The Effect of Addition of Gd, La into YVO$_4$:Eu^{3+} Red Phosphor

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Abstract

The effect of doping Gd, La for Y into YVO$_4$:Eu^{3+} red phosphor on its photoluminescence(PL) intensity has been investigated. YVO$_4$:Eu-based phosphors were prepared by solid-state reaction at temperature above 1200 °C. Under UV excitation(254, 365 nm), it was measured that YVO$_4$:Eu^{3+} was superior to a commercial red phosphor (Y,Gd)BO$_3$:Eu^{3+} in terms of PL intensity and CIE color coordinates. When La, Gd were doped into YVO$_4$:Eu^{3+}, the change in the structure of the host material was observed. In result, when the (Y$_{1-x}$La$_x$)VO$_4$:Eu^{3+} phosphors were excited by 365 nm excitation, its PL intensity was improved up to about 30 % for the case of x being 0.4 ~ 0.6.

1. Objective and Background

Vacuum ultra violet(VUV) rays with 147 and 173 nm wavelength from xenon gas-mixture have been used as the main stimulation source of photoluminescence(PL) phosphor in conventional plasma display panels. Considering, however, luminous efficiency of phosphor by VUV excitation, VUV by xenon gas-mixture is a very poor source. The one of the main reasons for that is the relatively large Stokes shift(from 147-173 nm to approximately 400-700 nm) that limits the quantum efficiency of phosphor as low as 25%. Recently, near ultra violet(UV) emitted from N$_2$ gas–mixture has been of interest and attractive and studied by several groups for the application to PDPs because of its possibility in adjusting conventional high efficiency RGB phosphors for PDPs [1, 2].

YVO$_4$:Eu^{3+} red phosphor which is one of these high efficiency RGB phosphors is a strongly luminescing material which had been used as the red phosphor in cathode ray tubes for more than 20 years. Moreover, this phosphor is well excited by UV light, and the PL quantum yield of the europium emission is as high as 70% [3]. According to several reports, the Stokes shift

is about 10,000 cm^{-1} in YVO$_4$:Eu. This makes YVO$_4$:Eu^{3+} a very efficient red phosphor : excitation into the vanadate group (31,850 cm-1) is followed by energy migration from the vanadate group to Eu^{3+} centers [4].

La and Gd were investigated as host cations substituting Y to enhance the PL intensity by UV excitation. All three elements have the same valence electron configuration (d^{1}s^2) and are optically inert. Their ionic radii in the trivalent state are 1.14, 0.95, and 0.92 Å, respectively. In addition, they possess spherically symmetrical electronic structures and are characterized by considerable stability : Y^{3+} and La^{3+} have a noble gas electronic structure (f^0), and Gd^{3+} has a half-filled shell(f^7). Such configurations provide the basis for effective host crystal structures of which excitation energy might be dissipated. Moreover, when combined with proper anions, these cations from host materials exhibit no absorption in the visible region and hence are white in body color.

The aim of this study is to suggest a method to improve the PL intensity of YVO$_4$:Eu^{3+} red phosphor which is a good candidate phosphor for PDP application, and understand the effect of doping Gd, La for Y into YVO$_4$:Eu^{3+} red phosphor on its PL intensities. And the correlation between the structure of the host materials and PL intensities has been considered.

2. Results and Discussion

lanthanide orthovanadates were prepared by solid-state reactions. For the synthesis of these phosphors, high purity yttrium oxide(Y$_2$O$_3$), gadolinium oxide(Gd$_2$O$_3$), lanthanum oxide(La$_2$O$_3$), vanadium oxide(V$_2$O$_5$), and europium oxide(Eu$_2$O$_3$) were taken as the starting chemicals. For present studies, we fixed the dopant europium concentration as 0.05 mole [5]. Chemicals in the following compositions were mixed thoroughly by using ethanol as a solvent for mixing.

$Y_{0.05}VO_4{:}Eu_{0.05}$	$Y_{0.05}VO_4{:}Eu_{0.05}$
$(Y_{0.8},\ Gd_{0.2})_{0.95}VO_4{:}Eu_{0.05}$	$(Y_{0.8},\ La_{0.2})_{0.95}VO_4{:}Eu_{0.05}$
$(Y_{0.6},\ Gd_{0.4})_{0.95}VO_4{:}Eu_{0.05}$	$(Y_{0.6},\ La_{0.4})_{0.95}VO_4{:}Eu_{0.05}$
$(Y_{0.4},\ Gd_{0.6})_{0.95}VO_4{:}Eu_{0.05}$	$(Y_{0.4},\ La_{0.6})_{0.95}VO_4{:}Eu_{0.05}$
$(Y_{0.2},\ Gd_{0.8})_{0.95}VO_4{:}Eu_{0.05}$	$(Y_{0.2},\ La_{0.8})_{0.95}VO_4{:}Eu_{0.05}$
$Gd_{0.95}VO_4{:}Eu_{0.05}$	$La_{0.95}VO_4{:}Eu_{0.05}$

Initially these oxides were calcined at 900 °C for 10 hrs and then calcined at 1200 °C for 20 hrs. After these procedure, the phosphors were light yellow in color, due to the presence of the vanadium, and emitted a bright-red color under a UV source.

Figure 1 shows the PL spectra of $YVO_4{:}Eu^{3+}{}_{0.05}$ red phosphor excited by 254 nm. It has been reported that the pure YVO_4 shows blue emission by itself, but when Eu substitutionally replaces Y in the host material, the very sharp peaks in red region appeared instead of broad band blue emission. The emission spectra of $YVO_4{:}Eu^{3+}$ shown in Fig. 1 present the characteristics of Eu^{3+} emission transitions arising mainly from the $^5D_0$ level to the $^7F_J(J{=}0,1,2,3,4)$ manifolds. Among these transitions, the structurally sensitive electric dipole $^5D_0 \rightarrow {}^7F_2$ was most dominant.
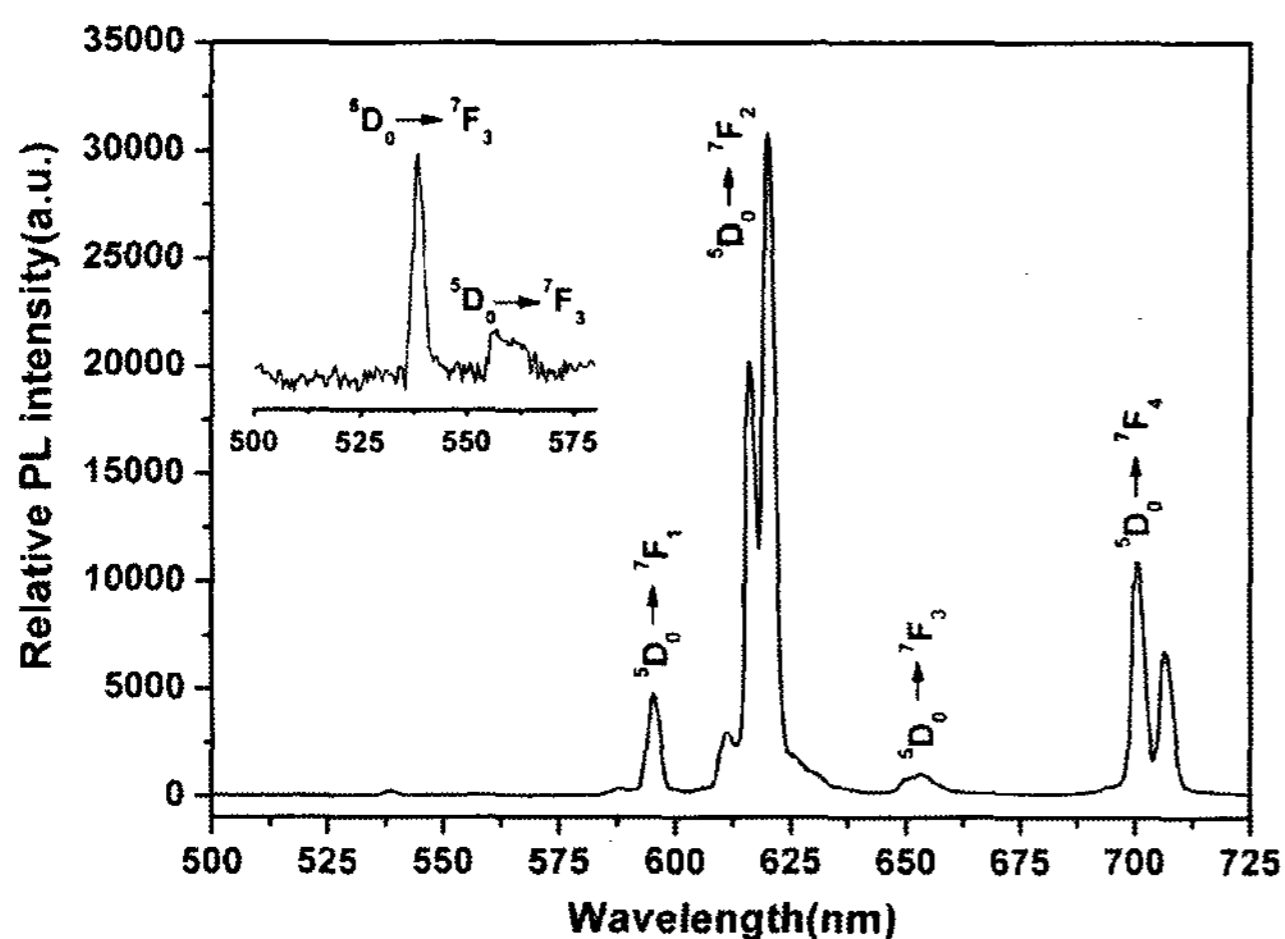

Figure 1. PL spectra of $YVO_4{:}Eu^{3+}$ red phosphor

Figure 2 shows the PL intensities of red phosphors excited by 254 nm and 365nm, relatively. Commercial red phosphor $(Y,Gd)BO_3{:}Eu^{3+}$ and $Y_2O_3{:}Eu^{3+}$ were used as reference phosphors. And $YVO_4{:}Eu$-based phosphors were prepared as mentioned previously.

Under UV excitation, the PL intensity of $(Y,Gd)BO_3{:}Eu^{3+}$ was very weaker than those of the other red phosphors and $YVO_4{:}Eu^{3+}$ showed very strong and sharp red emission. From several reports, it has been known that under VUV excitation $(Y,Gd)BO_3{:}Eu$ is superior to $Y_2O_3{:}Eu$ and $YVO_4{:}Eu$, however, under UV excitation the latters are much more efficient than the former [6].
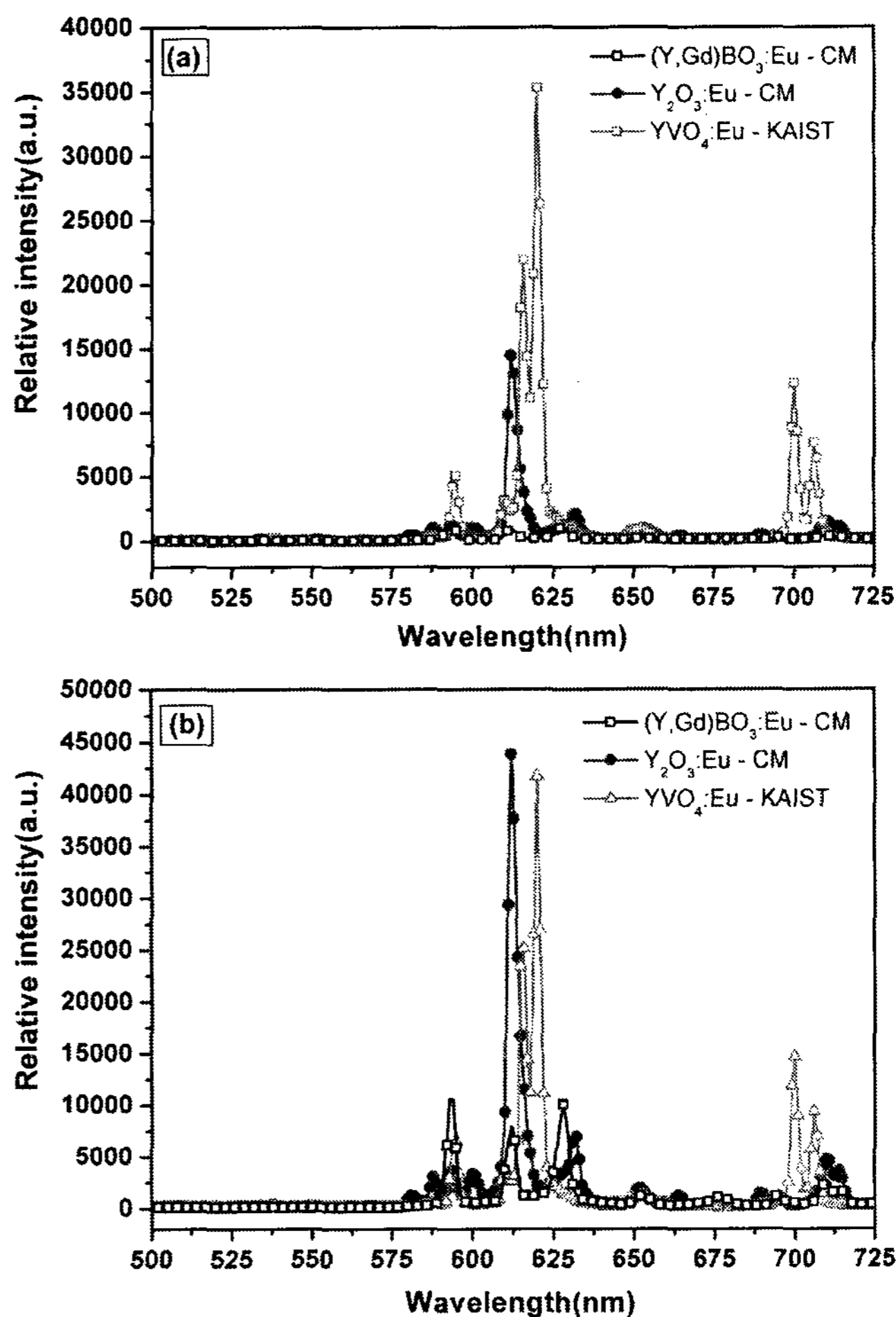

Figure 2. PL intensities of red phosphors such as the $(Y,Gd)BO_3{:}Eu^{3+}$, $Y_2O_3{:}Eu^{3+}$, and $YVO_4{:}Eu^{3+}$ excited by (a) 254 nm and (b) 365nm, respectively

Table 1 shows the CIE color coordinates of the red phosphors excited by 254 nm. $YVO_4{:}Eu^{3+}$ and $Y_2O_3{:}Eu^{3+}$ show the remarkably good color purity. $(Y,Gd)BO_3{:}Eu^{3+}$ excited by 254 nm shows the very poor propertiy which is the same by VUV excitation. Among these phosphors, $YVO_4{:}Eu^{3+}$ shows the best CIE color coordinates.

Table 1. CIE color coordinates of red phosphors

Compound	x	y
$(Y,Gd)BO_3:Eu^{3+}$	0.528	0.333
$Y_2O_3:Eu^{3+}$	0.628	0.338
$YVO_4:Eu^{3+}$	0.662	0.325

Figure 3 shows the PL intensity variation when Gd, La was added into YVO_4 structure. With increasing the amount of Gd addition, there were no big differences in the PL intensity of $(Y_{1-x}Gd_x)VO_4:Eu^{3+}$ excited by 254 and 365 nm sources, respectively. In the case of La addition, however, a little different phenomenon was measured. In detail, when $(Y_{1-x}La_x)VO_4:Eu^{3+}$ was excited by 254 nm, its intensity decreased linearly as the amount of La addition incre-
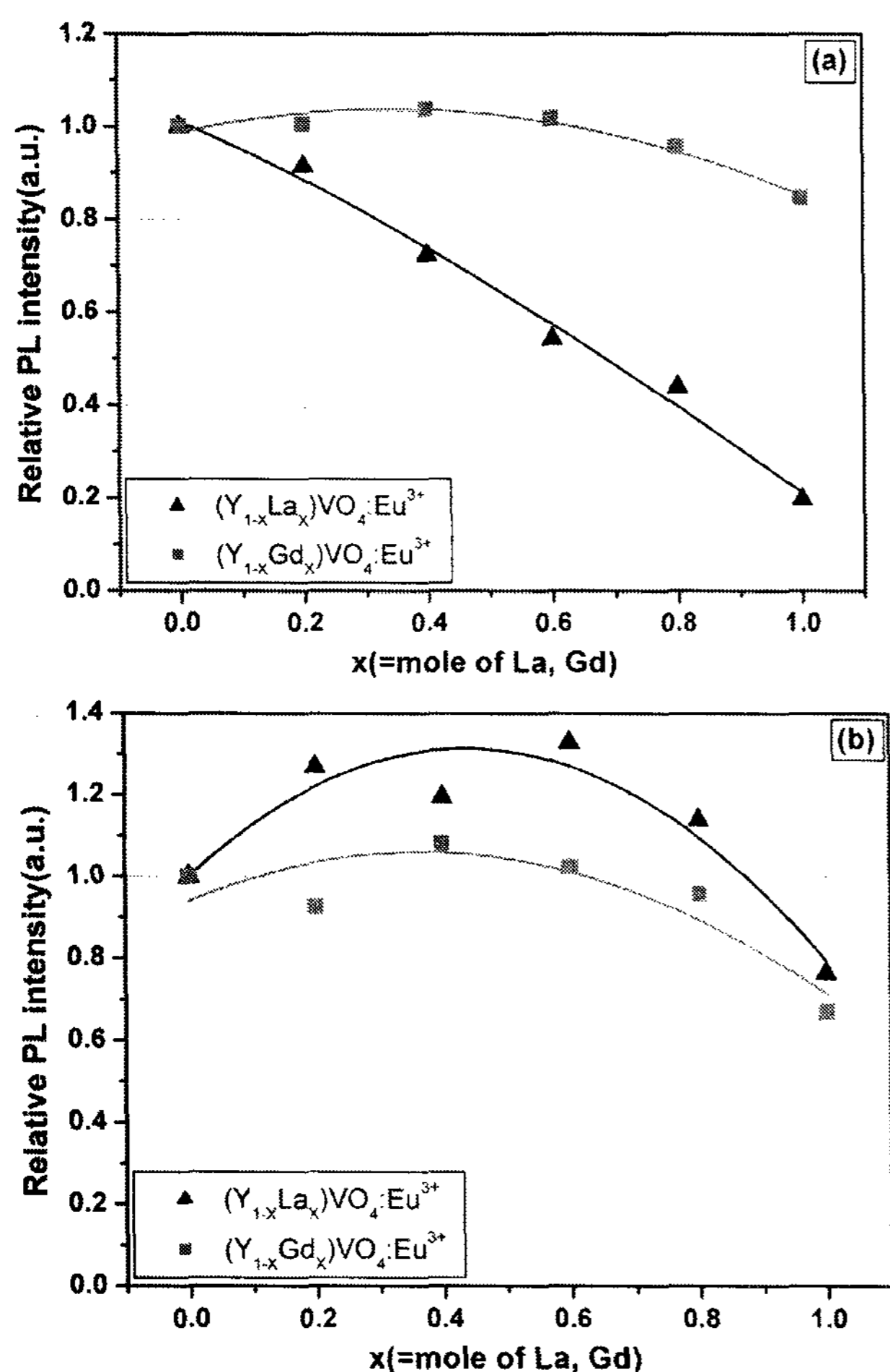
aeased. But under 365 nm excitation, PL intensity was improved up to about 30 % when La was added into YVO_4 in the range of 0.4 ~ 0.6 mole. These differences between Gd and La addition may be explained by inspecting a structural change of YVO_4 with doping Gd and La, which was caused by the difference of ionic radius and crystal formation between Gd and La. And the differences between 254 nm and 365 nm excitation in La addition may be explained by different emission mechanisms of activator ions, which are either direct excitation of activator ions or charge transfer from host [7]. The high PL intensity of $(Y_{1-x}La_x)VO_4:Eu^{3+}$ under 365 nm excitation was believed to be due to direct excitation of Eu^{3+} ion.
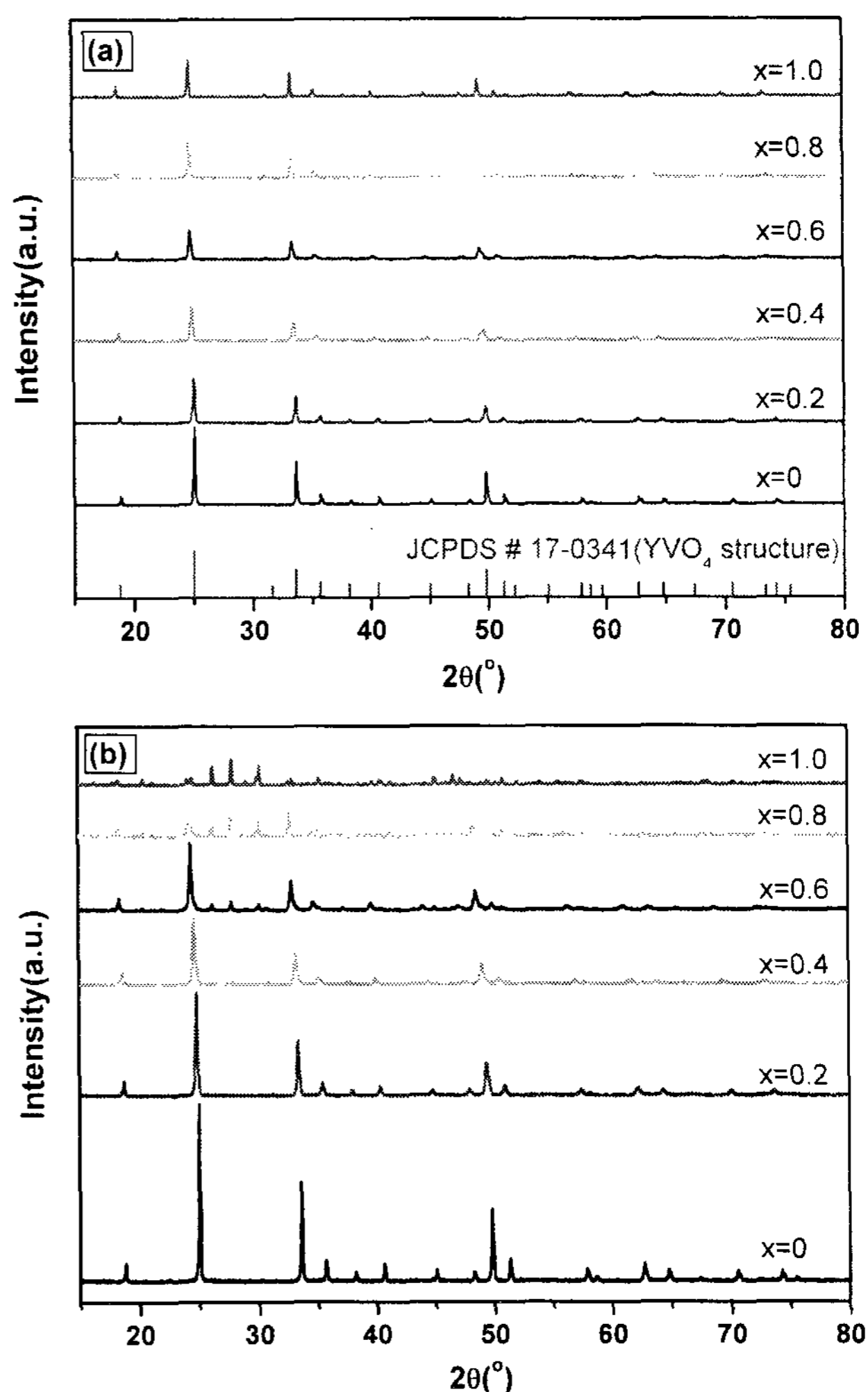

Figure 3. Relative PL intensities of red phosphors such as $(Y_{1-x}Gd_x)VO_4:Eu^{3+}$ and $(Y_{1-x}La_x)VO_4:Eu^{3+}$ excited by (a) 254 nm and (b) 365nm, relatively

Figure 4. XRD curves of (a) $(Y_{1-x}Gd_x)VO_4:Eu^{3+}$, (b) $(Y_{1-x}La_x)VO_4:Eu^{3+}$ calcined at 1200 °C. (x=0~1.0)

Figure 4 shows X-ray diffraction patterns of YVO_4, $GdVO_4$, and $LaVO_4$. YVO_4 and $GdVO_4$ have the same crystal structure which is tetragonal with a little different lattice constant. $LaVO_4$ is monoclinic. In result, crystal symmetry of $LaVO_4$ is very poor among these host materials. But, generally it is well known that low symmetry of rare earth site gives the increasing the probability of radiative transitions(within the 4f-electron shell) through destruction of parity forbiddenness [8]. And the phenomenon that the high PL intensity of $(Y_{1-x}La_x)VO_4:Eu^{3+}$ in Fig. 3(b) can be explained by concept of hypersensitive transition. Additionally, it is well known that the emission color of Eu^{3+}-activated phosphor is almost completely determined by its crystal structure.

3. Conclusion

In this work, we have studied the PL characteristics of $YVO_4:Eu^{3+}$ to apply it for PDPs using near UV excitation and the effect of Gd, La addition into $YVO_4:Eu^{3+}$ red phosphor on its PL intensity and crystal structure. Under UV excitation(254, 365 nm), it was found that $YVO_4:Eu^{3+}$ is superior to a commercial red phosphor $(Y,Gd)BO_3:Eu^{3+}$ in terms of PL intensity and CIE color coordinates. And with increasing the amount of La and Gd addition into $YVO_4:Eu^{3+}$, the variation in the crystal structure of YVO_4 was observed. Especially, when the $(Y_{1-x}La_x)VO_4:Eu^{3+}$ phosphors were excited by 365 nm source, its PL intensity was improved up to about 30 % in the range of x being 0.4 ~ 0.6. From the results in this study, it was found that a close correlation between the emission of $YVO_4:Eu^{3+}$ and the crystal symmetry of Eu^{3+} ion site existed.

4. Acknowledgements

5. Reference

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