Luminescence of Eu^{3+} and Sm^{3+} Doped Potassium Tungstate Phosphor

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Abstract

The luminescent properties of Eu^{3+} and Sm^{3+} doped potassium tungstate phosphor are investigated. The $K_{4-3x}(WO_4)_2$: Eu$^{3+}_x$,Sm$^{3+}_y$ phosphor is produced by firing the mixed precursors, followed by re-firing with a flux. The re-firing process results in the defect-free surface and uniform growth of the particles. The strong absorption in the region of ultra violet light is observed due to the $4f$-$4f$ electron transitions of the Eu^{3+} and Sm^{3+} ions. The doping concentration of europium into potassium tungstate is relatively high, compared to other host materials. It is revealed that the crystal structure is a monoclinic with space group, $C2/c$. This crystal structure facilitated the Eu^{3+} ions to be located with the Eu-Eu distance larger than 5 Å so that concentration quenching does not occur even at high doping concentration. The excitation spectrum could be adjusted by the introduction of the samarium. A small amount of the Sm^{3+} ions that acts as a sensitizer increases the energy absorption peak around 405 nm.

Keywords : europium, samarium, potassium tungstate, phosphor, LED, flux

1. Introduction

The light emitting diode (LED) has drawn great attention as a future illuminator for solid-state lighting. There are several approaches in the white light source using the LED. Among them, the phosphor-based white light source is the most promising. In this system, the three phosphors of red, green, and blue absorbs the UV light from the UV-LED, and generates the white light. Even though the phosphors to be applied in the white emitting LED are currently being developed, the red phosphor still has problems of low brightness and chemical instability [1]. Therefore, there is increasing demand for a new red phosphor that can be applied in the white emitting LED. Most phosphors show a strong energy absorption tendency in the wavelength region of less than 300nm due to the charge transfer and $4f^n$-$4f^{n-1}5d$ transition [2]. However, the LED used in solid-state lighting provides UV light of within the range of 380 to 480nm, which necessitates, the new red phosphor to be excited by these wavelengths and have high brightness.

The europium among rare earths has been used as an activator in the red phosphors because of the strong red emission. However, most of host lattice materials applied in a red phosphor can be doped by remarkably small amount of europium (0.01~0.05 mol%) due to concentration quenching. Therefore, a large quantity of europium should be used in the new host lattice to absorb the UV light. It has been known that the cations in self-emitting phosphors, such as calcium tungstate and sodium tungstate, can be substituted by activator ions up to 100% [3,4].

In this study, potassium tungstate was used as a host material. The europium and samarium were co-doped into the crystal as the activator and sensitizer. The conditions in a production process were optimized to produce the uniform-sized particles. The role of the europium and samarium was investigated from the excitation and emission spectra. Especially, the effect of crystal structure and local environment of Eu^{3+} ion on the luminescence was given the most attention.

2. Experiments

In this study, K_2CO_3, WO_3, Eu_2O_3, and Sm_2O_3 (Kojundo Chemical Lab Co., 99.9 %) were used as starting materials. The mixture of oxides composed of $K_{4-3x}(WO_4)_2$: Eu$^{3+}_x$,

Sm^{3+}_y was prepared by ballmilling for 10 h. After drying, the mixture was fired in a box furnace at 800~950 °C for 2 h. The as-produced powder was re-fired at 900 °C for 2 h with a flux of boron oxide. The re-fired powder was soaked in warm water during ultrasonication to remove the residual flux. After complete dissolution of the flux, the powder was collected from the solution by centrifuging.

Powder morphology was observed by scanning electron microscope (SEM, JSM-6360, JEOL, Japan). The phase and crystalline structure were analyzed using X-ray diffractometer (XRD, M18XHF-SRA, MAC Science Co., Japan). The XRD data were analyzed using Rietveld method. To investigate the change of structure and phase with respect to the firing temperature, a differential temperature analysis (DTA, DSC910S, TA Instrument, USA) was performed. The excitation and emission spectra were measured at a room temperature using a spectrofluorometer (JASCO, FP-6500, Japan).

3. Results and Discussion

3.1 Effect of Firing Conditions

The phase and crystal structure of the potassium tungstate phosphor depend on firing temperature. The DTA result of Fig. 1(a) shows the several peaks indicating the occurrence of reactions. The XRD results of Fig. 1(b) shows that the undesired phases, such as $Eu_2(WO_4)_3$ and K_2WO_4, were formed at the firing temperature lower or higher than 900 °C. By comparing the results of DTA and XRD, it was confirmed that K_2WO_4 and $Eu_2(WO_4)_3$ were favored at the firing temperature lower than 800 °C and higher than 1000 °C, respectively. Based on this, we can conclude that the optimum firing tem-perature for the production of the $K_{1.6}(WO_4)_2$: $Eu^{3+}_{0.8}$ phosphor is 900 °C. The powders fired at 900 °C were re-fired at 900 °C with a flux. The re-firing process led to the uniform growth of the particles and the breaking of agglomeration as shown in Fig. 2. The surface of the re-fired particles seemed defect-free. When the powder was re-fired with a flux, the emission intensity was increased due to the uniform particle size and defect-free surface. Fig. 3 shows the excitation and emission spectra of the powders with respect to the firing temperature. (The re-firing temperature was fixed to 900 °C.) The excitation spectra of
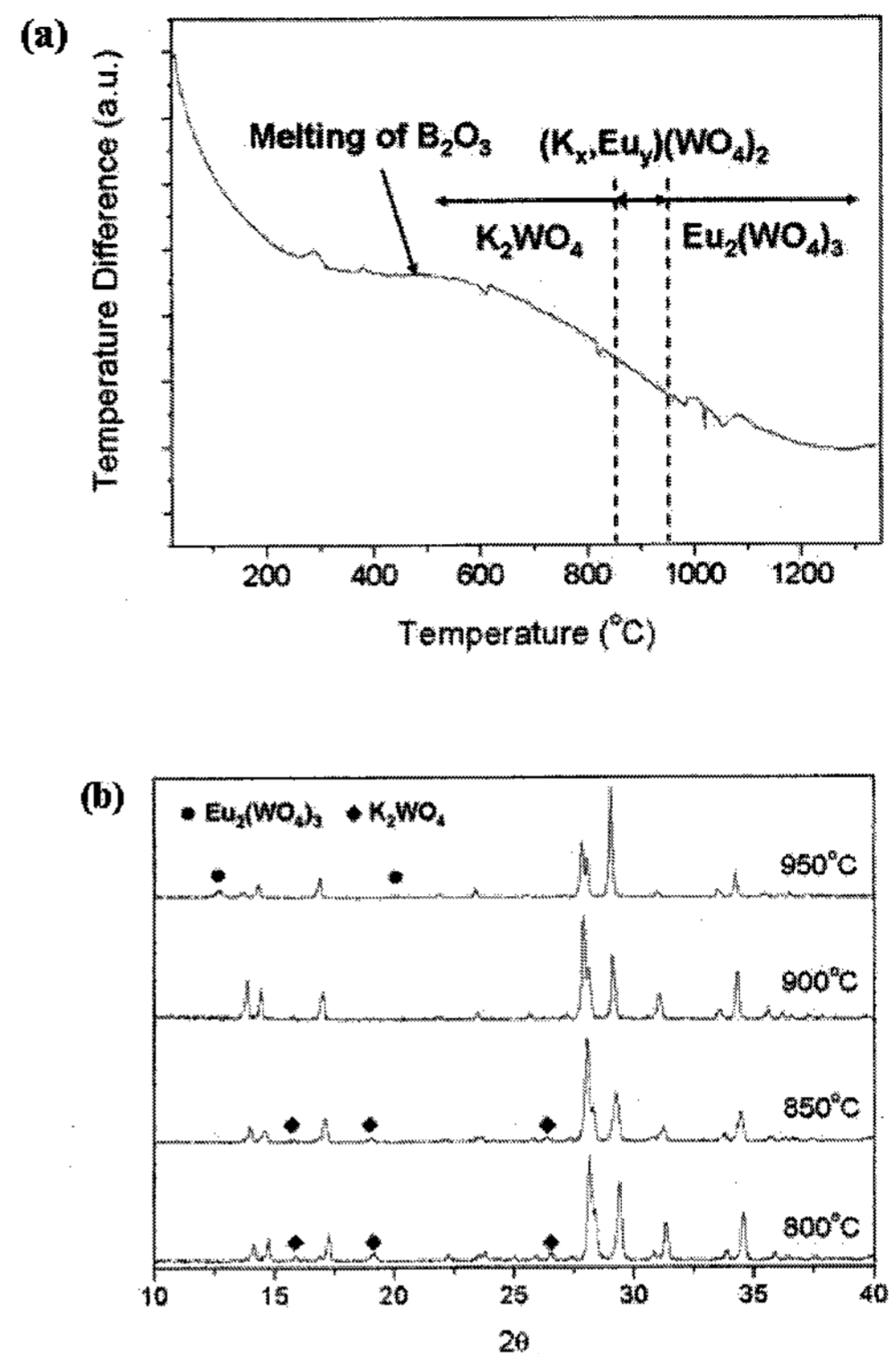

Fig. 1. (a) DTA result of the mixture of starting powders and (b) XRD results of the $K_{1.6}(WO_4)_2$: $Eu^{3+}_{0.8}$ powders fired at different temperatures for 2 h.

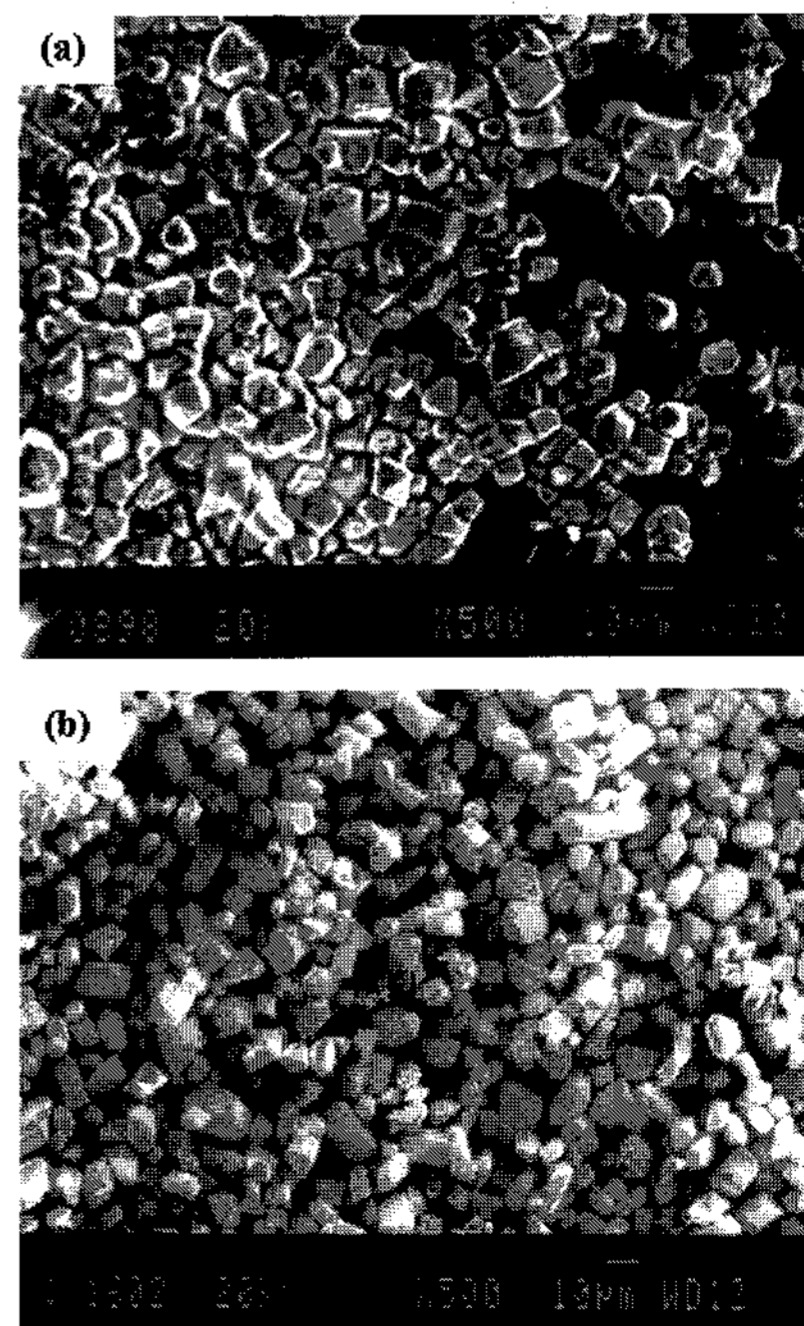Fig. 2. SEM micrographs of the $K_{1.6}(WO_4)_2$:$Eu^{3+}_{0.8}$ powders (a) fired at 900°C for 2h and (b) re-fired at 900°C for 2h with a flux.
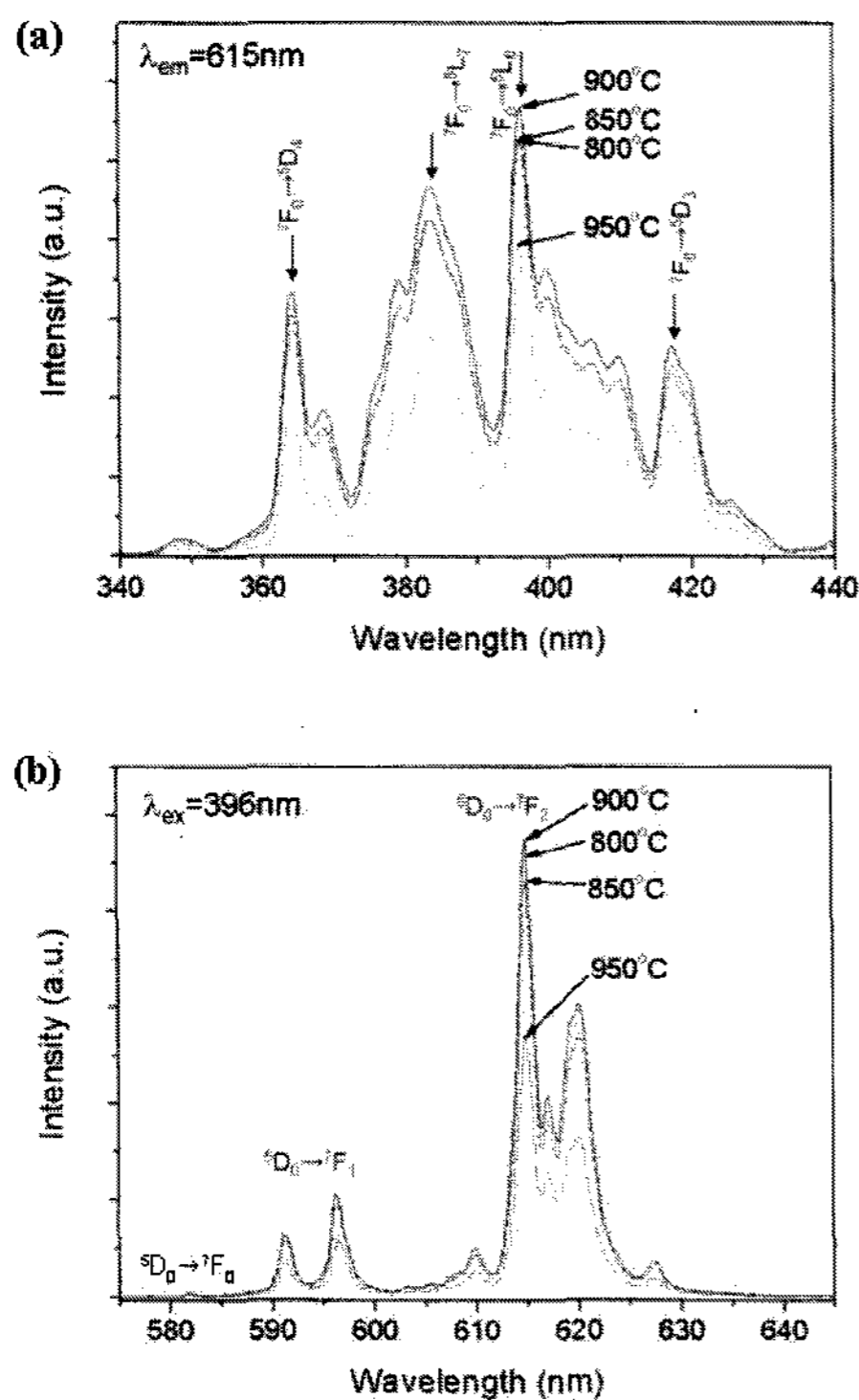
Fig. 3. (a) Excitation and (b) emission spectra of the $K_{1.6}(WO_4)_2$: $Eu^{3+}_{0.8}$ powders fired at different temperatures for 2 h, followed by re-firing at 900 °C for 2h with a flux.

Fig. 3(a) indicates that the $K_{1.6}(WO_4)_2$: $Eu^{3+}_{0.8}$ absorbs a UV light at the range between 345 nm an 432 nm, which is attributed to the $4f$-$4f$ electron transition of the Eu^{3+} ions [5]. When excited by 396 nm, the phosphor fired at 900 °C showed relatively strong emission peaks as shown in Fig. 3(b).

3.2 Effect of Doping Concentration

In order to find out the effect of doping concentration on the luminescence, x value of $K_{4-3x}(WO_4)_2$: Eu^{3+}_x was varied. It was confirmed that the phosphor with x=0.8 displayed maximum brightness as shown in Fig. 4. Moreover, the relative increase in the intensities of 615 nm and 620 nm peaks which result in the improved chromaticity. The high doping concentration of the Eu^{3+} ions in the potassium tungstate phosphor is ascribed to the unique crystal structure that has a long distance among the Eu^{3+} sites. The details of crystal structure will be explained later.

The excitation spectra were adjusted by adding a small amount of samarium as shown in Fig. 5(a). The intensity of excitation peak at 405 nm was enhanced with increasing doping concentration of the samarium. When the
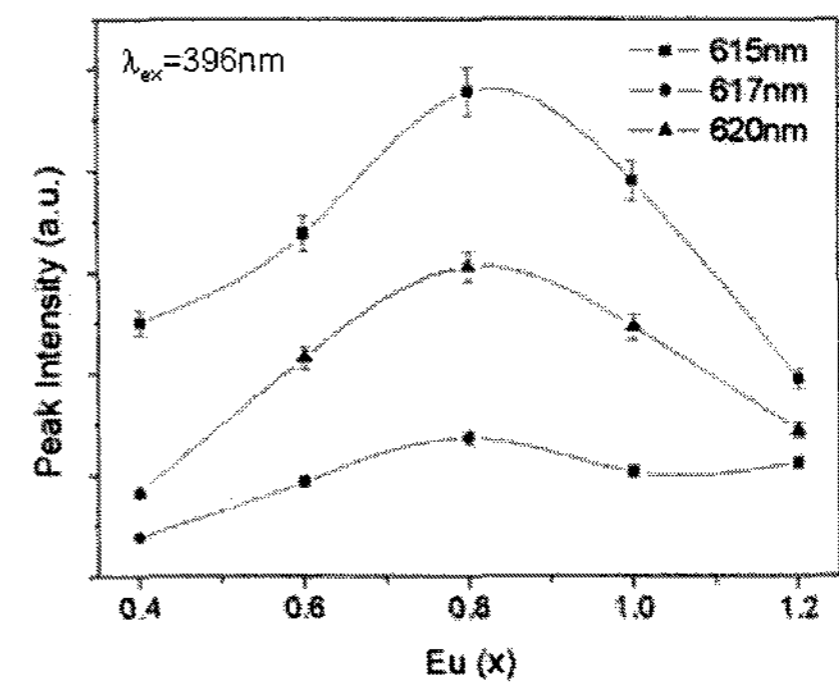

Fig. 4. Change in the emission intensities of three main peaks of the $K_{4-3x}(WO_4)_2$: Eu^{3+}_x powders with respect to the doping concentration of the Eu^{3+} ions.
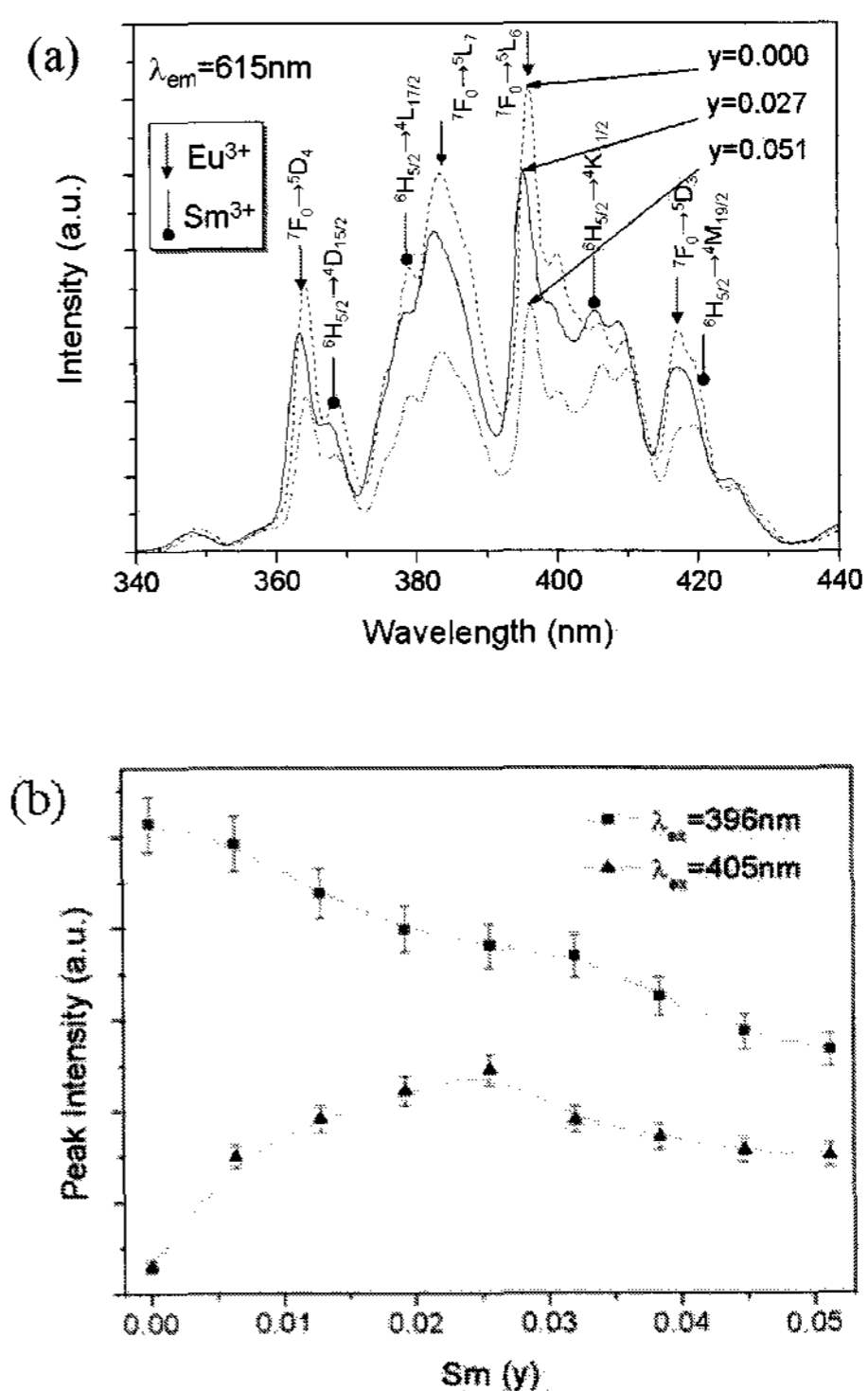

Fig. 5. (a) Excitation spectra and (b) change in the emission intensities of $K_{1.6}(WO_4)_2$:$Eu^{3+}_{0.8}$, Sm^{3+}_y powders with respect to the doping concentration of the Sm^{3+} ions. The two types of arrows in (a) indicate the energy level transitions of the Eu^{3+} and Sm^{3+} ions, respectively.

$K_{1.6}(WO_4)_2$: $Eu^{3+}_{0.8}$,Sm^{3+}_y phosphor was excited by 396 nm and 405 nm, the change in the peak intensities was different according to the excitation wavelength as shown in Fig. 5(b). The absorptions of 396 nm and 405nm wavelengths are assigned to the $^7F_0 \rightarrow ^5L_6$ transition of the Eu^{3+} ions and the $^6H_{5/2} \rightarrow ^4K_{1/2}$ transition of the Sm^{3+} ions,
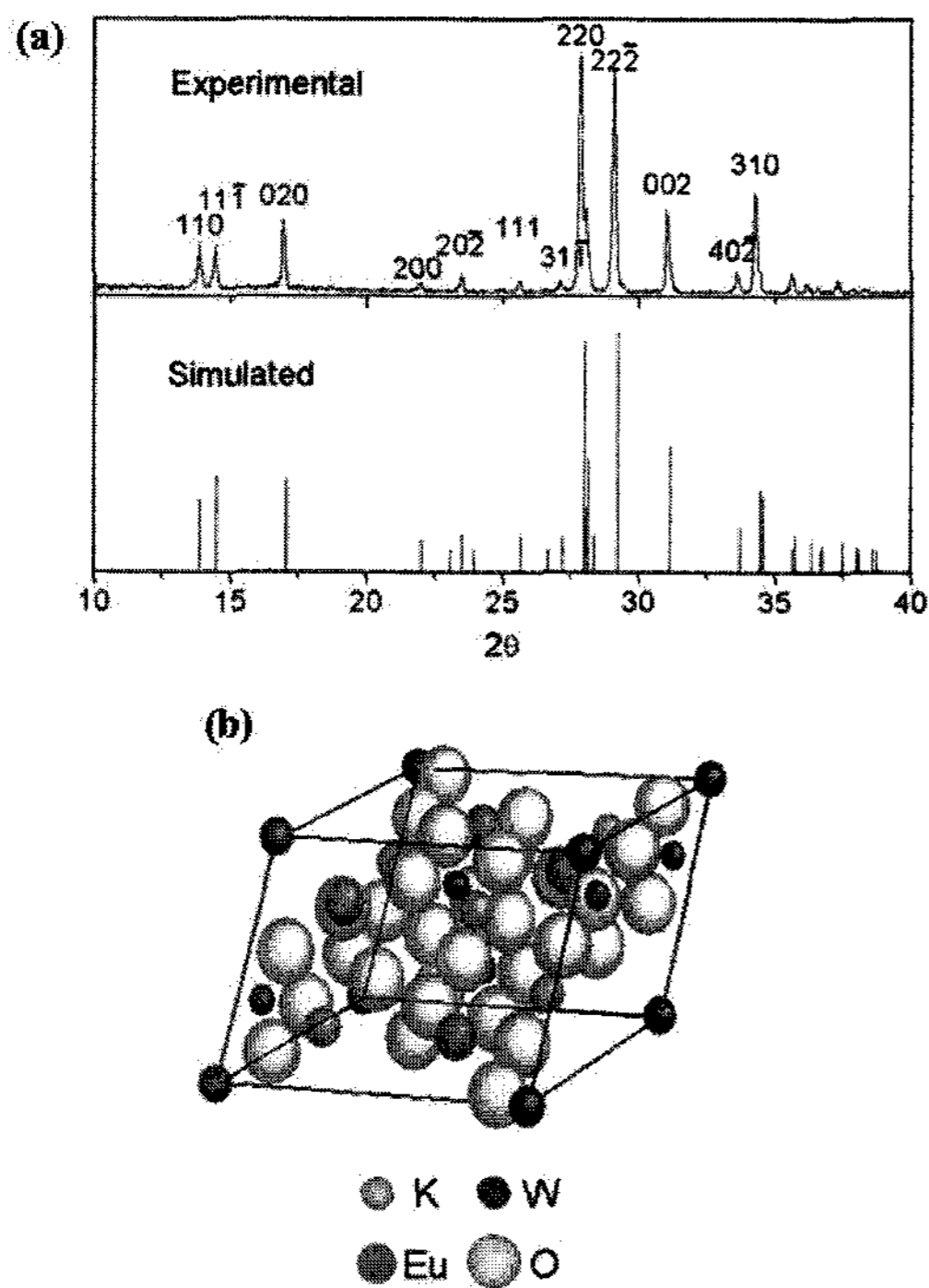
(a)

(b)

Fig. 6. (a) Experimental and simulated results of the X-ray diffraction pattern and (b) crystal structure of the $K_{4-3x}(WO_4)_2$: Eu^{3+}_x phosphor.

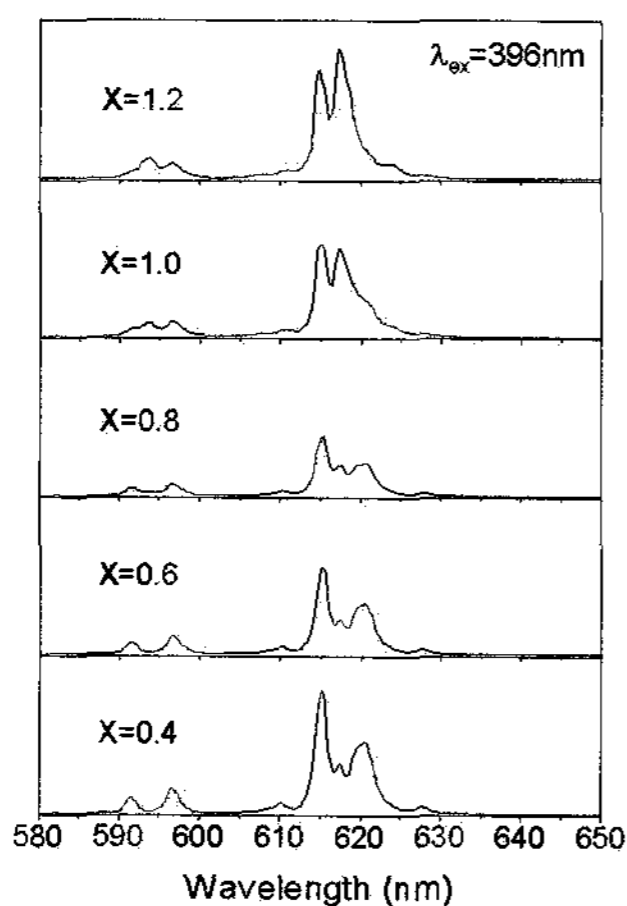Fig. 7. Emission spectra of the $K_{(4-3x)/2}(WO_4)_2$:Eu^{3+}_x phosphor.

respectively. When the concentration of the Sm^{3+} ions increased, the emission by 396 nm kept decreasing due to the Eu-Sm energy transfer, while the emission by 405 nm increased due to the $4f$-$4f$ electron transition of the Sm^{3+} ions. When the doping concentration of the Sm^{3+} ions increased to $y=0.027$, the peak intensity of the phosphor excited by 405 nm decreased. This shows that the excitation wavelength of the $K_{4-3x}(WO_4)_2$: Eu^{3+}_x,Sm^{3+}_y phosphor
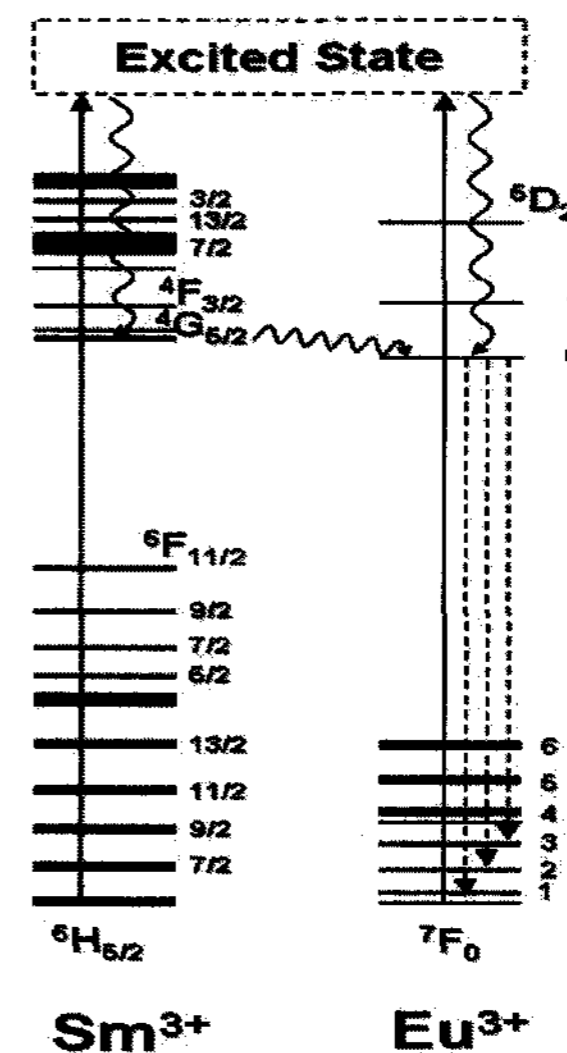

Fig. 8. Schematic representation of energy transfer and emission processes in the rare earths ions.

can be optimized by changing the doping concentration of the Sm^{3+} ions according to the wavelength that the LED.

3.3 Analysis of Crystal Structure

Using the Rietveld method, it was found that the crystal structure of the $K_{4-3x}(WO_4)_2$: Eu^{3+}_x,Sm^{3+}_y phosphor is a monoclinic with space group of $C2/c$. Fig. 6(a) shows that the experimental XRD result corresponds to the simulated one. The Eu^{3+} ions are located in the sites of the K^+ ions and surrounded by oxygen in the crystal as shown in Fig. 6(b). The Eu-O distance in this crystal is so small (~2.405 Å) that the energy level splitting in large numbers can be generated by a strong crystal field. Fig. 7 shows that, when the composition of $K_{(4-3x)/2}(WO_4)_2$: Eu^{3+}_x is prepared in order to generate the more vacancies in the K^+ sites, the number of energy level splitting in the $^5D_0 \rightarrow {}^7F_2$ transition is reduced due to the increase of the Eu-O distance, i.e., a weak crystal field. However, as the Eu-Eu distance in the crystal is larger than 5Å, the exchange transfer of the absorbed energy among Eu^{3+} ions becomes difficult, meaning that the concentration quenching rarely occurs [6]. Therefore, the fact that the doping concentration of the Eu^{3+} ions in the potassium tungstate phosphor is relatively high compared to other host lattice materials can be explained in terms of the unique crystal structure of the $K_{4-3x}(WO_4)_2$: Eu^{3+}_x,Sm^{3+}_y phosphor.

The schematic representation of Fig. 8 briefly shows how the rare earths in the potassium tungstate phosphor

absorbs energy (UV light) and emits a red light. Based on the fact that emission due to the Sm^{3+} ions is not observed and the excitation of the Sm^{3+} ions leads to the emission of the Eu^{3+} ions, it can be concluded that the Sm^{3+} ions acts as a sensitizer in the potassium tungstate phosphor.

4. Conclusions

The Eu^{3+} and Sm^{3+} doped potassium tungstate phosphor was produced by the solid-state reaction, followed by re-firing with a flux. The strong energy absorption in the region of the ultra violet light can be explained by the $4f$-$4f$ electron transitions of the Eu^{3+} and Sm^{3+} ions. In addition, it was found that a large amount of the Eu^{3+} ions doped into the host material facilitated the phosphor to absorb the UV light from the LED more efficiently. The excitation spectrum could be adjusted by adding a small amount of Sm^{3+} ions, which act as a

sensitizer. The long Eu-Eu distance and short Eu-O distance in a monoclinic crystal led to the more energy level splitting and high doping concentration of the Eu^{3+} ions.

References

[1] E. F. Schubert and J. K. Kim, *Science,* **308**, 1274 (2005).

[2] G. Blasse and B. C. Grabmaier, Luminescent Materials (Springer-Verlag, New York, 1994), p.42.

[3] R. C. Ropp, Luminescence and the Solid State (Amsterdam-Oxford, New York-Tokyo, 1991), p. 305.

[4] G. Gouedard, D. Husson, C. Sauteret, F. Auzel, and A. Migus, *J. Opt. Soc. Am. B,* **10**, 2358 (1993).

[5] Z. X. Cheng, S. J. Zhang, J. R. Han, H. C. Chen, X. S. Liu, Y. Y. Yang, and J. Yang, *Cryst. Res. Technol.,* **36**, 135 (2001).

[6] S. Shionoya and W. M. Yen, Phosphor Handbook (CRC Press, Boca Raton, Boston, 2000), p. 185.