



**Fast luminescence from rare-earth-codoped BaSiF<sub>6</sub>  
nanowires with high aspect ratios**

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## Fast luminescence from rare-earth-codoped BaSiF<sub>6</sub> nanowires with high aspect ratios

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Inorganic materials with short radiative decay time are highly desirable for fast optical sensors. This paper reports fast photoluminescence (PL) from a series of barium hexafluorosilicate (BaSiF<sub>6</sub>) superlong nanowires with high aspect ratios, codoped with Ce<sup>3+</sup>/Tb<sup>3+</sup>/Eu<sup>3+</sup> ions, with subnanosecond decay time. Solvothermally synthesized BaSiF<sub>6</sub> nanowires exhibit a uniform morphology, with an average diameter less than 40 nm and aspect ratios of over several hundreds, grown in c-axis direction with {110} surfaces. The PL emission from the codoped BaSiF<sub>6</sub> nanowires, when excited by a 254 nm source, is dependent on Tb<sup>3+</sup> concentration, and the energy transfer from Ce<sup>3+</sup> to Tb<sup>3+</sup> and to Eu<sup>3+</sup> ions allows efficient emissions in the visible spectra when excited by a near UV source. Annealing BaSiF<sub>6</sub> nanowires at 600 °C in vacuum produced barium fluoride (BaF<sub>2</sub>) nanowires composed of nanocrystals. Both BaSiF<sub>6</sub> and BaF<sub>2</sub> nanowires exhibit fast emissions in the visible spectra, with enhanced intensities compared with their codoped microparticle counterparts. The decay time of codoped BaSiF<sub>6</sub> nanowires is found to be shorter than that of codoped BaF<sub>2</sub> nanowires. The energy transfer is also observed in their cathodoluminescence spectra with high-energy irradiation.

### Introduction

Historically, rare-earth (RE) ions have been successfully used to dope scintillators/phosphors to ameliorate their luminescent properties. Trivalent Tb<sup>3+</sup> and Eu<sup>3+</sup> ions are extensively used as activators due to their characteristic green and red emission bands, respectively. Eu<sup>3+</sup> ions are attractive for their intense red emission; while Tb<sup>3+</sup> ions exhibit a weak and narrow absorption in the UV regions due to the narrow linewidth of Eu<sup>3+</sup> 4f–4f absorption transitions and low oscillator strength.<sup>1</sup> Generally, the emission from Eu<sup>3+</sup> ions are enhanced by various sensitizers such as Ce<sup>3+</sup> and Eu<sup>2+</sup> with 4f–5d allowed transitions, coupled with Tb<sup>3+</sup> or Gd<sup>3+</sup> ions as bridges to transfer the energy between Ce<sup>3+</sup> and Eu<sup>3+</sup> by minimizing the metal-metal charge transfer quenching, which otherwise equally quenches the emission from the sensitizer and

activator ions.

Alkaline earth fluorides are reckoned as ideal hosts for a large number of inorganic scintillators/phosphors, owing to their unique chemical stability and favourable photoluminescence (PL) characteristics, such as electron-acceptor behaviour, large optical-transmission domain, high resistivity and anionic conductivity.<sup>2</sup> Among them, barium hexafluorometallates are established as fluorescent host matrix in the recent years, for example, BaSiF<sub>6</sub> (BSF),<sup>3</sup> BaGeF<sub>6</sub>,<sup>4</sup> BaTiF<sub>6</sub>,<sup>5</sup> and BaSnF<sub>6</sub>,<sup>6</sup> doped with Mn<sup>4+</sup> for commercial LEDs with luminescent decay time in the order of microseconds. The possible energy transfer mechanisms in BaSiF<sub>6</sub> matrix codoped with Ce<sup>3+</sup> and Tb<sup>3+</sup> ions are discussed in the literature, while the influences of doping and crystal size on decay time are obscure.<sup>7,8</sup> These PL materials could be promising in the applications such as color multiplexing,<sup>9</sup> temperature sensing,<sup>10</sup> biosensing,<sup>11</sup> optical sensors,<sup>12</sup> cell imaging,<sup>13</sup> and photodynamic therapy,<sup>14</sup> etc. BSF is a chemically stable and optically transparent material,<sup>15</sup> and was used as a scintillator for high-energy γ-ray detection.<sup>16</sup>

PL with short radiative decay time is essential for fast optical sensors.<sup>17</sup> Surface functionalized phosphors with short decay time have found applications, such as biological imaging,<sup>18</sup> sensing,<sup>19,20</sup> drug delivery-discovery,<sup>21</sup> clinical diagnosis,<sup>22</sup> energy harvesting,<sup>23</sup> etc. Currently, fluorescence lifetime imaging is the major application that requires fluorophores with short decay time.<sup>24</sup>

Herein, superlong BSF nanowires with high aspect ratios, codoped with Ce<sup>3+</sup>, Tb<sup>3+</sup>, and Eu<sup>3+</sup> RE ions, were synthesized by a growth-controllable reverse micelle-solvothermal method,

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<sup>‡</sup> Electronic Supplementary Information (ESI) available: [Low-magnification image of BaSiF<sub>6</sub> nanowires, EDS results of BaSiF<sub>6</sub> and BaF<sub>2</sub> nanowires, SEM images of the microparticles, proposed mechanism of nanowire formation, TGA results of BaSiF<sub>6</sub> nanowires, PL and PLE spectra of unary doped BaSiF<sub>6</sub> and BaF<sub>2</sub> nanowires, PL spectra at different doping and excitation, mechanism of energy transfer, structure of BaSiF<sub>6</sub> and BaF<sub>2</sub>, CIE data and the details on the estimation of PL decay time.]. See DOI: 10.1039/x0xx00000x

and the doping in BSF nanowires was optimized for the best energy transfer bridge between  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$  ions. Further, BSF was decomposed at a high-temperature in vacuum to yield  $\text{BaF}_2$  (BF), a well-known fast scintillator for radiation detection with the shortest decay time of 0.8 ns among all inorganic scintillators.<sup>25,26</sup> The PL emission and decay time were also compared with the respective microparticle counterparts. These nanowires were further studied using cathodoluminescent (CL) emission spectra under high-energy irradiation. Significantly shortened decay time in subnanosecond has been observed from the codoped high-aspect-ratio BSF nanowires.

## Experimental

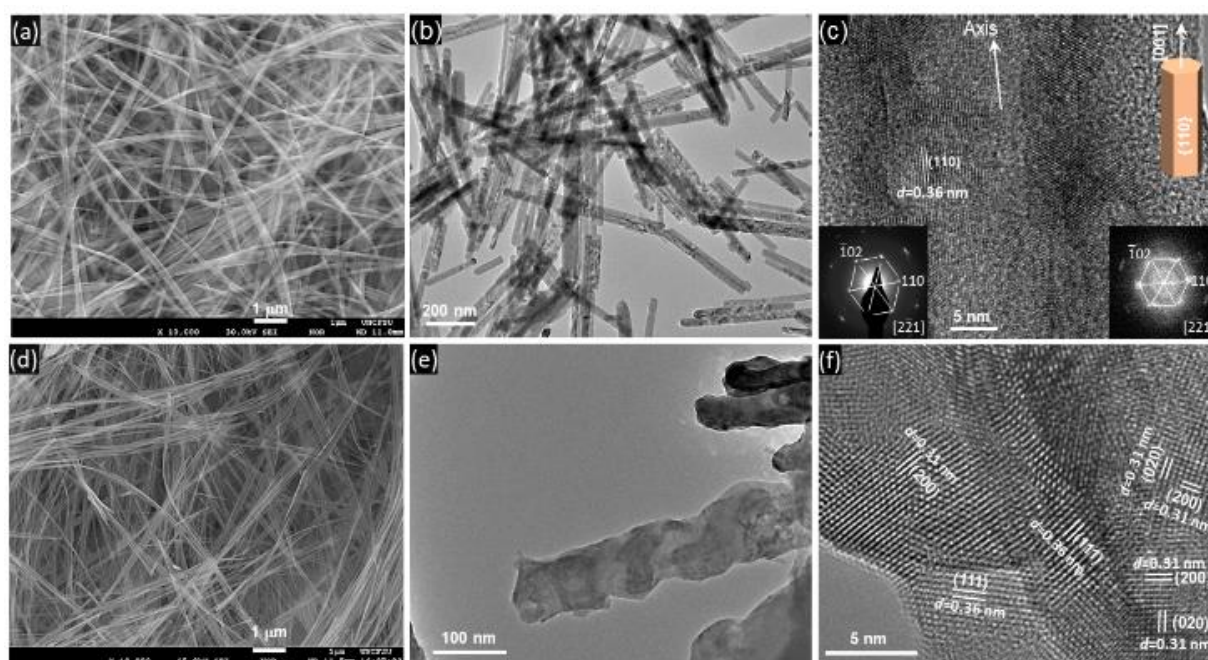
### Sample Preparation of pure and doped $\text{BaSiF}_6$ nanowires

All the nanowires were synthesized using a solvothermal method in a quaternary system of cetyltrimethylammonium bromide (CTAB)/water/cyclo-hexane/1-pentanol. All the chemicals were analytical grade and used without any purification. In the typical process, two identical solutions of 25 mL cyclohexane mixed with 2 g of CTAB (VWR International, LLC.) and 1 mL 1-pentanol (Sigma Aldrich) were prepared first. To prepare pure  $\text{BaSiF}_6$  nanowires; to one of the above solutions is added with 1 mL of 1 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (VWR International, LLC.) in water and the other with 1 mL of 1 M  $\text{SiO}_2$  (Sigma Aldrich) dissolved in 10% hydrofluoric acid (HF with concentration >40%, Sigma Aldrich). The precursor solutions were added drop wise at a rate of 2 mL  $\text{h}^{-1}$  under a vigorous stirring at 700 rpm. In this step, both the solutions gradually became transparent. After 30 min of vigorous stirring, both the solutions were mixed together and stirred for another 10 min. The mixed solution was then transferred to 100 mL Teflon-lined autoclaves and heated for 12 h at 120 °C.

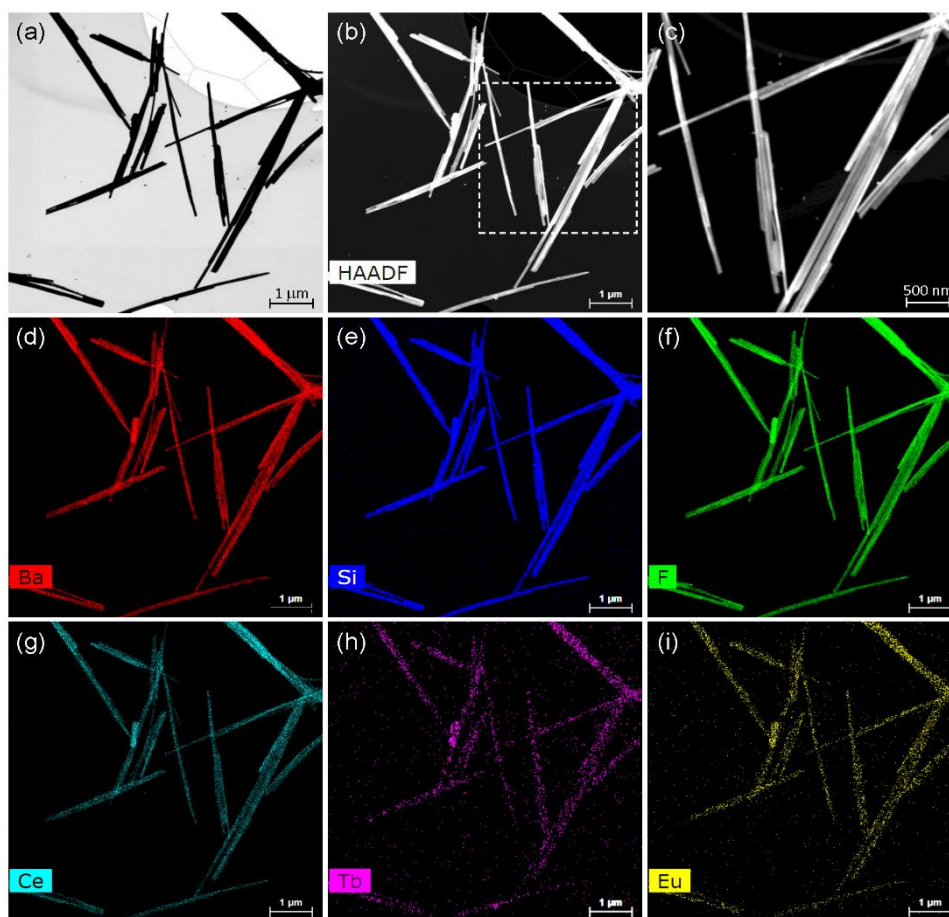
After 12 h the solution was cooled naturally to room temperature and were washed with ethanol and water several times and dried in vacuum at 80 °C for overnight. The doped nanowires were made using the similar method, in which respective molar percentage of the RE chlorides  $\text{CeCl}_3$ ,  $\text{EuCl}_3$ , and  $\text{TbCl}_3$  (Beantown Chemical, Hudson) were added to the  $\text{BaCl}_2$  solution, and the aforesaid procedure was followed. To obtain nanowires of  $\text{BaF}_2$ , the  $\text{BaSiF}_6$  nanowires were heated in vacuum at 600 °C for 12 h at a heating rate of 1 °C  $\text{min}^{-1}$ . The microparticle samples were prepared by the direct mixing of 2 mL each of 1 M  $\text{BaCl}_2$  solution containing the respective RE chlorides and 1M  $\text{SiO}_2$  in 10% HF, followed by heating in autoclave at 120 °C for 12 h. The doped  $\text{BaSiF}_6$  nanowires are represented as  $\text{BSF}:x\text{Ce}-y\text{Tb}-z\text{Eu}$  and doped  $\text{BaF}_2$  nanowires as  $\text{BF}:x\text{Ce}-y\text{Tb}-z\text{Eu}$ , where  $x$ ,  $y$  and  $z$  are molar percentages of  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$  ions, respectively, with respect to  $\text{Ba}^{2+}$  ions.

### Characterization

For scanning electron microscopy (SEM) observation and chemical compositional analysis, the samples were coated with ~10 nm carbon and observed in a JEOL field-emission JXA-8530F electron probe microanalyzer (EPMA), equipped with an X-ray energy-dispersive spectrometer (EDS) for chemical compositional analysis, and a xClent IV Advanced B Hyperspectral Cathodoluminescence detector for CL spectra. The imaging was done in SEM mode using the EPMA. Samples for transmission electron microscopy (TEM) were prepared in pure ethanol solutions, sonicated for 30 min to break the long nanowires and then dispersed on carbon-film supported grids. The grids were observed in an FEI field-emission Tecnai F20ST at 200 kV, and HRTEM was carried out using the Argonne chromatic aberration-corrected TEM (ACAT, a FEI Titan 80-300 ST) with both spherical  $C_s$  and chromatic  $C_c$  aberration corrections at 200 kV. For EDS mapping, FEI Talos F200X



**Fig. 1** (a) SEM and (b) TEM images of BSF nanowires; (c) HRTEM image of BSF with SAED (left) and FT (right) patterns inserted; (d) SEM and (e) TEM images of BF nanowires; and (f) HRTEM image of BF nanowire showing nanoparticles.



**Fig. 2** (a) TEM image of BSF:2Ce-7Tb-5Eu nanowires showing the area for mapping, and (b) corresponding HAADF image. (c) Magnified image from the framed area in (b) showing individual nanowires. (d)–(i) Elemental maps by EDS showing the distributions of Ba, Si, F, Ce, Tb and Eu, respectively.

TEM/STEM instrument was used at 200 kV. The imaging was done in the STEM mode using a high-angle annular dark-field imaging (HAADF) detector, and the elemental maps of selected elements were collected using the X-ray EDS signals. Fourier-transform infrared (FTIR) spectra (Shimadzu IRPrestige-21) were recorded in transmission mode by KBr pellet method in the wave number range of  $300\text{--}4,000\text{ cm}^{-1}$  at an average of 32 scans. The stability of nanowires at high temperature was studied using thermogravimetric analysis (TGA) (Shimadzu DTG-60). The X-ray diffraction (XRD) patterns of the samples were obtained using Rigaku MiniFlex 600 X-ray diffractometer in a scan range of  $10\text{--}90^\circ$ . The photoluminescent spectra of the samples were obtained in powder form using Shimadzu RF-5301PC spectrofluorophotometer at room temperature. Using an Edinburgh instruments minitau, time-correlated single photon counting (TCSPC) experiments were performed to measure the PL decay dynamics. The samples were excited with 56 ps laser pulses at a wavelength of 405 nm and the emission was monitored at 594 nm. PL decay was detected using single photon counting photomultiplier tube (PMT). The time resolution of the configuration was  $\sim 100$  ps. The mol. % of the dopants in both BSF and BF nanowires are obtained using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer 8000).

## Results and discussion

### Morphology and Structure

The one-dimensional growth of BSF nanowires is observed with SEM and TEM (Fig. 1a and b) of the samples. A quantitative measurement of the nanowires from the TEM images, without surface coating, indicates that the average diameter is 35.8 nm with a standard deviation of 5.4 nm, based on 20 measurements. The length is typically in the range of  $10\text{--}50\ \mu\text{m}$  from low-magnification SEM images (Fig. S1), giving the aspect ratio over several hundreds. A magnified high-resolution TEM (HRTEM) image is shown in Fig. 1c, with a selected-area electron diffraction (SAED) pattern inserted showing the nature of a single crystal with a rhombohedral structure within the nanowire. Although the sample is quickly damaged because no surface coating was applied, lattice fringes are still clearly visible, showing  $\{110\}$  planes parallel to the nanowire surfaces. The inserted Fourier transformation (FT) pattern from the HRTEM image is consistent with the SAED pattern from this nanowire. The nanowire axis is along its  $[001]$  direction. Such a rhombohedral (or hexagonal) structure facilitates the growth along its  $c$ -axis under the controlled conditions. Even though the nanowire morphology of BSF is retained after converting them to BF nanowires (Fig.



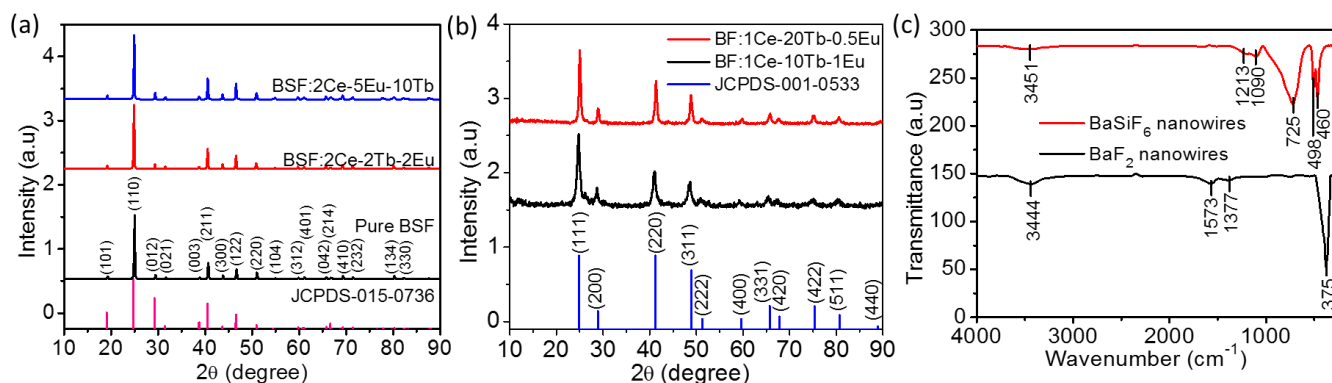


Fig. 3 XRD patterns of representative (a) BSF and (b) BF nanowires; and (c) FTIR Spectra of pure BSF and BF nanowires.

1d) in vacuum at 600 °C, BF nanowires are polycrystalline in nature, as evident from TEM and HRTEM images (Fig. 1e and f). The nanowire composition and uniform distribution of the dopants throughout the nanowires are confirmed by EDS mapping (Fig. 2) and point analyses (Fig. S2a and b). The size/shape of the nanowires is unaffected by doping. The SEM images of BSF and BF microparticles are shown in Fig. S3. A proposed mechanism of BSF nanowire formation (Fig. S4) is described in the ESI<sup>†</sup>.

The XRD pattern confirms the pure crystalline nature of BSF nanowires (Fig. 3a) and the sharp peak with extremely high intensity along preferred (110) reflection, demonstrating that the nanowire surfaces are {110}. The XRD patterns of BSF nanowires are indexed as the rhombohedral BaSiF<sub>6</sub> (JCPDS data file No. 15–0736), with space group of  $R\bar{3}m$  and lattice parameters of  $a=0.7185$  nm and  $c=0.7010$  nm, consistent with the TEM results. For every Ba<sup>2+</sup> ion in BSF, the coordination towards fluorine is twelve. The BSF nanowires are stable up to a temperature of 400 °C, as shown from TGA analysis (Fig. S5), and then the weight is lost gradually until 600 °C by releasing SiF<sub>4</sub> to derive BaF<sub>2</sub>.<sup>27</sup> The XRD patterns of BF nanowires are indexed to standard BaF<sub>2</sub> JCPDS data file No. 01–0533 (Fig. 3b),

with space group of  $Fm\bar{3}m$  and lattice parameter of  $a=0.62$  nm. No impurity phases are observed, indicating that the dopant ions are occupied at the lattice sites of Ba<sup>2+</sup> ions. However, the charge is compensated between the trivalent RE<sup>3+</sup> ions and the divalent Ba<sup>2+</sup> ions through defects such as interstitial fluoride ions and/or defect aggregation (cluster formation).<sup>28</sup> The actual molar percentage of the dopants in the nanowires with respect to barium ions obtained using ICP-OES are presented in Table S1, which are basically consistent with the nominal compositions. In the Fourier-transform infrared (FTIR) spectra of BSF and BF nanowires, as shown in Fig. 3c, the peaks 725, 498 and 460 cm<sup>-1</sup> are assigned to the various vibrations of octahedral SiF<sub>6</sub><sup>2-</sup> ions<sup>29</sup> of BSF, the peak at 375 cm<sup>-1</sup> is attributed to the Ba–F stretching of BF, respectively, and the remaining peaks are due to the several vibrational modes of adsorbed water molecules.

#### Photoluminescence emissions

The PL and photoluminescence excitation (PLE) spectra of co-doped BSF and BF nanowires reveal that excitation and emission bands are characteristic to the dopant ions (Fig. 4a and b, S6). In the emission spectrum of Ce<sup>3+</sup>-doped nanowires, broad peak in the UV region at 335 nm is due to the excitation

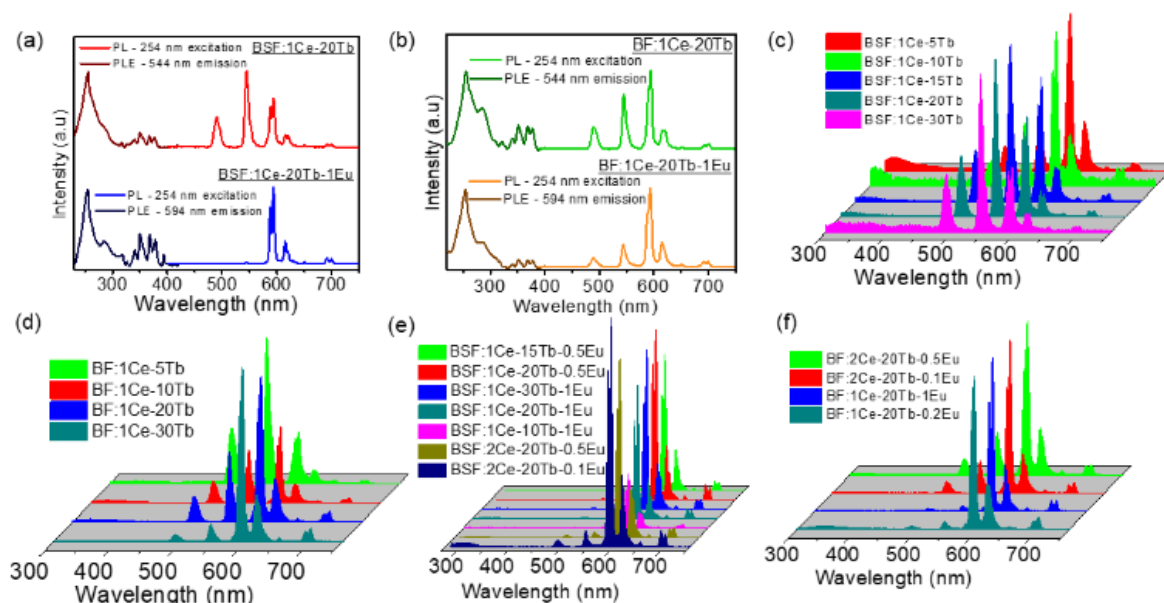


Fig. 4 (a, b) PL and PLE spectra of representative binary- and ternary-doped BSF and BF nanowires; (c) PL spectra of BSF:1Ce-yTb; (d) BF:1Ce-yTb; (e) BSF:xCe-yTb-zEu; and (f) BF:xCe-yTb-zEu nanowire phosphors under 254 nm excitation.

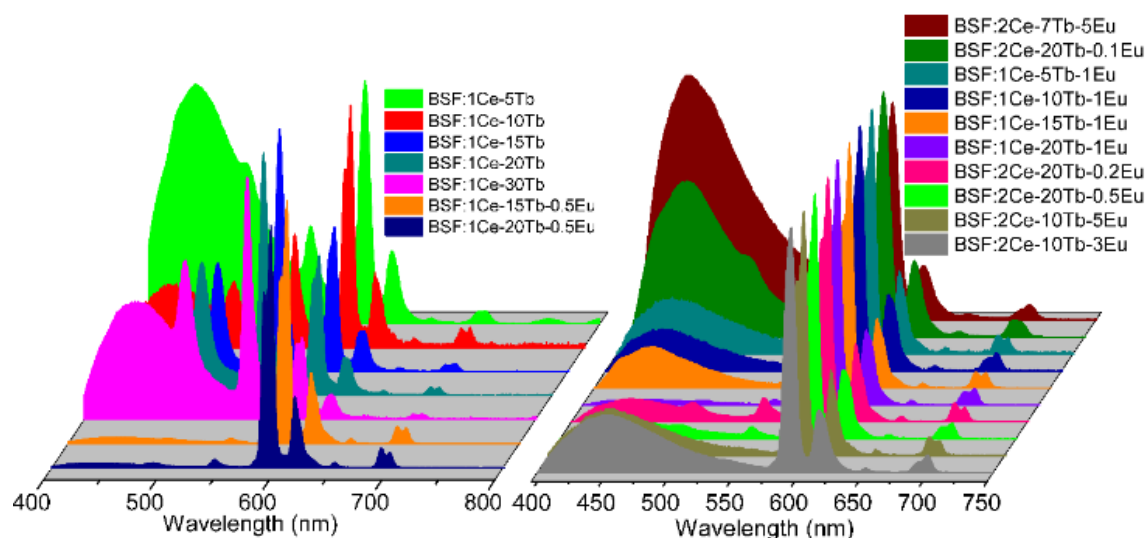


Fig. 5 PL spectra of codoped BaSiF<sub>6</sub> nanowires excited by 376 nm wavelength.

of electrons from  $4f$  to  $5d$  state and the subsequent relaxation to ground state comprising a doublet  $^2F_{5/2}$  and  $^2F_{7/2}$ , respectively, of Ce<sup>3+</sup> ions<sup>30,31</sup> and it is host depended.<sup>32</sup> The spectrum of Eu<sup>3+</sup> doped nanowires has emissions in the region 570 to 700 nm, originated from the excited state  $^5D_0$  to the ground states  $^7F_j (j = 0 - 4)$ ;<sup>33</sup> and Tb<sup>3+</sup> doping results in the sharp peaks noticed at 488, 544, 590 and 620 nm, originated from  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$ , and  $^5D_4 \rightarrow ^7F_3$   $4f-4f$  transitions of Tb<sup>3+</sup>, respectively.<sup>34</sup>

In the PLE spectrum monitored at 335 nm emission (Fig. S6) of Ce<sup>3+</sup> doped nanowires, the absorption close to 254 nm corresponds to  $5d \rightarrow 4f$  transition of Ce<sup>3+</sup> ions. On Tb<sup>3+</sup> doping, PLE spectrum monitored at 544 nm emission exhibits several bands at 225–400 nm relates to the  $4f^8 \rightarrow 4f^7 5d^1$  transition of Tb<sup>3+</sup> ion.<sup>35</sup> In the PLE spectrum of BSF:1Ce–20Tb–1Eu (Fig. 4a), an additional peak appears at 393 nm which is also present in the PLE spectrum of BSF:5Eu (Fig. S6), due to Eu<sup>3+</sup> ions in addition to the  $4f^8 \rightarrow 4f^7 5d^1$  transition of the Tb<sup>3+</sup> ion. The PLE spectra of codoped samples in Fig. 4a and b exhibit features by adding the PLE spectra of individual unary doped samples as shown in Fig. S6a and b.

The PL emission spectra of BSF:1Ce– $y$ Tb and BF:1Ce– $y$ Tb nanowires for an excitation wavelength of 254 nm are shown in Fig. 4c and d, respectively. There is no substantial difference in the emission band positions of BF and BSF nanowires doped with Ce<sup>3+</sup> and Tb<sup>3+</sup> ions. Fig. S7 also shows the PL emission from binary-doped samples.

In general, the emission lines from both Ce<sup>3+</sup> and Tb<sup>3+</sup> doped BSF and BF nanowires are consistent with the sum of emissions from singly-doped nanowires, but the intensity of emissions from binary-doped nanowires are significantly improved by the presence of Ce<sup>3+</sup> ions. The emission line arising from Ce<sup>3+</sup> ions near 335 nm is negligible as compared with the emissions from Tb<sup>3+</sup> ions, indicating the complete energy transfer between those ions. On a close observation, when BSF nanowires doped with Ce<sup>3+</sup> and Tb<sup>3+</sup> ions, the dominant emission line is at 544 nm, whereas it is at 590 nm in all BF nanowires. This difference in the emission intensity of

BSF and BF nanowires is in connection with the symmetry of dopant site in the respective lattices. In BSF, the dopants replace Ba<sup>2+</sup> ions with  $D_{3d}$  point symmetry;<sup>36</sup> however, in BF the dopants occupy lattice site of Ba<sup>2+</sup> with cubic symmetry (Fig. S8).

As shown in Fig. 4e and f, both BSF and BF nanowires display strong emission lines at 594 and 615 nm, corresponding to the emission from Eu<sup>3+</sup> ions, originate from  $^5D_0 \rightarrow ^7F_j (j = 1, 2)$  transitions, respectively. Intensity of the emission in orange-red region is increased significantly by the addition of Tb<sup>3+</sup> ions while the concentrations of Ce<sup>3+</sup> and Eu<sup>3+</sup> are kept constant. The emission line at 335 nm appears when the Ce<sup>3+</sup> concentration is 2% and Eu<sup>3+</sup> is 0.5% (Fig. S9a and b). The characteristic emissions of doped BF nanowires are akin to those of BSF nanowires, besides the superior emissions arising from the Tb<sup>3+</sup> ions as compared with those in BSF matrix, which can be attributed to reordering of dopant ions in the lattice with less structural defects after heating at 600 °C. The emission at 594 nm ( $^5D_0 \rightarrow ^7F_1$ ) is associated with magnetic dipole transition and 615 nm ( $^5D_0 \rightarrow ^7F_2$ ) is due to electronic dipole transition.

The magnetic dipole transition dominates when Eu<sup>3+</sup> is situated at a site coinciding with a center of symmetry, and electronic dipole transition prevails when Eu<sup>3+</sup> ions occupy a site lacks the inversion symmetry. Since the intensity of the 594 nm peak is higher than the 615 nm peak, one can confirm that the Eu<sup>3+</sup> ions occupy the site of Ba<sup>2+</sup> ions in BSF with a center symmetry. The peak intensity ratio between ( $^5D_0 \rightarrow ^7F_2$ ) and ( $^5D_0 \rightarrow ^7F_1$ ) transition is a measure of distortion around the Eu<sup>3+</sup> ions.<sup>37</sup> On comparing above ratios of BSF:5Eu and BSF: $x$ Ce– $y$ Tb–5Eu, it is concluded that the doping of Ce<sup>3+</sup> and Tb<sup>3+</sup> does not alter the neighborhood of Eu<sup>3+</sup> ions, as there is no significant difference in the same. In contrary, the 594 nm and 615 nm emission ratio of BF nanowires is higher than that of BSF nanowires, indicating the difference in the symmetry of the dopant sites in the respective crystal lattices.

From the PLE spectra, the excitation of binary- and ternary-doped BSF nanowires are possible by 376 nm source (Fig. 5), with a broad blue emission originated from  $\text{Tb}^{3+}$  ions assigned to the transitions ( $^5D_3 \rightarrow ^7F_j$  ( $j = 0, 1, 2, 3, 4$ ) due to the relaxation of the ions excited by the direct source band and sharp orange-red emission bands corresponding to the transition  $^5D_0 \rightarrow ^7F_j$  ( $j=0, 1, 2, 3, 4$ ) of  $\text{Eu}^{3+}$  ions. The resultant CIE coordinates are presented in Fig. S10 and Table S2. A slight change in the  $\text{Eu}^{3+}$  doping can bring an appreciable change in the emission and the dopant ratio can be optimized to attain blue, red, and white light emission. The energy transfer mechanism is discussed in the ESI<sup>†</sup>.

The luminescent emission of nanowires and microparticles are compared and shown Fig. S11. The fluorescence emission bands of both the samples are the same but the emissions from nanowires are intensified than microparticles though doped with the same ratio of RE ions, due to their increased surface area with more active dopants on the surfaces.

### Photoluminescence decay dynamics

The time-resolved PL decay dynamics of representative codoped BSF and BF nanowires for the emission at 594 nm (corresponding to  $^5D_4 \rightarrow ^7F_4$  of  $\text{Tb}^{3+}$  in binary  $x\text{Ce}-y\text{Tb}$ , or  $^5D_0 \rightarrow ^7F_1$  transitions of  $\text{Eu}^{3+}$  ions in ternary  $x\text{Ce}-y\text{Tb}-z\text{Eu}$  doped nanowires) are shown in Fig. 6a and b, and the overall decay time and the parameters for the remaining nanowires are listed in Table 1. The decay time curves can be fitted to a double exponential and the equations used in the estimation of decay time are presented in the ESI<sup>†</sup>. The fast ( $\tau_1$ ) and slow ( $\tau_2$ ) decay time components of the samples are perhaps due to two different recombination centers of  $\text{Tb}^{3+}$  or  $\text{Eu}^{3+}$  ions: one on the distorted lattice sites close to the surface and the other from the bulk of the nanowires.<sup>38</sup> On a comparison made among the decay times of different  $\text{Tb}^{3+}$  content (Table 1) in  $\text{BSF}:x\text{Ce}-y\text{Tb}$  and  $\text{BSF}:x\text{Ce}-y\text{Tb}-z\text{Eu}$  nanowires, the decay time is decreased monotonically with increasing  $\text{Tb}^{3+}$  concentration, which strongly supports the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$

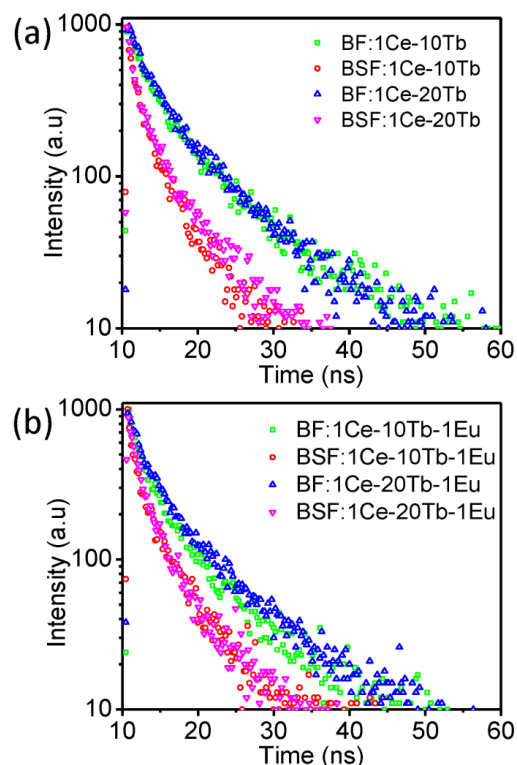


Fig. 6 Comparison on decay time of representative samples of (a)  $\text{BSF}:1\text{Ce}-y\text{Tb}$  and  $\text{BF}:1\text{Ce}-y\text{Tb}$ , and (b)  $\text{BSF}:1\text{Ce}-y\text{Tb}-1\text{Eu}$  and  $\text{BF}:1\text{Ce}-y\text{Tb}-1\text{Eu}$ .

ions; considering the fact that the contribution from cross relaxation to nonradiative relaxation increases with increasing concentration which ultimately decreases the decay time of the activators.<sup>39</sup> The lowest decay time is expected for optimal  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  contents with maximum energy transfer.<sup>40</sup> The decay time in ternary-doped nanowires are shorter than binary-doped ones because of the energy exchange between  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$  ions, as a result, rapid relaxation of the excited ions can take place through more different pathways than binary-doped samples.

Table 1 Parameters of exponential fit and average decay time of codoped BSF and BF nanowires

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\alpha_1$	$\alpha_2$	Adj. $R^2$	$\tau_{\text{avg}}$ (ns)
BSF:1Ce-10Tb	0.92	4.77	$4.45 \times 10^8$	2922.74	0.9949	0.92
BSF:1Ce-20Tb	0.88	5.28	$5.31 \times 10^8$	2452.88	0.9944	0.88
BSF:1Ce-5Tb-1Eu	1.02	5.98	$2.34 \times 10^7$	1779.38	0.9957	1.02
BSF:1Ce-10Tb-1Eu	0.9	5.56	$8.73 \times 10^7$	1956.85	0.9943	0.9
BSF:1Ce-20Tb-1Eu	0.82	5.94	$1.01 \times 10^7$	1602.17	0.996	0.82
BSF:1Ce-30Tb-1Eu	0.81	5.25	$3.16 \times 10^8$	2146.58	0.995	0.81
Micro-BSF: 1Ce-20Tb	1.81	90.81	$3.23 \times 10^5$	76.78	0.9853	1.81
Micro-BSF: 1Ce-20Tb-1Eu	1.78	150.53	1258.17	71.39	0.9876	1.78
BF:1Ce-10Tb	2.38	9.89	$5.95 \times 10^4$	1035.51	0.9964	2.38
BF:1Ce-20Tb	2.1	10.18	$1.13 \times 10^5$	7371.52	0.9953	2.1
BF:1Ce-10Tb-1Eu	1.69	8.6	$3.56 \times 10^5$	1338.96	0.9946	1.69
BF:1Ce-20Tb-1Eu	1.48	8.34	$9.54 \times 10^5$	1190.09	0.9946	1.48
Micro-BF: 1Ce-20Tb	2.5	17.71	$5.65 \times 10^4$	292.76	0.9892	2.5
Micro-BF: 1Ce-20Tb-1Eu	1.52	9.61	$7.99 \times 10^5$	1200.72	0.9929	1.62

The PL decay time recorded for these nanowires is shorter than the decay time reported in the literature, due to the dopant occupancy in the lattice sites and crystal size effect.<sup>41–43</sup> The PL transitions from dopants occupying the center of symmetry (like BSF) has a faster decay time, whereas the one occupying the lattice sites with inversion symmetry (like BF) has a slower decay time.<sup>41</sup> In Mn<sup>4+</sup> doped BSF, the Mn<sup>4+</sup> occupying the Si<sup>4+</sup> site in BSF has a  ${}^2E_g \rightarrow {}^4E_{2g}$  spin- and parity-forbidden transition with slow decay time  $\sim 6.5$  ms (monitored at 634 nm emission);<sup>3</sup> whereas, the RE dopants occupy Ba<sup>2+</sup> site in BSF, and the decay time is significantly shortened, e.g., Pr<sup>3+</sup>-doped BSF powder with 70 ns decay time when excited by 187 nm source and the emission monitored between 200–450 nm.<sup>37</sup> The size effect on decay time is also prevalent.<sup>43</sup> The fast component  $\tau_1$  of the decay time for BSF microparticles is increased by nearly two times and the slow component  $\tau_2$  is increased by  $\sim 17$  times in BSF:1Ce–20Tb and  $\sim 25$  times in BSF:1Ce–20Tb–1Eu, respectively, in comparison with the corresponding nanowires. The fact that slow component of microparticles is longer than that of BSF nanowires confirm the assumption of its origin from the bulk of the sample. The effect of deep traps in the bulk of the nanowires is trivial due to increased surface defects, whereas in microparticles the deep traps dominate over the surface defects.<sup>44</sup> In BF microparticles,  $\tau_1$  and  $\tau_2$  of nanowires are increased only by a small fraction compared with the BF nanowires, and the average decay time of the BF samples is approximately 1.5–2 ns. Yet another study on Nd<sup>3+</sup>-doped BaF<sub>2</sub> nanoparticles showed decay time of 350–900 ns whereas the decay time of polycrystalline sample was 3,000 ns (excited by 488 nm and emission monitored at 1,052 nm).<sup>45</sup> The decay time reported for BaF<sub>2</sub> bulk doped with Ce<sup>3+</sup> ions is  $\sim 27$  ns (excited by 289 nm source and emission monitored at 323 nm),<sup>46</sup> and Pr<sup>3+</sup> is  $\sim 20$  ns (excited by 205 nm and emission monitored at 230 nm).<sup>47</sup> The present nanowires exhibit short decay time by the presence of surface traps, which actually can transfer the energy to luminescent centers.<sup>48</sup>

The average decay time of BSF nanowires is shorter than that of BF nanowires. The dopant ions in BF is more symmetric (cubic symmetry) than the one in BSF lattice ( $D_{3d}$  point symmetry) and the forbidden  $f-f$  transitions are favorable for dopants at a lower symmetry site, hence one can expect a shorter decay time.<sup>49</sup>

On accounting the phonon energy of the lattices, the lattice distortions can increase the phonon energy. The non-radiative relaxations of RE ions are influenced by the phonon frequencies of the host lattices.<sup>50</sup> The reciprocal of decay time,  $\tau$  is determined by radiative emission, nonradiative relaxation and cross relaxation between the adjacent ions.<sup>51</sup> Therefore the total relaxation rate can be expressed as (Equation 1)

$$\tau^{-1} = \sum \tau_{NR}^{-1} + \sum \tau_R^{-1} + P_{CR} \quad (1)$$

Where,  $\sum \tau_R^{-1}$  is the radiative (photon) emission and  $\sum \tau_{NR}^{-1}$  is the nonradiative (multiphonon) emission rates. The term PCR is the rate of cross relaxation between the adjacent ions.

The decay time of BSF and BF samples doped with the same composition of RE elements, the contribution from PCR is assumed to be the same and hence,  $\sum \tau_R^{-1}$  and  $\sum \tau_{NR}^{-1}$  are the major factors contributing to the decay time.  $\sum \tau_R^{-1}$  is dependent on the site symmetry and environment of the dopant ions whereas  $\sum \tau_{NR}^{-1}$  is determined by the lattice phonon energy. Therefore, the decay time can be changed either by the local symmetry of the RE ion in the host lattice or by the phonon energy of the host, unless the level of doping is changed.<sup>51</sup>

The non-radiative relaxation is, in turn, related to the number of phonons as in Equation 2,

$$\tau_{NR}^{-1} = A \exp(-Bp) \quad (2)$$

Where  $A$  and  $B$  are constants,  $p$  is the number of phonons which can be calculated using equation 3,

$$p = \Delta E / \hbar \omega \quad (3)$$

Where  $\Delta E = 16,835 \text{ cm}^{-1}$  (corresponding to the fluorescence at 594 nm, the energy gap corresponding to the transitions  ${}^5D_4 \rightarrow {}^7F_4$  of Tb<sup>3+</sup> and  ${}^5D_0 \rightarrow {}^7F_1$  of Eu<sup>3+</sup> ions, respectively) and  $\hbar \omega$  is the energy of phonons, in wave numbers, of the crystal lattice.

The lattice phonon energy,  $\hbar \omega$ , can be approximated to the lowest vibration energies in the IR spectra of BSF and BF and are 480 and 375  $\text{cm}^{-1}$ , respectively. The corresponding number of phonons are 35 and 45 for BSF and BF, respectively. From Equation 1, one can conclude that with an increase in the number of phonons  $p$ ,  $\sum \tau_{NR}^{-1}$  decreases and as a result the decay time increases. Hence it is recognized that the difference in the luminescent decay time among BSF and BF doped samples can be accompanied to the difference in the radiative and nonradiative relaxation mechanisms associated with the crystal structure of the host matrix and the phonon energy of the host. To be precise, it is a competition among the radiative and nonradiative decay rates.<sup>52</sup>

#### Cathodoluminescence characteristics

The CL spectra of the codoped BSF and BF nanowires and microparticles are recorded using high-energy electrons to excite scintillation for radiation detection,<sup>54</sup> and representative CL spectra are shown in Fig. 7. Both pure BSF and BF nanowires exhibit strong CL emissions in the visible range. The CL spectrum of pure BSF nanowires is intense with broad bands at 390 and 510 nm, respectively, whereas pure BF nanowires exhibit a broad band at 390 nm. The common peak at 390 nm (3.18 eV) in the CL spectra of both BSF and BF nanowires implies that it has the same origin, from the  $2p F^- \rightarrow 5p \text{ Ba}^{2+}$  cross-over transition of electrons,<sup>54</sup> which is in turn due to the holes generated in cations during their ionization by the high energy source. The band at 510 nm (2.43 eV) from BSF nanowires is conceived as the radiative recombination of the self-trapped excitons (STE), the electron-hole pairs restricted by a self-induced lattice distortion, and the radiative relaxation restores the original defect-free structure.<sup>55</sup>



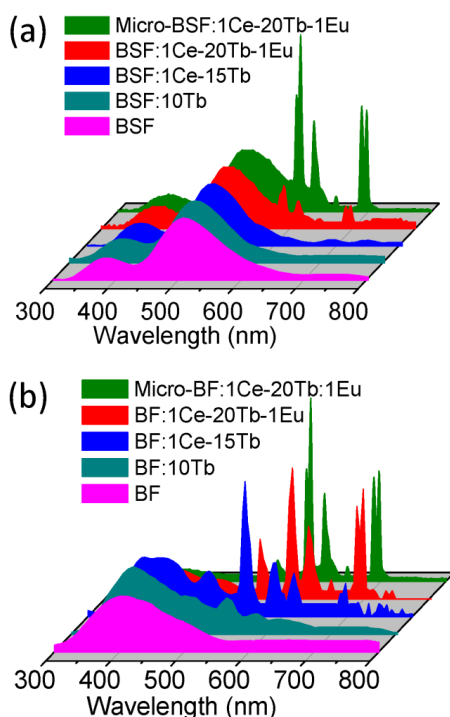


Fig. 7 Cathodoluminescent emission of pure and unary doped (a) BSF and (b) BF nanowires.

While comparing the CL emissions from the doped and pure nanowires, the emissions from  $\text{Tb}^{3+}$  doped nanowires are similar to those of pure BSF nanowires, as shown in Fig. 7a. However, weak characteristic emissions from  $\text{Tb}^{3+}$  ions appear in the presence of  $\text{Ce}^{3+}$  ions from BSF:1Ce–15Tb nanowires, indicating the energy transfer between the ions. The energy transfer is also observed in BSF:1Ce–20–Tb–1Eu nanowires with the characteristic emissions from  $\text{Eu}^{3+}$  ions. In doped BF nanowires, as shown in Fig. 7b, an ample improvement in CL emissions is observed than BSF nanowires especially by the presence of  $\text{Ce}^{3+}$  ions as in BF:1Ce–15Tb and BF:1Ce–20Tb–1Eu nanowires. Therefore, one can conclude that the energy from the cross-over transition excite the  $\text{Ce}^{3+}$  ions and the energy transfer from  $\text{Ce}^{3+}$  ions subsequently excite  $\text{Tb}^{3+}/\text{Eu}^{3+}$  ions. An effective energy transfer is not found in codoped BSF nanowires, in which the energy transfer is partial due to the presence of STE's.

The CL emissions from the micro-sized particles are superior to the nanowires. In nanowires, the mean-free path of the electron/hole ( $\sim 30$  nm) and the size of the nanowires are comparable, therefore, the charge carriers can be either captured by the surface defects or leave the nanoparticles.<sup>56</sup> As a result, luminescence quenching-induced low luminescence intensities are apparent from nanowires than microparticles. Strong characteristic emission from the dopants is observed in the CL spectrum of microparticles than the same noticed from the nanowires. Hence, it is concluded that the CL emission also follows the energy transfer mechanism observed in photoluminescence and the ions are excited by the energy associated with the transitions of the lattice.

## Conclusions

In summary, photoluminescent and cathodoluminescent RE ion-doped  $\text{BaSiF}_6$  nanowires were synthesized using a growth-controlled solvothermal method and annealing the  $\text{BaSiF}_6$  nanowires at  $600^\circ\text{C}$  in vacuum yielded  $\text{BaF}_2$  nanowires. TEM and XRD analyses of these nanowires were conducted. The influence of various doping of  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Eu}^{3+}$  RE ions on the photoluminescence of  $\text{BaSiF}_6$  and  $\text{BaF}_2$  nanowires were studied. The PL monitored when excited by 254 nm sources, is associated with the respective energy transfer between  $\text{Ce}^{3+}$ – $\text{Tb}^{3+}$ – $\text{Eu}^{3+}$  ions. The doped nanowires excited by 376 nm source also could produce a wide emission in the visible range. The decay time of codoped  $\text{BaSiF}_6$  nanowires was found to be shorter than that of codoped  $\text{BaF}_2$  nanowires. Codoping with  $\text{Ce}^{3+}$ – $\text{Tb}^{3+}$ – $\text{Eu}^{3+}$  provides an efficient way to shorten the decay time of  $\text{BaF}_2$  with visible emission. With intense emissions in the visible range with short decay time, these easy-grown and superlong nanowires with high aspect ratios may be used for fast luminescence sensing applications.

## Conflicts of interest

There are no conflicts to declare.

## Authors' contributions

G. George conducted the sample synthesis and PL measurements, and prepared the manuscript; S.L Jackson and Z.R. Mobley conducted the sample processing and preparation; B.R. Gautam conducted the decay dynamics; D. Fang attended the experimental design and data analysis; J. Peng, D. Luo and J. Wen conducted the TEM work; J.E. Davis and D. Ila conducted the research on scintillation; and Z. Luo designed the experiment, conducted the EPMA/CL measurement and revised the manuscript.

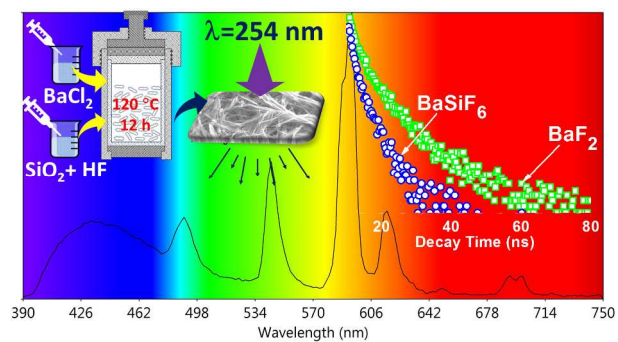
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Solvothermally synthesized rare-earth-doped superlong  $\text{BaSiF}_6$  nanowires with high aspect ratios with subnanosecond decay time.