Preparation and Photoluminescence Properties of Transparent Red-Emitting Suspension of BaMoO$_4$:Eu$^{3+}$,Na$^+$ Nanophosphor for a Three-Band White LED

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The white LED as an energy-efficient form of electrical lighting that is used widely for general white lighting sources.$^{1,2}$ The development of the blue InGaN LED chip has made it possible to produce a conventional two-band white LED by coating a yellow-emitting Y$_2$AlO$_2$:Ce phosphor onto a blue LED chip. The combination of blue emission from a blue LED chip and yellow emission form a Y$_2$AlO$_2$:Ce phosphor is perceived as white light by the human eye. Nevertheless, these two-band white LEDs are unable to produce all the nature-equivalent colors, particularly in the red region.

To improve the color rendering index of a white LED, the three-band white LED has been fabricated by coating a mixture of a green- and red-emitting phosphors onto a blue LED chip.$^{3-6}$ Ca$_3$SiO$_5$:Eu$^{2+}$, Ba$_2$Si$_2$N$_2$:Eu$^{3+}$, NaY(W,Mo)O$_4$:Eu$^{3+}$, CaMoO$_4$:Eu$^{3+}$, and Y$_2$(MoO$_4$)$_2$:Eu$^{3+}$ have been used red-emitting phosphors for three-band white LED because these phosphors show strong absorptions at 465 nm and strong emissions in the red region.$^{11-16}$ Most of these phosphors can be synthesized by simple solid state reactions, and a few micron-sized phosphors have been obtained. When micron-sized inorganic phosphors are coated on a blue LED chip, a large fraction of the blue light is lost by back scattering due to the micron-sized phosphors. Inorganic nanophosphors do not show any scattering effect in the visible region. Therefore, inorganic nanophosphors need to be developed for a highly efficient white LED by reducing back scattering. On the other hand, nanophosphors agglomerate easily in solvents, and little is known regarding the preparation of a suspension of inorganic nanophosphors. This paper reports the first simple method for preparing a transparent suspension of BaMoO$_4$:Eu$^{3+}$,Na$^+$ nanophosphors and the feasibility of this BaMoO$_4$:Eu$^{3+}$,Na$^+$ suspension for a three-band white LED.

Figure 1 shows the powder X-ray diffraction (XRD) patterns of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor prepared by a hydrothermal process at 80 °C. The XRD patterns of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor matched the tetragonal BaMoO$_4$ (JCPDS 29-0193, $a = 0.5580$ nm, $c = 1.2821$ nm). Since Eu$^{3+}$ and Na$^+$ ions substitute for Ba$^{2+}$ ions in the host BaMoO$_4$ structure, it was confirmed that the host BaMoO$_4$ was synthesized without impurities according to the XRD patterns. Figure 2(a) and 2(b) shows the excitation and emission spectra of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor, respectively. BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor shows strong absorption in the ultraviolet region at approximately 300 nm, which is due to the O$^-$ → Mo charge transfer transition in BaMoO$_4$. The excitation spectrum also consisted of a series of absorption lines between 350 and 500 nm, which corresponds to the absorption transitions of Eu$^{3+}$. The strongest absorption at 467 nm is similar to the emission wavelength of the blue LED chip of 465 nm. The emission peaks at 592, 614, 652, and 702 nm correspond to the characteristic emission from the $^5$D$_0$ → $^5$F$_j$ ($j = 1, 2, 3, 4$) transitions of Eu$^{3+}$. Because the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor shows strong absorption at 465 nm and strong emission at 614 nm with chromaticity coordinates of $x = 0.62$ and $y = 0.34$, which is close to the National Television Standard Committee (NTSC) red coordinates of $x = 0.67$ and $y = 0.33$. The chromaticity coordinates of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor were $x = 0.62$ and $y = 0.34$, which is suitable as the red-emitting phosphor for a three-band white LED pumped by the blue LED chip.

The synthetic temperature is one of the most important experimental variables for preparing a bright emitting inorganic phosphor. To determine the adequate synthetic temperature, the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphors were prepared by a hydrothermal reaction at various temperatures. Figure 3 shows the emission spectra of BaMoO$_4$:Eu$^{3+}$,Na$^+$ prepared at various temperatures. The emission of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor showed strong absorption in the ultraviolet region at approximately 300 nm, which is due to the O$^-$ → Mo charge transfer transition in BaMoO$_4$. The excitation spectrum also consisted of a series of absorption lines between 350 and 500 nm, which corresponds to the absorption transitions of Eu$^{3+}$. The strongest absorption at 467 nm is similar to the emission wavelength of the blue LED chip of 465 nm. The emission peaks at 592, 614, 652, and 702 nm correspond to the characteristic emission from the $^5$D$_0$ → $^5$F$_j$ ($j = 1, 2, 3, 4$) transitions of Eu$^{3+}$. Because the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor shows strong absorption at 465 nm and strong emission at 614 nm with chromaticity coordinates of $x = 0.62$ and $y = 0.34$, BaMoO$_4$:Eu$^{3+}$,Na$^+$ is suitable as the red-emitting phosphor for a three-band white LED pumped by the blue LED chip.

![Figure 1](image1.png)

Figure 1. XRD patterns of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor prepared by a hydrothermal reaction at 80 °C.
phosphors prepared at temperatures ranging from 60 °C to 140 °C. The excitation wavelength was fixed to 465 nm, which is the emission wavelength of the blue LED. The emission intensity at 614 nm increased with increasing temperature to 80 °C, and then decreased gradually with increasing temperature to 140 °C. Therefore, the brightest emission was obtained for BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphors prepared at 80 °C.

The photoluminescence intensity depends strongly on the concentration of activators. In general, the intensity of phosphors increases with increasing amount of activator at lower concentrations and decreases at higher concentrations due to the interaction between activators, which is known as a concentration quenching effect. To examine the emission intensity dependence of the activator concentration, several BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphors were prepared using various Eu$^{3+}$ and Na$^+$ concentrations with following formula, Ba$_{1-2x}$MoO$_4$:xEu$^{3+}$,xNa$^+$. Figure 4 shows the emission spectra of the Ba$_{1-2x}$MoO$_4$:xEu$^{3+}$,xNa$^+$ phosphors with x = 0.05, 0.10, 0.15, 0.20, and 0.25. The emission intensity of the Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ phosphor increased with increasing Eu$^{3+}$ concentration up to 20 mol % but decreased with further increases in the Eu$^{3+}$ concentration. Therefore, the brightest red emission was obtained using Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ prepared by a hydrothermal reaction at 80 °C.

Figure 5(a) shows a transmission electron microscopy (TEM) image of the Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ phosphor. The fringe pattern of an individual Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ phosphor in the high-resolution TEM (HRTEM) image showed a spacing of 0.33 nm, which corresponds to the (112) plane of tetragonal BaMoO$_4$, as shown in Figure 5(b). The inset in Figure 5(b) shows the fast Fourier transform (FFT) patterns of the Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ phosphor corresponding to the lattice fringe.

A highly transparent BaMoO$_4$:Eu$^{3+}$,Na$^+$ suspension was prepared by dispersing the Ba$_{0.60}$MoO$_4$:0.20Eu$^{3+}$,0.20Na$^+$ phosphor in toluene, as shown in Figure 6(a). This suspension was quite stable without sedimentation. This suspension was stable without agglomeration due to oleic acid and oleylamine, which were used as capping agents. Because the BaMoO$_4$:Eu$^{3+}$,Na$^+$ nanophosphors are capped by oleic acid
Experimental Section

Ba(NO₃)₂ (Aldrich), (NH₄)₂MoO₄·4H₂O (Aldrich), Eu(NO₃)₃·6H₂O (Aldrich), NaNO₃ (Aldrich), sodium oleate (TCI), oleic acid (Aldrich) and oleylamine (TCI) were used as received. In a typical synthesis of Ba₂MoO₄·0.2Eu³⁺, 0.2Na⁺ phosphor, 0.12 mol of Ba(NO₃)₂, 0.04 mol of NaNO₃ and 0.04 mol of Eu(NO₃)₃·6H₂O were dissolved in 10 mL of water. 1.218 g of sodium oleate, 5 mL of oleic acid, 5 mL of oleylamine and 40 mL of hexane were then added to the above solution with vigorous stirring for 1 h. 0.0286 mol of (NH₄)₂MoO₄·4H₂O was dissolved in 10 mL of water. After mixing the two optically transparent solutions, the mixed solution was transferred to a 100 mL Teflon-lined autoclave. For the preparation of BaMoO₄·Eu³⁺,Na⁺ phosphor, a hydrothermal reaction was used at temperatures ranging from 60 °C to 140 °C for 16 h. After finishing the hydrothermal reaction, the BaMoO₄·Eu³⁺,Na⁺ solution in the hexane layer was separated from the bottom solution of an aqueous layer using a separating funnel. This solution in a hexane was centrifuged at 4000 rpm for 15 min, and a clear top solution was obtained by separating the bottom nontransient solution. The BaMoO₄·Eu³⁺,Na⁺ phosphor was obtained by
adding 40 mL of ethanol to the clear solution by precipitation. The precipitate was centrifuged, washed several times with water and ethanol, and dried at 60 °C for 12 h. To prepare the BaMoO$_4$:Eu$^{3+}$,Na$^+$ suspension, 0.1 g of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor was dispersed in 4 mL of toluene in a 10 mL vial for 10 min.

The structures of the as-prepared BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor 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 transmission electron microscopy (TEM, JEOL JEM-3010). The excitation and emission spectra of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ phosphor was measured using a photoluminescence spectrometer (DARSA, PSI). A blue LED (Nichia, NSPB500S, $\lambda_{\text{max}}$ = 465 nm) was used to excite the BaMoO$_4$:Eu$^{3+}$,Na$^+$ suspension. A hand-held 12 W UV lamp (Uvitec, $\lambda_{\text{max}}$ = 254 nm) was used for UV excitation of the BaMoO$_4$:Eu$^{3+}$,Na$^+$ suspension.

References