Tunable full-color-emitting La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor for application to warm white-light-emitting diodes

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La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} showed three emission bands when excited by ultraviolet light. A blue emission originates from Eu^{2+}, whereas both green and red emissions originate from Mn^{2+}. The luminescent mechanism is explained invoking the energy transfer of Eu^{2+}→Mn^{2+} and Mn^{2+}(tetrahedral site)→Mn^{2+}(octahedral site). This energy transfer was confirmed by faster decay times of the blue and green emissions as energy donors. The emitted color of La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} can be easily tailored from blue to red through variations of the Mn^{2+} content. The white-light-emitting diode fabricated via a combination of an ultraviolet light-emitting diode (λ_{peak}=385 nm) with La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} showed a warm white light (T_c=3559 K). © *2006 American Institute of Physics.* [DOI: 10.1063/1.2398887]

Recently, the field of solid-state lighting based on GaN semiconductors has seen remarkable breakthroughs in efficiency.[1] Essentially, it is expected that white-light-emitting diodes (LEDs) can offer advantages of high brightness, reliability, low power consumption, and a long life time compared to conventional light bulbs and fluorescent lamps.[2] The conventional way involves combining a blue LED with a yellow-emitting Y$_3$Al$_5$O$_{12}$:Ce^{3+} phosphor. This method is relatively easy to perform and the device has been commercialized. However, there are several problems present with this type of white LED, including a blue-yellow color separation (halo effect) and temperature and current dependence of both the chromaticity and spectrum shape.

In order to overcome these disadvantages, a combination of ultraviolet (UV) LEDs with red, green, and blue phosphor blends has been studied.[2–4] The resultant type of white LED can offer superior color uniformity, a high color rendering index, and excellent light quality. However, the luminous efficiency of these white LEDs is low due to the reabsorption of the emission color; moreover, their manufacturing cost is high. In contrast, if an UV-pumped white LED using a single-phased full-color-emitting phosphor becomes available, it would have the following advantages: There would be no reabsorption of the blue light by green or red phosphors and no requirement to mix two or three phosphors. Therefore a single-phased full-color-emitting phosphor for UV-pumped white LEDs would most likely enhance the luminous efficiency and color reproducibility of a white light source.[4] Kim *et al.* investigated single-phased full-color-emitting phosphors[4,5] in which the color of the emission is fixed. In this case, if the color of the emitted radiation is to be changed, another phosphor must be added. In this study, the emission color of a single-phased La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor can be easily tailored from blue to red via a variation of the Mn^{2+} content.

This study reports the structural and optical properties of the La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor. In addition, the energy transfer mechanism of the La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor was investigated, and white LEDs were fabricated via a combination of UV LED chip (385 nm) with the La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor.

The La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphors were prepared via a conventional solid-state reaction method. Proper amounts of high purity (>99.99%) starting materials La$_2$O$_3$, Al$_2$O$_3$, Eu$_2$O$_3$, and MnO (all from Aldrich Co.) were mixed together. The solution was air dried for 3 h at room temperature. Samples were fired at 1500 °C for 4 h under a reducing atmosphere. Crystalline phases of the samples were analyzed by x-ray diffraction (Rigaku, D/max-IIIC). Photoluminescence characteristics were analyzed on the basis of emission and excitation spectra at room temperature using a DARSA PRO 5100 Photoluminescence System (Korea). A mixture of the phosphor and epoxy resin was coated onto an UV LED chip (385 nm). The white LED was operated with various forward currents.

The x-ray diffraction pattern of the La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor is shown in Fig. 1. The pattern was found to be in good agreement with one registered in JCPDS regardless of the content of the activators, indicating that the sample is of a single phase. Distorted magnetoplumbite (La$_{0.827}$Al$_{11.9}$O$_{19.09}$) has a space group of $P6_3/mmc$ and has 12-coordinated La sites and three different Al sites of 4, 5, and 6 coordinations in a unit cell.[6] Stevels has proposed that La^{3+} sites are substituted by Eu^{2+} ions and that tetrahedral and octahedral sites are substituted by Mn^{2+} ions.[7]

Figures 2(a) and 2(b) show the photoluminescence (PL) and photoluminescence excitation (PLE) spectra for the La$_{0.827}$Al$_{11.9}$O$_{19.09}$:Eu^{2+},Mn^{2+} phosphor, respectively. As shown in Fig. 2(a), the PL spectrum was composed of blue, green, and red emission bands located at 450, 525, and 660 nm, respectively. The blue emission band at 450 nm was attributed to the typical $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions that replaced La^{3+} ions.[8] The green (525 nm) and red (660 nm) emission bands were ascribed to the $^4T_1 \rightarrow {}^6A_1$

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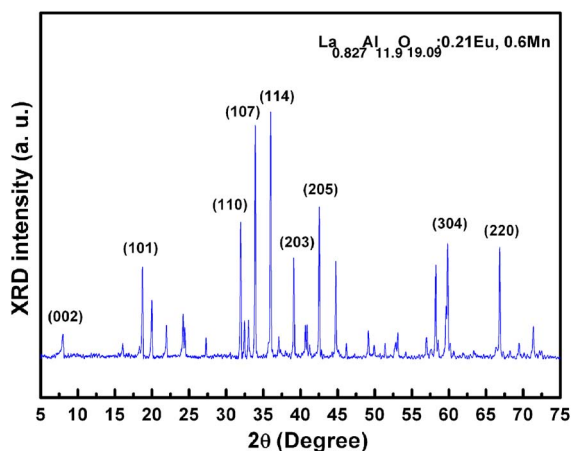[b]Author to whom correspondence should be addressed; FAX: +82-42-864-3310; electronic mail: dyj@kaist.ac.kr

FIG. 1. (Color online) X-ray diffraction pattern of $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor.

transition of $3d^5$ levels of Mn^{2+} ions which substituted into tetrahedral sites and octahedral sites of Al^{3+} ions, respectively.[4,7] Generally, as the crystal field at an octahedral site is stronger than that of a tetrahedral site,[5] the red emission band is ascribed to Mn^{2+} ions in an octahedral oxygen environment. The red emission band is approximately at 660 nm; its full width at half maximum is nearly 90 nm. These characteristics clearly indicate that the emission observed is not due to Mn^{4+} ions, which give rise to emission spectra consisting of several fairly sharp lines around 650 nm.[9] As shown in Fig. 2(b), the PLE spectra monitored at 450, 525, and 660 nm show very similar shapes. The main
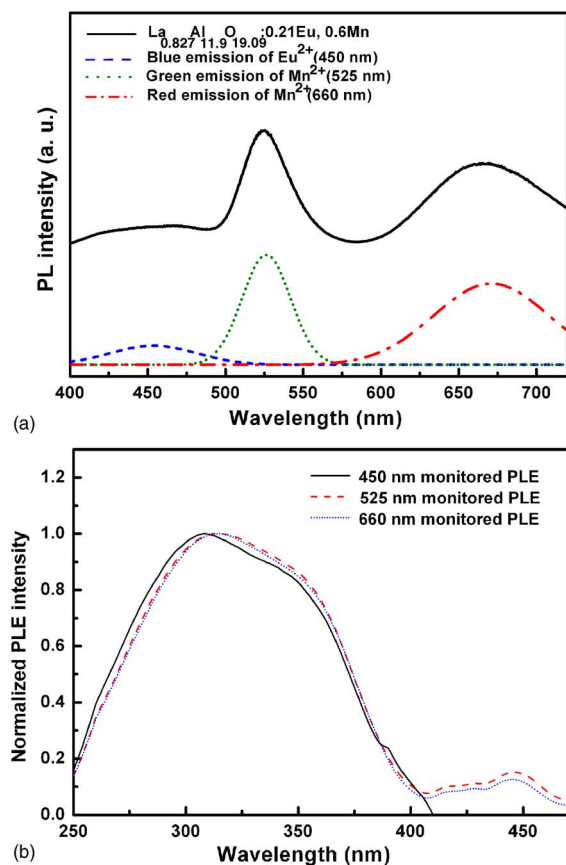

FIG. 2. (Color online) (a) PL spectra of $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor and deconvolution of blue, green, and red bands. (b) PLE spectra monitored at 450, 525, and 660 nm of $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor.
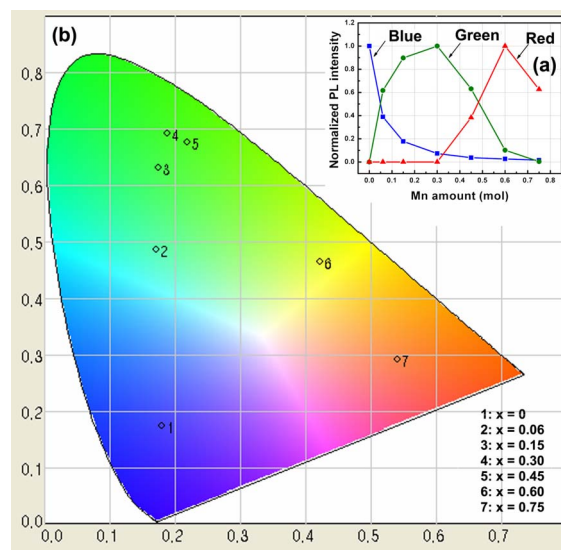

FIG. 3. (Color online) (a) Dependence of the normalized emission intensity of blue, green, and red in $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$,$xMn^{2+}$ phosphor on the amount of Mn^{2+}. (b) CIE chromaticity diagram for $La_{0.827}Al_{11.9}O_{19.09}$: $0.18Eu^{2+}$,xMn^{2+} phosphor with Mn^{2+} amounts (λ_{ex}=370 nm).

excitation bands in the range of 250–400 nm were caused by $4f^7 \rightarrow 4f^65d^1$ transitions of Eu^{2+} ions and the excitation bands peaking in the range of 425 and 450 nm were due to $^6A_1 \rightarrow {}^4E_g$, $^4A_1$ (^4G) and $^6A_1 \rightarrow {}^4T_{2g}$ ^4G transitions of the $3d^5$ level of the Mn^{2+} ions, respectively.[7,8] Thus, the curves suggest that the luminescence of both the green and red colors emitted by Mn^{2+} ions is mainly excited by Eu^{2+} ions. Given that the $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor has a strong PLE band at an UV region, it is a suitable phosphor for UV-pumped white LEDs.

Figure 3(a) shows the dependence of the normalized PL intensity of blue, green, and red emissions on the amount of Mn^{2+}. When the $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$ phosphor was not doped with Mn^{2+} ions, it emitted only a blue emission. With an increase in the Mn^{2+} content, the blue emission considerably decreased and the green emission increased. This phenomenon is attributed to the energy transfer from Eu^{2+} to Mn^{2+} on tetrahedral sites which emit a green emission. In addition, when $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$,$xMn^{2+}$ phosphors were doped with over 0.3 mol of Mn^{2+}, the red emissions increased and the green emissions decreased. This phenomenon is believed to have resulted from the energy transfer from Mn^{2+} at tetrahedral sites to Mn^{2+} at octahedral sites. The CIE chromaticity coordinates for $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$,$xMn^{2+}$ (x=0–0.75) phosphors with Mn^{2+} contents are shown in Fig. 3(b). The emitting colors of $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$,$xMn^{2+}$ (x=0–0.75) phosphors can constitute a full-color phosphor and be easily tailored from a blue to a red emission by simply controlling the Mn^{2+} contents.

In order to confirm the energy transfer between Eu^{2+} and Mn^{2+}, which can explain the luminescent mechanism in the $La_{0.827}Al_{11.9}O_{19.09}$:$Eu^{2+}$,$Mn^{2+}$ phosphor, the decay times of the luminescence from Eu^{2+} and Mn^{2+} were measured. The decay curves of the 450 nm emission of Eu^{2+} and the 525 nm emission of Mn^{2+} in $La_{0.827}Al_{11.9}O_{19.09}$:$0.18Eu^{2+}$,$xMn^{2+}$ phosphors are presented in Figs. 4(a) and 4(b), respectively. As described by Blasse and Grabmaier,[10] it is well established that the decay behavior can be expressed by
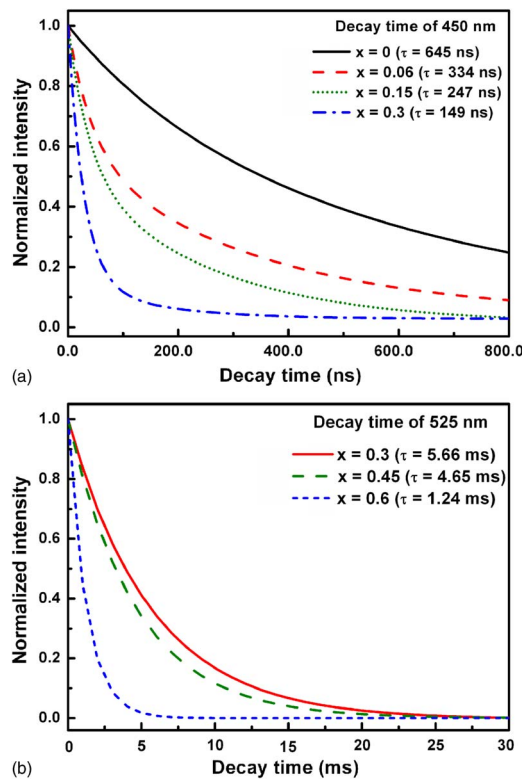
(a)

(b)

FIG. 4. (Color online) Decay curves of (a) Eu^{2+} (450 nm) and (b) Mn^{2+} (525 nm) emission bands of $La-Al-O:0.18Eu^{2+},xMn^{2+}$.

$$I = I_0 \exp(-t/\tau), \tag{1}$$

where I and I_0 are the luminescence intensities at times t and 0, respectively, and τ is the luminescence lifetime. On the basis of Eq. (1) and the decay curves in Fig. 4(a), the decay time values of the 450 nm emission of Eu^{2+} were determined to be 645, 334, 247, and 149 ns for $La_{0.827}Al_{11.9}O_{19.09}:0.18Eu^{2+},xMn^{2+}$ with $x=0$, 0.06, 0.15, and 0.30, respectively. According to Dexter's formulation,[11] the energy transfer rate is given by

$$P(R) \propto \frac{Q_A}{R^b \tau_D} \int \frac{f_D(E)F_A(E)}{E^c} dE, \tag{2}$$

where τ_D is the decay time of the donor emission, Q_A is the total absorption cross section of the acceptor ion, R is the distance between the donor and the acceptor, and b and c are parameters dependent on the type of energy transfer. The probability functions $f_D(E)$ and $F_A(E)$ represent the observed shapes of the donor emission band and the acceptor absorption band, respectively. Thus, according to Eq. (2), it becomes clear that the energy transfer rate (P) is in inverse proportion to the decay time (τ_D). Accordingly, the decay time of the luminescence from Eu^{2+} decreased as the Mn^{2+} contents increased, which is a strong evidence of an energy transfer from the blue emission of Eu^{2+} to the green absorption of Mn^{2+}.[4,12] Additionally, as represented in Fig. 4(b), the decay time values of the 525 nm emission band of Mn^{2+} were determined to be 5.66, 4.65, and 1.24 ms for $La_{0.827}Al_{11.9}O_{19.09}:0.18Eu^{2+},xMn^{2+}$ with $x=0.30$, 0.45, and 0.60, respectively. From this result in which the decay time of the green emission of Mn^{2+} was decreased as the red emission increased, it is evident that the energy transfer occurs from Mn^{2+} at tetrahedral sites to Mn^{2+} at octahedral sites.
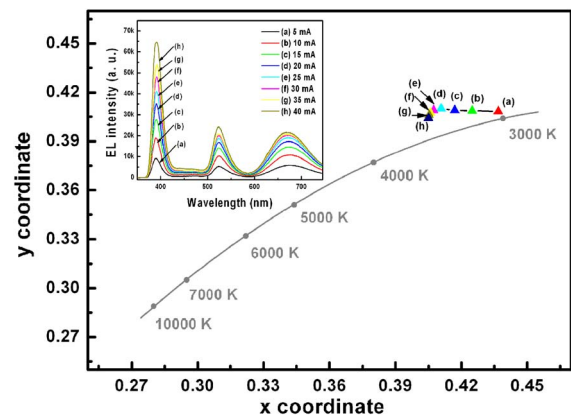

FIG. 5. (Color online) Luminescence spectra and CIE chromaticity coordinates of UV-pumped white LED with $La_{0.827}Al_{11.9}O_{19.09}:0.21Eu^{2+},0.6Mn^{2+}$ phosphor at various forward currents (5–40 mA).

Figure 5 shows the luminescence spectra and CIE chromaticity coordinates of an UV-pumped white LED with the $La_{0.827}Al_{11.9}O_{19.09}:0.21Eu^{2+},0.6Mn^{2+}$ phosphor under various forward currents (5–40 mA). The emission spectra consist of four bands: emission by UV LED and blue, green, and red emissions by the $La_{0.827}Al_{11.9}O_{19.09}:Eu^{2+},Mn^{2+}$ phosphor peaking at 385, 450, 525, and 660 nm, respectively. The fabricated warm white LED showed CIE chromaticity coordinates of $(x=0.40-0.43, y=0.40-0.41)$ and color temperatures of $(T_c \approx 3100-3600$ K) which were positioned within the range of warm white light. The color properties changed little on a forward-bias operation. Thus, a warm white LED with high color stability could be obtained with a forward-bias operation.

In conclusion, the luminescent properties of the $La_{0.827}Al_{11.9}O_{19.09}:Eu^{2+},Mn^{2+}$ phosphor were investigated. The phosphor showed the three emission bands of blue, green, and red. The blue emission originates from Eu^{2+} ions and the green and red emissions originate from Mn^{2+} ions, respectively. The emitting color of $La_{0.827}Al_{11.9}O_{19.09}:Eu^{2+},Mn^{2+}$ could be easily tailored from blue to red by varying the Mn^{2+} content. The white LED fabricated using a 385 nm chip with $La_{0.827}Al_{11.9}O_{19.09}:Eu^{2+},Mn^{2+}$ showed a warm white light with good color stability against the input power. This study indicates that $La_{0.827}Al_{11.9}O_{19.09}:Eu^{2+},Mn^{2+}$ can potentially serve as a single-phased full-color-emitting phosphor for an UV-pumped warm white LED.

[1] S. Nakamura, M. Senoh, and T. Mukai, Appl. Phys. Lett. **62**, 2390 (1993).
[2] S. Neeraj, N. Kijima, and A. K. Cheetham, Chem. Phys. Lett. **387**, 2 (2004).
[3] Y. Hu, W. Zhuang, H. Ye, D. Wang, S. Zhang, and X. Huang, J. Alloys Compd. **390**, 226 (2005).
[4] J. S. Kim, P. E. Jeon, Y. H. Park, J. C. Choi, and H. L. Park, Appl. Phys. Lett. **82**, 3696 (2004).
[5] J. S. Kim, J. S. Kim, T. W. Kim, S. M. Kim, and H. L. Park, Appl. Phys. Lett. **86**, 91912 (2005).
[6] N. Iyi, Z. Inoue, S. Takekawa, and S. Kimura, J. Solid State Chem. **54**, 70 (1984).
[7] A. L. N. Stevels, J. Lumin. **20**, 99 (1979).
[8] J. Qiu, K. Miura, N. Sugimoto, and K. Hirao, J. Non-Cryst. Solids **213–214**, 266 (1997).
[9] A. Bergstein and W. B. White, J. Electrochem. Soc. **118**, 1166 (1971).
[10] G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer, Berlin, 1994), p. 96.
[11] D. J. Dexter, J. Chem. Phys. **21**, 836 (1953).
[12] W.-J. Yang, L. Luo, T.-M. Chen, and N.-S. Wang, Chem. Mater. **17**, 3883 (2005).