Research Paper

Cation Substitution Induced Enhanced Photoluminescence Properties of Gd$_{2(1-x-y)}$Y$_{2x}$Mo$_4$O$_{15}$:2yEu$^{3+}$ Phosphors for Indoor Lighting

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Received May 17, 2018; accepted May 29, 2018

Abstract We reported a new method to enhance the photoluminescence (PL) properties of Eu$^{3+}$ ions doped Gd$_2$Mo$_4$O$_{15}$ phosphors via cation substitution. With the aid of conventional sol-gel method, a series of Eu$^{3+}$ ions doped Gd$_{2(1-x-y)}$Y$_{2x}$Mo$_4$O$_{15}$ phosphors were prepared. The prepared samples emitted red light when excited at 393 nm. Moreover, when part of the Gd$^{3+}$ ions was substituted by the Y$^{3+}$ ions, the PL emission intensity of the studied samples was enhanced and the optimal doping concentration for Y$^{3+}$ ions was 30 mol%. The calculated CIE coordinate (0.663,0.337) was situated in the red region. Furthermore, the thermal quenching behaviors of the synthesized Eu$^{3+}$ ions doped Gd$_{2(1-x)}$Y$_x$Mo$_4$O$_{15}$ phosphors were studied. At last, we also packaged a red-emitting light-emitting diode device by integrating the obtained phosphors and a near-ultraviolet chip to verify the applications of the Eu$^{3+}$ ions doped Gd$_{2(1-x)}$Y$_x$Mo$_4$O$_{15}$ phosphors for indoor lighting.

Keywords: Rare-earth, Phosphors, Indoor lighting, WLEDs

I. Introduction

Recently, the rare-earth (RE) ions doped inorganic luminescent materials have been intensively researched because of their potential applications in various fields, such as in vitro cell imaging, solid-state lighting, plant growth, solar cells and sensors [1-5]. Compared with conventional lamps, the interest in phosphor-converted white light-emitting diodes (WLEDs), which show satisfactory properties of low energy consumption, high luminous efficiency, ecofriendly, long lifetime white light-emitting diodes (WLEDs), which show conventional lamps, the interest in phosphor-converted growth, solar cells and sensors [1-5]. Compared with color-emitting phosphor, particularly the phosphor which can generate red emission under NUV/blue light irradiation, is very important to enhance the optical performance of the phosphor-converted WLEDs.

In comparison with other RE ions, the Eu$^{3+}$ ion, which possesses narrow red emission at about 615 nm ($^5$D$_0$ → $^7$F$_2$) when it occupies the sites without inversion center, is a good red-emitting activator [10,11]. It is clear that the PL emission intensities of the RE ions rely on the luminescent materials. As is known, low phonon energy usually contributes to low nonradiative (NR) transition possibility, resulting in strong photoluminescence (PL) performance in RE ions doped materials [12]. Currently, molybdate has been widely studied as a luminescent host material for RE ions due to their merits of high stability and strong absorption in the UV region [13,14]. Yan et al. reported that the NaGd(MoO$_4$)$_2$:Dy$^{3+}$/Eu$^{3+}$ compounds, which emitted with color-controllable emissions under NUV light excitation, were suitable for phosphor-converted WLEDs applications [15]. Furthermore, Li et al. also pointed out that the Sm$^{3+}$-doped Lu$_3$MoO$_9$ phosphors were promising candidates for simultaneous WLEDs and temperature sensing [16]. Nevertheless, more efforts are still required to further enhance the optical performance of RE ions doped molybdates to extend their applications. In this work, the Eu$^{3+}$ ions doped Gd$_{3(1-x)}$Y$_x$Mo$_4$O$_{15}$ phosphors were synthesized through sol-gel technique. With the aid of the X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM), PL excitation (PLE) and PL emission spectrum, the final products were characterized.

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Additionally, a red-emitting LED device, which consisted of the prepared compounds and a NUV chip, was developed to verify the feasibility of the studied samples for practical application in indoor lighting.

II. Experimental Procedure

A series of Gd$_{x_1}$(Y$_{0.6}$Mo$_{15}$)$_3$O$_{24}$:Eu$^{3+}$ (Gd$_{x_2}$Y$_2$Mo$_4$O$_{15}$:Eu$^{3+}$; $y=0.5$; $x=0.0, 0.1, 0.2, 0.3$ and $0.4$) compounds were successfully sintered through a conventional critic acid based sol-gel route. The chemicals, such as Gd(NO$_3$)$_3$:6H$_2$O, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Y(NO$_3$)$_3$:6H$_2$O, Eu(NO$_3$)$_3$:5H$_2$O and critic acid, were applied as the raw materials. According to the designed chemical formula, the Y(NO$_3$)$_3$:6H$_2$O, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Eu(NO$_3$)$_3$:5H$_2$O and Gd(NO$_3$)$_3$:6H$_2$O were weighted and added in 200 ml of de-ionized water. Subsequently, the critic acid (the molar ratio of total metal ions to critic acid of 1:2), which played the role as the chelating agent, was weighted and poured into the aforementioned solution. Afterwards, the mixture was sealed and heat-treated at 80°C under strong agitation. After 30 min agitation, the lid was shifted and the obtained solution was kept at 80°C to evaporate gradually. Then, the obtained wet-gel was put in oven and heat-treated at 120°C to form the xerogel. Finally, the final products were obtained after calcination at 700°C for several hours.

The X-ray diffractometer (Bruker D8 Advance), spectrofluorometer (Scinco FluroMate FS-2) and FE-SEM (LEO SUPRA 55, Carl Zeiss) were employed to characterize the final products. The temperature was tuned by a thermocouple (NOVA ST540). The multi-channel spectroradiometer (OL 770) was adopted to examine the electroluminescence (EL) performance of the developed red-emitting LED device.

III. Results and Discussion

Figure 1 shows the typical XRD pattern of the Gd$_{x_1}$(Y$_{0.6}$Mo$_{15}$)$_3$O$_{24}$:Eu$^{3+}$ phosphors prepared at 700°C. As presented, the detected XRD peaks matched with the Joint Committee on Powder Diffraction Standards card of 53-0358 which suggested that the studied phosphors possessed single monoclinic phase. Based on the strongest diffraction peaks, the average crystallite size ($D$) of the Gd$_{x_1}$(Y$_{0.6}$Mo$_{15}$)$_3$O$_{24}$:Eu$^{3+}$ phosphors was estimated utilizing the Scherrer formula of $D = k \lambda / \beta \cos \theta$, here the values of $k$ and $\lambda$ were fixed at 0.94 and 1.54, respectively, while, in present work, the values of $\beta$ and $\theta$ were 0.083 and 25.73, respectively. As a consequence, the average crystallite size for the Gd$_{x_1}$(Y$_{0.6}$Mo$_{15}$)$_3$O$_{24}$:Eu$^{3+}$ phosphors prepared at 700°C was calculated to be about 105.12 nm.

The FE-SEM images of the typical Gd$_{x_2}$Y$_2$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds are shown in Figure 2 to characterize the morphology of the resultant phosphors. It can be seen from Figure 2 that the studied compounds possessed aggregated microparticles. Furthermore, when the Y$^{3+}$ ion content was elevated from 0 to 40 mol%, the microstructure of the synthesized samples did not change, implying that the morphology performance of the studied compounds was independent of the Y$^{3+}$ ion concentration.

The luminescent properties of Gd$_{x_2}$Y$_{0.6}$Mo$_{15}$:Eu$^{3+}$ phosphors at room temperature were examined by PL excitation (PLE) and PL emission spectra. It can be seen from Figure 3(a) that the PLE spectrum consisted of an intense broad charger transfer (CT) band and pairs of sharp bands. Specially, the broad CT band with a central wavelength at 303 nm was due to overlapped transitions of O$^2\rightarrow$Eu$^{3+}$ and O$^2\rightarrow$Mo$^{6+}$, whereas the residual narrow peaks at 362, 376, 382, 393, 415 and 465 nm rising from 4f-4f transitions of Eu$^{3+}$ ions from $^7F_0$ to the $^5D_4$, $^5D_4$, $^5G_3$, $^5L_6$, $^5D_3$ and $^3D_2$ excited levels, respectively [17,18]. In comparison, the excitation bands at 303 and 393 nm exhibited the relatively strong intensity. Among them, the peak at 303 nm belonged to deep UV light, while the excitation band with a wavelength of 393 nm pertains to
is widely accepted that the Eu\(^{3+}\) ions are populated at the low symmetry sites, the \(^{5}D_0\rightarrow^{7}F_2\) transition will take the domination in the luminescent spectrum. Otherwise, the yellow emission (\(^{5}D_0\rightarrow^{7}F_1\)) will be stronger than the red emission when the Eu\(^{3+}\) ions situate the high symmetry sites with inversion center [19,20]. On the basis of the result deduced from PL emission spectrum, one obtains that the sites took up by the activator (Eu\(^{3+}\)) in the studied system had low symmetry.

In order to explore the effect of Y\(^{3+}\) ion concentration on the PL properties of the studied samples, series of Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) phosphors were prepared and their PL spectra excited at 393 nm are shown in Figure 3(b). As disclosed, the luminescent profiles as well as the emission bands were hardly changed when the Y\(^{3+}\) ions were added. Nevertheless, it can be seen from Figure 3(c) that the PL emission properties were found to rely on the dopant content and the strongest PL emission intensity was obtained when the Y\(^{3+}\) ion concentration was 30 mol\%\(_{\text{Y}}\), suggesting that the cation substitution is an promising route to modality the PL emission properties of Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) compounds. Nevertheless, when the Y\(^{3+}\) ion concentration was over 30 mol\%\(_{\text{Y}}\), the concentration quenching effect occurred and the PL emission intensity began to decrease. From the detected PL spectrum, the typical CIE coordinates of the Gd\(_{0.4}\)Y\(_{0.6}\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) were elevated and its value was (0.663,0.337), as described in Figure 3(d). It is obvious that this obtained CIE coordinate was comparable with the ideal red light (0.670,0.330) [21]. Moreover, it is obvious that the studied samples can emit glaring visible red light when excited at NUV light. As results, the Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) compounds, which possessed admirable PL properties, may have potential applications in indoor illuminations. On the other hand, to better explain the involved NUV-induced-visible emission mechanism in the studied material system, the simplified energy level diagram of Eu\(^{3+}\) ions in the Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) compounds was molded and demonstrated in Figure 3(e). Under 393 nm light irradiation, electrons were firstly moved from the ground state to the \(^{5}L_6\) excited level. Afterwards, the NR transition occurred and the populated electrons decayed to \(^{5}D_0\) level. At last, the radiative transitions of \(^{5}D_0\rightarrow^{7}F_1\), \(^{5}D_0\rightarrow^{7}F_2\), \(^{5}D_0\rightarrow^{7}F_3\) and \(^{5}D_0\rightarrow^{7}F_4\) took place, resulting in the achieved characteristic emissions of Eu\(^{3+}\) ions.

Figure 4(a) displays the PL spectra of the Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) compounds in the temperature range of 303-483 K. Obviously, a gradual decrement in the PL emission intensity of Gd\(_{1-x}Y_x\)Mo\(_4\)O\(_{15}\):Eu\(^{3+}\) phosphors was seen when the surrounding temperature was increased. The thermal quenching effect can be responsible for this phenomenon. Furthermore, compared with that of at 303 K,
the PL emission intensity of the studied compounds at 423 K kept 65.7%, indicating that the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors had admirable thermal stability. In addition, the involved activation energy was elevated by employing the following formula [22]:

$$\ln\left(\frac{I_b}{I_0} - 1\right) = \ln A - \frac{\Delta E}{kT}$$  \hspace{1cm} (1)

In this expression, the $I_b$, $I_0$, $A$, $\Delta E$ and $k$ denote PL emission intensity at room temperature, PL emission intensity at temperature $T$, coefficient, activation energy and Boltzmann constant, respectively. From the plot of $\ln(I_b/I_0 - 1)$ vs. $1/kT$, one knows that the experimental data can be linearly fitted and the slope was revealed to be -0.282 (see Figure 4(c)). Hence, the involved activation energy for the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors was as high as 0.282 eV. Additionally, it is well known that the NR transition ratio per unit time ($\alpha$) can be estimated by the following equation [23]:

$$\alpha = s \exp\left(-\frac{\Delta E}{kT}\right)$$  \hspace{1cm} (2)

where $s$ is assigned to the frequency factor, $\Delta E$ is related to the activation energy, $k$ represents the Boltzmann constant and $T$ is the temperature. Since $s$, $k$ and $T$ are coefficients, it is clear that larger $\Delta E$ can result in smaller $\alpha$ as well as stronger PL emission intensity at elevated temperature. In comparison with that of other Eu$^{3+}$ ions doped molybdates, such as Na$_{0.5}$Gd$_{0.5}$Mo$_2$O$_7$:Eu$^{3+}$ ($\Delta E = 0.235$ eV) and Na$_3$Gd(PO$_4$)(MoO$_4$):Eu$^{3+}$ ($\Delta E = 0.22$ eV) [22,24], the $\Delta E$ value of the prepared compounds was much larger, further indicating that the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds had admirable thermal stability.

A LED device was prepared through coating the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors onto the surface of a NUV chip so as to verify the practical applications of the as-prepared compounds. Figure 4(d) illustrates the room temperature EL spectrum of the developed LED device. It is evident that the band with a central wavelength at around 405 nm was attributed to the InGaN NUV chip and the other four peaks, which centered at 594, 615, 650 and 704 nm, were due to the emissions of Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors. Besides, when the forward basis current was 100 mA, as displayed in the inset of Figure 4(d), the packaged LED device can emit dazzling red light with CIE coordinate of (0.569,0.272). These observed results further confirm that the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds were appropriate for NUV chip-based WLEDs.

IV. Conclusions

Under NUV light excitation, all the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds emitted unique emissions of Eu$^{3+}$ ions. Moreover, the red emission ($^2$D$_{5/2}$ → $^2$F$_{5/2}$) was the strongest one in the measured PL emission spectrum compared with other bands. The PL emission intensity of the studied samples was found to be dependent on the Y$^{3+}$ ion concentration. When the Y$^{3+}$ ion concentration 30 mol%, the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds showed the optimum luminescent performance. The resultant samples were found to possess excellent thermal stability and the activation energy was demonstrated to be 0.282 eV. With the help of the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors and a LED chip with emission wavelength of 405 nm, a red-emitting LED device was packaged. These results demonstrate that the cation substitution is an efficient approach to modify the PL emission behaviors of the Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ phosphors and the synthesized Gd$_{1-2x}$Y$_x$Mo$_4$O$_{15}$:Eu$^{3+}$ compounds are potential candidates for indoor lighting as red-emitting components.

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