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Enhanced luminescence intensity of novel red-emitting phosphor -$Sr_3Lu_2(BO_3)_4$:Bi^{3+},Eu^{3+} via energy transfer

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Abstract

Bi^{3+}/Eu^{3+} co-activated $Sr_3Lu_2(BO_3)_4$ was successfully synthesized via a solid state reaction. The optimal concentration of Bi^{3+},Eu^{3+} and Bi^{3+}/Eu^{3+} are 1 mol%, 60 mol% and 1 mol%/20 mol%, respectively. The emission spectra of $Sr_3Lu_2(BO_3)_4$:Bi^{3+}, Eu^{3+} gives three peaks located at 405 nm, 489 nm which were attributed to Bi^{3+} S_6 (blue) and C_2 (green) site symmetry, respectively and 610 nm which was ascribed to Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) transition. The emission intensity of Bi^{3+} decreases with increasing Eu^{3+} content which indicates that a efficient energy transfer occurred in the $Sr_3Lu_2(BO_3)_4$ host. The relative intensity of $Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+},0.20Eu^{3+} excited at 327 nm and 370 nm was remarkably enhanced by 201% and 265%, respectively, via the energy transfer from Bi^{3+} to Eu^{3+}. The results indicate that $Sr_3Lu_2(BO_3)_4$:Bi^{3+}, Eu^{3+} is a potential novel red-emitting phosphor for UV LED applications.

Keywords: Bi^{3+}/Eu^{3+} co-doping; Red-emitting phosphor; Solid state reaction

Background

Recently, there has been a rapid increase in the number of researches on white-light emitting diodes (W-LEDs) and it has begun replacing conventional lighting sources due to its advantages such as high brightness, high energy efficiency, low power consumption, longer working performance and low environmental risk [1-6]. The common fabrication of W-LEDs involves a blue-emitting InGaN chip and a yellow emitting phosphor $Y_3Al_5O_{12}$:Ce^{3+} (YAG) [1,2,7]. However, this combination displays low color rendering index (*Ra*) of ~80 and high color temperature which is due to the insufficiency of red emission in the visible spectrum [5]. Thus, it is very essential to search for new red phosphors that can be efficiently excited at around 400 nm [8].

Eu^{3+} rare earth ions have drawn much attention of scientists in obtaining a red-emitting due to its lowest excited level $^5D_0$ of the $4f^6$ configuration which is located below the $4f^6$5d configuration and it principally displays very sharp red emission lines at $^5D_0$-$^7F_2$ transition around 610 ~ 618 nm [8,9]. Most of the red-emitting phosphors are efficiently excited at around 393 nm [10,11] originating from $^7F_0$-$^5L_6$ transition which is parity forbidden therefore it exists as a sharp peak and cannot absorb the excitation energy efficiently. In order to improve and broaden the excitation spectrum of Eu^{3+} ions, one of the common strategies is by introducing Bi^{3+} as a sensitizer. Liu et al. [1] found that the luminescence intensity and quantum efficiency of ZnB_2O_4:Bi^{3+}, Eu^{3+}

phosphors were much higher than that of $ZnB_2O_4:Eu^{3+}$ phosphors by co-doping Bi^{3+} into the host via an energy transfer process. The optimized-composition of $ZnB_2O_4:Eu^{3+}$, Bi^{3+} was even superior to that of commercial phosphor, $La_2O_2S:Eu^{3+}$. Zhou et al. [4] reported that the enhanced luminescence properties and energy transfer mechanism of $Ca_3Sn-Si_2O_9:Bi^{3+}$, Eu^{3+} phosphors by a solid state reaction. Zhu et al. [9] investigated the energy transfer phenomena of Bi^{3+}/Eu^{3+} co-doped $Ca_{10}(PO_4)_6 F_2$ phosphors for UVLED applications. Park et al. [12] discovered that with increasing the content of Bi^{3+} on Eu^{3+}/Bi^{3+} co-doping $YVO_4:Eu^{3+}$ phosphors, it demonstrate a shifting of the excitation band to a longer wavelength due to the energy transfer from Bi^{3+} to Eu^{3+}. Single-phased phosphors have attracted much attention in the fabrication of white LED and borate compounds are good candidates because they can be easily synthesized and are chemically stable. To the best of our knowledge, spectral and laser properties of Er:Yb $Sr_3Lu_2(BO_3)_4$ have been reported and it have manifested good spectral properties. Moreover, a study was carried on the luminescent characteristics of $Sr_3(RE)_2(BO_3)_4:Dy^{3+}$ (RE = Y, La, Gd) for white LED applications and provided a significant evidence.

To the best of our knowledge, there has been no reported study on the luminescence properties of Bi^{3+}/Eu^{3+} co-doped $Sr_3Lu_2(BO_3)_4$. In this study, crystal structure, phase purities as well as luminescence and energy transfer mechanism of $Sr_3Lu_2(BO_3)_4:Bi^{3+}$, Eu^{3+} phosphors were firstly investigated. The results demonstrate that $Sr_3Lu_2(BO_3)_4:Bi^{3+}$, Eu^{3+} is a potential red-emitting phosphor for UVLED applications.

Methods

Polycrystalline powder samples were prepared via a solid state reaction. The starting materials used were $SrCO_3$ (99.99%, Aldrich), H_3BO_3 (99.99%, Strem), Lu_2O_3 (99.99% Aldrich), Eu_2O_3 (99.99%, Aldrich) and Bi_2O_3 (99.99%Aldrich) were weighed in stoichiometric ratios and were homogeneously mixed and ground in agate mortar then transferred in alumina crucibles and sintered at 1200°C for 8 hours in air. The products were cooled down to ambient temperature and pulverized for further analysis.

The phase purity of the as-synthesized samples were characterized using X-ray diffraction (XRD) patterns with Cu Kα radiation (λ = 0.15418 Å) generated at 45 kV and 30 mA. Data were collected in the 2θ range of 10–80° with a scan speed of 5°/min. The PL/PLE spectra of Bi^{3+}/Eu^{3+} co-doped $Sr_3Lu_2(BO_3)_4$ phosphors were measured at room temperature and recorded by a Spex Fluorolog-3 spectrophotometer equipped with 450 W Xenon light source. All the spectra were measured with a scan rate of 150 nm min^{-1}. The Commission International de l'Eclairage (CIE) chromaticity coordinates were measured by a Laiko DT-101 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan).

Results and discussion

XRD and crystal structure analyses

The XRD patterns of $Sr_3Lu_2(BO_3)_4$ doped with (a) 1 mol% Bi^{3+}, (b) 60 mol% Eu^{3+} and (c) 1 mol% Bi^{3+}/20 mol% Eu^{3+} and (d) standard pattern of ICSD 10213 are shown in Figure 1. The results show that the as-synthesized $Sr_3Lu_2(BO_3)_4$ and Bi^{3+}, Eu^{3+} or Bi^{3+}/Eu^{3+} co-doped $Sr_3Lu_2(BO_3)_4$ are in well consistent with standard pattern of ICSD 10213, indicating that single-phased phosphors were successfully obtained by a solid state reaction. In addition, there are no notable peak shifts white doping Bi^{3+} and Eu^{3+} ions into the host,

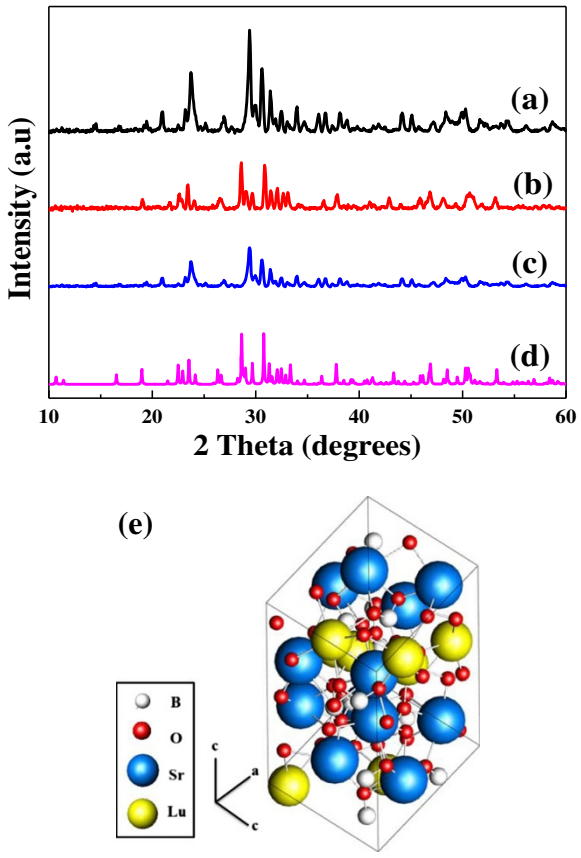

Figure 1 XRD patterns of $Sr_3Lu_2(BO_3)_4$ doped with (a) 1 mol% Bi^{3+}, (b) 60 mol% Eu^{3+} and (c) 1 mol% Bi^{3+}/ 20 mol% Eu^{3+} , (d) ICSD 10213 and (e) crystal structure of $Sr_3Lu_2(BO_3)_4$.

which demonstrates that Bi^{3+} and Eu^{3+} ions are completely dissolved in the host lattice as a solid solution by occupying the Lu^{3+} sites due to their similar ionic radii of 0.977 Å, 1.11 Å and 1.07 Å for Lu^{3+}, Bi^{3+} and Eu^{3+}, respectively [4,13]. The host phosphor belongs to $Sr_3RE_2(BO_3)_4$ (RE: Gd^{3+}, Y^{3+}, La^{3+} and Lu^{3+}) system which has an orthorhombic structure with P*c*21*n* space group. The lattice parameters of $Sr_3Y_2(BO_3)_4$ has lattice parameters of $a = 8.701(1)$ Å, $b = 15.984(8)$ Å, $c = 7.381(2)$ Å and $\alpha = \beta = \gamma = 90°$ [14,15]. Furthermore, the longer distance among the rare-earth ions in the crystal structure of $Sr_3Y_2(BO_3)_4$ results in higher doping concentration of Eu^{3+} [14].

Figure 1(e) displays the crystallographic structure. The $Sr_3Lu_2(BO_3)_4$. Lu^{3+} ions occupy two distinct crystallographic sites Lu_1 and Lu_2 and each Lu^{3+} has an eight-fold coordination that forms LuO_8 polyhedra. The bond valence of Lu_1 is stronger compared to Lu_2, therefore Bi^{3+} and Eu^{3+} occupies the Lu^{3+} site. Figure 1. XRD patterns of $Sr_3Lu_2(BO_3)_4$ doped with (a) 1 mol% Bi^{3+}, (b) 60 mol% Eu^{3+}, (c) 1 mol% Bi^{3+}, 20 mol% Eu^{3+}, (d) ICSD 10213 and (e) crystal structure of $Sr_3Lu_2(BO_3)_4$.

Photoluminescence properties of $Sr_3Lu_2(BO_3)_4$:Bi^{3+}phosphors

The PL and PLE of spectra of $Sr_3Lu_{1.8}(BO_3)_4$:$0.20Bi^{3+}$ phosphor are illustrated in Figure 2. When the samples are excited at 327 nm and 335 nm, the emission spectra displays three broad bands centering at 356 nm, 405 nm emitting blue color and 485 nm emitting green color however if the phosphors are excited at 370 nm, the emission spectra contains one

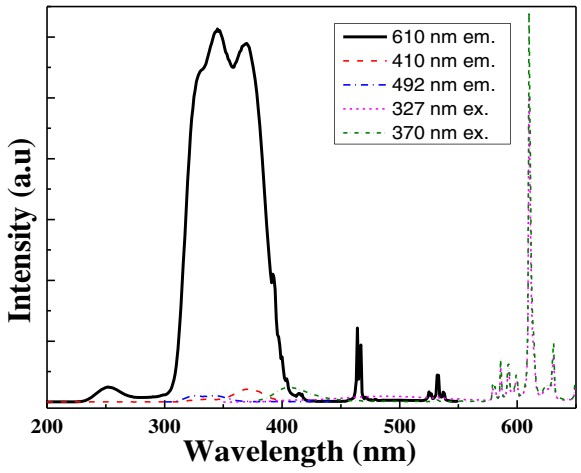

Figure 2 PL and PLE spectra of as-synthesized $Sr_3Lu_{1.80}(BO_3)_4$:0.20Bi^{3+} phosphor.

broad band with peak maximum at 404 nm. Varying the excitation wavelengths from 320 ~ 370 nm greatly affects the emission spectra of $Sr_3Lu_2(BO_3)_4$:×%Bi^{3+}. Therefore, the energy distribution of blue and green emission is highly dependent on the excitation wavelengths.

The excitation spectrum monitored at 492 nm (green emission) consists of two peaks at 326 nm and 342 nm respectively meanwhile the excitation spectrum monitored at 410 nm (blue emission) consists of a weak broad band at 334 nm and a strong broad band at 371 nm. If the Bi^{3+} ion is asymmetrically coordinated, the Stokes shift of Bi^{3+} is large. Therefore, the blue emission and green emission originates from S_6 and C_2 symmetry respectively [15].

Figure 3 shows the energy level diagram of Bi^{3+} under S_6 and C_2 symmetry. The emission band with maximum peaks at 356 nm and 405 nm are attributed to $^3A_u \rightarrow {}^1A_g$ and $^3E_u \rightarrow {}^1A_g$ of S_6 respectively. On the other hand, the excitation peaks at 335 nm and 370 nm found at site S_6 are ascribed to $^1A_g \rightarrow {}^3A_u$. The green emission band with maximum peak at 485 nm is due to $^3B \rightarrow {}^1A$ transition while the excitation peaks at 327 nm and 335 nm responsible for the green emission due to $^1A \rightarrow {}^3B$ transition under C_2 site symmetry of Bi^{3+}[15].

The $Sr_3Lu_2(BO_3)_4$:Bi^{3+} phosphors display efficient luminescence properties at ambient temperature. The luminesce properties of various concentrations of Bi^{3+} in the

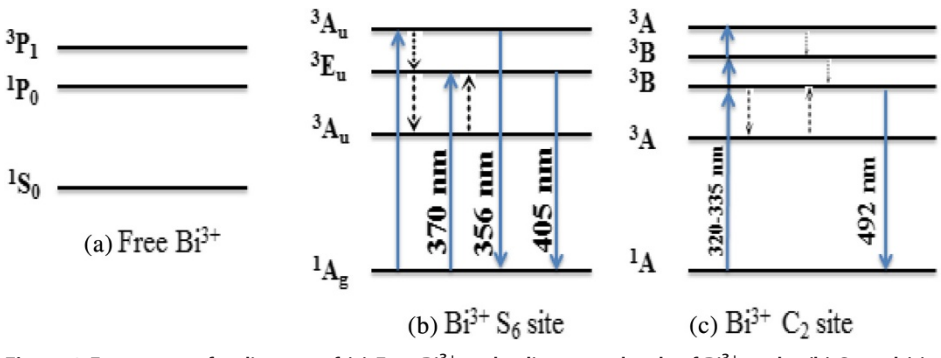

Figure 3 Energy transfer diagram of (a) Free Bi^{3+} and split energy levels of Bi^{3+} under (b) S_6 and (c) C_2 site symmetry.

range of 0.005-0.15. in $Sr_3Lu_2(BO_3)_4$ host are shown in Figure 4. It was noticeable that the emission intensity increased with the increasing amount of Bi^{3+} concentration until 1 mol%, and began to decrease due to concentration quenching. Generally, concentration quenching of luminescence was attributable to the energy migration existing among the activator ions at high concentration. During this migration process, the excitation energy would be diminished at a quenching site, causing a decrease in the luminescence [3]. Thus, the optimum concentration of Bi^{3+} in $Sr_3Lu_2(BO_3)_4$:Bi^{3+} was determined to be 0.01. It was also notable in the emission bands that the luminescent centers of Bi^{3+} at S_6 and C_2 quench simultaneously although they have different Stokes shift and concentration. C_2 has higher concentration of Bi^{3+} than that of S_6 which is essential for concentration quenching. However, higher Stokes shift leads to lower spectral overlap, offsetting the concentration quenching effect. Ju et al. [15] proposed that the energy transfer from Bi^{3+} under C_2 site to Bi^{3+} under S_6 site may be the reason to this phenomenon. As shown in Figure 3, the emission band of Bi^{3+} under C_2 overlaps the excitation band of Bi^{3+} under S_6. Conversely, if the emission band of Bi^{3+} under C_2 does not overlap the excitation band of Bi^{3+} under S_6 it cannot overlap its own excitation band which at situated at much higher energy. Moreover, the excitation spectra of Bi^{3+} at C_2 coincides with the excitation spectra of Bi^{3+} at S_6 from 300 nm – 350 nm although they have different absorption profiles but nonetheless, this is an obvious evident for Bi^{3+}-Eu^{3+} energy transfer.

Figure 5 shows the normalized intensity of $Sr_3Lu_2(BO_3)_4$:Bi^{3+} phosphors excited at 327 nm, 335 nm and 370 nm. The emission intensity of the phosphors gradually increased with the increasing amount of Bi^{3+} until 0.01 mole and started to decrease when the concentration of Bi^{3+} was further increased. Also, the emission intensity with respect to Bi^{3+} concentration was consistent among the three excitation wavelengths.

Photoluminescence properties of $Sr_3Lu_2(BO_3)_4$:Eu^{3+}phosphors

The photoluminescence of $Sr_3Lu_2(BO_3)_4$:Eu^{3+} phosphors are displayed in Figures 6. The emission spectra excited at 393 nm displays sharp peaks at 578 nm, 591 nm, 610 nm, 650 nm and 700 nm which were attributed to the $^5D_0 \rightarrow {}^7F_J$ (J = 0,1,2,3,4) transitions of Eu^{3+} ions respectively. The highest peak which was situated at 610 nm produced a red-emitting phosphor. Due to the absence of inversion symmetry and the break of parity selection rules, $^5D_0 \rightarrow {}^7F_2$ electric dipole is the strongest transition [4]. The excitation spectrum of $Sr_3Lu_2(BO_3)_4$:Eu^{3+} is also scrutinized. The broad band at 230 nm – 280 nm was due to the charge transfer band transition coming from ion O_2^- to Eu^{3+}. The narrow bands and sharp peaks found at 300 nm – 500 nm were ascribed to the intra-configurational *4f*-*4f* transitions of Eu^{3+}.

Figure 7a shows the emission spectra of $Sr_3Lu_{2-y}(BO_3)_4$:yEu^{3+} phosphors with x = 0.20, 0.40, 0.60 and 0.80 under 393 nm excitation. The emission spectra are dominated by a large peak located at 610 nm ascribed to the $^5D_0 \rightarrow {}^7F_2$ transition this indicates that the Eu^{3+} ions occupy non-inversion symmetry sites which is in accordance to the point group C_1. Figure 7b shows the relationship of the luminescence intensity at 610 nm as a function of its doping concentration (x) excited at 393 nm. Initially, the emission intensity increases as the doping concentration of Eu^{3+} increases due to the increase of absorption centers and reaches a maximum of 60 mol% and eventually drops with further increase in the concentration due to concentration quenching.

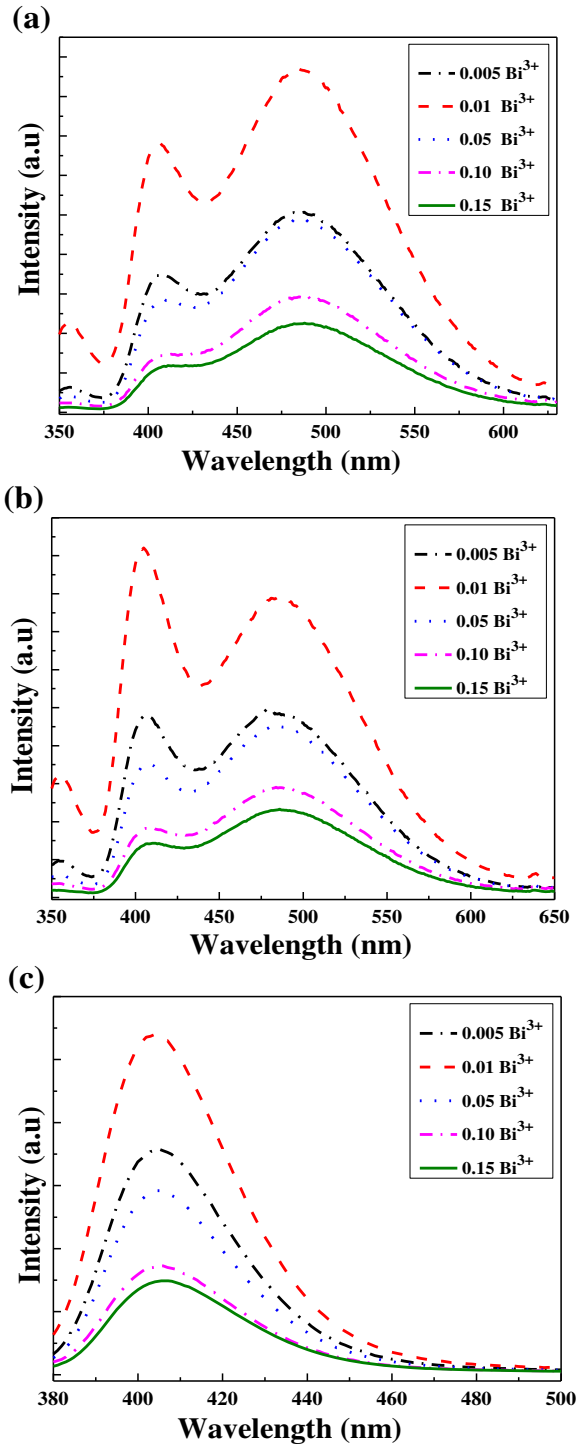

Figure 4 Emission spectra of as-synthesized $Sr_3Lu_2(BO_3)_4$:xBi^{3+} phosphor excited at (a) 327 nm, (b) 335 nm and (c) 370 nm.

Photoluminescence properties of $Sr_3Lu_{1.99-y}(BO_3)_4$:$0.01Bi^{3+}$, yEu^{3+} phosphors

The emission and excitation of spectra of $Sr_3Lu_{1.79}(BO_3)_4$:$0.01Bi^{3+}$, $0.20Eu^{3+}$ phosphors are depicted in Figure 8. The emission spectra were investigated and analyzed by exciting the sample at 327 nm and 370 nm. The emission spectra contain broad bands from

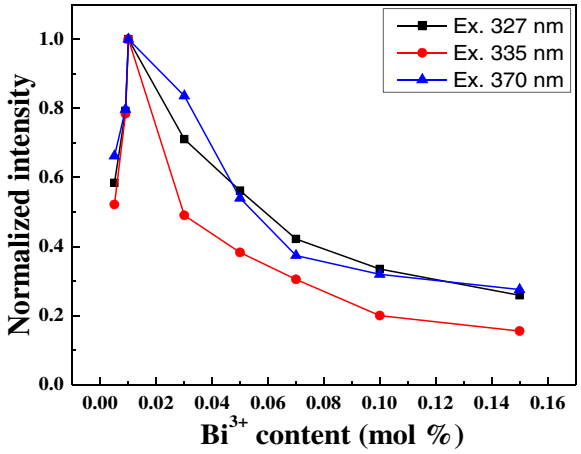

Figure 5 Normalized intensity of as-synthesized $Sr_3Lu_2(BO_3)_4$:xBi^{3+} phosphor excited at 327 nm, 335 nm and 370 nm.

350 nm - 580 nm which are attributed to the emission properties of Bi^{3+} while the sharp lines ranging from 580 nm – 650 nm are due to the Eu^{3+} intra-configurational 4*f*-4*f* located at transitions while the emission spectrum monitored at 410 nm contains two absorption peaks situated at which 334 nm and 371 nm. On the other hand, the excitation spectra monitored at 492 nm consist of two peaks located at 326 nm and 342 nm which is identical to the excitation spectra of $Sr_3Lu_2(BO_3)_4$:Bi^{3+}. The excitation spectra monitored at 610 nm contains broad excitation bands at around 300 nm – 400 nm which could be ascribed to the absorption of Bi^{3+}. The narrow peaks were due to the intra-configurational 4*f*-4*f* transitions of Eu^{3+} located at 593 nm ($^5D_0 \rightarrow {}^7F_0$), 599 nm ($^5D_0 \rightarrow {}^7F_1$), 610 nm ($^5D_0 \rightarrow {}^7F_2$) and 631 nm ($^5D_0 \rightarrow {}^7F_3$). Spectral overlap between the emission band of the sensitizer and absorption band of the activator is essential to have an efficient energy transfer [13]. The spectral overlap of Bi^{3+} emission with the Eu^{3+} excitation spectra situated at 464 nm and 533 nm indicates successful energy transfer from Bi^{3+} to Eu^{3+}.

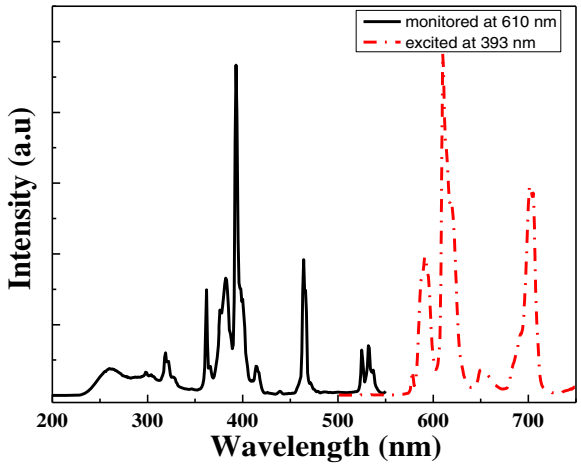

Figure 6 PL and PLE spectra of as-synthesized $Sr_3Lu_{1.20}(BO_3)_4$:0.80Eu^{3+} phosphor.

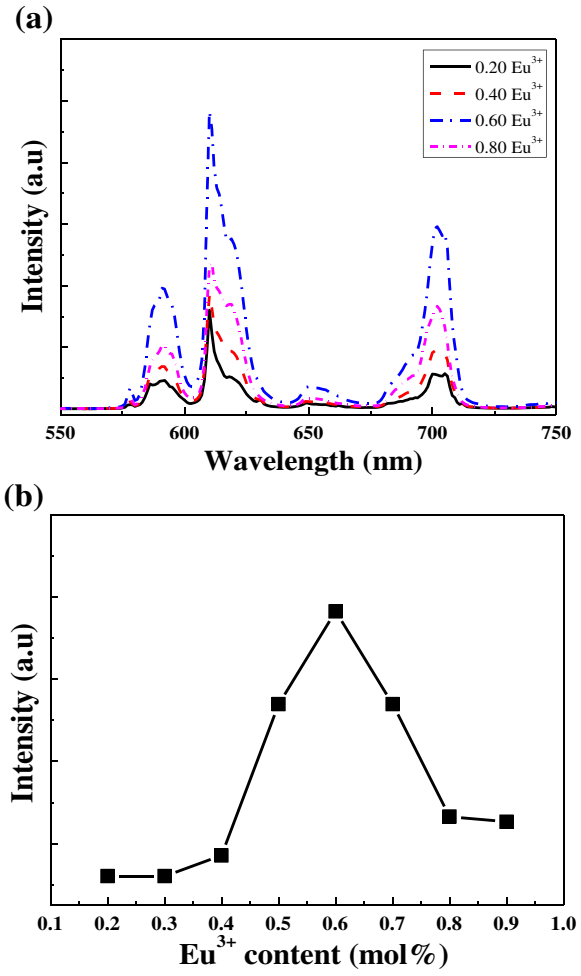

Figure 7 (a) Emission spectra of $Sr_3Lu_{2-y}(BO_3)_4$:yEu^{3+} (b) Emission Intensity as a function excited at 393 nm.

Figures 9a and 9b exhibit the emission spectra of $Sr_3Lu_{1.99-y}(BO_3)_4$:$0.01Bi^{3+}$, yEu^{3+} phosphors with varying concentrations of Eu^{3+} (y = 0.05, 0.10, 0.15, 0.20, 0.25, 0.35) excited at 327 nm and 370 nm respectively. It was apparent that the energy absorbed by Bi^{3+} was transferred to Eu^{3+} and the emission of Bi^{3+} was quenched at higher Eu^{3+} concentration. Moreover, the figure indicates that the optimum concentration of Bi^{3+} co-activated Eu^{3+} was $Sr_3Lu_{1.79}$ $(BO_3)_4$:$0.01Bi^{3+}$, $0.20Eu^{3+}$ and the intensity decreases eventually with a further increase in Eu^{3+} concentration.

Figure 10 further proves the energy transfer from Bi^{3+} to Eu^{3+}. It is evident that the intensity of Bi^{3+} decreases with the increase in Eu^{3+} concentration. This shows that the energy absorbed by Bi^{3+} is transferred to Eu^{3+}. Aside from spectral overlap, efficient energy transfer requires strong interactions it includes radiative transfer via photons which is almost distance independent and nonradiative transfer associated with the resonance between the acceptor and the donor that can be either an exchange interaction or multipolar interaction [15-19]. To calculate the critical transfer distance (R_c) between the activators Bi^{3+} and Eu^{3+} the following equation is considered:

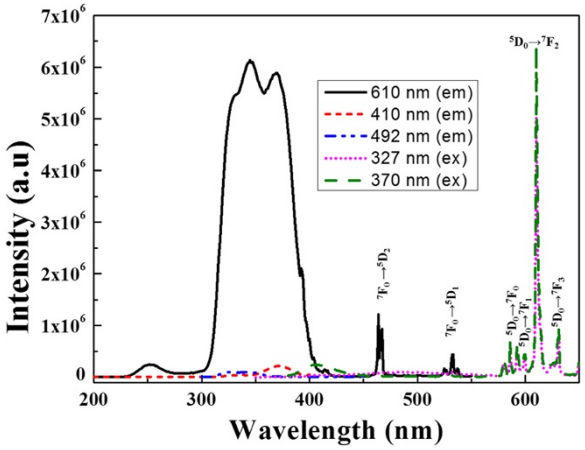

Figure 8 PL/PLE Spectra of as-synthesized $Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+}, 0.20Eu^{3+} phosphor.

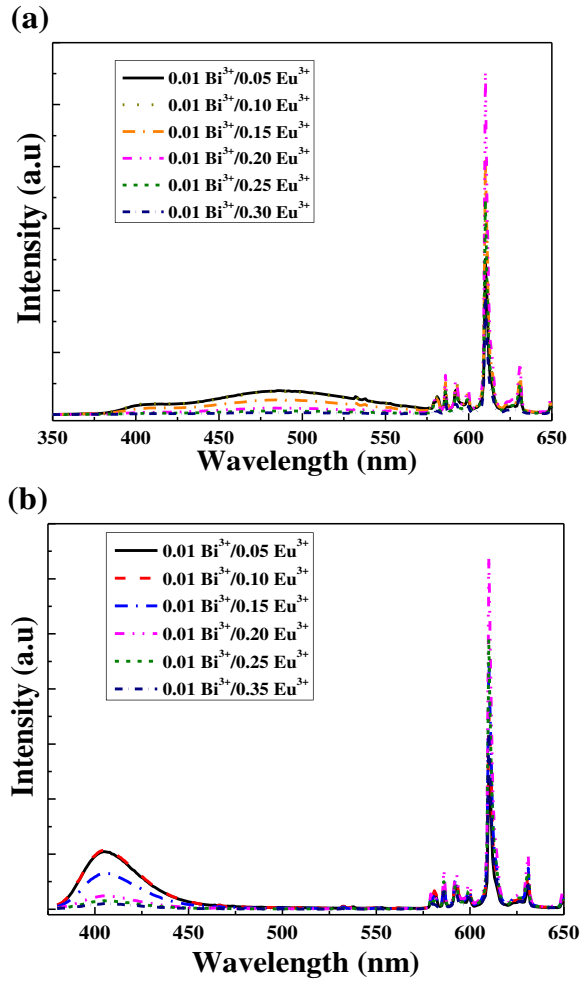

Figure 9 Emission spectra of as-synthesized $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+}, yEu^{3+} phosphor excited at (a) 327 nm and (b) 370 nm.

$$R_c = 2\left(\frac{3V}{4\Pi X_c N}\right)^{1/3} \quad (1)$$

where V = 1077.54 Å^3 is the volume of the unit cell, $X_c = 0.21$ which is the total concentration of Bi^{3+} and Eu^{3+} at maximum luminescence intensity [16] and N = 8 which represents the number of Lu^{3+} ions [20]. The critical distance of Bi^{3+} and Eu^{3+} was calculated to be 10.70 Å. In an exchange interaction, the critical distance should be shorter than 5 Å thus, it is rational to hypothesize that the mechanism involved is multipolar interaction [16-19]. According to Dexter's energy transfer expressions of multipolar interaction [16-19] and Reisfeld's transfer approximation [16,17] the following relation can be obtained:

$$\frac{\eta_o}{\eta} \propto C_{Bi+Eu}^{\eta/3} \quad (2)$$

where η_o and η are the luminescence quantum efficiency the sensitizer (Bi^{3+}) in the absence and presence of the activator (Eu^{3+}) respectively. The ratio of η_o/η can be estimated by the ratio of the relative luminescence intensities, I_{so}/I_s without and with the activator. C is the total concentration of Bi^{3+} and Eu^{3+} ions and $n = 6$, 8, 10 which corresponds to dipole-dipole, dipole- quadrupole and quadrupole-quadrupole interaction [16-19]. The relationships between I_{so}/I_s and C_{Bi+Eu} excited at 327 nm is illustrated in Figure 11(a), (b) and (c). It is evident that graph for n = 6 has the best-fitted linearity for both excitation. Therefore, the energy transfer from Bi^{3+} to Eu^{3+} was due to dipole-dipole interaction.

In order to further understand the energy transfer from Bi^{3+} to Eu^{3+} it is of high importance to discuss the energy transfer efficiency (η_T) from the sensitizer to the activator depicted in Figure 12 and expressed by:

$$\eta_T = 1 - \frac{Is}{Iso} \quad (3)$$

where I_s and I_{so} are the emission intensity of Bi^{3+} with and without Eu^{3+}, respectively. The η_T of $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+}, yEu^{3+} was calculated as a function varying

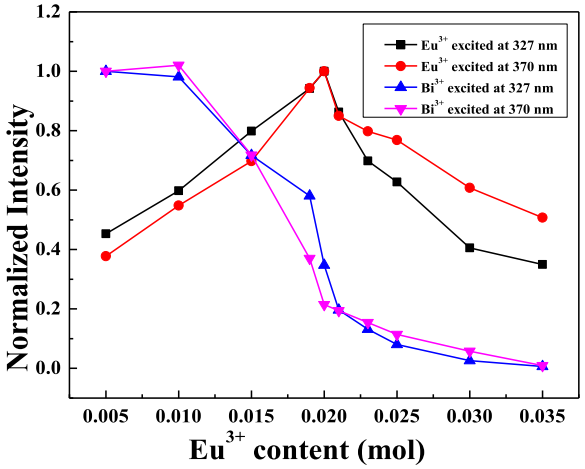

Figure 10 Normalized PL intensity of as-synthesized $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+}, yEu^{3+} phosphor.

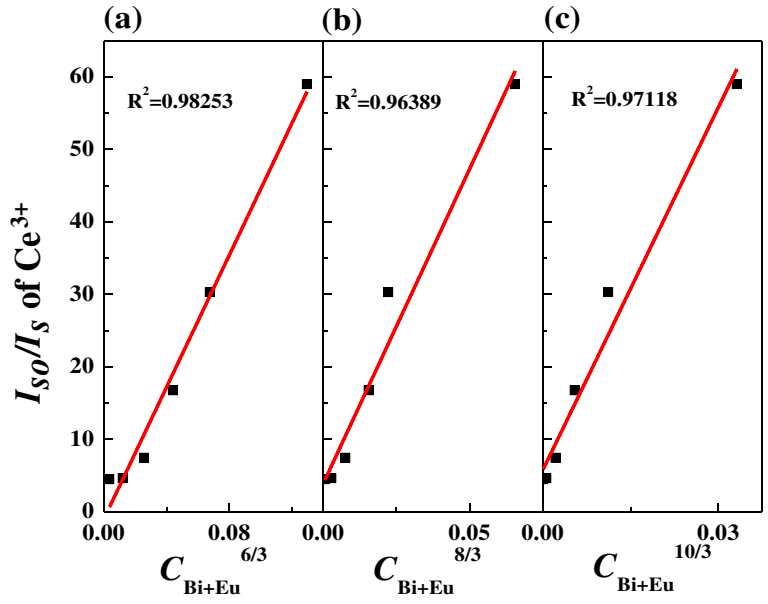

Figure 11 Dependence of I_{so}/I_s of Bi^{3+} on (a) $C^{6/3}_{(Bi+Eu)}$, (b) $C^{8/3}_{(Bi+Eu)}$ and $C^{10/3}_{(Bi+Eu)}$ excited at 327 nm.

concentration of Eu^{3+} which demonstrated that the energy transfer efficiency increases as the amount of activator Eu^{3+} increases.

With the intention of further investigating the energy transfer between Bi^{3+} and Eu^{3+}, the photoluminescence curve of Bi^{3+} in $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+},yEu^{3+} phosphors excited at 327 nm were measured and the corresponding lifetime (τ) of S_6 and C_2 site of Bi^{3+} were calculated as depicted in Figure 13. Since the decay curves are not exponential, therefore the samples where characterized using the average lifetime (τ) and were calculated using the following equation:

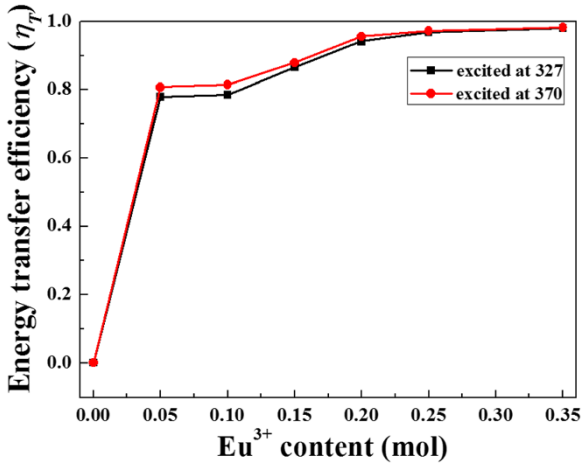

Figure 12 Energy transfer efficiency η_T of as-synthesized $Sr_3Lu_{1.99-y}(BO_3)_4$:$_{0.01}Bi^{3+}$, yEu^{3+} phosphor excited at 327 nm and 370 nm as a function of Eu^{3+} concentration.

$$\tau = \frac{\int_0^\infty I(t)tdt}{\int_0^\infty I(t)dt} \tag{4}$$

where *I(t)* is the intensity at time t. In the inset of Figure 13, the corresponding lifetime (τ) of each samples were given and calculated as 111.83 μs, 107.94 μs, 89.76 μs, 13.90 μs, 9.93 μs and 7.58 μs for $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+},yEu^{3+} (y = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) respectively and it is evident that as the doping concentration of Eu^{3+} increases, the τ of Bi^{3+} decreases which confirms the energy is successfully transferred from the sensitizer to the activator [9,16].

The schematic energy transfer diagram between Bi^{3+} and Eu^{3+} is presented in Figure 14. Upon excitation at 327 nm, 335 nm and 370 nm the Bi^{3+} are stimulated from the ground state ^1S_o to excited state $^3P_1$. In Figure 3, it was presented that there are two sites in level $^3P_1$, S_6 and C_2 site which are responsible for the blue and green emission of Bi^{3+} [20]. Subsequently, the absorbed energy can be transferred to the $^5D_4$ and level of Eu^{3+} and the emission of Bi^{3+} is quenched as the concentration of Eu^{3+} increases. The excited state of Eu^{3+} at $^5D_4$ relaxes non-radiatively to the lowest component of ^5D accompanied by broad emission bands as shown in Figure 9a-b and successively returns to its ground state $^7F_0$.

CIE coordinates

The chromaticity coordinates of the phosphor $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+}, yEu^{3+} and its corresponding relative intensity are calculated and presented in Table 1 and Figure 15, respectively. It depicts that the co-activation of Bi^{3+} and Eu^{3+} has increased the $^5D_0 \rightarrow {}^7F_2$ attributed to Eu^{3+} which was responsible for its red emission. At 327 nm excitation, the relative intensity of $Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+}, 0.20Eu^{3+} was enhanced by 201% although, its CIE coordinates indicates that it has an orange hue. On the other hand, when excited at 370 nm, the intensity was improved by 265% and according to its CIE coordinates, it has a bright red hue. Figure 16 shows the PL spectra of composition-optimized SLBO:Bi,

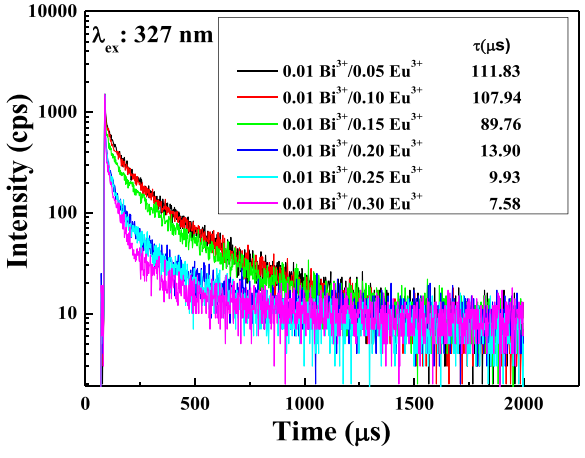

Figure 13 Photoluminescence decay curves of Bi^{3+} in $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+},yEu^{3+} phosphors excited at 327 nm.

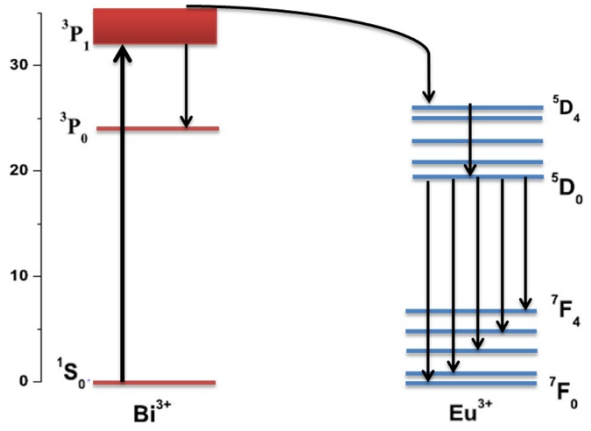

Figure 14 Schematic energy diagram of Bi^{3+} and Eu^{3+} in $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+},yEu^{3+}.

Eu phosphor and commercial red-emitting phosphor – Y_2O_3:Eu^{3+} (KX-681, Kasei co.) under excitation of 393 nm. The inset in Figure 16 displays the phosphor images of these two phosphors excited at 365 nm in UV box. The PL intensity of SLBO is about 32% of commercial phosphor. The measurement of quantum efficiency (QE) for SLBO and Y_2O_3:Eu^{3+} are carried out under excitation of 393 nm in the integrating sphere. The QE of SLBO and Y_2O_3:Eu^{3+} were determined to be 28% and 91%, respectively. It is believed that the QE could be further improved by tuning synthetic parameters, such as starting materials, synthetic approach and fluxes. The inset in Figure 16 also demonstrates that as-synthesized SLBO:Bi,Eu phosphor gives a bright and intense red hue.

Conclusions

$Sr_3Lu_2(BO_3)_4$:Bi^{3+}, Eu^{3+} were effectively synthesized by a solid state reaction and pure phase phosphors were successfully synthesized. Changing the excitation wavelengths from 320 ~ 370 nm greatly affects the emission spectra of $Sr_3Lu_2(BO_3)_4$:Bi^{3+}. Hence,

Table 1 CIE coordinates and relative intensity of SLBO:Bi^{3+},$Eu^{3\pm}$ phosphors

Phosphors	Excitation Wavelength (nm)	CIE chromaticity coordinates		$^5D_0 \rightarrow {}^7F_2$ relative intensity
		x	*y*	
$Sr_3Lu_{1.94}(BO_3)_4$:0.01Bi^{3+},0.05Eu^{3+}	327	0.3087	0.3182	1.00
$Sr_3Lu_{1.89}(BO_3)_4$:0.01Bi^{3+},0.10Eu^{3+}	327	0.3386	0.3199	1.32
$Sr_3Lu_{1.84}(BO_3)_4$:0.01Bi^{3+},0.15Eu^{3+}	327	0.4029	0.3266	1.65
$Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+},0.20Eu^{3+}	327	0.5191	0.3395	2.01
$Sr_3Lu_{1.74}(BO_3)_4$:0.01Bi^{3+},0.25Eu^{3+}	327	0.5303	0.3393	1.38
$Sr_3Lu_{1.64}(BO_3)_4$:0.01Bi^{3+},0.35Eu^{3+}	327	0.5365	0.3386	1.11
$Sr_3Lu_{1.94}(BO_3)_4$:0.01Bi^{3+},0.05Eu^{3+}	370	0.3678	0.1870	1.00
$Sr_3Lu_{1.89}(BO_3)_4$:0.01Bi^{3+},0.10Eu^{3+}	370	0.4039	0.2065	1.45
$Sr_3Lu_{1.84}(BO_3)_4$:0.01Bi^{3+},0.15Eu^{3+}	370	0.4772	0.2512	1.85
$Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+},0.20Eu^{3+}	370	0.5800	0.3356	2.65
$Sr_3Lu_{1.74}(BO_3)_4$:0.01Bi^{3+},0.25Eu^{3+}	370	0.4186	0.3377	2.03
$Sr_3Lu_{1.64}(BO_3)_4$:0.01Bi^{3+},0.35Eu^{3+}	370	0.4201	0.3377	1.34

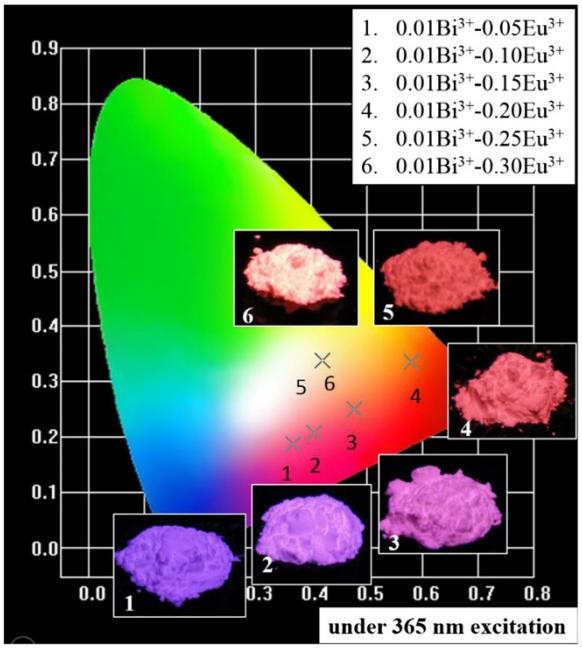

Figure 15 CIE coordinates of as-synthesized $Sr_3Lu_{1.99-y}(BO_3)_4$:0.01Bi^{3+}, yEu^{3+} phosphors and the inset indicates the representative samples und 365 nm UV light.

the energy distribution of blue and green emission is highly dependent on the excitation wavelengths. The concentration quenching for $Sr_3Lu_{2-x}(BO_3)_4$:xBi^{3+}, $Sr_3Lu_{2-y}(BO_3)_4$:yEu^{3+} and Sr_3Lu_{2-x-y} $(BO_3)_4$:xBi^{3+}, yEu^{3+} are 1 mol%, 60 mol% and 20 mol%, respectively. The spectral overlap of the emission spectra of Bi^{3+} and the excitation band of Eu^{3+} depicts an efficient energy transfer from Bi^{3+} to Bi^{3+} Moreover, it was shown that the emission intensity of Bi^{3+} quenches as the concentration of Eu^{3+} increases hence, the energy absorbed by Bi^{3+} was transferred to Eu^{3+}. The critical distance of Eu^{3+} was determined to be 10.7 Å. The relative intensity of $Sr_3Lu_{1.79}(BO_3)_4$:0.01Bi^{3+}, 0.20Eu^{3+} at 327 nm and 370 nm

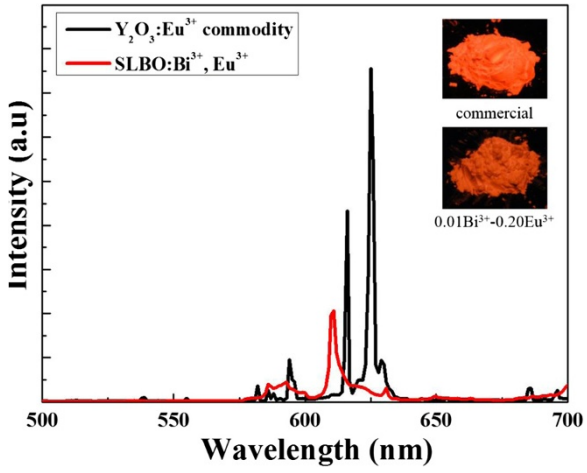

Figure 16 PL spectra of composition-optimized $Sr_3Lu_{1.79}$ $(BO_3)_4$:0.01Bi^{3+}, 0.20Eu^{3+} phosphor and Y_2O_3:Eu^{3+} commercial phosphor excited at 393 nm. Inset: these two phosphors excited at 365 nm in UVBOX.

were dramatically enhanced by 201% and 265%, respectively. The results indicate that $Sr_3Lu_2(BO_3)_4$:Bi^{3+}, Eu^{3+} is a potential novel red-emitting UV LED phosphor for display application.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
IVBM performed the experiment, analyzed the data and wrote the paper. PCL refined the graphs, tables and other essential information about this paper. WRL guided and scrutinized all the experiments and edited the paper. All the authors discussed and analyzed the results and commented on the manuscript. All authors read and approved the final manuscript.

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IVBM and PCL are both taking their Master's Degree in Chung Yuan Christian University, ROC Taiwan. WRL has a Ph.D. degree and is currently an assistant professor in Chung Yuan Christian University and is affiliated with Industrial Technology Research Institute of Taiwan (ITRI), ROC Taiwan.

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