

## Effect of Bi<sup>3+</sup> addition on photoluminescence of (Y,Gd)(V,P)O<sub>4</sub>:Eu phosphor

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### Abstract

*The structural and optical properties on Bi<sup>3+</sup> addition in (Y,Gd)(V,P)O<sub>4</sub>:Eu<sup>3+</sup> red phosphor were investigated. With the addition of Bi<sup>3+</sup>, the band edge in excitation spectrum shifts toward longer wavelength region, resulting in remarkable enhancement of the red emission intensity at 619 nm.*

### 1. Introduction

One of the potential markets of white LEDs is LCD backlight. The backlight should have a full range of visible light as well as high brightness. The white light generated from a blue-LED chip and a yellow phosphor could not meet the requisition for LCD backlight because of a low color rendering index (CRI) and no full range of visible light. A suggested solution to overcome this problem is to use a UV LED with a primary emission of 350-410 nm instead of the blue LED, in which the UV LED chip is used as the excitation source and combined with red, green, and blue phosphors. The mixture of these tricolor lights makes excellent white light. To successfully generate the white light through phosphor-combined UV LED, the phosphor materials should work under long-wavelength UV and have high emission efficiency.

YVO<sub>4</sub>:Eu<sup>3+</sup> had been extensively studied for many years [1-6] because of the efficient energy transfer from the vanadate group (VO<sub>4</sub><sup>3-</sup>) to Eu<sup>3+</sup> activator. This phosphor emits intense emission under UV and VUV excitation. On the other hand, YVO<sub>4</sub> host material belongs to a tetragonal crystal system, which is formed from chains of alternating edge-sharing VO<sub>4</sub> and YO<sub>8</sub>. So the Eu<sup>3+</sup> ion could be firmly coordinated by eight O<sup>2-</sup> ions in YVO<sub>4</sub> when they are substituted into Y<sup>3+</sup> sites. Accordingly, YVO<sub>4</sub>:Eu<sup>3+</sup> has desirable absorption and excellent chemical stability [7].

Recently, it was reported that the composition-optimized (Y,Gd)(V,P)O<sub>4</sub>:Eu can serve as an alternative phosphor to replace a widely used commercial red phosphor for PDP such as (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> or Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> [8, 9]. However this red phosphor exhibits low absorption property in the wavelength region of 350-410 nm.

In this work, the Bi<sup>3+</sup> ions were added into (Y,Gd)(V,P)O<sub>4</sub>:Eu red phosphor to promote the excitation property at the wavelength region of 350-410 nm. The influence of the Bi<sup>3+</sup> addition on the luminescent characteristics of (Y<sub>0.5-x</sub>Gd<sub>0.4</sub>Eu<sub>0.1</sub>Bi<sub>x</sub>)(V<sub>0.8</sub>P<sub>0.2</sub>)O<sub>4</sub> phosphor was investigated.

### 2. Experimental

The (Y<sub>0.5-x</sub>Gd<sub>0.4</sub>Eu<sub>0.1</sub>Bi<sub>x</sub>)(V<sub>0.8</sub>P<sub>0.2</sub>)O<sub>4</sub> red phosphor compositions optimized under UV excitation were prepared by a solid-state reaction. For the preparation of samples, stoichiometric amounts of Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, Eu<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> were weighed and mixed in an agate mortar. The mixture was heated at 1200 °C for 8 h in ambient air. After firing, the phosphor samples were gradually cooled to room temperature in the furnace. In order to analyze the crystalline phase of the synthesized phosphors, phase identifications were performed using a Rigaku D/MAX-2200V diffractometer with Cu K $\alpha$  ( $\lambda=1.5406$  Å) radiation. The operation voltage and current were maintained at 40 kV and 40 mA, respectively. The XRD profiles were collected in a range  $10^\circ < 2\theta < 65^\circ$ . The excitation and emission spectra of samples under UV ray excitation were measured using a spectrophotometer with a Xe flash lamp. All measurements were performed at room temperature.

### 3. Results and discussion

The crystal phases of the  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  ( $0 \leq x \leq 0.1$ ) phosphor particles were determined by X-ray powder diffraction, as shown in Fig. 1. The XRD patterns for all samples shows to be a single phase corresponding to the JCPDS card 17-0341 of yttrium vanadate. As the result, it is inferred that the phosphors are isostructural to  $YVO_4$  in a tetragonal crystal system with space group  $I4_1/amd$  and the doping of  $Eu^{2+}$  and  $Bi^{3+}$  ions into the  $(Y,Gd)(V,P)O_4$  lattice does not conduct any significant change in crystal structure of the host.

Fig. 2 shows the excitation spectra of the  $Bi^{3+}$ -doped  $(Y,Gd)(V,P)O_4:Eu$  phosphors emitted at 619 nm. It can be seen that the excitation spectra consist of a broad band and several sharp peaks at the longer wavelength region. The broad excitation band can be deconvoluted to two excitation bands centered at about 260 nm and 320 nm, respectively. The excitation band at 260 nm is attributed to charge transfer involving the Y, Gd-O components and the excitation band at 320 nm is originated from the V, P-O components of the mixture [10-12]. Also, a weak band at 390-405 nm has been identified to be corresponding to the f-f transition of the trivalent Eu ions [13]. The excitation spectrum of  $(Y_{0.5}Gd_{0.4}Eu_{0.1})(V_{0.8}P_{0.2})O_4$  phosphor without  $Bi^{3+}$  additive constitutes a broad peak in the wavelength range between about 225 nm and 350 nm. Whereas the absorption bands in the spectra of  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  with  $x = 0.03, 0.05$  and  $0.10$  are positioned in the wavelength region of 225 – 375 nm. Accordingly,

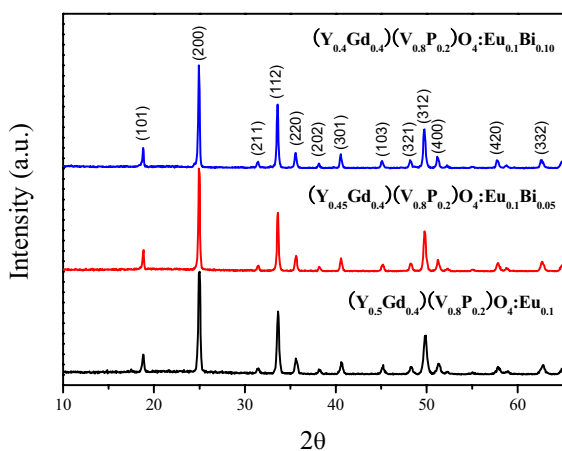


Fig. 1. XRD patterns of  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  ( $0 \leq x \leq 0.1$ ) samples fired at 1200 °C for 8 h.

the band edge shifts toward longer wavelength with addition of  $Bi^{3+}$ . These wavelength shifts occur due to the extra absorption involving the Bi-O component in addition to the V, P-O charge transfer bands. It makes the excitation intensity under NUV relatively strong and makes the phosphors suitable to be used for the excitation of 365 nm.

Concentration dependence of the relative excitation intensities of  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  phosphor at 342 nm and 396 nm are presented in Fig. 3. In the excitation spectra, the excitation intensity at 342 nm reaches a maximum at the  $Bi^{3+}$  concentration of 5 mol%, however, the intensity at 396 nm having a maximum at the  $Bi^{3+}$  concentration of 0 mol% decreases continuously with increasing  $Bi^{3+}$  content.

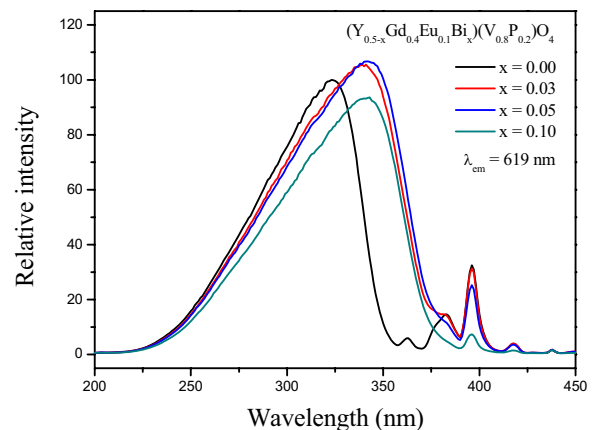


Fig. 2. Photoluminescence excitation spectra of the  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  phosphors.

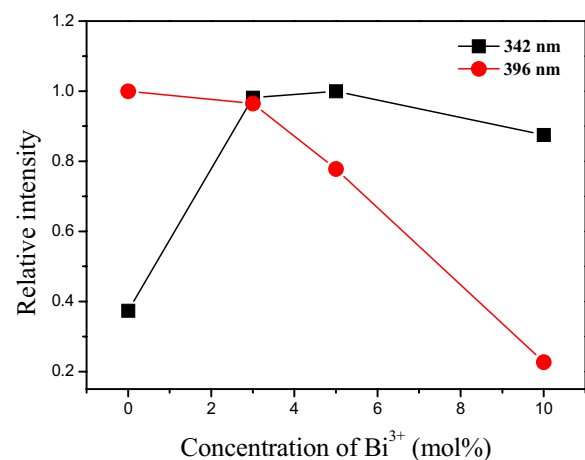
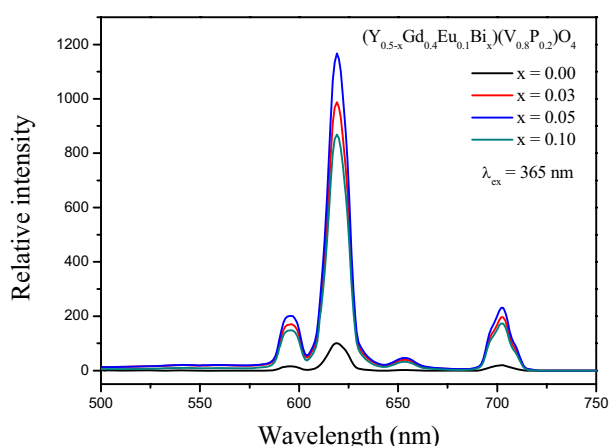


Fig. 3. Dependence of the relative excitation intensities of  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  phosphor at 342 nm and 396 nm with Bi concentration changes.



**Fig. 4. Photoluminescence emission spectra of the  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  phosphors.**

#### 4. Summary

$Bi^{3+}$ -doped  $(Y,Gd)(V,P)O_4:Eu$  phosphors were synthesized by solid-state reaction. The crystal structure and the luminescence properties of the phosphors under UV excitation were investigated. It was confirmed that the phosphors exhibiting single phase were formed by heat-treatment at 1200 °C for 8 h. With increasing  $Bi^{3+}$  content, the band edge of the excitation spectrum was shifted toward longer wavelength region. At the  $Bi^{3+}$  concentration of 5 mol%, the phosphor under the excitation of 365 nm most efficiently emitted red light centered at 619 nm. From the results, it could be concluded that the addition of  $Bi^{3+}$  ion enhances remarkably the luminescence intensity.

#### 5. References

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These results indicate that the sensitization effect of the  $Bi^{3+}$  ion on the  $Eu^{3+}$  emission varies with the  $Bi^{3+}$  concentration [14]. The total energy transfer efficiency depends on the probability of energy transfer from  $Bi^{3+}$  to  $Eu^{3+}$  as well as that between  $Bi^{3+}$  ions. At low concentration range of  $Bi^{3+}$  ion, the distance between  $Bi^{3+}$  and  $Eu^{3+}$  with the increase of  $Bi^{3+}$  content decreases and the energy transfer efficiency from  $Bi^{3+}$  to  $Eu^{3+}$  increases. For relatively high  $Bi^{3+}$  concentration, however, the efficient energy transfer between  $Bi^{3+}$  ions is predominant than that between  $Bi^{3+}$  and  $Eu^{3+}$  due to the short distance between  $Bi^{3+}$  ions. This phenomenon increases non-radiative process in luminescent mechanism of the phosphor. As a result, the energy transfer probability from  $Bi^{3+}$  to  $Eu^{3+}$  can be determined by a function of the  $Bi^{3+}$  concentration.

The emission spectra of  $(Y_{0.5-x}Gd_{0.4}Eu_{0.1}Bi_x)(V_{0.8}P_{0.2})O_4$  phosphors are presented in Fig. 3. Under the excitation at 365 nm, there are four peaks at 596, 619, 654 and 702 nm, respectively, which are  $^5D_0 \rightarrow ^7F_J$  ( $J = 1, 2, 3, 4$ ) transition emission of  $Eu^{3+}$ . The dominant red emission centered at 619 nm is attributed to the electric dipole transition of  $Eu^{3+}$  from  $^5D_0$  to  $^7F_2$ , indicating the location of  $Eu^{3+}$  ion at the site of non-inversion symmetry. With increasing  $Bi^{3+}$  content, the luminescent intensity of the phosphor is increased up to the  $Bi^{3+}$  concentration of 5 mol%. When the concentration of  $Bi^{3+}$  is 5 mol%, the emission intensity is about 12 times compared to the height of  $(Y_{0.5}Gd_{0.4}Eu_{0.1})(V_{0.8}P_{0.2})O_4$  phosphors.