Low-Temperature Synthesis of LiEuMo$_2$O$_8$ Red Phosphor for a White-Light-Emitting Diode

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The Eu^{3+}-activated double molybdate red phosphor, LiEuMo$_2$O$_8$ was prepared by a sol-gel process using inorganic salts as starting materials. A precursor prefired at 500°C for 240 min was subsequently annealed at 600°C for 240 min in Ar. The crystal structure, surface morphology and luminescent properties were analyzed by an X-ray diffractometer, a field emission scanning electron microscope and a fluorescent spectrophotometer. The obtained LiEuMo$_2$O$_8$ shows a strong excitation band near 395 and 466 nm and intensely red-emission lines at 616 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transitions on Eu^{3+} at 395 nm of light excitation.

Keywords: phosphor, LiEuMo$_2$O$_8$, sol-gel

1. INTRODUCTION

White-light-emitting diodes (LED) represent a remarkable resource in the 21st century because they are environmentally friendly and energy-saving. A white LED can be obtained by combining an InGaN blue LED with a yellow phosphor (Y$_3$Al$_5$O$_{12}$:Ce^{3+}).[1,2] However, this combination has some drawbacks, i.e., the overall efficiency is decreased when the color temperature of the devices is low, and the output wavelength is deficient in the red region of the visible light spectrum. Although the products of white LEDs have a general color rendering index (Ra) of ~ 85, which is sufficient for universal illumination, white LEDs are not applicable for certain medical applications and architectural lighting purposes due to the deficient red emission. Additionally, white light can be produced by other methods, assembling red, green and blue phosphors. These three phosphor-converted white LEDs maintain a very high color-rendering index and offer the greatest potential for high-efficiency solid-state light (SSL) using a near-ultra violet (UV) LED chip. The red light-emitting phosphors used for improving the Ra and tuning color temperature of white-light LEDs remain limited commercially to sulfide-based materials such as CaS: Eu^{2+}, SrY$_2$S$_4$:Eu^{2+}, and ZnCdS: Cu, Al.[3,4] However, the efficiency of the commercial red phosphor for blue and near-UV GaN-based LED, is approximately eight times lower than those of the blue and green phosphors; moreover, this sulfide-based phosphor is chemically and thermally unstable. To achieve a phosphor-converted white LED with these three phosphors, it is imperative to develop new effective red phosphors that are suitable for near-UV LED chips. Therefore, the lack of proper red phosphors becomes a bottleneck for the creation of SSL devices.

Recently, attractive research fields have been started to find a stable inorganic rare earth-based red phosphor with high absorption in the near-UV/blue spectral region. Interesting alternative red phosphors include materials doped with Eu^{3+}, which fluoresces via the $^5D_0 \rightarrow {}^7F_2$ transition at ~ 615 nm when the ion is present in a non-centro-symmetric site. Molybdates activated by trivalent europium ions (LEM, LiEuMo$_2$O$_8$) show efficient red-light emission in the near-UV radiation.[5-7] Double molybdates ABM$_2$O$_8$ (A: monovalent metal, B: trivalent rare earth, M: Mo^{6+}), which share a scheelite-like iso-structure, show excellent thermal and hydrolytic stability and are considered to be efficient luminescent host materials. LEM is typically produced from metal oxides in a conventional solid-state reaction at above 1000°C. These approaches usually require high temperatures, time-consuming heating processes and subsequent grinding. In addition, aggregation and an inhomogeneous shape are unavoidable, and these factors inhibit the absorp-

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tion of the excitation energy and therefore reduce the emission intensity.

The simple and economical sol-gel process is one of the most important techniques in conjunction with these products, as it offers many advantages over the conventional solid-state method, such as higher uniformity of the particle size distribution, non-agglomeration and greater photoluminescent intensity.[8] In this work, red-emitting LEM was prepared at a low temperature of 600°C in a sol-gel method.

2. EXPERIMENTAL PROCEDURE

The red phosphor LEM was prepared with a sol-gel method using lithium acetate dehydrate ($C_2H_3LiO_2 \cdot 2H_2O$), europium (III) nitrate pentahydrate [$Eu(NO_3)_3 \cdot 5H_2O$], and ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$]. Ammonium molybdate and lithium dehydrate were dissolved with H_2O, and europium (III) nitrate pentahydrate and citric acid were dissolved with a diluted HNO_3 solution. A homogeneous sol heated at 80°C for 120 min was converted to brown resin. The precursor sol was dried at 120°C for 24 h in air and was then prefired at 500°C for 240 min in air. Finally, the prefired white powder was annealed in a tube furnace at 600°C for 240 min in Ar (heating rate: 3°C/min).

X-ray diffraction (XRD) of the samples was examined on a D-Max-1200 (Rigaku, Japan). The morphologies of the samples were measured on a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Photoluminescent excitation and emission measurements were carried out using a fluorescent spectrophotometer (F4500, Hitachi, Japan).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the LEM. The LEM has scheelite structure with the space group $I4_1/a$ and unit cell parameters of $a = 0.5201$ nm and $c = 1.1334$ nm. In this structure, Li^+ and Eu^{3+} occupy an eight-coordinated site, and Mo^{6+} fills the four-coordinated sites. As the size of Li^+ is very small compared to its coordination environment, the Li^+ may not stay at the center of the LiO_8 cage. Rather, it may move towards the four-oxygen planar along the a-, b- or c-axes randomly. Due to the different valence states and difference in the ion sizes between M ($Mo^{6+} = 0.041$ nm) and Eu^{3+} (0.107 nm), Eu^{3+} is expected to occupy the Li^{2+} (0.068 nm) site in this phosphor.[9] The XRD pattern reveals that the LEM is single-phased and consistent with JCPDS 52-1848. Moreover, the doped Eu ion has little influence on the host structure.

During the application of phosphors to SSL, the size distribution and shape of the particles are very important. Figure 2 shows a FE-SEM image of the LEM powder after it was
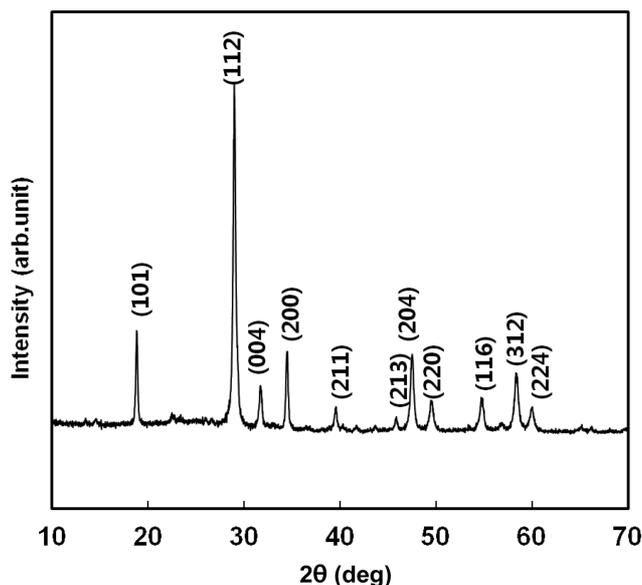

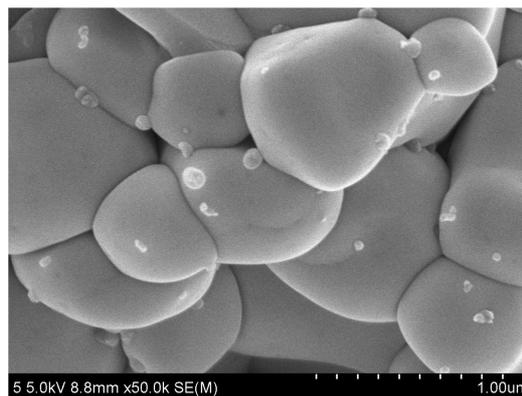**Fig. 1.** XRD pattern of the LEM red phosphor after annealing at 600°C.

Fig. 2. FE-SEM image of the LEM red phosphor after annealing at 600°C.

annealed at 600°C. The particle size of the sample is approximately ~ 1 μm, and it shows a spherically shaped surface morphology. The phosphor particles exhibited regular and homogeneous morphology characteristics without any visible admixture of any impurity phases. Hence, they are suitable for the fabrication of SSL devices.

The excitation and emission spectra excited by near-UV at 395 nm at an ambient temperature are illustrated in Fig. 3. As shown in Fig. 3(a), the intense broad band in the short wavelength range < 350 nm is assigned as the charge-transfer band (CTB) originating from the oxygen to the molybdenum transition. However, the CTB of Eu^{3+} - O^{2-} was not clearly observed in the excitation spectra, which may have been due to the possible overlap of the CTB with that of the molybdate group.[5] A previous study[6] indicated that the main source of excitation was related to the charge transfer
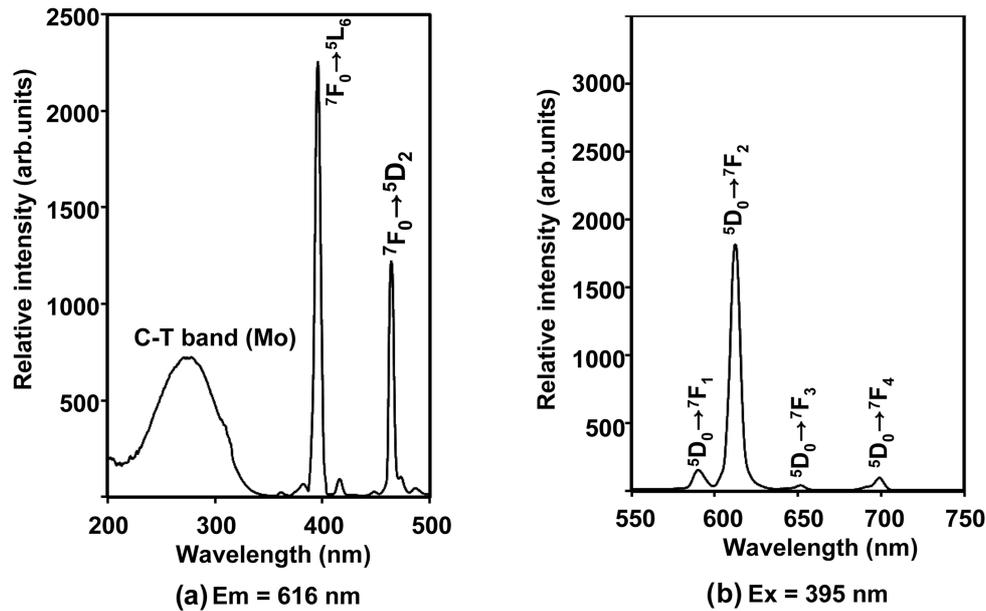
Fig. 3. Excitation (a) and emission (b) spectra of the LEM.

transition of the MoO_4^{2-} group while that of Eu-O made less contribution to the excitation. The Eu^{3+} excitation spectra cover the range from the long-wavelength UV to the visible green region (350 nm to 500 nm). In the range from 350 nm to 500 nm, the sample shows the characteristic intraconfigurational 4f-4f emissive transitions of the Eu^{3+}: $^7F_0 \rightarrow ^5D_4$ transition at 360 nm, the $^7F_0 \rightarrow ^5L_7$ transition at 380 nm, the $^7F_0 \rightarrow ^5L_6$ transition at 395 nm, the $^7F_0 \rightarrow ^5D_3$ transition at 416 nm, and the $^7F_0 \rightarrow ^5D_2$ transition at 466 nm. The lines at 395 nm and 466 nm are the two strongest of these observed lines and match the near-UV and the blue LED chips well; additionally, their intensities are much stronger than that of the CTB. Between the luminescent center and the crystal lattice, two couplings are performed in luminescent materials. The first is strong coupling (MoO_4^{2-} group) with a high Huang-Rhys factor. The other is weak coupling (Eu^{3+} ions) with a low Haung-Rhys factor.[10] Generally, strong coupling of the CTB is predominant, whereas weak coupling of the CTB (Eu^{3+}) is subdominant. When the CTB (Mo^{6+}) is excited, the energy absorbed from the charge-transfer state is efficiently transferred to an Eu^{3+} ion by a non-radiative mechanism, and generates red-light emission of the $^5D_0 \rightarrow ^7F_J$ transition of Eu^{3+}.

Figure 3 (b) shows the PL spectra of the LEM under 395 nm near-UV excitation. The spectra consist of sharp lines with wavelengths ranging from 570 nm to 710 nm, which are associated with the $^5D_0 \rightarrow ^7F_J$ (J = 1, 2, 3, 4) transitions from the excited Eu^{3+} to the ground state. The main emission peak is the $^5D_0 \rightarrow ^7F_2$ transitions of Eu^{3+} at 616 nm; other transitions from $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ located in the range of 570 nm to 710 nm are weak. The

strong emission peak around 616 nm, which allows the Eu^{3+} to occupy the center of asymmetry in the host lattice, and the relatively weak peaks around 698 nm are due to the electric dipole energy transition of $^5D_0 \rightarrow ^7F_{2, 4}$. The weak emissions of 591 nm and 650 nm are ascribed to the magnetic dipole transition of $^5D_0 \rightarrow ^7F_{1, 3}$. The electric dipole allowed transition would be dominant when Eu^{3+} occupies the lattice site of a noncentrosymmetric environment in the scheelite phases.[11] For this reason, the intensity of $^5D_0 \rightarrow ^7F_{2, 4}$ was found to be much stronger than those of $^5D_0 \rightarrow ^7F_{1, 3}$. The ratio ($I_{616}$ / I_{591}) between the strong emission at 616 nm due to the electric dipole transition of $^5D_0 \rightarrow ^7F_2$ and the weak emission at 591 nm due to the magnetic dipole transition of $^5D_0 \rightarrow ^7F_1$, as used in lanthanide-based systems as a probe of the cation local surroundings,[12] is estimated to be 1 : 0.085. This value is comparable to previous work pertaining to red-emitting (Ca, Eu, M)WO₄ (M = Mg, Zn, Li) with a scheelite structure caused by a solid-state reaction.[10] Shi *et al.*[10] found that the $^5D_0 \rightarrow ^7F_2$ transition emission intensity of Eu^{3+} increases significantly with the incorporation of Mg^{2+}, Zn^{2+} or Li^+ ions into CaMoO₄. Generally, in the tetragonal system of CaWO₄ and LiMoO₄, Eu^{3+} ions substitute partially for Ca^{2+} or Li^+ ions and have S_4 site symmetry. Doping with Mg^{2+}, Zn^{2+} or Li^+ into CaWO₄ results in the enhancement of I_{616}/I_{591}.[10] As shown in Fig. 3(b), the transition $^5D_0 \rightarrow ^7F_2$ is much stronger than the transition $^5D_0 \rightarrow ^7F_1$, which suggests that the Eu^{3+} is located in a distorted (or asymmetric) cation environment. Other transitions from ^5D_J (J = 1, 3, 4) are relatively weak, which is advantageous when seeking to obtain high-quality red light.

Sol-gel-derived Eu^{3+}-activated double molybdate red phos-

phor showing a homogeneous surface and particle shape, which are favorable the luminescent properties due to the lower level of contamination or the fewer dead layers on the phosphor surface, are exceptionally attractive as a near-UV or blue convertible phosphor. Moreover, compared with a solid-state reaction, the temperature of the preparation is reduced by at least 400°C.

5. CONCLUSION

In summary, scheelite-type LEM red phosphor for a white-LED was prepared at 600°C by a sol-gel process. The XRD pattern reveals that the sample is single-phased and that the doped Eu ion has little influence on the host structure. For the Eu^{3+} excitation spectra, the lines at 395 nm and 466 nm are the two strongest sharp lines. They matched well with those of near-UV and the blue LED chips. The PL spectra at 395 nm near-UV excitation shows that the main emission peak is the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 616 nm; other transitions from $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ located in the range of 570 nm to 710 nm are weak. Compared with a solid-state reaction, the temperature of the preparation is reduced at least 400°C.

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