



## White-Light-Emitting Diodes Using Red-Emitting LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> Phosphors

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The fundamental luminescence and chromaticity properties of a class of red-emitting phosphors LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> under near-UV excitation have been investigated. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra reveal that the absorption is mainly attributed to O → Mo(W) charge transfer at 300 nm and the Eu<sup>3+</sup> transitions in near-UV and visible regions, and red emissions are assigned to intraconfigurational 4f-4f transitions of Eu<sup>3+</sup>. Both PL and PLE intensity were found to increase with increasing doped Mo content. The intensity of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> emission of Eu<sup>3+</sup> activated at 394 nm was found to reach a maximum when the relative ratio of Mo/W was 2:0. The CIE chromaticity coordinates were found to be (0.66, 0.33) for LiEu(MoO<sub>4</sub>)<sub>2</sub> and it reached the same level as the commodity phosphor Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>. A white-light-emitting diode fabricated using the composition-optimized LiEu(MoO<sub>4</sub>)<sub>2</sub> and the matching green- and blue-emitting phosphors shows that the quality of red color reproduction based on LiEu(MoO<sub>4</sub>)<sub>2</sub> was found to be much higher and improved than that using La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2731042] All rights reserved.

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Solid-state lighting (SSL) using light-emitting diode (LED) and phosphor materials to generate white light is the current research focus in the lighting industry. SSL technology has several advantages over conventional fluorescent lamps such as reduced power consumption, compactness, efficient light output, and longer lifetime. The availability of white light (WL)-LEDs should open up a great number of exciting new application fields: white light sources to replace traditional incandescent and fluorescent lamps, and backlights for portable electronics, medical, and architecture lightings, etc.<sup>1</sup> In the first WL-LED produced in 1996, an excellent method using a blue-LED chip in combination with a phosphor that exhibits yellow emission under blue excitation was proposed.<sup>2</sup> The yellow-emitting phosphor is trivalent-cerium-activated yttrium aluminum garnet (YAG), (Y,Gd)<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup>.<sup>3</sup> The luminous efficacy ( $\eta_L$ ) of commercial WL-LEDs is above 25 lm/W at a forward-bias current ( $I_f$ ) of 20 mA at room temperature. This value is higher than the efficacy of an incandescent lamp (15 lm/W) but lower than that of fluorescent tubes (75 lm/W).<sup>4</sup> Nowadays, the products of WL-LEDs have a general color-rendering index ( $R_a$ ) of 75-80, which is enough for universal illumination.<sup>5</sup> However, the WL-LEDs based on blue LED plus yellow phosphor have several disadvantages, including the halo effect of blue/yellow color separation and poor color-rendering properties caused by lack of red component in the spectrum.

There are two solutions proposed to solve the problems. One method is to excite multiphosphors using near-ultraviolet (n-UV) LED sources.<sup>4,6</sup> The other method employing a blue-LED chip and yellow-emitting YAG and sulfide phosphors was proposed in order to improve its color-rendering property. However, the sulfide-based phosphors are inherently chemically unstable and the lifetime of the sulfide materials is deficient under excitation with ultraviolet irradiation.<sup>7</sup> It is regarded to be very difficult to use sulfide phosphors in WL-LEDs for general illumination. Hence, there has been a widespread and growing interest in developing new families of red-emitting phosphors with high absorption in the near-UV to blue region. In this work we report a class of new red-emitting phosphors LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub>, based on which along with experimentally optimized green- and blue-emitting phosphors a WL-LED was fabricated and its performance was investigated.

### Experimental

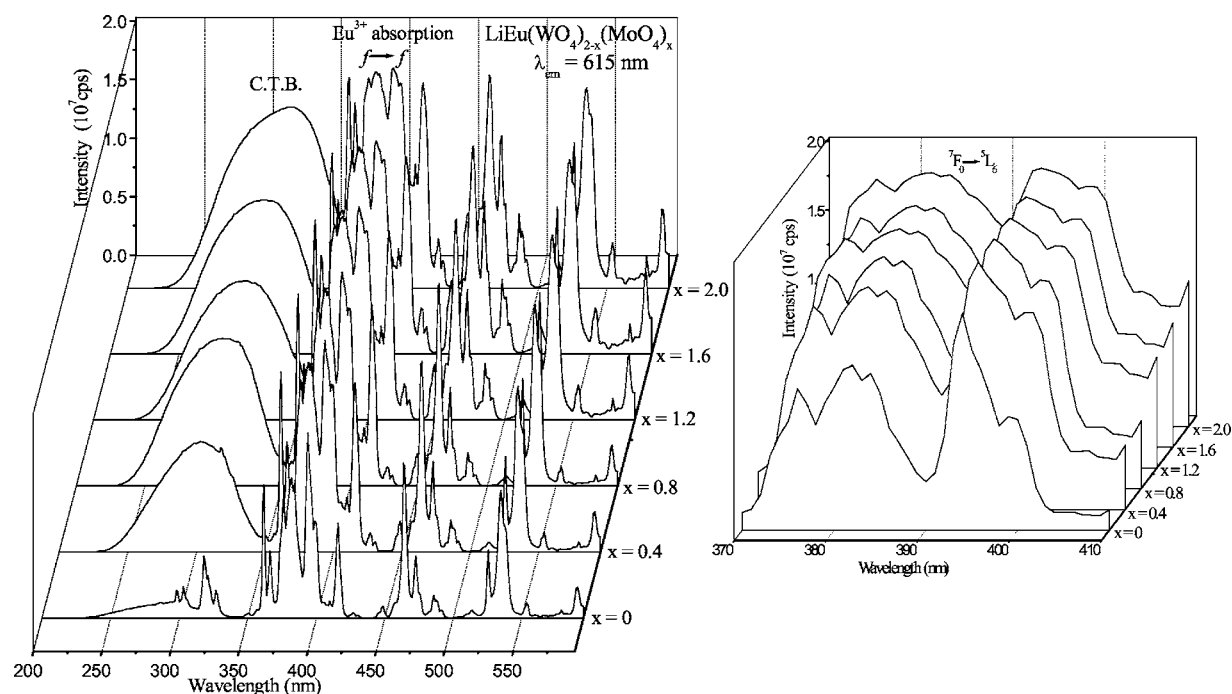
The samples of LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> phosphors were prepared by first ballmilling the reactant mixture consisting of a stoichiometric amount of Li<sub>2</sub>CO<sub>3</sub> (99.9%), Eu<sub>2</sub>O<sub>3</sub> (99.99%), MoO<sub>3</sub> (99.9%), and WO<sub>3</sub> (99.9%) (all from Aldrich Chemicals, Milwaukee, WI, USA.) for 20–30 min and then fired at 600–800°C for several hours. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> (0 ≤ x ≤ 2.0) were measured by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., NJ, USA) equipped with a 450 W Xe light source and double excitation monochromators. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates for all samples were determined by a Laiko DT-100 color analyzer equipped with a charge-coupled device (CCD) detector (Laiko Co., Tokyo, Japan). To compare the performance of LiEu(MoO<sub>4</sub>)<sub>2</sub> and the commodity of La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> (Kasei Optonix KX-681B) phosphors in the application of SSL, phosphor-conversion WL-LEDs were fabricated. Based on standard LED technology, the first WL-LED was fabricated by using an n-UV LED chip (average  $\lambda_{em}$  = 392 nm Cree, Catalog no. C395MB290-S0100) in pumping BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> (Kasei optonix KX-661), (Ba,Sr)-Si-Al-O:Eu<sup>2+</sup>,Dy<sup>3+</sup> (Nantex RU-G534) and LiEu(MoO<sub>4</sub>)<sub>2</sub> phosphors simultaneously. The above-mentioned BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> and Eu<sup>2+</sup>,Dy<sup>3+</sup>-codoped (Ba,Sr)-Si-Al-O phosphors have been tested to be excellent commodities because of their nontoxicity, thermal stability, and intense luminescence properties. The phosphors were encapsulated in a transparent epoxy resin (KBIN A2015). The second WL-LED based on La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> and the same green- and blue-emitting phosphors was also fabricated at the same collocation for comparison. The optimized weight ratio of R[LiEu(MoO<sub>4</sub>)<sub>2</sub>]:G:B phosphors is 0.92:0.06:0.02, whereas that for the R(La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>):G:B phosphors combination is 0.69:0.23:0.08. This ratio change depends on the target color of the white region. The relative emission spectra of n-UV chip WL-LED based on LiEu(MoO<sub>4</sub>)<sub>2</sub> and La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> operated at room temperature and at  $I_f$  of 20 mA were measured using a 50 cm single-grating monochromator.

### Results and Discussion

Rietveld structural refinement was carried out by using the GSAS software package and reported elsewhere.<sup>8,9</sup> Briefly, both LiEu(WO<sub>4</sub>)<sub>2</sub> and LiEu(MoO<sub>4</sub>)<sub>2</sub> are found to be isostructural with KEu(MoO<sub>4</sub>)<sub>2</sub>, which are crystallized in the triclinic space group  $P\bar{1}$  with  $a = 10.4287(3)$  Å,  $b = 5.2079(1)$  Å,  $c = 6.7350(2)$  Å,

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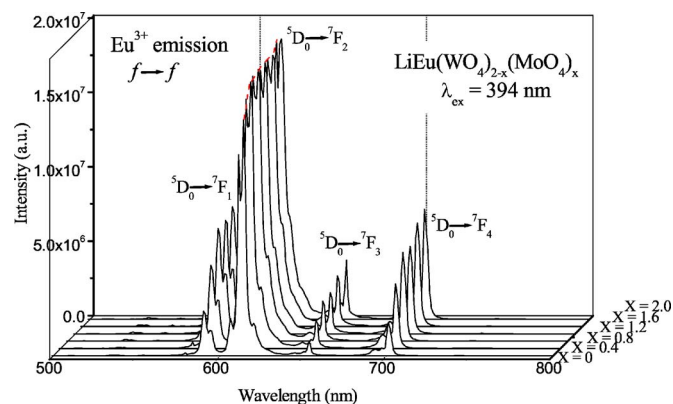
**Figure 1.** PLE spectra for  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  phosphors with  $x = (a) 0, (b) 0.4, (c) 0.8, (d) 1.2, (e) 1.6,$  and  $(f) 2.0$ .

$\alpha = 112.764(5)^\circ$ ,  $\beta = 112.716(3)^\circ$ ,  $\gamma = 89.930(3)^\circ$ ,  
 $V = 306.372(2) \text{ \AA}^3$ ,  $Z = 2$  for  $\text{LiEu}(\text{WO}_4)_2$ , and  $a = 10.4094(3) \text{ \AA}$ ,  
 $b = 5.1989(2) \text{ \AA}$ ,  $c = 6.7540(2) \text{ \AA}$ ,  $\alpha = 112.686(3)^\circ$ ,  
 $\beta = 112.575(2)^\circ$ ,  $\gamma = 90.043(4)^\circ$ ,  $V = 306.604(4) \text{ \AA}^3$ ,  $Z = 2$  for  
 $\text{LiEu}(\text{MoO}_4)_2$ .<sup>9</sup> The final weighted-profile  $R$  values ( $R_{\text{wp}}$ ) of 6.69%  
and 4.29% were reported by Chiu et al. for  $\text{LiEu}(\text{WO}_4)_2$  and  
 $\text{LiEu}(\text{MoO}_4)_2$ , respectively.<sup>9</sup>

Figure 1 shows the PLE spectra of six samples with selected compositions of  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  ( $x = 0, 0.4, 0.8, 1.2, 1.6, 2.0$ ) monitored at 615 nm that is attributed to  $^5\text{D}_0 \rightarrow ^5\text{F}_2$  emission of  $\text{Eu}^{3+}$  ions. The intense broad band at near 300 nm is assigned as the charge-transfer (CT) transition originated from  $\text{O} \rightarrow \text{W}$  or  $\text{O} \rightarrow \text{Mo}$  (i.e., ligand to metal charge transfer). However, the CT band of  $\text{Eu}^{3+}\text{-O}^{2-}$  was not clearly observed in the excitation spectra, which could be due to possible overlap of the CT band with that of tungstate or molybdate group. In the range from 350 to 550 nm, all samples show characteristic intraconfigurational 4f-4f absorption transitions of  $\text{Eu}^{3+}$ : sharp  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  transition for 394 nm,  $^7\text{F}_0 \rightarrow ^5\text{D}_2$  transition for 465 nm, and  $^7\text{F}_1 \rightarrow ^5\text{D}_1$  transition for 535 nm. As compared with the  $\text{O} \rightarrow \text{Mo}(\text{W})$  CT band, remarkable changes were observed in the intensity of characteristic absorptions of  $\text{Eu}^{3+}$  ion in the PLE spectra shown in Fig. 1, respectively; the maximum absorption of the  $\text{Eu}^{3+} \ ^7\text{F}_0 \rightarrow ^5\text{L}_6$  peak becomes stronger with increasing doped molybdenum content. A three-dimensional (3D) spectral representation at the right of Fig. 1 shows the expanded PLE spectra in the spectral range of 370–410 nm for comparison in detail.

Figure 2 shows the Mo-content dependence of PL spectra for  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  ( $x = 0, 0.4, 0.8, 1.2, 1.6, 2.0$ ) phosphors excited by n-UV radiation at 394 nm. The spectra essentially consist of sharp emissions with wavelengths ranging from 580 to 720 nm, which are associated with the  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 1, 2, 3, 4$ ) multiplet transitions from the excited levels of  $\text{Eu}^{3+}$  to the ground state, although no emission corresponding to tungstate or molybdate is observed. However, the presence of an absorption band due to a tungstate or molybdate group in the excitation spectrum of  $\text{Eu}^{3+}$ , when monitored for  $\text{Eu}^{3+}$  emission (at 615 nm), very likely suggests that

the energy absorbed by the  $\text{WO}_4^{2-}/\text{MoO}_4^{2-}$  group is transferred to  $\text{Eu}^{3+}$  levels nonradiatively. That is to say, the emission corresponding to  $\text{Eu}^{3+}$  ions has been observed under excitation of the CT band of either the  $\text{WO}_4^{2-}$  or  $\text{MoO}_4^{2-}$  group. This occurrence is known as “host-sensitized” energy transfer.<sup>10</sup> However, the intensity of  $\text{Eu}^{3+}$  emission is weaker with CT band excitation when compared to that due to  $\text{Eu}^{3+}$  excitation. This observation reveals that the energy transfer from the  $\text{MoO}_4^{2-}/\text{WO}_4^{2-}$  group to  $\text{Eu}^{3+}$  is inefficient, which was proposed to be strongly dependent on the bond angles of  $\text{O}-\text{Mo}(\text{W})-\text{O}$  and  $\text{Mo}(\text{W})-\text{O}-\text{Eu}^{3+}$  by Blasse and Brill.<sup>11</sup> The presence of multiplets in the emission spectra is attributed to the  $(2J + 1)$  Stark components of J-degeneracy splitting. The  $^5\text{D}_0$  is an unsplit singlet band, simplifying in a significant way the application of the group theory and of electronic transition selection rules. In general, the  $\text{Eu}^{3+}$  emission lines are hypersensitive, that is to say, they are highly sensitive to the environment. The electric-dipole transition would be dominant when  $\text{Eu}^{3+}$  occupied the lattice site of a non-centrosymmetric environment in the scheelite phases. The



**Figure 2.** PL spectra of  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  ( $x = 0, 0.4, 0.8, 1.2, 1.6, 2.0$ ) under 394 nm near-UV excitation.

**Table I. Comparison of excitation ( ${}^7F_0 \rightarrow {}^5L_6$ ) and emission ( ${}^5D_0 \rightarrow {}^7F_2$ ) intensity of  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  ( $x = 0-2$  in steps of 0.4)**

Compositions	Intensity ( $10^7$ cps)	
	$\lambda_{\text{em}} = 615$ nm	$\lambda_{\text{ex}} = 394$ nm
$\text{LiEu}(\text{WO}_4)_2$	1.582	1.215
$\text{LiEu}(\text{WO}_4)_{1.6}(\text{MoO}_4)_{0.4}$	1.803	1.612
$\text{LiEu}(\text{WO}_4)_{1.2}(\text{MoO}_4)_{0.8}$	1.817	1.742
$\text{LiEu}(\text{WO}_4)_{0.8}(\text{MoO}_4)_{1.2}$	1.820	1.746
$\text{LiEu}(\text{WO}_4)_{0.4}(\text{MoO}_4)_{1.6}$	1.824	1.794
$\text{LiEu}(\text{MoO}_4)_2$	1.885	1.889

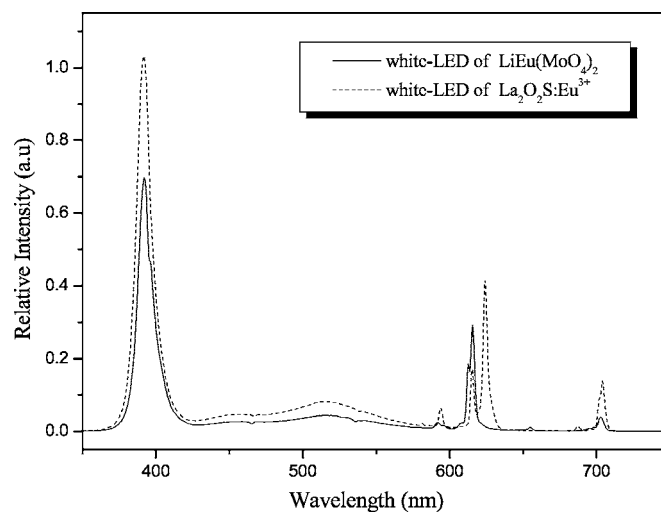
sharp and intense lines all have  ${}^5D_0$  as the emitting level, though transitions from  ${}^5D_1$  and  ${}^5D_2$  levels are also present with a much lower intensity. This feature, common to all molybdates previously studied,<sup>12-14</sup> is probably related to the high-energy phonons of the molybdate (or tungstate) groups, which favor nonradiative de-excitation  ${}^5D_J$  of toward  ${}^5D_0$ .<sup>15</sup> The intensity of  ${}^5D_0 \rightarrow {}^7F_{2,4}$  (electric-dipole transition) was found to be much stronger than that of  ${}^5D_0 \rightarrow {}^7F_{1,3}$  (magnetic-dipole transition), although the intensity of  ${}^5D_0 \rightarrow {}^7F_0$  was not clearly observed. The major emission of  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  was found at 615 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ), which corresponds to red emission. Other transitions of  $\text{Eu}^{3+}$  from the  ${}^5D_J$  excited levels to  ${}^7F_J$  ground states, for instance,  ${}^5D_0 \rightarrow {}^7F_J$  located at 570–720 nm and  ${}^5D_1 \rightarrow {}^7F_J$  located at 520–570 nm, are both very weak; therefore, the more saturated CIE chromaticity benefited greatly by the reasoning.

When the molybdenum content is increased, the lithium europium double tungsto-molybdate shows stronger red emission at 615 nm by exciting at 394 nm. As indicated in Fig. 2, the intensity of  ${}^5D_0 \rightarrow {}^7F_{1,2,3,4}$  transition was all found to increase with the increasing Mo/W content; however, the relative ratio of  ${}^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_2$  was found to change insensibly with Mo/W content. The  $I-\lambda$  curve of  ${}^5D_0 \rightarrow {}^7F_2$  reaches a maximum when the relative ratio of Mo/W is 2:0, as revealed in Table I. The reason for this observation may be due to the advent of ion pair interaction between  $\text{Eu}^{3+}$  ions, which is expected to be much stronger in molybdate than in tungstate crystal because of the differences in the  $\text{Eu}^{3+} - \text{Eu}^{3+}$  distance in molybdate [average distance 3.86(6) Å] and that in tungstate [average distance 3.9(1) Å] phosphors.<sup>9</sup> One of the possibilities is that the distance between two  $\text{Eu}^{3+}$  ions can affect the energy transfer between the two ions.

The CIE color coordinates ( $x, y$ ) and relative luminance of the red-emitting phosphors investigated in this work are tabulated in Table II. For the series of  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  phosphors with different Mo/W ratios, the experimental CIE ( $x, y$ ) coordinates indicate that as the concentration of Mo increases, the  $x$  value increases

**Table II. Comparison of CIE chromaticity coordinates of phosphors investigated in this work [ $\lambda_{\text{ex}} = 394$  nm for  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$ ;  $\lambda_{\text{ex}} = 342$  nm for the commodity of  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ ].**

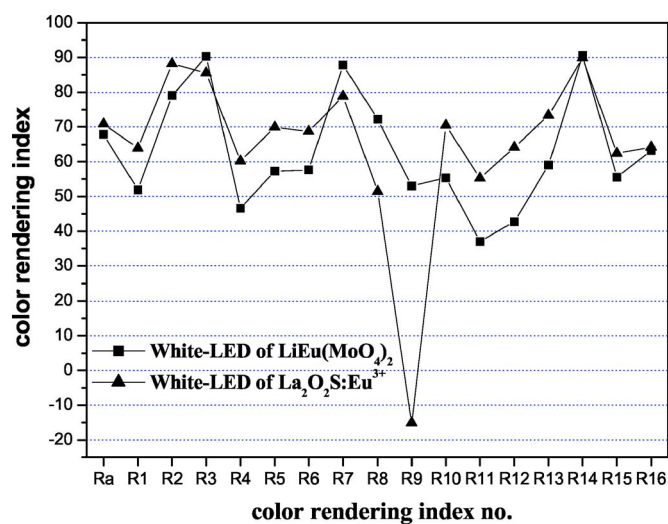
Phosphor compositions	CIE color coordinates ( $x, y$ )	Relative luminance (a.u.)
$\text{LiEu}(\text{WO}_4)_2$	(0.65, 0.35)	0.8
$\text{LiEu}(\text{WO}_4)_{1.6}(\text{MoO}_4)_{0.4}$	(0.65, 0.34)	0.9
$\text{LiEu}(\text{WO}_4)_{1.2}(\text{MoO}_4)_{0.8}$	(0.65, 0.34)	1.0
$\text{LiEu}(\text{WO}_4)_{0.8}(\text{MoO}_4)_{1.2}$	(0.65, 0.34)	1.1
$\text{LiEu}(\text{WO}_4)_{0.4}(\text{MoO}_4)_{1.6}$	(0.65, 0.34)	1.2
$\text{LiEu}(\text{MoO}_4)_2$	(0.66, 0.33)	1.4
$\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$	(0.66, 0.33)	1.0

**Figure 3.** The EL spectra of n-UV chip-based WL-LED with  $\text{LiEu}(\text{MoO}_4)_2$  and  $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  phosphors and a forward-bias current of 20 mA, respectively.

while  $y$  value decreases slightly, and the chromaticity was found to shift away from red toward deep-red. A similar observation to change relative Mo/W ratios has also been witnessed by Sivakumar and Varadaraju in the  $\text{AgLa}_{0.95}\text{Eu}_{0.05}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  ( $x = 0-2$ ) system,<sup>16</sup> and they argued that minor distortions in the crystal structure play a crucial role in determining the luminescence properties in these systems. In addition, the absorption of the sample is considered to be one of the decisive factors in evaluating the relative luminance of LED phosphors. In our work the phosphor samples and commodity were prepared by solid-state reactions and their particle sizes were estimated to be in the micrometer range, as we measure the relative luminance of the samples whose size was reasonably assumed to be micro-sized.

We also found that with increasing doped Mo content the relative luminance increases from 0.8 ( $x = 0$ ) to 1.4 ( $x = 2.0$ ) monotonically. The CIE chromaticity coordinates were found to be (0.66, 0.33) for  $\text{LiEu}(\text{MoO}_4)_2$ , and it reached the same level as the commodity phosphor  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  (Kasei Optonix P22-RE3, the optimal excitation  $\lambda_{\text{ex}} = 342$  nm).  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  phosphor was traditionally used in color television and it is a red-emitting candidate for SSL application at present. We have also observed that the CIE chromaticity coordinates of  $\text{LiEu}(\text{MoO}_4)_2$  approach that [i.e., (0.67, 0.33)] for the NTSC red. Consequently, our investigation results indicate that  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  can be used as a better near-UV conversion phosphor as compared to  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  in the application as a red-emitting phosphor for WL-LEDs. In addition,  $\text{LiEu}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x$  also emits light in the red region under 465 nm blue light excitation. Therefore, the new phosphor can be combined with a blue chip and YAG phosphor to WL-LEDs with higher  $R_a$ .

Furthermore, phosphor-conversion LED lamps were fabricated by precoating blue/green/red phosphors onto n-UV LED chips prior to packaging into LED lamps. Figure 3 shows the comparison of LED emission spectra of the WL-LED based on an n-UV chip,  $\text{LiEu}(\text{MoO}_4)_2$ , and  $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  at a  $I_f$  of 20 mA, respectively, where  $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  is currently a popular red-emitting phosphor for WL-LED application. We observed three bands in the LED emission spectra and the shorter-wavelength peak located at 392 nm originated directly from the n-UV LED chip. The broad emission band located at 430–580 nm originated from the blue and green phosphors, and the sharp emission located at 590–720 nm, respectively, originated from the red-emitting phosphor. The observation of a short-wavelength emission indicates that n-UV light emitted from



**Figure 4.** CRI variation of WL-LEDs based on an n-UV chip, LiEu(MoO<sub>4</sub>)<sub>2</sub>, and the commodity of La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> at an  $I_f$  of 20 mA, respectively.

the LED chips was not completely absorbed by the precoated phosphors in our LED lamps. It is also well known that down-conversion efficiency depends strongly on phosphor composition and phosphor grain size.<sup>17</sup> Therefore, it is necessary to develop high-quality phosphors and a well-controlled packaging process to improve the output intensity of phosphor-converted LED lamps.

When the two WL-LEDs were operated at a  $I_f$  of 20 mA at room temperature, color temperature ( $T_{cp}$ ) and the luminous efficacy ( $\eta_L$ ) were found to be 5551 K and 6 lm/W for the WL-LED based on LiEu(MoO<sub>4</sub>)<sub>2</sub>, and 6782 K and 10 lm/W for the other WL-LED based on La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>, respectively. The CIE chromaticity of WL-LED based on LiEu(MoO<sub>4</sub>)<sub>2</sub> and that based on La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> were found to be (0.33, 0.33) and (0.31, 0.34), respectively. However, compared to commercial WL-LEDs (>25 lm/W) at a forward-bias current ( $I_f$ ) of 20 mA at room temperature, the luminous efficacy ( $\eta_L$ ) observed for our n-UV + blue/green/red white LED lamps was still insufficient, probably due to the inherently weak f-f absorption of Eu<sup>3+</sup> and the lower efficacy of the LED chip (about 8–10 mW). Figure 4 shows the color-rendering index variation for WL-LEDs based on an n-UV chip, LiEu(MoO<sub>4</sub>)<sub>2</sub>, and La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> operated at an  $I_f$  of 20 mA, respectively. The CRI value of the WL-LED of LiEu(MoO<sub>4</sub>)<sub>2</sub> ( $Ra \approx 67.8$ ) is close to the other WL-LED fabricated with a commodity of La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> ( $Ra \approx 70.8$ ). The performance of the former is still deficient in the proportions of visible emission spectrum in the WL-LED of LiEu(MoO<sub>4</sub>)<sub>2</sub>. Above all, some of the CRI values for WL-LED based on LiEu(MoO<sub>4</sub>)<sub>2</sub> are clearly larger than those of that based on La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>. In particular, the CRI no. 9 value (that shows color reproduction quality in the red region) of LiEu(MoO<sub>4</sub>)<sub>2</sub> is 53.05, which is much higher and improved than that using La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> (-15.20). Therefore, LiEu(MoO<sub>4</sub>)<sub>2</sub> can be used as a red-emitting component in fabrication of phosphor-conversion WL-LEDs.

Formerly, Narukawa et al. have reported the fabrication of n-UV + blue/yellow WL-LED lamps.<sup>18</sup> It has been shown that the optical properties of such n-UV + blue/yellow WL-LED lamps were excellent with a high color-rendering index,  $Ra$ , of 85. Compared to their n-UV + blue/yellow WL-LED lamps, the color-rendering index,  $Ra$ , of 67.8 observed for our n-UV + blue/green/red WL-LED

lamps was lower, possibly imputed to inherently weak absorption and emission attributed to Eu<sup>3+</sup> f-f transition. The selection of blue or green phosphor still demands improvement (R1–R12 are both low). Our investigation results suggest that although LiEu(MoO<sub>4</sub>)<sub>2</sub> was demonstrated to show potential for general illumination approaching the commodity of La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>, further study is needed to improve our n-UV + blue/green/red WL-LED efficiency. Furthermore, the new sulfide-free phosphor of LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> can be combined with blue chip and YAG phosphor to form WL-LEDs with higher  $Ra$ , a commodity of which La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> is unable to achieve.

## Conclusions

We have successfully synthesized a class of novel red-emitting LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> phosphors by solid-state reaction technique at high temperature. The luminescence properties under near-UV excitation of the double tungsto-molybdate phosphors have been investigated. Chromaticity characteristics and comparative luminance for the LiEu(WO<sub>4</sub>)<sub>2-x</sub>(MoO<sub>4</sub>)<sub>x</sub> phosphors have also been measured and compared with a commodity phosphor Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>. We also fabricated WL-LEDs by integrating an n-UV LED chip, the LiEu(MoO<sub>4</sub>)<sub>2</sub> phosphor, and optimized matching green- and blue-emitting phosphors. The  $Ra$  value of the WL-LED based on LiEu(MoO<sub>4</sub>)<sub>2</sub> was found to be 67.8, approaching that of the other WL-LED ( $Ra \approx 70.8$ ) based on the commodity of La<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> when operated at a forward-bias current ( $I_f$ ) of 20 mA. Notably, the CRI no. 9 value showing color reproduction in the red region has been improved from -15.20 to 53.05 for the WL-LEDs using LiEu(MoO<sub>4</sub>)<sub>2</sub> as the red-emissive component.

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