative light yield measured as a function of absorbed γ -ray energy is shown in Fig. 10a. The new scintillators, $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$, showed highly proportional responses that deviate less than 2% from an ideal proportional response over the measured energy range of 14.4 to 662 keV. As we previously stated, the energy resolution R of a scintillator at energy E is experimentally determined from the FWHM of the full energy photopeak in the pulse height spectrum. However, several factors [33] contribute to the peak width such that:

$$R^2 = R_M^2 + R_{nPR}^2 + R_{inh}^2$$

where R_M is the contribution from PMT gain and photoelectron detection Poisson statistics, R_{nPR} is the contribution from the non-proportional response, and R_{inh} is the contribution from crystal inhomogeneity [34]. In other words, in order to achieve energy resolutions lower than 3%, scintillator crystals must be homogeneous and the light yield must be proportional to the absorbed gamma-ray energy and so far this is valid statement for the detector sizes measured in this work.

The scintillation decays of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% have primary components of $\sim 1 \mu\text{s}$ with longer secondary components. The scintillation time profiles of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% are shown in Fig. 10b. The data were fitted with double exponential decay functions. For $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% the primary decay component of 910 ns accounted for $\sim 81\%$ of the total emitted light while the secondary decay component of 4900 ns accounted for the rest of the light. Similarly, $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% showed a primary component of 720 ns (67%) and secondary component of 3100 ns. The primary component of the decay time for both crystals can be attributed to 5d-4f radiative transition in Eu^{2+} , with a slight delay from the ionization and energy migration process (compared Eu^{2+} PL lifetime), while the secondary long component could be due to the possible presence of shallow charge traps. In general, the scintillation decay time profiles shown for $\text{KBa}_2\text{I}_5:\text{Eu}^{2+}$ and $\text{K}_2\text{BaI}_4:\text{Eu}^{2+}$ are typical for Eu^{2+} -doped scintillators.

8a.

8b.

Fig 8a. Pulse height spectra measured for $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% at 661.7 keV with an energy resolution 2.4% of a cleaved piece ($\sim 2 \times 2 \times 1 \text{ mm}^3$) and (8b) 2.7% energy resolution of a $5 \times 8 \times 13 \text{ mm}^3$ specimen. 8c. The energy resolution of the 59.5 keV full absorption peak is 7.6%. One can also clearly distinguish the 13.95 keV, 17.8 keV, and 20.8 keV, the Neptunium X-ray photoelectric absorption peaks, the 26.35 keV ^{241}Am peak, and the iodine K α escape peak.

Fig 9a. ^{137}Cs pulse height spectra measured for $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% with an energy resolution of 2.9% for a cleaved piece ($\sim 2 \times 2 \times 1 \text{ mm}^3$) and (9b) 3.0% energy resolution of a $5 \times 5 \times 7 \text{ mm}^3$ specimen.

Fig 10a. The light yield proportionality of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% showed a deviation of less than 2% from the ideal response. 10b. The scintillation decay of $\text{KBa}_2\text{I}_5:\text{Eu}$ 4% and $\text{K}_2\text{BaI}_4:\text{Eu}$ 7% has primary components of $\sim 1 \mu\text{s}$ with longer secondary components.

Table 4. Comparison of scintillation properties.

	KBa ₂ I ₅ :Eu	K ₂ BaI ₄ :Eu	NaI:Tl [3]	CsBa ₂ I ₅ :Eu [5]	SrI ₂ :Eu [4]	KSr ₂ I ₅ :Eu [9]
RL emission max (nm)	444	448	415	432	435	445
Primary scintillation decay time (ns)	910	720	230	1000	1000	990
Light yield (ph/MeV)	90,000	63,000	38,000	80,000	100,000	94,000
ER @ 662 keV	2.4%	2.9%	7.1%	2.3%	2.6%	2.4%

4. Summary

In this work we report the structural analysis and scintillation characterization of two new scintillators, KBa₂I₅:Eu 4% and K₂BaI₄:Eu 7%. A summary of the crystal structure data and single-crystal X-ray diffraction refinement results can be found in Table 1. Both compounds have exceptional scintillation properties, in particular the energy resolutions are lower than 3% at 662 keV. A summary of the scintillation properties are shown in Table 4. KBa₂I₅:Eu²⁺ and K₂BaI₄:Eu²⁺ have highly proportional photon responses which indicate that even better energy resolutions may be achieved as the crystal quality is improved. Future work will focus on the improvement of the optical clarity and the optimization of growth parameters for larger size crystals.

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6. References

- [1] C.W.E. van Eijk, Inorganic scintillators in medical imaging detectors, Nuc. Instruments and Meth. Phys. Res. Sect. A, 509 (2003), pp. 17-25.
- [2] T.B.G. K. E. Nelson, and D. A. Knapp, The Effect of Gamma-Ray Detector Energy Resolution on the Ability to Identify Radioactive Sources, LLNL-TR-411374, (2009).
- [3] M. Moszynski, M. Balcerzyk, W. Czarnacki, M. Kapusta, W. Klamra, P. Schotanus, A. Syntfeld, M. Szawlowski, Study of pure NaI at room and liquid nitrogen temperatures, Nuc. Sci. Symp. Conf. Record, 2002 IEEE2002, pp. 346-351 vol.341.
- [4] N. Cherepy N. Cherepy, G. Hull, A. Drobshoff, S. Payne, E. van Loef, C. Wilson, K. Shah, U. Roy, A. Burger, L. Boatner, W. Choong W. Moses, Strontium and barium iodide high light yield scintillators, App. Phys. Lett. 2008.
- [5] E.D. Bourret-Courchesne, G. Bizarri, R. Borade, Z. Yan, S.M. Hanrahan, G. Gundiah, A. Chaudhry, A. Canning, S.E. Derenzo, Eu²⁺-doped Ba₂CsI₅, a new high-performance scintillator, Nuc. Instruments and Meth. Phys. Res. Sect. A, 612 (2009), pp. 138-142.
- [6] E.D. Bourret-Courchesne, G. Bizarri, S.M. Hanrahan, G. Gundiah, Z. Yan, S.E. Derenzo, BaBrI:Eu²⁺, a new bright scintillator, Nuc. Instruments and Meth. Phys. Res. Sect. A, 613 (2010), pp. 95-97.
- [7] M.S. Alekhin, S. Weber, K.W. Krämer, P. Dorenbos, Optical properties and defect structure of Sr²⁺ co-doped LaBr₃:5%Ce scintillation crystals, J. Lumin., 145 (2014), pp. 518-524.
- [8] E.V. van Loef, K.S. Shah, Advances in scintillators for medical imaging applications, 2014, pp. 92140A-92140A-92145.
- [9] L. Stand, M. Zhuravleva, A. Lindsey, C.L. Melcher, Growth and characterization of potassium strontium iodide: A new high light yield scintillator with 2.4% energy resolution, Nuc. Instruments and Meth. Phys. Res. Sect. A, 780 (2015), pp. 40-44
- [10] R. Borade, E. Bourret-Courchesne, S. Derenzo, Scintillation properties of CsBa₂Br₅:Eu²⁺, Nuc. Instruments and Meth. Phys. Res. Sect. A, 652 (2011), pp. 260-263.
- [11] M. Zhuravleva, L. Stand, H. Wei, C. Hobbs, L.A. Boatner, J.O. Ramey, K. Shah, A. Burger, E. Rowe, P. Bhattacharya, E. Tupitsyn, C.L. Melcher, Hygroscopicity evaluation of halide scintillators, Nuc. Sci. Symp. Conf. Record, 2013 IEEE2013, pp. 1-5.
- [12] G. Gundiah, Z. Yan, G. Bizarri, S.E. Derenzo, E.D. Bourret-Courchesne, Structure and scintillation of Eu²⁺-activated BaBrCl and solid solutions in the BaCl₂–BaBr₂ system, J. Lumin., 138 (2013), pp. 143-149.
- [13] G. Schilling, G. Meyer, Zeitschrift für anorganische und allgemeine Chemie, 622 (1996), pp. 759-765.
- [14] Rigaku (2005) CrystalClear. Rigaku Corporation, Tokyo, Japan.
- [15] Higashi, T. (2000) ABSCOR. Rigaku Corporation, Tokyo, Japan
- [16] G. M. Sheldrick, Acta Crystallogr. A64, 112-122 (2008); J. Farrugia, J. Appl. Cryst. 45, 849-854 (2012). ; Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G.L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. and Spagna, R., J. Appl. Cryst. 45, 351-356 (2012).
- [17] K. Momma and F. Izumi, J. Appl. Crystallogr. 41, 653-658 (2008).
- [18] L.M.Bollinger, in: G.E. Thomas (Ed.), Rev. Sci. Instr. 1961, pp. 1044-1050.
- [19] C.W.E. van Eijk, P. Dorenbos, E.V.D. van Loef, K. Krämer, H.U. Güdel, Energy resolution of some new inorganic-scintillator gamma-ray detectors, Radiation Measurements, 33 (2001), pp. 521-525.

- [20] Flick, K., Ternaere Chloride des Formeltyps A_2MCl_4 mit $A = K, Rb, Cs$ und $M = Eu, Sr, Ba, Pb$ als Strukturverwandte des Th_3P_4 -Typs. Ein Beitrag zum Problemkreis inkomensurabel modulierter Strukturen. Dissertation Universitaet Karlsruhe (1990) 1990, p1-p161.
- [21] M.S. Alekhin, J.T.M. de Haas, K.W. Kramer, I.V. Khodyuk, L. de Vries, P. Dorenbos, Scintillation properties and self absorption in $SrI_2:Eu^{2+}$, Nuc. Sci. Symp. Conf. Record, 2010 IEEE2010, pp. 1589-1599.
- [22] A. F. Molisch, B.P. Oehry, Radiation Trapping in Atomic Vapours, Oxford Sci. (1999).
- [23] B.W. Sturm, N.J. Cherepy, O.B. Drury, P.A. Thelin, S.E. Fisher, S.A. Payne, A. Burger, L.A. Boatner, J.O. Ramey, K.S. Shah, R. Hawrami, Effects of packaging $SrI_2(Eu)$ scintillator crystals, Nuc. Instruments and Meth. Phys. Res. Sect. A, 652 (2011), pp. 242-246.
- [24] U. Shirwadkar, E.V.D. van Loef, R. Hawrami, S. Mukhopadhyay, J. Glodo, K.S. Shah, New promising scintillators for gamma-ray spectroscopy: $Cs(Ba,Sr)(Br,I)_3$, Nuc. Sci. Symp. Conf. Record, 2011 IEEE2011, pp. 1583-1585.
- [25] U. Shirwadkar, R. Hawrami, J. Glodo, E.V.D. van Loef, K.S. Shah, Promising Alkaline Earth Halide Scintillators for Gamma-Ray Spectroscopy, IEEE Trans. Nucl. Sci, 60 (2013), pp. 1011-1015.
- [26] S. Lam, S. Swider, J. Fiala, A. Datta, S. Motakef, Microscale luminescence imaging of defects, inhomogeneities, and secondary phases in halide scintillators, Nuc. Instruments and Meth. Phys. Res. Sect. A
- [27] D.H. Gahane, N.S. Kokode, P.L. Muthal, S.M. Dhopte, S.V. Moharil, Luminescence of Eu^{2+} in some iodides, Optical Materials, 32 (2009), pp. 18-21.
- [28] P. Dorenbos, Energy of the first $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} in inorganic compounds, J. Lumin., 104 (2003), pp. 239-260.
- [29] A. Pushak, V. Vistovskyy, A. Voloshinovskii, T. Demkiv, J. Dacyuk, A. Gektin, S. Myagkota, Luminescence of Eu^{2+} -doped Me-containing aggregates (Me= Ca, Sr, Ba) in KI matrix.
- [30] D.H. Gahane, N.S. Kokode, P.L. Muthal, S.M. Dhopte, S.V. Moharil, Luminescence of Eu^{2+} in some iodides, J. Alloys and Compd., 484 (2009), pp. 660-664.
- [31] J. Glodo, E.V. Van Loef, N.J. Cherepy, S.A. Payne, K.S. Shah, Concentration Effects in Eu Doped SrI_2 , IEEE Trans. Nucl. Sci, 57 (2010), pp. 1228-1232.
- [32] G. Bizarri, E.D. Bourret-Courchesne, Y. Zewu, S.E. Derenzo, Scintillation and Optical Properties of $BaBrI:Eu^{2+}$ and $CsBa_2I_5:Eu^{2+}$, IEEE Trans. Nucl. Sci, 58 (2011), pp. 3403-3410.
- [33] P. Dorenbos, Fundamental Limitations in the Performance of Ce^{3+} , Pr^{3+} , and Eu^{2+} Activated Scintillators, IEEE Trans. Nucl. Sci, 57 (2010), pp. 1162-1167.
- [34] M.S. Alekhin, D.A. Biner, K.W. Krämer, P. Dorenbos, Optical and scintillation properties of $CsBa_2I_5:Eu^{2+}$, J. Lumin., 145 (2014), pp. 723-728.