

Red-emitting LiEuW₂O₈ phosphor for white emitting diodes prepared by sol–gel process

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Scheelite-type LiEuW₂O₈ (LEW) phosphors with the optical function of color conversion from near-UV to red were prepared by sol–gel method using a lithium acetate dehydrate, europium(III) nitrate pentahydrate, and tungsten(VI) chloride as starting materials. Viscous mixing sol was pre-fired at 300 °C for 120 min in air and then white powder precursor was finally annealed at 500–800 °C for 240 min in Ar. From an X-ray diffraction analysis, all the samples are isostructural and belong to the tetragonal system of scheelite-type. The main emission peak is ⁵D₀ → ⁷F₂ transitions of Eu³⁺ at 615 nm, other transitions from the ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ located at 570–700 nm range are weak. The characteristic emission of WO₄²⁻ in LEW is quenched absolutely and only red-light emission of Eu³⁺ appears. Crystallinity, surface properties and red-emission by near-ultraviolet (395 nm) were improved by high-temperature annealing.

Keywords: phosphors, sol–gel, near-UV, red-light emission.

1. Introduction

Recently, great progress has been made as regards the solid-state lighting (SSL) device based on GaN light-emitting diode (LED), since the LEDs with high efficiency and various emission wavelengths are available [1, 2]. White LED is a remarkable resource because it is environment-friendly and energy-saving in the 21st century. White LED can be obtained by combining an InGaN blue LED emitting at 465 nm with a broad-band yellow phosphor, *e.g.*, Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) [3–5]. However,

such a combination has some drawbacks, *i.e.*, the overall efficiency is decreased rapidly when the correlated color temperature of the device is low, and the output light is deficient in the red region of the visible light spectrum. In addition to the blue LED/yellow phosphor approach, white light can be produced by other methods, such as assembling red, green and blue LEDs in one device; a mixture of the tri-color lights generates white light, and a combination of a near-ultra violet (UV) LED (370–410 nm) with red, green and blue phosphors; by this approach, the tri-color phosphors are excited by near-UV emitted by the LED. The use of red, green and blue light-emitting phosphors coated on the near-UV LED chip, is the focus in material and luminescence research nowadays. Three phosphors-converted white LEDs maintain a very high color-rendering index ($R_a > 90$) and are believed to offer the greatest potential for high efficiency SSL [6, 7]. However, the efficiency of the commercially available red phosphors, $Y_2O_2S:Eu^{3+}$ for blue and near-UV GaN based LED, is about eight times less than that of the blue and green phosphors, and this sulfide-based phosphor is chemically unstable. For achieving the three phosphors-converted white LED, it is imperative to develop new effective red phosphors suitable for near-UV LED chips. Therefore, the lack of proper red phosphors becomes the bottleneck for the SSL devices.

Recently, much attention has been paid to making superior red phosphor for white LED. Previously reported scheelite-type compound, $LiEuW_2O_8$ (LEW), written as ABM_2O_8 (A: monovalent metal, B: trivalent rare earth, M: Mo^{6+} or W^{6+}), exhibits high red emission efficiency under excitation of blue light [8]. LEW has attractive photoluminescent properties; *i*) the red emission due to $4f-4f$ transition of Eu^{3+} when excited by UV, blue or green light, *ii*) concentration quenching hardly occurs in scheelite-type LEW [9–11]. This weak concentration quenching property is known to be due to the W–O covalent bond [9, 10].

LEW was mostly produced from metal oxides by conventional solid-state reaction at above 1000 °C [11]. As far as we know, there is little information on a successful sol–gel synthesis of LEW red phosphor.

In this paper, we report the preparation of LEW phosphors with the optical function of color conversion from near-UV to red by sol–gel method. In particular, we focused on the preparation parameter of annealing temperature.

2. Experimental

For the synthesis of LEW, stoichiometric mixtures of lithium acetate dehydrate ($C_2H_3LiO_2 \cdot 2H_2O$), europium(III) nitrate pentahydrate [$Eu(NO_3)_3 \cdot 5H_2O$], and tungsten(VI) chloride (WCl_6) were dissolved with H_2O_2 and iso-propanol, respectively. A weighed quantity of urea (NH_2CONH_2) was added to the solution at 100 °C. The molar ratio of urea to the total concentration of metal ions was adjusted to 1.5. After mixing, a homogeneous colorless solution was obtained. The solvent was slowly evaporated off from the solution at 100 °C and a colorless precursor with high viscosity was obtained. Subsequently, the precursor was pre-fired in a dry oven at

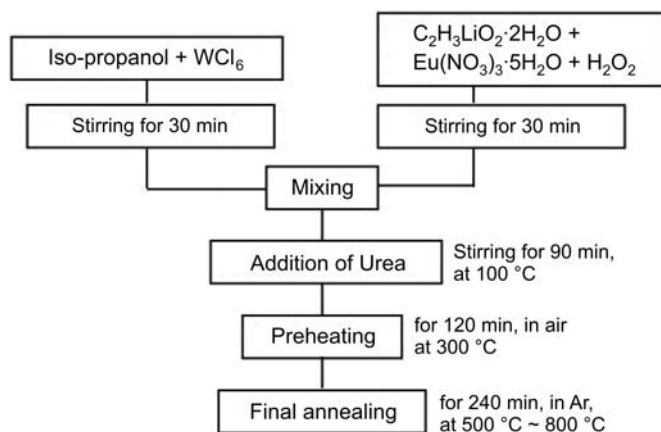


Fig. 1. Experimental flow chart.

300 °C for 120 min in air to obtain white powder. Finally, the dried powder was annealed in a tube furnace at 500, 600, 700, and 800 °C for 240 min in Ar (heating rate: 3 °C/min). Figure 1 shows the experimental flow chart.

X-ray diffraction profiles were measured using an X-ray diffractometer (XRD, D-Max-1200, Rigaku, Japan), equipped with a CuK α radiation source and a graphite monochromator. Particle size and shapes were observed by field emission–scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The excitation and emission spectra were recorded on a fluorescent spectrophotometer (F4500, Hitachi, Japan).

3. Results and discussion

The structural analysis of isomorphous LiY(MoO₄)₂ [8] shows that the scheelite-type LEW has the following crystallographic properties: *i*) the crystal structure belongs to a tetragonal system with its space group of I4₁/a, *ii*) randomly distributed dodecahedra of LiO₈ and EuO₈ are surrounded by WO₄ tetrahedral units. Figure 2 gives the XRD patterns of LEW as a function of annealing temperature. All the samples are isostructural and belong to the tetragonal system of scheelite-type. In this work, isomorphous NaYW₂O₈ (JCPDS No. 48-886) is used for the purpose of comparison, since the crystal structure analysis of LEW has not been reported yet and NaYW₂O₈ exhibits an identical diffraction pattern to the bulk LEW [12]. In this structure, W⁶⁺ occupies the tetrahedral sites constructed with O²⁻ composing WO₄²⁻ anion complex. Li²⁺ is eight-coordinated with O²⁻, forming a distorted cube. The dopant Eu³⁺ occupies the Li²⁺ site. Since there is no significant shift in the peak location, we can consider that the doped Eu³⁺ has little influence on the host structure.

When the pre-fired white gel was annealed at 500 °C and above, only the scheelite-type LEW phase appeared, and no peaks from impurities were present. This result clearly indicated that sol–gel method effectively decreases the annealing temperature for obtaining a single phase of scheelite-type LEW.

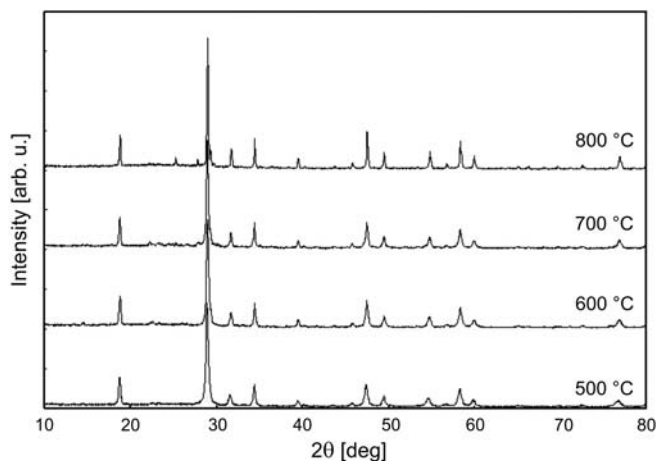


Fig. 2. XRD patterns of LEW powders as a function of annealing temperature.

The major diffraction peak at $2\theta \approx 29^\circ$ (112) reflection and other diffraction peaks occurred at $2\theta \approx 18.8^\circ$ (101), 31.7° (004), 34.4° (200) and 47.5° (204), corresponding to the LEW structure, as shown in Fig. 2. With an increase of annealing temperature, the full widths at half-maximum (FWHM) decrease from 0.2362° at 500°C to 0.1378° at 800°C , while the peak intensity shows an increase with annealing temperature, as shown in Table 1. These results indicate that the LEW prepared by sol-gel and heat treated at a high temperature can be expected to have high crystallinity.

Based on the XRD data, the lattice parameter has been estimated to be $a = 0.5201 \sim 0.5207 \text{ \AA}$ and $c = 1.1253 \sim 1.1309 \text{ \AA}$, as shown in Tab. 2. These values are similar to the reference value of $a = 0.5208 \text{ \AA}$ and $c = 1.1282 \text{ \AA}$ for bulk LEW [13].

Figure 3 shows the FE-SEM image of LEW powders according to the annealing temperature. With an increase of annealing temperature, the particle size increases. At 800°C , the mean size of the particles is about $1 \mu\text{m}$, which is suitable for

Table 1. The peak intensity and FWHM of (112) reflection from LEW.

Temperature	Peak intensity	FWHM [$^\circ$]
500°C	2650	0.2362
600°C	2754	0.2360
700°C	2775	0.1771
800°C	3339	0.1378

Table 2. Lattice parameters for the LEW according to the annealing temperature.

Lattice parameter	Ref. [13]	Annealing temperature [$^\circ\text{C}$]			
		500	600	700	800
a [\AA]	0.5208	0.5207	0.5207	0.5204	0.5201
c [\AA]	1.1282	1.1309	1.1268	1.1273	1.1253

fabrication of the SSL devices. For the powders annealed at a temperature below 700°C , the surface of the sample is coarser than that of the sample annealed at 800°C and the shape of the samples is irregular. Therefore, the emission intensity of the samples annealed at below 700°C may be lower than that of the sample annealed at 800°C due to the greater surface scattering.

The excitation and emission spectra of LEW excited by near-UV (395 nm) at ambient temperature as a function of annealing temperature are illustrated in Fig. 4. The luminescence intensity of LEW increases with an increase of annealing temperature, which is because the crystallinity of LEW phosphor increases with annealing temperature, as shown in Fig. 2 and Tab. 1.

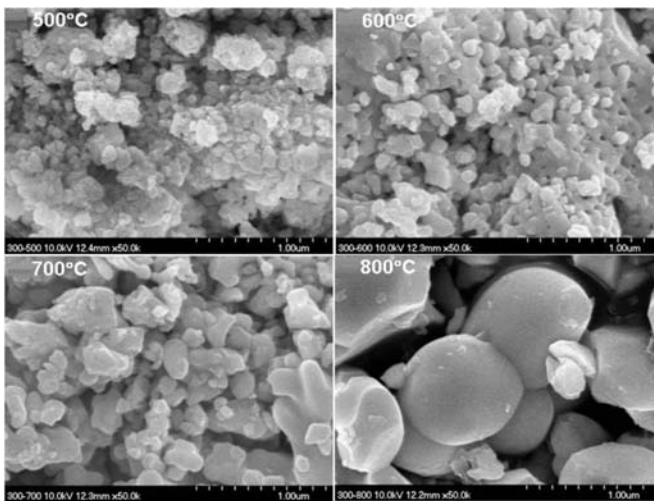


Fig. 3. FE-SEM images of LEW powders as a function of annealing temperature.

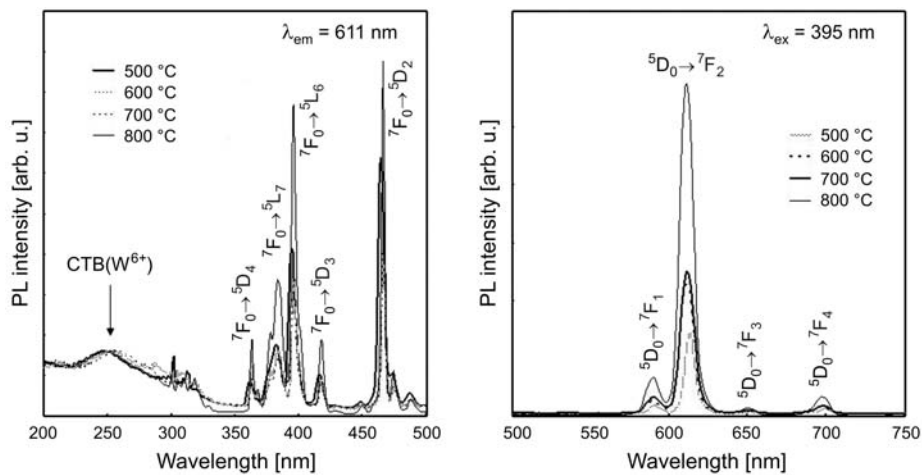


Fig. 4. Excitation and emission spectra of LEW prepared at $500\text{--}800^\circ\text{C}$.

The broad excitation curve near 250 nm is assigned as the charge-transfer band (CTB) originated from oxygen to tungsten within the WO_4^{2-} group, as discussed by SIVAKUMAR and VARADARAJU [14]. The Eu^{3+} excitation spectra of the LEW cover the ranges from long-wavelength UV to visible green-light region (300–500 nm). In the range from 300 to 500 nm, all samples show characteristic intraconfigurational $4f-4f$ emissive transitions of Eu^{3+} : ${}^7F_0 \rightarrow {}^5D_4$ transition for 364 nm, ${}^7F_0 \rightarrow {}^5L_7$ transition for 384 nm, ${}^7F_0 \rightarrow {}^5L_6$ transition for 396 nm, ${}^7F_0 \rightarrow {}^5D_3$ transition for 418 nm, and the ${}^7F_0 \rightarrow {}^5D_2$ transition for 466 nm.

Between the luminescent center and the crystal lattice, two couplings are performed in luminescent materials. One is the strong coupling (WO_4^{2-} group) with high Huang–Rhys factor. The other belongs to the weak coupling (Eu^{3+} ions) with low Huang–Rhys factor [15]. Generally, the strong coupling of CTB (W^{6+}) is predominant, whereas the weak coupling of CTB (Eu^{3+}) is subordinate. When CTB (Eu^{3+}) is excited, the energy absorbed from charge-transfer state is efficiently transferred to Eu^{3+} ion by a non-radiative mechanism, and generates red-light emission of the ${}^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+} . However, in this work, CTB in the range 200–300 nm for WO_4^{2-} group is remarkably weak, compared to that of $\text{LiEuMo}_2\text{O}_8$ [11], and the $f-f$ transitions of Eu^{3+} dominate the excitation process. Comparing the LEW phosphors prepared in this work, the Eu^{3+} transitions in LEW excitation spectra at a high annealing temperature show more effective absorption at near-UV (396 nm) and blue (466 nm), and these wavelengths coincide with those of commercial GaN-based LED.

As regards the annealing temperature the emission spectra are similar, corresponding to typical $4f$ level specific transitions of Eu^{3+} . The main emission peak is ${}^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} at 615 nm, other transitions from ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ located at the range 570–700 nm are weak. The characteristic emission of WO_4^{2-} in LEW is quenched absolutely and only red-light emission of Eu^{3+} appears. The strong emission peak around 615 nm and relatively weak peak around 699 nm is due to the electric dipole energy transition of ${}^5D_0 \rightarrow {}^7F_{2,4}$. The weak emissions of 592 nm and 651 nm are ascribed to the magnetic dipole transition of ${}^5D_0 \rightarrow {}^7F_{1,3}$. The electric-dipole allowed transition would be dominant if Eu^{3+} occupied the lattice site of noncentrosymmetric environment in the scheelite phases [16]. For this reason, the intensity of ${}^5D_0 \rightarrow {}^7F_{2,4}$ was found to be much stronger than that of ${}^5D_0 \rightarrow {}^7F_{1,3}$. When the annealing temperature is increased, the LEW shows stronger red emission at 615 nm by exciting at near-UV wavelength of 395 nm. The reason for this may be that the emission intensity of LEW phosphor depends strongly on the particle shape and size distribution. A narrow size distribution and spherical-like morphology are necessary for the phosphor with good luminescent properties [17]. Compared with the LEW annealed at below 700 °C, the sample annealed at 800 °C has a homogeneous surface and particle shape (see Fig. 4), which are favorable as regards the luminescent properties because of the lesser contamination or fewer dead layers on the phosphor surface. Furthermore, the doping of Eu^{3+} is easier and more effective in sol–gel process than traditional solid-state reaction since all of the starting materials are mixed at the molecular level.

4. Conclusions

Crystalline scheelite-type LEW phosphors for white-LED were prepared at 500–800 °C by using a sol–gel method. The crystal structure, particle shape and luminescent properties under near-UV (395 nm) excitation of the phosphor have been investigated according to the annealing temperature. In the emission spectra, the strongest emission is the electric dipole transition red emission ${}^5D_0 \rightarrow {}^7F_2$ (615 nm), while the magnetic dipole transition orange emission ${}^5D_0 \rightarrow {}^7F_{1,3}$ (592 and 651 nm) is subordinate. Compared with the LEW annealed at below 700 °C, the sample annealed at 800 °C has a high crystallinity, a homogeneous surface and particle shape, which are favorable as regards to luminescent properties because of the lesser contamination or fewer dead layers on the phosphor surface.

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