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Synthesis and luminescence properties of $Eu_{2-x}Y_xW_2O_9$

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Abstract

The luminescence properties of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.8$) were studied. These samples were prepared by solid-state reaction. The purpose of this work was to see the luminescence variations due to the amount of Y^{3+} ions and preparation temperatures. The samples 0–50 mol% Y^{3+}-doped and fired at 900–1100 °C showed a single phase. In them, 20 mol% Y^{3+}-doped and fired at 1100 °C showed high emission intensity at the range of 614 nm. On the other hand, 30 mol% Y^{3+}-doped samples fired at 1150 and 1200 °C included $Eu_2W_3O_{12}$ as another component. The highest luminescence intensity was shown in 30 mol% Y^{3+}-doped and fired at 1150 °C. It seems that another component related to the high luminescence intensity in these phosphors.

Keywords: $Eu_2W_2O_9$; Yttrium; Phosphor; X-ray diffraction; Luminescence

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1. Introduction

It has been investigated that near UV-LED combined with three component RGB emitters as a white LED phosphor. In RGB phosphors, red emitting phosphor is most difficult for single excitation source from 380 to 410 nm. And luminescence intensity of red one is lower than that of green and blue ones. The color purity in the phosphors for the fluorescent lamp is very important to make pure white color. There are considerable numbers of lanthanum tungstates, have been performed as a red emitting phosphor [1]. Nowadays, fluorescent materials find a wide variety of applications. Phosphors need good absorbers and efficient emitters. The important breakthrough of luminescent materials was the use of Eu^{3+}-activated materials as the red component for color television. Several previous investigations of compounds with $Ln_2W_2O_9$ formulation (Ln = La, Pr, Nd, Sm, Eu and Gd) have been done [2]. All the crystal structures of these compounds $Ln_2W_2O_9$ are monoclinic with space group $P2_1/c$ [3].

This work presents the preparation of these compounds, and focuses on the $Eu_2W_2O_9$. The synthesis and luminescence properties of Eu^{3+}-doped phosphors are many reported. It is our main interest to examine the luminescence of Y^{3+}-doped powder of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.8$) phosphor to change the concentration of Y^{3+} ions and preparation temperature. These were prepared by solid-state reaction. These compounds were confirmed by the X-ray powder diffraction (XRD) patterns and these absorption, excitation and emission spectra were measured. To change the concentration of Y^{3+} ions and preparation temperatures, we obtained some products which contained another constitution and luminescence properties, so we compared with these luminescence characteristics.

2. Experiment

2.1. Preparation

$Eu_{2-x}Y_xW_2O_9$ was prepared by a solid-state reaction. The starting materials were high-purity Eu_2O_3 (Shin-etsu Chemical Co. Ltd., 99.9%), Y_2O_3 (Shin-etsu Chemical Co. Ltd., 99.9%) and WO_3 (Allied Material, 99.9%) powders. Each

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preparation was ball-mill mixed in ethanol for 1 h and then dried. Placing in an alumina crucible, these mixtures were fired for 2 h at 900, 1000, 1100, 1150 or 1200 °C in air and were slowly lowered to room temperature. After firing step, these mixtures were smashed by mortar to keep off the flocculation. And then, smashed ones were sieved by 22 μm mesh pass to remove large products.

2.2. Characterization

All samples were confirmed by XRD patterns (MAC Science Co. Ltd., M21X system) and these lattice constant and cell volume were calculated. The Cu Kα radiation was selected by means of a graphite monochromator. The data were collected on thoroughly ground powders by a step-scanning mode in the 2θ range 5–90° with a step width of 0.02° and step time of 4 s. These particle sizes were measured by laser scanning microscope (Laser Tec. Co. Ltd., 1LM-21). The absorption spectra were recorded in photo acoustic (PA) experiment. The PA signal intensity was normalized by the signals from carbon black to eliminate the effects of optical conditions to the spectral responses. A 500 W xenon lamp was used for the PA experiment. The wavelength of the excitation light beam was scanned from 300 to 550 nm with a 5 nm step. The excitation and emission spectra were recorded on a fluorescence spectrophotometer (SPEX Fl-3-21Tau) equipped with two double-grating monochromators and a 450 W xenon lamp as the excitation source. All measurements were made at room temperature.

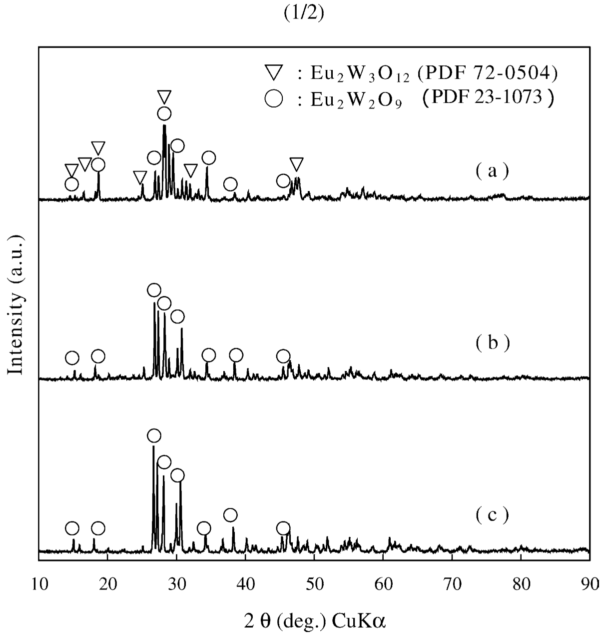

Fig. 1. XRD patterns of (a) $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, (b) $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and (c) $Eu_2W_2O_9$ fired at 1000 °C.

3. Results and discussion

Fig. 1 shows XRD patterns of $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and $Eu_2W_2O_9$ fired at 1000 °C. According to the XRD patterns, $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and $Eu_2W_2O_9$ fired at 1000 °C obtained a single phase, which is similar with the data of $Eu_2W_2O_9$ powder diffraction file (PDF) No. 23-1073. All samples of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.0$) fired at 900–1100 °C obtained as same phase. Moreover, the 30 mol% Y^{3+}-doped $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 and 1200 °C contained another component of $Eu_2W_3O_{12}$ (PDF No. 72-0504). In addition, more 50 mol% Y^{3+}-doped ones were included $Y_2W_3O_{12}$ (PDF No. 15-0546). This indicates that the obtained components are closely related to the concentration of Y^{3+} ions and preparation temperatures. All samples appear to be white in color and these particle sizes were 5–7 μm.

Fig. 2 shows relationship between cell volume and amount of doped Y^{3+} ions in $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.0$) fired at several temperatures. Cell volume of 0–50 mol% Y^{3+}-doped and fired at 900–1100 °C are reduced as addition of Y^{3+} ions, while more 30 mol% Y^{3+}-doped and fired at 1150 and 1200 °C does not see any variation. This indicates that the substitution of Y^{3+} ion to Eu^{3+} site does not occur in the samples, which doped more 30 mol% Y^{3+} ions and fired at 1150 and 1200 °C, for another component of $Eu_2W_3O_{12}$.

Fig. 3 shows PA spectra on $Eu_{2-x}Y_xW_2O_9$ ($x = 0$, 0.6, 1.0 and 1.4) fired at 1200 °C. These samples had broad peaks at 375–400, 450–475 and 520–540 nm, respectively. These were reduced as addition of Y^{3+} ions. This indicates that these broad peaks are related to the energy transitions of the Eu^{3+} ion. PA signal intensity at 450–475 nm was lower than that of

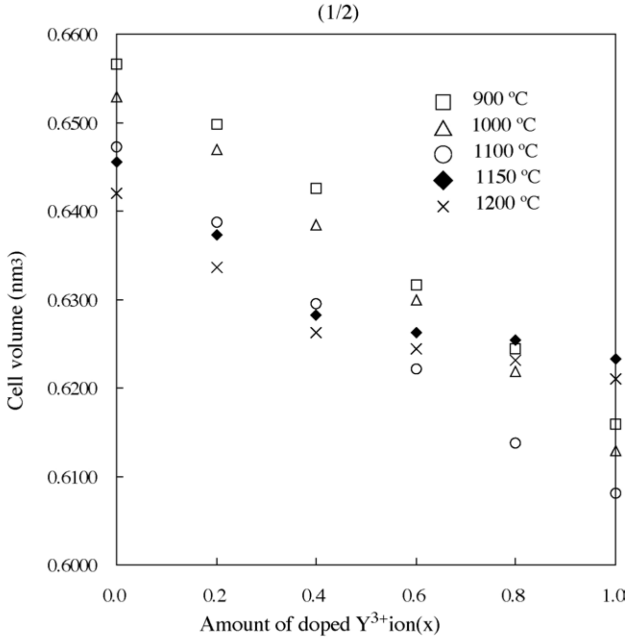

Fig. 2. Relationship between cell volume and amount of doped Y^{3+} ion (x) in $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.0$) fired at several temperatures.

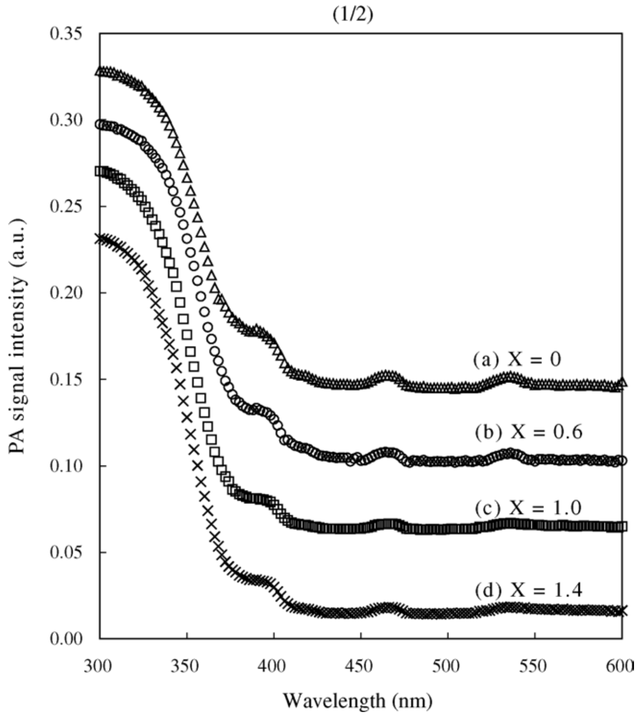

Fig. 3. PA spectra on $Eu_{2-x}Y_xW_2O_9$ fired at 1200 °C: (a) $x = 0$, (b) $x = 0.6$, (c) $x = 1.0$ and (d) $x = 1.4$.

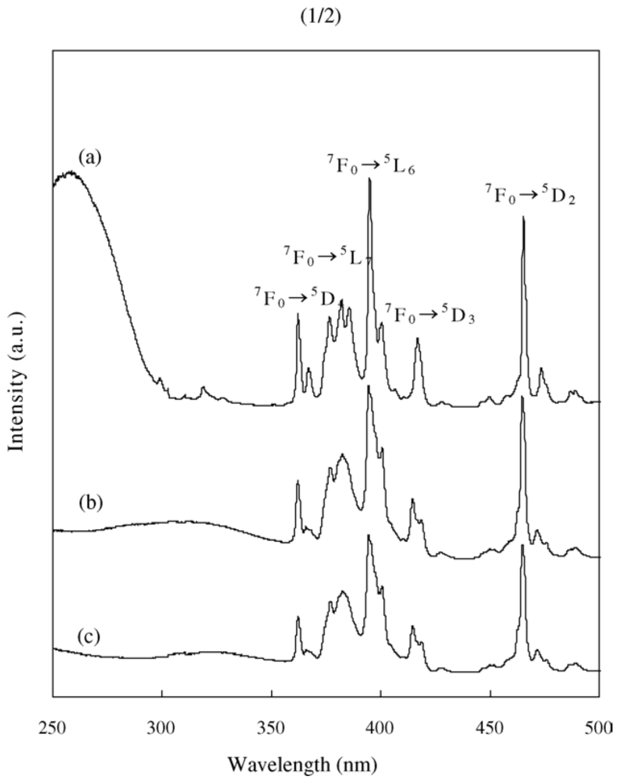

Fig. 4. Excitation spectra of (a) $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, (b) $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and (c) $Eu_2W_2O_9$ fired at 1000 °C ($\lambda_{em} = 614$ nm).

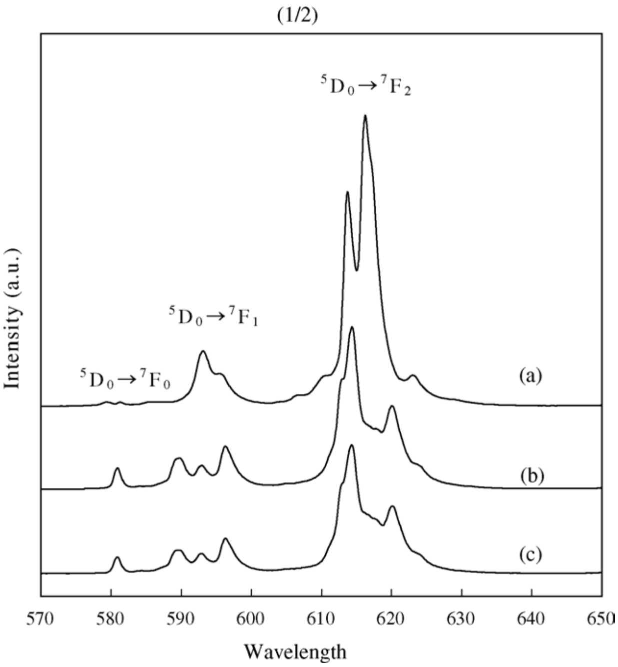

Fig. 5. Emission spectra of (a) $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, (b) $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and (c) $Eu_2W_2O_9$ fired at 1000 °C ($\lambda_{ex} = 395$ nm).

near UV region. The large PA signal intensity observed under 350 nm seems to the fundamental absorption. The samples fired at other temperatures showed absorption in same region.

Fig. 4 shows excitation spectra of $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and $Eu_2W_2O_9$ fired at 1000 °C as a typical example of the excitation spectra. It consists of the sharp lines due to the transitions of the Eu^{3+} ions. In this figure, these spectra display two sharp lines at 395 and 465 nm, respectively. These were ascribed to the $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions of Eu^{3+} ions [4]. On the other hand, 30 mol% Y^{3+}-doped $Eu_{1.4}Y_{0.6}W_2O_9$ showed the broad band with a maximum at about 262 nm. In these compounds, $Eu_2W_2O_9$ containing WO_6 octahedron in space group $P2_1/c$ and $Eu_2W_3O_{12}$ containing WO_4 units in space group $C2/c$, respectively [5]. It seems that this charge transfer in UV region is related to the O → W ligand to metal charge transfer (LMCT) state of WO_4 units in $Eu_2W_3O_{12}$ [5]. In this figure, the excitation spectrum of 30 mol% Y^{3+}-doped $Eu_{1.4}Y_{0.6}W_2O_9$ was larger than other two samples at 395 and 465 nm. The excitation spectra are also dependent on the emission wavelength.

Fig. 5 shows emission spectra of $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C, $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C and $Eu_2W_2O_9$ fired at 1000 °C. The spectra of them consist of several lines and these lines belong to transitions between the energy levels of Eu^{3+} ion. In this figure, emission spectra consist of three bands assigned to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–2) transitions. The most insensitive and deep red emission band is attributed to $^5D_0 \rightarrow {}^7F_2$ transition. In $Eu_2W_2O_9$ type structure, 20 mol% Y^{3+}-doped $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C

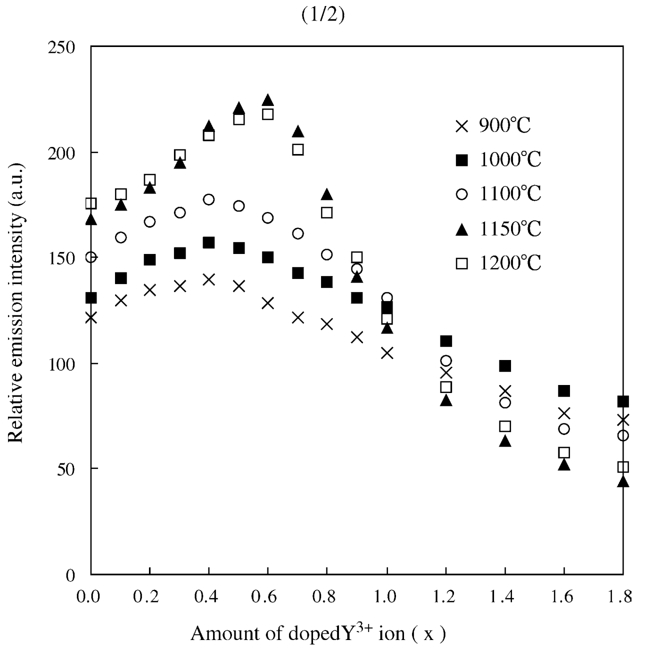

Fig. 6. The dependence of $^5D_0 \rightarrow {}^7F_2$ emission intensity on Y^{3+} concentration and preparation temperatures of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.8$) excited at 395 nm.

showed highest intensity at 614 nm. This indicates that the suitable substitution of Y^{3+} ion to Eu^{3+} site related to high luminescence efficiency. On the other hand, 30 mol% Y^{3+}-doped $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C observed highest intensity at 616 nm and this was the best phosphor in this study. It seems that this intensity is owing to second component $Eu_2W_3O_{12}$. This indicates that the broad band in the UV region of the excitation spectra operated efficient energy transfer from the tungstate group to Eu^{3+} ions [6].

Fig. 6 shows the dependence of $^5D_0 \rightarrow {}^7F_2$ emission intensity on Y^{3+} concentration and preparation temperatures of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.8$) excited at 395 nm. These values are integral of $^5D_0 \rightarrow {}^7F_2$ emission intensity and show many variations as addition of Y^{3+} ions. In $Eu_2W_2O_9$ type structure, higher luminescence performance was observed from 20–30 mol% Y^{3+}-doped phosphor and the best one was 20 mol% Y^{3+}-doped $Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C. This indicated that the suitable amount of Y^{3+} ions operated high luminescence intensities. Higher luminescence intensity was obtained 30 mol% Y^{3+}-doped and fired at 1150 and 1200 °C.

The best one was 30 mol% Y^{3+}-doped $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C for $Eu_2W_3O_{12}$. The luminescence intensities of more 50 mol% Y^{3+}-added phosphors were low for $Y_2W_3O_{12}$. This $Y_2W_3O_{12}$ shows negative thermal expansion along all three axes [7].

The relative luminescence brightness $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ for the measured emission levels of these phosphors were calculated [8]. These values are integral of each emission intensities and the calculated relative emission ratios were 3.33 ($Eu_2W_2O_9$ fired at 1000 °C), 3.62 ($Eu_{1.6}Y_{0.4}W_2O_9$ fired at 1100 °C) and 4.65 ($Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C), respectively. This indicated that $Eu_{1.4}Y_{0.6}W_2O_9$ fired at 1150 °C is promising candidates for bright red color emission.

4. Conclusions

In this paper, we have studied the luminescence properties of $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.8$) about the influences of Y^{3+} concentration and preparation temperatures at 900–1200 °C. XRD patterns of Y^{3+}-doped $Eu_{2-x}Y_xW_2O_9$ ($0 \leqq x \leqq 1.0$) fired at 900–1100 °C were fitted with that of $Eu_2W_2O_9$. In them, 20 mol% Y^{3+}-doped and fired at 1100 °C showed highest emission intensity. This indicates that the suitable substitution of Y^{3+} ion to Eu^{3+} ion site related to high luminescence efficiency. The obtained phosphor which 3.0 mol% Y^{3+}-doped and fired at 1150 and 1200 °C included $Eu_2W_3O_{12}$ and this related to the high luminescence intensity. In this study, concentration quenching does not occur in all prepared compounds.

The difference of several crystal structures is closely related to the excitation or emission spectra and these intensities. It is interesting to investigate the relation between the difference of coordinated polyhedra and luminescence properties in tungstates.

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