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Short communication

Sol–gel synthesis of red-emitting $LiEuW_2O_8$ powder as a near-ultraviolet convertible phosphor

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Abstract

$LiEuW_2O_8$ phosphor with the optical function of color conversion from near-UV to red wavelength was prepared by sol–gel method using inorganic salts as a starting material. Viscous mixing sol was prefired at 300 °C for 120 min in air and then white precursor was finally annealed at 800 °C for 240 min in Ar. Structural and photoluminescent properties of the sample were analyzed by an X-ray diffraction analysis, field emission-scanning electron microscope and a fluorescent spectrophotometer. The main emission peak is $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} at 615 nm, other transitions from the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ located at 570–700 nm range are weak. The characteristic emission of WO_4^{2-} in $LiEuW_2O_8$ is quenched absolutely and only red-light emission of Eu^{3+} appears.

Keywords: Phosphor; Sol–gel; Photoluminescent properties

1. Introduction

White LED can be obtained by combining a InGaN blue LED emitting at 465 nm with a broad-band yellow phosphor, e.g., $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) [1,2]. However, there are drawbacks in this combination because 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; the mixture of the tri-color lights present white light, and 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. Three phosphors-converted white LED maintain a very high-color-rendering index ($R_a > 90$) and were believed to offer the greatest potential for high-efficiency SSL [3,4]. 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, lack of proper red phosphors becomes the bottleneck for the SSL devices.

Recently, much attention has been paid to make superior red phosphor for white LED. Previously reported scheelite-type compound, $LiEuW_2O_8$ (LEW), can be 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 [5]. Most of LEW was produced from metal oxides by conventional solid-state reaction at above 1000 °C [6]. As far as we know, there is a little information on the successful sol–gel synthesis of LEW red phosphor.

In this work, we report the preparation of LEW phosphors with the optical function of color conversion from near-UV to red by sol–gel method.

2. Experimental

For the synthesis of LEW, stoichiometric mixtures of lithium acetate dehydrate ($C_2H_3LiO_2{\cdot}2H_2O$), europium(III) nitrate

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pentahydrate [$Eu(NO_3)_3 \cdot 5H_2O$], and tungsten(VI) chloride (WCl_8) 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, homogeneous colorless solution was obtained. The solvent was slowly evaporated off from solution at 100 °C and a colorless precursor with high viscosity was obtained. Subsequently the precursor pyrolyzed in a dry oven at 300 °C for 120 min in air to obtain white powder. Finally the dried powder was annealed in a tube furnace at 800 °C for 240 min in Ar (heating rate: 3 °C/min).

X-ray diffraction profiles were measured using an X-ray diffractometer (XRD, D-Max-1200, Rigaku, Japan). Particle shape was 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

On the basis of the structural analysis of isomorphic $LiY(MoO_4)_2$ [7], scheelite-type LEW has the following crystallographic properties: (i) the crystal structure belongs to a tetragonal system with its space group of $I4_1/a$, (ii) randomly distributed dodecahedra of LiO_8 and EuO_8 are surrounded by WO_4 tetrahedral units. Fig. 1 gives the XRD pattern of LEW. The sample is isostructural and belongs to the tetragonal system of scheelite-type. In this letter, isomorphic $NaYW_2O_8$ (JCPDS no. 48-886) is used to compare, since the crystal structure analysis of LEW has not been reported yet and $NaYW_2O_8$ exhibits an identical diffraction pattern to bulk LEW [8]. In this structure, W^{6+} occupies the tetrahedral sites constructed with O^{2-} composing $WO_4{}^{2-}$ anion complex. Li^{2+} is eight-coordinated with O^{2-}, forming a distorted cube. The dopant Eu^{3+} occupies the Li^{2+} site. Since there is no significant shift in the peak location, we can consider that the doped Eu^{3+} has little influence on the host structure. When the pyrolyzed white gel was annealed at 800 °C, the scheelite-type LEW phase and some Li_2WO_4 phase appeared.

The major diffraction peak at $2\theta \approx 29^\circ$ (1 1 2) reflection and other diffraction peaks occurred at $2\theta \approx 18.8^\circ$ (1 0 1), 31.7° (0 0 4), 34.4° (2 0 0) and 47.5° (2 0 4), corresponding to the LEW structure, as shown in Fig. 1. On the basis of XRD data, the lattice parameter has been estimated to be a = 0.5201 Å and c = 1.1253 Å. These values are similar to the reference value of a = 0.5208 Å and c = 1.1282 Å for bulk LEW [9].

Fig. 2 shows the FE-SEM image of LEW powder. The mean size of the particles is about 1 μm, which fit to fabricate of the SSL devices. The surface of the sample is homogeneous and the shape of the sample is regular. Therefore, the emission intensity of the sample may be high due to less surface scattering.

The excitation and emission spectra of LEW excited by near-UV (395 nm) at ambient temperature are shown in Fig. 3(a) and (b). 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 [10]. 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, sample shows characteristic intra-configurational 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 luminescent center and 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 [11]. 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 generate red-light emission of the ${}^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+}. However, in this work, CTB in 200–300 nm range for $WO_4{}^{2-}$ group is remarkably weak, compared with that of $LiEuMo_2O_8$ [6] and the f–f transitions of Eu^{3+} dominate the excitation process. The Eu^{3+} transitions in LEW excitation spectra show effective absorption at near-UV (396 nm) and blue (466 nm), and these wavelengths coincide with those of commercial GaN-based LED.

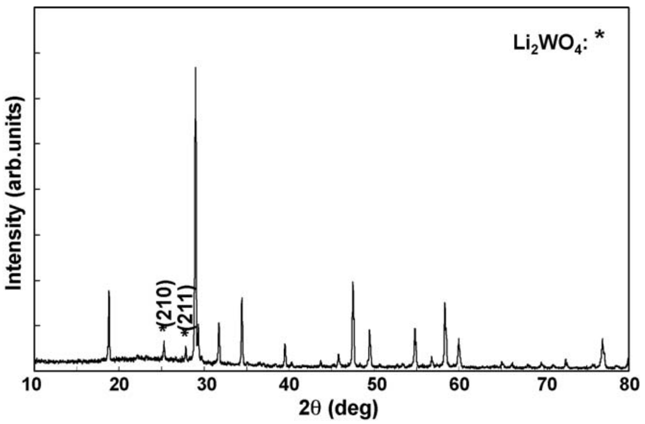

Fig. 1. XRD pattern of LEW powder.

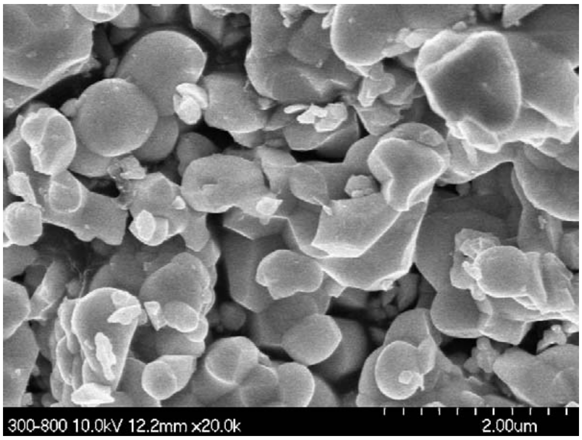

Fig. 2. FE-SEM image of LEW powder.

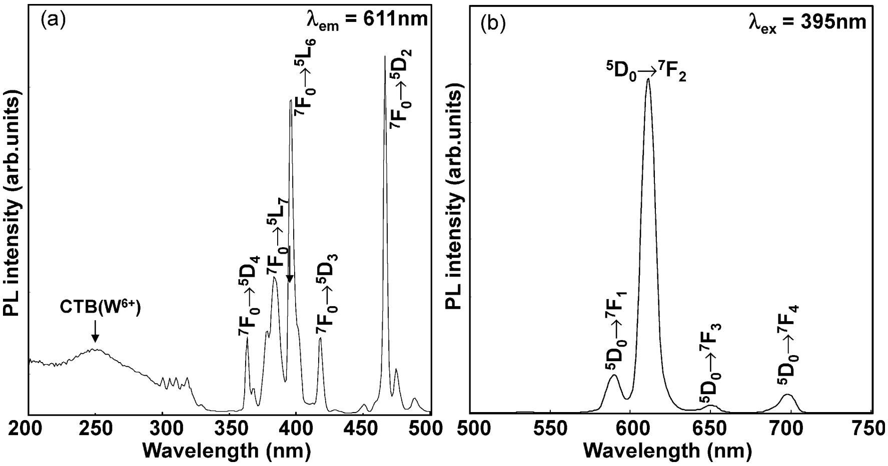

Fig. 3. Excitation (a) and emission (b) spectra of LEW.

As shown in Fig. 3(b), emission spectra show typical 4f levels 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 the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ located at 570–700 nm range 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 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 when Eu^{3+} occupied the lattice site of noncentrosymmetric environment in the scheelite phases [12]. For this reason, the intensity of $^5D_0 \rightarrow {}^7F_{2,4}$ was found to be much stronger than that of $^5D_0 \rightarrow {}^7F_{1,3}$.

A narrow size distribution and spherical-like morphology are necessary for the phosphor with good luminescent properties. The sample annealed at 800 °C has a homogeneous surface and particle shape (see Fig. 2), which are favorable to luminescent properties because of less contamination or fewer dead layers on the phosphor surface. Furthermore, doping of Eu^{3+} is more easy and effective in sol–gel process than traditional solid-state reaction since all of the starting materials are mixed at the molecular level. However, the intensity of Eu^{3+} emission is weaker when compared to that due to Eu^{3+} excitation and generally weak emission of $^5D_0 \rightarrow {}^7F_0$ (~580 nm) is absent [11]. This reveals that the energy transfer from the WO_4^{2-} group to Eu^{3+} is not efficient. More research on the pyrolysis and annealing conditions to improve luminescent properties will be done.

4. Summary

Crystalline scheelite-type LEW phosphors for white-LED were prepared by using a sol–gel method. 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. The sample annealed at 800 °C has a homogeneous surface and particle shape, which are favorable to luminescent properties.

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