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# Significantly enhanced photoluminescence and thermal stability of $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ via the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer: a blue-green phosphor for ultraviolet LEDs†

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A series of  $\text{Ce}^{3+}$ -,  $\text{Tb}^{3+}$ - and  $\text{Ce}^{3+}/\text{Tb}^{3+}$ -doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phosphors were synthesized by gas-pressure sintering (GPS). The energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  occurred in the co-doped samples, leading to a tunable emission color from blue to green under the 360 nm excitation. The energy transfer mechanism was controlled by the dipole–dipole interaction. The  $\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped sample had an external quantum efficiency of 46.7%, about 5.6 times higher than the  $\text{Tb}$ -doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phosphor (8.3%). The thermal quenching of the  $\text{Tb}^{3+}$  emission in  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:\text{Tb},\text{Ce}$  was greatly reduced from 74 to 30% at 250 °C, owing to the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ . The blue-green  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.05\text{Tb}$  phosphor was testified to fabricate a warm white LED that showed a high color rendering index of 90.2 and a correlated color temperature of 3570 K. The results suggested that the co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:\text{Ce},\text{Tb}$  phosphor could be a potential blue-green down-conversion luminescent material for use in UV-LED pumped wLEDs.

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## 1 Introduction

In recent years, white light-emitting diodes (w-LEDs) have drawn much attention due to their advantages over conventional lighting technologies, such as high efficiency, energy saving, environmental friendliness, compactness and longevity.<sup>1–10</sup> There are two common approaches to generate white light from LEDs.<sup>11–13</sup> The first one is to combine monochromatic blue, green and red LED chips to create white light. This method allows the production of high luminous efficacy but it also requires a complicated feedback electronic control which limits its application. The second one is to pump phosphor(s) with a blue, UV or near-UV LED chip (also called phosphor-converted w-LEDs), which promises cost effectiveness and ease of fabrication. Compared to the dichromatic wLEDs using the combination of a blue LED chip and a yellow-emitting

phosphor (e.g., YAG: $\text{Ce}^{3+}$ ), multi-phosphor-converted wLEDs driven by an UV LED chip enable to provide a super-high color rendering index (CRI > 90) and the excellent quality of light that can be widely used in supermarkets, surgical operations, museums, *etc.*<sup>14–20</sup> To realize this, highly efficient and thermally stable red, green and blue phosphors that can be excited by UV light are required.<sup>21–24</sup>

To develop green or green-to-blue emitting phosphors for such applications, one of the strategies is to co-dope  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  in one phosphor host, and to apply the energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  to realize the tunable color and enhanced photoluminescence properties.<sup>25–28</sup> For example, Wang *et al.* reported a novel blue-green emitting phosphor  $\text{NaBaScSi}_2\text{O}_7:\text{Ce}^{3+},\text{Tb}^{3+}$  with an internal quantum efficiency (IQE) of 36%.<sup>29</sup> Xiao *et al.* addressed that the green emission of  $\text{Tb}^{3+}$  in  $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Ce}^{3+},\text{Tb}^{3+}$  at 423 K could remain 92% of its intensity at room temperature.<sup>30</sup> Du *et al.* found that in the blue-green emitting phosphor  $\text{LaSi}_3\text{N}_5:0.09\text{Ce}^{3+},0.12\text{Tb}^{3+}$  the  $\text{Tb}^{3+}$  luminescence had a higher thermal stability than the  $\text{Ce}^{3+}$  luminescence at 423 K (~90% vs. ~70% of the initial luminescence).<sup>31</sup> Zhang *et al.* investigated the green phosphor  $\text{LaOBr}:\text{Ce}^{3+},\text{Tb}^{3+}$ , and observed that the green emission at 433 K could maintain 90–100% of its intensity at room-temperature.<sup>32</sup>

Among the huge number of luminescent materials for wLEDs, the rare-earth doped (oxy)nitride phosphors have drawn much attention due to their abundant emission color, high

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† Electronic supplementary information (ESI) available: Ionic radii (Å) of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  for the given coordination number (CN) (Table S1) and EDS spectrum of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$  (Fig. S1). See DOI: 10.1039/c8ra07011c



conversion efficiency and small thermal quenching.<sup>33–45</sup>  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  are the mostly used activators in (oxy)nitride phosphors, leading to a variety of interesting luminescent materials for white LEDs, such as  $\alpha$ -sialon: $\text{Eu}^{2+}$ ,  $\beta$ -sialon: $\text{Eu}^{2+}$ ,  $\text{CaAlSiN}_3$ : $\text{Eu}^{2+}$ ,  $\text{Sr}[\text{LiAl}_3\text{N}_4]$ : $\text{Eu}^{2+}$ ,  $\text{La}_3\text{Si}_6\text{N}_{11}$ : $\text{Ce}^{3+}$ , and *etc.*<sup>46–50</sup> On the other hand, to the best of our knowledge, there are very limited investigations on co-doped (oxy)nitride phosphors. Liu *et al.* reported the greatly enhanced luminescence in  $\gamma$ -alox: $\text{Mn}^{2+}$  by co-doping  $\text{Eu}^{2+}$ , which enables to a promising green phosphor for near-UV LEDs.<sup>51</sup> Song *et al.* realized the tunable emission colors in  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  co-doped  $\text{SrSi}_2\text{O}_2\text{N}_2$  *via* the energy transfer between  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$ .<sup>52</sup> Therefore, it has great opportunities to develop (oxy)nitride phosphors with enhanced photoluminescence properties by realizing the efficient energy transfer in them.

$\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  is a good host for  $\text{Ce}^{3+}$  or  $\text{Eu}^{2+}$  that has intense blue emissions under the UV excitation.<sup>3,53</sup> Moreover,  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ : $\text{Ce}^{3+}$  also shows smaller thermal quenching than other phosphors in system La–Si–N–O–Ce.<sup>54</sup> In this work, we attempt to investigate the photoluminescence of  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ , and to apply the energy transfer strategy to enhance photoluminescence properties of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ : $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ . The photoluminescence properties and the energy transfer mechanism of the co-doped materials will be investigated and discussed.

## 2 Experimental

A series of  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Ce}^{3+}/\text{Tb}^{3+}$ -doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  ( $\text{La}_3\text{-Si}_8\text{N}_{11}\text{O}_4$ : $y\text{Ce}$ ,  $x\text{Tb}$ ,  $y = 0\text{--}0.15$ ,  $x = 0\text{--}0.30$ ) powder samples were synthesized *via* the high temperature solid-state reaction method.  $\alpha$ - $\text{Si}_3\text{N}_4$  (SN-E10, Ube Industries, Tokyo, Japan), LaN (laboratory made),  $\text{La}_2\text{O}_3$  (Shin-Etsu Chemical Co., Tokyo, Japan), CeN (laboratory made) and TbN (laboratory made) were thoroughly mixed with mortar and pestle for 15 min in a nitrogen-field glovebox ( $\text{H}_2\text{O} < 1$  ppm,  $\text{O}_2 < 1$  ppm). The powders were put into BN crucibles and fired at 1800 °C for 2 h under 1.0 MPa nitrogen atmosphere. After firing, the samples were gradually cooled to room temperature in the furnace under the  $\text{N}_2$  protection. Finally, the fired powders were finely ground using a mortar for further measurements.

The crystalline phase of the synthesized samples was collected on an X-ray diffraction (XRD, Smart Lab, Rigaku, Tokyo, Japan) operating at 40 kV and 40 mA and using  $\text{Cu}\alpha_1$  radiation ( $\lambda = 1.54056$  Å). A step size of  $0.02^\circ$  with a scan speed of  $10^\circ$  per minute over the  $2\theta$  range  $5\text{--}80^\circ$ .

Energy-dispersive X-ray spectroscopy (EDS) and mapping measurements of the cross-section particles were carried out at room temperature with a Hitachi SU-8000 scanning microscope at an accelerating voltage of 5 kV. SEM and cathodoluminescence (CL) measurements were performed using a field emission scanning electron microscope (SEM, Hitachi S4300, Tokyo, Japan) equipped with a CL system (Horiba MP32S/M, Horiba, Tokyo, Japan).

High-resolution transmission electron microscopy (TEM) images and the EDS mapping were recorded using a JEM-

3100FEF electron microscope (JEOL, Tokyo, Japan) fitted with the field emission gun at accelerating voltage of 300 kV.

Photoluminescence spectra at room temperature were analyzed with a Hitachi F-4500 spectrophotometer equipped with a Xe lamp. The diffuse reflectance spectra were measured with a UV-vis spectrophotometer (Ubest V560, Jasco, Tokyo, Japan), using a Spectralon diffusive white standard for calibration.

The fluorescence lifetime measurement was taken on a time-correlated single-photon counting fluorometer (TemPro, Horiba Jobin-Yvon, Tokyo, Japan) equipped with a NanoLED-370 nm with a pulse duration full width at half-maximum of  $\sim 1$  ns.

The temperature-dependent photoluminescence was measured in the range of  $25\text{--}250$  °C with a multichannel Photal MCPD-7000 detector, using a Xe lamp as an excitation source. The quantum efficiency (QE) measurements were done using a multichannel spectrometer (MCPD-7000, Otsuka Electronics, Tokyo, Japan), with a Xe lamp as an excitation source, and the  $^{\text{a}}\text{BaSiO}_4$  white standard was used for calibration. The external ( $\eta_0$ ) and internal ( $\eta_i$ ) QEs were calculated according to the following equations:<sup>55</sup>

$$\eta_0 = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda E(\lambda) d\lambda}$$

$$\eta_i = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda \{E(\lambda) - R(\lambda)\} d\lambda}$$

where  $E(\lambda)/h\nu$ ,  $E(\lambda)/h\nu$  and  $E(\lambda)/h\nu$  are the number of photons in the excitation, reflectance and emission spectra of the phosphor sample, respectively.

A white LED was fabricated by using a UV-LED chip (365 nm) and  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ :0.01Ce,0.05Tb (blue-green),  $\text{SrSi}_2\text{N}_2\text{O}_2$ :Eu (green) and  $\text{Sr}_2\text{Si}_5\text{N}_8$ :Eu (red) phosphors. The optical properties of the white LED were measured using an integrated sphere spectroradiometer system (LHS-1000, Everfine Co., Hangzhou, China). The operated current and voltage were 300 mA and 3.756 V, respectively.

## 3 Results and discussion

### 3.1 Phase identification

The XRD patterns of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ :1%Ce, $x\text{Tb}$  doped with varying  $\text{Tb}^{3+}$  concentrations ( $x = 0\text{--}0.3$ ) are shown in Fig. 1. All the diffraction peaks of the selected samples agree well with the standard data of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  (JCPDS card #48-1597), and no impurity phase is identified. It indicates that the doping of Ce and Tb does not change the phase purity of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  host. Moreover, the lattice parameters of samples decrease with increasing the Tb concentration ( $x$ ), as seen in Fig. 2. As reported by Grins *et al.*,  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  has two different La sites, with La1 being coordinated by 4 O/N and 2 O atoms and La2 atom coordinated by 5 O/N, 2 O and 1 N atoms (Fig. 1b).<sup>56</sup> According to the effective ionic radius of cations with varying coordination numbers (CN), the radius of both  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  is smaller than that of  $\text{La}^{3+}$ , as is listed in Table S1.<sup>†</sup><sup>57</sup> Therefore,



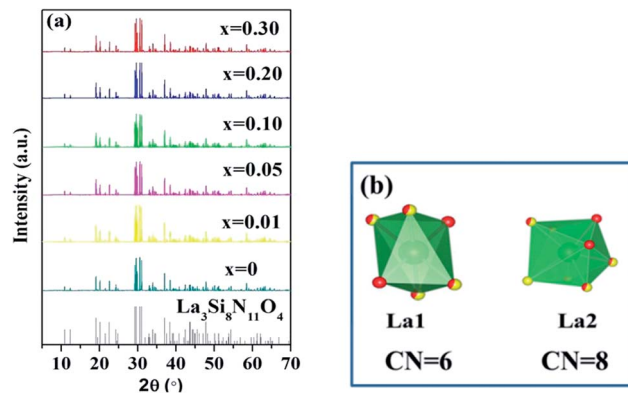


Fig. 1 XRD patterns of (a)  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},x\text{Tb}$  ( $x = 0-0.3$ ) and (b) the coordination environment of La1 and La2 in the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  host.

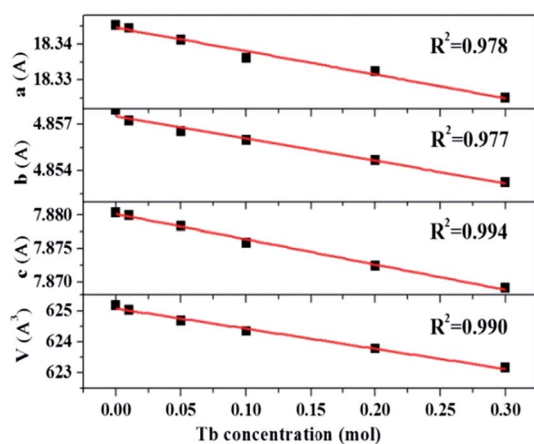


Fig. 2 Lattice parameters ( $a$ ,  $b$  and  $c$ ) and volume ( $V$ ) of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},x\text{Tb}$  ( $x = 0-0.3$ ).

when  $\text{La}^{3+}$  is partially replaced by  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  ions, the lattice parameters and the cell volume of the substituted samples will shrink to some extent, which is in line with the reduction of the lattice parameters.

### 3.2 SEM and TEM

In order to further confirm the composition uniformity of the samples, the SEM and TEM observations of the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$  phosphor were carried out, as illustrated in Fig. 3 and 4. The elemental mapping images evidence that La, Si, N, O, Ce and Tb are homogeneously distributed within the phosphor particles, which indicates that both Ce and Tb ions are accommodated in the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  lattice. As seen in Fig. 4a and c, Ce and Tb are distributed uniformly in the sample that is well crystallized. The  $d$ -spacing of the (11-2) crystal plane is 0.299 and 0.300 nm for  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$  and  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ , respectively. It further confirms the successful introduction of  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  into the lattice. The ratio of  $(\text{La} + \text{Ce} + \text{Tb})/\text{Si}$  is 0.396, which is close to the theoretical ratio of 0.375 (3 : 8), as is shown in Fig. S1.†

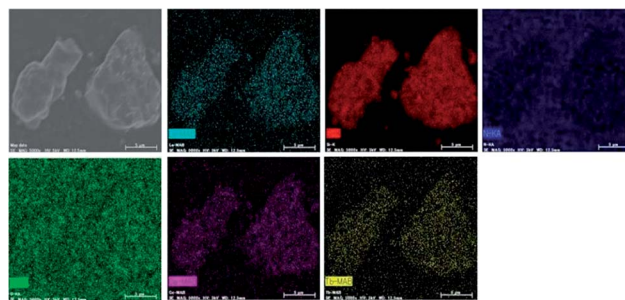


Fig. 3 SEM image and elemental mapping of La, Si, N, O, Ce, and Tb in  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$ .

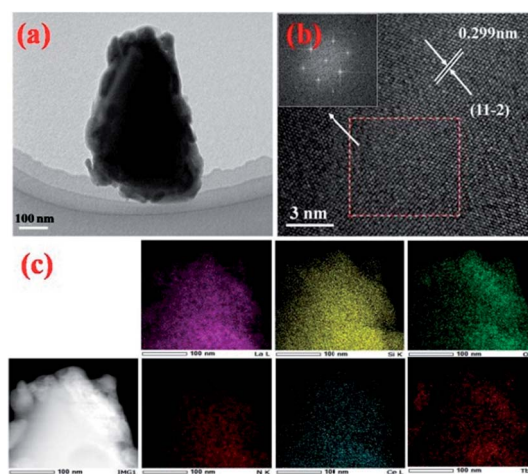


Fig. 4 (a) TEM image, (b) HRTEM images, and (c) elemental mapping of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$ . The inset of (b) shows the fast Fourier transforms of the HRTEM image.

### 3.3 Photoluminescence properties

The excitation and emission spectra of single- and co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phosphors are described in Fig. 5. As seen in Fig. 5a, the PLE spectrum of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}$ , monitored by 423 nm, consists of three distinct bands centered at 257, 340, and 360 nm, respectively. The strong PLE band at 340–370 nm matches well with the near-UV LED chip, indicating that the phosphor could be used in white LEDs. Under the 360 nm excitation, the phosphor exhibits a broad asymmetric emission band covering the spectral range of 380–500 nm and a maximum emission at 423 nm. The emission is assigned to the  $5d \rightarrow 4f$  electronic transitions of  $\text{Ce}^{3+}$ . The emission band can be divided into two sub-bands centered at 413 nm ( $24\,213\text{ cm}^{-1}$ ) and 442 nm ( $22\,624\text{ cm}^{-1}$ ) by Gaussian fitting (Fig. 4d). The energy difference between two sub-bands is about  $1589\text{ cm}^{-1}$ , which is close to  $2000\text{ cm}^{-1}$  (energy difference between  ${}^2\text{F}_{7/2}$  and  ${}^2\text{F}_{5/2}$  of  $\text{Ce}^{3+}$ ).

Fig. 5b shows the PL and PLE of the single  $\text{Tb}^{3+}$  doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  sample. The emission spectrum consists of several sharp peaks at 489, 543, 580 and 620 nm, which are assigned to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$  ( $j = 6, 5, 4, 3$ ) transitions of  $\text{Tb}^{3+}$ , respectively. The excitation spectrum is composed of a strong broad band spanning 200 to 400 nm, and has a maximum at 284 nm and a weak





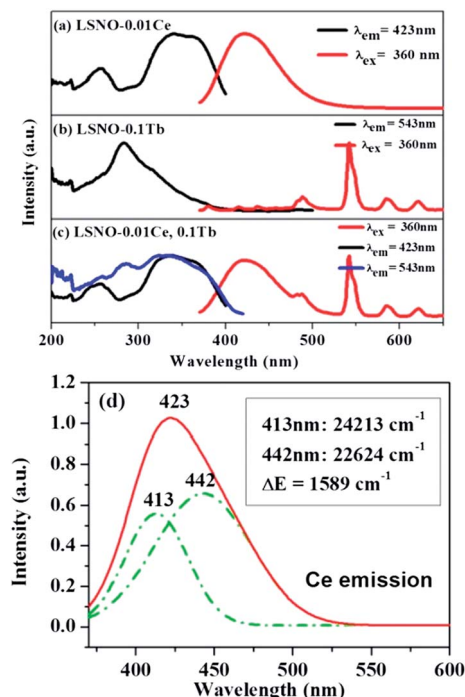


Fig. 5 PL and PLE of (a)  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}$ , (b)  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.05\text{Tb}$  and (c)  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, 0.05\text{Tb}$ , and (d) Gaussian splitting of the emission spectrum of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}$ .

band at  $\sim 480$  nm. It corresponds to the f-f electronic transitions of  $\text{Tb}^{3+}$ . It is clearly shown that there is a great spectral overlap between the emission band of  $\text{Ce}^{3+}$  and the excitation band of  $\text{Tb}^{3+}$ , which indicates the possibility of energy transfer from  $\text{Ce}^{3+}$  (sensitizer) to  $\text{Tb}^{3+}$  (activator) according to the Dexter theory.<sup>58</sup>

To confirm the energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  in  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$ , the photoluminescence properties of the co-doped samples were investigated, as shown in Fig. 5c. Clearly, the PLE spectrum monitored at 543 nm of  $\text{Tb}^{3+}$  exhibits not only a strong absorption band of  $\text{Tb}^{3+}$  in the range of 260–300 nm, but also contains a characteristic excitation band of  $\text{Ce}^{3+}$  in the spectral range of 300–400 nm. Additionally, the stronger  $\text{Tb}^{3+}$  emission appears under the excitation at 360 nm in the co-doped sample. It implies that the energy transfer from Ce to Tb occurs, and the emission of  $\text{Tb}^{3+}$  is significantly enhanced under the near-UV excitation (*i.e.*, 360 nm).

### 3.4 Cathodoluminescence (CL) spectra and mapping

Compared to PL with the weak excitation energy (photon: 0.5–6 eV), CL has the stronger excitation source (e-beam: 2–300 keV), which thus enables to provide the information of localized luminescence. As shown in Fig. 6, the CL images of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, 0.20\text{Tb}$ , taken at 418 nm ( $\text{Ce}^{3+}$ ) and 544 nm ( $\text{Tb}^{3+}$ ), are quite similar. It indicates that both the  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  emissions are from the same host lattice. Furthermore, with increasing  $x$  value from 0 to 0.20, the 418 nm emission decreases (from  $2.01 \times 10^5$  to  $1.52 \times 10^5$  cps), while the 544 nm emission increases (from 0 to  $0.58 \times 10^5$  cps). This is an evidence of the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ .

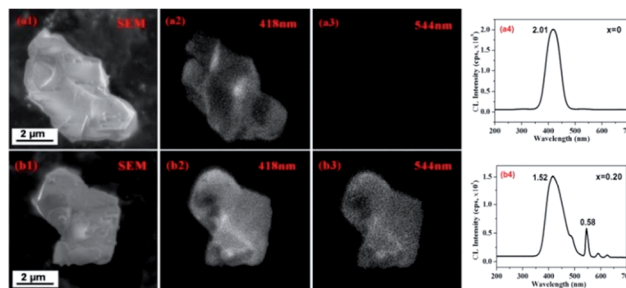


Fig. 6 SEM images (a1 and b1), CL images taken at 418 nm (a2 and b2) and 544 nm (a3 and b3) and CL spectra (a4 and b4) of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}$  and  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, 0.20\text{Tb}$ .

### 3.5 Energy transfer mechanism

Fig. 7 shows the emission spectra of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, x\text{Tb}$  with varying  $\text{Tb}^{3+}$  concentrations ( $x = 0-0.3$ ) under the 360 nm excitation. The PL intensity of  $\text{Ce}^{3+}$  decreases whereas the luminescence of  $\text{Tb}^{3+}$  at 543 nm increases, which intuitively supports the occurrence of the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ . The energy transfer efficiency ( $\eta_T$ ) can be computed by the following equation:<sup>51</sup>

$$\eta_T = 1 - I/I_0$$

where  $I_0$  and  $I$  are the emission peak intensity of  $\text{Ce}^{3+}$  in the absence and presence of  $\text{Tb}^{3+}$ , respectively. With increasing the  $\text{Tb}^{3+}$  doping concentration, the energy transfer efficiency increases and reaches the maximum of 59.1% when the  $\text{Tb}^{3+}$  concentration is 0.30, as shown in Fig. 7b.

The change of the fluorescence decay time is used to further verify the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$  in the  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, x\text{Tb}$  sample. The decay time of the 423 nm emission of  $\text{Ce}^{3+}$  nearly keeps unchanged with increasing the  $\text{Tb}^{3+}$  concentration, which is different from the change in peak emission intensity, as shown in Fig. 8. The reason for the unobvious change of lifetime and the decrease of emission intensity is that, the energy transfer rate is faster than the radiative transfer rate in the process of the electronic transitions of  $5d \rightarrow 4f$  of  $\text{Ce}^{3+}$  ions, and the fast energy transfer rate

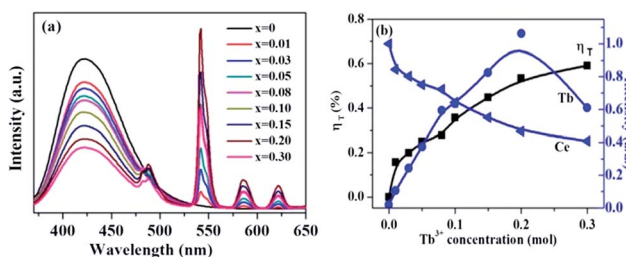


Fig. 7 (a) PL spectra of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}, x\text{Tb}$  with varying  $\text{Tb}^{3+}$  concentrations ( $x = 0-0.3$ ) under 360 nm excitation, and (b) the normalized peak intensity of the  $\text{Tb}^{3+}$  emission at 543 nm and the  $\text{Ce}^{3+}$  emission at 423 nm, and the energy transfer efficiency  $\eta_T$  as a function of the Tb concentration.



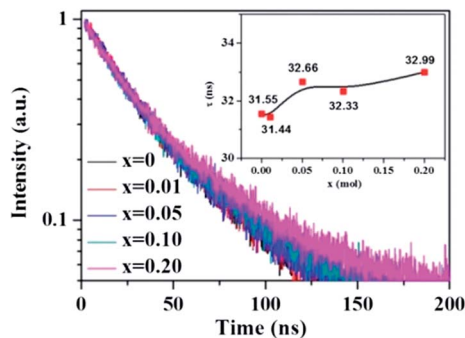


Fig. 8 Fluorescence decay curves and decay times of Ce<sup>3+</sup> in La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.01Ce,*x*Tb under 370 nm excitation and monitored at 423 nm.

can quench the emission intensity while not affect the life time. It is also true in the Ba<sub>2</sub>Y<sub>5</sub>B<sub>5</sub>O<sub>17</sub>:Ce,Tb phosphor.<sup>30</sup>

According to the energy transfer theory proposed by Dexter, concentration quenching is due to the energy transfer from one activator to another until an energy sink in the lattice is reached. As put forward by Blasse, the critical distance ( $R_{Ce-Tb}$ ) between Ce<sup>3+</sup> and Tb<sup>3+</sup> ions can be calculated as below:<sup>59</sup>

$$R_{Ce-Tb} = 2[3V/4\pi x_c N]^{1/3}$$

where  $N$  is the number of available sites for the dopant in the unit cell,  $V$  is the volume of the unit cell, and  $x_c$  is the total of the concentration of Ce<sup>3+</sup> and Tb<sup>3+</sup> at which the luminescence of Ce<sup>3+</sup> is half compared to the sample containing no Tb<sup>3+</sup> ions. In this work,  $N = 24$ ,  $V \approx 1272 \text{ \AA}^3$ , and  $x_c = 0.19$ . Thus, the  $R_{Ce-Tb}$  distance is calculated to be about 8.07 Å. It is well known that if the critical distance between sensitizer and activator is much bigger than 4 Å, the energy transfer from Ce<sup>3+</sup> and Tb<sup>3+</sup> mainly takes place *via* multipolar interaction rather than exchange interaction.<sup>60</sup> On the basis of the Dexter's energy transfer expression of multipolar interaction and Reisfeld's approximation, the following equation can be given as:<sup>60</sup>

$$I_0/I \propto C^{n/3}$$

where  $C$  is the sum of the content of Ce<sup>3+</sup> and Tb<sup>3+</sup>. The plots of ( $I_0/I$ ) versus  $C^{n/3}$  with  $n = 6, 8$ , and 10 correspond to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole

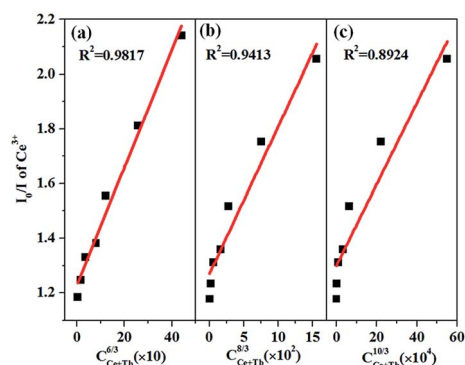


Fig. 9 Dependence of  $I_0/I$  of Ce<sup>3+</sup> on (a)  $C^{n/3}$ , (b)  $C^{n/3}$ , and (c)  $C^{n/3}$ .

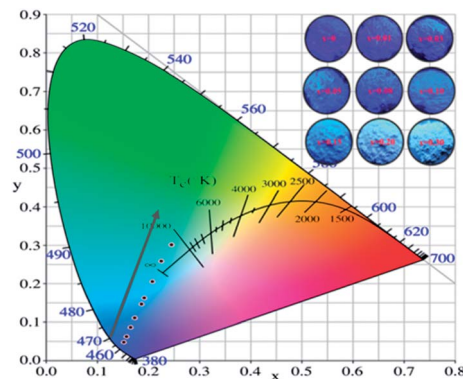


Fig. 10 CIE chromaticity coordinates and the color of La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.01Ce,*x*Tb phosphors under the 365 nm irradiation.

interactions, respectively. Fig. 9 illustrates the relationships between ( $I_0/I$ ) versus  $C$ . A linear relationship is well fitted at  $n = 6$ , which clearly indicates that the energy transfer mechanism is dipole-dipole interaction.

The Commission International de l'Eclairage (CIE) 1931 chromaticity coordinates of the La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.01Ce,*x*Tb were calculated, as shown in Fig. 10. The color can be changed from blue (0.1523, 0.0483) at  $x = 0$  to green (0.2455, 0.3013) at  $x = 0.3$ . The green emission of Tb<sup>3+</sup> dominates the luminescence when  $x$  is up to 0.1, which could be used as a potential green-emitting phosphor in near-UV LED driven white LEDs.

### 3.6 Quantum efficiency

The absorption, internal and external quantum (IQE and EQE) efficiencies of single- and co-doped La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:Ce,Tb samples under different wavelength excitations are shown in Fig. 11. Due to the stronger absorption in co-doped sample, the absorption, IQE and EQE of the La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.01Ce,0.05Tb under 360 nm excitation are about 55, 76.3 and 46.7%, while those of La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.05Tb are about 11, 77.7 and 8.3%, respectively. The PL intensity of Tb<sup>3+</sup> is improved by about 9 times under 360 nm excitation due to the strong energy transfer from Ce<sup>3+</sup> to Tb<sup>3+</sup>, as shown in Fig. 12.

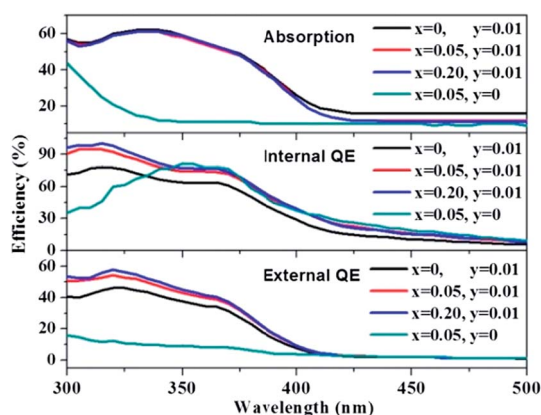


Fig. 11 Absorption, quantum efficiency of La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:0.01Ce,*x*Tb ( $x = 0, 0.05, 0.20$ ) and La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:*y*Ce,*x*Tb ( $y = 0, x = 0.05$ ).



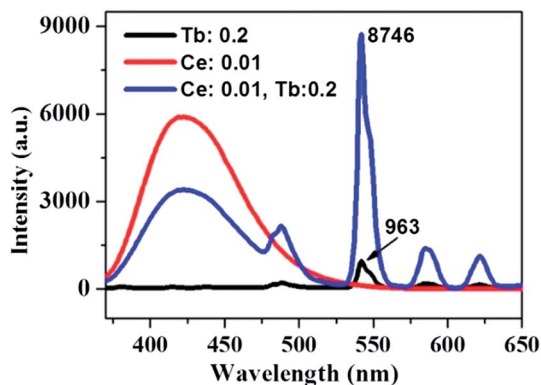


Fig. 12 PL spectra of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.2\text{Tb}$ ,  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}$  and  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.2\text{Tb}$  under the 360 nm excitation.

### 3.7 Thermal quenching

Thermal stability of a phosphor is an indispensable factor that cannot be neglected for its application in white LEDs. Fig. 13 shows the temperature-dependent luminescence of the Ce-, Tb-single doped and co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  samples under 360 nm excitation. For the  $\text{Ce}^{3+}$  emission at 423 nm, the thermal quenching is nearly equivalent for both the single- and co-doped samples. On the other hand, for the  $\text{Tb}^{3+}$  emission, the  $\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  samples show smaller thermal quenching than either the  $\text{Ce}^{3+}$ - or the  $\text{Tb}^{3+}$ -doped sample, which indicates that the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$  contributes significantly to the enhanced thermal stability.

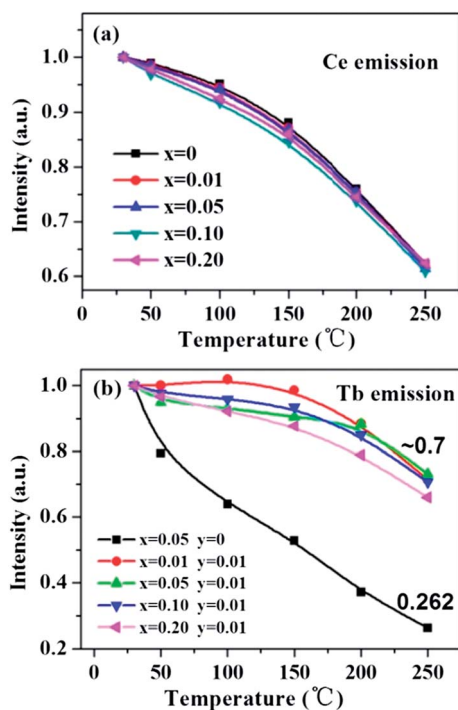


Fig. 13 Temperature dependence of (a) the Ce emission intensity in  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce}_x\text{Tb}$  and (b) the Tb emission intensity in  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:y\text{Ce}_x\text{Tb}$  ( $y = 0, 0.05$ ).

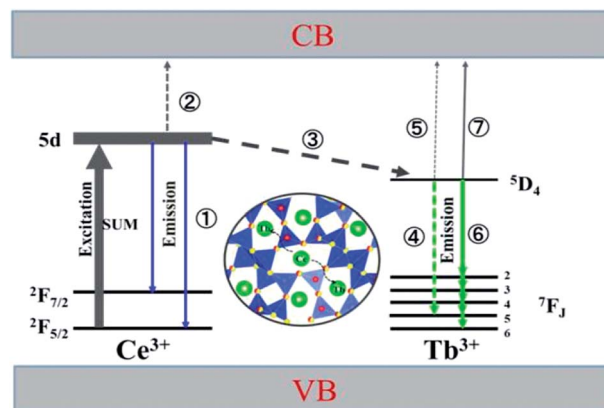


Fig. 14 The model of the  $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$  energy transfer and the emission processes of  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$ .

Based on the thermal activation model, the excited 5d electrons of  $\text{Ce}^{3+}$  will be mainly involved in three processes, as illustrated in Fig. 14.<sup>30</sup> The first process (1), defined as  $N_{\text{EM}}$ , is the intrinsic emission electrons of the lowest 5d state of  $\text{Ce}^{3+}$ . The second process (2), defined as  $N_{\text{TQ}}$ , is the thermal activation electrons and equal to  $Ae^{-\Delta E/kT}$  ( $A$  is a constant,  $\Delta E$  is the activation energy for thermal quenching, and  $k$  is Boltzmann constant). And the third process (3), named as  $N_{\text{ET}}$ , is the energy transfer electrons between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$ . Therefore, the energy transfer efficiency ( $\eta_{\text{ET}}$ ) can be written as:

$$\eta_{\text{ET}} = \frac{N_{\text{ET}}}{N_{\text{SUM}}} = \frac{N_{\text{ET}}}{N_{\text{EM}} + N_{\text{TQ}} + N_{\text{ET}}} \quad (1)$$

As the thermal quenching behavior of the  $\text{Ce}^{3+}$  luminescence of the single- and co-doped samples is almost the same, the luminescence of  $\text{Ce}^{3+}$  changes very little at a certain temperature. It indicates that the change in energy transfer rate is mainly attributed to the thermal activation electrons rather than the intrinsic emission electrons when the temperature increases. Therefore, the number of energy transfer electrons increases, which thus contributes to the increased  $\text{Tb}^{3+}$  luminescence in the co-doped samples.

At the same time, the electrons, coming from the energy transfer of  $\text{Ce}^{3+}$ , will be separated into process 4 ( $N_{\text{EM-Ce}}$ ) and process 5 ( $N_{\text{TQ-Ce}}$ ), which stands for the intrinsic emission and thermal activation electrons of  $\text{Tb}^{3+}$ . That is to say, the emission of  $\text{Tb}^{3+}$  does not contain the intrinsic emission of  $\text{Tb}^{3+}$  (process 6,  $N_{\text{EM-Tb}}$ ) but it originated from the energy transfer from  $\text{Ce}^{3+}$ . Therefore, the temperature-dependent luminescence of  $\text{Tb}^{3+}$  in the single-doped ( $\eta_{\text{EM-S-Tb}}$ ) and the co-doped sample ( $\eta_{\text{EM-C-Tb}}$ ) can be calculated by the following equations:

$$\eta_{\text{EM-S-Tb}} = \frac{N_{\text{EM-Tb}}}{N_{\text{EM-Tb}} + N_{\text{TQ-Tb}}} \quad (2)$$

$$\eta_{\text{EM-C-Tb}} = \frac{N_{\text{ET}} \frac{N_{\text{EM-Ce}}}{N_{\text{EM-Ce}} + N_{\text{TQ-Ce}}} + N_{\text{EM-Tb}}}{N_{\text{ET}} + N_{\text{EM-Tb}} + N_{\text{TQ-Tb}}} \quad (3)$$





where  $N_{TQ-Tb}$  is the thermal activation electrons of the intrinsic  $Tb^{3+}$ . For the co-doped phosphor, we may infer that the electrons coming from the energy transfer of  $Ce^{3+}$  mainly contribute to the emission rather than thermal activation, and the emission of  $Tb^{3+}$  hence shows a higher thermal stability. If  $N_{EM-Ce}$  is smaller than  $N_{TQ-Ce}$ , the emission of  $Tb^{3+}$  would exhibit a lower thermal stability than that in the single-doped sample.

Additionally, as the temperature increases from 30 to 250 °C, the CIE chromaticity coordinates of  $La_3Si_8N_{11}O_4:0.01Ce,0.20Tb$  show a small variation (Fig. 15). Compared to the CIE  $x$  value, the CIE  $y$  value has a greater change. It is mainly due to the increasing ratio of the  $Tb^{3+}$  emission intensity to the  $Ce^{3+}$  one. This agrees well with the faster quenching of the  $Ce^{3+}$  emission with increasing the temperature, as discussed above.

As aforementioned, the temperature-dependent luminescence of  $Tb^{3+}$  ( $\eta_{EM-C-Tb}$ ) will be enhanced owing to the increased number of electrons from  $Ce^{3+}$  ( $N_{ET}$ ) via the energy transfer. As seen in Fig. 16, the emission intensity of  $Tb^{3+}$  in  $La_3Si_8N_{11}O_4:yCe, 0.05Tb$  ( $y = 0-0.20$ ) samples is enhanced as the  $Ce^{3+}$  concentration increases. It indicates that the higher  $Ce^{3+}$  concentration generates more electrons that are transferred to  $Tb^{3+}$ , which is well accordance with the analysis from eqn (1) and (3). Moreover, the change of the decay time of  $La_3Si_8N_{11}O_4:yCe,0.05Tb$  ( $y = 0-0.20$ ) also provides the evidence that more electrons are transferred from  $Ce^{3+}$  to  $Tb^{3+}$  with increasing the  $Ce^{3+}$  concentration, as shown in Fig. 17. In addition, as shown in Fig. 18, the thermal quenching of the  $Tb^{3+}$  emission in the co-

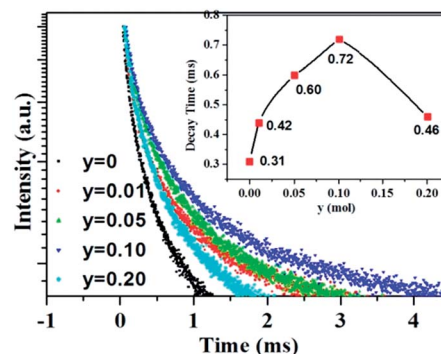


Fig. 17 Luminescence decay curves of the  $La_3Si_8N_{11}O_4:yCe,0.05Tb$  ( $y = 0-0.20$ ) samples under 370 nm excitation, monitored by the peak wavelength of  $Tb^{3+}$  (544 nm).

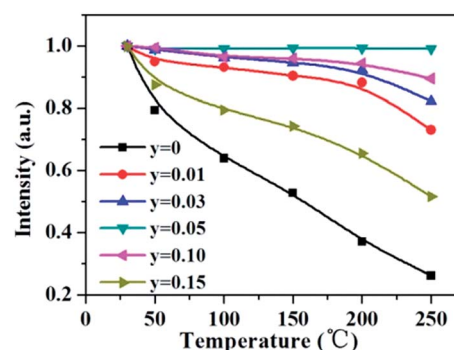


Fig. 18 Temperature dependence of the  $Tb^{3+}$  emission intensity in  $La_3Si_8N_{11}O_4:yCe,0.05Tb$  ( $y = 0-0.15$ ) under the 360 nm excitation.

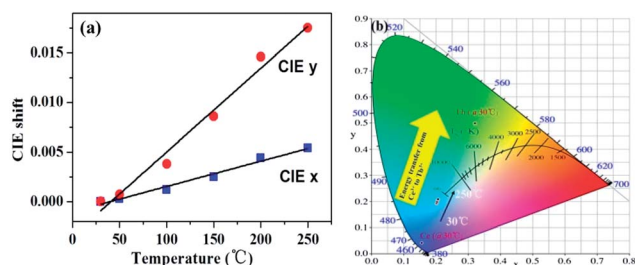


Fig. 15 Temperature-dependent (a) CIE chromaticity coordinates and (b) the color point shift of  $La_3Si_8N_{11}O_4:0.01Ce,0.20Tb$  sample.

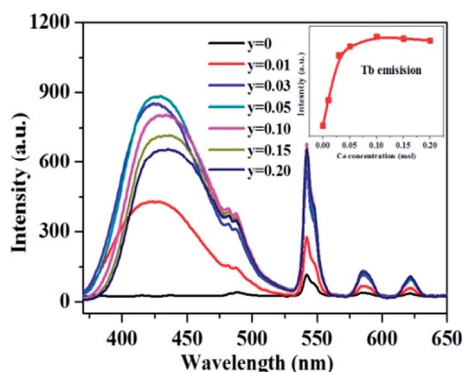


Fig. 16 PL spectra and the peak intensity of  $Tb^{3+}$  emission under 360 nm excitation in the  $La_3Si_8N_{11}O_4:yCe,0.05Tb$  ( $y = 0-0.15$ ) samples.

doped  $La_3Si_8N_{11}O_4:yCe,0.05Tb$  ( $y = 0-0.20$ ) samples is smaller than that in the single-doped sample. When the  $Ce^{3+}$  concentration increases, the thermal stability of the  $Tb^{3+}$  emission gradually enhances. At 200 °C, the emission intensity of the single-doped sample ( $La_3Si_8N_{11}O_4:0.05Tb$ ) declines by 63%, whereas it loses only by 10% in the co-doped samples ( $La_3Si_8N_{11}O_4:yCe,0.05Tb$ ,  $y = 0.01-0.10$ ). The small reduction in luminescence of  $Tb^{3+}$  in the co-doped samples implies that the energy transfer from  $Ce^{3+}$  to  $Tb^{3+}$  dominantly contributes to the emission of  $Tb^{3+}$ . The thermal quenching of the sample at  $y = 0.15$  becomes much larger than others, which may be due to the increased lattice distortion caused by the substitution of La by Ce and Tb.

### 3.8 Applications in white LEDs

In order to testify the suitability of the blue-green  $La_3Si_8N_{11}O_4:0.01Ce,0.05Tb$  phosphor in white LEDs, it was mixed with  $SrSi_2N_2O_2:Eu$  (green) and  $Sr_2Si_5N_8:Eu$  (red) phosphors to form a phosphor blend, and then pumped by a UV-LED chip (365 nm). As seen in Fig. 19, the white LED has the chromaticity coordinates of  $x = 0.391$ ,  $y = 0.361$ , a correlated color temperature (CCT) of 3570 K and a high color rendering index (CRI) of 90.2. The luminous efficiency of this white LED is as low as  $4.4 \text{ lm W}^{-1}$ , which is mainly due to the low efficiency of the UV-LED



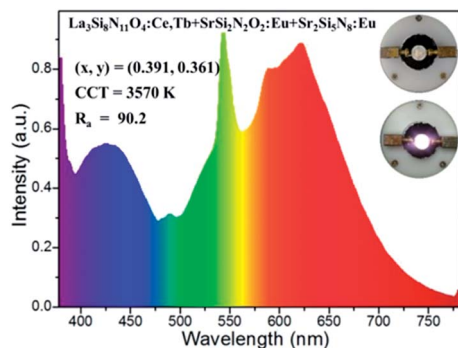


Fig. 19 The electroluminescence spectrum of the white LED using a UV-LED chip (365 nm) and  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.05\text{Tb}$ ,  $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$  and  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$  phosphors. The inset shows images of the white LED (power off and on).

chip ( $0.78 \text{ lm W}^{-1}$ ). These results demonstrate that the title phosphor could be a promising blue-green phosphor for use in UV-LED driven white LEDs.

## 4 Conclusions

The energy transfer between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  was realized in the co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  phosphors. The emission color could be tuned from blue ( $\text{Ce}^{3+}$ ) to green ( $\text{Tb}^{3+}$ ) under the 360 nm excitation, and the  $\text{Tb}^{3+}$  luminescence of the co-doped sample was improved by 9 times owing to the energy transfer of  $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ . The external quantum efficiency of  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{-Ce},0.05\text{Tb}$  was 46.7% under the 360 nm excitation, which is much higher than that of 8.3% for  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.05\text{Tb}$ . The thermal quenching of the co-doped samples was significantly reduced, with the luminescence loss of  $\text{Tb}^{3+}$  emission decreasing from 74 to 30% at  $250^\circ\text{C}$ . A UV-LED driven white LED using  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.05\text{Tb}$ ,  $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$  and  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$  phosphors was fabricated, and it had a correlated color temperature of 3570 K, a high color rendering index of 90.2, and a luminous efficacy of  $4.4 \text{ lm W}^{-1}$ . It indicates that the  $\text{Ce}^{3+}/\text{Tb}^{3+}$  co-doped  $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4$  ( $\text{La}_3\text{Si}_8\text{N}_{11}\text{O}_4:0.01\text{Ce},0.05\text{Tb}$ ) would be an interesting blue-green phosphor for UV LEDs.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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