

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

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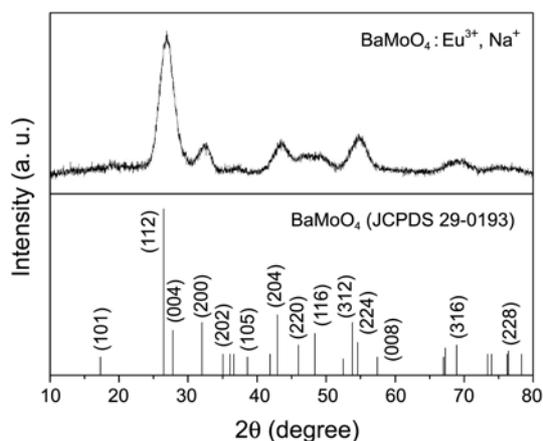
The white LED as an energy-efficient form of electrical lighting that is used widely for general white lighting sources.<sup>1,2</sup> The development of the blue InGaN LED chip has made it possible to produce a conventional two-band white LED by coating a yellow-emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  phosphor onto a blue LED chip.<sup>3-6</sup> The combination of blue emission from a blue LED chip and yellow emission from a  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  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.<sup>7-10</sup>  $\text{CaS}:\text{Eu}^{2+}$ ,  $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ,  $\text{NaY}(\text{W},\text{Mo})_2\text{O}_8:\text{Eu}^{3+}$ ,  $\text{CaMoO}_4:\text{Eu}^{3+}$ , and  $\text{Y}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$  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.<sup>11-16</sup> 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.<sup>17-20</sup> This paper reports the first simple method for preparing a transparent suspension of  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  nanophosphors and the feasibility of this  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  suspension for a three-band white LED.

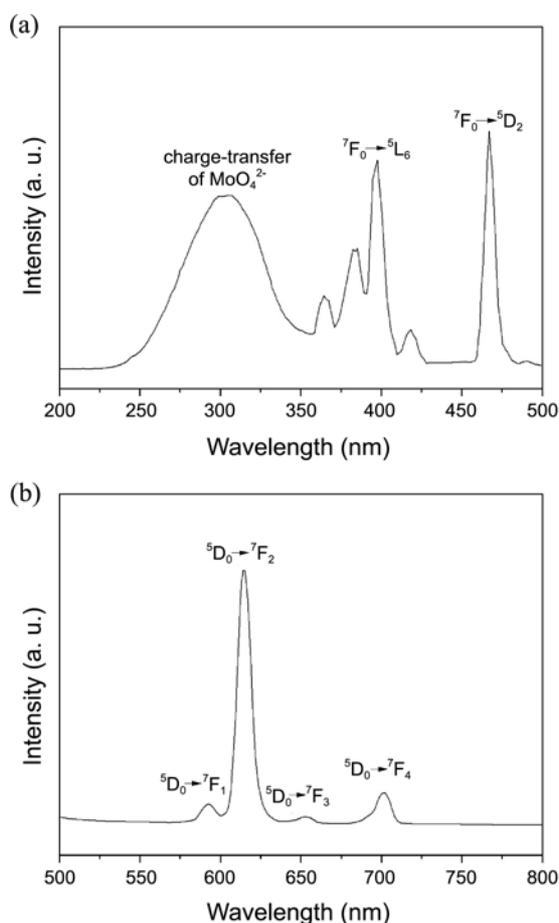
Figure 1 shows the powder X-ray diffraction (XRD) patterns of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor prepared by a hydrothermal process at 80 °C. The XRD patterns of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor matched the tetragonal  $\text{BaMoO}_4$  (JCPDS 29-0193,  $a = 0.5580$  nm,  $c = 1.2821$  nm). Since  $\text{Eu}^{3+}$  and  $\text{Na}^+$  ions substitute for  $\text{Ba}^{2+}$  ions in the host  $\text{BaMoO}_4$  structure, it was confirmed that the host  $\text{BaMoO}_4$  was synthesized without impurities according to the XRD patterns. Figure 2(a) and 2(b) shows the excitation and

emission spectra of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor, respectively.  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor shows strong absorption in the ultraviolet region at approximately 300 nm, which is due to the  $\text{O} \rightarrow \text{Mo}$  charge transfer transition in  $\text{BaMoO}_4$ .<sup>21</sup> The excitation spectrum also consisted of a series of absorption lines between 350 and 500 nm, which corresponds to the absorption transitions of  $\text{Eu}^{3+}$ .<sup>22</sup> 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  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $J = 1, 2, 3, 4$ ) transitions of  $\text{Eu}^{3+}$ .<sup>23</sup> The chromaticity coordinates of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor were  $x = 0.62$  and  $y = 0.34$ , which is close to the National Television Standard Committee (NTSC) red coordinates of  $x = 0.67$  and  $y = 0.33$ .<sup>24</sup> Because the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor shows strong absorption at 465 nm and strong emission at 614 nm with chromaticity coordinates of  $x = 0.62$  and  $y = 0.34$ ,  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  is suitable as the red-emitting phosphor for a three-band white LED pumped by the blue LED chip.

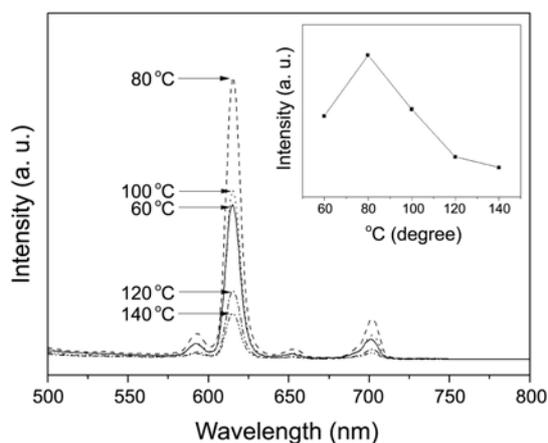
The synthetic temperature is one of the most important experimental variables for preparing a bright emitting inorganic phosphor. To determine the adequate synthetic temperature, the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphors were prepared by a hydrothermal reaction at various temperatures. Figure 3 shows the emission spectra of  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$



**Figure 1.** XRD patterns of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor prepared by a hydrothermal reaction at 80 °C.

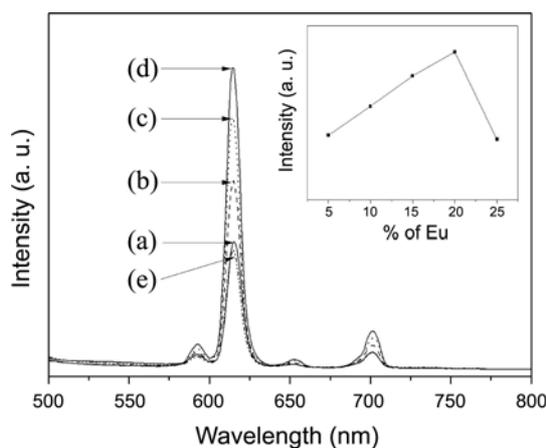


**Figure 2.** (a) Excitation ( $\lambda_{em} = 614$  nm) and (b) emission ( $\lambda_{ex} = 465$  nm) spectra of the  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  phosphor.



**Figure 3.** Emission spectra ( $\lambda_{ex} = 465$  nm) of the  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  phosphors prepared by a hydrothermal reaction at temperatures between  $60$  °C and  $140$  °C. The inset shows the relative intensity at  $614$  nm as a function of the hydrothermal temperature.

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



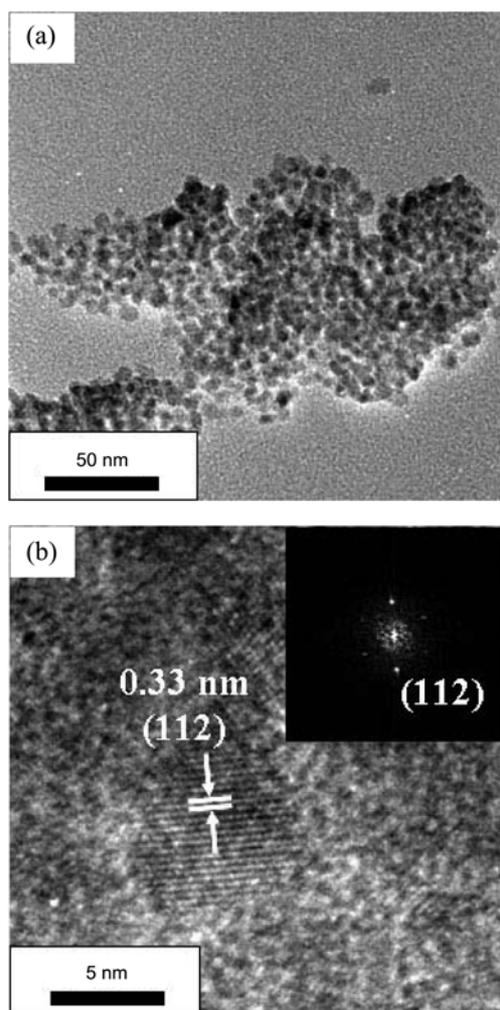
**Figure 4.** Emission spectra ( $\lambda_{ex} = 465$  nm) of the  $\text{Ba}_{(1-2x)}\text{MoO}_4:x\text{Eu}^{3+}, x\text{Na}^+$  phosphors with different  $x$  values; (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20, and (e) 0.25. The inset shows the relative intensity of the  $\text{Ba}_{(1-2x)}\text{MoO}_4:x\text{Eu}^{3+}, x\text{Na}^+$  phosphors at  $614$  nm as a function of  $x$ .

emission was obtained for  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  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  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  phosphors were prepared using various  $\text{Eu}^{3+}$  and  $\text{Na}^+$  concentrations with following formula,  $\text{Ba}_{(1-2x)}\text{MoO}_4:x\text{Eu}^{3+}, x\text{Na}^+$ . Figure 4 shows the emission spectra of the  $\text{Ba}_{(1-2x)}\text{MoO}_4:x\text{Eu}^{3+}, x\text{Na}^+$  phosphors with  $x = 0.05, 0.10, 0.15, 0.20,$  and  $0.25$ . The emission intensity of the  $\text{Ba}_{(1-2x)}\text{MoO}_4:x\text{Eu}^{3+}, x\text{Na}^+$  phosphor increased with increasing  $\text{Eu}^{3+}$  concentration up to  $20$  mol % but decreased with further increases in the  $\text{Eu}^{3+}$  concentration. Therefore, the brightest red emission was obtained using  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+}, 0.20\text{Na}^+$  prepared by a hydrothermal reaction at  $80$  °C.

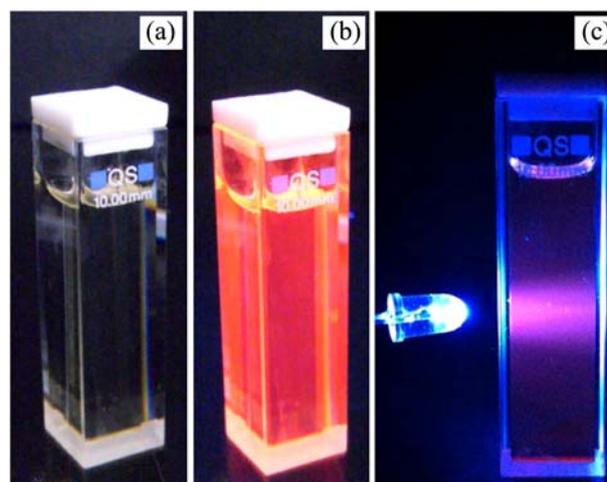
Figure 5(a) shows a transmission electron microscopy (TEM) image of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+}, 0.20\text{Na}^+$  phosphor. The mean diameter is approximately  $7$  nm. These nanophosphors are suitable for reducing back scattering. The fringe pattern of an individual  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+}, 0.20\text{Na}^+$  phosphor in the high-resolution TEM (HRTEM) image showed a spacing of  $0.33$  nm, which corresponds to the (112) plane of tetragonal  $\text{BaMoO}_4$ , as shown in Figure 5(b). The inset in Figure 5(b) shows the fast Fourier transform (FFT) patterns of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+}, 0.20\text{Na}^+$  phosphor corresponding to the lattice fringe.

A highly transparent  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  suspension was prepared by dispersing the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+}, 0.20\text{Na}^+$  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  $\text{BaMoO}_4:\text{Eu}^{3+}, \text{Na}^+$  nanophosphors are capped by oleic acid



**Figure 5.** (a) TEM and (b) HRTEM images of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  phosphor. The inset in (b) shows FFT patterns of the individual  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  phosphors.

and oleylamine, the outer parts of the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  nanophosphors are hydrophobic, and the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  nanophosphors are quite stable in non-polar solvents, such as toluene. When the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  suspension was irradiated with a 254 nm hand-held UV lamp, intense red emission was observed, as shown in Figure 6(b). Figure 6(c) shows a photograph of the pink-emitting of  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  suspension that was excited by the blue LED. The pink-emitted color of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  suspension pumped by the blue LED was different from the red-emitting of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  suspension excited by the UV lamp. This pink-emitting color of the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  suspension pumped by the blue LED was generated by additive color mixing of the red-emitted by  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  phosphors and the blue light emitted by the blue LED. Therefore, the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  suspension can be used as a red-emitting material for a three-band white LED. Generally, a LED lens is formed by curing epoxy resins at 130 °C for 8 h. Future studies will develop a curing process using epoxy resins including suspensions of red- and green-emitting nano-



**Figure 6.** Transparent suspensions of  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  phosphors in toluene (a) in daylight and (b) under the irradiation of a 254 nm hand-held UV lamp. (c) Photograph of the pink-emission from the  $\text{Ba}_{0.60}\text{MoO}_4:0.20\text{Eu}^{3+},0.20\text{Na}^+$  suspension excited by the blue LED.

phosphors for the fabrication of a three-band white LED.

In conclusion,  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphors, 7 nm in diameter, were prepared from a hydrothermal reaction of  $\text{Ba}(\text{NO}_3)_2$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ,  $\text{NaNO}_3$ , and  $\text{Eu}(\text{NO}_3)_3$ . A highly transparent suspension was obtained by dispersing the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor in toluene without agglomeration. A transparent suspension of  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  nanophosphors was easily excited by the blue LED and emitted strong red luminescence. A transparent suspension of  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  is a good candidate for red-emitting phosphors for bright emitting three-band white LEDs pumped by a blue LED chip with the least back scattering.

## Experimental Section

$\text{Ba}(\text{NO}_3)_2$  (Aldrich),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Aldrich),  $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{NaNO}_3$  (Aldrich), sodium oleate (TCI), oleic acid (Aldrich) and oleylamine (TCI) were used as received. In a typical synthesis of  $\text{Ba}_{0.6}\text{MoO}_4:0.2\text{Eu}^{3+},0.2\text{Na}^+$  phosphor, 0.12 mol of  $\text{Ba}(\text{NO}_3)_2$ , 0.04 mol of  $\text{NaNO}_3$  and 0.04 mol of  $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  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  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  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  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor, a hydrothermal reaction was used at temperatures ranging from 60 °C to 140 °C for 16 h. After finishing the hydrothermal reaction, the  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  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 nontransparent solution. The  $\text{BaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  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<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> suspension, 0.1 g of the BaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> phosphor was dispersed in 4 mL of toluene in a 10 mL vial for 10 min.

The structures of the as-prepared BaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> phosphor were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using Cu K $\alpha$  radiation. The morphology of the products was observed by transmission electron microscopy (TEM, JEOL JEM-3010). The excitation and emission spectra of the BaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> 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<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> suspension. A hand-held 12 W UV lamp (Uvitec,  $\lambda_{\text{max}} = 254$  nm) was used for UV excitation of the BaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> suspension.

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