The Optical Properties of $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ Phosphors for White LED

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Bright yellow $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors were synthesized. White LED was obtained by the combination of non-absorbed blue emission from a blue LED itself and yellow emission from $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors. The crystal structures and optical properties of $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors were investigated.

Key Words : Phosphors, White LED

Introduction

Recently, there has been much interest in light-emitting diode (LED) that emit light from ultraviolet to infrared. Major developments in wide band gap III-V nitride compound semiconductors have led to the commercial production of high-efficiency LED.[1-5] Traditional colored LED has proven themselves in signal, as indicator lights and in automotive lighting. White LED is important in expanding LED applications toward general lighting, where the opportunities are enormous. Recently, efficient blue and green LED devices were developed. Green and blue InGaN technology makes possible the first white light LED. LED manufacturers produced a white light by simply mixing red, green, and blue LED (multiple LED). Unfortunately, the multiple LED produces a poor white. The variation of LED color properties due to manufacturing tolerances makes the multiple LED impractical. Moreover, the various LED experience different light output degradation rates, which will produce different color temperature over the time.

To solve these problems, blue LED chips coated with a $Y_3Al_5O_{12}$:Ce phosphor was used to provide a white light with correlated color temperatures ranging from 4,000 to 11,000 K.[6,7] $Y_3Al_5O_{12}$:Ce phosphor emit broad yellow luminescence.[8] White light can be obtained by the combination of non-absorbed blue emission from blue LED and broad yellow emission from $Y_3Al_5O_{12}$:Ce phosphor. This simple structure avoids the need to control a consistent red-green-blue emission ratio from multiple LED. However, the optical properties of $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors for white LED has scarcely been published. In this paper, the optical properties of $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors are presented for the application of white LED. Especially, the substitution effects of Gd and Ga ions in $(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors were elucidated and optimized for white LED application.

Experimental Section

$(Y_{1-x}Gd_x)_{3-z}(Al_{1-y}Ga_y)_5O_{12}$:$Ce_z$ phosphors were prepared

by solid-state reaction. The starting material were Y_2O_3, Gd_2O_3, Al_2O_3, Ga_2O_3, and CeO_2. BaF_2 was used for flux. These materials were obtained from AMR(advanced material resource), Rhodia Chimie, Ceralox, and Chameleon Reagent and used without further purification. These starting materials were weighed out in stoichiometric quantities, ground together in a mortar, and then placed in an alumina crucible in a box furnace. For example, Y_2O_3 (2.16 mol), Gd_2O_3 (0.54 mol), Al_2O_3 (4.00 mol), Ga_2O_3 (1.00 mol), and CeO_2 (0.60 mol) were mixed for $(Y_{0.8}Gd_{0.2})_{2.7}(Al_{0.8}Ga_{0.2})_5O_{12}$:$Ce_{0.3}$. The Ce^{3+} concentration was fixed. About 2%(w/w) of BaF_2 was mixed with total metal oxides. The mixtures were calcined at 1550 °C for 4 hours.

X-Ray powder diffraction patterns were recorded on a Phillips PW1800 diffractometer using Cu-K_α radiation. Diffraction patterns were taken over the range of $10^o < 2\theta < 90^o$ with a scan rate of 1° in 2θ/min. Excitation and emission spectra were measured using a spectrophotometer with a 0.275 m triple grating monochromator (Acton Research Co.), PHV400 photomultiplier tube, and a 500W Xe-lamp light source. The incident beam is perpendicular to the surface of the sample, and the observation angle is equal to 45° with normal to excitation source.

A blue LED (NSPB500, Nichia Chemical Industries) which had a peak emission wavelength of 465 nm was used in this work. The phosphor was dispersed in a 10 wt% poly-vinyl-alcohol (PVA, polymerization degree: 200) aqueous solution (1 : 4 by weight) applied on the poly-ethylene-terephthalate (PET) film. The white LED was prepared by coating this suspension film onto the outer sphere of blue LED. The relative amounts of phosphor are controlled by thickness of applied phosphor layer on PET film. Chromaticity of the LED was measured using 15 cm diameter integration sphere with photoluminescence measurement.

Results and Discussion

In the Y_2O_3-Al_2O_3 system, there are three different phases: YAM ($Y_4Al_2O_9$, yttrium aluminum monoclinic), YAP (YAlO₃, yttrium aluminum perovskite), and YAG ($Y_3Al_5O_{12}$, yttrium aluminum garnet). Even if the synthesis of YAG is performed with a stoichiometric mixture of Y_2O_3 and Al_2O_3, other

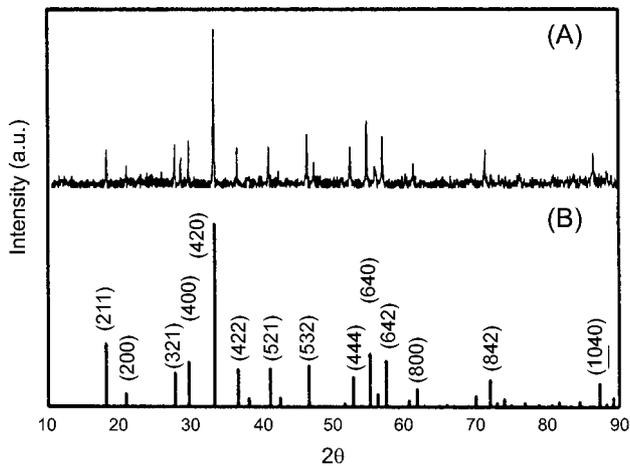*Corresponding Author. e-mail : ydhuh@dankook.ac.kr

Figure 1. X-ray diffraction patterns and Miller indices of (A) $Y_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor and (B) cubic $Y_3Al_5O_{12}$ crystal.

Figure 3. The plot of a (Å) of the crystal constant with different contents of the Ga (y) in $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors.

phases, YAM and YAP, often coexist as by-products. Ohno and Abe reported that YAM appeared first, YAP second, and YAG last, as the firing temperature was increased.[9] In the synthesis with BaF_2, the firing temperatures that gave the highest peak intensity for YAM and YAP were 200-300 ºC lower than those for samples fired without BaF_2. Only YAG was synthesized above 1500 ºC when BaF_2 was used.[9] In this work, $(Y_{1-x}Gd_x)_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors with various compositions were synthesized at 1550 ºC, where $0.0 \leq x \leq 0.8$ and/or $0.0 \leq y \leq 0.8$. Figures 1(A) and 1(B) show the X-ray diffraction patterns of $Y_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor synthesized and calculated powder pattern of cubic YAG, respectively.[10] Figure 1 indicates that only single cubic YAG phase is formed for synthesizing the $Y_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor.

The crystal structure of YAG is cubic with a = 12.016(3) Å.[10] The crystal structure of GAG ($Gd_3Al_5O_{12}$, gadolinium aluminum garnet) and YGaG ($Y_3Ga_5O_{12}$, yttrium gallium garnet) are also cubic with a = 12.11 Å, a = 12.273(1) Å,
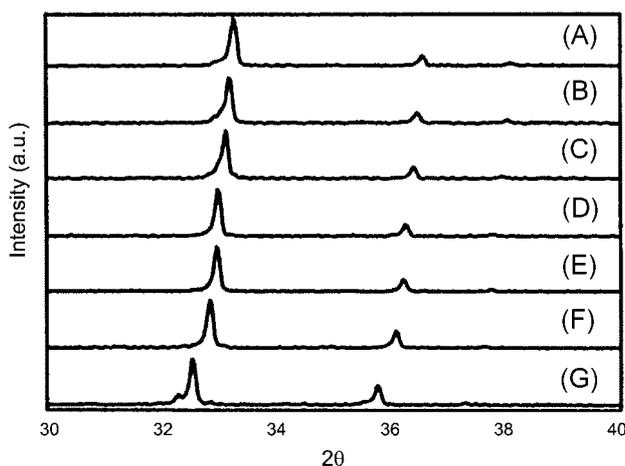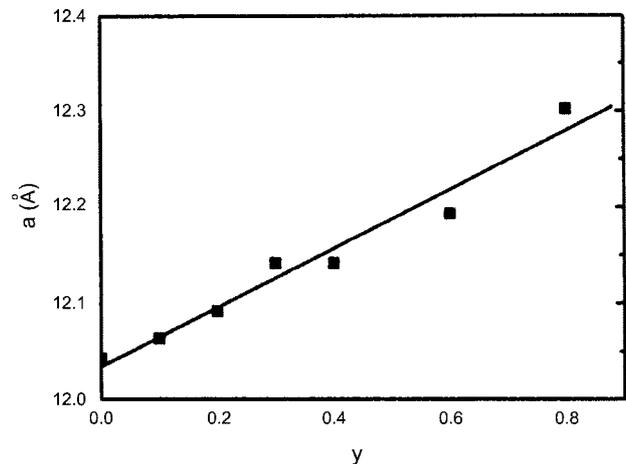

Figure 2. (420) and (422) diffraction peaks of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors with different contents of Ga. (A) y = 0.0, (B) y = 0.1, (C) y = 0.2, (D) y = 0.3, (E) y = 0.4, (F) y = 0.6, and (G) y = 0.8.

respectively.[11,12] Figure 2 shows the X-ray diffraction patterns of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors in which a portion of the Al is replaced with Ga. The (420) and (422) peaks are shifted to the lower angle as the Ga increases. These are caused by the difference in lattice parameter between YAG and YGaG. The lattice parameter of YGaG (a = 12.27 Å) is larger than that of YAG (a = 12.01 Å), since the ionic radius of Ga^{3+} (0.62 Å) is larger than that of Al^{3+} (0.51 Å).[10,12,13] The correlation between crystal constant (a) and Ga mole fraction (y) of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors is shown in Figure 3 and can be expressed in the following equation, a (Å) = $12.04 + 0.26 \cdot y$. The XRD results indicated that $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors were well synthesized as we expected. Similar results were obtained for $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors with following equation, a (Å) = $12.01 + 0.09 \cdot x$. This is caused that the crystal constant of GAG (a = 12.11 Å) is slightly larger than that of YAG (a = 12.01 Å), because of the slightly larger ionic radius of Gd^{3+} (0.94 Å) compared with that of Y^{3+} (0.90 Å).[10,11,13]

The ground and excited electronic configurations of Ce^{3+} ion are $4f^1$ and $5d^1$, respectively. Since the $5d \rightarrow 4f$ transition is parity allowed, the emission transition is an allowed one. Therefore, cerium-activated YAG ($Y_{3-z}Al_5O_{12}:Ce_z$) is known as an efficient phosphor for three decades. Its yellow luminescence can be excited by blue photons. The system $Y_{3-z}Al_5O_{12}:Ce_z$ is ideally suited for luminescence conversion of blue light emitting diode (blue LED). Because blue and yellow are complementary colors, white light emitting diode (white LED) can be obtained by the combination of non-absorbed blue emission from blue LED and broad yellow emission from $Y_{3-z}Al_5O_{12}:Ce_z$ phosphor.

Figure 4 shows emission spectra of $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors, where the wavelength of excitation source (λ_{ex}) is fixed at 465 nm. The λ_{em} is shift to longer wavelength as the content of Gd (x) is increased in $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors. This agrees with Hollway's result. They reported that the substitution of smaller Lu^{3+} ion for the Y^{3+} shifts the bands toward the blue, while substitution of the larger La^{3+} and Gd^{3+} ions shift the bands toward the red in
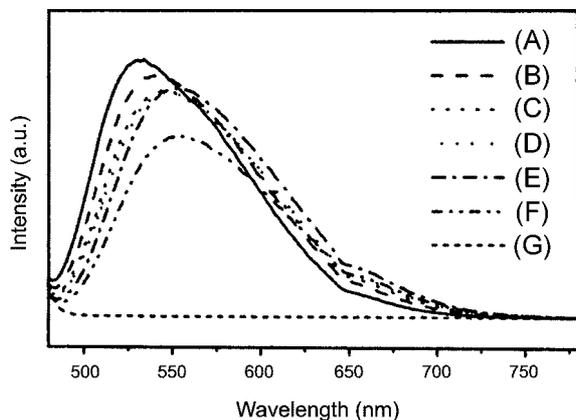
Figure 4. Emission spectra of $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors with $\lambda_{ex} = 465$ nm at different values of (A) x = 0.0, (B) x = 0.1, (C) x = 0.2, (D) x = 0.3, (E) x = 0.4, (F) x = 0.6, and (G) x = 0.8.
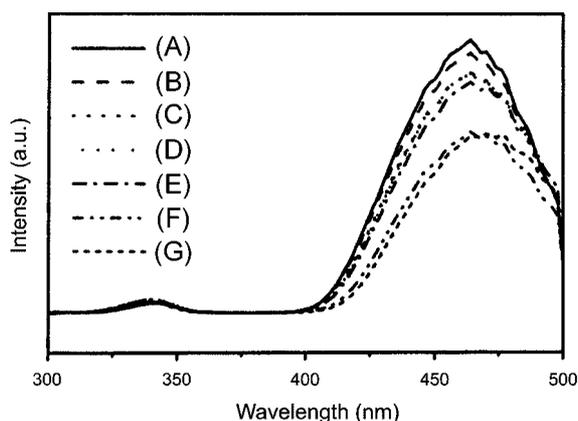

Figure 5. Excitation spectra of $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors with $\lambda_{em} = 540$ nm at different values of (A) x = 0.0, (B) x = 0.1, (C) x = 0.2, (D) x = 0.3, (E) x = 0.4, (F) x = 0.6, and (G) x = 0.8.

$(Y_{1-x}M_x)_{3-z}Al_5O_{12}:Ce_z$ (M = Lu, La, Gd).[8] And the maximum intensity of emission (I_{em}) is decreased as the content of Gd is increased in $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$, since $Gd_{2.7}Al_5O_{12}$: $Ce_{0.3}$ does not exhibit fluorescence. Figure 5 shows excitation spectra of $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$, where the wavelength of emission (λ_{em}) is fixed at 540 nm. There is no shift in the excitation peaks (λ_{ex}) with increasing the content of Gd. However, the maximum intensity of excitation (I_{ex}) is decreased as the Gd increases. Figure 6 and 7 show emission and excitation spectra of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ at $\lambda_{ex} = 465$ nm and $\lambda_{em} = 540$ nm, respectively. Both λ_{em} and λ_{ex} are shift to shorter wavelength as the content of Ga (y) increases. I_{em} and I_{ex} are also decreased as the content of Ga increases.

Unfortunately, we can't fabricate the white LED since we have no machines for LED chip mounting, wire bonding, and mold resin sealing. In order to investigate the optical properties of white LED, we generate the white LED which $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor films are coated onto the outer sphere of blue LED. Even though, it is not the way to fabricate the white LED, this method is easy to generate and test the white LED. Figure 8 shows the photoluminescence spectra of various LED's where different amounts of
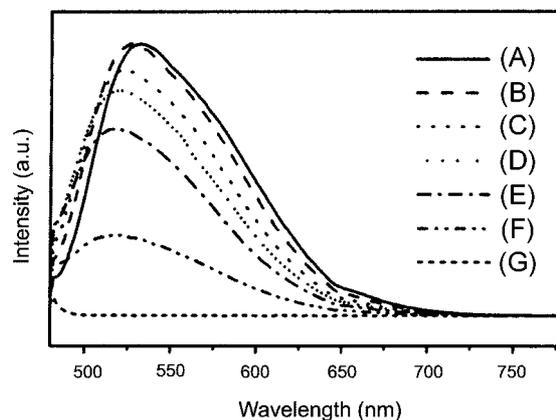

Figure 6. Emission spectra of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors with $\lambda_{ex} = 465$ nm at different values of (A) y = 0.0, (B) y = 0.1, (C) y = 0.2, (D) y = 0.3, (E) y = 0.4, (F) y = 0.6, and (G) y = 0.8.
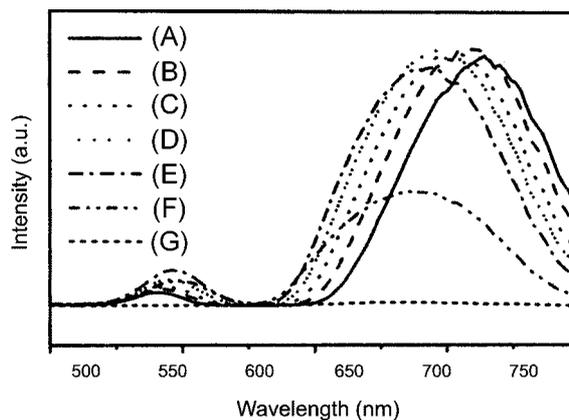

Figure 7. Excitation spectra of $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors with $\lambda_{em} = 540$ nm at different values of (A) y = 0.0, (B) y = 0.1, (C) y = 0.2, (D) y = 0.3, (E) y = 0.4, (F) y = 0.6, and (G) y = 0.8.
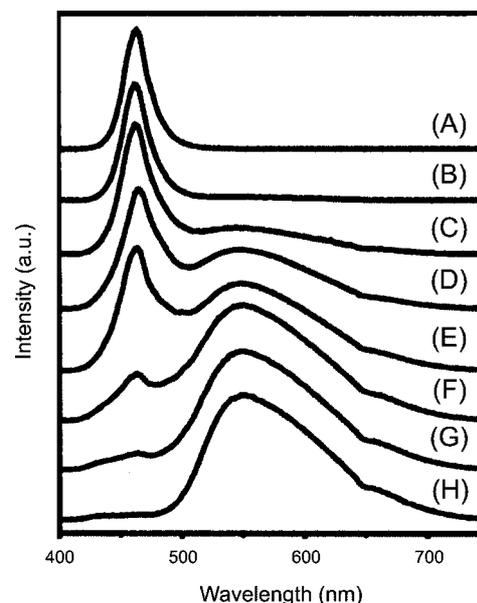

Figure 8. Photoluminescence spectra of various LED's where different amounts of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors are coated. No phosphor is used (A). The amounts of phosphor is increasing from (B) to (H).

Figure 9. Chromaticity diagram of various LED's where different amounts of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors are coated. No phosphor is used (A). The amounts of phosphor is increasing from (B) to (H).
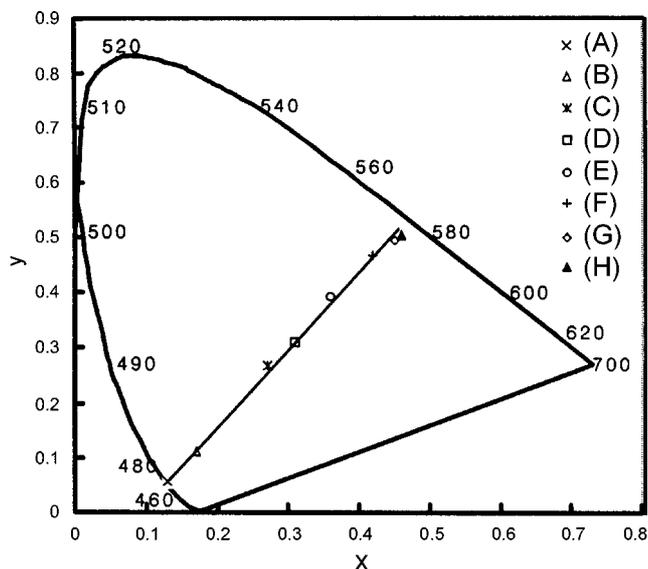
$(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors films are coated onto the outer sphere of the blue LED. The distinct emission peaks of LED's appear at 465 and at 550 nm which are due to the blue LED itself and $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ emission under the blue LED excitation, respectively. When the concentration of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ is increased, the intensity of 465 nm is decreased, while that of 550 nm is increased simultaneously. The CIE (Commission International de l'Eclairage) chromaticity coordinates of photoluminescence spectra of blue and yellow emitting LED are shown in Figure 9. The CIE chromaticity coordinates of the blue LED are x = 0.13 and y = 0.08. As the concentration of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ is increased, the color approaches yellow regions which is the color of emitting $(Y_{0.6}Gd_{0.4})_{2.7}$-$Al_5O_{12}:Ce_{0.3}$. The color corresponding to any point on CIE line, the law of lever rule can be applied with appropriate amounts of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$. In near ranges with x = 0.3 and y = 0.3 for the CIE chromaticity coordinates, we can obtain a white LED.

There are three commercial blue LED's, which emit light at 430, 450, and 465 nm, respectively. In order to choose the proper composition of phosphor, we have to know the emission wavelength of blue LED used. For example, $(Y_{0.8}Gd_{0.2})_{2.7}(Al_{0.8}Ga_{0.2})_5O_{12}:Ce_{0.3}$ is good candidate for white LED when blue LED at 450 nm was used, since its λ_{em} and λ_{ex} are 560 nm and 450 nm, respectively. $(Y_{0.8}Gd_{0.2})_{2.7}$-$(Al_{0.8}Ga_{0.2})_5O_{12}:Ce_{0.3}$ is strongly excited by 450 nm blue LED which can act as a primary light source and emit wavelength of 560 nm. White light can be obtained by mixing of 450 nm and 560 nm emissions. The intensities of

450 nm and 560 nm emissions can be controlled by choosing the proper amount of $(Y_{0.8}Gd_{0.2})_{2.7}(Al_{0.8}Ga_{0.2})_5O_{12}:Ce_{0.3}$ phosphor which is coated on the blue LED. In this way, we can generate various color temperatures of white emitting LED by choosing a proper composition and amounts of phosphor, even if a different kind of blue LED was used.

Conclusion

We synthesized yellow emitting $(Y_{1-x}Gd_x)_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors with various compositions. The crystal structures and optical properties of $(Y_{1-x}Gd_x)_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors were investigated. While there is no shift in λ_{ex}, the λ_{em} is shift to longer wavelength with increasing the content of Gd in $(Y_{1-x}Gd_x)_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors. Both λ_{em} and λ_{ex} are shift to shorter wavelength as the content of Ga increases in $Y_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphors. White LED can be obtained by the combination of non-absorbed blue emission from blue LED and broad yellow emission from $(Y_{1-x}Gd_x)_{2.7}(Al_{1-y}Ga_y)_5O_{12}:Ce_{0.3}$ phosphor, since blue and yellow are complementary colors. We choose the $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor for making the white LED with the 465 nm emitting blue LED, since it absorbs the 465 nm and emits the 550 nm. To investigate the optical properties of white LED, $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphors films are coated onto the outer sphere of the blue LED. When the amount of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ is increased, the intensity of 465 nm is decreased, while that of 550 nm is increased simultaneously. By taking the proper amount of $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$, we can obtain a white LED in near ranges with x = 0.3 and y = 0.3 for the CIE chromaticity coordinates.

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