Photoluminescence characteristics of Bi^{3+}-sensitized YVO_4:Eu^{3+} phosphor

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Abstract: *A possibility of YVO_4:Eu^{3+} phosphor as a red phosphor for the application to ultraviolet (UV) light emitting diodes (LEDs) was investigated. Bi was used as a sensitizer for Eu^{3+} to improve photoluminescence (PL) intensity in the longer wavelengths region than 350 nm and Bi^{3+}-sensitized YVO_4:Eu^{3+} phosphor was characterized in terms of crystal structure, and PL excitation/emission spectra. Addition of Bi 0.15 mol into YVO_4:Eu^{3+} phosphor improved its PL intensity by 12 times under 365 nm UV radiation. However, a new broad band spectrum at around 552 nm appeared besides very sharp spectrum at 619 nm of Eu^{3+} ion. By the addition of Bi, PLE intensity in the longer wavelengths than 330 nm was improved. CIE color coordinates of $Y_{0.95-x}VO_4$:$Eu_{0.05}{}^{3+}$,$Bi_x{}^{3+}$ phosphor was distributed from red to orange region because of the emission (552 nm) of Bi.*

Keywords: YVO_4:Eu^{3+},Bi^{3+}; phosphor; sensitizer; UV-pumped white LED

Introduction

Today lighting and display industries are focused upon developing efficient high-intensity LEDs that produce white light. This is crucial in order for LEDs to be able to compete with incandescent and fluorescent lighting systems. However, since white light is actually composed of many colors, and LEDs produce monochromatic colors, this poses a considerable challenge for LED technology. Presently, engineers have developed three systems for producing white light with LEDs; (1) Mixing red, green and blue (RGB) LEDs, (2) UV LEDs with RGB phosphor coatings, and (3) blue LEDs with yellow phosphor coatings [1].

Recently there has been renewed interest in creating a white source using a UV-emitting LED to pump a trio of RGB-emitting phosphors, the UV LED-pumped white LED. The UV light is completely adsorbed by the phosphors, and the mixed RGB output appears white much the same as an RGB mixed LED array. However, we have to consider the inherent disadvantages such as a quantum deficit indispensably existing in UV LED-pumped white LED system using UV LED and RGB phosphors. The quantum deficit between the UV pump and the phosphors, especially the low-energy red phosphor, dissipates significant energy and makes this approach inherently less efficient than either the RGB or

the blue LED-pumped white LED systems for generating white light [2].

Among red phosphors for UV radiation, it is well known that YVO_4:Eu^{3+} phosphor is well excited by UV light, and the PL quantum yield of the europium emission is as high as 70% [3]. Considering the application to UV-LED, however, an absorption efficiency of YVO_4:Eu^{3+} phosphor in the longer wavelengths than 350 nm should be improved more than ever. There are several reports to improve the quantum efficiency of red phosphor excited by UV radiation via synthesis route and composition variation. One of the simplest methods to improve absorption efficiency of phosphor in UV region near to violet light instead of changing a host lattice of phosphor is using a sensitizer [4, 5].

We have studied a possibility of YVO_4:Eu^{3+} phosphor as a red phosphor for the application to UV LED-pumped white LEDs. Bi^{3+} ion was used as a sensitizer for Eu^{3+} to improve PL intensity under UV radiation. And Bi^{3+}-sensitized YVO_4:Eu^{3+} phosphor was characterized in terms of crystal structure, and PL excitation/emission spectra.

Experiment

Sample preparation: To synthesize $Y_{1-x}VO_4$:Eu^{3+},$Bi_x{}^{3+}$ phosphors, high purity yttrium oxide (Y_2O_3, 99.99%, Aldrich), vanadium oxide (V_2O_5, 99.99 %, Aldrich), europium oxide (Eu_2O_3, 99.99 %, Aldrich), and bismuth oxide (Bi_2O_3, 99.99+ %, Aldrich) were used as raw materials. For the present study, the amount of dopant europium fixed at 0.05 mol. Chemicals in the following compositions were mixed thoroughly by using ethanol as a solvent for mixing.

Initially these oxide samples were calcined at 900 °C for 10 hrs and then calcined at 1200 °C for 20 hrs. After these procedures, the phosphors were light yellow in body color due to the presence of vanadium, and emitted a bright-red color under UV radiation. Subsequently, the synthesized samples were washed with distilled water to remove the useless resultants, filtered, and dried at 80 °C.

X-ray diffraction (XRD) measurement: Crystalline phases of the samples were analyzed by XRD (Rigaku, D/max-IIIC(3kw) with Cu-K (λ = 1.542 Å) radiation operating

at 40 kV and 45 mA. The scan rate was 3 $^{\circ}$/min and covered the range between 15 and 60 $^{\circ}$.

PL/PLE measurement: To investigate luminescence properties, PL was measured by PL spectrometers using Xenon lamp (500 W) in UV range.

Results and discussion

Fig. 1 shows the PL intensity of YVO_4:Eu^{3+},Bi^{3+} phosphors monitored at 619 nm which comes from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. To investigate the role of Bi as a sensitizer, the amount of Bi from 0.01 to 0.6 mol was used. PL intensity of YVO_4:Eu^{3+},Bi^{3+} phosphors excited by 254nm showed gradual decrease while YVO_4:Eu^{3+},Bi^{3+} phosphors excited by 365nm showed a drastic increase and subsequent decrease, which is similar to the case of YVO_4:Eu^{3+},Bi^{3+} phosphors excited by 254nm. Addition of Bi 0.15mol into YVO_4:Eu^{3+} phosphor improved its PL intensity by 12 times.
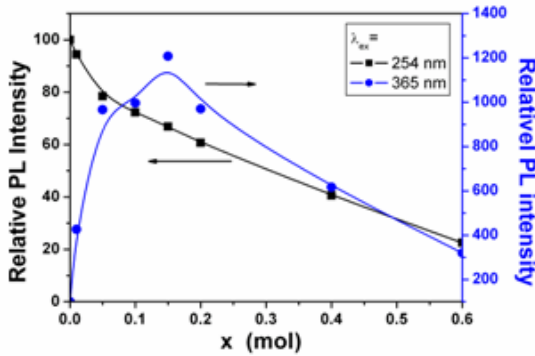

Figure 1. Relative PL intensity of $Y_{1-x}VO_4$:Eu^{3+},Bi_x^{3+} phosphor by 254 nm and 365 nm (monitored at 619 nm).

As shown in Fig. 2, PLE analysis was carried out to investigate the effect of Bi as a sensitizer in YVO_4:Eu^{3+} phosphor. PL intensities of YVO_4:Eu^{3+},Bi^{3+} phosphors excited by UV radiation from 250 to 500 nm were monitored. As the amount of Bi increased, PLE intensity in shorter wavelengths than 330 nm decreased. However, a new PLE spectrum appeared in the longer wavelengths than 330 nm. Spectral overlap around 330 nm was appeared. PLE spectrum observed at around 255 nm is a charge transfer band which is due to the charge transfer between Eu and O. Broad band spectrum observed at 317 nm is assigned to absorption of VO_4^{3-} molecular group. And the new broad band spectrum observed at around 337 nm might be absorption of $6s^2 \rightarrow 6s6p$ of Bi ion.

Fig. 3 shows XRD data of the phosphors prepared. In the case that the amount of Bi is more than 0.2 mol, additional phase, tetragonal $BiVO_4$ phase (*) appeared. And the XRD pattern which comes from (200) plane of YVO_4 tetragonal phase shifted to much smaller angle from 25.04 to 24.86 $^{\circ}$. It is thought that the peak shift to a smaller angle might be caused by mismatch of ionic radius (Y=1.02, Bi=1.17 Å). In other words, as the

amount of Bi increase, the lattice of unit cell must be expanded.

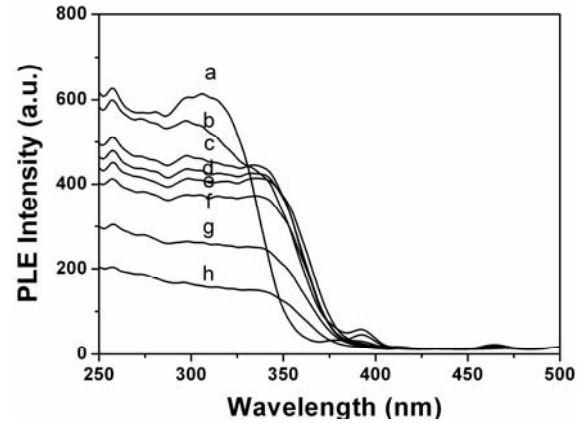**Figure 2**. PLE spectra of $Y_{1-x}VO_4$:Eu^{3+},Bi_x^{3+} phosphor (λ_{em} = 619 nm) : (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.4, and (h) 0.6 mol.

Fig. 4 shows a volume fraction of $BiVO_4$ phase existed in the phosphor screen prepared. The volume fraction of $BiVO_4$ was calculated with the following formula.

$$V_{BiVO4} = I_{BiVO4\,(200)}/(I_{BiVO4\,(200)} + I_{YVO4\,(200)}). \qquad (1)$$

where V_{BiVO4} is the volume fraction of $BiVO_4$, $I_{BiVO4(200)}$ is the XRD maximum intensity of (200) plane of $BiVO_4$, $I_{YVO4(200)}$ is the XRD maximum intensity of (200) plane of YVO_4.

From the calculation of volume fraction of $BiVO_4$, it became clear that the amount of additional $BiVO_4$ phase increased linearly as the amount of Bi increased. Even if Eu ion is doped into $BiVO_4$, Eu in $BiVO_4$ does not act as a luminescent center, which is confirmed from the experiment. Actually Eu can not be doped in $BiVO_4$, it forms $EuVO_4$ precipitates in $BiVO_4$ phase. Therefore, it is believed that the origin of the decreased PL intensity of the phosphor screen when the amount of $BiVO_4$ was more than 0.2 mol is due to the existence of additional non-luminescent $BiVO_4$ phase.
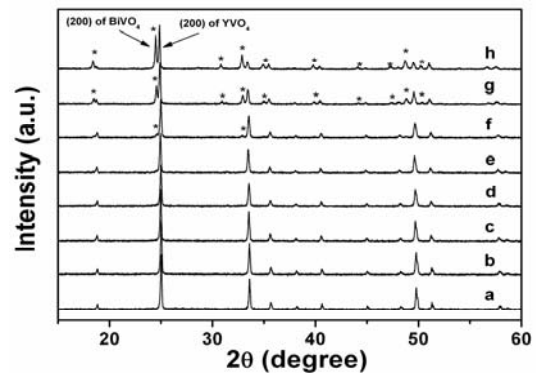

Figure 3. XRD patterns of $Y_{1-x}VO_4$:Eu^{3+},Bi_x^{3+} phosphors ; x = (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.4, and (h) 0.6 mol. (*) indicates XRD patterns of $BiVO_4$ phase.
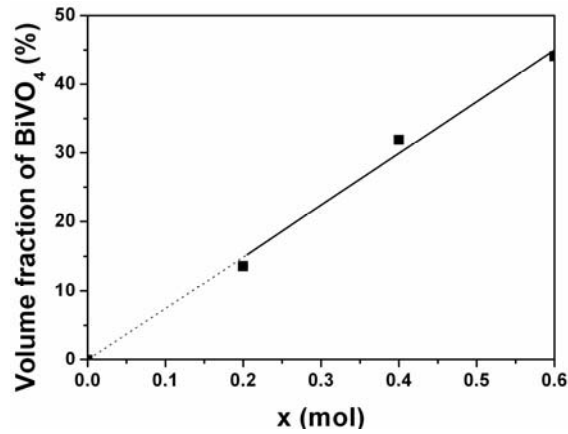
Figure 4. Volume fraction of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors.

Fig. 5 shows PL spectra of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors ($0 \leq x \leq 0.15$) excited by 337 nm. A new broad band spectrum at around 552 nm appeared besides very sharp spectrum coming from $^3D_0$ to ^7F_J (J=0, 1, 2, 3, 4) transition in Eu^{3+} ion. Broad band spectrum is assigned to $6s6p \rightarrow 6s^2$ transition in Bi^{3+} ion. From the consideration of PLE spectra and PL spectra, it is believed that both VO_4^{3-} molecule and Bi ion in YVO_4 host lattice absorbs 337 nm UV radiation. After that, some of the energies absorbed by Bi^{3+} ion emits green light (557 nm) and others are transferred from Bi^{3+} ion and VO_4^{3-} to Eu^{3+} ion, subsequently emit red light via $^3D_0$ to ^7F_J (J=0, 1, 2, 3, 4).

Bi in $YVO_4:Eu^{3+}$ phosphor acts as a sensitizer. Generally, roles of a sensitizer are to absorb the excitation energy and then transfer the energy to an activator which is a luminescent center. To be a good sensitizer, it should not play a role as a luminescent or quenching center but energy transfer process from a sensitizer to an activator should be very efficient. As observed in the PL spectra, however, energy transfer process from Bi^{3+} to Eu^{3+} ion doesn't seem to be very efficient.

The maximum energy transfer from a sensitizer to an activator occurs when there is a spectral overlap of emission of the sensitizer and the excitation of an activator
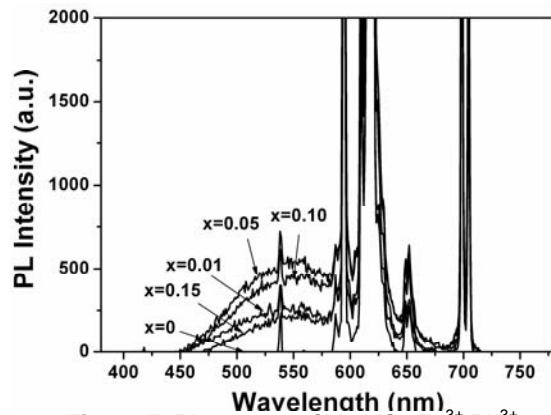
ion. But this may not be the only criteria. Even if the emission of sensitizer is below the emission of activator, the energy transfer from the sensitizer to an activator occurs. The emitted energy of Bi^{3+} ion may be reabsorbed by Eu^{3+} activator ion thereby enhancing the red emission of Eu^{3+} ion in small amounts [5-7].

As shown in Fig. 6, to investigate the energy transfer process from Bi^{3+} to Eu^{3+} ion, variation of maximum PL intensity of Bi^{3+} and Eu^{3+} ion was observed as a function of the amount of Bi. Broad band spectrum observed at around 552 nm due to Bi^{3+} ion increased up to 0.05 mol and then decreased. Maximum PL intensity at 619 nm due to Eu^{3+} ion, however, increased up to 0.1 mol and then decreased with much the same slope as Bi^{3+} ion. The sensitization effect of Bi^{3+} ion on the Eu^{3+} activator ion varied with Bi^{3+} ion concentration. And this phenomenon can be explained by energy transfer probability.

There are electric (or magnetic) multipole-multipole interaction and exchange interaction in the interaction between sensitizer (S) and activator (A). Postulating that the dipole-dipole interaction plays an important role in the energy transfer between Bi^{3+} and Eu^{3+} ion, the probability of energy transfer is given by the following equation [6].

$$P_{SA}(dd) = \frac{3\hbar^4 c^4 Q_A}{4\pi R^6 n^4 \tau_S}\left(\frac{\varepsilon}{x^{1/2}\varepsilon^c}\right)^4 \cdot \int \frac{f_S(E)f_A(E)}{E^4}dE \quad (2)$$

where P_{SA} is the probability of energy transfer, Q_A is the absorption cross section of A, R is the distance between S and A, n is the refractive index of host lattice, τ_s the radiative decay time of S. On the other hand, $\left(\varepsilon / x^{1/2}\varepsilon_c\right)^4$ is the local electric field, x is dielectric constant. The integral represents the overlap between the normalized S emission and A excitation band.

The distance in which the energy transfer between S and A can occur is defined as R_c. Considering structural factors, R_c can be described by the following equation.

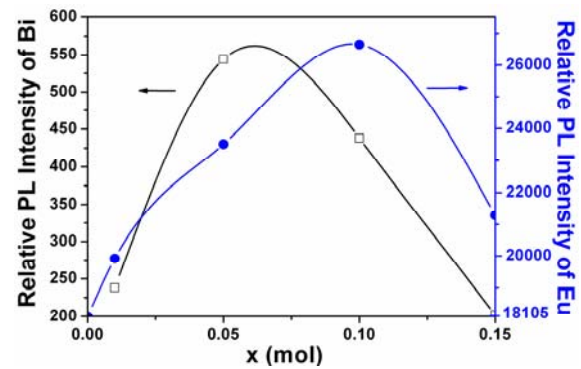$$R_c^6 \approx 2\left(\frac{3V}{4\pi X_c N}\right)^{1/3} \quad (3)$$

Figure 6. Variation of PL intensity of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors ($0 \leq x \leq 0.15$) ; Emission spectra of Bi and Eu were monitored at 552 nm and 619 nm, respectively.

Figure 5. PL spectra of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors ($0 \leq x \leq 0.15$).

where X_c is the Eu^{3+} and Bi^{3+} ion concentration and N is the number of Bi^{3+} and Eu^{3+} ions in the unit cell.

In this case, as Bi^{3+} concentration increases, the distance between Bi^{3+} and Eu^{3+} ion decreases, subsequently the energy transition probability increases and consequently red light by Eu^{3+} increases. However, in the case that the amount of Bi^{3+} became bigger than 0.1 mol, PL intensity due to $^3D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion decreased. This might be due to the effect of structural change on a radiation transition of Eu^{3+} ion by Bi addition or the lower energy transfer probability between Bi^{3+} to Eu^{3+} ion than between Bi^{3+} ions.

Fig. 7 shows the relative PL luminance of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors ($0 \leq x \leq 0.15$) excited by 255, 310, and 337 nm, respectively. The luminance of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors is determined by relative spectral area between broad band spectrum of Bi^{3+} and sharp spectrum of Eu^{3+} ion, and this spectrum area can be changed by the amount of Bi^{3+} addition. $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors ($0 \leq x \leq 0.15$) excited by 255 and 310 nm UV radiations showed almost the same luminance as $YVO_4:Eu^{3+}$ phosphor. On the other hand, $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phosphors excited by 337 nm UV radiation showed 2.5 times better luminance than before.
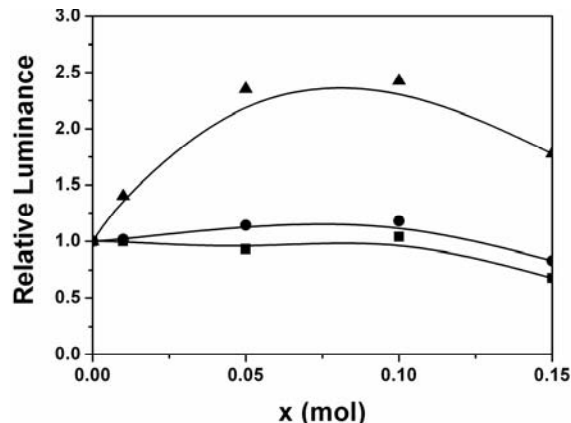

Figure 7. Relative luminance of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phos- phor ($0\leq x \leq 0.15$) excited by (■) 255, (●) 310, and (▲) 337 nm.

The CIE color coordinates of $YVO_4:Eu^{3+},Bi^{3+}$ phosphors were shown in Fig. 8. Up to 0.05 mol of Bi^{3+} ion, CIE color coordinates had shifted to yellow light. When the amount of Bi ion, however, was more than 0.05 mol, it had shifted to red light again. This is because the broad band spectrum at around 552 nm which is introduced by Bi^{3+} ion can affect the CIE color coordinates of $YVO_4:Eu^{3+}$ phosphor.

Conclusion

We have studied the photoluminescence characteristics of Bi^{3+}-sensitized $YVO_4:Eu^{3+}$ phosphor for the applica- tion to UV-pumped white LEDs. $YVO_4:Eu^{3+}$ phosphor

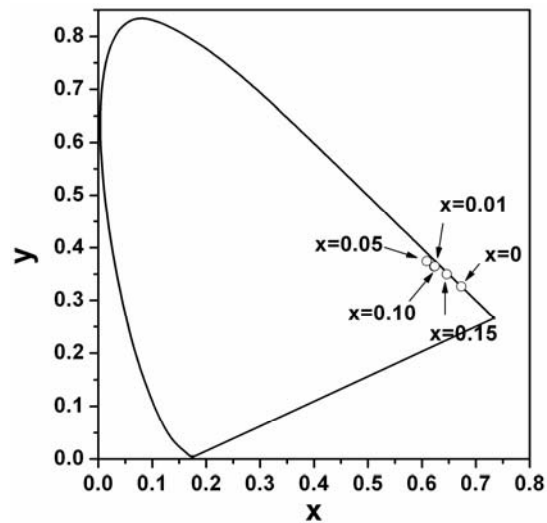**Figure 8.** CIE color coordinates of $Y_{1-x}VO_4:Eu^{3+},Bi_x^{3+}$ phos- phor ($0\leq x \leq 0.15$) excited by 337 nm.

without Bi ion seems to have no strong absorption below 350 nm. However, an absorption efficiency of the $YVO_4:Eu^{3+},Bi^{3+}$ phosphor around the region near 365 nm excitation was greatly enhanced up to 12 times because the energy absorption due to $6s^2 \rightarrow 6s6p$ transition of Bi ion occurred. PLE intensity of charge transfer band (255 nm) and VO_4^{3-} molecule (317 nm) with Bi amount decreased gradually. However, PLE intensity in the longer wavelengths than 330 nm increased. CIE color coordinates of $Y_{0.95-x}VO_4:Eu_{0.05}^{3+},Bi_x^{3+}$ phosphor was distributed from red to orange region because of the emission (552 nm) of Bi. It was thought that PL intensity from Eu^{3+} ion has correlation with the amount of Bi^{3+} ion. Taking all the results into consideration, it is believed that improved PL intensity of $YVO_4:Eu^{3+}$ is due to energy transfer from Bi^{3+} ion to Eu^{3+} ion but the efficiency of energy transfer is poor.

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