Appl Phys B (2009) 95: 715–720
DOI 10.1007/s00340-009-3484-1

Applied Physics B
Lasers and Optics

Improvement of electroluminescent property of blue LED coated with highly luminescent yellow-emitting phosphors

H.S. Jang · Y.-H. Won · D.Y. Jeon

Received: 24 August 2008 / Revised version: 9 February 2009 / Published online: 2 April 2009

Abstract White light-emitting diodes (WLEDs) were fabricated by combining InGaN-based blue light-emitting diodes (LEDs) with highly luminescent $Tb_3Al_5O_{12}$:Ce^{3+} (TAG:Ce), $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce), and Sr_3SiO_5:Eu^{2+} (SS:Eu). The TAG:Ce-based WLED showed a color rendering index (R_a) of 79 and a luminous efficiency (η_L) of 34.1 lm/W at 20 mA. The YAG:Ce-based WLED and the SS:Eu-based WLED showed low R_a values of 75 and 57 but high luminous efficiency values of 38.9 and 41.3 lm/W at 20 mA, respectively. When a mixture of YAG:Ce and SS:Eu was coated on a blue LED and the resultant WLED operated at 20 mA, the WLED showed a highly bright white light similar to daylight ($\eta_L = 40.9$ lm/W, color temperature $T_c = 5{,}716$ K, and $R_a = 76$). Moreover, the WLED showed stable color coordinates against a considerable variation of applied current.

PACS 76.30.Kg · 78.55.-m · 85.60.Jb

H.S. Jang · Y.-H. Won · D.Y. Jeon (✉)
Department of Materials Science and Engineering,
Korea Advanced Institute of Science and Technology, 373-1,
Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea
e-mail: dyj@kaist.ac.kr
Fax: +82-42-3503310

Present address:
H.S. Jang
Department of Chemistry, Purdue University, West Lafayette,
IN 47907, USA
e-mail: msekorea@purdue.edu

Present address:
Y.-H. Won
School of Materials Engineering, Purdue University,
West Lafayette, IN 47907, USA
e-mail: ywon@purdue.edu

1 Introduction

White light-emitting diodes (WLEDs) have been studied extensively due to their excellent properties such as low power consumption, long operating time, and environmental benefit (no mercury) [1–4]. Due to these excellent properties, WLEDs are expected to be new light sources in the illumination field. There are several methods for generating WLEDs [5–8]. Currently, of these, a blue light-emitting diode (LED) coated with a yellow-emitting phosphor has been commercialized because it satisfies both of the following requirements: a high luminous flux and simple structure. In addition, the cost of an WLED of this type is lower than that of WLEDs composed of red, green, and blue LED chips in a single package due to its having a relatively simple structure compared to the WLEDs composed of three chips [9, 10]. The most frequently used yellow-emitting phosphor is $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce). However, because YAG:Ce emits a greenish-yellow light, the emission from an InGaN-based blue LED coated with YAG:Ce is deficient in the red spectral region and its color rendering property is poor [3]. To improve the color rendering property of WLEDs, Sheu et al. used a near ultraviolet (n-UV) LED [11]. Fabricated with three different phases of phosphors, the n-UV LED-pumped WLEDs lead, firstly, to a decrease in luminous efficiency due to reabsorption of emissions, and, secondly, also to an increase in manufacturing cost. Won et al. and Kim et al. introduced single-phase full-color-emitting phosphors for an n-UV LED-pumped WLED [12–15]. Wu et al., on the other hand, reported on a blue LED precoated with green/red phosphors, but the luminous efficiency was low and the red-emitting phosphor showed luminescence saturation as the applied current was increased [16]. In addition, red-emitting Eu^{2+}-activated sulfide phosphors are chemically unstable and show much weaker emission intensities than YAG:Ce. Recently, Xie et al. and Kimura et al. reported that high brightness and good color rendering properties were achieved with nitride green/red phosphor-converted (pc) WLEDs [17, 18]. However, both high firing temperature (>1600°C) and high N_2 pressure (>5 atm) are necessary to synthesize nitride phosphors [19–21]. In this study, we used oxide-based highly luminescent yellow-emitting phosphors such as YAG:Ce, $Tb_3Al_5O_{12}$:Ce^{3+} (TAG:Ce), and Sr_3SiO_5:Eu^{2+} (SS:Eu). They have different peak wavelengths, and various WLEDs with different color coordinates were fabricated. Two yellow-emitting phosphors were blended with each other to achieve bright WLEDs with high color rendering index (R_a). In addition, the current stability of the fabricated WLEDs was investigated.

2 Experimental

To obtain high luminous efficiency and a good color rendering property, we used various eminent yellow-emitting phosphors in the fabrication of blue LED-pumped WLEDs.

First, we separately synthesized the highly luminescent yellow-emitting phosphors, YAG:Ce, TAG:Ce, and SS:Eu, using a solid-state reaction method [3, 22]. High purity oxides such as Y_2O_3 (Aldrich, 99.99%), Al_2O_3 (Sumitomo AKP-50), CeO_2 (Aldrich, 99.999%) were used to synthesize YAG:Ce. Ce of 2 mol% was incorporated into a YAG host lattice. In the case of the synthesis of TAG:Ce, Tb_4O_7 (Aldrich, 99.999%) was used instead of Y_2O_3. The photoluminescence (PL) intensity was optimized when 2 mol% Ce was incorporated into a $Tb_3Al_5O_{12}$ host. And $SrCO_3$ (Aldrich, 99.995%), SiO_2 (Kojundo chem., 99.9%), and Eu_2O_3 (Aldrich, 99.99%) were used as raw materials for the synthesis of SS:Eu. SS:Eu showed maximum PL intensity when the activator concentration was 1 mol%. These yellow-emitting phosphors showed a higher PL intensity than the commercial YAG:Ce phosphor. After the synthesis, each phosphor was mixed with epoxy and applied as a coating onto InGaN-based blue LEDs. Next, to improve the electroluminescence (EL) property of the WLEDs, YAG:Ce was mixed with SS:Eu and then the mixture was coated on the blue LED. In addition, the PL excitation (PLE) and the PL of the phosphors were characterized with the DARSA PRO 5100 PL System (PSI Trading Co., Ltd., Korea) using a xenon lamp (500 W). Finally, we evaluated the EL properties of the WLEDs by using a charge-coupled device detector attached to the PL system, and we obtained the luminous efficiencies of the WLEDs by using an integrating sphere. All the spectra were measured at room temperature.

3 Results and discussion

Figure 1 shows the normalized PLE and PL spectra of various yellow-emitting phosphors, and the EL spectrum of a blue LED. As shown in Fig. 1, the main bands of the PLE spectra for the three phosphors (YAG:Ce, TAG:Ce, and SS:Eu) overlapped well with the emission band of the blue LED. In both the YAG:Ce and the TAG:Ce, the Ce^{3+} ions occupy the dodecahedral sites in the host lattices, and in both cases, the crystal field splitting of Ce^{3+} is large and the energy difference between the 4f level and the lowest 5d band is about 22,000 cm^{-1}, which corresponds to the energy of blue light [3]. Two phosphors also emit yellow light via the spin and parity allowed transition of $4f^05d^1 \rightarrow 4f^1$. As shown in Fig. 1, the YAG:Ce phosphor emits a greenish-yellow light that peaked at about 565 nm and the TAG:Ce phosphor emits a yellow light that peaked at about 578 nm. In the case of SS:Eu, the Eu^{2+} ions at the octahedral sites in the host emit a yellowish-orange light that peaked at about 586.5 nm via the transition from $4f^65d^1$ to $4f^7$ [2]. Since the emission spectrum of one phosphor differs slightly from those of the other phosphors, a white light can be tuned by combining a blue LED with another available yellow-emitting phosphor.

Figure 2 shows the Commission Internationale de l'Eclairage (CIE) color coordinates of the three yellow-emitting phosphors and the InGaN-based blue LED (460 nm chip). If two or three of the phosphors are mixed together, the mixture may show the CIE color coordinates between *a* and *c* as in Fig. 2. Therefore, any CIE color coordinates of a pc LED can be generated in the triangle of *acd*. When a WLED is fabricated, its color temperature (T_c) can be tailored from 2,700 to 20,000 K. Figure 2 also shows the CIE color coordinates of the pc LEDs (◊, △, and □). The inset of Fig. 2 shows the digital camera image of luminescence of the fabricated pc LEDs operating at 20 mA. When

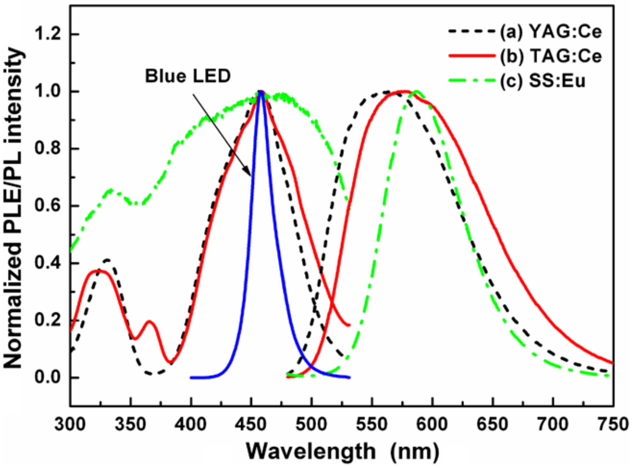

Fig. 1 Normalized PLE and PL spectra of various yellow-emitting phosphors: (**a**) YAG:Ce, (**b**) TAG:Ce, and (**c**) SS:Eu, respectively

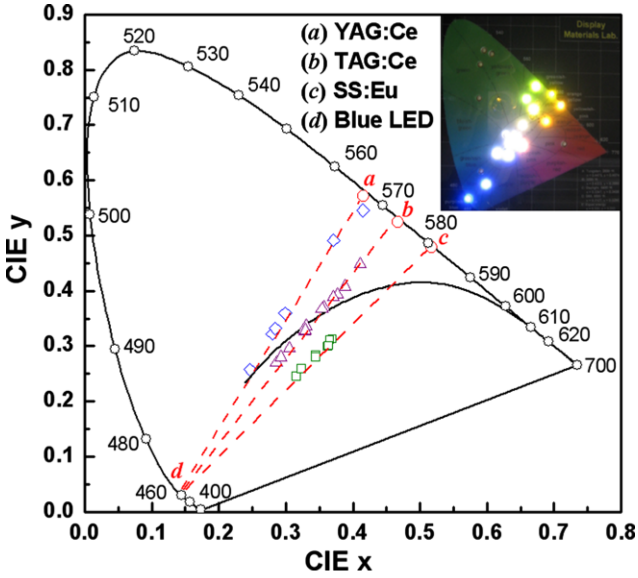

Fig. 2 The CIE color coordinates of (**a**) YAG:Ce, (**b**) TAG:Ce, (**c**) SS:Eu, and (**d**) blue LED, respectively; the CIE color coordinates of YAG:Ce-based, TAG:Ce-based, and SS:Eu-based LEDs are depicted as ◇, △, and □, respectively. *Inset* is a photograph showing emissions of various pc LEDs

the ratio of YAG:Ce to the epoxy was increased, the CIE color coordinates of the pc LED (◇) moved toward point *a* along the line *ad*. When the ratio of TAG:Ce to the epoxy was increased, the CIE color coordinates of the pc LED (△) moved toward point *b* along the line *bd*. And when the ratio of SS:Eu to the epoxy was increased, the CIE color coordinates of the pc LED (□) moved toward point *c* along the line *cd*.

Figure 3 shows the EL spectra of four pc WLEDs under the following forward currents of direct current (DC): 10, 20, 30, 40, 50, and 60 mA. When the applied current was 20 mA, the TAG:Ce-based WLED showed the best color rendering property ($R_a = 79$) but the lowest luminous efficiency ($\eta_L = 34.1$ lm/W). And it showed natural white light ($T_c = 5{,}026$ K). The YAG:Ce-based WLED showed an η_L of 38.9 lm/W and R_a of 75. The YAG:Ce-based WLED showed a cool white light ($T_c = 7{,}756$ K), while the SS:Eu-based WLED showed a warm white light ($T_c = 3{,}387$ K). The SS:Eu-based WLED showed the highest luminous efficiency ($\eta_L = 41.2$ lm/W) of the four pc WLEDs but a poor color rendering property ($R_a = 57$) due to the green spectral deficiency of SS:Eu. To obtain highly efficient natural white light, we coated a mixture of YAG:Ce and SS:Eu on an InGaN-based blue LED.

Figure 4 shows the CIE color coordinates of WLEDs combining blue LEDs and the mixtures of YAG:Ce and SS:Eu with various mixing ratios of YAG:Ce and SS:Eu. The mixing ratios of YAG:Ce to SS:Eu are as follows. YAG:Ce : SS:Eu = 3:2, 3:3, 3:4, 4:2, 4:3, and 4:5. The coated amount of the mixture of the phosphors and epoxy was also varied to optimize the optical property of the WLED. The CIE color coordinates of WLEDs fabricated using mixed phosphors were observed between a straight line connecting the CIE color coordinates of YAG:Ce-based WLEDs and that connecting the CIE color coordinates of SS:Eu-based WLEDs. As the amount of SS:Eu in the two phosphor mixtures was increased, T_c of the fabricated WLEDs decreased. With regard to the R_a of the fabricated WLEDs, when SS:Eu was mixed with YAG:Ce, R_a of the WLED increased due to the stronger red spectral component ascribed to the emission from SS:Eu. However, when the ratio of SS:Eu to YAG:Ce exceeded 2:3 (the ratio $>$SS:Eu/YAG:Ce = 0.67), the R_a of the WLEDs decreased due to imbalance among emission bands (blue, yellow, and orange bands). In our experiments, the optimized mixing ratio of YAG:Ce to SS:Eu was 3:2. In Fig. 4, D65 is a standard illuminant whose correlated color temperature is 6,500 K and “A” is a standard illuminant which has the profile of a black body radiator at 2,856 K [23].

The mixed phosphor-based WLED showed highly efficient daylight-like white light ($\eta_L = 40.9$ lm/W, $T_c = 5{,}716$ K) and its R_a was 76 which was much larger than that of the SS:Eu-based WLED. In terms of luminous efficiency, the value of 40.9 lm/W for the mixed phosphor-based WLED is higher than the corresponding values for the YAG:Ce-based WLED (38.9 lm/W) and the TAG:Ce-based WLED (34.1 lm/W). All the WLED samples showed higher efficiencies than commercial WLEDs (15–30 lm/W according to Ref. [5]). Table 1 summarizes the optical properties of the pc WLEDs. When we increased the applied current from 10 to 60 mA, the EL intensities of the blue and yellow bands of the four WLEDs increased. That is, the higher the applied current, the stronger the blue emission. The stronger blue emission was absorbed by the yellow-emitting phosphors, and the yellow emissions were enhanced as shown in Figs. 3(a) to (d). Although some phosphors (e.g. $(Ca_{1-x}Sr_x)S:Eu^{2+}$) have shown saturation in the emission at a current greater than 30 mA [16], each yellow-emitting phosphor in this study showed a superior property whereby the emission intensity increases without saturation as a function of the applied current. Similarly, the emission intensity of the mixed phosphor (YAG:Ce + SS:Eu) was not saturated at a high forward current of 60 mA. As shown in Fig. 3(d), the intensity of the yellow band of the WLED became stronger as the applied current was increased.

Although none of the yellow-emitting phosphors showed the saturation, the CIE color coordinates of the WLEDs varied with increasing applied current. Figure 5(a) shows the CIE color coordinates of the WLEDs under the following applied currents: 10, 20, 30, 40, 50, and 60 mA. In the case of the WLEDs that used YAG:Ce or TAG:Ce, the CIE color coordinates shifted towards the blue region as the applied

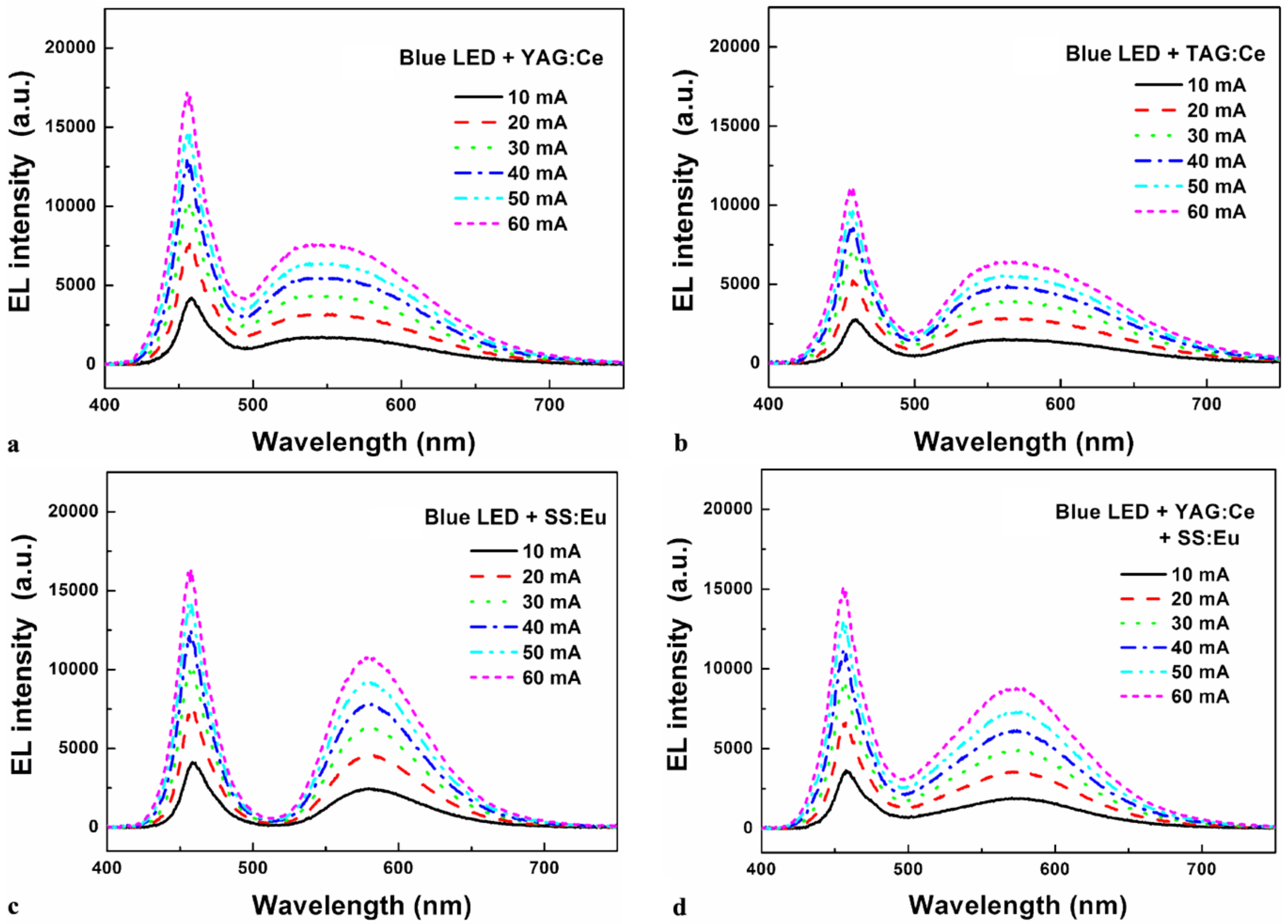

Fig. 3 EL spectra of WLEDs using (**a**) YAG:Ce, (**b**) TAG:Ce, (**c**) SS:Eu, and (**d**) YAG:Ce + SS:Eu under various currents (DC 10, 20, 30, 40, 50, and 60 mA)

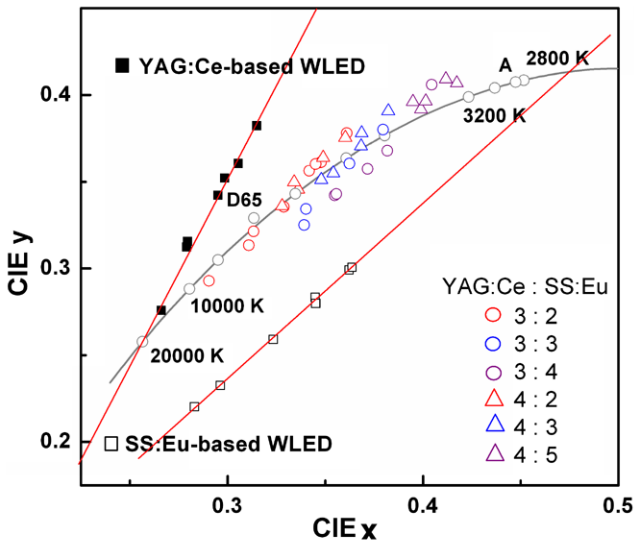

Fig. 4 The CIE color coordinates of WLEDs using mixed phosphor having various mixing ratios of YAG:Ce and SS:Eu (YAG:Ce : SS:Eu = 3:2, 3:3, 3:4, 4:2, 4:3, and 4:5)

current was increased. It indicates that the degree of the increase in yellow emissions is smaller than that of the increase in blue emissions.

In the case of the TAG:Ce-based WLED, the variation in the CIE color coordinates was large [(0.3449, 0.3478) at 10 mA → (0.3408, 0.3349) at 60 mA]. Furthermore, the CIE color coordinates of the YAG:Ce-based WLED changed from (0.2923, 0.3281) at 10 mA to (0.2903, 0.3171) at 60 mA. In the case of the SS:Eu-based WLED, however, the CIE color coordinates changed only slightly [(0.3635, 0.3025) at 10 mA → (0.3623, 0.3010) at 60 mA]. When a blue LED was combined with the mixed phosphor (YAG:Ce + SS:Eu), the CIE color coordinates changed only slightly in relation to variations in the applied current [(0.3282, 0.3363) at 10 mA → (0.3276, 0.3310) at 60 mA].

Figure 5(b) shows the variation in the CIE color coordinates of the four WLEDs. There is clearly a difference $(\Delta x, \Delta y)$ between the CIE color coordinates at 10 mA and when the applied current was increased. In the case of the TAG:Ce-based WLED, the difference $(\Delta x, \Delta y)$ between the CIE color coordinates increased drastically as the applied current was increased. On the other hand, the CIE

Table 1 Optical properties of various WLEDs at 20 mA

Phosphor coated on a blue LED	CIE color coordinates (x, y)	T_c (K)	R_a	Luminous efficiency (lm/W)	Driving current stability (10–60 mA)
YAG:Ce	(0.2921, 0.3246)	7756	75	38.9	medium
TAG:Ce	(0.3439, 0.3435)	5026	79	34.1	poor
SS:Eu	(0.3632, 0.3011)	3387	57	41.3	excellent
YAG:Ce + SS:Eu	(0.3280, 0.3340)	5716	76	40.9	good

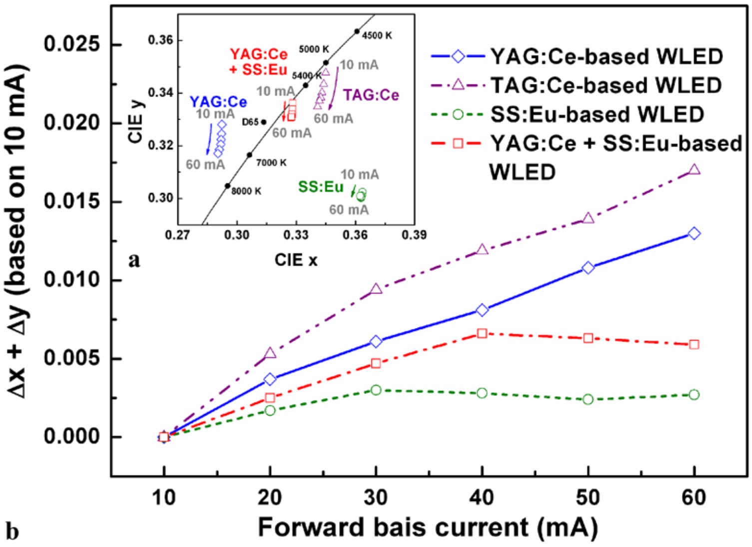

Fig. 5 (**a**) The CIE color coordinates of the pc WLEDs and (**b**) the variation of the CIE color coordinates of the pc WLEDs as a function of the applied current (DC 10, 20, 30, 40, 50, and 60 mA)

color coordinates of the SS:Eu-based WLED were very stable when the applied current was increased. In addition, when the forward current was increased, the mixed phosphor (YAG:Ce + SS:Eu)-based WLED showed more stable color coordinates than both the YAG:Ce-based WLED and the TAG:Ce-based WLED. Consequently, by coating the mixed phosphor on a blue LED chip, we improved the current stability of the CIE color coordinates as well as the color rendering property of the WLED, and the WLED showed a high luminous efficiency.

To explain the color stability of the WLEDs against the increase of the forward current, photoluminescence of the phosphors was considered separately from LED luminescence since different types of phosphors were coated on the same blue LEDs. When the applied current is increased, the number of photons emitted from the blue LED increases and the temperature of the LED chip increases [24]. As a result, the ambient temperature of the LED chip also increases. These two factors, photon number and temperature, influence the phosphor luminescence. In order to investigate the effect of excitation light intensity on the luminescence of three yellow-emitting phosphors (YAG:Ce, TAG:Ce, and SS:Eu), we carried out the PL measurement with different light intensities. When we remeasured the PL spectra, we used several neutral density (ND) filters to adjust the incident light intensity. The initial light intensity (without ND filter) is depicted as 100% in Fig. 6. From Fig. 6, the emission intensities of these three yellow-emitting phosphors decreased linearly with the decrease of the intensity of the excitation light. It indicates that the luminescence of these three yellow-emitting phosphors has a linear relationship with the incident light. Therefore, it is believed

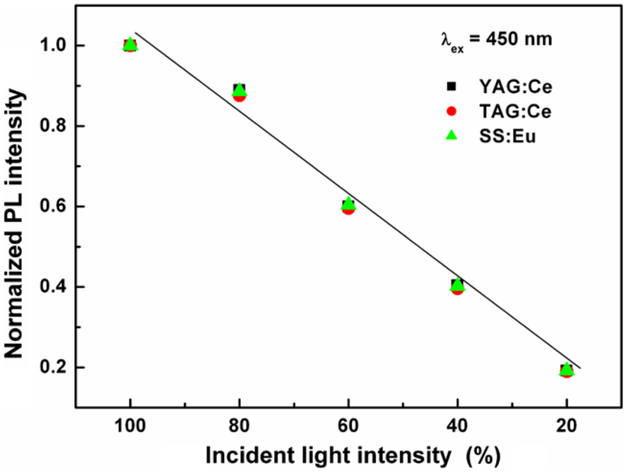

Fig. 6 Normalized PL intensities of yellow-emitting YAG:Ce, TAG:Ce, and SS:Eu phosphors under various incident light intensities

that the change of the luminescence of the phosphor in the WLED was mainly affected by the temperature change of the WLEDs. In general, the luminescence intensity of the phosphor decreased with increasing temperature [21]. According to Park et al., the thermal stability of SS:Eu is better than that of YAG:Ce [2]. And there is a report that the thermal stability of YAG:Ce is better than that of TAG:Ce [25]. The thermal stability trends of the phosphors in these two reports are consistent with the trend of the variation of the CIE color coordinates of the WLEDs which were fabricated by using YAG:Ce, TAG:Ce, and SS:Eu, respectively. When we compared the thermal stability of the yellow-emitting phosphors from the literature [2, 25], the thermal stability of SS:Eu was the best and the thermal stability of TAG:Ce was the worst among the three phosphors [2, 25]. This explains why the SS:Eu-based WLED showed the most stable color coordinates against the increase of a forward current. In addition to the current stability of the WLEDs, other stabilities, such as thermal stability, are under further investigation.

4 Summary

In summary, bright pc WLEDs were fabricated by using the eminent yellow-emitting YAG:Ce, TAG:Ce, and SS:Eu phosphors, respectively. The TAG:Ce-based WLED showed a bright natural white ($\eta_L = 34.1$ lm/W, $T_c = 5{,}026$ K) with good color rendering property, but its CIE color coordinates were unstable when the applied current was increased. On the other hand, the YAG:Ce-based WLED showed bright cool white light and the SS:Eu-based WLEDs showed bright warm white light, but in both cases, the color rendering properties were not satisfactory. The WLED with the mixed phosphor (YAG:Ce + SS:Eu) showed highly bright natural white light ($\eta_L = 40.9$ lm/W, $T_c = 5{,}716$ K) and an improved color rendering property ($R_a = 76$); in addition, its CIE color coordinates were stable against an increase of the applied current.

Acknowledgement This work was supported by the Center for Electronic Packaging Materials (ERC) of MOST/KOSEF.

References

1. S. Nakamura, T. Mukai, M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994)
2. J.K. Park, C.H. Kim, S.H. Park, H.D. Park, S.Y. Choi, Appl. Phys. Lett. **84**, 1647 (2004)
3. H.S. Jang, W.B. Im, D.C. Lee, D.Y. Jeon, S.S. Kim, J. Lumin. **126**, 371 (2007)
4. M.G. Craford, Proc. SPIE **4776**, 1 (2002)
5. H.-S. Chen, C.-K. Hsu, H.-Y. Hong, IEEE Photonics Technol. Lett. **18**, 193 (2006)
6. J.K. Sheu, C.J. Pan, G.C. Chi, C.H. Kuo, L.W. Wu, C.H. Chen, S.J. Chang, Y.K. Su, IEEE Photonics Technol. Lett. **14**, 450 (2002)
7. H.S. Jang, D.Y. Jeon, Appl. Phys. Lett. **90**, 041906 (2007)
8. H.S. Jang, H. Yang, S.W. Kim, J.Y. Han, S.-G. Lee, D.Y. Jeon, Adv. Mater. **20**, 2696 (2008)
9. H.S. Jang, D.Y. Jeon, Opt. Lett. **32**, 3444 (2007)
10. S. Nakamura, G. Fasol, *The Blue Laser Diode: GaN Based Light Emitters and Lasers* (Springer, Berlin, 1997)
11. J.K. Sheu, S.J. Chang, C.H. Kuo, Y.K. Su, L.W. Wu, Y.C. Lin, W.C. Lai, J.M. Tsai, G.C. Chi, R.K. Wu, IEEE Photonics Technol. Lett. **15**, 18 (2003)
12. Y.-H. Won, H.S. Jang, W.B. Im, J.S. Lee, D.Y. Jeon, Appl. Phys. Lett. **89**, 231909 (2006)
13. J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, S.I. Mho, G.C. Kim, Appl. Phys. Lett. **84**, 2931 (2004)
14. J.S. Kim, P.E. Jeon, Y.H. Park, J.C. Choi, H.L. Park, G.C. Kim, T.W. Kim, Appl. Phys. Lett. **85**, 3696 (2004)
15. S.H. Lee, J.H. Park, S.M. Son, J.S. Kim, H.L. Park, Appl. Phys. Lett. **89**, 221916 (2006)
16. H. Wu, X. Zhang, C. Guo, J. Xu, M. Wu, Q. Su, IEEE Photonics Technol. Lett. **17**, 1160 (2005)
17. R.-J. Xie, N. Hirosaki, N. Kimura, K. Sakuma, M. Mitomo, Appl. Phys. Lett. **90**, 191101 (2007)
18. N. Kimura, K. Sakuma, S. Hirafune, K. Asano, N. Hirosaki, R.-J. Xie, Appl. Phys. Lett. **90**, 051109 (2007)
19. R.-J. Xie, N. Hirosaki, M. Mitomo, K. Uheda, T. Suehiro, X. Xu, Y. Yamamoto, T. Sekiguchi, J. Phys. Chem. B **109**, 9490 (2005)
20. R.-J. Xie, N. Hirosaki, T. Suehiro, F.-F. Xu, M. Mitomo, Chem. Mater. **18**, 5578 (2006)
21. R.-J. Xie, N. Hirosaki, M. Mitomo, K. Sakuma, N. Kimura, Appl. Phys. Lett. **89**, 241103 (2006)
22. H.S. Jang, W.B. Im, D.Y. Jeon, in *Proc. 12th International Display Workshops* (2005), p. 539
23. http://en.wikipedia.org/wiki/Standard_illuminant#Illuminant_A
24. L. Jayasinghe, Y. Gu, N. Narendran, Proc. SPIE **6337**, 63370V (2006)
25. A.A. Setlur, A.M. Srivastava, H.A. Comanzo, G. Chandran, H. Aiyer, M.V. Shankar, S.E. Weaver, Proc. SPIE **5187**, 142 (2004)