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Near-UV light excited Eu^{3+}, Tb^{3+}, Bi^{3+} co-doped $LaPO_4$ phosphors: Synthesis and enhancement of red emission for WLEDs

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Abstract

A series of single-phase Eu^{3+}, Tb^{3+}, Bi^{3+} co-doped $LaPO_4$ phosphors were synthesized by solid-state reaction at 800 °C. Crystal structures of the phosphors were investigated by X-ray diffraction (XRD). A monoclinic phase was confirmed. The excitation (PLE) and emission (PL) spectra showed that the phosphors could emit red light centered at 591 nm under the 392 nm excitation, which is in good agreement with the emission wavelength from near-ultraviolet (n-UV) LED chip (370–410 nm). The results of PLE and PL indicated that the co-doped Tb^{3+} and Bi^{3+} could enhance emission of Eu^{3+} and the fluorescent intensities of the phosphors excited at 392 nm could reach to a maximum value when the doping molar concentration of Tb^{3+} and Bi^{3+} is about 2.0% and 2.0%, respectively. The co-doping Tb^{3+} and Bi^{3+} ions can strengthen the absorption of near UV region. They can also be efficient to sensitize the emission of Eu^{3+}, indicating that the energy transfer occurs from Tb^{3+} and Bi^{3+} to Eu^{3+} ions. From further investigation it can be found that co-doping Tb^{3+} and Bi^{3+} ions can also induce excitation energy reassignment between $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ in these phosphors, and result in more energy assignment to $^5D_0$–$^7F_2$ emission in $LaPO_4$:Eu^{3+}, Tb^{3+}, Bi^{3+}. Our research results displayed that $La_{0.94}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$, $Bi^{3+}_{0.02}$ could be a new one and could provide a potential red-emitting phosphor for UV-based white LED.

Keywords: A. Sintering; Inorganic compounds; Phosphor; Luminescence; UV-based white LED

1. Introduction

In recent years, search for new phosphors and other materials which can be employed in white light-emitting diodes (W-LEDs) and in the field of integrated optics has been studied intensively [1–6]. Moreover, great efforts have been devoted for synthesis of lanthanide phosphate phosphors due to their merit of a large Stokes shift, a long life time, sharp fluorescence in comparison with traditional materials [7–11]. Although, Eu^{3+}, Tb^{3+} co-doped phosphors and energy transfer between Tb^{3+} and Eu^{3+} has been investigated since years [12–17], to the best of our knowledge, Eu^{3+}, Tb^{3+} co-doped lanthanide phosphate phosphors for UV-LED chip-based W-LEDs has been seldom reported. It is interesting that, in some literatures, rare earth ions co-doped $LaPO_4$ phosphors have also been used in the studies of W-LEDs [18–23], such as $LaPO_4$:Ce^{3+}, Tb^{3+} [18–20], LaPO4:Eu^{3+}, Sm^{3+} [21], $Sr_3La(PO_4)_3$:Sm^{3+}, Eu^{3+} [22], $NaGd(PO_3)_4$:Tb^{3+}, Eu^{3+} [23] and $LaPO_4$:Ce^{3+}, Tb^{3+}, Eu^{3+} [24]. It suggests that Eu^{3+}, Tb^{3+} co-doped $LaPO_4$ may be a novel Eu^{3+}, Tb^{3+} co-doped phosphors, and also present energy transfer between Tb^{3+} and Eu^{3+}. Many reports revealed that the doped Bi^{3+} is

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efficient to sensitize the emission of rare earth ions [3,25–28]. So, there is reason to believe that such Bi^{3+} enhanced effect will be observed in Eu^{3+}, Tb^{3+} co-doped $LaPO_4$. Different raw materials, sensitized ions and synthesis methods will result in different luminescent properties of Eu^{3+}, Tb^{3+} co-doped phosphors with different crystallization temperature, crystallite size and morphology. So, new host materials and synthesis methods for Eu^{3+}, Tb^{3+} co-doped phosphors still need to be studied and innovated further, as well as their luminescent properties.

Here we report the synthesis and luminescent properties of a series of Eu^{3+}, Tb^{3+} and Bi^{3+} co-doped $LaPO_4$. The sensitization effect on the emission of Eu^{3+} produced by the doped Tb^{3+} is novel and different from other Eu^{3+}, Tb^{3+} co-doped phosphors reported by previous literatures [4]. Calcining active precursors is a common way to prepare metal-doped phosphate materials [29,30]. In the present work, Eu^{3+}, Tb^{3+} and Bi^{3+}co-doped $LaPO_4$ phosphors were synthesized from calcining their active precursors.

2. Experimental

All chemicals were reagent-grade pure and purchased from the Sinopharm Chemical Reagent Co. Ltd., China. X-ray powder diffraction (XRD) was performed at a scanning rate of 5°/min from 5° to 70° for 2θ at room temperature by using a Rigaku D/max 2500 V diffractometer. It was equipped with a graphite monochromator by utilizing monochromatic Cu$K\alpha$ radiation (λ=0.154178 nm). Excitation and emission spectra were recorded at room temperature by a Shimadzu RF-53001 spectrophotometer equipped with a xenon lamp as the excitation source.

For $La_{0.96}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$ phosphor, in a typical synthesis method, with a molar ratio of La:Eu:Tb:P=0.96:0.02:0.02:1.00, La_2O_3 (4691.7 mg, 14.40 mmol), $Eu(NO_3)_3 \cdot 6H_2O$ (267.6 mg, 0.60 mmol), and $Tb(NO_3)_3 \cdot 6H_2O$ (271.8 mg, 0.60 mmol) powders were added into a mortar and ground for 15 min. Then, $(NH_4)_3PO_4 \cdot 3H_2O$ (6093.5 mg, 30.0 mmol) powder was added into the above mixture. The resulting mixture was carefully ground for 30 min. The reaction mixture gradually became damp. Then a paste formed quickly. The paste was dried at 120 °C for 3 h, then calcined at 300 °C for 3 h, and finally calcined at 800 °C for 3 h to obtain the phosphor $La_{0.96}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$. Synthetic procedures of $La_{0.98}PO_4$:$Eu^{3+}_{0.02}$, $La_{0.98}PO_4$:$Tb^{3+}_{0.02}$ and $La_{0.94}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$, $Bi^{3+}_{0.02}$ are same as those of $La_{0.96}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$.

3. Results and discussion

Fig. 1 shows the XRD patterns of four representative samples calcined at 800 °C for 3 h. In Fig. 1, all the diffraction peaks of the samples are indexed and are in agreement with that of the pure monoclinic $LaPO_4$ phase standard data (PDF Card 84-0600). For example, the indexed results of the sample (d) are as follows: a=0.684541 (3) nm, b=0.710426 (3) nm, c=0. 652771 (2) nm; α=90°, β=103.3366 (2)°, γ=90°, which are in agreement with that of monoclinic $LaPO_4$ (PDF Card 84-0600) with space group $P2_1/n(14)$ and cell parameters: a=0. 6825 nm, b=0.7057 nm and c=0.6482 nm (α=90°, β=103.21° and γ=90°). It illustrates that $La_{0.94}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$, $Bi^{3+}_{0.02}$ has the same structure as $LaPO_4$. Fig. 1, shows that the calcined sample has good crystallinities and no other impurities in the samples.

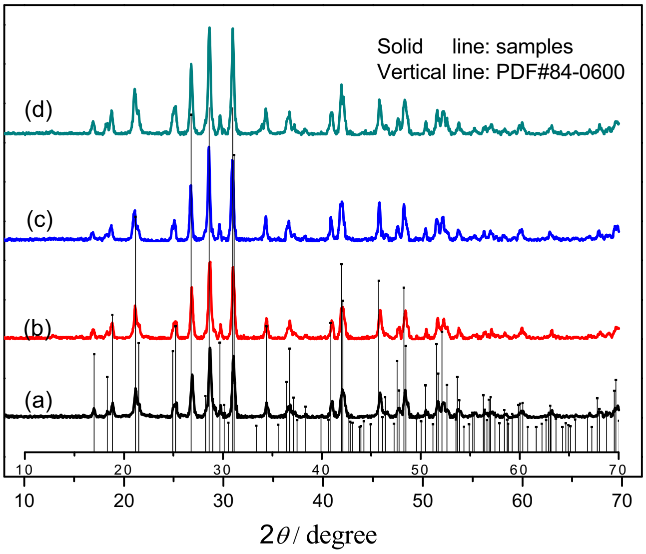

Fig. 1. XRD patterns of samples, calcined at 800 °C for 3 h: (a) LaPO4:$Tb_{0.02}$; (b) LaPO4:$Eu_{0.02}$; (c) LaPO4:$Eu_{0.02}$, $Tb_{0.02}$; (d) LaPO4:$Eu_{0.02}$, $Tb_{0.02}$, $Bi_{0.06}$.

The fluorescent properties of $La_{0.98}PO_4$:$Tb^{3+}_{0.02}$, $La_{0.98}PO_4$:$Eu^{3+}_{0.02}$, and $La_{0.98}PO_4$:$Eu^{3+}_{0.02}$, $Tb^{3+}_{0.02}$ were explored by the photoluminescence excitation (PLE) and emission (PL) spectra at room temperature (Fig. 2). The PLE and PL spectra of $LaPO_4$:$Tb^{3+}_{0.02}$ is shown in Fig. 2a(i). It is noticed that no excitation peaks are found between 385 and 460 nm for $La_{0.98}PO_4$:$Tb^{3+}_{0.02}$. In the PL spectrum, four emission peaks at 487, 542, 583 and 618 nm can be respectively assigned to the $^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$, $^5D_4$–$^7F_4$, and $^5D_4$–$^7F_3$ transitions of Tb^{3+} [19,20], and the green emission at 542 nm ($^5D_4$–$^7F_5$) is the strongest one. Fig. 2a(ii) shows the PLE and PL spectra of $La_{0.98}PO_4$:$Eu^{3+}_{0.02}$. There are several excitation peaks among the range of 350–530 nm, and the strongest one is at 392 nm. Four emission peaks centered at 590, 616, 651 and 690 nm are belonged to the transitions from excited $^5D_0$ level to ^7F_J (J=1–4) ground level of the $4f^6$ configuration in Eu^{3+} ion [21,31-33]. The strongest splitting peak is observed at 591 nm. Meanwhile, three strong splitting peaks present at 591, 611 and 619 nm. Fig. 2a(iii) shows the PLE and PL spectra of $La_{0.96}PO_4$:$Eu^{3+}_{0.02}$,$Tb^{3+}_{0.02}$. Among excitation peaks in the range of 330–530 nm, the strongest one is at 392 nm. In PL, emission bands of Eu^{3+} are appeared when excitation by 392 nm, while no emission peaks of Tb^{3+} are found in the PL spectrum. This indicates that Tb^{3+} cannot be efficiently excited by 392 nm, which is in agreement with the literatures [5,33].

Fig. 2b shows comparative PLE and PL spectra of three samples. Fig. 2b indicates that the doped Tb^{3+} is effective to extend the absorption of near-UV light centered at 392 nm for