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Tunable full color emission from single-phase $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ phosphors

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Abstract

Tunable full color emissive $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ ($0 \leq x \leq 0.09$) phosphors peaked at 481 nm (blue), 574 nm (yellow), 592 nm (orange), and 617 nm (red) were synthesized in air by high temperature solid-state reaction route. The as-synthesized phosphors were characterized by X-ray powder diffraction (XRD), photoluminescence excitation (PLE) and photoluminescence (PL) spectra. The PLE spectra in the range from 200 to 500 nm include an Eu–O charge transfer band (CTB) and several 4*f*–4*f* transition peaks of Dy^{3+} and Eu^{3+}, indicating its potential application in white light emitting diodes (LEDs). The effect of Eu^{3+} concentration on the emission intensity of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ phosphors was investigated in detail and the optical concentration is found to be $x=0.005$. The CIE chromaticity coordinates for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ phosphors are simulated. With an increase in Eu^{3+} ion concentration, the chromaticity color coordinates can be tuned efficiently from the border of greenish white region to its equal-energy white light point, and eventually to red region. All the results imply that the studied $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ phosphors could be potentially used as white LEDs.

Keywords: Solid-state reaction; $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$x$$Eu^{3+}$ phosphors; Photoluminescence; White LEDs

1. Introduction

Recently, white light-emitting diodes (white LEDs) have been intensively studied as an attractive alternative to conventional lamps because of their excellent luminescent characteristics, good stability, high luminescence efficiency, as well as corrosion-free gas emission [1–3]. Generally, white light is generated by a GaN blue LED encapsulated with a yellow-emitting phosphor (YAG:Ce^{3+}) coating. However, a long-standing challenge is to possess excellent color rendering index for the white LEDs based on YAG:Ce^{3+} phosphor [4]. To solve this problem, researchers present a strategy to explore the single-host full-color emitting phosphors for near ultraviolet (NUV) pumped white LEDs [5–7]. Many studies have been focused on doping one or more activators in one matrix. For example, Dy^{3+} is widely used as a potential activator for white-emitting phosphors due to its yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) emissions. Nevertheless, the CRI of Dy^{3+}-doped phosphors are very low because of its weak red light emission. Some activators with high efficiency red light emission, to some extent, can compensate this shortcoming [8–10], such as Eu^{3+} ions. Up to now, there are a few phosphors including $La_2Zr_2O_7$:Eu^{3+}, Dy^{3+} [11], $KCaBO_3$:Eu^{3+}, Dy^{3+} [12], Sr_2CeO_4:Eu^{3+}, Dy^{3+} [13], YVO_4:Eu^{3+}, Dy^{3+} [14], Sr_2SiO_4:Eu^{3+}, Dy^{3+} [15] which were developed for LEDs application.

In recent years, several materials of borate family, such as $LiCaBO_3$:M (M$=$$Eu^{3+}$, Sm^{3+}, Tb^{3+}, Ce^{3+}, Dy^{3+}) [16], $NaSrBO_3$:Ce^{3+} [17], $Li_6Y(BO_3)_3$:Eu^{3+} [18], $RE_{0.05}M_{0.95}BO_3$ (RE$=$$Eu^{3+}$, Tb^{3+}, M$=$In, Gd, La) [19] have been presented as promising phosphors for white LEDs. Among these phosphors, $LiSr_4(BO_3)_3$:Re (Re$=$$Ce^{3+}$, Eu^{2+} and Tb^{3+}) [20,21] phosphors have attracted much attention due to their advantages of excellent colorimetric purity, good luminescence characteristics, high chemical stability and low synthesis

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temperature. Previously, we reported $LiSr_4(BO_3)_3:Dy^{3+}$ as a single phase white emission phosphor for LEDs [22]. Similar with the common strategy in increasing the red component, Eu^{3+} co-doping $LiSr_4(BO_3)_3:Dy^{3+}$ phosphor was synthesized in this work to demonstrate tunable white light emission. The photoluminescence (PL) properties and the tunable properties were investigated in detail.

2. Experimental

Powder samples with stoichiometric composition of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ (x=0.0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.09) phosphors were synthesized by high temperature solid-state route. Raw materials of $SrCO_3$, H_3BO_3, Li_2CO_3 (Shanghai Chemical Reagent, A.R. grade) and Eu_2O_3, Dy_2O_3 (Shanghai Yuelong New Materials Co. Ltd., 99.99%) were mixed thoroughly in an agate mortar. The amount of H_3BO_3 was excess of 5% to compensate its evaporation losses during the synthesis process. The well-ground mixtures were calcined at 1000 °C for 300 min in air, then cooled down naturally to room temperature. The synthesis reaction could be described as follows:

$$Li_2CO_3+6H_3BO_3+(1.98-2x)SrCO_3+0.005Dy_2O_3$$
$$+xEu_2O_3\xrightarrow{1000\,^\circ C}(2.98-2x)CO_2+9H_2O$$
$$+2LiSr_{0.99-x}Dy_{0.01}(BO_3)_3:xEu^{3+}$$

The phase purity of the as-synthesized phosphors was investigated by X-ray powder diffraction spectroscopy (XRD) with a X-ray Difractometer (Brucker D8) with Cu-Ka radiation at 40 kV and 40 mA. The XRD patterns were collected in the range of $10^\circ \leq 2\theta \leq 80^\circ$. The PL and PLE spectra were recorded on a Hitachi F-7000 fluorescence spectrometer with a 150 W-xenon lamp. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the XRD patterns for the as-prepared $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ powder. Dominant phase $LiSr_4(BO_3)_3$ was identified for all samples as the diffraction peaks were in well agreement with standard card (JCPDS 17-0861) [23], accompanied with small amount of impurity phases of $Sr_3B_2O_6$ (JCPDS 35-0144) (marked as * in Fig. 1) [24]. The occurrence of impurity is owing to the sublimation loss of Li_2O at the temperature of 1000 degree during the synthesized procedure. The main peaks are sharp suggesting that the structures of the crystalloid are well crystallized and the $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors have been successfully prepared. Moreover, the incorporation of Dy^{3+} and Eu^{3+} ions did not change the structure of $LiSr_4(BO_3)_3$ due to the low dopant concentrations.

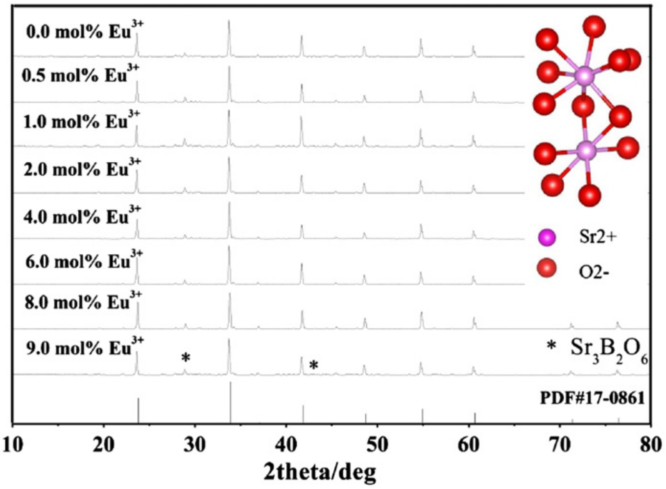

Fig. 1. X- ray diffraction patterns of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ powders (Inset: the Sr coordinationpolyhedral in $LiSr_4(BO_3)_3$. The pink and red spheres represent Sr^{2+} and O^{2-}, respectively.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$LiSr_4(BO_3)_3$ crystallizes in the cubic space group $Ia\overline{3}d$ with large lattice parameters: a=14.95066(5) Å and V (cell volume)=3341.80(2) Å^3. As shown in the inset of Fig. 1, there are two different crystallographic sites for Sr atoms in the $LiSr_4(BO_3)_3$ compound. The Sr(I) atom is coordinated to six oxygen atoms, forming a distorted octahedron, and it is centrosymmetric (16a). While the Sr(II) atom is eight-coordinated to oxygen atoms, forming a $Sr(II)O_8$ polyhedron, and it is noncentrosymmetric (48f) [23]. It is well known that an acceptable percentage difference in ion radii between the doped and substituted ions must not exceed 30%, which suggests that Dy^{3+} ions (1.027 Å, CN=8) and Eu^{3+} ions (0.092 Å, CN=8) may prefer to substitute Sr^{2+} (1.260 Å, CN=8) cation ions rather than Li^+ (0.059 Å, CN=4) [25]. Therefore, the general formula of the investigated phosphors is described as $LiSr_{4-x\text{-}y}(BO_3)_3{:}xDy^{3+}$, yEu^{3+}, where x and y denote the substitution ratio of both Dy^{3+} and Eu^{3+} for Sr^{2+} ions, respectively.

3.2. PL and PLE spectra

3.2.1. PL spectra

Fig. 2 shows the PLE spectrum (λ_{em}=617 nm) and PL spectra (λ_{ex}=272 nm) of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors, respectively. The emission bands of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors under 272 nm excitation are composed of orange (592 nm) and red (617 nm) emission peaks. Additionally, the emission shape and peak positions hardly vary with the increasing Eu^{3+} concentration. However, the emission intensity increases gradually and reaches a maximum intensity at x=0.08, then decrease dramatically due to the effect of concentration quenching.

Fig. 3 shows the PL spectra of $LiSr_{3.99}Dy_{0.01}(BO_3)_3$, $LiSr_{3.97}Eu_{0.03}(BO_3)_3$ and $LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3$ phosphors

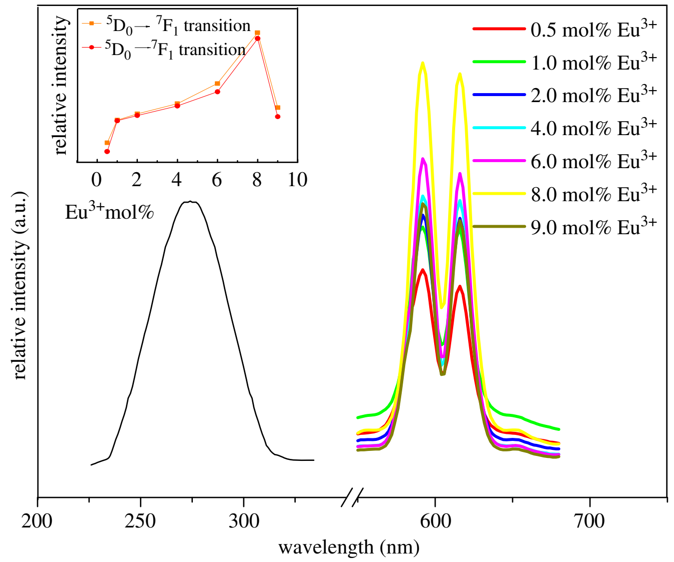

Fig. 2. PLE and PL spectra of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphor ($\lambda_{ex}=272$ nm, and $\lambda_{em}=616$ nm).

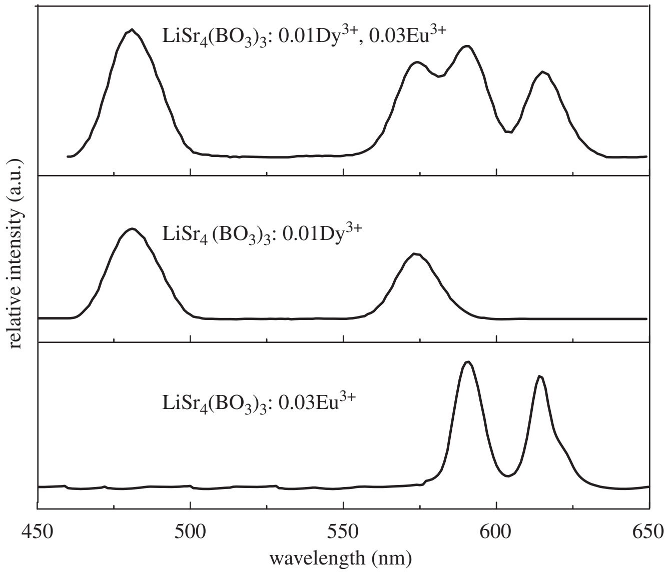

Fig. 3. The PL emission spectra of $LiSr_{3.99}Dy_{0.01}(BO_3)_3$, $LiSr_{3.97}Eu_{0.03}(BO_3)_3$ and $LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3$ phosphors ($\lambda_{ex}=386$ nm).

excited by 386 nm light. For $LiSr_{3.99}Dy_{0.01}(BO_3)_3$ phosphor, the observed PL spectrum exhibits two strong bands centered at 481 nm (blue) and 574 nm (yellow), which are corresponded to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively. From PL spectra of $LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3$ phosphors excited by 386 nm, the prominent emission peaks at 481, 574, 592 and 617 nm could be observed. The peaks at 481 and 574 nm correspond to transitions of Dy^{3+} ions, and others are assigned to transitions of Eu^{3+} ions. In a word, both Eu^{3+} and Dy^{3+} ions can be excited simultaneously by 386 nm light.

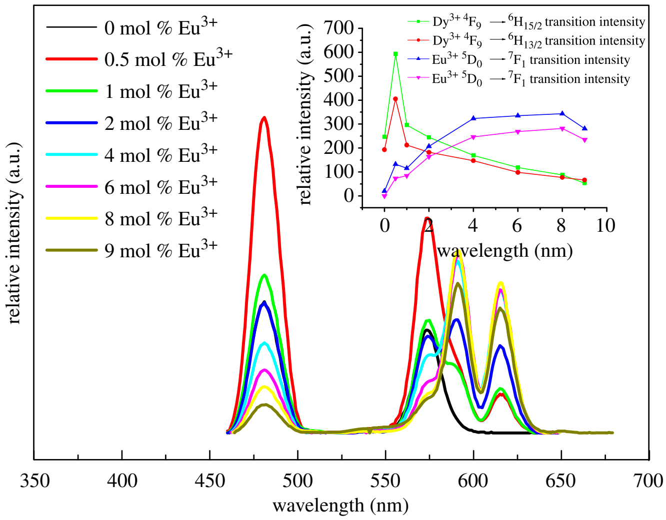

Fig. 4. PL spectra of phosphor $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ excited by 386 nm (the insert represents concentration dependence of the emission intensity for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ excited by 386 nm).

Fig. 4 shows the PL spectra of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors excited by 386 nm, and the inset shows the corresponding concentration dependence of the characteristic emission intensity for both Dy^{3+} and Eu^{3+} ions. As shown in the inset of Fig. 4, the transition emission intensity of Dy^{3+} and Eu^{3+} is plotted as a function of Eu^{3+} concentration (x mol%) in $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ samples. Although the concentration of Dy^{3+} is fixed constant, significant change of the its emission in $LiSr_4(BO_3)_3$ is observed by varying the Eu^{3+} concentration in the range from $x=0.5$ to 9 mol%. Both the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission intensity of Dy^{3+} increase with the increase of Eu^{3+} concentration (x) because energy transfer from Eu^{3+} to Dy^{3+} ions [12,14], and reaches a maximum value at $x=0.005$, finally decreases with further increasing Eu^{3+} concentration because of the concentration quenching effect. Similarly, the emission intensity of both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition is dependent on the Eu^{3+} content which is similar to those of Dy^{3+} ions. Meanwhile, both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition emission intensity of Eu^{3+} increases with the increase of Eu^{3+} concentration, and reaches a maximum value at 8 mol%, finally decreases with increasing Eu^{3+} ions due to the concentration quenching.

It is well known that the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic dipole transition is prominent when Dy^{3+} is located at high symmetry. In our case, the blue emission ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) at 481 nm is stronger than the yellow emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) at 574 nm, which illustrates that Dy^{3+} ions occupy a high-symmetry site in the investigated $LiSr_4(BO_3)_3$ host. Also, the orange emission ($^5D_0 \rightarrow {}^7F_1$) is stronger than the red emission ($^5D_0 \rightarrow {}^7F_2$) of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors, which indicates that Eu^{3+} is located in a centrosymmetric position in the $LiSr_4(BO_3)_3$ matrix. In a word, as depicted in Fig. 1, Dy^{3+} and Eu^{3+} ions prefer to substitute the Sr^{2+} in the 16a position in the $LiSr_4(BO_3)_3$ compound.

The concentration quenching of the luminescence is due to the energy transfer from one activator to another until all energy is consumed. For this reason, it is necessary to obtain the critical distance (R_c), that is, the critical separation between donor (activators) and acceptors (quenching site). The critical distance R_c of the energy transfer between the activators ions in the $\mathrm{LiSr_{3.99-\mathit{x}}Dy_{0.01}(BO_3)_3}$:$x\mathrm{Eu^{3+}}$ phosphors can be estimated according to the following equation [26]:

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

where x_c is the critical concentration, N is the number of $\mathrm{Sr^{2+}}$ ions in the unit cell and V is the volume of the unit cell. To obtain the strongest emission for $\mathrm{Dy^{3+}}$, by taking the experimental and analytic values of x_c, N and V (0.005, 64 and 3341.80 Å^3, respectively), the critical transfer distance of $\mathrm{Eu^{3+}}$ in $\mathrm{LiSr_{3.99-\mathit{x}}Dy_{0.01}(BO_3)_3}$:$x\mathrm{Eu^{3+}}$ phosphors is found to be about 27.05 Å. Similarly, for $\mathrm{Eu^{3+}}$, the critical transfer distance is 10.75 Å.

3.2.2. PLE spectra

Fig. 5(a) and (b) shows the PLE spectra of $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphors monitored at 481 nm and 617 nm, respectively. The PLE spectrum of $\mathrm{LiSr_{3.97}qEu_{0.03}(BO_3)_3}$ phosphors monitored at 617 nm is also shown in Fig. 5(c) for comparison. For the PLE spectrum of $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphors monitored at 481 nm, it is indicated that the excitation spectrum in the range 300–460 nm comes from the ground state of $^6\mathrm{H}_{15/2}$ to the excited states of $4f^9$ electronic configurations of the $\mathrm{Dy^{3+}}$ ions, which are located at 324 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^4\mathrm{M}_{17/2}$), 350 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^6\mathrm{P}_{7/2}$), 364 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^4\mathrm{I}_{11/2}$), 388 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^4\mathrm{I}_{13/2}$), 427 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^4\mathrm{G}_{11/2}$) and 454 nm ($^6\mathrm{H}_{15/2}\rightarrow{}^4\mathrm{I}_{15/2}$) [25]. In comparison with Fig. 5(c), the typical excitation peaks of $\mathrm{Eu^{3+}}$ in $\mathrm{LiSr_4(BO_3)_3}$ cannot be found.

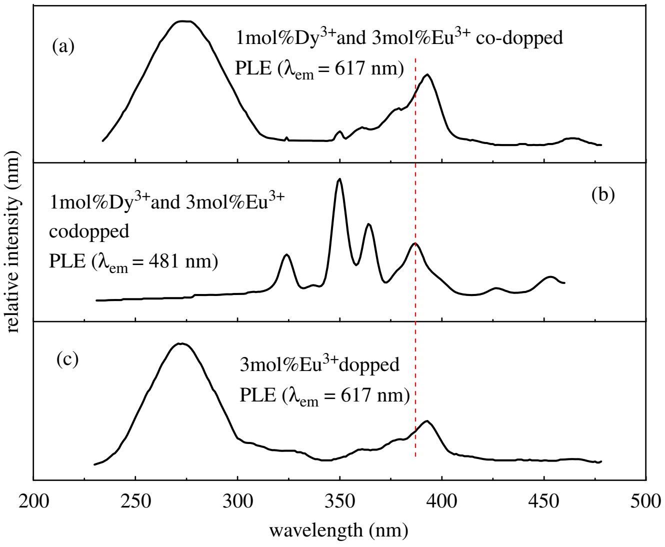

Fig. 5. The PLE spectra of $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphors under $\lambda_{\mathrm{em}}=617$ nm (a) and 481 nm (b), respectively. The PLE spectrum of $\mathrm{LiSr_{3.97}Eu_{0.03}(BO_3)_3}$ phosphors under $\lambda_{\mathrm{em}}=617$ nm is shown in (c).

In the case of PLE spectrum of $\mathrm{LiSr_{3.97}Eu_{0.03}(BO_3)_3}$ phosphor, it is clear that it consists of a broad band and a group of sharp peaks in the visible and UV region. The broad excitation band centered at 272 nm can be attributed to the CTB transition arising from $\mathrm{O^{2-}}$ ion to $\mathrm{Eu^{3+}}$ ion, which suggests that the phosphor is a possible candidate for fluorescent lamps. The sharp peaks are ascribed to the intra-configurational $4f$–$4f$ transitions of $\mathrm{Eu^{3+}}$ in the host: $^7\mathrm{F}_0\rightarrow{}^5\mathrm{D}_4$, $^7\mathrm{F}_0\rightarrow{}^5\mathrm{G}_2$, $^7\mathrm{F}_0\rightarrow{}^5\mathrm{L}_6$ and $^7\mathrm{F}_0\rightarrow{}^5\mathrm{D}_2$ at wavelengths 361, 380, 393 and 464 nm, respectively [18]. The PLE spectrum (Fig. 5c) monitored at 616 nm shows typical transitions characteristics of $\mathrm{Eu^{3+}}$, meanwhile, the co-doped system (Fig. 5a) shows additional excitation band at about 350 nm which is corresponded to solely $\mathrm{Dy^{3+}}$ ion, $^6\mathrm{H}_{15/2}\rightarrow{}^6\mathrm{P}_{3/2}$ excitation transition. This is an indication of possible inter-ion energy transfer from $\mathrm{Eu^{3+}}$ to $\mathrm{Dy^{3+}}$ ions ($^5\mathrm{L}_6\rightarrow{}^4\mathrm{F}_{9/2}$). The similar results were reported in Refs. [12,15]. Accordingly, electronic transitions as well as energy transfer process in $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphor is schematically illustrated in Fig. 6. According to Fig. 6, the energy absorbed by $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphors may be divided into two parts, one of which is directly absorbed by $\mathrm{Eu^{3+}}$ and $\mathrm{Dy^{3+}}$ ions, and then leads to f–d and f–f electron transitions; another part is absorbed by $\mathrm{LiSr_4(BO_3)_3}$ host. When excited by 273 nm, the charge will transfer from $\mathrm{Eu^{3+}}$ to $\mathrm{O^{2-}}$ ion. With the excitation of $\mathrm{Eu^{3+}}$ ions from ground state to higher levels, $^5\mathrm{L}_6$, some part of the absorbing energy relaxed into the $^4\mathrm{F}_{9/2}$ level of $\mathrm{Dy^{3+}}$ and brought about the emission.

The excitation band of $\mathrm{LiSr_{3.96}Dy_{0.01}Eu_{0.03}(BO_3)_3}$ phosphor matches well with the NUV emitting of InGaN chip, implying a potential application of the investigated phosphor in NUV-pumped white LEDs.

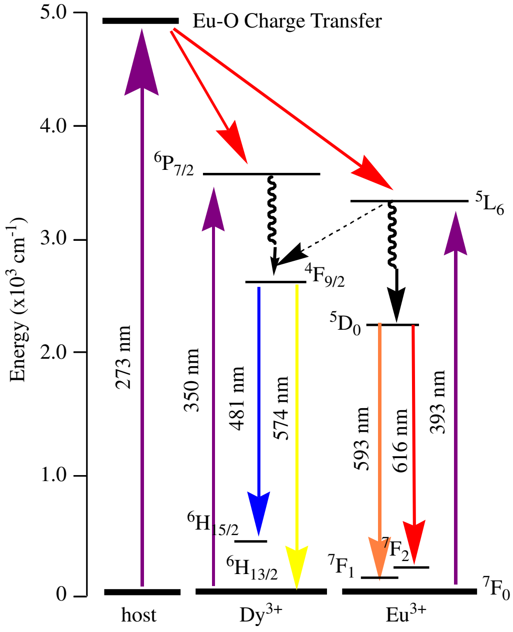

Fig. 6. The schematic energy levels of $\mathrm{LiSr_{4-\mathit{x}-\mathit{y}}(BO_3)_3}$:$x\mathrm{Dy^{3+}}$, $y\mathrm{Eu^{3+}}$.

3.3. Simulation of white light emission from $LiSr_{4-x}(BO_3)_3$:xDy^{3+} phosphors

Generally, the relative intensity ratio of the yellow (574 nm) to blue (481 nm) emission (Y/B ratio) and the relative intensity ratio of red (617 nm) emission to the orange (592 nm) (R/O ratio) can be used to examine the structural distortion around Dy^{3+} and Eu^{3+} ions, respectively. The Y/B ratios and R/O ratios for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors under 386 nm excitation are calculated and also listed in Table 1. Correspondingly, Fig. 7 represents Eu^{3+}-doped concentration dependence of the Y/B ratios and R/O ratios for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$. It is obvious that Y/B ratios are strongly affected by the co-doped Eu^{3+} ions, when Dy^{3+}-doped concentration is fixed constant. Y/B ratios increase with the increase of Eu^{3+} concentration. The distortion of Dy^{3+} ions located in the crystal lattices increases with the increasing Eu^{3+} concentration owing to the substitution of smaller Eu^{3+} ions for the larger Sr^{2+} ions in $LiSr_4(BO_3)_3$. It is also well known that $^4F_{9/2}$–$^6H_{13/2}$ transition of Dy^{3+} belongs to hypersensitive transitions with $\Delta J=2$. When Dy^{3+} is located at a low-symmetry local site (without an inversion center), this emission transition dominates in emission spectra, otherwise the blue emission is dominant [8]. As presented previously, Dy^{3+} is located at a high symmetry in $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphor. When the Eu^{3+} ions are introduced into the host, the structural distortion around Dy^{3+} ions is aggravated and the symmetry becomes lower. Therefore, Y/B ratios increase with the increase of Eu^{3+}-doped concentration. The reasonable interpretation is suitable for the change trend R/O ratios. It is very interesting to note that Y/B ratios of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ ($x=0.005$, 0.01 and 0.02) is smaller than that of $LiSr_{3.99}Dy_{0.01}(BO_3)_3$, as shown in the purple circle, which is worth further studying.

Color coordinate is an important parameter for phosphors in white LED application. The chromaticity color coordinates for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors are simulated and also listed in Table 1. The corresponding Commission International de I'Eclairage (CIE) 1931 *x–y* chromaticity diagram is presented in Fig. 8, and the inset simultaneously shows the enlarged spectrum for color coordinate (*x*) value from 0.260 to 0.600. The dot * in CIE-1931 chromaticity diagram shows the ideal white light chromaticity coordinates with (0.333, 0.333) value. Generally, the closer the CIE chromaticity coordinates to dot *, the higher the white-light-emitting quality. As indicated by a grass green line with arrows in Fig. 8, with the increase of Eu^{3+} ions, the chromaticity color coordinates can be tuned efficiently from the border of greenish white region to its equal-energy white light point, and eventually to red region. When $x=0.005$, color coordinate (*x*, *y*) value is (0334, 0.353), which is very close to the ideal white light (dot *). When $0.005 < x < 0.02$, the investigated phosphors can emit warm white light. In a word, it is possible to obtain the ideal white and warm white emission for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors by appropriate concentration adjustment of both Dy^{3+} and Eu^{3+} ions.

Table 1
Ratios of Y/B, R/O and chromaticity color coordinations for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors by 386 nm light excitation.

$LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$		Dy^{3+}	Eu^{3+}	Color coordination	
		Y/B ratio	R/O ratio	*x*	*y*
a	$x=0.00$	0.781	/	0.307	0.307
b	$x=0.005$	0.682	0.553	0.334	0.353
c	$x=0.01$	0.716	0.730	0.375	0.360
d	$x=0.02$	0.743	0.752	0.441	0.366
e	$x=0.04$	0.809	0.762	0.505	0.379
f	$x=0.06$	0.830	0.803	0.533	0.377
g	$x=0.08$	0.885	0.822	0.551	0.378
h	$x=0.09$	1.245	0.836	0.558	0.391

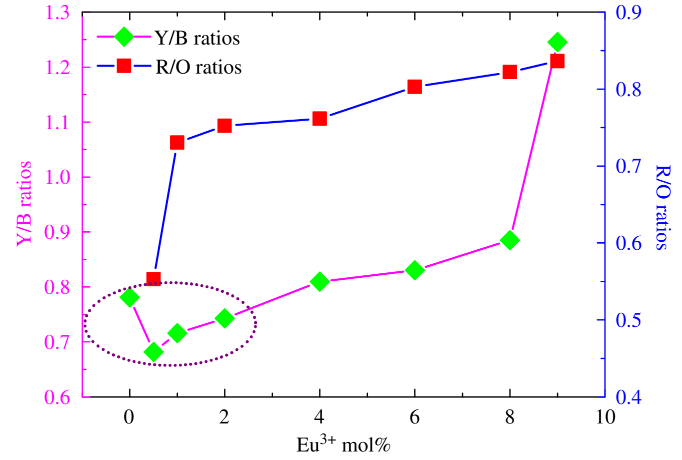

Fig. 7. Eu^{3+}-doped concentration dependence of the Y/B ratios and O/R ratios for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ excited by 386 nm.

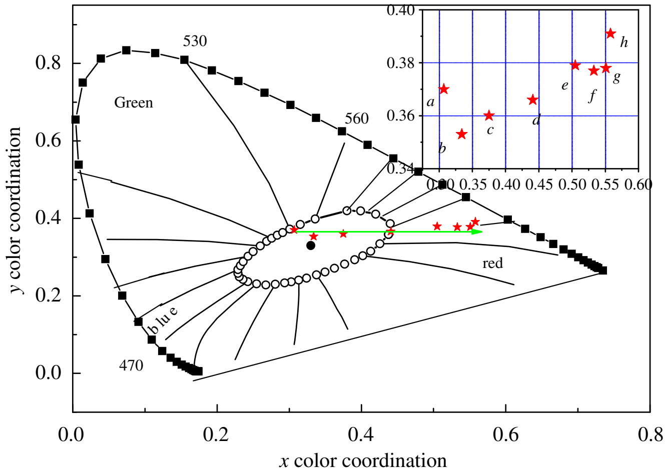

Fig. 8. CIE coordinate diagram of $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3$:$xEu^{3+}$ phosphors by 386 nm light.

4. Conclusions

In summary, a single-phased white-light-emitting phosphor, $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$, was prepared by the conventional solid-state reaction. The study showed that the $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors could be excited by near-ultraviolet (NUV) light in the region of 200–500 nm, and the emission bands are centered at 481 nm (blue), 574 nm (yellow), 592 nm (orange) and 616 nm (red) excited by 386 nm light. To obtain the strongest emission for Dy^{3+}, the critical transfer distance of Eu^{3+} in $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors is found to be about 27.05 Å. Similarly, the critical transfer distance is 10.75 Å for the strongest emission of Eu^{3+} at $x=0.08$. The CIE chromaticity coordinates for $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors suggest that the emission color of the obtained phosphors can be tunable from greenish to white and eventually to red by simply adjusting the amount of Eu^{3+} ions. All the results indicate that the $LiSr_{3.99-x}Dy_{0.01}(BO_3)_3{:}xEu^{3+}$ phosphors show potential application in NUV-pumped white LEDs to be free of complicated phosphor blending operation.

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