



Cite this: *RSC Adv.*, 2019, 9, 4295

# Luminescence properties and energy transfer of $\text{K}_3\text{LuF}_6:\text{Tb}^{3+}, \text{Eu}^{3+}$ multicolor phosphors with a cryolite structure†

Dan Yang,<sup>a</sup> Libing Liao,<sup>ID</sup> \*<sup>a</sup> Qingfeng Guo,<sup>ID</sup> \*<sup>bc</sup> Lefu Mei,<sup>\*,a</sup> Haikun Liu,<sup>a</sup> Tianshuai Zhou<sup>a</sup> and Huan Ye<sup>bc</sup>

In recent years, compounds with a cryolite structure have become excellent hosts for luminescent materials. In this paper,  $\text{Tb}^{3+}$  doped and  $\text{Tb}^{3+}/\text{Eu}^{3+}$  co-doped  $\text{K}_3\text{LuF}_6$  phosphors were prepared via a high temperature solid phase sintering method. The XRD, SEM, as well as photoluminescence excitation (PLE) and emission (PL) spectra were measured to investigate the structure and luminescence properties of the as-prepared samples. In the  $\text{Tb}^{3+}/\text{Eu}^{3+}$  co-doped  $\text{K}_3\text{LuF}_6$  samples, both characteristic emission spectra of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  could be observed and the emission color of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+}, x\text{Eu}^{3+}$  phosphors could be adjusted from green to yellowish pink and the corresponding CIE values could be regulated from (0.2781, 0.5407) in the green area to (0.4331, 0.3556) in the yellowish pink area by controlling the concentration ratio of  $\text{Eu}^{3+}/\text{Tb}^{3+}$ . In addition, the energy transfer mechanism in  $\text{Tb}^{3+}/\text{Eu}^{3+}$  co-doped  $\text{K}_3\text{LuF}_6$  was calculated to be a quadrupole–quadrupole interaction from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  based on the Dexter's equation.

Received 7th December 2018

Accepted 15th January 2019

DOI: 10.1039/c8ra10059d

rsc.li/rsc-advances

## 1. Introduction

Fluoride compounds are potential hosts for luminescent materials due to their suitable chemical stability and excellent luminous properties, and as such, have received a lot of attentions over the past few decades.<sup>1–4</sup> Cryolite is an important kind of fluoride compound, the chemical formula of which can be expressed as  $\text{M}_3\text{NF}_6$ , where M represents monovalent cations such as alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ) and  $\text{NH}_4^+$ , and the sites of N can be occupied by trivalent cations, that is  $\text{Al}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ga}^{3+}$ , etc.<sup>5,6</sup> In addition, the N sites can also be occupied by rare earth ions by isomorphic replacement in the cryolite lattice, such as  $\text{K}_3\text{GaF}_6$ ,<sup>7</sup>  $\text{K}_3\text{InF}_6$ ,<sup>8</sup> and  $\text{K}_3\text{LuF}_6$ .<sup>9</sup> Since the luminescence behavior of rare earth ions depends on the matrix, it is significant to explore novel cryolite luminescent materials.

On the other hand, multicolor single-phase phosphors occupy an important seat in the field of luminescent materials. In particular, rare-earth ion-doped luminescent materials mixed with blue and UV LEDs are fabricated to produce white light. However, a traditional single-color single-phase strategy

usually requires a complicated synthetic process, multiple excitation wavelengths with different responses of the various dopants to the excitation wavelength and reabsorption of the dopant.<sup>10</sup> Single excitation wavelength excited phosphors with multicolor emissions (cyan-emitting, blue-green-emitting, and blue-red-emitting phosphors) can efficiently avoid the above problems and make it easier to obtain a phosphor with high luminous efficiency, excellent color rendering index (CRI), good thermal and chromatic stability. Accordingly, multicolor single-phase phosphors have received attention over the past few decades.<sup>11–13</sup>

Energy transfer is an important way to realize single-phase multicolor phosphors, which have been investigated in abundant hosts.<sup>14</sup> As we know, energy transfer is achieved by ion pairs from a sensitizer to activator, such as  $\text{Eu}^{2+}/\text{Tb}^{3+}$ ,  $\text{Ce}^{3+}/\text{Eu}^{2+}$ ,  $\text{Ce}^{3+}/\text{Dy}^{3+}$ ,  $\text{Tb}^{3+}/\text{Eu}^{3+}$ ,  $\text{Er}^{3+}/\text{Sm}^{3+}$ ,  $\text{Tm}^{3+}/\text{Dy}^{3+}$  and so on.<sup>15–20</sup> Due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  electronic transitions,  $\text{Eu}^{3+}$ -doped luminescent materials can emit strong red light.<sup>21</sup>  $\text{Tb}^{3+}$  has been widely used together with  $\text{Eu}^{3+}$  to produce multicolor emission by means of energy transfer, such as in  $\text{CaMoO}_4:\text{Tb}^{3+}/\text{Eu}^{3+}$ ,<sup>22</sup>  $\text{Ba}_2\text{La}_3(\text{SiO}_4)_3\text{F}:\text{Tb}^{3+}/\text{Eu}^{3+}$ , and<sup>23</sup>  $\text{Na}_2\text{MgSiO}_4:\text{Tb}^{3+}/\text{Eu}^{3+}$ .<sup>24</sup> However, until now, there have been no reports on the crystal structure, luminescence properties and energy transfer investigations of multicolor-emitting  $\text{K}_3\text{LuF}_6:\text{Tb}^{3+}, \text{Eu}^{3+}$  phosphors with a cryolite structure.

In the present work,  $\text{Tb}^{3+}$  and  $\text{Tb}^{3+}/\text{Eu}^{3+}$  activated cryolite-type  $\text{K}_3\text{LuF}_6$  compounds were synthesized in a simple way and the crystal structure and luminescence properties, as well as the energy transfer mechanism between  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in  $\text{K}_3\text{LuF}_6$

<sup>a</sup>Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences, Beijing 100083, China. E-mail: clayl@cugb.edu.cn; mlj@cugb.edu.cn

<sup>b</sup>School of Gemology, China University of Geosciences, Beijing 100083, China

<sup>c</sup>Jewelry and Mineral Materials Laboratory of Experimental Teaching Demonstration Center, Beijing, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra10059d



were thoroughly studied. Benefiting from the crystal field environment of the cryolite-type samples, the emission color of  $\text{K}_3\text{LuF}_6:\text{Tb}^{3+},\text{Eu}^{3+}$  could be continuously regulated from green to yellowish pink by changing the content ratio of  $\text{Tb}^{3+}/\text{Eu}^{3+}$ .

## 2. Experimental section

### 2.1. Materials and synthesis

$\text{K}_3\text{LuF}_6:x\text{Tb}^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.10, 0.12$  and  $0.13$ ) and  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0.03, 0.05, 0.07, 0.10$  and  $0.13$ ) phosphors were prepared *via* a high temperature solid-state method. The raw materials included  $\text{K}_2\text{CO}_3$  (AR),  $\text{Lu}_2\text{O}_3$  (99.99%),  $\text{NH}_4\text{HF}_2$  (AR),  $\text{Eu}_2\text{O}_3$  (99.99%) and  $\text{Tb}_4\text{O}_7$  (99.99%). Firstly, the raw materials were weighed according to the stoichiometric ratios of the reactions and were then ground in a mortar for nearly 10 min, resulting in a uniform mixture. Considering the loss of fluorine sources at high temperatures, a 30% excess of  $\text{NH}_4\text{HF}_2$  was required during the weighing process. Secondly, the mixture was moved to a furnace and heated at heating rate of  $4^\circ \text{min}^{-1}$  and was maintained at  $800^\circ \text{C}$  for 3 h under an argon atmosphere. Finally, the systems were naturally cooled down to room-temperature and evenly re-ground prior to characterization.

### 2.2. Characterization

The powder X-ray diffraction (PXRD) measurements of the phosphors were performed using a Bruker Corporation D8 powder X-ray diffractometer (Germany) equipped with a  $\text{Cu } \alpha$  radiation source at  $0.15406 \text{ nm}$ , a tube voltage of  $40 \text{ kV}$  and a tube current of  $40 \text{ mA}$ . The step scanning rate used was  $8^\circ \text{min}^{-1}$  over the  $2\theta$  range from  $10^\circ$  to  $70^\circ$ . Morphological analysis of the compounds was carried out using a scanning electron microscope (SEM, JSM-6701F, Hitachi, Japan). The photoluminescence (PL) and photoluminescence excitation behavior were measured using a Hitachi F-4600 fluorescence spectrophotometer at room temperature, with a xenon lamp ( $400 \text{ V}, 150 \text{ W}$ ) acting as the light source.

## 3. Results and discussion

### 3.1. Crystal structure

The PXRD patterns of the as-prepared  $\text{K}_3\text{LuF}_6:x\text{Tb}^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.1, 0.12$  and  $0.13$ ) and  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) phosphors are shown in Fig. 1(a) and (b). The standard PXRD pattern of  $\text{K}_3\text{LuF}_6$  (JCPDS no. 27-467) is shown as a reference. As shown in Fig. 1(a) and (b), all of the PXRD patterns of the as-prepared  $\text{K}_3\text{LuF}_6:\text{Tb}^{3+}$

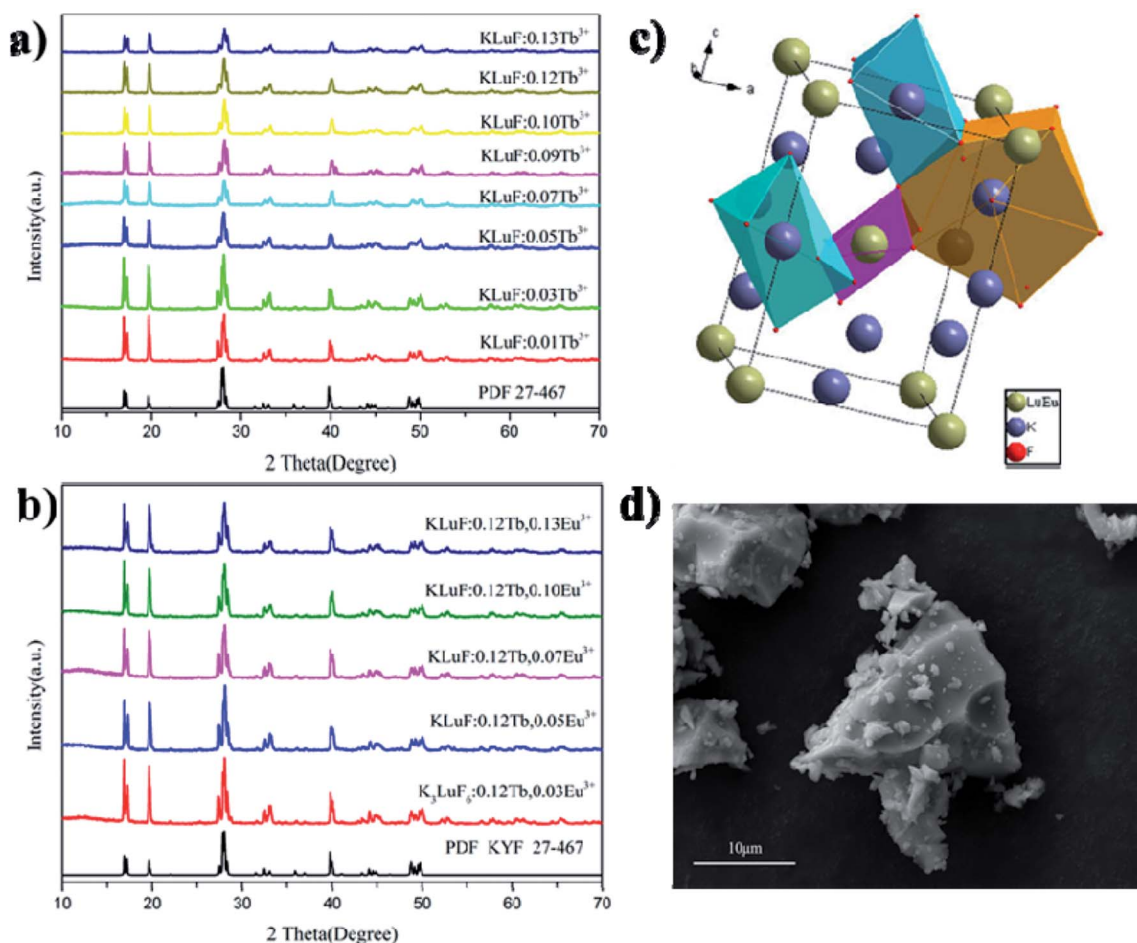


Fig. 1 (a) The PXRD patterns of the as-prepared  $\text{K}_3\text{LuF}_6:x\text{Tb}^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.10, 0.12$  and  $0.13$ ) and (b)  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0.03, 0.05, 0.07, 0.10$  and  $0.13$ ) phosphors, (c) the crystal structure of  $\text{K}_3\text{LuF}_6$ , and (d) the SEM image of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},0.07\text{Eu}^{3+}$  sample.

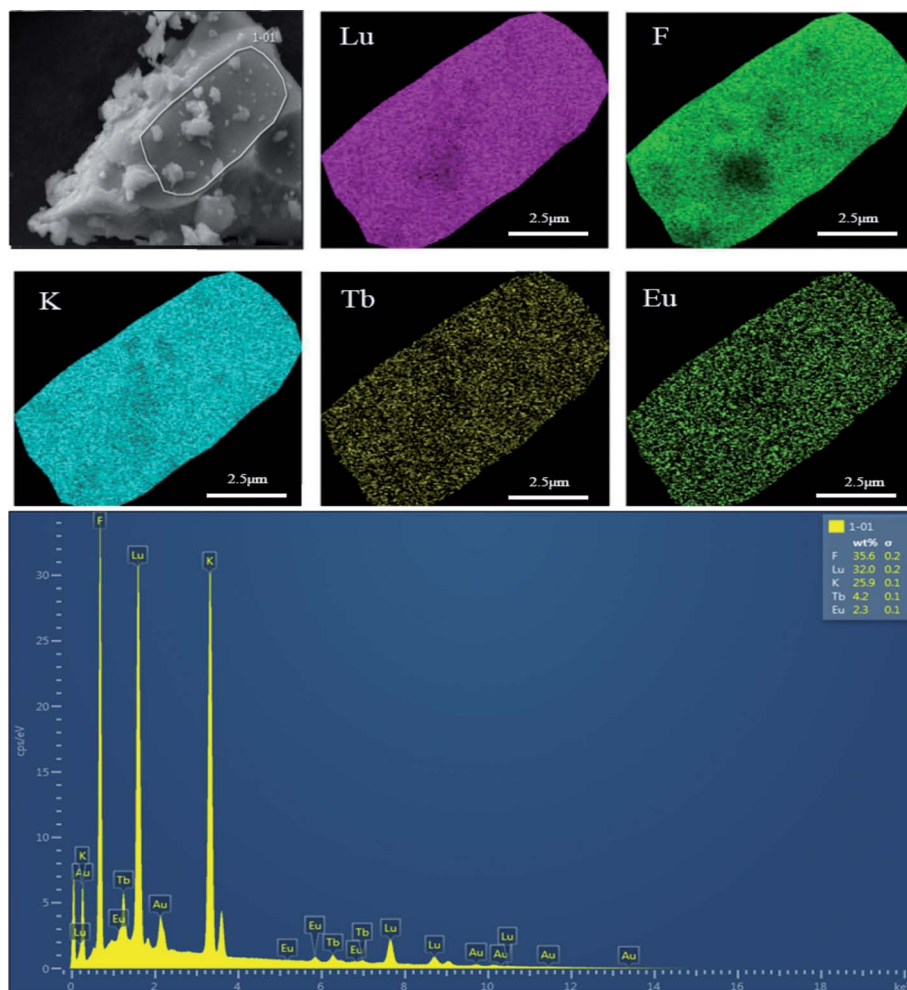


Fig. 2 SEM image, elemental mapping images and EDX spectrum of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},0.07\text{Eu}^{3+}$  phosphor.

and  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},\text{Eu}^{3+}$  samples can be accurately assigned to the standard card of  $\text{K}_3\text{LuF}_6$ , without the appearance of any impurity peaks, which indicates that the introduction of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in  $\text{K}_3\text{LuF}_6$  does not bring about any significant changes in the crystal structure. Fig. 1(c) shows the crystal structure of  $\text{K}_3\text{LuF}_6$ , which belongs to a monoclinic phase with a space group of  $P2_1/n$ . As depicted in Fig. 1(c), the Lu atom coordinates to six F atoms forming  $[\text{LuF}_6]$  octahedra, with the Lu atom in the centre. Two nonequivalent sites for the K atoms can be found in the crystal structure of  $\text{K}_3\text{LuF}_6$ , that is, twelve-coordinated K and six-coordinated K. Based on the charge balance and effective ionic radii,  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  were thought to occupy the sites of  $\text{Lu}^{3+}$ . Fig. 1(d) shows the SEM image of  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},0.07\text{Eu}^{3+}$ , which indicates the prepared sample with an irregular shape and the particle size ranges from a few hundred nanometers to dozens of microns (Fig. 2).

The elemental composition and distribution of the prepared  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},0.07\text{Eu}^{3+}$  were investigated and the results are shown in Fig. 3. In addition, the elemental composition and distribution of the prepared  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.10, \text{ and } 0.13$ ) are shown in Fig. S1–S6,<sup>†</sup> among which the Au element was introduced to enhance the conductivity of the material during testing. The particles in all the

samples seem like blocks with aggregation. The energy-dispersive X-ray (EDX) spectrum illustrates the existence of elemental K, Lu, F, Tb, and Eu in the sample, except for in the  $\text{Tb}^{3+}$  single-doped sample. Moreover, the elemental mapping results confirmed that all of the elements in the sample were homogeneously distributed over the whole area.

### 3.2. Photoluminescence properties and energy transfer process

Fig. 3(a) shows the PLE ( $\lambda_{\text{em}} = 550 \text{ nm}$ ) and PL ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ) spectra of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+}$  phosphor. As depicted in Fig. 3(a), the PLE spectrum of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+}$  sample shows typical transitions of  $\text{Tb}^{3+}$  ranging from 310 to 460 nm, attributed to  ${}^7\text{F}_6\text{-}{}^5\text{H}_7$  (315 nm),  ${}^7\text{F}_6\text{-}{}^5\text{D}_2$  (340 and 351 nm),  ${}^7\text{F}_6\text{-}{}^5\text{D}_4$  (357 nm),  ${}^7\text{F}_6\text{-}{}^5\text{D}_3$  (375 nm), and  ${}^7\text{F}_6\text{-}{}^5\text{G}_6$  (440 nm), respectively. The excitation peak at 375 nm ( ${}^7\text{F}_6\text{-}{}^5\text{D}_3$ ) is the most intense, matching well with near ultraviolet light LED chips, indicating that this sample has the potential for application in LEDs. When the phosphor was monitored at 375 nm, the PL spectrum of the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+}$  sample exhibited several peaks located at 488/499, 540/550, 586/599, and 624 nm, respectively. These peaks can be assigned as the characteristic

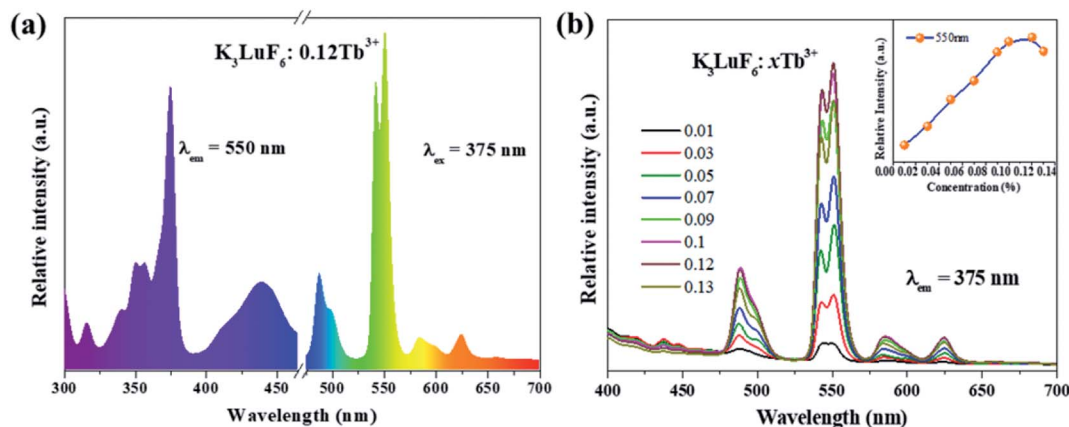


Fig. 3 (a) The photoluminescence excitation (PLE) ( $\lambda_{em} = 550$  nm) and emission (PL) ( $\lambda_{ex} = 375$  nm) spectra of the  $K_3LuF_6:0.12Tb^{3+}$  phosphor, and (b) the emission PL spectra ( $\lambda_{ex} = 375$  nm) of the  $K_3LuF_6:xTb^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.10, 0.12$  and  $0.13$ ) phosphors. The inset depicts the relative emission-intensity trends for the 550 nm peak ( $^5D_4-^7F_3$ ) in terms of the  $Tb^{3+}$  concentration.

emission of  $^5D_4-^7F_n$  ( $n = 6, 5, 5$  and  $3$ ). Fig. 3(b) shows the emission PL spectra of the  $K_3LuF_6:xTb^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.1, 0.12$  and  $0.13$ ) phosphors monitored at 375 nm, and the inset depicts the relative emission-intensity trends for the 550 nm peak ( $^5D_4-^7F_3$ ) regarding the  $Tb^{3+}$  concentration. Upon 375 nm excitation, all of the PL spectra of the  $K_3LuF_6-xTb^{3+}$  samples showed characteristic  $Tb^{3+}$  emission peaks, attributed to  $J = 6, 5, 4$ , and  $3$ . It is well known that the emission intensity of the  $^5D_3-^7F_j$  ( $J = 6, 5, 4$ , and  $3$ ) transitions of  $Tb^{3+}$  are quenched upon an increase in the  $Tb^{3+}$  concentration, ascribed to the cross-relaxation effect regarding the  $^5D_3-^7F_j$  levels.<sup>25-27</sup> Meanwhile, the emission intensity for the 550 nm ( $^5D_4-^7F_3$ ) peak increased upon an increase in the concentration of the  $Tb^{3+}$  concentration up to  $K_3LuF_6:0.12Tb^{3+}$ , and then it decreased due to concentration quenching.<sup>28</sup> Thus, the  $Tb^{3+}$  doping concentration was fixed at 0.12 (mol) for the co-doping of  $Tb^{3+}$  and  $Eu^{3+}$  in  $K_3LuF_6$ .

In order to further investigate the possibility of energy transfer behavior between  $Tb^{3+}$  and  $Eu^{3+}$  in  $K_3LuF_6$ ,

$K_3LuF_6:0.12Tb^{3+}, xEu^{3+}$  ( $x = 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) phosphors were prepared. The PLE and PL spectra of the  $Tb^{3+}$  and  $Eu^{3+}$  single-doped, as well as  $Tb^{3+}/Eu^{3+}$  co-doped  $K_3LuF_6$  phosphors are shown in Fig. 4. Under 393 nm excitation, the as-prepared  $K_3LuF_6:0.1Eu^{3+}$  sample shows sharp peaks at 579, 590, 613, 624, and 656 nm in Fig. 4(a), which are due to the  $^5D_0-^7F_0, ^5D_0-^7F_1, ^5D_0-^7F_2, ^5D_0-^7F_3,$  and  $^5D_0-^7F_4$  transitions of  $Eu^{3+}$ , respectively. In addition, the emission intensity of the peak at 613 nm is the highest among the transitions of  $Eu^{3+}$ , as shown in Fig. 4(b). When monitored at 613 nm, the PLE spectrum of  $K_3LuF_6:0.1Eu^{3+}$  exhibits a series of sharp excitation bands between 300 and 500 nm, centered at 318, 361, 379, 393, and 414 nm, which can be attributed to the  $^7F_0-^5H_5, ^7F_0-^5D_4, ^7F_0-^5L_6, ^7F_0-^5L_7$  and  $^7F_0-^5D_3$  transitions, respectively.<sup>29,30</sup> The strongest excitation peak can be obviously observed at 393 nm. The PLE and PL spectra of the  $K_3LuF_6:0.12Tb^{3+}, 0.1Eu^{3+}$  phosphor are illustrated in Fig. 4(b). As shown in Fig. 4(c), when the co-doped sample was excited by near ultraviolet light at 375 nm, both characteristic emission peaks of  $Tb^{3+}$  and  $Eu^{3+}$  could be

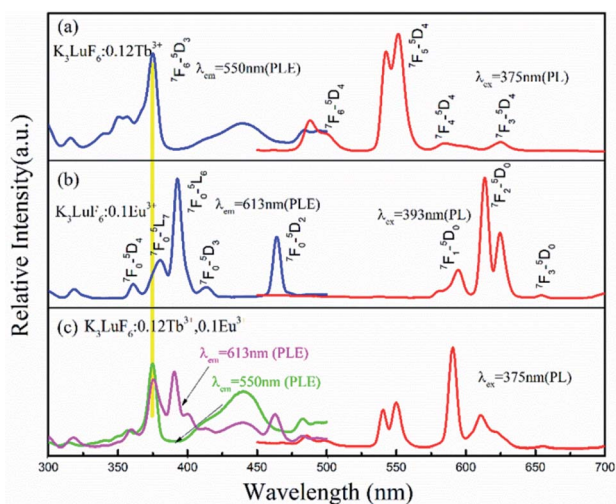


Fig. 4 The PLE and PL spectra of (a)  $K_3LuF_6:0.12Tb^{3+}$ , (b)  $K_3LuF_6:0.1Eu^{3+}$ , and (c)  $K_3LuF_6:0.12Tb^{3+}, 0.1Eu^{3+}$ .

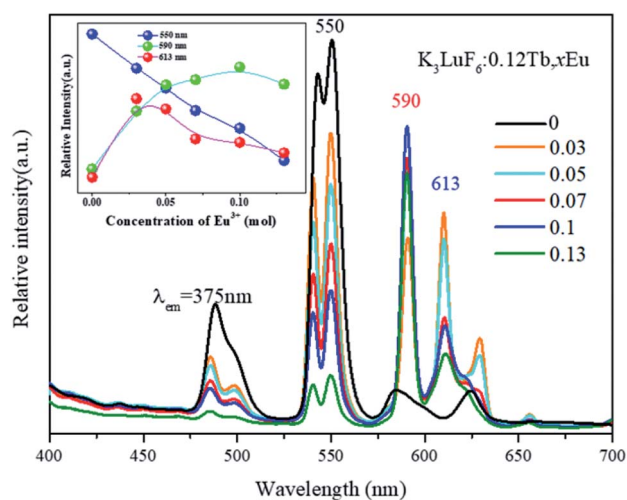


Fig. 5 The PL spectra of  $K_3LuF_6:0.12Tb^{3+}, xEu^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) under excitation at 375 nm. The inset shows the relative emission intensities at 550, 590, and 613 nm.

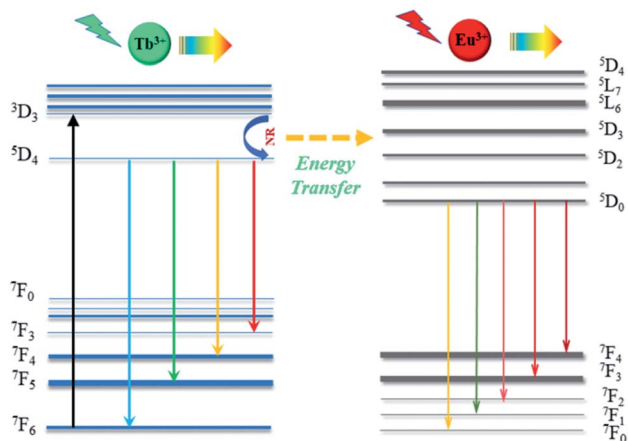


Fig. 6 Energy levels of the possible energy transfer mechanism from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$ .

observed in the PL spectrum, indicating that energy transfer may occur between  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in  $\text{K}_3\text{LuF}_6$ . Moreover, when monitored by 613 nm light, which is the typical emission wavelength of  $\text{Eu}^{3+}$ , the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},0.1\text{Eu}^{3+}$  phosphor showed a characteristic excitation peak (375 nm) of  $\text{Tb}^{3+}$ , while the peak at 375 nm could not be found in the excitation spectrum. Therefore, energy transfer from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  exists in the  $\text{K}_3\text{LuF}_6$  host and the emission color for  $\text{K}_3\text{LuF}_6:\text{Tb}^{3+}/\text{Eu}^{3+}$  can be regulated according to different energy transfer efficiencies by adjusting the ratio of  $\text{Eu}^{3+}/\text{Tb}^{3+}$ .<sup>31</sup> However, when the monitoring light was changed to 550 nm, the excitation spectrum of the co-doped sample did not exhibit the typical  $\text{Eu}^{3+}$  excitation

peak. Therefore, it could be inferred that the energy transfer process is irreversible in this system.

To further investigate the energy transfer process, the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) samples were synthesized using the same method. The PL spectra of  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) under the excitation of 375 nm were recorded and the results are shown in Fig. 5. The inset shows the relative emission intensity at 550, 590, and 613 nm, respectively. Upon 375 nm excitation and with increasing  $\text{Eu}^{3+}$  concentration, the emission intensity of Tb at 550 nm ( ${}^5\text{D}_4\text{-}{}^7\text{F}_3$  transitions) decreases all the time and the emission intensity of  $\text{Eu}^{3+}$  at 590 nm ( ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  transitions) increases and reaches a maximum at  $x = 0.10$ , after which the emission intensity decreases, caused by the concentration quenching of  $\text{Eu}^{3+}$  itself.<sup>32</sup> The results indicate that energy transfer occurs from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in the  $\text{K}_3\text{LuF}_6$  host. The emission intensity of  $\text{Eu}^{3+}$  at 613 nm ( ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  transitions) increases and reaches a maximum at  $x = 0.03$ , then the emission intensity decreases upon an increase in the  $\text{Eu}^{3+}$  concentration, which can be ascribed to the concentration quenching of  $\text{Eu}^{3+}$ .

Fig. 6 shows energy levels of the possible energy transfer mechanism between  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$ . As depicted in Fig. 6, the  $\text{Tb}^{3+}$  electrons in the  ${}^7\text{F}_6$  ground state energy level can be excited by n-UV light and jump to the  ${}^5\text{D}_3$  excited state level. Then, they relax to the  ${}^5\text{D}_4$  transition state due to multi-phonon relaxation. As is known, the excited states are not stable, and  $\text{Tb}^{3+}$  can exhibit green light when the electrons leap back from  ${}^5\text{D}_4$  to  ${}^7\text{F}_j$  ( $j = 6, 5, 4$ , and  $3$ ) with non-radiative processes from  ${}^5\text{D}_3$  to  ${}^5\text{D}_4$ .

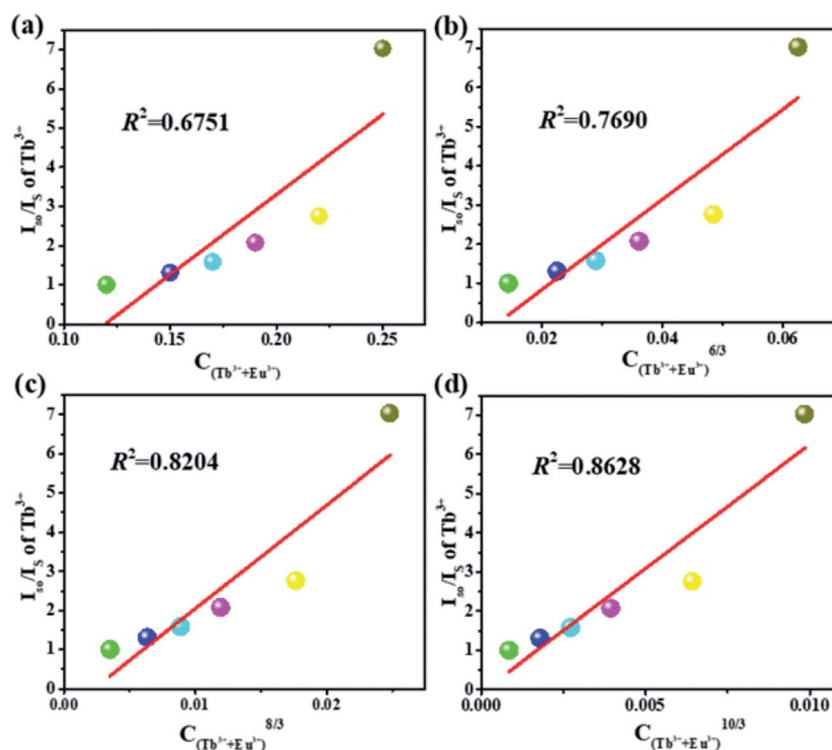
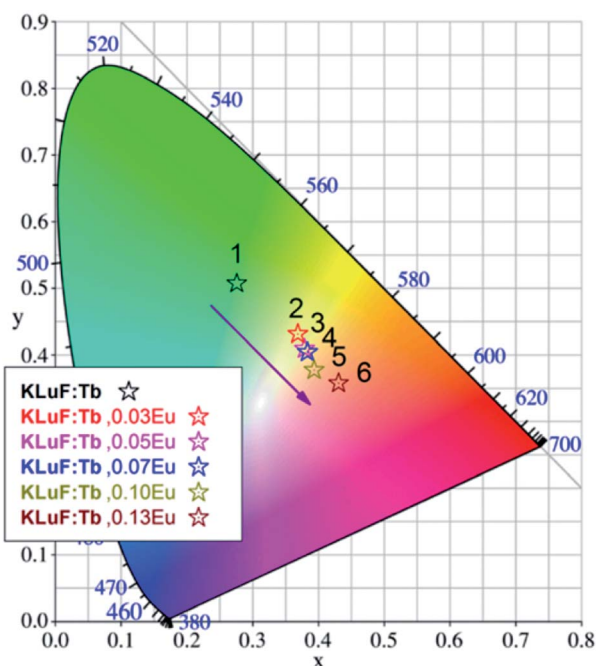


Fig. 7 Dependence of  $I_{50}/I_5$  of  $\text{Tb}^{3+}$  on (a)  $C$ , (b)  $C^{6/3}$ , (c)  $C^{8/3}$  and (d)  $C^{10/3}$  for the  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) samples.

**Table 1** The CIE chromaticity coordinates of the  $\text{K}_3\text{LuF}_6:0.12\text{-Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.10$  and  $0.13$ ) samples under 375 nm excitation

| No. | $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$ | ( $x, y$ )       |
|-----|---|------------------|
| 1   | $x = 0$   | (0.2781, 0.5047) |
| 2   | $x = 0.03$  | (0.3710, 0.4289) |
| 3   | $x = 0.05$  | (0.3812, 0.4069) |
| 4   | $x = 0.07$  | (0.3857, 0.4019) |
| 5   | $x = 0.10$  | (0.3958, 0.3750) |
| 6   | $x = 0.13$  | (0.4331, 0.3556) |



**Fig. 8** The CIE chromaticity coordinate diagram of the  $\text{K}_3\text{LuF}_6:0.12\text{-Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.10$  and  $0.13$ ) samples under 375 nm excitation.

On the other hand, some  $\text{Tb}^{3+}$  electrons transfer their energy from the  $^5\text{D}_4$  ( $\text{Tb}^{3+}$ ) level to the excited state of  $\text{Eu}^{3+}$  ( $^5\text{D}_1$  and  $^5\text{D}_2$ ) by cross-relaxation, and then the  $\text{Eu}^{3+}$  ( $^5\text{D}_1$  and  $^5\text{D}_2$ ) electrons relax to the  $^5\text{D}_0$  level in a non-radiative process, resulting in  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j = 0, 1, 2, 3,$  and  $4$ ) transitions of  $\text{Eu}^{3+}$ , which produce a red emission color.

In order to further understand the energy transfer mechanism of multi-polar interactions between the Tb and Eu ions in this system, the Dexter equation can be applied, as follows:<sup>33,34</sup>

$$(\eta_{s0}/\eta_s) \propto C^{n/3} \quad (1)$$

in which  $\eta_{s0}$  is the quantum efficiency of  $\text{Tb}^{3+}$  in the absence of  $\text{Eu}^{3+}$  and  $\eta_s$  in the presence of  $\text{Eu}^{3+}$ ,  $C$  represents the total concentration of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$ ,  $n$  is a constant value, 3, 6, 8 or 10, corresponding to the exchange, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively.<sup>35,36</sup> The value of  $\eta_0/\eta_s$  can be approximately calculated from the ratio of the photoluminescence intensity ( $I_{s0}/I_s$ ).

Furthermore, Fig. 7 shows the  $I_{s0}/I_s$  vs.  $C^{n/3}$  ( $n = 3, 6, 8,$  or  $10$ ) correlation diagram of these phosphors. When  $n = 10$ , an optical linear relationship was observed, which corresponds to the quadrupole-quadrupole interaction between  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in  $\text{K}_3\text{LuF}_6$ .

The CIE chromaticity coordinate diagram of the  $\text{K}_3\text{-LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0, 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) phosphors under 375 nm excitation was calculated on the basis of the corresponding emission spectra, which are depicted in Table 1 and Fig. 8. As shown in Table 1 and Fig. 8, the emission color of  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  can change from green (0.2781, 0.5407) to yellowish pink (0.4331, 0.3556) upon an increase in the concentration of  $\text{Eu}^{3+}$ . Therefore,  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  can be efficiently excited by 375 nm as an adjustable luminescence material for use in n-UV LEDs.

## 4. Conclusions

In summary, single-phase  $\text{K}_3\text{LuF}_6:x\text{Tb}^{3+}$  ( $x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.1, 0.12$  and  $0.13$ ) and  $\text{K}_3\text{LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  ( $x = 0.03, 0.05, 0.07, 0.1$  and  $0.13$ ) samples were successfully prepared via a high temperature solid-state phase sintering method. In order to determine the energy transfer mechanism between the  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions, the photoluminescence properties and decay lifetimes were measured, and the results showed an energy transfer mechanism from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{K}_3\text{LuF}_6$ , determined as a quadrupole-quadrupole interaction. Characteristic emissions for both  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  can be observed in the PL spectrum of the co-doped phosphors at an excitation of 375 nm ( $\text{Tb}^{3+}$ ), while the luminescent colors of the  $\text{K}_3\text{-LuF}_6:0.12\text{Tb}^{3+},x\text{Eu}^{3+}$  samples can be regulated by changing the concentration of  $\text{Eu}^{3+}$ . All of the above results show that the phosphor could be an ideal single-phase multicolor phosphor.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This present work is supported by the National Natural Science Foundation of China (Grant No. 41672044).

## References

- M. Runowski and S. Lis, Synthesis of lanthanide doped  $\text{CeF}_3:\text{Gd}^{3+}, \text{Sm}^{3+}$  nanoparticles, exhibiting altered luminescence after hydrothermal post-treatment, *J. Alloys Compd.*, 2016, **661**, 182–189.
- M. Runowski, J. Marciniak, T. Grzyb, D. Przybylska, A. Shyichuk, B. Barszcz, A. Katrusiak, S. Lis, A. Katrusiak and S. Lis, Lifetime Nanomanometry – High-Pressure Luminescence of Up-converting Lanthanide Nanocrystals- $\text{SrF}_2:\text{Yb}^{3+}, \text{Er}^{3+}$ , *Nanoscale*, 2017, **9**, 16030–16037.
- L. Qin, P. Q. Cai, C. L. Chen, J. Wang, S. Kim, Y. L. Huang and H. J. Seo, Optical performance of the  $\text{Ba}_5\text{Al}_3\text{F}_{19}:\text{Eu}^{2+}$  blue

- phosphors with high thermal stability, *J. Alloys Compd.*, 2018, **738**, 372–378.
- 4 V. D. Shcherbakov and A. S. Nizamutdinov, Study of  $\text{Mn}^{2+}$  luminescence in  $\beta\text{-PbF}_2$ , *J. Lumin.*, 2019, **194**, 321–326.
- 5 T. T. Deng, E. H. Song and Y. Y. Zhou, Tailoring photoluminescence stability in double perovskite red phosphors  $\text{A}_2\text{BAlF}_6:\text{Mn}^{4+}$  (A = Rb, Cs; B = K, Rb) via neighboring-cation modulation, *J. Mater. Chem. C*, 2017, **5**, 12422–12429.
- 6 D. Yang, L. B. Liao, Q. F. Guo, L. J. Wang, L. F. Mei, H. K. Liu and T. S. Zhou, A novel phosphor of  $\text{Eu}^{3+}$ -activated  $\text{Na}_3\text{GaF}_6$ : Synthesis, structure, and luminescence properties, *J. Lumin.*, 2019, **194**, 321–326.
- 7 T. T. Deng, E. H. Song and Y. Y. Zhou, Stable narrowband red phosphor  $\text{K}_3\text{GaF}_6:\text{Mn}^{4+}$  derived from hydrous  $\text{K}_2\text{GaF}_5$  ( $\text{H}_2\text{O}$ ) and  $\text{K}_2\text{MnF}_6$ , *J. Mater. Chem. C*, 2017, **5**, 9588–9596.
- 8 S. K. Saroj, P. Rawat, M. Gupta, G. V. Prakash and R. Nagarajan, Double perovskite  $\text{K}_3\text{InF}_6$  as upconversion phosphor and its structural transformation by rubidium substitution, *Eur. J. Inorg. Chem.*, 2018, **44**, 4826–4833.
- 9 J. K. Cao, F. F. Hu, L. P. Chen, H. Guo, C. K. Duan and M. Yin, Wide-range thermometry based on green up-conversion luminescence of  $\text{K}_3\text{LuF}_6:\text{Yb}^{3+}/\text{Er}^{3+}$  bulk oxyfluoride glass ceramics, *J. Am. Ceram. Soc.*, 2017, **100**, 2108–2114.
- 10 P. Du and J. S. Yu, Self-activated multicolor emissions in  $\text{Ca}_2\text{NaN}_2(\text{VO}_4)_3:\text{Eu}^{3+}$  phosphors for simultaneous warm white light-emitting diodes and safety sign, *Dyes Pigm.*, 2017, **147**, 16–23.
- 11 C. L. Liao, R. P. Cao, W. D. Wang, W. Hu, G. T. Zheng, Z. Y. Luo and P. Liu, Photoluminescence properties and energy transfer of  $\text{NaY}(\text{MoO}_4)_2:\text{R}$  (R =  $\text{Sm}^{3+}/\text{Bi}^{3+}$ ,  $\text{Tb}^{3+}/\text{Bi}^{3+}$ ,  $\text{Sm}^{3+}/\text{Tb}^{3+}$ ) phosphors, *Mater. Res. Bull.*, 2018, **97**, 490–496.
- 12 B. Han, Y. Z. Dai, J. Zhang, B. B. Liu and H. Z. Shi, Development of near-ultraviolet-excitable single-phase white-light-emitting phosphor  $\text{KBaY}(\text{BO}_3)_2:\text{Ce}^{3+}, \text{Dy}^{3+}$  for phosphor-converted white light emitting-diodes, *Ceram. Interfaces*, 2018, **44**, 14803–14810.
- 13 Q. F. Guo, C. L. Zhao, Z. Q. Jiang, L. B. Liao, H. K. Liu, D. Yang and L. F. Mei, Novel emission-tunable oxyapatite-type phosphors: Synthesis, luminescent properties and the applications in white light emitting diodes with higher color rendering index, *Dyes Pigm.*, 2017, **139**, 361–371.
- 14 B. Li, X. Y. Huang and J. Lin, Single-phased white-emitting  $\text{Ca}_3\text{Y}(\text{GaO})_3(\text{BO}_3)_4:\text{Ce}^{3+}, \text{Tb}^{3+}, \text{Sm}^{3+}$  phosphors with high-efficiency: Photoluminescence, energy transfer and application in near-UV-pumped white LEDs, *J. Lumin.*, 2019, **205**, 115–121.
- 15 P. L. Li, Z. J. Wang, Q. L. Guo and Z. P. Yang, Luminescence and energy transfer of 432 nm blue LED radiation-converting phosphor  $\text{Ca}_4\text{Y}_6\text{O}(\text{SiO}_4)_6:\text{Eu}^{2+}, \text{Mn}^{2+}$  for warm white LEDs, *RSC Adv.*, 2015, **5**, 4448–4453.
- 16 L. Li, X. H. Tang, Z. J. Wu, Y. F. Zheng, S. Jiang, X. Tang, G. T. Xiang and X. J. Zhou, Simultaneously tuning emission color and realizing optical thermometry via efficient  $\text{Tb}^{3+}/\text{Eu}^{3+}$  energy transfer in whitlockite-type phosphate multifunctional phosphors, *J. Alloys Compd.*, 2018, **780**, 266–275.
- 17 Y. L. Zhu, Y. J. Liang, M. F. Zhang, M. H. Tong, G. G. Li and S. Wang, Structure, luminescence properties and energy transfer behavior of color-adjustable  $\text{Sr}_3\text{Gd}_2(\text{Si}_3\text{O}_9)_2:\text{Ce}^{3+}, \text{Tb}^{3+}/\text{Mn}^{2+}$  phosphors, *RSC Adv.*, 2015, **5**, 98350–98360.
- 18 C. Y. Xu, Y. H. Song, H. X. Guan, Y. Sheng, P. C. Ma, X. Q. Zhou, Z. Shi and H. F. Zou, The photoluminescence, thermal properties and tunable color of  $\text{Na}_{1-x}\text{Al}_{1+2x}\text{Si}_{1-2x}\text{O}_4:x\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Dy}^{3+}$  via energy transfer: a single-component multicolor-emitting phosphor, *Phys. Chem. Chem. Phys.*, 2017, **19**, 22197–22209.
- 19 K. Li and R. V. Deun, Photoluminescence and energy transfer properties of a novel molybdate  $\text{KBaY}(\text{MoO}_4)_3:\text{Ln}^{3+}$  ( $\text{Ln}^{3+} = \text{Tb}^{3+}, \text{Eu}^{3+}, \text{Sm}^{3+}, \text{Tb}^{3+}/\text{Eu}^{3+}, \text{Tb}^{3+}/\text{Sm}^{3+}$ ) as a multicolor emitting phosphor for UV w-LEDs, *Dalton Trans.*, 2018, **47**, 6995–7004.
- 20 M. M. Jiao, Q. F. Xu, M. L. Liu, C. L. Yang and Y. J. Yu, Efficient green phosphor realized by  $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$  energy transfer in  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$  for ultraviolet white light-emitting diodes, *Phys. Chem. Chem. Phys.*, 2018, **20**, 26995–27002.
- 21 L. Li, W. X. Chang, W. Y. Chen, Z. S. Feng, C. L. Zhao, P. F. Jiang, Y. J. Wang, X. J. Zhou and A. Suchocki, Double perovskite  $\text{LiLaMgWO}_6:\text{Eu}^{3+}$  novel red-emitting phosphors for solid state lighting: Synthesis, structure and photoluminescent properties, *Ceram. Int.*, 2017, **43**, 2720–2729.
- 22 S. D. Li, Q. Y. Meng, S. C. Lü and W. J. Sun, Study on optical temperature sensing properties of  $\text{Tb}^{3+}, \text{Eu}^{3+}$  co-doped  $\text{CaMoO}_4$  phosphor, *J. Lumin.*, 2018, **200**, 103–110.
- 23 X. X. Ma, L. B. Liao, Q. F. Guo, H. K. Liu, T. S. Zhou and L. F. Mei, Luminescence properties and energy transfer investigations of  $\text{Ba}_2\text{La}_{2.85-x}\text{Tb}_{0.15}\text{Eu}_x(\text{SiO}_4)_3\text{F}$  multicolor phosphor, *RSC Adv.*, 2018, **8**, 27332–27341.
- 24 X. M. Zhu and Z. F. Zhou, Photoluminescence and energy transfer mechanism of a novel tunable color phosphor  $\text{Na}_2\text{MgSiO}_4:\text{Tb}^{3+}, \text{Eu}^{3+}$ , *J. Lumin.*, 2017, **188**, 589–594.
- 25 S. Lee and S. Park, Preparation and luminescent properties of  $\text{Tb}^{3+}$  and  $\text{Tb}^{3+}-\text{Ce}^{3+}$  doped  $\text{Ba}_9\text{Y}_2\text{Si}_6\text{O}_{24}$  phosphors, *J. Lumin.*, 2013, **143**, 215–218.
- 26 Z. X. Shi, J. Wang and X. Guan, Upconversion multicolor tuning of  $\text{NaY}(\text{WO}_4)_2:\text{Tb}^{3+}$  with  $\text{Eu}^{3+}$  doping, *J. Rare Earths*, 2018, **36**, 911–916.
- 27 M. M. Shang, S. Huang and J. Lin, Multicolor emissions and photoluminescence properties for  $\text{Ca}_3\text{Al}_4\text{ZnO}_{10}:\text{Ce}^{3+}/\text{Eu}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$  phosphors, *J. Lumin.*, 2018, **204**, 493–498.
- 28 T. A. Safeera and E. I. Anila, An investigation on the luminescence quenching mechanism of  $\text{ZnGa}_2\text{O}_4:\text{Tb}^{3+}$  phosphor, *J. Lumin.*, 2019, **205**, 277–281.
- 29 X. Y. Li, X. T. Wei, Y. G. Qin, Y. H. Chen, C. K. Duan and M. Yin, The emission rise time of  $\text{BaY}_2\text{ZnO}_5:\text{Eu}^{3+}$  for non-contact luminescence thermometry, *J. Alloys Compd.*, 2016, **657**, 353–357.
- 30 X. J. Zhou, L. N. Chen, S. Jiang, G. T. Xiang, L. Li, X. Tang, X. B. Luo and Y. Pang,  $\text{Eu}^{3+}$  activated  $\text{LiSrVO}_4$  phosphors: Emission color tuning and potential application in temperature sensing, *Dyes Pigm.*, 2018, **151**, 219–226.
- 31 F. F. Hu, Z. M. Zhao, F. F. Chi, X. T. Wei and M. Yin, Structural characterization and temperature-dependent

- luminescence of  $\text{CaF}_2:\text{Tb}^{3+}/\text{Eu}^{3+}$  glass ceramics, *J. Rare Earths*, 2017, **35**, 536–541.
- 32 Z. H. Li, H. Y. Ma, N. Li, Y. Du and Q. Y. Shao, New phosphors of  $\beta\text{-BaB}_2\text{O}_4:\text{RE}^{3+}$  ( $\text{RE}^{3+} = \text{Eu}^{3+}, \text{Tb}^{3+}$ ), *J. Alloys Compd.*, 2018, **747**, 340–347.
- 33 L. G. Van Uitert, Characterization of energy transfer interactions between rare earth ions, *J. Electrochem. Soc.*, 1967, **114**, 1048–1053.
- 34 D. L. Dexter and J. H. Schulman, Theory of Concentration Quenching in Inorganic Phosphors, *J. Chem. Phys.*, 1954, **22**, 1063–1070.
- 35 X. Zhang, P. He, L. Zhou, J. Shi and M. Gong, Energy transfer and luminescent properties of a green-to-red colour tunable  $\text{Tb}^{3+}, \text{Eu}^{3+}$  co-doped  $\text{K}_2\text{Y}(\text{WO}_4)(\text{PO}_4)$  phosphor, *Mater. Res. Bull.*, 2014, **60**, 300–307.
- 36 B. Li, B. Devakumar, L. W. Jin, L. L. Sun and X. Y. Huang, Synthesis, energy transfer and photoluminescence properties of thermal stable multicolour-emitting  $\text{Ca}_3\text{Gd}(\text{AlO})_3(\text{BO}_3)_4:\text{Tb}^{3+}, \text{Eu}^{3+}$  phosphors, *J. Lumin.*, 2018, **204**, 386–393.