Photoluminescence characteristics of Bi$^{3+}$-sensitized YVO$_4$:Eu$^{3+}$ phosphor

Jong Hyuk Kang$^{1*}$, Dong Chin Lee$^{2}$, Sun Jin Yun$^{3}$, Duk Young Jeon$^{4}$

$^1$Dept. of Materials Sci. and Eng., Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon, 305-701, Korea
$^2$Production team 2, HD display center, LCD business, Samsung electronics Co., Ltd 200 Myeongam-ri, Tangjeong-myeon, Asan-city, Chungcheongnam-do, 336-841, Korea
$^3$IT-Convergence and Component Laboratory, Electronics and Telecommunications Research Institute 161 Gajung-dong, Yuseong-gu, Daejeon, 305-700, Korea
$^4$ariel75@kaist.ac.kr

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$_{0.95}$, VO$_{4.05}$, Eu$_{0.05}$, Bi$_{0.15}$ 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 absorbed 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$_{0.05}$, Bi$_{0.15}$ phosphors, high purity yttrium oxide (Y$_2$O$_3$, 99.99%, Aldrich), vanadium oxide (V$_2$O$_5$, 99.99 %, Aldrich), europium oxide (Eu$_2$O$_3$, 99.99 %, Aldrich), and bismuth oxide (Bi$_2$O$_3$, 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$_\alpha$ ($\lambda$ = 1.542 Å) radiation operating
at 40 kV and 45 mA. The scan rate was 3 °/min and covered the range between 15 and 60 °.

**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 YVO₄:Eu³⁺,Bi³⁺ phosphors monitored at 619 nm which comes from \(^{5}D_{0} \rightarrow ^{7}F_{2}\) transition of Eu³⁺ 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 YVO₄:Eu³⁺,Bi³⁺ phosphors excited by 254 nm showed gradual decrease while YVO₄:Eu³⁺,Bi³⁺ phosphors excited by 365 nm showed a drastic increase and subsequent decrease, which is similar to the case of YVO₄:Eu³⁺,Bi³⁺ phosphors excited by 254 nm. Addition of Bi 0.15 mol into YVO₄:Eu³⁺ phosphor improved its PL intensity by 12 times.

As shown in Fig. 2, PLE analysis was carried out to investigate the effect of Bi as a sensitizer in YVO₄:Eu³⁺ phosphor. PL intensities of YVO₄:Eu³⁺,Bi³⁺ 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 VO₄³⁻ molecular group. And the new broad band spectrum observed at around 337 nm might be absorption of 6s² → 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 BiVO₄ phase (*) appeared. And the XRD pattern which comes from (200) plane of YVO₄ tetragonal phase shifted to much smaller angle from 25.04 to 24.86 °. 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.

Fig. 4 shows a volume fraction of BiVO₄ phase existed in the phosphor screen prepared. The volume fraction of BiVO₄ was calculated with the following formula.

\[
V_{\text{BiVO}_4} = \frac{I_{\text{BiVO}_4(200)}}{I_{\text{BiVO}_4(200)} + I_{\text{YVO}_4(200)\text{}}}
\]

where \(V_{\text{BiVO}_4}\) is the volume fraction of BiVO₄, \(I_{\text{BiVO}_4(200)}\) is the XRD maximum intensity of (200) plane of BiVO₄, \(I_{\text{YVO}_4(200)}\) is the XRD maximum intensity of (200) plane of YVO₄.

From the calculation of volume fraction of BiVO₄, it became clear that the amount of additional BiVO₄ phase increased linearly as the amount of Bi increased. Even if Eu ion is doped into BiVO₄, Eu in BiVO₄ does not act as a luminescent center, which is confirmed from the experiment. Actually Eu can not be doped in BiVO₄, it forms EuVO₄ precipitates in BiVO₄ phase. Therefore, it is believed that the origin of the decreased PL intensity of the phosphor screen when the amount of BiVO₄ was more than 0.2 mol is due to the existence of additional non-luminescent BiVO₄ phase.
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].

\[
P_{S\rightarrow A}(dd) = \frac{3\hbar^4 c^4 Q_A}{4\pi R^6 n^4 \tau_S} \int \left( \frac{E}{x^{11/2} \epsilon_x} \right)^4 \frac{f_S(E) f_A(E)}{E^4} dE
\]

where \(P_{S\rightarrow A}\) 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, \(\tau_S\) the radiative decay time of S. On the other hand, \(\left( \frac{E}{x^{11/2} \epsilon_x} \right)^4\) 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.

\[
R_c^6 \approx \left( \frac{3V}{4\pi X N} \right)^{1/3}
\]
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 $^5D_0 \rightarrow ^7F_2$ 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$^{3+}$ 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$^{3+}$ 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$^{3+}$ 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$^{3+}$ phosphors excited by 337 nm UV radiation showed 2.5 times better luminance than before.

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 application to UV-pumped white LEDs. YVO$_4$:Eu$^{3+}$ phosphor 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$_{0.05}$,Bi$_x$; 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.

References