

## Luminescence of $\text{Eu}^{3+}$ and $\text{Sm}^{3+}$ Doped Potassium Tungstate Phosphors

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### Abstract

*The luminescent properties of  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  doped potassium tungstate phosphor were investigated. The  $\text{K}_{4-3x}(\text{WO}_4)_2:\text{Eu}_x,\text{Sm}_y$  phosphor was produced by firing the mixed precursors, followed by re-firing with a flux. The re-firing process provided the clean surface to the particles. The excitation spectra showed that the strong absorption in the region of ultra violet light occurred due to the high europium doping concentration. The incorporation of europium to potassium tungstate was easier, compared to other host materials. The excitation spectra could be controlled by the small addition of samarium. The increase of energy absorption around 405nm was assigned to the  $\text{Sm}^{3+}$  ions. The comparison between real x-ray diffraction and simulated one revealed that the crystal structure of  $\text{K}_{4-3x}(\text{WO}_4)_2:\text{Eu}_x,\text{Sm}_y$  phosphor is monoclinic with a space group,  $\text{C2/c}$ .*

### 1. Introduction

The demand for a red phosphor applicable to the LED (light emitting diode) has been increased. The low brightness of a red phosphor excited by ultra violet light (UV) has caused difficulties to establish the white-emitting LED for lightening system. Most of phosphors shows the strong absorption in the region less than 300nm through the charge transfer or  $4f^n-4f^{n-1}5d$  transition.[1] However, a light emitting diode provides the UV light with ~400nm wavelength. Therefore, the design of a new phosphor material, which can be excited by UV light and have high brightness, has been focused recently.

The europium among rare earths has been used as an activator because of the absorption of UV light within  $4f$  levels and emission of a red light. However, most of host lattice structure applied in a red phosphor can be doped by europium with a range of 0.01~0.05 mol%. In order to emit more photons, a new host lattice, which can be doped by the europium of higher concentration, has been required. In the crystals used for a self-emitting phosphor such as calcium tungstate

and sodium tungstate, it has been known that cation can be substituted by an activator ion up to 100%.[2]

In this study, potassium tungstate was used as a host lattice. The europium and samarium were doped into the crystal as an activator. The conditions in a process were optimized to produce the uniform-sized and surface-modified phosphor particles. The role of europium and samarium was investigated from the emission and excitation spectra. Especially, the effect of crystal structure and local environment of  $\text{Eu}^{3+}$  ion on the luminescence was focused.

### 2. Experimental

As starting materials,  $\text{K}_2\text{CO}_3$ ,  $\text{WO}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Sm}_2\text{O}_3$  (Kojundo Chemical Lab Co., 99.9%) were used. The mixture of oxides was prepared to be a composition of  $\text{K}_{4-3x}(\text{WO}_4)_2:\text{Eu}_x,\text{Sm}_y$ , followed by ballmilling for 10h. After drying, the mixture was fired in a box furnace at 800~950°C for 2h. To produce the uniform-sized and surface-modified phosphor, the powder was re-fired at 800~1200°C for 2h with a flux of boron oxide (1wt%). The re-fired powder was soaked in warm water during ultrasonication to remove the residual flux. After complete dissolution of a flux, the powder was separated from a solution by centrifuging and dried in an oven of 80°C.

Powder morphology was observed by scanning electron microscope (SEM, JSM-6360, JEOL, Japan). The phase and crystalline structure was 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, differential temperature analysis (DTA, DSC910S, TA Instrument, USA) was used. The excitation and emission spectra were measured at a room temperature using a spectrofluorometer (JASCO, FP-6500, Japan). The EXAFS analysis was conducted to reveal the local environment of  $\text{Eu}^{3+}$  ion in a 7C beam line of Pohang accelerator laboratory.

### 3. Results and Discussion

#### 3.1 Effect of Firing Conditions

The optimum firing temperature was 900°C. At the firing temperature lower or higher than 900°C, the undesired phases were found. It corresponded to the DTA result. The fired powders have different morphologies with respect to the temperature as shown in figure 1. The luminescent properties were improved through re-firing process with a flux. The re-firing and flux leads to the uniform growth of particles as shown in figure 2. Moreover, the surface is modified to reduce the defects. Figure 7 shows the excitation and emission spectra of fired and re-fired powders. When the powder was fired and re-fired at 900°C, the emission intensity of 615nm was strongest as shown in figure 3(c).

#### 3.2 Effect of doping concentration

When the compound of  $K_{4-3x}(WO_4)_2:Eu_x,Sm_y$  was examined to find out the effect of europium doping concentration on the luminescence, optimum europium doping concentration was  $x=0.8$  as shown in figure 4, which is higher than the doping concentration used in other phosphors. The excitation spectra showed the lowered excitation band of host lattice (~250nm), while the increased one of europium (~400nm). The strongest excitation peak was found to be at 396nm.

The addition of small amount of samarium increased the intensity of excitation peak at 405nm as shown figure 5. In conclusion, the fine tuning of excitation peak was feasible.

#### 3.3 Analysis of Crystal Structure

When Rietveld method was used, the crystal structure of  $K_{4-3x}(WO_4)_2:Eu_x,Sm_y$  phosphor was found out to be a monoclinic with a space group of,  $C2/c$ . A europium ion is located in the potassium site and surrounded by oxygen as shown figure 6.

Fourier transform of Eu  $L_{2,3}$  edge EXAFS function of figure 7 shows oxygen is close to the  $Eu^{3+}$  ion. It give rise to the more splitting of emission lines around 615nm.

### 4. Conclusions

The  $K_{4-3x}(WO_4)_2:Eu_x,Sm_y$  phosphor can be used in white-emitting LED, which is composed of three phosphors (R, G, B) and UV-LED. The morphology of powder was improved by re-firing process with a

flux. The re-fired phosphor give a bright red light by UV absorption. The improved luminescent properties of  $K_{4-3x}(WO_4)_2:Eu_x,Sm_y$  phosphor is attributed to the high doping concentration and crystal structure with a short Eu-O distance. Moreover, the fine tuning of excitation peaks by the addition of samarium enable the  $K_{4-3x}(WO_4)_2:Eu_x,Sm_y$  phosphor to be applied in the UV-LED that provides UV light of 390~410.

### 5. References

- [1] G. Blasse, and B. C. Grabmaier, Luminescent Materials, Springer-Verlag, New York, 42-44, 1994.
- [2] R. C. Ropp, Luminescence and the Solid State, Amsterdam-Oxford, New York-Tokyo, 1991.

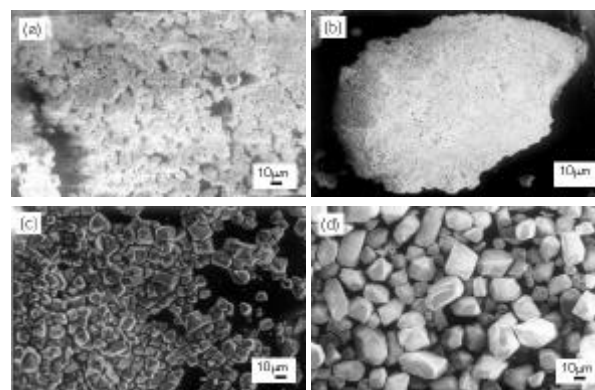


Figure 1. SEM micrographs of  $K_{1.6}(WO_4)_2:Eu_{0.8},Sm_{0.0256}$  powders fired at different temperature, (a) 800°C, (b) 850°C, (c) 900°C, (d) 950°C for 2h.

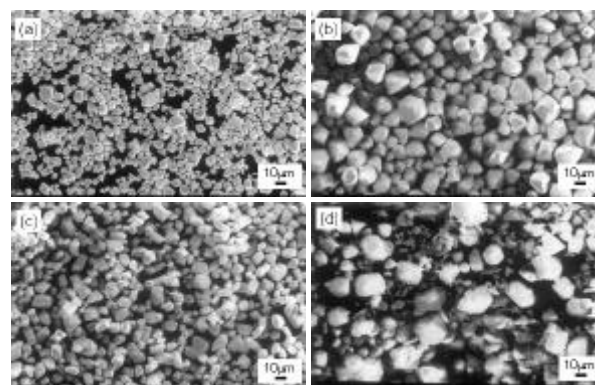


Figure 2. SEM micrographs of  $K_{1.6}(WO_4)_2:Eu_{0.8},Sm_{0.0256}$  powders fired at different temperature, (a) 800°C, (b) 850°C, (c) 900°C, (d) 950°C for 2h, followed by re-firing at 900°C for 2h with a flux.

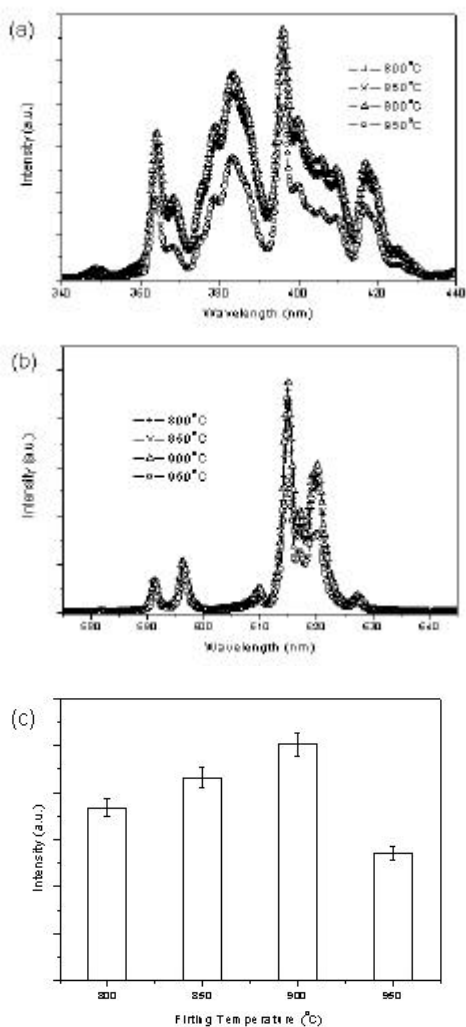


Figure 3. (a) excitation and (b) emission spectra of  $K_{1.6}(WO_4)_2:Eu_{0.8},Sm_{0.0256}$  powders fired at different temperature for 2h, followed by re-firing at 900°C for 2h with a flux. The intensities of 615nm emission peak in powders fired at different temperature were plotted as shown in (c).

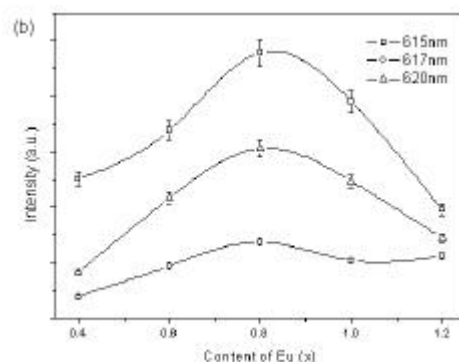
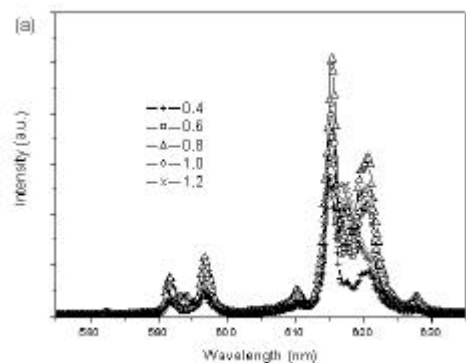


Figure 4. (a) emission spectra and (b) emission intensities of three main peaks of  $K_{4-3x}(WO_4)_2:Eu_x$  powders.

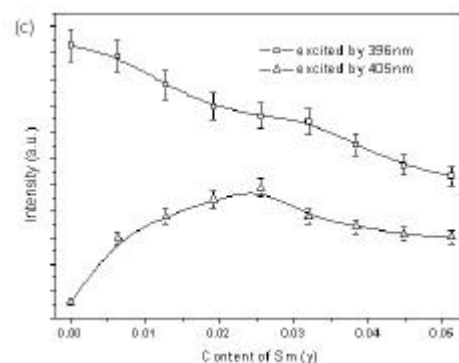
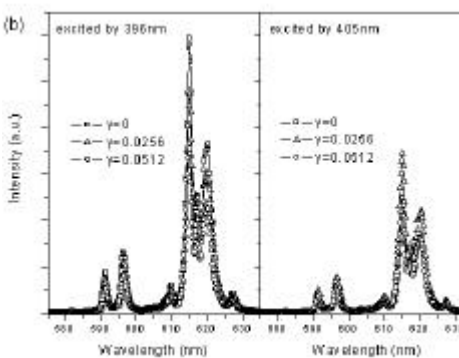
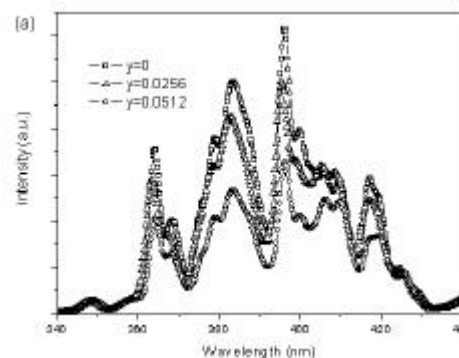


Figure 5. (a) excitation and (b) emission spectra of  $K_{1.6}(WO_4)_2:Eu_{0.8},Sm_y$  powders. The emission spectra were measured in the powders excited by 396nm and 405nm respectively. The intensities of 615nm emission peak in powders excited by 396nm and 405nm were plotted as shown in (c).

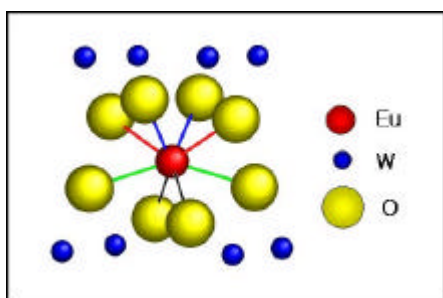


Figure 6. Local structure of  $Eu^{3+}$  in  $K_{1.6}(WO_4)_2:Eu_{0.8}$  phosphor.

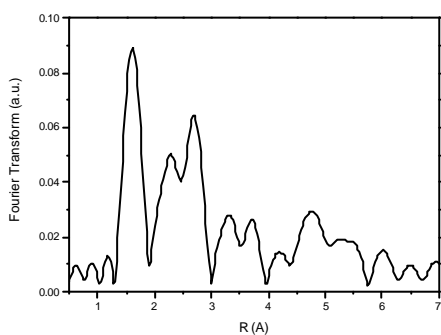


Figure 7. Fourier transform of  $Eu L_2$  edge EXAFS function.