ZnB₂O₄:Bi³⁺,Eu³⁺: a highly efficient, red-emitting phosphor

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Abstract: The novel red phosphor of Eu³⁺-Bi³⁺ co-activated ZnB₂O₄ was prepared by a solid-state reaction. The composition-optimized (Zn₁₀₋ₓEuₓ)₂O₄ phosphor exhibits a dominant emission peak at 610 nm (³D₀−²F₂) with CIE coordinates of (0.63, 0.36) under the excitation at 393 nm. By co-doping Bi³⁺ ions in ZnB₂O₄:Eu³⁺, the emission intensity and quantum efficiency can be efficiently enhanced by an increment of 14% and 6%, respectively. The luminescence performance and thermal stability of (Zn₁₀₋ₓBiₓEuₓ)₂O₄ phosphor were found to be superior to that of the commodity phosphor, La₂O₃:Eu³⁺. The red-emitting borate phosphor may be potentially useful in the fabrication of white light-emitting diodes (LEDs).

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1. Introduction

In the last decade, there has been a dramatic increase in the number of research on white light-emitting diodes (LEDs) as a new light source for general lighting and displays [1]. The conversional white light illumination are mostly composed of blue-emitting InGaN chip and yellow phosphor, typically Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG) [2,3], which exhibits high luminescence efficiency and chemical stability. The combination of blue chip and YAG, however, show a lower color rendering index ($R_a$) of ~80 due to the lack of red color contribution. Thus, developing new red phosphors, which can be efficiently excited by either 460 or 405 nm LEDs is a very crucial issue. For seeking suitable red phosphors, sulfides and oxysulfides, such as Ca$_2$Eu$^{2+}$, SrS:Eu$^{2+}$, La$_2$O$_3$:Eu$^{3+}$, and Y$_2$O$_2$:Eu$^{3+}$, were reported to be efficiently excited under 460 or 405 nm. Nevertheless, the drawbacks of these compounds are sensitive to moisture, giving a poor chemical stability. Recently, nitrates and oxynitrates [4–8] demonstrate good potential as red phosphors due to their good thermal stability. Hence, it is urgent to search for new red phosphor with low cost and high chemical stability. From the points of view, the oxide-based hosts with Eu$^{3+}$ have been widely investigated [9–12]. It has been well known that in some hosts, Bi$^{3+}$ or Sm$^{3+}$ was proven to be a very good sensitizer for Eu$^{3+}$ with not only enhancing the luminescent performance but also broadening the excitation spectrum. Datta [13] investigated the role of Bi$^{3+}$ in YVO$_4$:Eu$^{3+}$ and showed an increase in luminescence intensity of almost 200% as Bi$^{3+}$ is incorporated into the (Y$_{0.95}$Eu$_{0.05}$)VO$_4$ lattice. Neeraj et al. [14] reported the excitation band of Bi$_{1-x}$Ln$_{x}$VO$_4$ system doped with Eu$^{3+}$ or Sm$^{3+}$ can be broadened by choosing suitable sensitizers. Park et al. [15] investigated the effect of Bi$^{3+}$, Eu$^{3+}$ codoping on the excitation of Eu$^{3+}$ in YVO$_4$:Bi$^{3+}$,Eu$^{3+}$ and concluded that with increasing Bi$^{3+}$ dopant content, the excitation range was found to shift to longer wavelength. Wang et al. [16] also demonstrated that the incorporation of Bi$^{3+}$ and Sm$^{3+}$ into NaEu(MoO$_4$)$_2$ host can both broaden the excitation band and enhance the emission intensity of Eu$^{3+}$ under 395/405nm. Chi et al. [17] found that Bi$^{3+}$-doped Y$_2$O$_3$:Eu is used as red phosphors with very high efficiency. Recently, Li et al [18] reported photoluminescence (PL) and thermoluminescence (TL) of Zn(BO$_2$)$_2$:Tb$^{3+}$ and concluded that the phosphor exhibited potential application in gamma-rays TL dosimeter. To the best of our knowledge, the luminescence properties of Bi$^{3+}$/Eu$^{3+}$ – co-activated ZnB$_2$O$_4$ have not been reported yet. Hence, the aim of this study is to investigate and examine the luminescence properties of a new red phosphor, ZnB$_2$O$_4$:Bi$^{3+}$,Eu$^{3+}$. The improvement of luminescence intensity through energy transfer from co-doped sensitizer Bi$^{3+}$ to activator Eu$^{3+}$ in ZnB$_2$O$_4$ host will also be discussed in this work.

2. Experimental

Polycrystalline samples of ZnB$_2$O$_4$:Eu$^{3+}$ and ZnB$_2$O$_4$:Bi$^{3+}$,Eu$^{3+}$ powders were synthesized by conventional solid state reaction, starting from ZnO, H$_2$B$_2$O$_5$, Eu$_2$O$_3$, and Bi$_2$O$_3$. The raw materials were weighed out in stoichiometric proportions and the mixtures were then fired at 850°C for 10 h under ambient atmosphere. The detailed measurements of photoluminescence (PL), photoluminescence excitation (PLE), Commission International de l’Eclairage (CIE)
chromaticity, and diffuse reflectance (DR) spectra were carried out under ambient atmosphere and described in our previous work [19].

3. Results and discussion

3.1. XRD patterns and atom structure of synthesized ZnB$_2$O$_4$

As reported in the JCPDS card No. 39-1126, ZnB$_2$O$_4$, crystallizes in a cubic (space group: Im-3m (229)) structure with lattice constant: $a = 7.473$ Å and $Z = 6$. Figure 1 shows the XRD patterns of the as-synthesized ZnB$_2$O$_4$, Zn$_{0.9}$Eu$_{0.1}$B$_2$O$_4$, and Zn$_{0.8}$Eu$_{0.1}$Bi$_{0.1}$B$_2$O$_4$ samples. These XRD patterns were found to be consistent with that reported in JCPDS card No. 39-1126 and no peak shifting was observed in the XRD patterns of ZnB$_2$O$_4$:Eu or ZnB$_2$O$_4$:Bi,Eu samples.

![Fig. 1. XRD patterns of (a) ZnB$_2$O$_4$, (b) (Zn$_{0.9}$Eu$_{0.1}$)B$_2$O$_4$ and (c) (Zn$_{0.8}$Eu$_{0.1}$Bi$_{0.1}$)B$_2$O$_4$. The standard XRD pattern of ZnB$_2$O$_4$ is taken from JCPDS Card No. 39-1126. The internal standard silicon is labeled with a star.](image)

The decrease in crystallinity of ZnB$_2$O$_4$:Eu,Bi with increasing Eu$^{3+}$ and Bi$^{3+}$ dopant content was observed from the XRD patterns, which can be attributed to the variation of charges of dopants that results in the defect formation in the lattice. Little impurity phases, such as H$_3$BO$_3$ and B$_2$O$_3$ were observed at 2$\theta$ = 29.7°, 30.2°, 30.9°, 31.3°, 31.6° and 32.1° in Fig. 1b and 1c, respectively. The intensity of impurity phases are too small that the effect on luminescence of ZnB$_2$O$_4$:Eu or ZnB$_2$O$_4$:Bi,Eu could be neglected. The XRD data shown in Fig. 1 indicated the as-prepared ZnB$_2$O$_4$ samples were almost pure phase with highly crystallinity. It is known that the ionic radii ($r$) of Zn$^{2+}$ (CN = 4) and B$^{3+}$ (CN = 3) are 0.60 Å and 0.21 Å [20], respectively. As a result of the ionic radius of B$^{3+}$ is too small, it is difficult for these elements to replace B$^{3+}$ in the ZnB$_2$O$_4$. Hence, in this study, it is believed that the Zn$^{2+}$ sites are substituted of Eu$^{3+}$ and Bi$^{3+}$ in the lattice.

3.2. The UV excitation spectrum under Bi$^{3+}$/Eu$^{3+}$ activators

Figure 2 shows the reflectance spectra of pure ZnB$_2$O$_4$ and tri-valance ions (such as Bi, Eu or Bi-Eu) activated–ZnB$_2$O$_4$. The spectrum of pure ZnB$_2$O$_4$ host (Fig. 2(a)) exhibited the fundamental absorption edge at ~380 nm. For doping 10 mol% Eu$^{3+}$ in ZnB$_2$O$_4$, two absorption bands peaks at ~280 nm and 393 nm are observed in the spectrum. The former is attributed to the O$^-$-Eu$^{3+}$ charge transfer band (CTB); the latter is resulting from $f$-$f$ transition of Eu$^{3+}$ ($^5$D$_{0}$$\rightarrow$$^3$L$_{6}$). While solely doping 1 mol % Bi$^{3+}$, a very broad absorption band between 250 nm to 390 nm is observed, which could be responsible for the 6s6p excitation state of Bi$^{3+}$ [21].
Fig. 2. Reflectance spectra of as-synthesized samples: (a) ZnB$_2$O$_4$; (b) Zn$_{0.9}$B$_2$O$_4$:Eu$_{0.1}$; (c) Zn$_{0.89}$B$_2$O$_4$:Bi$_{0.01}$Eu$_{0.1}$; (d) Zn$_{0.8}$B$_2$O$_4$:Bi$_{0.1}$Eu$_{0.1}$; and (e) Zn$_{0.99}$B$_2$O$_4$:Bi$_{0.01}$.

For Zn$_{0.89}$B$_2$O$_4$:Bi$_{0.01}$Eu$_{0.1}$ and Zn$_{0.8}$B$_2$O$_4$:Bi$_{0.1}$Eu$_{0.1}$, the spectra show that with increasing the Bi$^{3+}$ content, the absorption band shifts to longer wavelength. It was found that the absorption edges were almost overlapping in ZnB$_2$O$_4$, ZnB$_2$O$_4$:1%Eu, ZnB$_2$O$_4$:3%Eu and ZnB$_2$O$_4$:5%Eu. The unobserved absorption edge for ZnB$_2$O$_4$:10%Eu may be due to its relatively strong luminescence. The detector of reflector received higher luminescence while excitation wavelength in the range of 350~400 nm.

Fig. 3. PL/PLE spectra of as-synthesized (Zn$_{0.9}$Eu$_{0.1}$)B$_2$O$_4$ excited at 393 nm. The inset represents the effect of Eu$^{3+}$ concentration on the PL intensity.

The PL and PLE spectra of ZnB$_2$O$_4$:0.1Eu$^{3+}$ are shown in Fig. 3. A broad excitation band observed at 250~280 nm can be attributed to the O$^2-$-Eu$^{3+}$ charge transfer (CT) transition. The sharp excitation peaks between 300 and 550 nm are due to the typical f-f transition of Eu$^{3+}$. The strongest line absorption in the excitation spectrum is located at 393 nm, which is resulting from the $^7$F$_0$$\rightarrow$$^5$L$_6$ transition. The PL spectrum exhibits typically Eu$^{3+}$ line emission at 578 nm ($^5$D$_0$$\rightarrow$$^7$F$_0$), 585, 590, 600 nm ($^5$D$_0$$\rightarrow$$^7$F$_1$), 610, 621 nm ($^5$D$_0$$\rightarrow$$^7$F$_2$), 651 nm ($^5$D$_0$$\rightarrow$$^7$F$_3$) and 689 nm ($^5$D$_0$$\rightarrow$$^7$F$_4$). It has been reported that the highly intense line at $^5$D$_0$$\rightarrow$$^7$F$_1$ is due to magnetic dipole transition, while strong emission at $^5$D$_0$$\rightarrow$$^7$F$_2$ is attributed to the electric dipole transition which is observed at 610 nm ($^5$D$_0$$\rightarrow$$^7$F$_2$) indicating that Eu$^{3+}$ ion occupied the site of non-inversion symmetry [22]. The $^5$D$_0$$\rightarrow$$^7$F$_0$ transition at 578 nm is observed in (Zn$_{0.9}$Eu$_{0.1}$)B$_2$O$_4$ revealing that Eu$^{3+}$ occupied a site with C$_v$, C$_{3v}$ or C$_i$ symmetry [23]. The inset displays that the PL intensity of Eu$^{3+}$ excited at 393 nm as a function of Eu$^{3+}$ concentration. It can be seen that the optimal dopant concentration of Eu$^{3+}$ is 10 mol %. Below 10 mol%, the PL intensity of the emission peaks were found to increase with increasing Eu$^{3+}$ content, while above 10 mol%, it decreased with the increasing Eu$^{3+}$ content.
The former observation could be attributed to the distance between Eu$^{3+}$ ions is too far away that the intensity is proportional to the content of Eu$^{3+}$. The latter observation is presumably due to the concentration quenching of Eu$^{3+}$ ions.

Figure 4 shows the PL spectra of ZnB$_2$O$_4$ with different content of Eu$^{3+}$. The inset in Fig. 4 displayed the intensity ratio of 583 nm and 609 nm. In this study, the dominant emission peak was varied with the content of Eu$^{3+}$.

Figure 4 shows the PL spectra of ZnB$_2$O$_4$ with different content of Eu$^{3+}$. The inset in Fig. 4 displayed the intensity ratio of 583 nm and 609 nm. In this study, the dominant emission peak was varied with the content of Eu$^{3+}$. The ratio of $^5$D$_{0}$ – $^7$F$_{1}$/$^5$D$_{0}$ – $^7$F$_{2}$ was different with the increase of Eu$^{3+}$ concentrations. The results indicate that there are more than one Eu sites in the lattice. The excitation and emission wavelengths of Bi$^{3+}$ observed at 380 nm and 485 nm are corresponded to the $^1$S$_0$→$^1$P$_1$ and $^3$P$_1$→$^1$S$_0$ transitions [24]. The emission band of Bi$^{3+}$ was found to overlap with the excitation bands of Eu$^{3+}$ ions, especially at 393 nm ($^5$F$_{0}$→$^5$L$_{6}$ transition) and 464 nm ($^5$F$_{0}$→$^5$D$_{2}$ transition), respectively. It is well known that for effective energy transfer to occur, an overlap of the emission region of the sensitizer, said Bi$^{3+}$ in this study, and the absorption region of the activator, namely Eu$^{3+}$ was necessary. We also investigated the emission intensity of (Zn$_{0.9}$Eu$_{0.1}$)B$_2$O$_4$ doped with 1, 3, 5, 10, 15 and 20 mol % of Bi$^{3+}$. Similar to Eu$^{3+}$ doping in ZnB$_2$O$_4$, an optimal doping concentration of Bi$^{3+}$ was also found to be 10 mol %. With Eu$^{3+}$/Bi$^{3+}$ codoping in ZnB$_2$O$_4$, the optimal composition was determined to be (Zn$_{0.8}$Bi$_{0.1}$Eu$_{0.1}$)B$_2$O$_4$. Thus, it can be concluded that in ZnB$_2$O$_4$, Bi$^{3+}$ is a sensitizer for the luminescence of Eu$^{3+}$ and with the Bi$^{3+}$ codoped in ZnB$_2$O$_4$:Eu$^{3+}$, the PL intensity and brightness can be significantly improved by an increment of 16% and 52%, respectively. As compared to the red-emitting phosphor La$_2$O$_2$S:Eu$^{3+}$ the intensity and integrated area of ZnB$_2$O$_4$:Eu$^{3+}$,Bi$^{3+}$ were found to be 95% and 104% of those of the commodity, respectively.

### 3.3 PL spectra and relative emission intensity dependence of temperature effect

For the application of high power LEDs, the thermal stability tests of phosphors are shown in Fig. 5. In general, the luminescence intensity decreases with increasing temperature. The thermal quenching phenomena observed in phosphors are generally attributed to (a) the degradation of host structure, (b) the oxidation of activators, and (c) the interruption of energy transfer processes between host and activator. Figure 5 displays the PL spectra of (Zn$_{0.8}$Bi$_{0.1}$Eu$_{0.1}$)B$_2$O$_4$ excited at 393 nm with varied temperatures ranging from 25°C to 300°C. The PL spectra of (Zn$_{0.8}$Bi$_{0.1}$Eu$_{0.1}$)B$_2$O$_4$ were found to show little change with increasing temperature except the intensity.

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In comparison, the luminescence of La$_2$O$_2$S:Eu$^{3+}$ commodity was also carried out under the same condition. The inset in Fig. 5 shows the comparison of the temperature-dependent PL intensity or thermal quenching behavior for (Zn$_{0.8}$Bi$_{0.1}$)B$_2$O$_4$ and La$_2$O$_2$S:Eu$^{3+}$. The PL intensity of La$_2$O$_2$S:Eu$^{3+}$ was firstly observed to increase before reaching its maximum value at 100°C and dramatically decreased with increasing temperature. The thermal behavior of (Zn$_{0.8}$Bi$_{0.1}$)B$_2$O$_4$ is a “irreversible” process, meaning that while the temperature returns to room temperature, the PL intensity cannot go back to its original value. The increase of PL intensity at lower temperature was probably due to the red shift of excitation band of La$_2$O$_2$S:Eu$^{3+}$ at ~395 nm[25]. As for (Zn$_{0.8}$Bi$_{0.1}$)B$_2$O$_4$, the inset of Fig. 5 shows a linear decay in PL intensity with increasing temperature, which may result from the interruption of energy transfer processes between host and activator. The study on the thermal quenching of luminescence indicates that ZnB$_2$O$_4$:Eu,Bi can serve as a potential candidate as a red-emitting phosphor in the application high power phosphor-converted LEDs.

4. Conclusion

A new red-emitting phosphor, ZnB$_2$O$_4$:Eu$^{3+}$,Bi$^{3+}$, was synthesized by solid state reactions for the first time. The optimized compositions of ZnB$_2$O$_4$ co-doping Eu$^{3+}$ and Eu$^{3+}$/Bi$^{3+}$ are ZnB$_2$O$_4$:10%Eu and ZnB$_2$O$_4$:10%Eu,10%Bi, respectively. The introduction of Bi$^{3+}$ ions successfully enhances both emission intensity and quantum efficiency by 14% and 6%, respectively. The present results indicate that the novel red emitting phosphor is a suitable candidate for the application on NUV white LEDs.

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