Research Paper

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

Peng Du and Jae Su Yu*

Department of Electronic Engineering, Institute for Wearable Convergence Electronics, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Republic of Korea

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Abstract We reported a new method to enhance the photoluminescence (PL) properties of Eu^{3+} ions doped $\text{Gd}_2\text{Mo}_4\text{O}_{15}$ phosphors via cation substitution. With the aid of conventional sol-gel method, a series of Eu^{3+} ions doped $\text{Gd}_{2(1-x-y)}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}$ 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 $\text{Gd}_{2(1-x-y)}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}$ 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 $\text{Gd}_{2(1-x-y)}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}$ 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 *et al.*, is increasing and the phosphor-converted WLEDs are also thought of as the next generation indoor/outdoor lighting source [6,7]. Up to date, two available approaches have been developed to prepare the phosphor-converted WLEDs. The first strategy is utilizing a blue LED chip to pump the yellow-emitting phosphor. However, the white light obtained from the above method usually exhibits unsatisfied correlated color temperature and color rendering index because of the insufficient red-emitting component in the luminescent spectrum [8]. Another route that can be applied to generate the white light with high colorific performance is using the near-ultraviolet (NUV) chip to excite the hybrid red-green-blue (RGB) emitting phosphors [9]. Clearly, developing highly efficient single 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 ($^3\text{D}_0 \rightarrow ^7\text{F}_2$) 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 $\text{NaGd}(\text{MoO}_4)_2:\text{Dy}^{3+}/\text{Eu}^{3+}$ 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_2MoO_6 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 $\text{Gd}_{2(1-x-y)}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}$ 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.

*Corresponding author
E-mail: jsyu@khu.ac.kr

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 $\text{Gd}_{2(1-x-y)}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:2y\text{Eu}^{3+}$ ($\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$; $y = 0.5$; $x = 0.0, 0.1, 0.2, 0.3$ and 0.4) compounds were successfully sintered through a conventional citric acid based sol-gel route. The chemicals, such as $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and citric acid, were applied as the raw materials. According to the designed chemical formula, the $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were weighted and added in 200 ml of de-ionized water. Subsequently, the citric acid (the molar ratio of total metal ions to citric 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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors was estimated utilizing the Scherrer formula of $D = k\lambda/\beta\cos\theta$, here the values of k and λ were fixed at 0.94 and 1.54, respectively, while, in present work, the values of β and θ were 0.083 and 25.73° , respectively. As a consequence, the average crystallite size for the $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors prepared at 700°C was calculated to be about 105.12 nm.

The FE-SEM images of the typical $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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

Figure 1. XRD pattern of $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors sintered at 700°C .

Figure 2. FE-SEM images of $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.3$ and (d) $x = 0.4$.

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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ and $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$, whereas the residual narrow peaks at 362, 376, 382, 393, 415 and 465 nm rising from 4f-4f transitions of Eu^{3+} ions from $^7\text{F}_0$ to the $^5\text{D}_4$, $^5\text{G}_2$, $^5\text{G}_3$, $^5\text{L}_6$, $^5\text{D}_3$ and $^5\text{D}_2$ 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

Figure 3. (a) PLE and PL spectra of $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors. (b) PL spectra of the $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors. (c) Dependence of the PL emission intensities on the Y^{3+} ion concentration. (d) CIE chromaticity diagram of the $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors. (e) Simplified energy level diagram of Eu^{3+} ions. Inset shows the luminescent image excited by 365 nm light lamp.

Figure 4. (a) Temperature-dependent PL emission spectra of $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors. (b) Normalized PL emission intensity of $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors as a function of temperature. (c) Plot of $\ln(I_0/I - 1)$ vs. $1/kT$. (d) EL spectrum of the fabricated LED device under 100 mA. Inset shows the image of the developed LED device.

the NUV light. In terms of the practical applications in WLEDs, the studied compounds were anticipated to be pumped by NUV light rather than deep UV light. Thus, in present work, the 393 nm light was selected as the excitation wavelength. From Figure 3(a), it is obvious that the red emission from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition prevailed in the luminescent spectrum under 393 nm excitation. Apart from the strong red emission, other emissions at around 594 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 650 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and 704 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) were also found in the PL spectrum [17,18]. It is widely accepted that the Eu^{3+} ions have two characteristic emission bands in the red ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and yellow ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) regions [19,20]. Specifically, the

emission intensity of the hypersensitive electronic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red emission) is distinctly affected by local crystal field, whereas that of the magnetic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (yellow emission) is insensitive to the chemical circumstance. Usually, when the Eu^{3+} ions are populated at the low symmetry sites, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition will take the domination in the luminescent spectrum. Otherwise, the yellow emission ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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%, suggesting that the cation substitution is a promising route to modality the PL emission properties of $\text{Gd}_2\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds. Moreover, when the Y^{3+} ion concentration was over 30 mol%, the concentration quenching effect occurred and the PL emission intensity began to decrease. From the detected PL spectrum, the typical CIE coordinates of the $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors, 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds was molded and demonstrated in Figure 3(e). Under 393 nm light irradiation, electrons were firstly moved from the ground state to the $^5\text{L}_6$ excited level. Afterwards, the NR transition occurred and the populated electrons decayed to $^5\text{D}_0$ level. At last, the radiative transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ took place, resulting in the achieved characteristic emissions of Eu^{3+} ions.

Figure 4(a) displays the PL spectra of the $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds in the temperature range of 303–483 K. Obviously, a gradual decrement in the PL emission intensity of $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors had admirable thermal stability. In addition, the involved activation energy was elevated by employing the following formula [22]:

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln A - \frac{\Delta E}{kT} \quad (1)$$

In this expression, the I_0 , I , A , ΔE 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 $\ln(I_0/I - 1)$ 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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors was as high as 0.282 eV. Additionally, it is well known that the NR transition ratio per unit time (α) can be estimated by the following equation [23]:

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

where s is assigned to the frequency factor, ΔE 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 ΔE can results in smaller α as well as stronger PL emission intensity at elevated temperature. In comparison with that of other Eu^{3+} ions doped molybdates, such as $\text{Na}_{0.5}\text{Gd}_{0.5}\text{MoO}_4:\text{Eu}^{3+}$ ($\Delta E = 0.235$ eV) and $\text{Na}_2\text{Gd}(\text{PO}_4)(\text{MoO}_4):\text{Eu}^{3+}$ ($\Delta E = 0.22$ eV) [22,24], the ΔE value of the prepared compounds was much larger, further indicating that the $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds had admirable thermal stability.

A LED device was prepared through coating the $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors. Besides, when the forward bias 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds were appropriate for NUV chip-based WLEDs.

IV. Conclusions

Under NUV light excitation, all the $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds emitted the unique emissions of Eu^{3+} ions. Moreover, the red emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) 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 $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_{0.4}\text{Y}_{0.6}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ 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 $\text{Gd}_2\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ phosphors and the synthesized $\text{Gd}_{1-2x}\text{Y}_{2x}\text{Mo}_4\text{O}_{15}:\text{Eu}^{3+}$ compounds are potential candidates for indoor lighting as red-emitting components.

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