White light emission from blue and near ultraviolet light-emitting diodes precoated with a Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ phosphor

Ho Seong Jang and Duk Young Jeon$^*$

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea
$^*$Corresponding author: dyj@kaist.ac.kr

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White-light-emitting diodes (WLEDs) were fabricated by combining a yellow Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ phosphor with a blue light-emitting diode (LED) (460 nm chip) or a near ultraviolet (n-UV) LED (405 nm chip), respectively. Color temperature ($T_c$) of Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$-based WLEDs could be tuned from 6500 to 100,000 K (blue LED pumping) and from 4900 to 50,000 K (n-UV LED pumping) without mixing with other phosphors. The blue LED-pumped WLED showed excellent white light (luminous efficiency=31.7 lm/W, $T_c$=6857 K) at 20 mA. This WLED showed a stable color coordinates property against an increase of the forward current. An n-UV LED-pumped WLED also showed bright white light (25.0 lm/W, 5784 K) at 20 mA. © 2007 Optical Society of America

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Light-emitting diodes (LEDs) have been intensively researched in recent years [1–3]. White-light-emitting diodes (WLEDs), in particular, have excellent properties; low power consumption, a long life span, and a rugged structure. Furthermore, in contrast with fluorescent lamps, they offer the environmental benefit of not using mercury [4]. As a result, WLEDs are expected to facilitate the introduction of new concepts in lighting technology. WLEDs can be generated by several methods [5–7]. Among these, a combination of a blue LED and a yellow phosphor is widely used because this approach yields high luminous flux and involves a lower cost than WLEDs composed of red, green, and blue LEDs [3]. The most frequently used yellow phosphor, Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$(YAG:Ce), absorbs blue light from a blue LED and emits yellow light. However, because the photoluminescence excitation (PLE) intensity of YAG:Ce is very weak in the deep blue [or near ultraviolet (n-UV)] spectral region, YAG:Ce is not applicable to n-UV LED-pumped WLEDs. In the case of Eu$^{3+}$-activated yellow phosphors, although they can be applied to both n-UV LEDs and blue LEDs, the bandwidth of their emission is narrower than that of YAG:Ce. Thus, the color rendering property of Eu$^{3+}$-activated yellow phosphor-based WLEDs is not satisfactory [8,9]. Recently, Xie et al. reported oxynitride phosphor-based WLEDs that showed high efficiencies of 46–55 lm/W and a color rendering index ($R_a$) of 60–72 [10,11], and we reported Ce$^{3+}$-activated silicate phosphor [12]. Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ shows a strong and broad PLE band peaking at 415 nm, and thus white light can be generated from n-UV LEDs as well as blue LEDs by coating this phosphor onto these LEDs. In addition, since the emission wavelength of Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ is adjusted by changing the amount of Ce$^{3+}$, the color temperature ($T_c$) and color coordinates of Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$-based WLEDs can be controlled without mixing different kinds of phosphors.

In this Letter, the optical properties of WLEDs combining a blue LED with Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ and combining a n-UV LED with Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ are reported. In addition, the color stability of fabricated WLEDs was investigated under various forward currents.

Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ samples were synthesized by a solid-state reaction method [12]. The concentration of Ce$^{3+}$ was varied from 0.2 to 2.5 mol%. To investigate luminescent properties of the phosphor, photoluminescence (PL) was characterized with a DARS A PRO 5100 PL System [Professional Scientific Instrument Company (PSI) Korea]. The excitation wavelength was 460 nm. WLEDs were fabricated using blue LEDs (460 nm chip) and n-UV LEDs (405 nm chip), respectively. To fabricate WLEDs, Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ was mixed with transparent epoxy resin and coated onto LED chips. The optical properties of the fabricated WLEDs were evaluated using an integrating sphere at 20 mA, and their color stability was investigated under various forward currents (10→70 mA).

Figure 1(a) shows the normalized PL spectra of Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ under 460 nm excitation. As the amount of Ce$^{3+}$ in Sr$_3$SiO$_5$ was increased, the peak wavelength of Ce$^{3+}$ emission shifted toward a longer wavelength. With an increase of the peak wavelength of the Ce$^{3+}$ emission, the body color of the phosphor changed from greenish-yellow to yellow. In addition, a redshift in the color coordinates of the Sr$_3$SiO$_5$:Ce$^{3+}$,Li$^+$ samples occurred as shown in Fig. 1(b). Redshift of Ce$^{3+}$ emission in other host lattices has also been reported [13,14]. According to Setlur and Srivastava the color shift at higher Ce$^{3+}$ concentrations is primarily due to inhomogeneous broaden-
ing of the Ce³⁺ emission band leading to energy transfer between intrinsic higher energy Ce³⁺ sites and lower energy Ce³⁺ sites [14]. As the amount of Ce³⁺ was increased, the distance between the Ce³⁺ ions decreased and the probability of energy transfer among Ce³⁺ ions increased. The probability of Ce³⁺ ions at higher levels of 5d to relax or make an energy transfer to lower 5d levels of Ce³⁺ ions in the same or different sites increases with an increase of the Ce³⁺ ions. With the redshift, the PL intensity of Sr₃SiO₅ :Ce³⁺ ,Li⁺ was changed with varying Ce³⁺ concentration. The concentration of luminescence quenching was found to be 0.8 mol% of Ce³⁺ in our previous work [12]. The PL intensity of Sr₂₋₂ₓSiO₅ :ₓCe³⁺ ,ₓLi⁺ increased as the amount of Ce³⁺ was increased until x=0.024. However, when x exceeded 0.024, the PL intensity of the phosphor decreased with increasing Ce³⁺ concentration. Although the Sr₂.95₂SiO₅ :0.02₄Ce³⁺ ,0.02₄Li⁺-based WLED showed high luminous efficiency (ηlm > 40 lm/W), it showed cool white. On the other hand, the Sr₂.₈₅₂SiO₅ :0.0₇₅Ce³⁺ ,0.0₇₅Li⁺-based WLED, the luminous efficiency of which was 31.7 lm/W, showed a daylightlike white. Therefore, in the study, the focus of the investigation is on the optical properties of Sr₂.₈₅₂SiO₅ :0.0₇₅Ce³⁺ ,0.0₇₅Li⁺-based WLED.

The Commission Internationale de l’Eclairage (CIE) color coordinates of fabricated phosphor-converted (pc) LEDs combining LEDs (blue LEDs or n-UV LEDs) with Sr₃SiO₅ :Ce³⁺ ,Li⁺ samples are shown in Fig. 2. Chromaticity properties of the fabricated pc LEDs were characterized at 20 mA. Open squares express the CIE color coordinates of Sr₃₋₂ₓSiO₅ :ₓCe³⁺ ,ₓLi⁺ (0.02₄<x<0.0₇₅) under 460 nm excitation [Fig. 2(a)] and under 405 nm excitation [Fig. 2(b)], respectively. In Fig. 2(a), the open triangles indicate the CIE color coordinates of blue LED-pumped pc LEDs using Sr₂.₉₅₂SiO₅ :0.0₂₄Ce³⁺ ,0.0₂₄Li⁺ (0.8 mol% Ce³⁺). The open circles represent the CIE color coordinates of blue LED-pumped pc LEDs using Sr₂.₆₅₂SiO₅ :0.₀₇₅Ce³⁺ ,0.₀₇₅Li⁺ (2.5 mol% Ce³⁺). The color temperature (Tₑ) of WLEDs fabricated by combining blue LEDs with Sr₃SiO₅ :Ce³⁺ ,Li⁺ could be tuned from 6500 to 100,000 K. In Fig. 2(b), the open triangles indicate the CIE color coordinates of n-UV LED-pumped pc LEDs using Sr₂.₉₅₂SiO₅ :0.0₂₄Ce³⁺ ,0.0₂₄Li⁺. Open circles represent the CIE color coordinates of the n-UV LED-pumped pc LEDs using Sr₂.₆₅₂SiO₅ :0.₀₇₅Ce³⁺ ,0.₀₇₅Li⁺. Tₑ of the WLEDs fabricated by combining n-UV LEDs with Sr₃SiO₅ :Ce³⁺ ,Li⁺ could be tuned from 4900 to 50,000 K. Optical properties of WLEDs that have the nearest chromaticity to the blackbody locus are as follows. The blue LED-pumped WLED using Sr₂.₆₅₂SiO₅ :0.₀₇₅Ce³⁺ ,0.₀₇₅Li⁺ showed bright white light (31.7 lm/W), Tₑ of 6857 K, and Ra of 81. The n-UV LED-pumped WLED using Sr₂.₆₅₂SiO₅ :0.₀₇₅Ce³⁺ ,0.₀₇₅Li⁺ also showed bright white light (25.0 lm/W), Tₑ of 5784 K, and Ra of 69. In both cases, the luminous efficiencies are comparable to that of commercial WLEDs (15–30 lm/W) [15] and higher than that of conventional incandescent lamps (16–18 lm/W) [9]. The color rendering in-
dices of the Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$-based WLEDs are larger than the $R_a$ (60) of fluorescent lamps; in the case of the blue LED-pumped WLED, the $R_a$ (81) is much larger than that of fluorescent lamps [9].

Figure 3(a) shows the electroluminescence (EL) spectra of blue LED-pumped WLED under the following forward currents of direct current (dc): 10–70 mA. The CIE color coordinates of the WLED under various currents are indicated in Fig. 3(b). When the applied current was increased from 10 to 70 mA, intensities of the blue and yellow bands of the WLED increased without luminescence saturation. The variation of the CIE color coordinates of the blue LED-pumped WLED using Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$ was smaller than that of a YAG:Ce-based WLED as shown in Fig. 3(b). The CIE color coordinates of the Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$-based WLED changed from (0.3061, 0.3104) at 10 mA to (0.3023, 0.3108) at 70 mA. Furthermore, there was little change in the $T_c$ and $R_a$.

The EL spectra of the n-UV LED-pumped WLED are depicted in Figs. 4(a) and 4(b). Although the amount of increase of the yellow band was very small, there was no saturation in luminescence as shown in Fig. 4(b). The amount of increase of the deep blue band from the n-UV LED was large, while that of the yellow band from the phosphor was small. However, the n-UV LED-pumped WLED showed stable color coordinates property [(0.3275, 0.3227) at 10 mA–(0.3182, 0.3111) at 70 mA]. This can be explained as follows. Because deep blue light (405 nm) is less sensitive to the human eye than blue light (460 nm) [16], the difference between the increase of the deep blue band and that of the yellow band is not large when visual spectral sensitivity is applied to the EL spectra.

In summary, WLEDs were fabricated by combining a yellow Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$ phosphor with blue LEDs or n-UV LEDs. Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$-based WLEDs displayed various white light ranging from natural white to cool white without mixing additional phosphors. A blue LED-pumped WLED coated with Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$ showed excellent white light. It also showed stable color coordinates, $T_c$, and $R_a$ against an increase of forward current. White light was also generated by combining an n-UV LED with Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$. Thus, the Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$-based WLED is a promising light source for general illumination.

References