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Luminescence properties and energy transfer in Tb³⁺ and Eu³⁺ co-doped Ba₂P₂O₇ phosphors

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The Ba₂P₂O₇:Tb³⁺, Eu³⁺ phosphors were synthesized by a high temperature solid-state reaction method in air atmosphere and their crystal structures, lifetime, luminescence properties, and energy transfer mechanism were investigated in detail. A series of characteristic emissions of Ba₂P₂O₇:Tb³⁺, Eu³⁺ phosphors were observed in the emission spectra at around 545 nm, 593 nm, and 613 nm when excited at 378 nm. The energy-transfer mechanism from Tb³⁺ to Eu³⁺ in Ba₂P₂O₇ is determined by a dipole-dipole interaction. The emission intensity of Ba_{2-x}P₂O₇:xEu³⁺ was enhanced by doping charge compensation Li⁺, Na⁺ and K⁺. The CIE coordinates of the phosphors can be tuned from blue-green through white, to yellow and finally to orange-red with changing the Eu³⁺/Tb³⁺ ratio. The average decay time of Eu³⁺ increases from 2.10 to 5.81 ms with the concentration of Tb³⁺ increasing from 2% to 8%, and reaches the maximum at 0.08, and is shortened when the concentration of Tb³⁺ goes beyond 8%.

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1. Introduction

Nowadays, as the next-generation lighting and display systems, the white light-emitting diodes (WLEDs) are attracting much attention due to their environmental friendliness, reliability, and low power consumption.^{1-5,28,29} In general, the manufacture of white light phosphors follows one of two routes. One approach is to mix monochromatic (red/green/blue) phosphors in the best proportion, the other approach is to excite yellow phosphors using blue or ultraviolet (UV) emitting chips.⁶ However, for phosphor mixtures, the strong re-absorption and nonuniformity of luminescence problems exist, this result gives rise to the loss of luminescence efficiency, properties, and multicolor emitting points. Compared with phosphor mixtures, a single phase phosphor has more advantages and overcomes these problems. So, the single phase phosphor is a very promising material.^{7-9,30,31}

Recently, more and more scholars focus on pyrophosphate phosphor materials which have the advantage of environmental friendliness, chemical stability, low power consumption, and high efficiency, *etc.*¹⁰ In the rare earth family, due to the existence of ⁵D₃-⁷F₅, and ⁵D₄-⁷F₅ transition, the Tb³⁺ ion doped phosphors which can emit blue and green light has been prepared in previous research. Meanwhile, Eu³⁺ ion is a red emitting activator due to its ⁵D₀-⁷F₂ transition.⁶ Accordingly, the Tb³⁺ and Eu³⁺ co-doped phosphors can generate simultaneous the red/green/blue emissions. At present, by means of the energy-transfer from a sensitizer to an activator, the multicolor emitting phosphor can be usually designed under ultraviolet

excitation, so by co-doping of Eu³⁺ and Tb³⁺ ions, the color emission may be tuned base on the energy transfer from Tb³⁺ to Eu³⁺. In some literatures, the Tb³⁺ and Eu³⁺ co-doped phosphors have been used in the studies of W-LEDs, such as Sr₂P₂O₇:Tb³⁺, Eu³⁺,⁶ KCaY(PO₄)₂:Tb³⁺, Eu³⁺,¹¹ LaPO₄:Tb³⁺, Eu³⁺, Bi³⁺.¹²

For all we know, for Ba_{1-x-y}P₂O₇:xEu³⁺, yTb³⁺ phosphors, its luminescence properties and the mechanism of Tb³⁺ → Eu³⁺ energy transfer have not been investigated in the previous study. In this study, the phosphors Ba₂P₂O₇:Tb³⁺, Eu³⁺ were synthesized by solid-state reaction method in air. The crystal structure, photoluminescence properties, color tunability, the mechanism of Tb³⁺ → Eu³⁺ energy transfer, and luminous efficiency of prepared samples were systematically studied.

2. Experimental

2.1. Sample synthesis

The powder samples Ba₂P₂O₇:Tb³⁺, Eu³⁺ were prepared by the conventional solid-state reaction in air. According to mole ratio of elements in Ba_{1.94-y}P₂O₇:0.06Tb³⁺, yEu³⁺, we calculated and weighed the raw materials BaCO₃ (A.R.), NH₄H₂PO₄ (A.R.), Tb₄O₇ (99.99%) and Eu₂O₃ (99.99%), and then the raw materials were fully ground in an agate mortar. Eventually, the mixtures in the alumina crucible was put into the muffle furnace and calcined at 1100 °C for 2 h. The samples were obtained after cooled to room temperature.

2.2. Sample characterization

The X-ray diffraction (XRD) patterns of the samples were recorded *via* using Japan Rigaku D/Max-2200 X-ray diffractometer with Cu-Kα radiation (λ = 0.15406 nm). The excitation and emission spectra were observed by the Hitachi F-4600

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fluorescence spectrophotometer. Fluorescence lifetime were investigated by using the Edinburgh FS5 fluorescence spectrophotometer. All the measurements above were carried out at room temperature.

3. Results and discussion

3.1. Structure characterization

Fig. 1a and b shows the X-ray diffraction patterns of $\text{Ba}_2\text{P}_2\text{O}_7\text{:Tb}^{3+}$, Eu^{3+} and $\text{Ba}_{1.88}\text{P}_2\text{O}_7\text{:0.06Eu}^{3+}$, 0.06M^+ (Li^+ , Na^+ , K^+) samples, respectively. All XRD patterns are found to agree well with standard data (JCPDS 30-0144) in the $\text{Ba}_2\text{P}_2\text{O}_7$. The results indicate that the $\text{Ba}_2\text{P}_2\text{O}_7$ host keep the crystal structure when the M^+ , Tb^{3+} and Eu^{3+} in small amount doping.

3.2. Luminescence properties of the $\text{Ba}_2\text{P}_2\text{O}_7\text{:Tb}^{3+}$, Eu^{3+}

Fig. 2a shows the excitation and emission spectra of $\text{Ba}_{1.94}\text{P}_2\text{O}_7\text{:0.06Eu}^{3+}$ phosphor. When monitored at 593 nm, several excitation peaks at 361 nm, 381 nm and 395 nm are obtained

and assigned to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ and ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transitions, respectively.^{12,13} In the emission spectrum of $\text{Ba}_{1.94}\text{P}_2\text{O}_7\text{:0.06Eu}^{3+}$ sample, under excitation at 395 nm, the feature emission peaks are observed at 593 and 613 nm. According to the Judd–Ofelt theory,^{14–16} the transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ is the magnetic dipole, and it is orange emission at 593 nm. While the transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ is the electric-dipole, it is red emission centered at 613 nm.

As we all know, the transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ (593 nm) is the magnetic dipole, and it is insensitive to distortion of the inversion symmetry, whereas the electric dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ (613 nm) is hypersensitive to it, and the intensity ratio (${}^5\text{D}_0\text{--}{}^7\text{F}_2$)/(${}^5\text{D}_0\text{--}{}^7\text{F}_1$) suggests the degree of distortion.¹⁶ In our experiment, the transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ (593 nm) was stronger than the ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ (613 nm), this result reveals Eu^{3+} ions mainly occupy the inversion symmetry lattice site.

Fig. 2b shows the excitation and emission spectra of $\text{Ba}_{1.94}\text{P}_2\text{O}_7\text{:0.06Tb}^{3+}$. When monitored at 545 nm, there are several excitation peaks between 300 and 380 nm, where the strongest one is at 378 nm (${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$).^{6,10} In the emission spectrum of

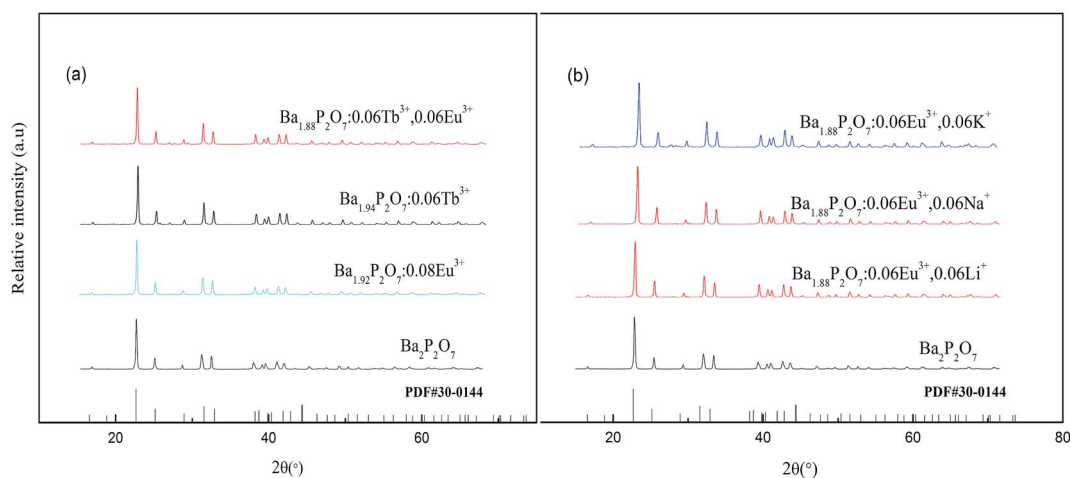


Fig. 1 XRD pattern of phosphors: (a) $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7\text{:xTb}^{3+}$, $y\text{Eu}^{3+}$, (b) $\text{Ba}_{1.88}\text{P}_2\text{O}_7\text{:0.06Eu}^{3+}$, 0.06M^+ (Li^+ , Na^+ , K^+).

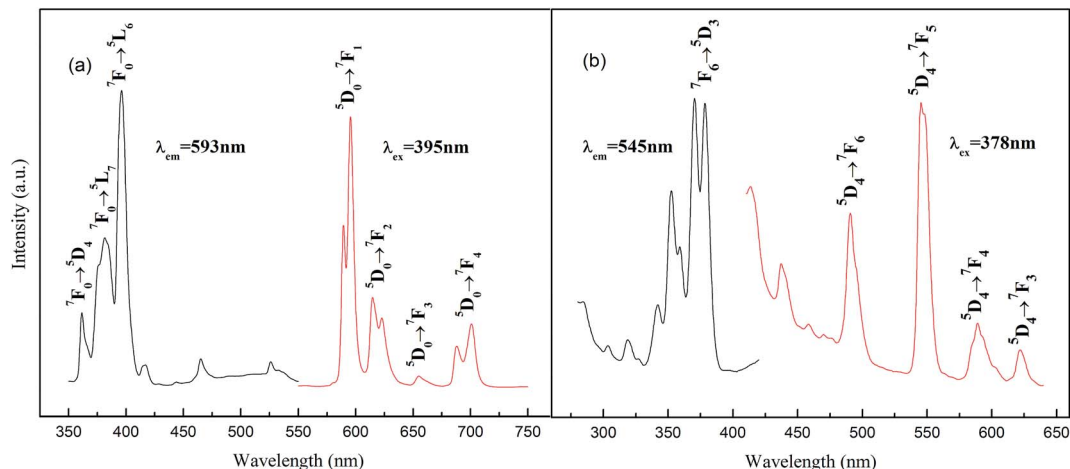


Fig. 2 Excitation and emission spectra of phosphor: (a) $\text{Ba}_{1.94}\text{P}_2\text{O}_7\text{:0.06Eu}^{3+}$, (b) $\text{Ba}_{1.94}\text{P}_2\text{O}_7\text{:0.06Tb}^{3+}$.



Ba_{1.94}P₂O₇:0.06Tb³⁺ sample, under excitation at 378 nm, the feature emission peaks are observed at 491, 545, 589, and 622 nm corresponding to ⁵D₄ to ⁷F₆, ⁷F₅, ⁷F₄, and ⁷F₃ transitions, respectively.^{6,11}

Fig. 3 shows the emission spectra of Ba_{1.94-y}P₂O₇:0.06Tb³⁺, yEu³⁺ samples excited at 378 nm. When doped the Eu³⁺ and Tb³⁺ in the Ba₂P₂O₇, the samples exhibit not only ⁵D₄ to ⁷F_{6,5,4,3} emission bands of the Tb³⁺ ions but also the ⁵D₀-⁷F_{1,2} emission of the Eu³⁺ ions. When the Tb³⁺ doping concentration is 0.06, we change the doping concentration of Eu³⁺ (the concentration of 0, 0.005, 0.015, 0.02, 0.04, 0.06 and 0.08, respectively), the emission intensities of 593 and 613 nm (⁵D₀-⁷F_{1,2}) of Eu³⁺ are enhanced and reaches the maximum at y = 0.06, meanwhile the emission intensity of Tb³⁺ is impaired. This indicated that the efficient probability is notably enhanced for energy transfer (Tb³⁺ → Eu³⁺). According to the above results, the optimal composition of Tb³⁺ and Eu³⁺ co-activated phosphor is Ba_{1.88}-P₂O₇:0.06Tb³⁺, 0.06Eu³⁺, which shows the strongest emission.

From the emission intensity of sensitizer, the energy-transfer efficiency (η_{ET}) from a sensitizer to an activator can be obtained as the following equation:^{8,9}

$$\eta_{ET} = 1 - \frac{I_s}{I_{s0}} \quad (1)$$

where I_{s0} is the intrinsic luminescent intensity of Tb³⁺, I_s is the luminescent intensity of Tb³⁺ in the presence of Eu³⁺. The energy transfer efficiencies from Tb³⁺ to Eu³⁺ excited at 378 nm are illustrated in Fig. 4. As a result, the energy transfer efficiency values from Tb³⁺ to Eu³⁺ were calculated to be 70%, 77.91%, 79.82%, 81.26%, and 79.07% for Ba_{1.94-y}P₂O₇:0.06Tb³⁺, yEu³⁺ samples, respectively. This result reveals that the η_{ET} increases with the increase of Eu³⁺ doping content, meaning that the energy transfer from Tb³⁺ to Eu³⁺ is very efficient.

In general, for the energy transfer from a sensitizer to an activator, there are two main aspects: one is exchange interaction (the typical critical distance is no more than 5 Å) and the other is multipolar interaction (the critical distance is longer than 10 Å).^{17,23,24} According to Blasse, the critical distance R_c for

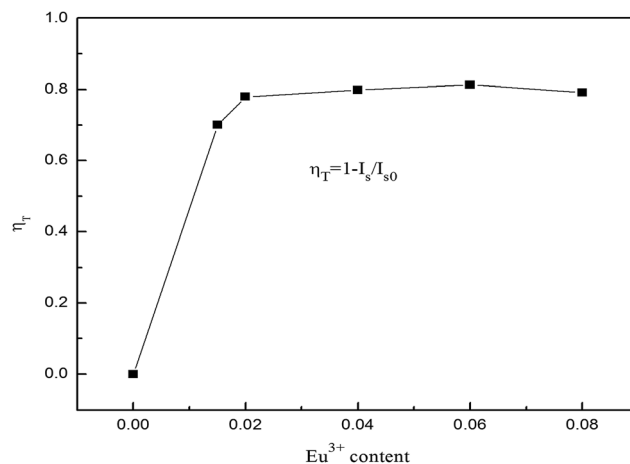


Fig. 4 Change of the energy transfer efficiency with increase of Eu³⁺ concentration.

energy transfer from the Tb³⁺ to Eu³⁺ ions can be calculated using the following equation:^{18,20,26,27}

$$R_c = 2 \left[\frac{3V}{4\pi x_c N} \right]^{1/3} \quad (2)$$

here, V is the unit cell volume, x_c is the critical concentration, and N is the coordinate number of molecules in the unit cell. For the Ba₂P₂O₇ host, $V = 543.87 \text{ \AA}^3$, $N = 3$, and $x_c = 0.065$ (total concentration of Tb³⁺ and Eu³⁺ when the Tb³⁺ emission intensity is half of that in the absence of Eu³⁺). According to the above equation, the value of R_c is 17.47 Å, and it is much larger than 5 Å. So the energy transfer from Tb³⁺ to Eu³⁺ ions happen in the way of electric multipolar interaction for this system.

In order to further verify the mechanism of energy transfer for Ba₂P₂O₇:Tb³⁺, Eu³⁺, Dexter's formula of multipolar interaction and Reisfeld's approximation are used as follows:^{19,21,22}

$$\frac{I_{s0}}{I_s} \propto C^{n/3} \quad (3)$$

herein, the C is the Eu³⁺ concentration, I_s is the luminescent intensity of Tb³⁺ in Ba₂P₂O₇:Tb³⁺, Eu³⁺, and I_{s0} is the intrinsic luminescent intensity of Ba₂P₂O₇:Tb³⁺. Based on the eqn (3), when $n = 6, 8$, and 10 correspond to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively.

The $I_{s0}/I_s - C^{n/3}$ ($n = 6, 8, 10$) plots for Ba_{1.94-y}P₂O₇:0.06Tb³⁺, yEu³⁺ (at excitation wavelength of 378 nm and emission wavelength of 545 nm) are shown in Fig. 5. It can be seen that when $n = 6$, the I_{s0}/I_s value follows the linear growth law much better than $n = 8$ or 10 . So the dipole-dipole mechanism is the mainly way for the energy transfer between Tb³⁺ and Eu³⁺ in Ba₂P₂O₇.

The energy-transfer mechanism of Tb³⁺ and Eu³⁺ are shown in Fig. 6. Upon 378 nm excitation, few excited Tb³⁺ ions is excited to higher energy level through Tb³⁺:⁷F₆-⁵D₃ transitions, then relaxed to lower energy levels through Tb³⁺:⁵D₃-⁷F_{5,4,3} non-radiative transitions and to its lower lying Tb³⁺:⁵D₄ metastable state relaxed to lower energy levels through Tb³⁺:⁵D₄-⁷F_{5,4,3} transitions.

The rest of the Tb³⁺:⁵D₃ level transfer their energy to the Eu³⁺:⁵G₂ level *i.e.* the energy transfer. A fast non-radiative decay

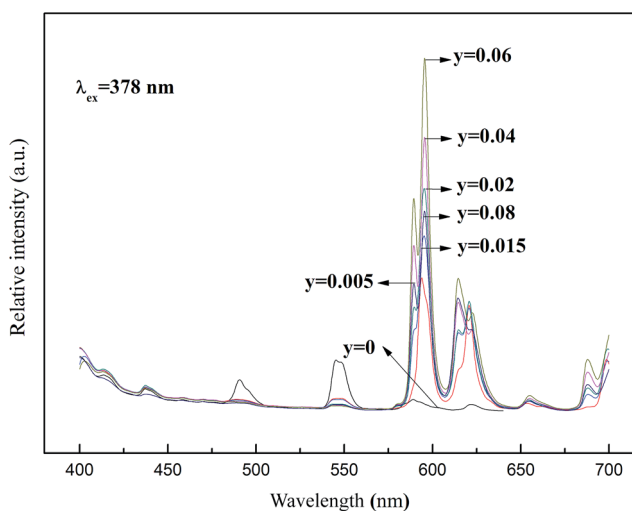


Fig. 3 The emission spectrum of Ba_{1.94-y}P₂O₇:0.06Tb³⁺, yEu³⁺.



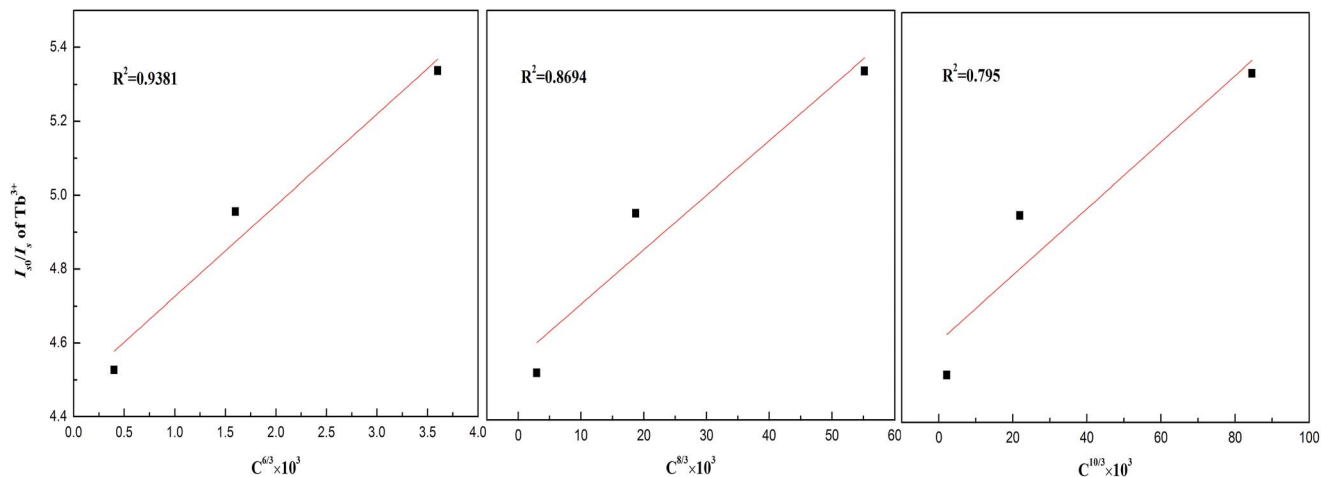


Fig. 5 Dependence of I_{613}/I_{593} of Dy^{3+} on $C^{6/3}$, $C^{8/3}$ and $C^{10/3}$.

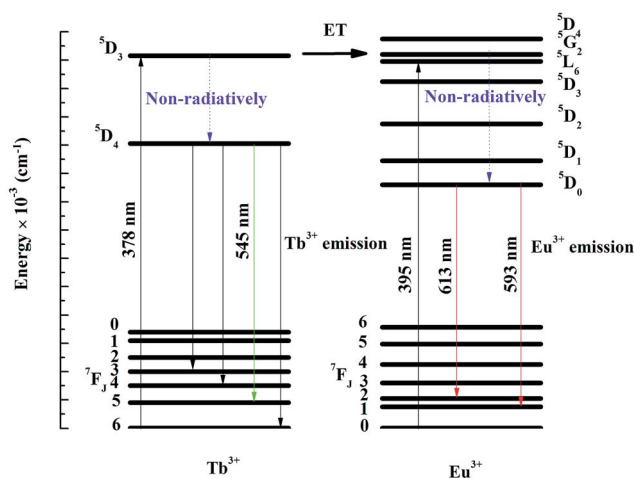


Fig. 6 Energy levels of Tb^{3+} and Eu^{3+} in $Ba_2P_2O_7$ phosphor.

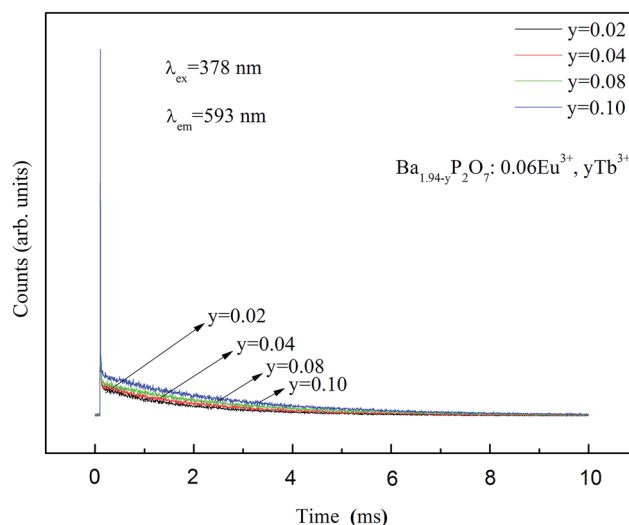


Fig. 7 PL decay curves of Eu^{3+} in $Ba_{1.94-y}P_2O_7:0.06Eu^{3+}, yTb^{3+}$.

from 5G_2 excited state increase the population of 5D_0 metastable state causing enhanced emission from Eu^{3+} ions through $^5D_0 \rightarrow ^7F_J$ ($J = 0-6$) transitions. Finally, the characteristic emission of Eu^{3+} at 593 and 613 nm was enhanced.

Fig. 7 shows luminescence decay for 5D_0 level of Eu^{3+} in $Ba_{1.94-y}P_2O_7:0.06Eu^{3+}, yTb^{3+}$ ($y = 2\%, 4\%, 8\%, 10\%$) excited at 378 nm and measured at 593 nm. The decay times of Eu^{3+} can be more accurate fitted *via* using second-order exponential decay mode as follows:²⁵

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (4)$$

where A_1 and A_2 are the fitting parameters, t is the time, τ_1 and τ_2 are the decay times for different exponential components, I is the phosphorescent intensity, respectively. The average decay time τ of Eu^{3+} can be expressed as the following equation:²⁵

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (5)$$

For $Ba_{1.94-y}P_2O_7:0.06Eu^{3+}, yTb^{3+}$ ($y = 0.02, 0.04, 0.08, 0.10$) phosphors, corresponding to the 5D_0 level of Eu^{3+} , when the samples are excited at 378 nm, the average lifetimes that calculated by eqn (5) are 2.10, 2.51, 5.81, and 2.65 ms, respectively. The average decay time of Eu^{3+} increases from 2.10 to 5.81 ms as the increase of the concentration of Tb^{3+} from 0.02 to 0.08, the results confirmed the exist of energy transfer from Tb^{3+} to Eu^{3+} ions.^{34,35} When the Tb^{3+} beyond 8% mol, the average decay time of Eu^{3+} is shortened oppositely, which is corresponding to the widely known concentration quenching effect happened in high concentration.

Due to Eu^{3+} and Ba^{2+} have similar radius, the Eu enter the lattice, and replace the position of the Ba^{2+} to form a point defect Eu_{Ba} which have a positive charge.^{32,33} In order to keep the charge balance, it can be implemented by doping alkali metal ions. For $Ba_{1.94}P_2O_7:0.06Eu^{3+}$ phosphors, we regard Li^+ (Li_2CO_3), Na^+ (Na_2CO_3) and K^+ (K_2CO_3) as charge compensations to stabilize the structure. The results are shown in Fig. 8.



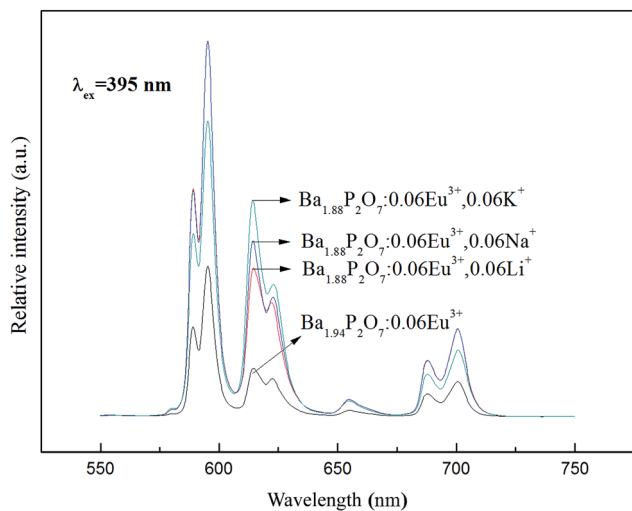


Fig. 8 Effect of Li^+ , Na^+ and K^+ on the emission spectrum of $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors.

When the M^+ (Li^+ , Na^+ , K^+) doping concentration are 0.06 respectively, the intensity of $\text{Ba}_{1.94}\text{P}_2\text{O}_7:0.06\text{Eu}^{3+}$ are all enhanced. The doping Na^+ enhanced emission intensity more than by doping Li^+ or K^+ at 593 nm, and the emission intensity at 613 nm is higher by doping K^+ .

Fig. 9 shows the CIE chromaticity diagram for $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors. According to the emission spectra, the values of CIE parameters of the $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors with different doping concentrations are summarized in Table 1. Under the excitation at 378 nm, the CIE coordinates of the phosphors can be tuned from blue-green (point

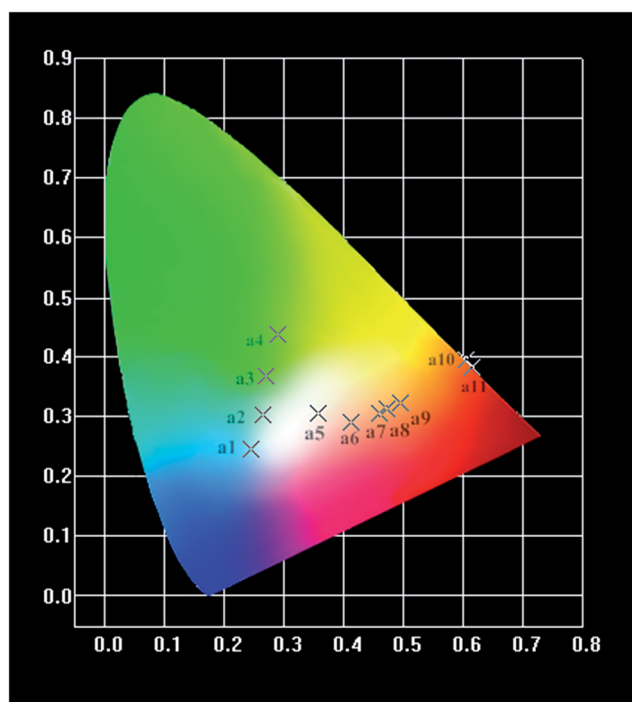


Fig. 9 CIE coordinates of the $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors.

Table 1 CIE chromaticity coordinates of the $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors

Point	Sample ($\lambda_{\text{ex}} = 378 \text{ nm}$)	CIE (x, y)
a1	$\text{Ba}_{1.98}\text{P}_2\text{O}_7:0.02\text{Tb}^{3+}$	(0.245, 0.244)
a2	$\text{Ba}_{1.94}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}$	(0.264, 0.303)
a3	$\text{Ba}_{1.92}\text{P}_2\text{O}_7:0.08\text{Tb}^{3+}$	(0.271, 0.368)
a4	$\text{Ba}_{1.75}\text{P}_2\text{O}_7:0.25\text{Tb}^{3+}$	(0.291, 0.437)
a5	$\text{Ba}_{1.939}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.001\text{Eu}^{3+}$	(0.358, 0.305)
a6	$\text{Ba}_{1.935}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.005\text{Eu}^{3+}$	(0.412, 0.289)
a7	$\text{Ba}_{1.92}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.02\text{Eu}^{3+}$	(0.459, 0.304)
a8	$\text{Ba}_{1.9}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.04\text{Eu}^{3+}$	(0.473, 0.312)
a9	$\text{Ba}_{1.88}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.06\text{Eu}^{3+}$	(0.496, 0.322)
a10	$\text{Ba}_{1.985}\text{P}_2\text{O}_7:0.015\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 395 \text{ nm}$)	(0.604, 0.395)
a11	$\text{Ba}_{1.94}\text{P}_2\text{O}_7:0.06\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 395 \text{ nm}$)	(0.616, 0.383)

a1, a2, a3, a4) to white (point a5), yellow (point a6, a7, a8, a9) and finally to the orange-red (point a10, a11) by changing the $\text{Eu}^{3+}/\text{Tb}^{3+}$ ratio. The CIE chromaticity coordinates associated with white luminescence (0.358, 0.305) of $\text{Ba}_{1.94-x}\text{P}_2\text{O}_7:0.06\text{Tb}^{3+}, 0.001\text{Eu}^{3+}$ sample (point a5) are very close to an ideal white chromaticity coordinates (0.33, 0.33). However, upon 395 nm excitation, the CIE chromaticity coordinates are associated with orange-red luminescence of $\text{Ba}_{2-x}\text{P}_2\text{O}_7:\text{xEu}^{3+}$ phosphor (point a10, a11). Above results indicate that the phosphors show merits of multicolor emissions in the visible region when excited by a single wavelength light.

4. Conclusion

In summary, the $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors were synthesized by a solid-state reaction at 1100 °C for 2 h. The $\text{Ba}_{2-x-y}\text{P}_2\text{O}_7:\text{xTb}^{3+}, \text{yEu}^{3+}$ phosphors can be effectively excited at 378 nm and have several emission peaks centered at 545 nm, 593 nm and 613 nm. The CIE coordinates of the phosphors can be tuned from blue-green to white, yellow and finally to the orange-red by changing the $\text{Eu}^{3+}/\text{Tb}^{3+}$ ratio. The emission intensity of $\text{Ba}_{2-x}\text{P}_2\text{O}_7:0.06\text{Eu}^{3+}$ was enhanced by doping charge compensation M^+ (Li^+ , Na^+ , K^+). The energy transfer from Tb^{3+} to Eu^{3+} in $\text{Ba}_2\text{P}_2\text{O}_7$ was demonstrated to be dipole-dipole interaction mechanism. The energy transfer efficiency in $\text{Tb}^{3+}-\text{Eu}^{3+}$ was approximately 81.26% at $x = 0.06$, $y = 0.06$, and for the $\text{Ba}_{1.94-y}\text{P}_2\text{O}_7:0.06\text{Eu}^{3+}, \text{yTb}^{3+}$ ($y = 0.02, 0.04, 0.08, 0.10$) phosphors, under excitation at 378 nm, the average lifetimes of Eu^{3+} were determined to be 2.10, 2.51, 5.81, and 2.65 ms, respectively.

Acknowledgements

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