Luminescent properties of Eu^{3+} doped α-Gd$_2$(MoO$_4$)$_3$ phosphor for white light emitting diodes

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Abstract

A novel red emitting phosphor α-Gd$_2$(MoO$_4$)$_3$:Eu^{3+} was developed for white light emitting diodes (LEDs). The phosphor was prepared by solid-state reaction. The effects of the flux content and the activator concentration on the crystal structure, morphology and luminescent properties were investigated by using XRD, SEM, and fluorescent spectra. These results showed that this phosphor can be effectively excited by ultraviolet (UV) (395 nm) and blue (465 nm) light, matching the output wavelengths of ultraviolet or blue LED chips. The α-Gd$_2$ (MoO$_4$)$_3$ phosphor may be a better candidate for solid state lighting application.
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1. Introduction

Since the commercial blue light emitting diodes (LEDs) was first reported by Nichia chemical Co. in 1994, much progress has been achieved on GaN-based LEDs [1–6]. Blue and near-UV light GaN-based LEDs can be used to excite longer wavelength emitting phosphor to realize white light emission. Nakamura pioneered this approach at Nichia Chemical Co. and the first white light emitting diodes became commercially available in 1997 [7–9]. The white light was obtained by combining a 465 nm blue light from the GaN-based LED and yellow light from the phosphor YAG:Ce. However, this light combination has exposed some drawbacks: firstly, the degradation rates of LEDs and phosphor are not isochronous, thus the white light point in the color coordinates scheme shifts with working time. Secondly, the ''white'' light from this combination route has an undesirable color balance, the deficiency of the red light in the visible spectra (around 600 nm) results in a low color rendering index [10]. So a novel red emitting phosphor for compensating the red component is needed in order to obtain white light with higher color rendering index.

Another approach for obtaining white light is to combine a near-UV LED (around 370–410 nm) with tri-color phosphors. The white light consists of the red, green, blue light emitted from the tri-color phosphors while excited by the near-UV LEDs [11,12]. In this case, the float of white color point can be eliminated because all the visible lights come from the tri-color phosphors. In order to realize this type of white LEDs, novel phosphors are required, since most of commercially applicable phosphors were developed on different purposes of applications and do not meet

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the white LEDs applications. The phosphors for LED applications that needs to be excited effectively by the near-UV light is lacking, especially the red one. Nowadays, the commercially applicable red emitting phosphors for white LED are divalent Eu ion activated sulfides. These sulfide phosphors are chemically unstable when exposed in the moisture environment. Therefore, there is an urgent demand upon the superior red emitting phosphors for white LEDs applications.

Eu^{3+}-doped materials, especially in which the Eu^{3+} ions occupy a non-centrosymmetric site in the host, have been widely used as the red emitting phosphors due to their intense $^5D_0 \rightarrow {}^7F_2$ emission in the red spectral region. Previous investigations [10,13] have showed that Eu^{3+}-doped molybdates and tungstates exhibited relatively strong absorption in the near-UV region and intense red emission with good color purity. These results suggest that Eu^{3+}-doped molybdates or tungstates may be the promising candidates as red emitting phosphors for the white LEDs applications.

Compared with CaWO$_4$, α-Gd$_2$(MoO$_4$)$_3$ is capable of accommodating higher Eu^{3+} content. Meanwhile, Eu^{3+} would be stable since taking the Gd^{3+} place in the crystal host α-Gd$_2$(MoO$_4$)$_3$. In order to test the performance of α-Gd$_2$(MoO$_4$)$_3$, trivalent europium ion (Eu^{3+}) activated α phase gadolinium triple molybdate (α-Gd$_2$(MoO$_4$)$_3$) phosphors with various Eu^{3+} concentration were prepared by solid-state reaction in air atmosphere. The influence of flux content and Eu^{3+} concentration on the crystal structure, morphology and spectroscopic properties were investigated.

2. Experimental

A set of phosphor Gd$_2$(MoO$_4$)$_3$:Eu^{3+} was prepared by solid state reaction in air atmosphere. According to a certain stoichiometric ratio, the starting materials: gadolinium oxide (Gd$_2$O$_3$, 99.99%), europium oxide (Eu$_2$O$_3$, 99.99%) and molybdenum oxide (MoO$_3$, 99.99%) were weighted. NH$_4$F with purity of 99.9% was used as flux to improve the chemical reaction. After these powders were blended and grounded thoroughly in an agate mortar, the homogeneous mixture was put into an alumina crucible and calcined in a muffle furnace at the temperature of 800 °C for 4 h.

The crystal structure of these phosphors was identified by a RigakuD/max- II B X-ray diffractometer (XRD) using Cu Kα ($\lambda = 1.54178$) radiation at 40 kV and 100 mA. The excitation and emission spectra of these powder phosphors were recorded with a Hitachi F-4500 with a 150 W Xe lamp. The spectral resolution was set up to be 0.2 nm for both the cases of emission and excitation spectrum measurement. SEM images were taken at a KYKY-1000 Scanning Electron Microscope (SEM). All the measurements were performed at room temperature (RT).

3. Results and discussion

Gd$_2$(MoO$_4$)$_3$ has several phases from RT to melting point (1160 °C) [14]. At RT Gd$_2$(MoO$_4$)$_3$ exists in both the monoclinic and orthorhombic phases depending on the synthesis procedure. If the crystal at RT is orthorhombic (Pba2), it will transform at 159 °C to the tetragonal phase P-42$_1$m; but if it is monoclinic at RT with space group C2/c, it will transform to tetragonal P-42$_1$m at 857 °C [14–17]. Compared with the tetragonal phase, monoclinic α-Gd$_2$(MoO$_4$)$_3$ is a stable phase at RT.

For the solid-state reaction, flux is often used to depress the sintering temperature, shorten the reaction time, and improve the crystallization. An ideal flux is one that can promote the reaction and strengthen the crystallization and the luminescence performance, and it usually does not react with the raw materials. In this work, different
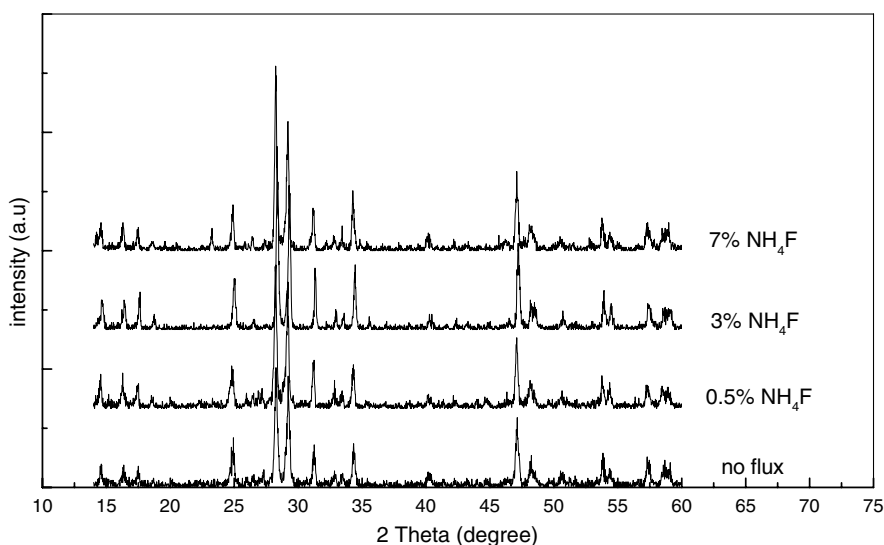

Fig. 1. XRD patterns of Gd$_{1.96}$(MoO$_4$)$_3$:Eu$_{0.04}^{3+}$ prepared at 800 °C with different amount of NH$_4$F as flux.

amount of NH_4F was used in the sample preparations to investigate the effects on the crystallization and the luminescence properties.

The XRD patterns of the $Gd_{1.96}(MoO_4)_3:Eu_{0.04}$ phosphors with different amount of flux NH_4F are presented in Fig. 1. Obviously, with an increase of flux content, the characteristic diffraction peaks of $Gd_2(MoO_4)$ appear and their intensities become more and more intense. Compared with the JCPDS card 25-0338, it is found that the as-prepared powders exist in only one phase, namely, monoclinic $Gd_2(MoO_4)$. There is no extraneous phase emerged.

Fig. 2 depicts the emission spectra for $Gd_{1.96}(MoO_4)_3:Eu_{0.04}^{3+}$ phosphor. The emission spectrum of $Gd_{1.96}(MoO_4)_3:Eu_{0.04}^{3+}$ excited by 465 nm light (showed in Fig. 2(b)) is composed of several narrow spectral lines in the range 500–750 nm. These lines could be assigned to the transitions from the initial state $^5D_0$ and $^5D_1$ to the final states ^7F_J ($J = 1$–4) (signed in Fig. 2(b)). It is well known that the emission intensity ratio of the $^5D_0 \rightarrow {}^7F_1$ to $^5D_0 \rightarrow {}^7F_2$ transitions strongly depend on the local symmetry of the Eu^{3+} ions in host lattice. When the Eu^{3+} ions occupy non-centrosymmetric sites, the ratio is smaller. The emission spectrum of the studied sample exhibits weak emission of $^5D_0 \rightarrow {}^7F_1$ transition at 590 nm and strong emission of $^5D_0 \rightarrow {}^7F_2$ at 613 nm, thus indicating that the Eu^{3+}ion is located at a non-centrosymmetric position in the matrix. The emission spectrum of $Gd_{1.96}(MoO_4)_3:Eu_{0.04}^{3+}$ phosphor excited by 395 nm is also demonstrated in Fig. 2(a). It is obvious that the profile of the emission spectrum excited by 395 nm is identical with that excited by 465 nm.

The excitation spectrum for monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} is shown in Fig. 3. A broad band located around 230–350 nm and several narrow lines centered at 395, 465, 535 nm are observed. The broad band is responsible for the charge transfer state absorption, and the narrow lines are corresponding to the f–f transitions from the ground state $^7F_0$ to the upper excited states $^5D_1$, $^5D_2$, $^5L_6$ of
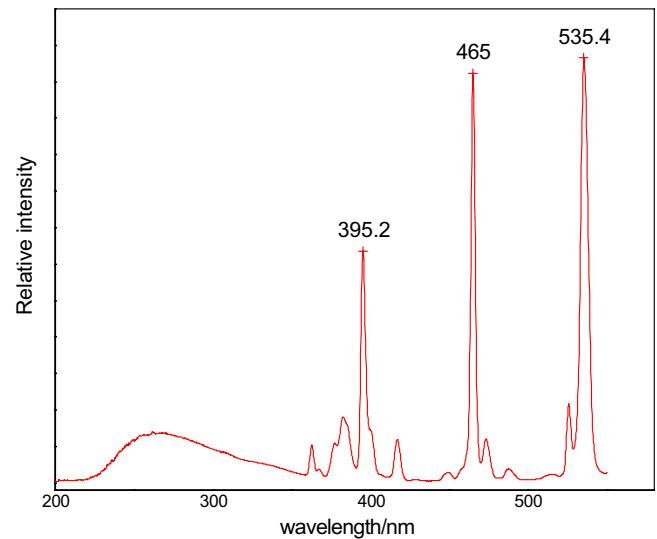

Fig. 3. Excitation spectrum of $Gd_{1.96}(MoO_4)_3:Eu_{0.04}^{3+}$ phosphor (monitoring 613 nm emission).

Eu^{3+}, respectively. For the as prepared samples, the intensities of mentioned f–f absorption transitions are higher than that of broad band. This phenomenon is also observed in some of other phosphor systems, such as $Ca_{1-2x}Eu_xLi_xMoO_4$ [5] and $NaM(WO_4)_{2-x}(MoO_4)_x:Eu^{3+}$(M = Gd, Y, Bi) [13]. Up to now, there is no reasonable explanation for this experimental phenomenon. Probably, this is due to the nature of WO_4^{2-} and MoO_4^{2-} groups and sites of Eu^{3+} occupied in the matrix. However, in $CaMoO_4$:Eu the charge transfer band is much more intense than the f–f transitions [10]. The work for exploring its physical mechanism is under way in our group. In any case, it is good phenomenon that this novel phosphor can strongly absorb ultraviolet (395 nm) and visible blue light (465 nm), and transform the excitation energy to the red radiation. The effective excitation wavelengths of 395 and 465 nm are nicely in agreement with the UV or blue output wavelengths of GaN-based LED chips.
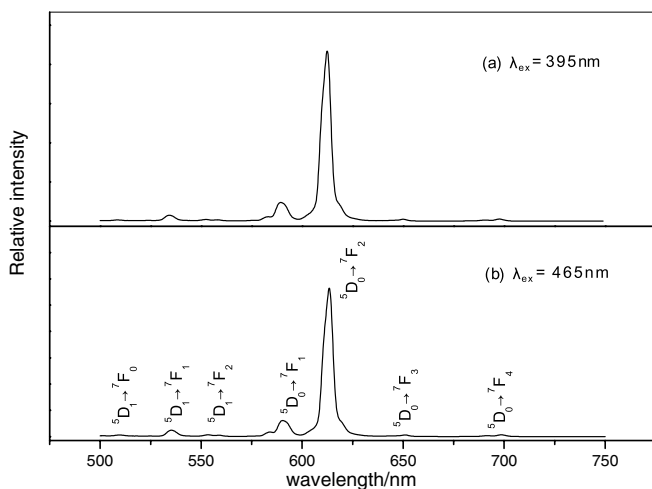

Fig. 2. Emission spectra of $Gd_{1.96}(MoO_4)_3:Eu_{0.04}^{3+}$ phosphor excited by 395 nm (a) and 465 nm (b), respectively.
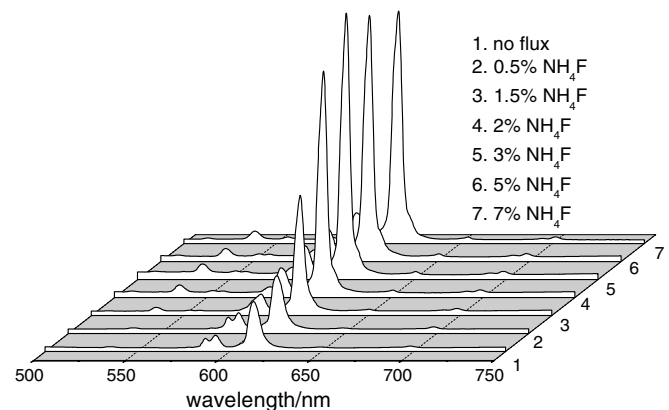

Fig. 4. The effect of flux on the luminescent intensity of phosphors under 395 nm excitation.

Fig. 4 shows the effect of flux content on the luminescent intensity of phosphor $Gd_{1.96}(MoO_4)_3:Eu^{3+}$ under near UV (395 nm) excitation. As increasing the flux dose up to wt 3%, the luminescent intensities are enhanced gradually. When the flux amount is more than wt 3%, the luminescent intensity keeps a constant. This phenomenon is in agreement with the crystallization of the phosphors showed in Fig. 1. When the amount of NH_4F is more than wt 3%, the resultant products may have better crystallization.

Fig. 5 shows the SEM images of $Gd_{1.96}(MoO_4)_3:Eu_{0.04}$ phosphors with different amount NH_4F flux used. Fig. 5(a) (without flux added) and (b) (wt 3% NH_4F added) show the regular and spherical-shape-like particles with uniform size of 2–3 μm, and there is no agglomeration found. It is well known that the phosphors with regular morphology and appropriate size can improve the packing density, slurry properties, and make the luminescence intensity uniform [18]. From this point of view, we believe that appropriate amount of flux is beneficial to the luminescent performance of phosphor on the devices. Fig. 5(c) shows the image of phosphors particles prepared with wt

7% NH_4F flux. The size of phosphor particles is about 2–3 μm, but the melting and agglomeration of the phosphor particles appeared. The agglomeration of phosphor particles is harmful to practical applications, especially for the application in the solid state lighting, since the light should come out by crossing the phosphor coating layer. So flux amount of wt 3% may be a better choice for synthesizing this phosphor.

Previous structural study [19] showed that rare earth molybdate with general formula $RE_2(MoO_4)_3$, where $RE^{3+} = Pr–Dy$, having similar structures. $Eu_2(MoO_4)_3$ can form a monoclinic α phase structure under 881 °C. The radius of $Eu^{3+}(0.95\,nm)$ is very close to that of $Gd^{3+}(0.94\,nm)$, therefore, $Eu_2(MoO_4)_3$ and $Gd_2(MoO_4)_3$ can form a solid solution. This point has been verified by XRD. In order to find a best doping concentration of Eu^{3+} in this novel phosphor, several samples with various Eu^{3+} concentrations were prepared. Integrated emission intensity under 395 nm excitation for each sample was calculated. The relationship between the emission intensity and the concentration of activator ion Eu^{3+} is shown in
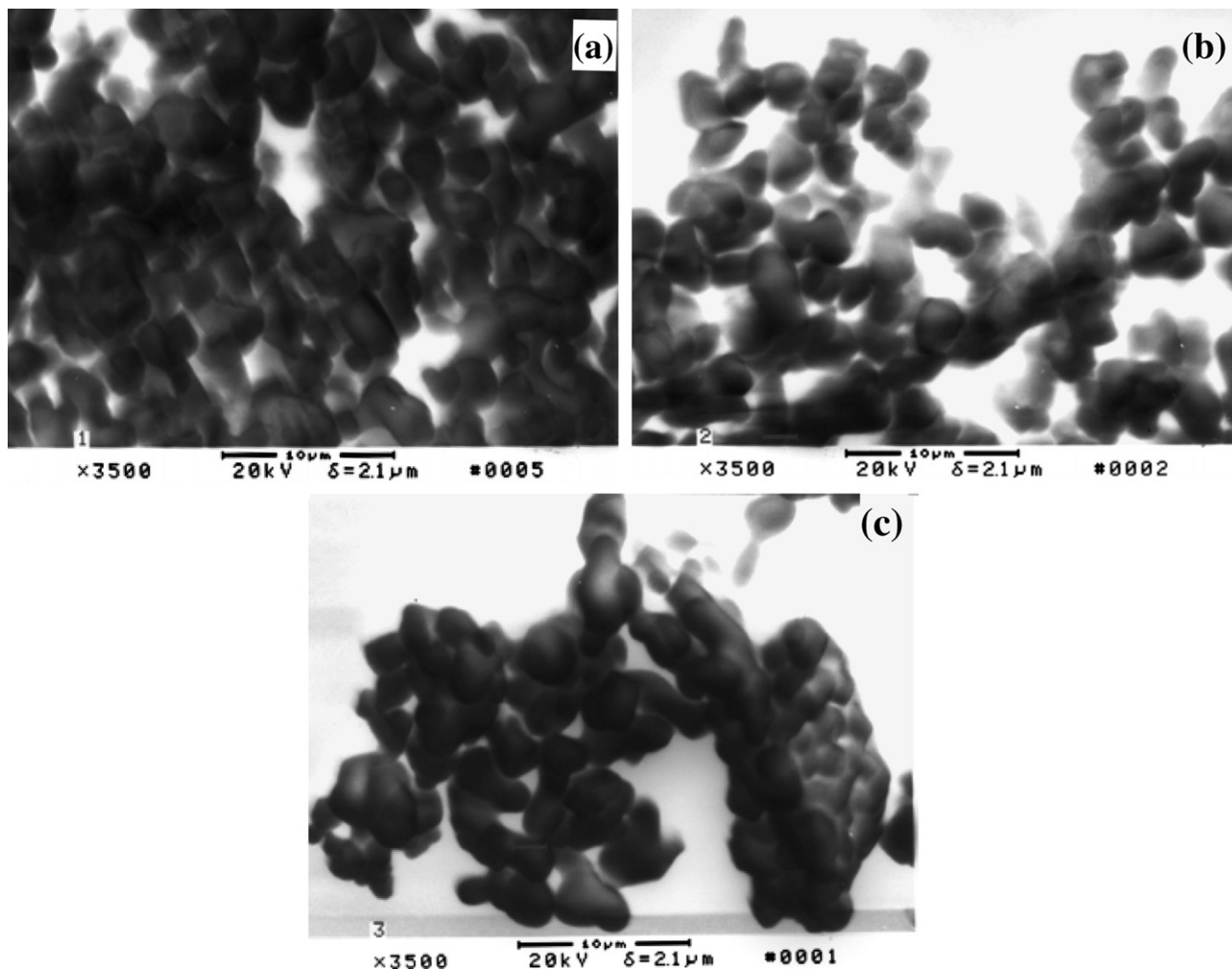

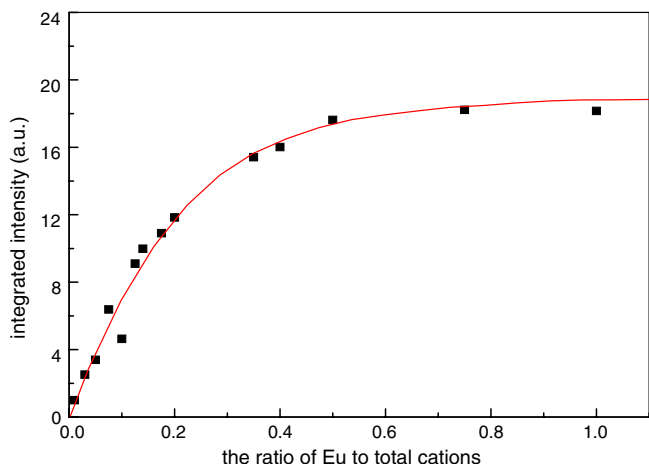Fig. 5. SEM images of $Gd_{1.96}(MoO_4)_3:Eu^{3+}_{0.04}$ phosphors particles prepared with (a) no flux, (b) 3% NH_4F, (c) 7% NH_4F.

Fig. 6. The relationship between Eu^{3+} ion concentration and emission intensity of the $Gd_2(MoO_4)_3:Eu^{3+}$ phosphor under 395 nm excitation.

Fig. 6. This result indicates a higher quenching concentration around 35 mol.% than 24 mol.% in $CaMoO_4$:Eu reported by Yunsheng Hu et.al. [10]. The difference in quenching concentration of two phosphors might be due to the difference in their crystal structure. α-$Gd_2(MoO_4)_3$ phases adopt scheelite (ABO_4)-related structures in which the lanthanide is co-ordinated to eight oxygens. The composition $Gd_2(MoO_4)_3$ may be written as $Gd_{2/3}(cat)_{1/3}MoO_4$ where cat denotes an Gd site vacancy in the scheelite structure. The Gd site vacancy are placed at every third of (220) planes of the scheelite structure in the α-$Gd_2(MoO_4)_3$ [20]. Compared with the scheelite structure $CaMoO_4$, Gd is diluted in α-$Gd_2(MoO_4)_3$, and thus the increase of the distance between rare earth ions results in $CaMoO_4$ induces a high quenching concentration.

4. Conclusions

In conclusion, α-$Gd_2(MoO_4)_3:Eu^{3+}$ has been successfully prepared by solid state reaction. This phosphor can be efficiently excited by UV (395 nm) and visible blue (465 nm) light nicely matching the output wavelengths of the UV and blue LED chips and emits the red light (613 nm). Appropriate amount of flux can improve crystallization and enhance the luminescence intensity. The quenching concentration in α-$Gd_2(MoO_4)_3:Eu^{3+}$ is much higher than in $CaMoO_4:Eu^{3+}$ due to the large distance between rare earth in the latter case.

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