Crystal structure, tunable luminescence and energy transfer properties of Na₃La(PO₄)₂:Tb³⁺,Eu³⁺ phosphors†

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A series of Tb³⁺ and/or Eu³⁺ doped Na₃La(PO₄)₂ phosphors were successfully synthesized and their crystal structure and photoluminescence (PL) properties were investigated in detail. Double phosphates with the compositions Na₃Tb(PO₄)₂ and Na₃Eu(PO₄)₂ were obtained by the substitution of Tb or Eu for La in the Na₃La(PO₄)₂ host. XRD pattern analysis indicates that these obtained compounds crystallize in the orthorhombic system with the space group Pbc₂₁. The crystal structure of the Na₃RE(PO₄)₂:RE = Tb, Eu is made up of isolated PO₄ tetrahedra and of sodium and RE atoms arranged in an ordered way. The REO₃ polyhedra are isolated from one another, resulting in a high critical concentration of Tb³⁺ or Eu³⁺ activators. Under excitation of near-ultraviolet (NUV) irradiation, Tb³⁺ doped Na₃La(PO₄)₂ shows a blue-greenish emission with a predominant peak at 546 nm, while the emission spectra of Eu³⁺-doped Na₃La(PO₄)₂ exhibits a reddish orange emission due to the 5D₀ → 7F₂ transitions of Eu³⁺ ions. The energy transfer from Tb³⁺ to Eu³⁺ in the Na₃La(PO₄)₂ host is demonstrated by the luminescence spectra and fluorescence decay dynamics. Meanwhile, the emission color of Na₃La(PO₄)₂:Tb³⁺,Eu³⁺ can be tuned from green to red through tuning the Tb³⁺/Eu³⁺ ratio. These results indicate that the Na₃La(PO₄)₂:Tb³⁺,Eu³⁺ phosphor exhibits broadband NUV absorption and green–reddish orange tunable emission, which might serve as a down-converting phosphor for NUV light-emitting diodes.

Introduction

Rare earth (RE) ions play an irreplaceable role in the development of lighting and display fields due to their abundant emission colors based on 4f–4f or 5d–4f transitions.1–3 Recently, RE³⁺ ion doped phosphors based on double phosphate hosts have drawn much attention because of their high luminous efficiency, low sintering temperature, high thermal and chemical stability, and low cost.4–7 Double phosphates of mono- and trivalent cations with the general formula M⁴⁺NM⁵⁺(PO₄)₂ (M⁴⁺ = Na, K; N⁵⁺ = Y, Sc, In, Fe, rare earth elements) have high thermal and chemical stability and their host absorption edge locates at a rather short wavelength (about 140–180 nm),6 making them excellent host materials for luminescent materials. M⁴⁺N⁵⁺(PO₄)₂ compounds crystallize in a trigonal, orthorhombic or monoclinic structure, depending on the type of M⁴⁺ or N⁵⁺ cations.7 Among them, Na₃RE(PO₄)₂ (RE = La–Tb) compounds crystallize orthorhombic with the glaserite-type structure. They are built up on isolated REO₃ polyhedral and PO₄ tetrahedra.8 The presence of this particular structure suggests that the lattice can accommodate other cations with similar radii and charges without significant changes to the structural frame.9 Furthermore, this structure can weaken the concentration quenching effect and the critical concentration of activator ions is much higher than that of conventional inorganic phosphors. Therefore, the structure and optical properties of Na₃RE(PO₄)₂-related phosphors have been extensively studied. A great number of glaserite-type phosphors, such as Na₃Y(PO₄)₂:Ce³⁺,10 Na₃La(PO₄)₂:Er³⁺,11 Na₂Gd(PO₄)₂:Ce³⁺,12 and Na₃RE(PO₄)₂:Yb³⁺ (RE = Y, La, Gd)13 have been reported. Meanwhile, most of the phosphors are single-colored, and combining different phosphors is applied when a multicolor emission is needed. However, this combination suffers from the disadvantages of reabsorption among phosphors and different degradation rates.14 Therefore, great efforts have been devoted to develop single-host phosphors with a multicolor emission to meet the increasing demand of different illumination applications. In order to achieve color tunable emitting in single-phase hosts, several strategies are used, including controlling the temperature,15 band-gap modulation,16 crystal field adjustment,17 the combination of multiple rare ions with various color emissions,18 and codoping ion pairs based on the energy transfer mechanism. Codoping different rare earth ions as sensitizers and activators in a single matrix is one of the most

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† Electronic supplementary information (ESI) available: F-7000 instrumental parameters; Fig. S1 Rietveld refinement of the powder XRD pattern of Na₃Tb₀.₅Eu₀.₅(PO₄)₂; Fig. S2 Rietveld refinement of the powder XRD pattern of Na₃(Tb₀.₅Eu₀.₅)(PO₄)₂. See DOI: 10.1039/c6ra26164g
popular methods to control the emission color via energy transfer processes.\textsuperscript{29} Additional, tunable multicolor emission can be realized in phosphors under a single excitation wavelength. The multicolor tuning of phosphors has been achieved by co-doping RE\textsuperscript{3+} ion into suitable host lattice, such as Eu\textsuperscript{3+}–Bi\textsuperscript{3+},\textsuperscript{20} Tb\textsuperscript{3+}–Dy\textsuperscript{3+} (ref. 21) and Tb\textsuperscript{3+}–Eu\textsuperscript{3+}.\textsuperscript{22–24}

It has been reported that Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} crystallizes in the orthorhombic structure.\textsuperscript{8} Eu\textsuperscript{3+} and Tb\textsuperscript{3+} ions are frequently used as red and green activators in luminescent materials.\textsuperscript{19} However, the luminescence properties of Tb\textsuperscript{3+} and/or Eu\textsuperscript{3+} ions in Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} host under near ultraviolet (NUV) light excitation have not been reported, and so far the energy transfer phenomenon from Tb\textsuperscript{3+} to Eu\textsuperscript{3+}. In this contribution, Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} was chosen as the host material. The structure, luminescence properties and chromaticity stability of Tb\textsuperscript{3+} and/or Eu\textsuperscript{3+} activated Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} samples are studied in detail. The energy transfer process between Tb\textsuperscript{3+} and Eu\textsuperscript{3+} ions as well as the potential luminescence mechanism has been analyzed in Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} host upon the excitation wavelength of 378 nm irradiation.

**Experimental**

Powder samples of Na\textsubscript{3}La\textsubscript{1−x}(PO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+} (x = 0–1.0), Na\textsubscript{3}La\textsubscript{1−y}(PO\textsubscript{4})\textsubscript{2}:yTb\textsuperscript{3+} (y = 0–1.0), Na\textsubscript{3}La\textsubscript{0.7}–0.3Tb\textsubscript{0.3}(PO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+} (x = 0–0.7), and Na\textsubscript{3}La\textsubscript{0.95}–0.05Eu\textsubscript{0.05}(PO\textsubscript{4})\textsubscript{2}:yTb\textsuperscript{3+} (y = 0–0.95) were prepared as follows. Stoichiometric amounts of analytical reagents Na\textsubscript{2}NO\textsubscript{3}, NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, and 99.99% pure La\textsubscript{2}O\textsubscript{3} were mixed. An appropriate amount of CO(NH\textsubscript{2})\textsubscript{2} was added as fuel. 99.99% pure Eu\textsubscript{2}O\textsubscript{3} and Tb\textsubscript{2}O\textsubscript{3} were dissolved in HNO\textsubscript{3} to convert into nitrate completely. These reagents were dissolved in water and then introduced into a muffle furnace maintained at 600 °C for 5 min. The obtained powder was subsequently ground in an agate mortar and then reacted at 900 °C for 4 h in air atmosphere. Finally, the products were gradually cooled to room temperature and reground for further measurements.

The phase purity of the products was checked by powder X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer (Bruker Co. Ltd., Karlsruhe, Germany) with Cu Kα radiation (λ = 1.5406 Å), operating at 40 kV and 40 mA. Structure refinements of XRD data were performed using the computer software General Structure Analysis System (GSAS) program.\textsuperscript{25} The luminescence emission and excitation spectra of the samples were measured on a fluorescence spectrophotometer (F-7000, Hitachi, Japan) equipped with a 150 W Xe light source. The luminescence decay data were collected on an Edinburgh FLS920 combined fluorescence lifetime and steady state spectrometer with a 450 W xenon lamp and 60 μF flash lamp. For comparison, all measurements were conducted at room temperature with the identical instrumental parameters.

**Results and discussion**

**Phase identification and crystal structure**

The XRD patterns of Tb\textsuperscript{3+} and/or Eu\textsuperscript{3+} doped Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} samples were measured at room temperature. Fig. 1 shows the powder XRD profiles of some representative samples. No records of Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2}, Na\textsubscript{3}Tb(PO\textsubscript{4})\textsubscript{2} and Na\textsubscript{3}Eu(PO\textsubscript{4})\textsubscript{2} are available in Joint Committee on Powder Diffraction Standards (JCPDS) or Inorganic Crystal Structure Database (ICSD). As shown in Table 1, the radius Nd\textsuperscript{3+} is quite close to that of La\textsuperscript{3+}, Eu\textsuperscript{3+} and Tb\textsuperscript{3+}.\textsuperscript{26} The compound Na\textsubscript{3}Nd(PO\textsubscript{4})\textsubscript{2} is isostructural with Na\textsubscript{3}RE(PO\textsubscript{4})\textsubscript{2} (RE = La, Eu and Tb). Therefore, the standard data of Na\textsubscript{3}Nd(PO\textsubscript{4})\textsubscript{2} (ICSD no. 100593) serve as a certified reference.\textsuperscript{27} As presented in Fig. 1a, most of the samples are consistent with the standard file of Na\textsubscript{3}Nd(PO\textsubscript{4})\textsubscript{2}, indicating that the obtained samples are single phase and heavily doping Tb and/or Eu ions do not change the crystal structure. This is attributed to that Tb\textsuperscript{3+} or Eu\textsuperscript{3+} occupies La\textsuperscript{3+} sites for their similar radii and identical valence. However, as an exceptional case, two additional weak diffraction peaks at 30.95° and 34.27° ascribed to Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} as a second phase can be discerned for the Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} sample. A small shift of the XRD peaks of the Na\textsubscript{3}RE(PO\textsubscript{4})\textsubscript{2} (RE = La, Eu, Tb) samples in comparison to the standard data of Na\textsubscript{3}Nd(PO\textsubscript{4})\textsubscript{2} can be observed in Fig. 1b. The characteristic peak (3 4 2) shifts to the higher angle as the RE\textsuperscript{3+} sites are substituted by the La\textsuperscript{3+} → Nd\textsuperscript{3+} → Eu\textsuperscript{3+} → Tb\textsuperscript{3+} with the decrease of ionic radii. According to Bragg’s diffraction equation, 2d sin θ = nλ, in which n is an integer, λ is the X-ray wavelength, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. The substitution of the La\textsuperscript{3+} ions in the crystallographic structure by the smaller Tb\textsuperscript{3+} or Eu\textsuperscript{3+} ions reduces the cell dimensions of the crystal, leading to the increase of the 2θ value.

**Table 1** The effective ionic radii of the different coordination sites of RE\textsuperscript{3+} in REO\textsubscript{3} (RE = La, Nd, Eu, Tb; y = 6, 7, 8)

| y  | La\textsuperscript{3+} | Nd\textsuperscript{3+} | Eu\textsuperscript{3+} | Tb\textsuperscript{3+} |
|----|---------------------|---------------------|---------------------|---------------------|
| 6  | 1.032               | 0.983               | 0.947               | 0.923               |
| 7  | 1.10                | —                   | 1.01                | 0.98                |
| 8  | 1.16                | 1.109               | 1.066               | 1.04                |
Reported by Salmon et al., Na$_3$Nd(PO$_4$)$_2$ crystallizes in $Pbc_1$ (no. 29) space group and orthorhombic crystal system (ICSD no. 100593). As shown in Fig. 1, solid solutions of Na$_3$RE(PO$_4$)$_2$ (RE = La, Eu and/or Tb) may exist due to the same valence and similar radii of these ions. Meanwhile, there are a lot of evidence about the iso-structural of orthorhombic Na$_3$Nd(PO$_4$)$_2$ with other sodium and rare-earth double orthophosphates Na$_3$RE(PO$_4$)$_2$ (RE = Y, La–Er). Here the crystal structure data of Na$_3$Nd(PO$_4$)$_2$ is used as a starting model to refine the crystal structure. Fig. 2a and b exhibit the experimental, calculated and difference results from the Rietveld refinement of the two end components Na$_3$Tb(PO$_4$)$_2$ and Na$_3$Eu(PO$_4$)$_2$, respectively. All of the observed peaks can be indexed to the corresponding data. We can conclude that the desired single-phase phosphors with a glaserite-type structure have been synthesized and the patterns have not changed by doping Tb$^{3+}$ and/or Eu$^{3+}$ ions. No other phase or impurity can be detected, confirming the formation of a single phase. The low values of $R_{wp}$, $R_p$ and $\chi^2$ shown in Table 2 indicate that the refined crystal structure data are reliable. Both Na$_3$Tb(PO$_4$)$_2$ and Na$_3$Eu(PO$_4$)$_2$ crystallize in the orthorhombic crystal system with space group $Pbc_1$ and $N = 24$. Their unit cell parameters differ from that of Na$_3$Nd(PO$_4$)$_2$ ($a = 15.874$ Å, $b = 13.952$ Å, $c = 18.470$ Å, $V = 4090.63$ Å$^3$), resulted from the substitution of Nd$^{3+}$ by Tb$^{3+}$ or Eu$^{3+}$. The Rietveld analysis shows that the samples are in crystalline phase and no phase mixture was observed. Rietveld plots of Na$_3$Tb$_{0.95}$Eu$_{0.05}$(PO$_4$)$_2$ and Na$_3$Tb$_{0.3}$Eu$_{0.7}$(PO$_4$)$_2$ are presented in Fig. S1 and S2 (in the ESI†), respectively. All of the observed peaks satisfy the reflection conditions, confirming the formation of a single phase with no impurities. The remarkable good fit between the experimental data and calculated line confirm the phase purity of the as-prepared samples.

Fig. 3a depicts the crystal structure of the Na$_3$RE(PO$_4$)$_2$ (RE = La, Eu, Tb) unit cell viewed along $a$-direction from the parallel projection, the coordination environment of RE$^{3+}$ sites, and the ideal glaserite structure. The Na$_3$RE(PO$_4$)$_2$ framework is made up of isolated PO$_4$ tetrahedron and [REO$_y$] ($y = 6, 7, 8$) polyhedron that arranged in an ordered way which results in the tunnel. The basic structure units are helical ribbons [REO$_y$] formed by six corner sharing [PO$_4$] tetrahedron that alternate “up” and “down.”. The pinwheels are linked through [PO$_4$] tetrahedra to form layers with alkali atoms located between the layers. Fig. 3b and c demonstrate the six kinds of RE sites in a unit cell along $b$-direction. The ribbons run along some

![Rietveld analysis patterns for X-ray powder diffraction data of Na$_3$Tb(PO$_4$)$_2$ (a) and Na$_3$Eu(PO$_4$)$_2$ (b) compounds.](image)

![Crystal structure of the Na$_3$RE(PO$_4$)$_2$ (RE = La, Eu, Tb) unit cell viewed along $a$-direction from the parallel projection (a); the coordination environment of different Nd$^{3+}$ sites in a unit cell (b); the expansion particular six kinds of Nd$^{3+}$ (c); the ideal glaserite structure of the K$_3$Na(SO$_4$)$_2$ (d).](image)
Luminescence properties of Tb\textsuperscript{3+} and/or Eu\textsuperscript{3+} doped Na\textsubscript{3}La\textsubscript{0.99}(PO\textsubscript{4})\textsubscript{2}:0.01Tb\textsuperscript{3+} phosphors

Fig. 4 illustrates the UV-vis excitation (PLE, \(\lambda_{em} = 546\) nm) and emission (PL, \(\lambda_{em} = 378\) nm) spectra of Na\textsubscript{3}La\textsubscript{0.99}(PO\textsubscript{4})\textsubscript{2}:xTb\textsuperscript{3+} with \(x = 0.01\text{--}1.0\). The PLE spectrum of Na\textsubscript{3}Tb(PO\textsubscript{4})\textsubscript{2} involves several sharp lines in the 280\textendash 420 nm range. The sharp f-f excitation lines at about 302, 317, 340, 351, 358, 368, 378 and 486 nm are assigned to \(7F_6\text{–}7H_7\), \(7F_6\text{–}7G_5\), \(7F_6\text{–}7D_2\), \(7F_6\text{–}7L_{10}\), \(7F_6\text{–}G_6\) and \(7F_6\text{–}D_4\), respectively. \(^{21}\) Under 378 nm NUV excitation, the PL spectrum of Na\textsubscript{3}La\textsubscript{0.99}(PO\textsubscript{4})\textsubscript{2}:0.01Tb\textsuperscript{3+} presents a group of \(5D_{3,4}\text{→}7F_j\) transitions: \(D_3 \rightarrow 7F_2 (415\text{ nm}),\) \(D_3 \rightarrow 7F_4 (437\text{ nm}),\) \(D_2 \rightarrow 7F_6 (490\text{ nm}),\) \(D_4 \rightarrow 7F_5 (546\text{ nm}),\) \(D_4 \rightarrow 7F_6 (586\text{ nm})\) and \(D_4 \rightarrow 7F_4 (623\text{ nm})\). With the increase of Tb\textsuperscript{3+} concentration (x), the blue emissions from the \(D_4 \rightarrow 7F_4\) transitions are quenched gradually, while the green emissions from the \(D_4 \rightarrow 7F_6,5,4,3\) transitions increase continuously. For the Tb\textsuperscript{3+} ion, the energy gap between the \(5D_3\) and \(5D_4\) levels is about 5915 cm\(^{-1}\), which is quite close to that between \(7F_6\) and \(7F_0\) levels (6000 cm\(^{-1}\)). \(^{21}\) Hence, if the Tb\textsuperscript{3+} concentration (y) is high enough, the emission from the \(5D_3\) level due to the cross relaxation via the resonant energy transfer process: Tb\textsuperscript{3+} (\(5D_3\)) + Tb\textsuperscript{3+} (\(7F_6\)) \(\rightarrow\) Tb\textsuperscript{3+} (\(5D_4\)) + Tb\textsuperscript{3+} (\(7F_0\)) and the green emission of the \(5D_4 \rightarrow 7F_2\) (546 nm) becomes predominant. \(^{31}\) The PL intensity of Tb\textsuperscript{3+} \(5D_4 \rightarrow 7F_2\) transition increases gradually with its concentration (x) increasing, and reaches a maximum at \(x = 1\). This result indicates that no concentration quenching exists in the Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} host among the Tb\textsuperscript{3+} ions. The Na\textsubscript{3}Tb(PO\textsubscript{4})\textsubscript{2} sample shows strong green emission under 378 nm NUV irradiation excitation, which makes it a potential green phosphor for NUV LED application.

The PLE spectrum of Na\textsubscript{3}Eu(PO\textsubscript{4})\textsubscript{2} and PL spectra of Na\textsubscript{3}La\textsubscript{1-x}(PO\textsubscript{4})\textsubscript{2}:yEu\textsuperscript{3+} (y = 0.01\text{--}1.0) are shown in Fig. 5. The PL spectrum consists of a weak broad band assigned to the charge-transfer transition (CTB) between Eu\textsuperscript{3+} and \(O^2\text{–}\), some narrow lines in the range of 230\textendash 320 nm (the strongest peak located at about 306 nm is due to Rayleigh scattering), and several sharp lines from 360\textendash 480 nm. These sharp lines correspond to the characteristic f \(\rightarrow\) f transitions of Eu\textsuperscript{3+} ions within its 4f\(^6\) configuration. They are ascribed to \(7F_0 \rightarrow 5D_4 (360\text{ nm}), 7F_0 \rightarrow 5G_7 (381\text{ nm}), 7F_0 \rightarrow 5L_6 (394\text{ nm}), 7F_0 \rightarrow 3D_4 (414\text{ nm}), 7F_0 \rightarrow 5D_2 (464\text{ nm})\) transitions of Eu\textsuperscript{3+} ion, respectively. Excitation into the \(7F_0 \rightarrow 5L_6\) transition of Eu\textsuperscript{3+} at 394 nm yields some characteristic emission lines from the \(3D_{0,1}\) excited states to the \(7F_j\) ground states, i.e., \(3D_1 \rightarrow 7F_1 (536\text{ nm}), 3D_1 \rightarrow 7F_2 (556\text{ nm}), 3D_0 \rightarrow 7F_1 (594\text{ nm}), 3D_0 \rightarrow 7F_2 (620\text{ nm}), 3D_0 \rightarrow 7F_3 (655\text{ nm})\), and \(3D_0 \rightarrow 7F_4 (703\text{ nm})\), respectively. \(^{24}\) However, the \(3D_0 \rightarrow 7F_0\) transition (about 580 nm) is very weak and can hardly be detected.

The two dominant bands at 594 (\(5D_0 \rightarrow 7F_1\) transition) and 620 nm (\(5D_0 \rightarrow 7F_2\) transition) confer on the sample an orange-red luminescence upon excitation with 394 nm light. It is known that the magnetic-dipole transition \(3D_0 \rightarrow 7F_1\) is insensitive to the symmetry of the Eu\textsuperscript{3+} site, while the forced electric dipole transition \(5D_0 \rightarrow 7F_2\) is hypersensitive to the local environment. \(^{35,36}\) Therefore, the intensity ratio \(R\) of \((5D_0 \rightarrow 7F_2) / (5D_0 \rightarrow 7F_1)\) gives a measure of the Eu\textsuperscript{3+} site symmetry in the lattice. A higher value of \(R\) (\(R > 1\)) suggests that Eu\textsuperscript{3+} locates at the site without inversion symmetry. Otherwise, Eu\textsuperscript{3+} ion locates at the site with inversion symmetry, leading to a lower value of \(R\) (\(1 > R > 0\)). \(^{37}\) As shown in Fig. 3d, Na\textsuperscript{+} has an inversion symmetric environment in the ideal glaserite structure of K\textsubscript{2}Na(SO\textsubscript{4})\textsubscript{2}. However, upon substitution of Na\textsuperscript{+} sites by RE\textsuperscript{3+},
there will be some distortion in NaO$_6$ octahedron. The Na$_3$-RE(PO$_4$)$_2$ structure seems to be a distorted glaserite structure. In this structure six different types of REO$_4$ polyhedra can be expected. Hence, the Eu$^{3+}$ ion may occupy six sites in the Na$_3$-RE(PO$_4$)$_2$ lattice, as shown in Fig. 3b and c. Here, the intensity of $^5$D$_0 \rightarrow ^7$F$_2$ is comparable with that of $^5$D$_0 \rightarrow ^7$F$_1$. The value of $R$ calculated is about 1.02, indicating that the Eu$^{3+}$ ions occupy a symmetric and a non-symmetric site almost equally. This agrees with the results of Eu$^{3+}$ doped K$_3$Y(PO$_4$)$_2$ (ref. 34) and Na$_3$Y(PO$_4$)$_2$ (ref. 38) but challenges the results of Eu$^{3+}$ doped Na$_3$La(PO$_4$)$_2$ lattice, as shown in Fig. 3b and c. Here, the intensity of Eu$^{3+}$ emission is dominated by Eu$^{3+}$ bands/lines, which are similar to that of monitoring the Tb$^{3+}$-emission, but shows large difference with that of Eu$^{3+}$ (Fig. 6b). Only several f-f transition lines of Eu$^{3+}$ are evidently observed (marked by stars in Fig. 6c). The presence of Tb$^{3+}$-related PLE bands/lines in the PLE spectrum of Eu$^{3+}$ emission clearly indicates the occurrence of energy transfer from Tb$^{3+}$ to Eu$^{3+}$. Upon 394 nm excitation ($^5$D$_0 \rightarrow ^7$F$_6$ of Eu$^{3+}$), only emission from Eu$^{3+}$ is observed, and the positions of all emission peaks are identical to those in Fig. 6b of Na$_3$-Eu(PO$_4$)$_2$. Excited at 378 nm UV irradiation ($^7$F$_6 \rightarrow ^5$G$_{5,6}$ of Tb$^{3+}$), the characteristic sharp emissions from both Eu$^{3+}$ and Tb$^{3+}$ can be detected, confirming that Tb$^{3+}$ can partially transfer excitation energy to Eu$^{3+}$ via its absorption of 4f state. Therefore, the relative intensities of these two emissions can be varied by adjusting the concentrations of the two activators through the principle of energy transfer.

**Fig. 6** PLE and PL spectra of Na$_3$Tb(PO$_4$)$_2$ (a), Na$_3$Eu(PO$_4$)$_2$ (b), and Na$_3$La$_{0.65}$(PO$_4$)$_2$:0.3Tb$^{3+}$,0.05Eu$^{3+}$ (c).

**Fig. 7** PL spectra ($\lambda_{ex}=378$ nm) of Na$_3$La$_{0.95-x}$(PO$_4$)$_2$:0.3Tb$^{3+}$,0.05Eu$^{3+}$ ($x=0.0-0.95$, a) and Na$_3$La$_{0.7-x}$(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ ($y=0-0.7$, b) phosphors together with their digital photographs under a 365 nm UV lamp.
Fig. 7 illustrates the variations of PL spectra and corresponding intensities of Na$_3$La$_{0.95-x}$(PO$_4$)$_2$:xTb$^{3+}$,0.05Eu$^{3+}$ and Na$_3$La$_{0.7-y}$(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ phosphors. The emission profile of all the Tb$^{3+}$/Eu$^{3+}$ codoped samples contain the characteristic sharp emission peaks of both Tb$^{3+}$ and Eu$^{3+}$ under excitation at 378 nm. The increasing concentrations of the Eu$^{3+}$ or Tb$^{3+}$ ions bring no obvious alteration in the intensity ratio of ($^5D_0 \rightarrow ^7F_2$)/($^5D_0 \rightarrow ^7F_1$), indicating that the degree of the local symmetry around Eu$^{3+}$ ions keeps constant. As shown in Fig. 7a, the PL intensities of Eu$^{3+}$ at 620 nm increase systematically with increasing the Tb$^{3+}$ concentration ($x$), because the increase of Tb$^{3+}$ concentration results in more sensitizers transferring the energy to Eu$^{3+}$ ions. Meanwhile, the Tb$^{3+}$ green emission intensity reaches its maximum at $x = 0.3$, and then decreases due to the concentration quenching effect with further increasing the Tb$^{3+}$ concentration ($x$). The inset of Fig. 7a depicts the dependences of the PL intensities ($^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$; $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$; $\lambda_{ex} = 378$ nm)) on the Tb$^{3+}$ concentration ($y$). The Eu$^{3+}$ PL intensity is enhanced about 11 times by codoping with Tb$^{3+}$. In Fig. 7b, the PL intensity of Tb$^{3+}$ decreases monotonously with the increase of Eu$^{3+}$ concentration from $y = 0$ to 0.7, while the Eu$^{3+}$ PL intensity increases to a maximum at $y = 0.7$. This observation indicates that the energy transfer from Tb$^{3+}$ to Eu$^{3+}$ ions can occur in current excitation condition in Tb$^{3+}$/Eu$^{3+}$ codoped Na$_3$La$_{0.7}$(PO$_4$)$_2$ phosphor. Therefore, the relative intensities of these two emissions can be varied by adjusting the concentrations of the two activators through the principle of energy transfer to realize the tunable emission color. The digital emission color photos were depicted in the inset of Fig. 7b, clearly indicating that the emission color can be tuned from green to reddish orange with increasing the Eu$^{3+}$ concentration ($y$).

Decay curves and energy transfer mechanism

It has been witnessed that an efficient energy transfer from Tb$^{3+}$ to Eu$^{3+}$ occurs in Na$_3$La$_{0.7}$(PO$_4$)$_2$ host. In order to further investigate the energy transfer between Tb$^{3+}$ and Eu$^{3+}$ in Na$_3$La$_{0.7}$(PO$_4$)$_2$, luminescent decay curves of Tb$^{3+}$ emission and Eu$^{3+}$ emission in Na$_3$La$_{0.7-y}$(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ ($y = 0–0.7$) samples have been measured. The decay curves monitored at 546 nm (Tb$^{3+}$ $^5D_4 \rightarrow ^7F_5$ transition) and 620 nm (Eu$^{3+}$ $^5D_0 \rightarrow ^7F_2$ transition) with excitation of 378 nm irradiation are presented in Fig. 8a and b, respectively.

It is found that the decay curves of Tb$^{3+}$ emission cannot be fitted in terms of a single-exponential function, but can be well fitted by a double-exponential function:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

(1)

where $I$ is the luminous intensity at time $t$; $A_1$ and $A_2$ are the fitting parameters; and $\tau_1$ and $\tau_2$ are rapid and slow lifetimes for exponential components, respectively. The decay process of these samples is characterized by an effective lifetime $\tau$, which can be calculated using eqn (2) as follows

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

(2)

Fig. 8 Luminescence decay curves of Tb$^{3+}$ 546 nm emission ($^5D_4 \rightarrow ^7F_5$) (a), Eu$^{3+}$ 620 nm emission ($^5D_0 \rightarrow ^7F_2$) (b) and the corresponding simulation curves (c).

The values of $\tau_{Tb}$ are calculated to be 3.70, 2.54, 1.33, 0.93 and 0.38 ms for Na$_3$La$_{0.7-y}$(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ phosphors with $y = 0$, 0.01, 0.05, 0.4 and 0.7. As shown in Fig. 9, the effective lifetime of Tb$^{3+}$ ions decreases with the increase of Eu$^{3+}$ due to the ET$\text{Tb} \rightarrow \text{Eu}$ process.

For the ET$\text{Tb} \rightarrow \text{Eu}$ process, the transfer probability ($P_{\text{Tb} \rightarrow \text{Eu}}$) can be expressed by eqn (3):

$$P_{\text{Tb} \rightarrow \text{Eu}} = 1/\tau - 1/\tau_0$$

(3)

where $P_{\text{Tb} \rightarrow \text{Eu}}$ is the energy transfer probability and $\tau$ and $\tau_0$ are the lifetimes for Tb$^{3+}$ with and without the Eu$^{3+}$ ions, respectively. In addition, the energy transfer efficiency ($\eta_{\text{Tb} \rightarrow \text{Eu}}$) can be evaluated using eqn (4),

$$\eta_{\text{Tb} \rightarrow \text{Eu}} = 1 - \tau/\tau_0$$

(4)

The values of $P_{\text{Tb} \rightarrow \text{Eu}}$ and $\eta_{\text{Tb} \rightarrow \text{Eu}}$ are calculated and are also shown in Fig. 9. Both the values of $P_{\text{Tb} \rightarrow \text{Eu}}$ and $\eta_{\text{Tb} \rightarrow \text{Eu}}$ increase obviously with increasing the Eu$^{3+}$ concentration ($y$), indicating that the energy-transfer process become more efficient with high Eu$^{3+}$ ion concentration.
Fig. 8b illustrates the decay curves of Eu³⁺ emission. All the decay curves of Eu³⁺ emission could be well fitted into singly exponential equation

\[ I(t) = I_0 \exp(-t/\tau) \]

where \( I_0 \) and \( I(t) \) are the intensities of Eu³⁺ emission at time \( t_0 \) and \( t \), respectively; \( \tau \) denotes the lifetimes for Eu³⁺. The calculated values of \( \tau_{\mathrm{Eu}} \) are 5.02, 4.21, 3.32 and 3.27 ms for \( y = 0.01, 0.05, 0.4 \) and 0.7 in Na₃Laₓ₀.₇₋ₓ(PO₄)₂₀.₃Tb³⁺₂ʸEu³⁺ phors. It is obvious that the Eu³⁺ decay curves recorded at the \( 5\,\text{D}_{0} \rightarrow 7\,\text{F}_{5} \) transition (620 nm) exhibit a rising step. The fluorescence intensity increases with increasing time, then reaching a maximum, and finally decreases until the decay process completes. Therefore, there are two different processes for the emission of Eu³⁺; decay process and build-up process. In the initial build-up process, the energy absorbed by the \( \text{F}_6 \rightarrow \text{G}_6 \) transition of Tb³⁺ ions is transferred to Eu³⁺ ions. This process is significantly influenced by the Eu³⁺ concentration. As shown in Fig. 8b, with increasing the Eu³⁺ concentration \( (y) \), the initial build-up process becomes faster and faster, suggesting that the ET \( \text{TB} \rightarrow \text{EU} \) process becomes more efficient with higher Eu³⁺ concentration.⁴³ When the Na₃Laₓ₀.₇₋ₓ(PO₄)₂₀.₃Tb³⁺₂ʸEu³⁺ samples are excited by 378 nm irradiation, the rate equations for the population densities in the \( \text{D}_4 \) level of Tb³⁺ and the \( \text{D}_0 \) of Eu³⁺ ion can be expressed as follows,⁴⁴

\[ \frac{dN_{\text{Tb}}}{dt} = -N_{\text{Tb}}/\tau_{\text{Tb}} - K_{\text{TB-EU}} N_{\text{Tb}} N_{\text{Eu}} \]  
\[ \frac{dN_{\text{Eu}}}{dt} = -N_{\text{Eu}}/\tau_{\text{Eu}} + K_{\text{TB-EU}} N_{\text{Tb}} N_{\text{Eu}} \]

where \( N_{\text{Tb}} \) and \( N_{\text{Eu}} \) are the population densities of the \( \text{D}_4 \) level of Tb³⁺ and the \( \text{D}_0 \) of Eu³⁺, respectively. \( K_{\text{TB-EU}} \equiv \text{ET} \text{Tb} \rightarrow \text{Eu} \) is the non-radiative energy transfer rate from the \( \text{D}_4 \) state of Tb³⁺ to \( \text{D}_0 \) of Eu³⁺. Then the fluorescence intensity \( I(t) \) of Eu³⁺ ions at 620 nm excited at 378 nm irradiation can be given as following equation:

\[ I(t) = N_{\text{Eu}}(t) = N_{\text{Eu}}/\tau_{\text{Eu}} \]
\[ = \frac{K_{\text{TB-EU}} N_{\text{Tb}}}{1/\tau_{\text{Eu}} - 1/\tau_{\text{TB}}} \left[ \exp\left(\frac{-t}{\tau_{\text{TB}}}\right) - \exp\left(\frac{-t}{\tau_{\text{Eu}}}\right) \right] \]

Using the measured values of \( \tau_{\text{Tb}} \) and \( \tau_{\text{Eu}} \), the simulation curves for Na₃La₀.₇₋ₓ(PO₄)₂₀.₃Tb³⁺₂ʸEu³⁺ samples are obtained as presented in Fig. 8c, which show two process for Eu³⁺ emission, being similar to the measured curves. That is to say, the theoretical results are consistent with the experimental observations.

In general, the energy transfer between the sensitizer and activator may take place via exchange interaction and multipolar interaction. The energy transfer mechanism can be determined using the following relationship:\²⁵

\[ \ln(I_0/I) \propto C \quad \text{and} \quad I_{50}/I_S \propto C^{1/3} \]

in which \( I_{50} \) and \( I_S \) are the luminescence intensities of Tb³⁺ in the absence and presence of Eu³⁺, respectively; \( C \) is the total concentration of Tb³⁺ and Eu³⁺; \( \ln(I_{50}/I_S) \propto C \) is corresponding to the exchange interaction; \( \alpha = 6, 8, \) and 10 are dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions. The relationships are illustrated in Fig. 10a–d, respectively for Na₃La₀.₇₋ₓ(PO₄)₂₀.₃Tb³⁺₂ʸEu³⁺ phors. The linear behavior was observed only when \( \alpha = 6 \), indicating that energy transfer from Tb³⁺ to Eu³⁺ in Na₃La(PO₄)₂ host occurs via a dipole–dipole interaction.

The scheme of energy transfer from Tb³⁺ to Eu³⁺ in Na₃La(PO₄)₂ host is demonstrated in Fig. 11. Tb³⁺ ions absorb the energy from 378 nm irradiation and are excited from the ground state of \( \text{F}_6 \) to the excited states of \( \text{D}_j \) (\( j = 2, 3, 4 \)). Some of the excited Tb³⁺ radiative transmit from \( \text{D}_4 \) to the ground state \( \text{F}_2 \) directly with relatively weaker blue light emission of 415 and 437 nm, and other excited Tb³⁺ relax to the lowest excited state \( \text{F}_2 \) through non-radiative transition, then radiative decay to the ground state \( \text{F}_0 \) with a strong green emission. When Eu³⁺ ions are codoped, part of the energy from \( \text{D}_4 \) to \( \text{F}_2 \) transition of Tb³⁺ will be transferred to Eu³⁺ through cross-relaxation due the obvious overlap between the \( \text{D}_4 \rightarrow \text{F}_2 \) emission of Tb³⁺ and \( \text{F}_{0,1,2} \rightarrow \text{D}_{0,1,2} \) absorption of Eu³⁺, then relax to the ground state \( \text{F}_0 \) of Eu³⁺ and finally radiative decay to the ground state \( \text{F}_0 \) with a reddish orange emission.⁴⁴

**CIE chromaticity coordinates of Na₃La(PO₄)₂:Tb³⁺,Eu³⁺**

The CIE chromaticity coordinates \((X, Y)\) for Na₃La₀.₇₋ₓ(PO₄)₂₀.₃Tb³⁺₂ʸEu³⁺ \((y = 0–0.7)\) samples were calculated in the case of 378 nm excitation and the results are shown in Fig. 12. The chromaticity coordinates of Na₃Eu(PO₄)₂ phosphor is also presented. The CIE chromaticity coordinates \((X, Y)\) changes from point \((0.2987, 0.5695)\) to point \((0.6203, 0.3505)\) with the increase of Eu³⁺ concentration \((y)\). The as formed Na₃La₀.₉₅₋ₓ(PO₄)₂хран³⁺₂ₓEu³⁺ \((x = 0–0.95)\) phosphors show typical reddish-orange luminescence. However, their CIE coordinates are too close to be distinguished from each other in a chromaticity diagram with the changes of the Tb³⁺ ion concentration, so they are not presented.

![Fig. 10](image-url)

**Fig. 10** Dependence of \(\ln(I_{50}/I_S)\) on \(C_{\text{Tb+Eu}}\) (a) and the dependence of \(I_{50}/I_S\) on \(C_{\text{Tb+Eu}}\)⁶/₅ (b), \(C_{\text{Tb+Eu}}\)⁸/₅ (c) and \(C_{\text{Tb+Eu}}\)¹₀/₅ (d).
The above equation should mathematically demonstrate the range of chromaticity coordinates that we can obtain by adjusting the Tb$^{3+}$ and Eu$^{3+}$ concentrations. It is obvious that the chromaticity coordinates for the Na$_3$La(PO$_4$)$_2$:Tb$^{3+}$,Eu$^{3+}$ phosphor falls on a line connecting the two chromaticity coordinates of Na$_3$La(PO$_4$)$_2$:Tb$^{3+}$ and Na$_3$La(PO$_4$)$_2$:Eu$^{3+}$, respectively. With increasing the Eu$^{3+}$ concentration ($y$), the chromaticity coordinate for Na$_3$La(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ phosphors move from the chromaticity point 1 of Na$_3$La$_{0.7}$(PO$_4$)$_2$:0.3Tb$^{3+}$ toward point 8 of Na$_3$Eu(PO$_4$)$_2$ along this straight line. The prepared Na$_3$La(PO$_4$)$_2$:Tb$^{3+}$,Eu$^{3+}$ phosphor exhibits efficient tunable emission in the visible-light region upon excitation with NUV irradiation, and might find potential applications in multicolor displays and other optoelectronic devices.

**Conclusions**

In a conclusion, a series of Tb$^{3+}$ and/or Eu$^{3+}$ doped Na$_3$La(PO$_4$)$_2$ phosphors have been successfully synthesized and their luminescence properties have been investigated in detail. The glaserite-like orthorhombic structure provides the Na$_3$La(PO$_4$)$_2$ host the possibility of doping with Tb$^{3+}$ or Eu$^{3+}$ ions without substantial luminescence quenching. Tb$^{3+}$ can efficiently sensitize Eu$^{3+}$ emission under NUV excitation. The energy transfer mechanism (Tb$^{3+} \rightarrow$ Eu$^{3+}$) was demonstrated to be dominated by a dipole-dipole interaction. The luminescence decay properties of Eu$^{3+}$ in Na$_3$La(PO$_4$)$_2$:Tb$^{3+}$,Eu$^{3+}$ samples under $^5$D$_{4}$-$^7$G$_{6}$ excitation (378 nm) within Tb$^{3+}$ ions were simulated with the energy transfer theory. The emission color of Na$_3$La$_{0.7}$(PO$_4$)$_2$:0.3Tb$^{3+}$,yEu$^{3+}$ phosphors can be tunable from green through yellow and red region by adjusting the Eu$^{3+}$ concentration. These results indicate that the as-synthesized phosphors may find potential applications as a color-tunable emitting material in solid state lighting.

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**Notes and references**

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\[ Y = 0.7782 - 0.7037X \]
