# Journal of Materials Chemistry C



# PAPER

Check for updates

Cite this: J. Mater. Chem. C, 2021, 9, 1721

# Dopant site-dependent luminescence from rare-earth doped dibarium octafluorohafnate Ba<sub>2</sub>HfF<sub>8</sub> nanocubes for radiation detection<sup>†</sup>

Vineet Kumar,<sup>a</sup> Gibin George, <sup>b</sup> <sup>a</sup> Jacob I. Hayes,<sup>a</sup> Yulin Lin,<sup>b</sup> Burak Guzelturk,<sup>c</sup> Jianguo Wen <sup>b</sup> <sup>b</sup> and Zhiping Luo <sup>b</sup>\*<sup>a</sup>

Development of new host materials containing heavy elements for radiation detection is highly desirable. In this work, dibarium octafluorohafnate,  $Ba_2HF_8$ , doped with rare-earth ions, was synthesized as cube-shaped nanocrystals *via* a facile hydrothermal method. The host lattice contains two  $Ba^{2+}$  crystallographic sites, and dopants on these sites exhibit site-dependent photoluminescence (PL), cathodoluminescence (CL) and X-ray excited radioluminescence (RL) characteristics. Single doping contents were optimized as 25 mol% Tb<sup>3+</sup> and 5 mol% Eu<sup>3+</sup>. In  $Ba_2HF_8:Tb^{3+}-Eu^{3+}$  codoped nanocrystals, preferrable occupation of  $Eu^{3+}$  and  $Tb^{3+}$  at two different  $Ba^{2+}$  sites in the host lattice was observed. The nanocubes exhibited enhanced emissions over micron sized particles. In PL, the presence of  $Tb^{3+}$  ions significantly enhanced the emission intensity of  $Eu^{3+}$  ions due to energy transfer from the  $Tb^{3+}$  to  $Eu^{3+}$  ions, while under high-energy irradiation in CL or RL,  $Tb^{3+}$  emission was intensified. X-ray induced RL with afterglow in seconds was observed. It was found that the codoped sample showed higher sensitivity than the singly doped sample, indicating that codoping is an effective strategy to develop a scintillator with this host structure for high-energy radiation detection.

Received 25th October 2020, Accepted 17th December 2020

DOI: 10.1039/d0tc05051b

rsc.li/materials-c

# Introduction

Inorganic fluorides are commonly used as host lattices for luminescent rare-earth (RE) ions for applications in solid-state lasing,<sup>1</sup> scintillation,<sup>2</sup> temperature sensing,<sup>3</sup> optical sensing,<sup>4</sup> *etc.* The key requirements of a host lattice for optical applications include low phonon energy and high chemical and temperature stability. Fluorides are suitable for RE doping due to their wide energy bandgap and therefore high optical transparency in the visible and ultraviolet regions.<sup>5,6</sup> In comparison with oxide-based systems, fluorides possess very low lattice vibrational energies; as a result, the quenching of the excited states of RE ions is minimal.<sup>7,8</sup> Tb<sup>3+</sup> and Eu<sup>3+</sup> ions have been used for various optical applications. In particular, the emission from Eu<sup>3+</sup> ions is used as a spectroscopic probe for identifying the local structure,<sup>9,10</sup> host–dopant energy transfer

dynamics,<sup>11,12</sup> point group symmetry,<sup>13</sup> etc. The luminescence of Eu<sup>3+</sup> is very sensitive to the local symmetry of its lattice site and affected by the selection rules. The emission magnitudes, induced by magnetic dipole (MD) transitions ( ${}^5D_0 \rightarrow {}^7F_1$ ) and electric dipole (ED) transitions ( ${}^5D_0 \rightarrow {}^7F_2$ ), reveal different crystallographic Eu<sup>3+</sup> sites in the host lattice with distinct site symmetry. Additionally, Tb<sup>3+</sup> is an intense green-emitting activator and acts as a sensitizer for codopants such as Eu<sup>3+</sup> and Sm<sup>3+</sup> ions. Site-dependent Eu<sup>3+</sup> and Eb<sup>3+</sup> luminescence will be addressed in this work.

Heavy elements with a high atomic number Z in a scintillator can absorb high-energy ionizing radiation.<sup>14,15</sup> Previously, numerous inorganic fluoride hosts doped with RE ions, such as  $BaF_{2}$ ,<sup>2</sup>  $BaLuF_{5}$ ,<sup>16</sup> and  $LiBaF_{3}$ ,<sup>17</sup> have been investigated owing to their characteristic luminescence behaviour for scintillation applications.  $Tb^{3+}$  doped  $BaLuF_{5}$  nanocrystals were synthesized by Cao *et al.*<sup>16</sup> for X-ray imaging. The reported decay time for  $Tb^{3+}$  emission was 2.88–4.02 ms, whereas  $Pr^{3+}$  doped  $BaY_2F_8$ prepared by Andrade *et al.*<sup>18</sup> exhibited a short decay time around 70 ns associated with the  $4f^15d^1 \rightarrow 4f^2$  transition of the  $Pr^{3+}$  ions. RE doped scintillators use dipole allowed transitions between the  $4f^n$  and  $4f^{n-1}5d^1$  states for a fast scintillation decay time.<sup>19</sup> However, the f–f transitions, which are forbidden by the parity selection rule, are characterized by a long lifetime.<sup>20</sup> RE doped phosphors also exhibit a long-lasting

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, Physics and Materials Science, Fayetteville State University, Fayetteville, NC 28301, USA. E-mail: zluo@uncfsu.edu

<sup>&</sup>lt;sup>b</sup> Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439, USA

<sup>&</sup>lt;sup>c</sup> X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Rietveld refinement and crystal structure of Ba\_2HfF\_6, XRD patterns, SEM images of microparticles, CIE coordinate data, and cathodoluminescence spectra. See DOI: 10.1039/d0tc05051b

luminescence activity, which is known as afterglow or persistent luminescence. Yamamoto *et al.*<sup>21</sup> found that the prolonged emission lifetime in blue-emitting CaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Nd<sup>3+</sup> and green emitting SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> phosphors is likely governed by the slow liberation of trapped charge carriers. Similarly, Liu *et al.*<sup>20</sup> reported a complex CaZnGe<sub>2</sub>O<sub>6</sub> oxide material that exhibits afterglow up to 5 min under UV excitation, which resulted from the recombination of electrons and holes trapped in the matrix exciting the Tb<sup>3+</sup> after the source is off.

Dibarium octafluorohafnate,  $Ba_2HfF_8$  (BHF), with a density of 6.05 g cm<sup>-3</sup>, <sup>22</sup> is a potential scintillator host containing heavy metal elements to absorb the radiation energy. RE doped BHF can down-convert high-energy radiation to the UV or visible region. To date, only one study of BHF luminescence has been carried out by Li et al., in which the photoluminescence (PL) properties of the BHF:Mn<sup>4+</sup> fluoride phosphor for red light emitting diodes were examined.<sup>23</sup> Nevertheless, the doping of RE<sup>3+</sup> along with CL and RL in this host material for radiation detection remains unexplored. In this research, BHF nanoparticles doped with Tb<sup>3+</sup> and Eu<sup>3+</sup> were synthesized, and their PL, CL, and RL properties were studied and optimized. Dopant site-dependent luminescence was found with this unique host structure. Strong steady-state emission upon X-ray excitation confirmed BHF as a brilliant scintillator, with afterglow for a few seconds.

## Experimental

#### Sample preparation

The starting materials used were BaCl<sub>2</sub>, TbCl<sub>3</sub>, EuCl<sub>3</sub>, HfO<sub>2</sub>, hydrofluoric acid (HF, 40 vol%), and cetyltrimethylammonium bromide (CTAB). In a typical synthesis procedure, CTAB (1.0 g) was dissolved in 40 mL of deionized water, followed by stirring for 1 h at ambient temperature. A 2.0 mL solution of 1.0 M BaCl<sub>2</sub> dissolved in deionized water was added dropwise into the CTAB solution under vigorous stirring, followed by the addition of 1.0 mL of 1.0 M Hf<sup>4+</sup> in 20 vol% HF solution. The mixture was kept at room temperature and stirred for another 30 min before being sealed in a Teflon-lined autoclave and aged statically at 160 °C under autogenous pressure for 12 h. The obtained product was separated and washed with water and ethanol repeatedly to remove any surfactants, and then dried at 100  $^\circ C$ for 3 h. The Tb<sup>3+</sup> and Eu<sup>3+</sup> doped BHF samples were prepared using the same procedure, except that the respective molar percentages of TbCl<sub>3</sub> and EuCl<sub>3</sub> were added to replace BaCl<sub>2</sub>.  $RE^{3+}$  was doped into the  $Ba^{2+}$  site, expressed as  $Ba_{2-x-y}$ HfF<sub>8</sub>:Tb<sub>x</sub>-Eu<sub>y</sub>, where x and y are the fractions of Tb<sup>3+</sup> and Eu<sup>3+</sup> ions, respectively. The synthesis method was slightly modified to prepare micron sized particles for comparison: no CTAB surfactant was used for the growth of micron sized particles, and the other conditions were the same as those in the nanoparticle synthesis. In this paper, all samples were prepared as nanoparticles using this hydrothermal method with CTAB, unless specifically indicated as micron sized particles without the use of CTAB.

#### Characterization

X-ray diffraction (XRD) was performed using a Rigaku MiniFlex 600 X-ray diffractometer in the range of 10°-80° at an interval of  $0.025^{\circ}$  and a scanning speed of  $0.075^{\circ}$  min<sup>-1</sup>. Structure refinement of XRD data was performed using the PDXL integrated X-ray powder diffraction software. The samples were characterized using a JEOL JXA-8530F field-emission electron probe microanalyzer (EPMA), equipped with an X-ray energydispersive spectrometer (EDS) for chemical compositional analysis and an xCLent IV Advanced B Hyperspectral CL detector for CL analysis. The imaging was done in the SEM mode using the EPMA at 15 kV and 20 nA, while different voltages (5-30 kV) were used to examine the electron beam power in the CL measurement. Samples for transmission electron microscopy (TEM) were prepared in pure ethanol solutions, which were sonicated for 1 min and then dispersed on carbon-film supported grids. The grids were observed using an FEI Talos F200X TEM/STEM instrument at 200 kV. The scanning TEM (STEM) imaging was done in the STEM mode using a high-angle annular dark-field (HAADF) imaging detector, and the elemental maps of the selected elements were collected using the X-ray EDS signals. The PL spectra of the powder samples were recorded using a Shimadzu RF-5301PC spectrofluorophotometer at room temperature. X-ray induced radioluminescence (RL) was measured using time-resolved X-ray induced optical luminescence setup at Beamline 11-ID-D in Advanced Photon Source, ANL, with an X-ray energy of 11.5 keV.

# Results and discussion

#### Phase identification and morphology

The powder XRD patterns of pristine and  $\text{RE}^{3+}$  doped samples are shown in Fig. 1. Ba<sub>2</sub>HfF<sub>8</sub> is isostructural to the orthorhombic Ba<sub>2</sub>ZrF<sub>8</sub> (JCPD 089-0863), with the *Pnma* (No. 62) space group.<sup>24</sup> All reflections are indexed to the pure orthorhombic phase and no impurity phase is observed even for the doped samples, indicating that the RE dopants occupy the BHF lattice. The charge difference between the trivalent RE<sup>3+</sup> ions and the divalent Ba<sup>2+</sup> lattice site is possibly compensated through interstitial fluoride ions, defect aggregation (cluster formation),<sup>25</sup>



Fig. 1 (a) XRD patterns of  $Ba_{2-x}HfF_8$ :Tb<sub>x</sub> samples; (b) demonstration of peak shift with an increase in Tb<sup>3+</sup> concentration, *x*.

Hf vacancies,<sup>26</sup> or even partial occupation on both Ba and Hf sites as observed in other systems.<sup>27</sup> The influence of Tb<sup>3+</sup> incorporation on the structure of BHF can be observed by examining the peak shift in the XRD pattern (Fig. 1b). With the increasing  $Tb^{3+}$  dopant concentration on the  $Ba^{2+}$  site, the most intense peak corresponding to the (211) plane at  $2\theta$  =  $25.24^{\circ}$  shifts toward the higher angle side. The radii of Ba<sup>2+</sup> and  $Tb^{3+}$  are 1.47 and 1.09 Å, respectively, when compared in an environment with a coordination number (CN) of nine. Hence, upon the substitution of Ba<sup>2+</sup> with Tb<sup>3+</sup> ions, the unit cell shrinks, leading to a shift of the XRD peaks toward a higher angle.<sup>28</sup> The diffraction intensity changes of some peaks are due to changes in structural factors caused by the incorporation of RE ions. The structure of Ba2ZrF8 was selected as the starting model for Rietveld refinement (Fig. S1a, ESI<sup>†</sup>).<sup>24</sup> A good fit between the experimental and refined data was obtained, and the refined structural parameters are listed in Table S1 (ESI<sup>+</sup>). From the Rietveld refinement of Ba<sub>2</sub>HfF<sub>8</sub>, the lattice constants are determined as a = 9.798 Å, b = 5.636 Å and c = 11.920 Å. The changes in lattice parameters with the RE doping are listed in Table S2 (ESI<sup> $\dagger$ </sup>). With an increase in the concentration of Tb<sup>3+</sup> ions from x = 0.0 to x = 0.5, the lattice volume contracts monotonically. The crystal structure of BHF is presented in Fig. S1b (ESI<sup>+</sup>), and the coordination polyhedra of barium and hafnium are shown in Fig. S1c-e (ESI<sup>+</sup>). In the lattice of BHF, Ba<sup>2+</sup> has two different coordination sites, namely Ba1 and Ba2, surrounded by twelve and ten fluorine ions, respectively (Fig. S1c and d, ESI<sup>†</sup>).

SEM imaging results reveal that, with the use of CTAB, the samples synthesized using the hydrothermal method exhibit cube-shaped nanoparticles, as shown in Fig. 2(a–d), for various concentrations of Tb<sup>3+</sup> ions, with the average size measured as  $509 \pm 50$  nm. However, there are some smaller particles. The EDS analysis confirmed the stoichiometric presence of the elements Ba, Hf, and F in the sample (Fig. 2e). However, without the use of CTAB in the synthesis, larger particles that are 1–2 µm in size with irregular shapes are obtained, as shown in Fig. S3 (ESI†).

The TEM image of the  $\text{Tb}^{3+}-\text{Eu}^{3+}$  codoped sample is shown in Fig. 3a, confirming the nanocube shape. The selected-area electron diffraction (SAED) pattern of a cube is shown in Fig. 3b, indicating the single-crystal nature that is indexed to the orthorhombic structure. From the high-resolution TEM (HRTEM) image in Fig. 3c, it is observed that the cube edge is along the (010) plane, so probably the cubes are grown along the three orthogonal planes. TEM-HAADF imaging is further used to characterize the elemental maps of the BHF:Tb<sup>3+</sup>-Eu<sup>3+</sup> sample. Fig. 4a shows the HAADF STEM image, showing the nanocubes. The elemental maps of Ba, Hf, F, Tb and Eu are shown in Fig. 4b–f, respectively, exhibiting the uniform distribution of these elements over the BHF nanocubes.

#### Photoluminescence studies of Tb<sup>3+</sup> and Eu<sup>3+</sup>

Steady-state normalized PL excitation (PLE) and PL spectra of  $BHF:Tb^{3+}$  and  $BHF:Eu^{3+}$  are presented in Fig. 5. The major bands of both samples are labelled with the corresponding



**Fig. 2** (a–d) SEM images of  $Ba_{2-x}HfF_8$ :Tb<sub>x</sub> samples (x = 0.0, 0.1 0.3, & 0.5, respectively); (e) EDS spectrum of the as-synthesized BHF nanocubes.

transitions. The UV-visible PLE spectrum of Ba1.5HfF8:Tb0.5 corresponding to  $\text{Tb}^{3+}$  emission ( ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{5}$ ) at 545 nm is shown in Fig. 5a. In the PLE spectrum, the sharp absorption lines represent the f-f transitions of  $Tb^{3+}$  from the  ${}^{7}F_{6}$  ground state to the different excited states of Tb<sup>3+</sup>. Fig. 5a also shows the emission spectrum of Ba<sub>1.5</sub>HfF<sub>8</sub>:Tb<sub>0.5</sub> under 350 nm excitation. The emission spectrum consists of f-f transitions within the 4f<sup>8</sup> configuration of Tb<sup>3+</sup>, which are  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  (485 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (545 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (585 nm), and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  (620 nm) transitions. The strongest one is located at 545 nm corresponding to the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of  $Tb^{3+}$ . Fig. 5b shows the UV-visible PLE spectrum of Ba<sub>1.9</sub>HfF<sub>8</sub>:Eu<sub>0.1</sub> with the Eu<sup>3+</sup> emission at 595 nm and the corresponding PL spectrum. The several sharp peaks observed represent the f-f transitions of  $Eu^{3+}$ from the  ${}^{7}F_{I}$  ground state to different excited states of Eu<sup>3+</sup>. For instance, the strongest transition line at 394 nm is associated with the  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$  transition. The emission curve in Fig. 5b is due to the direct excitation of Eu<sup>3+</sup> ions at 394 nm.

The emission from  $Eu^{3+}$  ions is highly sensitive to the coordination environment of  $Eu^{3+}$  ions in the crystal structure. As shown in Fig. 5b, the PL spectrum of  $Ba_{1,9}HfF_8:Eu_{0,1}$  consists of two major peaks: one at 595 nm due to the  ${}^5D_0 \rightarrow {}^7F_1$  MD



Fig. 3 (a) TEM image, (b) SAED pattern, and (c) HRTEM image showing the cube edge along the (010) plane of the orthorhombic structure.



Fig. 4 (a) TEM-HAADF images and (b–f) the corresponding elemental maps by EDS analysis of BHF:Tb $^{3+}$ -Eu $^{3+}$  nanocubes.

transition and the other at 615 nm due to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  ED transition. There is no large difference in their intensities. The MD transition is remarkable when Eu<sup>3+</sup> is situated at a site that coincides with a center of symmetry, and the ED transition is remarkable when Eu<sup>3+</sup> is situated at a site that lacks inversion symmetry.<sup>29</sup> As shown in Fig. S1 (ESI†), the Ba1 site is coordinated by twelve fluorine atoms with different Ba–F bond distances, while Ba2 is coordinated by ten fluorine atoms with slightly different Ba–F bond distances. The coordination polygon of Ba1 is a cuboctahedron with  $O_{\rm h}$  point symmetry, as shown in Fig. S1c (ESI†), whereas Ba2 is an axially bisected bicapped hexagonal prism with symmetry lower than  $O_{\rm h}$  point symmetry, as shown in Fig. S1d (ESI†). In BHF, Eu<sup>3+</sup> ions that occupy the Ba1 site with a center of symmetry exhibit 595 nm emission, and the Eu<sup>3+</sup> ions at the Ba2 site that lacks inversion

symmetry exhibit 615 nm emission. Therefore, in the Eu<sup>3+</sup> singly doped sample, Eu<sup>3+</sup> ions randomly occupy Ba1 and Ba2 sites, as there is no large difference in the intensities of these two peaks. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition exhibits splitting of the  ${}^{7}F_{1}$  level, which directly reflects the crystal-field splitting of the  ${}^{7}F_{1}$  level. In a cubic crystal-field, the  ${}^{7}F_{1}$  level is not split, while, at lower symmetry such as orthorhombic in BHF, the total removal of crystal field degeneracies results in splitting in the sublevels of  ${}^{7}F_{1}$ .<sup>30</sup>

Fig. 6a and b show the concentration-dependent PL spectra of  $Ba_{2-x}HfF_8:Tb_x$  (x = 0.1 to 0.6) and  $Ba_{2-y}HfF_8:Eu_y$  (y = 0.005 to 0.20), respectively. It is observed that the luminescence intensities of  $Tb^{3+}$  and  $Eu^{3+}$  are enhanced with an increase in their concentrations up to x = 0.50 and y = 0.10, respectively, and then decrease with x or y, due to concentration quenching. Concentration quenching is a well-known phenomenon in luminescent materials<sup>31</sup> because of the energy transfer between identical  $Eu^{3+}-Eu^{3+}$  and  $Tb^{3+}-Tb^{3+}$  ions. Consequently, the optimum dopant concentration is x = 0.50 (25 mol%) for  $Tb^{3+}$ and y = 0.10 (5 mol%) for  $Eu^{3+}$ .

#### Tb<sup>3+</sup> to Eu<sup>3+</sup> energy transfer

The Tb<sup>3+</sup> to Eu<sup>3+</sup> energy transfer in the BHF lattice is investigated in the present study. The overlap of the PLE band of Eu<sup>3+</sup> and the PL band of Tb<sup>3+</sup> in the spectral region of 300-500 nm (Fig. 7) suggests that the  $Tb^{3+}$  ions may act as good sensitizers for Eu<sup>3+</sup> emission. In the excitation spectra recorded at 595 nm of Eu<sup>3+</sup> emission and 545 nm of Tb<sup>3+</sup> emission of BHF:Tb<sup>3+</sup>-Eu<sup>3+</sup> nanocrystals (Fig. 7a), PLE bands are dominated by Tb<sup>3+</sup> absorption bands except a new peak designated as the Eu<sup>3+</sup> excitation peak, *i.e.* 394 nm ( ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ ). Fig. 7b presents the emission spectra of Ba<sub>1.485</sub>HfF<sub>8</sub>:Tb<sub>0.50</sub>-Eu<sub>0.015</sub> under excitation at different wavelengths. Upon 394 nm excitation ( ${}^{5}L_{6}$  of Eu $^{3+}$ ), only Eu<sup>3+</sup> exhibits emissions, and the emission peak positions are similar to those of singly doped Ba<sub>2</sub>HfF<sub>8</sub>:Eu<sup>3+</sup> shown in Fig. 5b, whereas, under 350 nm excitation ( ${}^{5}D_{I}$  of Tb ${}^{3+}$ ), emissions from both Eu<sup>3+</sup> and Tb<sup>3+</sup> can be detected. There were no excitation peaks corresponding to Eu<sup>3+</sup> ions at 350 nm (not shown here), confirming that Tb<sup>3+</sup> can partially transfer excitation energy to Eu<sup>3+</sup> via its excitation of the 4f state. It was observed that the intensity of Eu<sup>3+</sup> emission under 394 nm excitation is lower than that under 350 nm excitation, which is correlated with the respective excitation spectra. This observation indicates that direct excitation into the <sup>5</sup>L<sub>6</sub> energy level of Eu<sup>3+</sup> in this host is not efficient, while Tb<sup>3+</sup> acts as a sensitizer for efficient  $Eu^{3+}$  emission through  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer. Interestingly, the codoping of Tb<sup>3+</sup> ions influences the occupation of Eu<sup>3+</sup> at the Ba<sup>2+</sup> lattice site of BHF. As compared to the PL of BHF:Eu<sup>3+</sup> nanocrystals (Fig. 6b), the emission at 615 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) is much reduced compared to the emission at 595 nm  $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  with the codoping of Tb<sup>3+</sup> ions in the host lattice.<sup>32</sup> This observation implies that the Eu<sup>3+</sup> ions preferentially occupy a more symmetric Ba1 site (CN = 12), and  $Tb^{3+}$  ions occupy the relatively compact Ba2 (CN = 10) site, due to the smaller ionic radius of Tb<sup>3+</sup> than that of the Eu<sup>3+</sup> ions.<sup>32</sup> As a result, the Eu<sup>3+</sup> emission at 595 nm is more



Fig. 5 Normalized excitation and emission spectra of (a) Ba<sub>1.5</sub>HfF<sub>8</sub>:Tb<sub>0.5</sub> and (b) Ba<sub>1.9</sub>HfF<sub>8</sub>:Eu<sub>0.1</sub>.



Fig. 6 Emission spectra of (a) Ba<sub>2-x</sub>HfF<sub>8</sub>:Tb<sub>x</sub> ( $\lambda_{ex}$  = 350 nm) and (b) Ba<sub>2-y</sub>HfF<sub>8</sub>:Eu<sub>y</sub> ( $\lambda_{ex}$  = 394 nm). The insets show the variation in intensity of 545 nm and 595 nm peaks.

significant than that at 615 nm emission in Tb<sup>3+</sup>–Eu<sup>3+</sup> codoped nanocrystals.

Fig. 8 shows the emission spectra of  $Ba_{1.5-y}HfF_8$ :Tb<sub>0.50</sub>-Eu<sub>y</sub> upon excitation using a 350 nm source. With an increase in the Eu<sup>3+</sup> concentration (*y*), the emission intensity of Eu<sup>3+</sup> increases,



Fig. 7 Excitation (a) and emission (b) spectra of  $Ba_{1.485}HfF_8:Tb_{0.50}-Eu_{0.015}.$ 



Fig. 8 Normalized emission spectra at various  $Eu^{21}$  concentrations in  $Ba_{1.5-y}HfF_8$ :Tb<sub>0.50</sub>-Eu<sub>y</sub> under 350 nm excitation.

whereas that of the  $Tb^{3+}$  ions rapidly decreases, further indicating the energy transfer from  $Tb^{3+}$  to  $Eu^{3+}$ . The absolute

emission colors have changed continuously due to different ratios between the green band emission from  $\text{Tb}^{3+}$  ions and the orange-red emission from  $\text{Eu}^{3+}$  ions. At an  $\text{Eu}^{3+}$  concentration of y = 0.020, the total emission intensity is slightly lower than that at y = 0.015, and thus the optimized emission intensity is observed around y = 0.015. Fig. S4 (ESI<sup>†</sup>) shows the Commission Internationale de L'Eclairage (CIE) coordinates of the above series of samples. From Fig. S4 and Table S3 (ESI<sup>†</sup>), one can observe that the absolute emission is insignificant at  $\text{Eu}^{3+}$  concentrations above y = 0.002. In the codoped  $\text{Ba}_{1.5-y}$  HfF<sub>8</sub>:Tb<sub>0.50</sub>-Eu<sub>y</sub> nanocrystals, as mentioned previously, the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$  (615 nm) transition is weaker in comparison to the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$  (595 nm) transition, and an orange luminescence color is observed.<sup>33</sup>

The PL emissions of nanocubes and microparticles with the same composition as that of  $Ba_{1.485}HfF_8:Tb_{0.50}-Eu_{0.015}$  are compared, as shown in Fig. 9. Although the emission band features are the same, the emission from nanocubes is much intensified compared to that from micron sized particles due to their increased surface area with more active dopants on the surfaces.<sup>6</sup>

#### Cathodoluminescence

The CL properties of BHF:Tb<sup>3+</sup>, BHF:Eu<sup>3+</sup>, and BHF:Tb<sup>3+</sup>–Eu<sup>3+</sup> luminescent nanocrystals are examined, as shown in Fig. 10a. For comparison, the PL emission spectra of the corresponding samples are also shown in Fig. 10a. It is observed that the CL spectrum of singly doped Tb<sup>3+</sup> ions is similar to the PL spectrum, except for two new blue-emitting peaks at 415 nm and 437 nm, which are attributed to  ${}^5D_3 \rightarrow {}^7F_5$  and  ${}^5D_3 \rightarrow {}^7F_4$ transitions, respectively. The probable reason is the presence of high energy charged particles exciting the blue band of the Tb<sup>3+</sup> ions efficiently. For the Eu<sup>3+</sup> singly doped sample, the 615 nm emission ( ${}^5D_0 \rightarrow {}^7F_2$ ) in the CL spectrum is more intensified than the 595 nm emission ( ${}^5D_0 \rightarrow {}^7F_1$ ), when compared to its PL spectrum. The difference between the PL and CL emission bands may be related to the different excitation mechanisms of



Fig. 9 Comparison of the PL emission of the nanocubes and micro-particles with the composition  $Ba_{1.485}HfF_8:Tb_{0.50}-Eu_{0.015}$ .

the CL and PL processes.<sup>34</sup> Under electron beam irradiation, apart from the direct excitation of the dopant ions, charge transfer and host lattice assisted excitation occur.35-37 In the BHF lattice, Ba1 is surrounded by twelve F<sup>-</sup> ions while Ba2 by ten F<sup>-</sup> ions, and thus the Ba2 site is probably more accessible to electrons for excitation, causing enhanced 615 nm emission from Eu<sup>3+</sup> at the Ba2 site. In the Tb<sup>3+</sup>-Eu<sup>3+</sup> codoped sample, the CL emission spectrum shows strong  $Tb^{3+}$  emission (545 nm) besides the Eu<sup>3+</sup> emitting lines, in contrast to the PL emission, where Tb<sup>3+</sup> emission is weak due to the efficient Tb<sup>3+</sup> to Eu<sup>3+</sup> energy transfer. During the high-energy excitation, there are sufficient secondary electrons generated by the high-energy source enable the highest intensity of Tb<sup>3+</sup> ions embedded in the lattice. Since the content of Tb<sup>3+</sup> is much higher than that of  $Eu^{3+}$ , not all the portion of the  $Tb^{3+}$  ions energy be transfer to the Eu<sup>3+</sup> ions.<sup>38</sup> Hence the Tb<sup>3+</sup> emission is not quenched in the presence of the Eu<sup>3+</sup> ions under CL excitation. This feature can be potentially used to distinguish between high energy radiation and UV rays. The chromaticity coordinates are calculated from the spectra of the BHF:Tb<sup>3+</sup>-Eu<sup>3+</sup> sample. Under electron beam excitation, the chromaticity coordinates are determined to be x = 0.3759 and y = 0.4316, which are in the green zone (Fig. S5, ESI<sup>+</sup>). In contrast, under UV excitation, the chromaticity coordinates are determined to be x = 0.5350 and y = 0.4036, which are in the orange zone. Therefore, the BHF:Tb<sup>3+</sup>-Eu<sup>3+</sup> based phosphor may serve as a potential candidate to distinguish UV light from ionizing radiation.

The effects of source electron energy on the emission intensities of BHF:Tb<sup>3+</sup>, BHF:Eu<sup>3+</sup>, and BHF:Tb<sup>3+</sup>-Eu<sup>3+</sup> were evaluated by varying the voltage from 5 to 30 kV. The integral intensities of the major emission peaks with varying voltage are plotted in Fig. 10b and Fig. S5 (ESI<sup>+</sup>). The depth of penetration of the incident electrons is proportional to the accelerating voltage.33 With an increase in accelerating voltage, more secondary electrons are produced by the incident electrons, resulting in more RE<sup>3+</sup> ions being excited with higher CL intensities. No saturation voltage occurred in the experimental observation range. On comparing the Tb<sup>3+</sup> singly doped and Tb<sup>3+</sup>-Eu<sup>3+</sup> codoped samples with the same Tb<sup>3+</sup> content, it is observed that the Tb<sup>3+</sup>-Eu<sup>3+</sup> codoped sample is more sensitive to the electron beam power showing higher intensities at higher radiation energies, possibly due to the fact that Eu<sup>3+</sup> occupies the Ba1 site yielding more Tb<sup>3+</sup> at the Ba2 site, which favors the emission excited by secondary electrons.

#### Radioluminescence

Under X-ray excitation, the samples exhibit excellent RL emissions, as shown in Fig. 11a, from the selected BHF:Tb and BHF:Tb–Eu nanocubes. As discussed in the previous CL section, the fundamental luminescence mechanisms by UV and highenergy radiation are different. For X-ray excited RL, in contrast to the direct optical excitation wherein an electron within an activator is directly excited from the  $4f^n \rightarrow 4f^{n-1}5d^1$  levels, the X-ray excitation process is mainly defined as follows: the secondary electrons are first generated in the host lattice by absorbing the X-ray energy, which subsequently directly or



Fig. 10 (a) CL (colored) and PL (single line) spectra of singly doped  $Ba_{1.5}HfF_8$ :Tb<sub>0.50</sub> and  $Ba_{1.9}HfF_8$ :Eu<sub>0.1</sub> and codoped  $Ba_{1.485}HfF_8$ :Tb<sub>0.50</sub>-Eu<sub>0.015</sub>; (b) integral emission intensity as a function of electron beam energy in the range of 5–30 kV.



**Fig. 11** (a) Normalized RL emission spectra of  $Ba_{1.5}HfF_8:Tb_{0.50}$  and  $Ba_{1.485}HfF_8:Tb_{0.50}-Eu_{0.015}$  under X-ray excitation; (b) afterglow spectra of  $Ba_{1.485}HfF_8:Tb_{0.50}-Eu_{0.015}$  recorded at a slow time-gate (s). The inset shows the time-resolved RL at longer times of the same sample.

indirectly excite the luminescent centers in the host.<sup>39</sup> The characteristic emission bands of  ${\rm Tb}^{3+}$  and  ${\rm Eu}^{3+}$ , as observed in

Fig. 11a, are clearly consistent with the emissions from  $\mathrm{RE}^{3^+}$  ions.  $^{40}$ 

Fig. 11b shows the time-resolved RL spectra of BHF:Tb-Eu. The emission spectra were recorded in time gates of 0-7 s after the excitation X-ray shot, at a time interval of 500 ms, but only plotted at intervals of 1 s in the figure. The spectra show the afterglow phenomenon in the visible region. The emission intensity decreased two-fold in the first second and change slowly afterward from 2 to 7 s. This indicates the presence of at least two decay components: one is in seconds and the other is comparatively faster in ms. Preeti et al.41 have reported the luminescence decay of Tb<sup>3+</sup> ions in NaYF<sub>4</sub> with an average lifetime of  $\sim 4$  ms. Similarly, Chen et al. have reported the 543 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ) emission of the Tb<sup>3+</sup> ions under X-ray excitation in the ms range (2.7-3.3 ms) for Na<sub>5</sub>Gd<sub>9</sub>F<sub>32</sub>.<sup>42</sup> The afterglow emission could be due to the capture of electrons by energy traps when excited by X-rays.43,44 This material with X-ray afterglow characteristics could be used for potential future applications in high-energy radiation detection.

## Conclusions

A facile hydrothermal method was used to prepare cube-shaped  $Ba_2HfF_8$  nanocrystals, and the PL, CL and RL properties of singly and binary RE-doped  $Ba_2HfF_8$  were studied in detail. The single doping was optimized to be 25 mol% for  $Tb^{3+}$  and 5 mol% for  $Eu^{3+}$ . The host lattice contains two  $Ba^{2+}$  sites: Ba1 and Ba2, surrounded by twelve and ten fluorine ions, respectively. The luminescence characteristics were found to be dependent on the dopant site of this host structure. In the singly doped samples, RE ions randomly occupy the  $Ba^{2+}$  sites, while in the  $Tb^{3+}$ – $Eu^{3+}$  codoped samples PL emissions suggest the preferrable occupation of  $Eu^{3+}$  on Ba1 and of  $Tb^{3+}$  on Ba2.  $Tb^{3+}$  acts as a sensitizer for  $Eu^{3+}$  ions, resulting in enhanced emission from  $Eu^{3+}$  ions under UV excitation. The nanocubes with a smaller size exhibited stronger emission compared to the micron sized particles. However, in the CL and RL spectra

#### Paper

under high energy irradiation, the  $\text{Tb}^{3+}$  emission becomes intensified, causing the chromaticity shift from the UV-excited orange zone to the green zone. The X-ray excitation induced excellent emissions and afterglow was observed. The codoped sample was found to be more sensitive than the singly doped sample in the higher energy radiation range, indicating that codoping is an effective strategy to develop a scintillator with this host structure for high-energy radiation detection.

# Authors' contributions

V. Kumar and G. George contributed equally to the sample synthesis, XRD, SEM, PL and CL measurements, and manuscript preparation; J. I. Hayes conducted the sample processing and preparation; Y. Lin and J. Wen conducted the TEM analysis; B. Guzelturk conducted X-ray induced RL; and Z. Luo designed and supervised the experiment and revised the manuscript.

# Conflicts of interest

There are no conflicts of interest to declare.

# Acknowledgements

This research was funded by the US National Science Foundation (NSF; ECCS 1900837). The EPMA instrumentation was acquired through the U.S. Department of Defense grant W911NF-09-1-0011 and the xCLent CL system through the NSF MRI Program DMR 1626376. In this research, we used the resources of the Center for Nanoscale Materials and Advanced Photon Source, both of which are Office of Science user facilities, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

# References

- 1 M. J. Weber, *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, 1979, vol. 4, pp. 275–315.
- 2 J. Luo, S. Sahi, M. Groza, Z. Wang, L. Ma, W. Chen,
   A. Burger, R. Kenarangui, T.-K. Sham and F. A. Selim, *Opt. Mater.*, 2016, 58, 353–356.
- 3 M. Runowski, N. Stopikowska, D. Szeremeta, S. Goderski, M. Skwierczyńska and S. Lis, ACS Appl. Mater. Interfaces, 2019, 11, 13389–13396.
- 4 L. Nana, L. Ruiyi, S. Xiulan, W. Guangli and L. Zaijun, *Sens. Actuators, B*, 2020, **320**, 128408.
- 5 G. George, M. D. Simpson, B. R. Gautam, D. Fang, J. Peng, J. Wen, J. E. Davis, D. Ila and Z. Luo, *RSC Adv.*, 2018, **8**, 39296–39306.
- 6 G. George, J. I. Hayes, C. N. Collins, J. E. Davis, L. Yu, Y. Lin, J. Wen, D. Ila and Z. Luo, *J. Alloys Compd.*, 2021, 157591, DOI: 10.1016/j.jallcom.2020.157591.
- 7 C. M. Bender, J. M. Burlitch, D. Barber and C. Pollock, *Chem. Mater.*, 2000, **12**, 1969–1976.

- 8 M. Zhang, H. Fan, B. Xi, X. Wang, C. Dong and Y. Qian, *J. Phys. Chem. C*, 2007, **111**, 6652–6657.
- 9 R. Mani, H. Jiang, S. K. Gupta, Z. Li and X. Duan, *Inorg. Chem.*, 2018, 57, 935–950.
- 10 V. Kumar, A. F. Khan and S. Chawla, *J. Phys. D: Appl. Phys.*, 2013, **46**, 365101.
- 11 G. George, C. S. Edwards, J. I. Hayes, L. Yu, S. R. Ede, J. Wen and Z. Luo, *J. Mater. Chem. C*, 2019, 7, 14949–14961.
- 12 S. K. Gupta, M. Sahu, P. S. Ghosh, D. Tyagi, M. K. Saxena and R. M. Kadam, *Dalton Trans.*, 2015, 44, 18957–18969.
- 13 S. K. Gupta, P. S. Ghosh, A. K. Yadav, S. N. Jha, D. Bhattacharyya and R. M. Kadam, *Inorg. Chem.*, 2017, 56, 167–178.
- 14 Z. Luo, G. J. Moch, S. S. Johnson and C. C. Chen, *Curr. Nanosci.*, 2017, **13**, 364–372.
- 15 N. J. Cherepy, G. Hull, A. D. Drobshoff, S. A. Payne, E. van Loef, C. M. Wilson, K. S. Shah, U. N. Roy, A. Burger, L. A. Boatner, W.-S. Choong and W. W. Moses, *Appl. Phys. Lett.*, 2008, **92**, 083508.
- 16 J. Cao, W. Chen, L. Chen, X. Sun and H. Guo, *Ceram. Int.*, 2016, 42, 17834–17838.
- S. Kurosawa, A. Yamaji, J. Pejchal, Y. Yokota, Y. Ohashi,
  K. Kamada and A. Yoshikawa, *J. Mater. Sci.*, 2017, 52, 5531–5536.
- 18 A. B. Andrade, A. C. S. de Mello, M. V. dos, S. Rezende,
  S. L. Baldochi and M. E. G. Valerio, *J. Appl. Phys.*, 2014, 116, 053521.
- 19 C. W. E. van Eijk, P. Dorenbos and R. Visser, *IEEE Trans. Nucl. Sci.*, 1994, **41**, 738–741.
- 20 C. Liu, G. Che, Z. Xu and Q. Wang, J. Alloys Compd., 2009, 474, 250–253.
- 21 H. Yamamoto and T. Matsuzawa, J. Lumin., 1997, 72-74, 287-289.
- 22 ed. P. Villars and K. Cenzual, Ba2HfF8 Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in Springer Materials (online database). (https://materials. springer.com/isp/crystallographic/docs/sd\_1921789).
- 23 H. Li, Z. Yang, L. Luo, Q. Wang, Y. Chen, M. Rong, Q. Zhou and Z. Wang, *Opt. Mater.*, 2020, **107**, 110091.
- 24 A. Le Bail and J. P. Laval, *Eur. J. Solid State Inorg. Chem*, 1998, 35, 357-372.
- 25 C. Lorbeer, F. Behrends, J. Cybinska, H. Eckert and A.-V. Mudring, *J. Mater. Chem. C*, 2014, **2**, 9439–9450.
- 26 G. H. Jonker and E. E. Havinga, *Mater. Res. Bull.*, 1982, 17, 345–350.
- 27 M. Vega, P. Alemany, I. R. Martin and J. Llanos, *RSC Adv.*, 2017, 7, 10529–10538.
- 28 R. Chatterjee, S. Saha, D. Sen, K. Panigrahi, U. K. Ghorai, G. C. Das and K. K. Chattopadhyay, ACS Omega, 2018, 3, 788–800.
- 29 S. Chawla, M. Parvaz, V. Kumar and Z. Buch, *New J. Chem.*, 2013, **37**, 3991–3997.
- 30 K. Binnemans, Coord. Chem. Rev., 2015, 295, 1-45.
- 31 G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag, Berlin Heidelberg, 1994.
- 32 L. C. Thompson and S. C. Kuo, *Inorg. Chim. Acta*, 1988, **149**, 305–306.

- 33 Z. An, H. Zou, C. Xu, X. Zhang, R. Dong, Y. Sheng, K. Zheng,
  X. Zhou and Y. Song, ACS Sustainable Chem. Eng., 2019, 7, 3154–3163.
- 34 W. Zhao, S. An, B. Fan, S. Li and Y. Dai, *Int. J. Miner., Metall. Mater.*, 2012, **19**, 271–277.
- 35 H. Jiao, J. Wang, F. Liao, S. Tian and X. Jing, *J. Electrochem. Soc.*, 2004, **151**, H49.
- 36 D. Meiss and S. Kemmler-Sack, *Phys. Status Solidi A*, 1991, 124, 371–378.
- 37 X. Liu and J. Lin, J. Mater. Chem., 2007, 18, 221-228.
- 38 G. S. R. Raju, J. Y. Park, H. C. Jung, E. Pavitra, B. K. Moon, J. H. Jeong and J. H. Kim, *J. Mater. Chem.*, 2011, 21, 6136–6139.

- 39 W. Zhang, Y. Shen, M. Liu, P. Gao, H. Pu, L. Fan, R. Jiang, Z. Liu, F. Shi and H. Lu, *ACS Appl. Mater. Interfaces*, 2017, 9, 39985–39993.
- 40 K. Wahid, M. Pokhrel and Y. Mao, *J. Solid State Chem.*, 2017, 245, 89–97.
- 41 P. Padhye and P. Poddar, J. Mater. Chem. A, 2014, 2, 19189–19200.
- 42 W. Chen, J. Cao, F. Hu, R. Wei, L. Chen, X. Sun and H. Guo, *Opt. Mater. Express*, 2018, **8**, 41.
- 43 Z. Chen, Y. Pan, L. Xi, R. Pang, S. Huang and G. Liu, *Inorg. Chem.*, 2016, **55**, 11249–11257.
- 44 S. N. Menon, B. Dhabekar, E. Alagu Raja and M. P. Chougaonkar, *Radiat. Meas.*, 2012, 47, 236–240.