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Preparation and Photoluminescence Properties of Red-Emitting $Gd_2(MoO_4)_3$:Eu Phosphors for a Three-Band White LED

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White light-emitting diodes (white LEDs) are of great interest, particularly for their promising applications to solid state lightning. White LEDs have advantages over conventional electrical lightning including high efficiency, long lifetime and low energy consumption.[1-4] Commercial white LEDs were fabricated by a InGaN blue-emitting LED chip with $Y_3Al_5O_{12}$:Ce phosphors. In this device, white light was generated by additive color mixing of the blue light emitted by InGaN LEDs and the yellow light emitted by $Y_3Al_5O_{12}$:Ce phosphors.[5-7] However, these two-band white LEDs suffer from limited color rendering, and are unable to produce all nature-equivalent colors, particularly in the red region. To improve the color rendering index of white LEDs, three-band white LED should be developed using a blue chip as a pump source with a blend of green- and red-emitting phosphors. Many green- or red-emitting phosphors, such as $SrGa_2S_4:Eu^{2+}$ (green), β-SiAlON:Eu^{2+} (green), CaS:Eu^{2+} (red), $Ba_2Si_5N_8:Eu^{2+}$ (red), and $NaY(W,Mo)_2O_8:Eu^{3+}$ (red), have been developed for three-band white LEDs.[8-16] Red-emitting $R_2(MoO_4)_3:Eu^{3+}$ (R = Y, La, Gd) phosphors have been synthesized for three-band white LEDs.[17-20] Most of these phosphors were prepared using a solid state reaction. Therefore, new green- or red-emitting phosphors with good luminescent properties are needed for the next-generation white LEDs. This study reports simple methods for producing red-emitting $Gd_2(MoO_4)_3$:Eu nanophosphors using hydrothermal reactions of emulsions containing $Gd(NO_3)_3$, $Eu(NO_3)_3$, and $(NH_4)_2MoO_4$. Micron-sized $Gd_2(MoO_4)_3$:Eu phosphors were also prepared by calcining the $Gd_2(MoO_4)_3$:Eu nanophosphors.

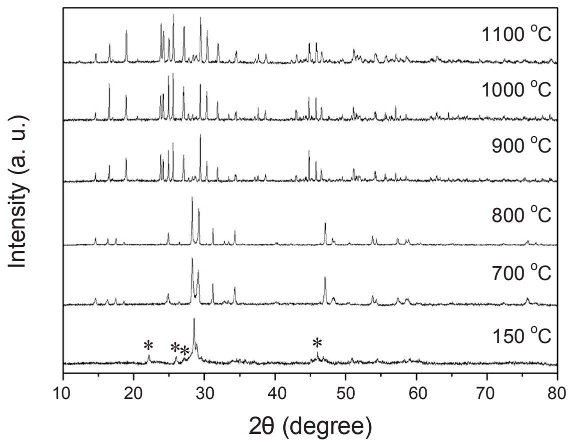

Figure 1. XRD patterns of the $Gd_2(MoO_4)_3$:Eu phosphors prepared by a hydrothermal reaction of the emulsions at 150 °C and post-calcination at temperatures ranging from 700 °C to 1100 °C.

Figure 1 shows XRD patterns of $Gd_2(MoO_4)_3$:Eu phosphors obtained using the hydrothermal method and post-calcination methods at different temperatures. In the case of temperatures ≤ 800 °C, most of the peaks corresponded to monoclinic $Gd_2(MoO_4)_3$(JCPDS 26-0655, a = 0.7575 nm, b = 1.1436 nm, c = 1.1424 nm). When a hydrothermal method was used at 150 °C, the materials began to crystallize with low intensity XRD peaks along with some unidentified peaks marked by the asterisks. In the case of reaction temperatures ≥ 900 °C, all the peaks were assigned to orthorhombic $Gd_2(MoO_4)_3$(JCPDS 20-0408, a = 1.0388 nm, b = 1.0416 nm, c = 1.0697 nm).

Figures 2(a) and 2(b) show the photoluminescence excitation and emission spectra of the $Gd_2(MoO_4)_3$:Eu nanophosphors obtained by the hydrothermal method, respectively. The excitation spectrum was obtained, where the emission wavelength (λ_{em}) was fixed at 613 nm. A broad charge transfer (O → Mo) band at approximately 300 nm and sharp peaks at 350 - 550 nm due to intra-configuration 4f-4f transitions Eu^{3+} were observed.[21] The emission spectrum was obtained at a fixed excitation wavelength (λ_{ex}) of 465 nm, which was the wavelength of a blue-emitting InGaN chip. The emission spectrum was composed of a few sharp peaks ranging from 550 to 750 nm, which were associated with the $^5D_J \rightarrow {}^7F_J$ transitions in Eu^{3+}. The strongest red emission peak at 613 nm was assigned to the $^5D_0 \rightarrow {}^7F_2$ transition. A commercial InGaN LED chip emits blue light at 465 nm. The requirement for a red-emitting phosphor for a three-band white LED is that the phosphor must have strong excitation near 465 nm, and strong emission at the red region.

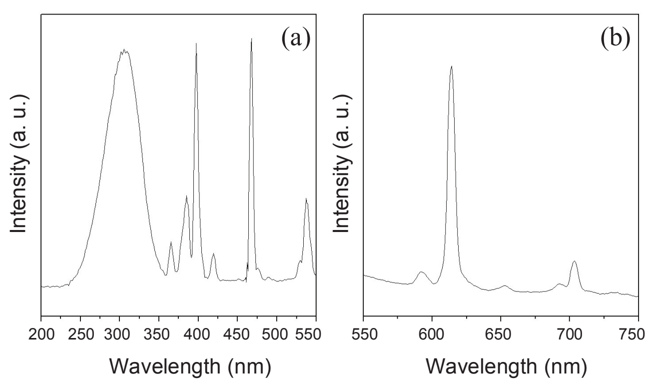

Figure 2. Photoluminescence (a) excitation (λ_{em} = 613 nm) and (b) emission (λ_{ex} = 465 nm) spectra of $Gd_2(MoO_4)_3$:Eu nanophosphors prepared by a hydrothermal reaction of the emulsions at 150 °C.

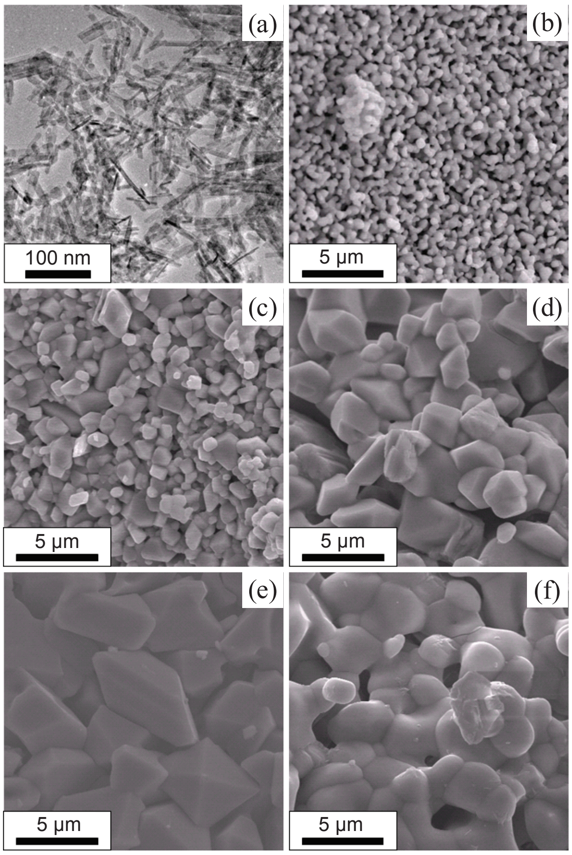

Figure 3. (a) TEM image of $Gd_2(MoO_4)_3$:Eu nanophosphor prepared by a hydrothermal reaction of the emulsions at 150 °C, and SEM images of the $Gd_2(MoO_4)_3$:Eu phosphors prepared by calcining the $Gd_2(MoO_4)_3$:Eu nanophosphor at various temperatures; (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, and (f) 1100 °C.

The $Gd_2(MoO_4)_3$:Eu phosphor showed strong excitation and emission at 466 nm and 613 nm, respectively. This suggests that $Gd_2(MoO_4)_3$:Eu is a good candidate for a red-emitting phosphor in a three-band white LED.

Figure 3(a) shows a TEM image of the $Gd_2(MoO_4)_3$:Eu nanophosphor obtained using the hydrothermal method. Rod-like $Gd_2(MoO_4)_3$:Eu crystals with average lengths and widths of 100 nm and 10 nm, respectively, were obtained. SEM showed that the particles aggregated to form larger sized particles up to 5 μm in size as the calcination temperature was increased, as shown in Figures 3(b) to 3(f). Figure 4 shows the photoluminescence spectra of the $Gd_2(MoO_4)_3$:Eu phosphors prepared by hydrothermal synthesis followed by calcination at temperatures between 700 °C and 1100 °C. The emission intensity increased gradually with increasing calcination temperature up to 1000 °C, then decreased sharply at 1100 °C, as shown in Figure 4.

To evaluate for the feasibility of a $Gd_2(MoO_4)_3$:Eu phosphor as a red-emitter for three-band white LED, a three-band LED fabricated by coating $Gd_2(MoO_4)_3$:Eu and $SrGa_2S_4$:Eu phosphors on a blue LED with a $Gd_2(MoO_4)_3$:Eu to $SrGa_2S_4$:Eu weight ratio of 7.0. $SrGa_2S_4$:Eu was used for the green-emitting phosphor pumped with InGaN blue LED light. $Gd_2(MoO_4)_3$:Eu phosphor prepared by hydrothermal followed by calcinated at 1000 °C was used for the fabrication of a three-band white LED.

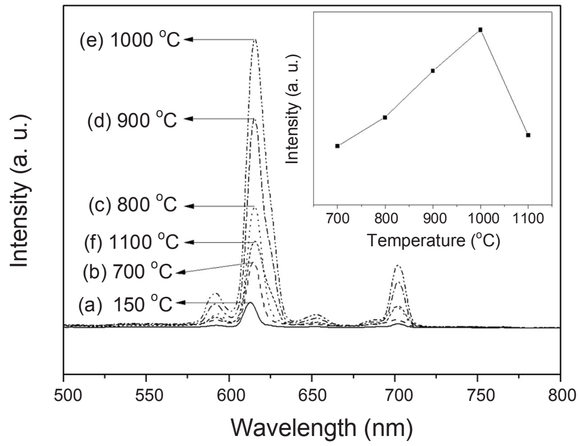

Figure 4. Photoluminescence emission spectra of the $Gd_2(MoO_4)_3$:Eu phosphors prepared by (a) hydrothermal reaction of the emulsions at 150 °C followed by calcination at various temperatures: (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, and (f) 1100 °C. The inset shows the relative emission intensity as a function of the calcination temperature.

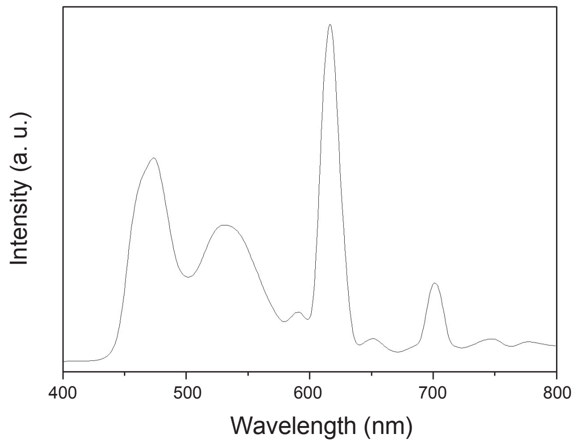

Figure 5. Photoluminescence spectra of a three-band white LED fabricated in this study.

Figure 5 shows the photoluminescence spectrum of a three-band LED fabricated in this study. The color range of light emitted by a three-band LED fabricated by coating $Gd_2(MoO_4)_3$:Eu and $SrGa_2S_4$:Eu phosphors on a blue-emitting InGaN LED chip is the region inside the triangle formed by connecting the chromaticity coordinate positions of the blue LED, $SrGa_2S_4$:Eu, and $Gd_2(MoO_4)_3$:Eu phosphors in the Commission International de l'Eclairage (CIE) diagram. The area of the region inside the triangle formed by connecting the National Television Standard Committee (NTSC) blue, green, and red coordinates was used as a reference for the color purity of a display panel. The chromaticity coordinates of the NTSC blue, NTSC green, and NTSC red were (0.14, 0.08), (0.21, 0.71), and (0.67, 0.33), respectively. The chromaticity coordinates of the blue LED, $SrGa_2S_4$:Eu, and $Gd_2(MoO_4)_3$:Eu phosphors were (0.13, 0.08), (0.28, 0.68), and (0.61, 0.33), respectively. The area of the triangle formed by connecting the positions of the blue LED, $SrGa_2S_4$:Eu, and $Gd_2(MoO_4)_3$:Eu phosphors was 79.2% of that of the NTSC triangle, which indicates that the color rendering of the

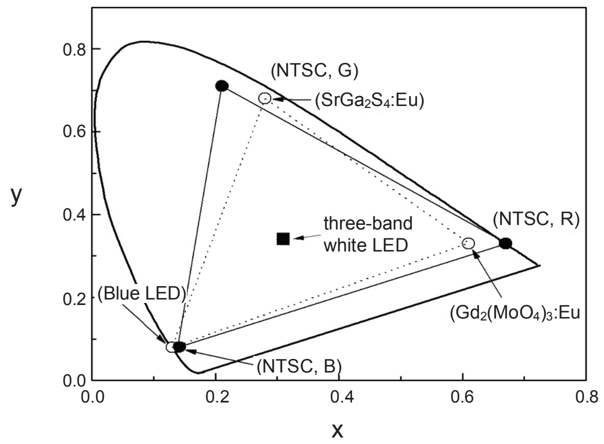

Figure 6. CIE diagram and chromaticity coordinates of NTSC blue, NTSC green, NTSC red, the blue InGaN LED chip, $SrGa_2S_4$:Eu (green phosphor), and $Gd_2(MoO_4)_3$:Eu (red phosphor). ■ represents the chromaticity coordinates of the three-band white LED fabricated in this study.

three-band white LED fabricated in this study is superior to that typically required for display panels. Figure 6 shows the CIE chromaticity coordinates of NTSC blue, NTSC green, NTSC red, the blue LED, $SrGa_2S_4$:Eu, and $Gd_2(MoO_4)_3$:Eu phosphors. The CIE chromaticity coordinate (x = 0.31, y = 0.34) with the color temperature of 6330 K for the three-band LED fabricated in this study was also shown in Figure 6.

In conclusion, $Gd_2(MoO_4)_3$:Eu nanophosphors were prepared using hydrothermal reaction emulsions of $Gd(NO_3)_3$, $Eu(NO_3)_3$, and $(NH_4)_2MoO_4$. The hydrothermal emulsion reaction, followed by calcination at 1000 °C, might be an effective synthetic strategy for preparing bright $Gd_2(MoO_4)_3$:Eu phosphors. The $Gd_2(MoO_4)_3$:Eu phosphor is an excellent candidate as a red-emitter for three-band white LEDs. The photoluminescence properties of the three-band white LED fabricated by coating a blue-emitting InGaN LED chip with $SrGa_2S_4$:Eu and $Gd_2(MoO_4)_3$:Eu phosphors was investigated. The color rendering of this white LED is excellent as a display light source.

Experimental Section

$Gd(NO_3)_3 \cdot 6H_2O$ (Aldrich), $Eu(NO_3)_3 \cdot 6H_2O$ (Aldrich), $(NH_4)_2MoO_4$ (Aldrich), cyclohexane (Aldrich), *n*-butanol (Aldrich) and cetyltrimethylammonium bromide (CTAB, TCI) were used as received. The $Gd_2(MoO_4)_3$:Eu nanophosphors were prepared by a hydrothermal reaction of a mixture of emulsions containing $Gd(NO_3)_3$ and $Eu(NO_3)_3$ with an emulsion containing $(NH_4)_2MoO_4$. The Eu^{3+} concentration was fixed to 12 mol % for synthesis. The CTAB/water/cyclohexane/*n*-butanol system was used to prepare the emulsions. Typically, 2 mL of an aqueous 0.44 M $Gd(NO_3)_3 \cdot 6H_2O$ and 0.06 M $Eu(NO_3)_3 \cdot 6H_2O$ solution were added to a solution containing 8 g CTAB, 40 mL cyclohexane, and 8 mL *n*-butanol with vigorous stirring. The $(NH_4)_2MoO_4$ emulsion was prepared by adding 2 mL of an aqueous 0.75 M $(NH_4)_2MoO_4$ solution to a solution containing 8 g CTAB, 40 mL cyclohexane, and 8 mL *n*-butanol with vigorous stirring. The two optically transparent solutions were mixed, a 60 mL aliquot of this solution was transferred to a 100 mL Teflon-lined autoclave, and the aliquot was heated to 150 °C for 12 h. The precipitates were centrifuged, washed several times with water and ethanol, and dried at 60 °C for 12 h. Micron-sized $Gd_2(MoO_4)_3$:Eu phosphors were also prepared by calcination of the $Gd_2(MoO_4)_3$:Eu nanophosphor at temperatures ranging from 700 to 1100 °C. The structures of the $Gd_2(MoO_4)_3$:Eu phosphors were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using Cu Kα radiation. The morphology of the products was observed by scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL JEM-3010). The photoluminescence excitation and emission spectra were measured using a spectrum analyzer (DARSA, PSI). A blue InGaN chip (NSPBS500S, Nichia, λ_{max} = 465 nm) was used to fabricate the three-band white LED. The three-band white LED was prepared by coating a phosphor film onto the outer sphere of a blue InGaN LED. The amount of phosphors was controlled by adjusting the thickness of the coating layer. $Gd_2(MoO_4)_3$:Eu and $SrGa_2S_4$:Eu phosphors were mixed with PAS ink (800 series, Jujo) and applied to a poly(ethylene terephthalate) (PET) film. The $SrGa_2S_4$:Eu phosphor was synthesized using a previously reported procedure.[8]

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