



Preparation of Tetra-Tungstate Red Phosphors and Corresponding White Light-Emitting Diodes

QIHUA ZENG^{1,*}, HONGBIN LIANG² and MENGLIAN GONG²

¹College of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, P.R. China

²School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, P.R. China

*Corresponding author: Fax: +86 20 39352128; Tel: +86 20 39352122; E-mail: qihuazeng@139.com

(Received: 18 June 2012;

Accepted: 22 April 2013)

AJC-13380

Eu³⁺-activated tungstate phosphors, Ca₉Gd_{2-x}Eu_xW₄O₂₄ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0), were prepared by the conventional solid-state reaction method. A systematic and exhaustive study for their photoluminescent properties was made. The tungstate phosphors show intensely red emission under 395 and 465 nm light excitation and good Commission International de l'Eclairage (CIE) chromaticity coordinates, therefore can get high colour purity of red emission. Excellent thermal stability for luminescence can also be observed for the tungstate phosphors. Bright red light-emitting diodes (LEDs) and white light-emitting diodes (WLEDs) were fabricated with Ca₉Eu₂W₄O₂₄ phosphor on *ca.* 395 nm-emitting InGaN chips and about 460 nm blue-emitting InGaN chips, respectively. The good performances of the LEDs demonstrate that the tungstate phosphor is suitable for application of near-UV (NUV) and blue InGaN-based WLEDs.

Key Words: Rare earth, Tungstate, Phosphor, Light-emitting diode.

INTRODUCTION

White-light-emitting diodes (WLEDs) have great potential for application in the lighting domain due to many advantages, such as high luminous efficiency, small volume, no environmental hazards. Currently, the dominant commercial method¹⁻³ to obtain white light is by combining a 460 nm blue chip with a yellow-emitting phosphor YAG:Ce³⁺. However, some problems for such "blue + yellow" WLEDs, such as low colour-rendering index, low luminous efficiency, high (6000-7000 K) colour temperature exist because of lack of red light^{2,3}. Another method to obtain a high efficient WLED with an appropriate colour temperature is by combining a near-UV LED (*ca.* 400 nm) chip with red, green and blue tri-colour phosphors⁴⁻⁷. The commonly used phosphors⁴⁻⁷ are blue phosphor BaMgAl₁₀O₁₇:Eu²⁺, green phosphor ZnS:Cu⁺/Al³⁺ and red phosphor Y₂O₂S:Eu³⁺. Among these phosphors, Y₂O₂S:Eu³⁺ shows some shortcomings: lower efficiency compared with that of blue and green phosphors and instability due to release of sulphide gas⁶. Therefore, it is urgent to search for new red phosphors with high efficiency, stability and no environmental hazards.

As important optical materials, tungstates and molybdates^{4,8-14} doped with rare earth have attracted particular interest. Neeraj *et al.*⁴ reported the promising red phosphors NaM(WO₄)_{2-x}(MoO₄)_x (M³⁺ = Gd³⁺, Y³⁺ and Bi³⁺) which exhibited strong *f-f* excitations of Eu³⁺ around 395 and 465 nm. Similar reports were also given in LiEuM₂O₈ (M = Mo, W)⁸ and

AgGd_{0.95}Eu_{0.05}(WO₄)_{2-x}(MoO₄)_x⁹ phosphors. However, little investigation on the performances of the LEDs fabricating with such tungstate phosphors has been reported. In our previous papers, several europium(III) ion-doped tungstates red phosphors were investigated^{12,13}. As systematic and further work, in the present paper, Eu³⁺-activated Ca₉Gd₂W₄O₂₄ phosphors have been studied in detail. Bright red and white LEDs were fabricated with Ca₉Eu₂W₄O₂₄ phosphor and about 395 nm emitting InGaN chips. WLEDs were also fabricated by combining Ca₉Eu₂W₄O₂₄ and YAG:Ce³⁺ with about 460 nm blue-emitting InGaN chips and the good performances of the WLEDs demonstrate that the tungstate phosphor can be a promising red component for the commercial YAG:Ce³⁺ WLEDs.

EXPERIMENTAL

Samples Ca₉Gd_{2-x}Eu_xW₄O₂₄ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0) are prepared by solid-state reaction. The stoichiometric mixtures of CaCO₃ (AR grade), WO₃ (AR grade) and M₂O₃ (99.99 % purity, M³⁺ = Eu³⁺, Gd³⁺) were first ground by using an agate mortar and pestle and then heated at 1400 °C for 4 h. Finally, the samples were ground into fine powder for characterization. Y₂O₂S:0.05Eu³⁺ was synthesized by Reddy's *et al.*¹⁴. The structure of the final products was examined by X-ray powder diffraction (XRD) using CuK_α radiation on Rigaku D/max 2200 vpc. The morphology of the samples was inspected using a JEOL JSM-6330F field emission scanning electron microscope (FESEM). Excitation and emission

spectra of the powdered phosphors were measured on a Fluorog-3-21 spectrometer (JOBIN YVON, America) at room temperature with a 450 W xenon lamp as excitation source and a cooled R928 photomultiplier tube run at 950 V in photon-counting mode. The luminescence decay curve was measured with an EDINBURGH FLS920 (UK) combined fluorescence lifetime and steady-state spectrometer. The emission spectra of the LEDs were recorded on a PMS-50 LED spectrophotocolourimeter (EVERFINE, China).

RESULTS AND DISCUSSION

X-Ray diffraction and morphology analysis: Fig. 1a shows the XRD patterns of the samples $\text{Ca}_9\text{Gd}_{2-x}\text{Eu}_x\text{W}_4\text{O}_{24}$ ($x = 0, 0.8, 1.2, 1.6, 2.0$). All curves are consistent with the JCPDS card 41-0186 ($\text{Ca}_9\text{Gd}_2\text{W}_4\text{O}_{24}$), showing that there is no detectable intermediate phase within the whole range of Eu^{3+} concentrations. The compound $\text{Ca}_9\text{Gd}_2\text{W}_4\text{O}_{24}$ is tetragonal and belongs to space group $I4_1/a$. The radius of Eu^{3+} (0.95 nm) is almost equal to that of Gd^{3+} (0.94 nm), therefore, Eu^{3+} and Gd^{3+} can form a solid solution in the host.

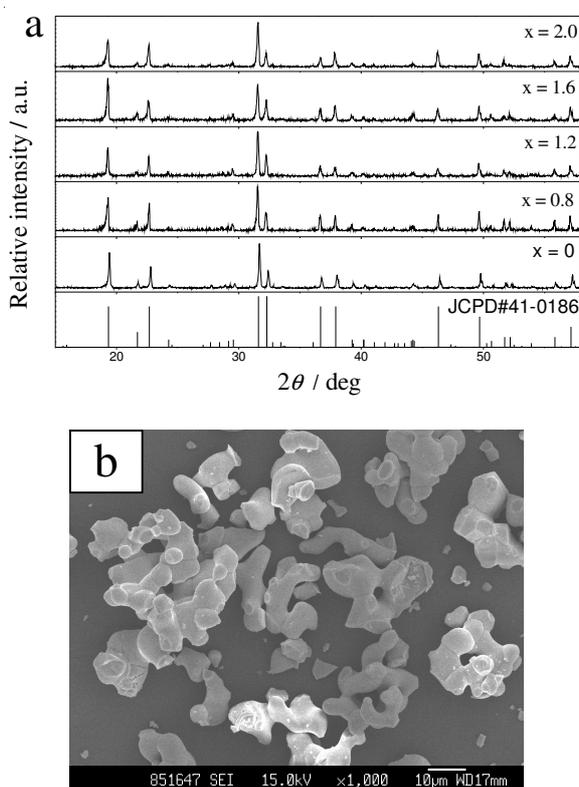


Fig. 1. (a) XRD patterns of $\text{Ca}_9\text{Gd}_{2-x}\text{Eu}_x\text{W}_4\text{O}_{24}$; (b) FESEM image of the crystalline $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ phosphor

Morphology and particle size are also important properties for phosphors. Fig. 1b shows the FESEM image of the crystalline $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$. The powder shows a uniform spindle-like morphology and an average particle size of 4–8 μm . Although, in view of application, the phosphors with spherical shape and small size are desirable, $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ phosphor can meet the demands of the LED application basically.

Luminescent properties: The profiles of photoluminescent spectra of all phosphors $\text{Ca}_9\text{Gd}_{2-x}\text{Eu}_x\text{W}_4\text{O}_{24}$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 1.8, 2.0$) are similar. Fig. 2a(1) shows

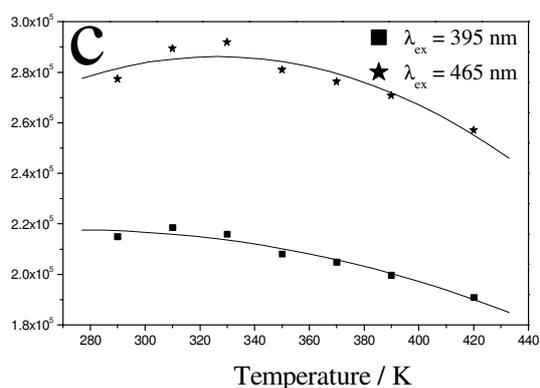
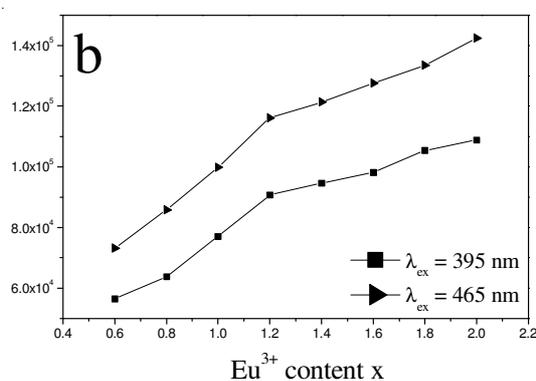
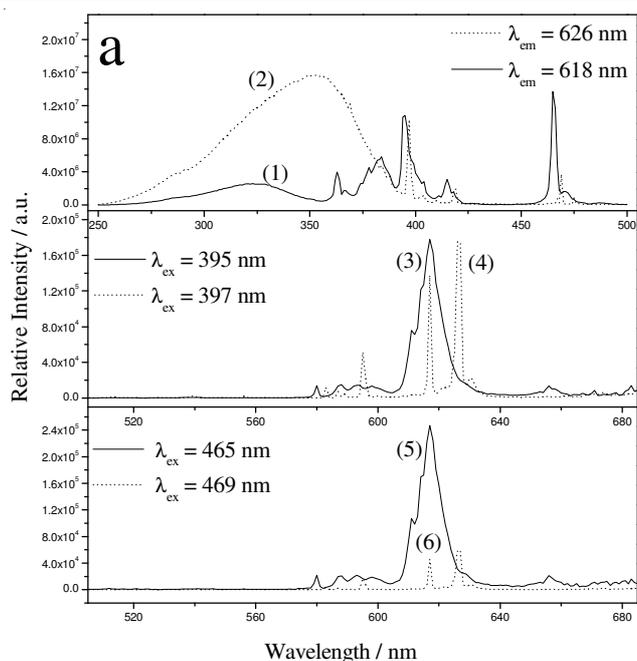


Fig. 2. (a) The excitation and emission spectra of $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$; (b) The emission intensity ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) of Eu^{3+} as a function of the doped Eu^{3+} concentration (x) in $\text{Ca}_9\text{Gd}_{2-x}\text{Eu}_x\text{W}_4\text{O}_{24}$; (c) The emission intensity ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) of Eu^{3+} as a function of temperature

the excitation spectrum of $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$. The broad band from 250–350 nm is attributed to the electric charge transfer (CT) of $\text{O}^{2-} \rightarrow \text{W}^{6+}$ and $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ and the sharp lines in the 360–500 nm range are attributed to $4f-4f$ transitions of Eu^{3+} ion: $^7\text{F}_0 \rightarrow ^5\text{D}_4$ at 364 nm, $^7\text{F}_0 \rightarrow ^5\text{L}_7$ at 384 nm, $^7\text{F}_0 \rightarrow ^5\text{L}_6$ at 395 nm, $^7\text{F}_0 \rightarrow ^5\text{D}_3$ at 416 nm and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ at 465 nm. Both excitations at 395 and 465 nm are very strong and the $^7\text{F}_0 \rightarrow$

5D_2 at 465 nm is the strongest absorption which may be favourable to resolve the problem of high colour temperature of YAG:Ce³⁺ WLEDs^{15,16}. The emission spectra of Ca₉Eu₂W₄O₂₄ under 395 and 465 nm excitation shown in Fig. 2a(3), (5) are composed of groups of the characteristic emission of Eu³⁺ ion. The main emission is $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ at 618 nm, which reveals that the Eu³⁺ ions occupy the lattice sites without inversion symmetry. Other *f-f* transitions of Eu³⁺, such as $^5D_0 \rightarrow ^7F_1$ ($J = 0, 1, 3, 4$) and $^5D_1 \rightarrow ^7F_1$ ($J = 0, 1, 2$) transitions are very weak, which is advantageous to obtain good Commission International de l'Eclairage (CIE) chromaticity coordinates (Table-1).

TABLE-1
RELATIVE EMISSION INTENSITY OF PHOSPHORS

Phosphor	Excitation wavelength (nm)	CIE chromaticity coordinates ^a		Relative integral intensity from 500-680 nm
		x	y	
Y ₂ O ₂ S:0.05Eu ³⁺	397	0.67	0.33	1.0
Ca ₉ Eu ₂ W ₄ O ₂₄	395	0.67	0.33	2.22
Y ₂ O ₂ S:0.05Eu ³⁺	469	0.67	0.33	0.33
Ca ₉ Eu ₂ W ₄ O ₂₄	465	0.66	0.34	3.23

^aNTSC standard values for red are $x = 0.67$, $y = 0.33$.

Fig. 2b shows the emission intensity ($^5D_0 \rightarrow ^7F_2$) of Eu³⁺ (under 395 and 465 nm excitation) as a function of its doping concentration (x) in Ca₉Gd_{2-x}Eu_xW₄O₂₄. With increasing Eu³⁺ content in the samples, the emission intensity increases and no concentration quenching occur. Ca₉Eu₂W₄O₂₄ exhibits the strongest emission intensity. Similar results are also observed in Na₅Eu(MoO₄)₄¹¹ and Na₅Eu(WO₄)₄ in which Pan *et al.*¹⁰ obtained single crystals of Na₅Eu(WO₄)₄ successfully by flux method. They reported that Eu³⁺ in Na₅Eu(WO₄)₄ occupy S₄ symmetric site and the compound with cell parameters ($a = 11.507$ Å and $c = 11.406$ Å; space group I4₁/a) had no concentration quenching due to the special structure of Eu-O-W-O-Eu.

As a comparison, the excitation and emission spectra of Y₂O₂S:0.05Eu³⁺ are also shown in Fig. 2a(2), (4), (6). Although Y₂O₂S:0.05Eu³⁺ exhibits a broad and strong absorption band around 250-370 nm, its absorptions ascribable to the $^7F_0 \rightarrow ^5L_6$ level transition (*ca.* 395 nm) and to the $^7F_0 \rightarrow ^5D_2$ level transition (*ca.* 465 nm) are very weak. Table-1 lists the comparison of integrated intensities in the range from 500-680 nm of Ca₉Eu₂W₄O₂₄ to that of Y₂O₂S:0.05Eu³⁺. Ca₉Eu₂W₄O₂₄ shows much stronger *f-f* transition absorptions at *ca.* 395 and 465 nm. Under *ca.* 395 nm excitation, the integrated intensity of Ca₉Eu₂W₄O₂₄ is *ca.* 2.22 times higher than that of Y₂O₂S:0.05Eu³⁺ while under *ca.* 465 nm excitation, the integrated intensity of Ca₉Eu₂W₄O₂₄ is *ca.* 9.78 times higher than that of Y₂O₂S:0.05Eu³⁺. Therefore Ca₉Eu₂W₄O₂₄ is more suitable to be excited by 395 nm-emitting or 465 nm-emitting InGaN/GaN chips.

As we know, a good thermal stability for luminescence is an important requirement for phosphors. Fig. 2c shows the emission intensity of Ca₉Eu₂W₄O₂₄ under 395 and 465 nm excitation as a function of temperature from 290-420 K. With the increase of the temperature, the emission intensity increases slightly at first and decreases slowly thereafter. Even when

the temperature reaches 420 K, the intensity only decreases by *ca.* 12 % and the fact indicates that Ca₉Eu₂W₄O₂₄ has superior high temperature luminescent behaviour.

The decay curve for $^5D_0 \rightarrow ^7F_2$ of the Eu³⁺ in Ca₉Eu₂W₄O₂₄ can be well fitted by a single-exponential function as $I = A \exp(-t/\tau)$ and the lifetime is 0.413 ms.

Fabricated light-emitting diode: Fig. 3a(1), (4) show the emission spectra of LEDs fabricated with the original near UV InGaN and blue InGaN chips, respectively. Fig. 3a(2) presents the emission spectrum of the red LED (Photo 2) fabricated with Ca₉Eu₂W₄O₂₄ and 395 nm-emitting InGaN chip. Obviously, the peak at *ca.* 395 nm depressed, which is originated by the absorption of the coated Ca₉Eu₂W₄O₂₄ and the peak at *ca.* 618 nm belongs to the $^5D_0 \rightarrow ^7F_2$ emission of Eu³⁺ in Ca₉Eu₂W₄O₂₄. Fig. 3a(3) presents the emission spectrum of the WLED (Photo 3) fabricated by combining a 395 nm-emitting chip with the red phosphor Ca₉Eu₂W₄O₂₄, a blue phosphor and a green phosphor which were all prepared by our team. The CIE chromaticity coordinates are (0.3517, 0.3553) which is located inside the white light domain (point C in Fig. 3b). The luminous efficiency reaches 2.44 lm/W which is high as compared with the value (0.33 lm/W) of the original near UV InGaN chip. The colour temperature is 4769 K. Unexpectedly, the colour rendering index is low (60), which may be due to the poor mixture of the used phosphors under the manual fabrication process. Thus the phosphor Ca₉Eu₂W₄O₂₄ is considered to be a candidate as a red component for a three-band WLED.

Fig. 3a(5), (6) show the emission spectra of the WLEDs fabricated by coating yellow YAG:Ce³⁺ and "red + yellow" (Ca₉Eu₂W₄O₂₄ and YAG:Ce³⁺) onto blue InGaN chips, respectively. Both WLEDs exhibits bright white emitting (photo 5 and 6) located inside the white light domain and the CIE chromaticity coordinates are (0.3075, 0.3376) for the YAG:Ce³⁺-WLED, (0.3181, 0.3403) for the "red + yellow"-WLED, respectively. The band between 462 and 490 nm in curve 6 is lower than that in curve 5 which is originated by the absorption of Ca₉Eu₂W₄O₂₄. And the broad band from 515-680 nm in curve 6 is stronger than that in curve 5 which is originated by the emission of Ca₉Eu₂W₄O₂₄. Therefore, compared with the WLED fabricated with commercial YAG:Ce³⁺ (point A in Fig. 3b), the CIE chromaticity coordinates of our WLEDs (point B in Fig. 3b) show red shift and the performances of the "red + yellow"-WLED were improved both on the colour-temperature and the luminous efficiency except for colour rendering index (Table-2). The reason for the low colour rendering index also may be due to the poor mixture of the used phosphors under the manual fabrication process. The results indicate that Ca₉Eu₂W₄O₂₄ can be a promising red component for the commercial YAG:Ce³⁺-WLEDs.

Conclusion

Analyzing photoluminescent properties of the phosphors and performance of related LEDs, the following results can be found. First, such tungstates phosphors show red emission excited by a near UV chip or a blue chip, therefore can be a promising red component for WLEDs. Second, all phosphors obtain good CIE chromaticity coordinates, therefore can get high colour purity of red emission. Third, such tungstates phosphors have excellent thermal stability. Fourth, the phosphors

TABLE-2
PERFORMANCE PARAMETERS OF THE LEDs

LED	Excitation wavelength (nm)	Excitation electric current (mA)	CIE chromaticity coordinates ^a		Efficiency (lm/W)	Colour temperature (K)	Colour rendering index
			x	y			
NUV InGaN chip	395	20	0.1840	0.0639	0.33	–	–
Red LED based on $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$	395	20	0.5669	0.2919	1.41	–	–
WLED made from $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ and a NUV chip	395	20	0.3517	0.3553	2.44	4769 K	60.0
Blue InGaN chip	460	20	0.1435	0.0483	10.75	–	–
WLED made from $\text{YAG}:\text{Ce}^{3+}$ and a blue chip	460	20	0.3075	0.3376	42.99	6710	81.0
WLED made from $\text{YAG}:\text{Ce}^{3+}$, $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ and a blue chip	460	20	0.3181	0.3403	44.71	6164	80.0

^aNTSC standard values for white are $x = 0.33$, $y = 0.33$.

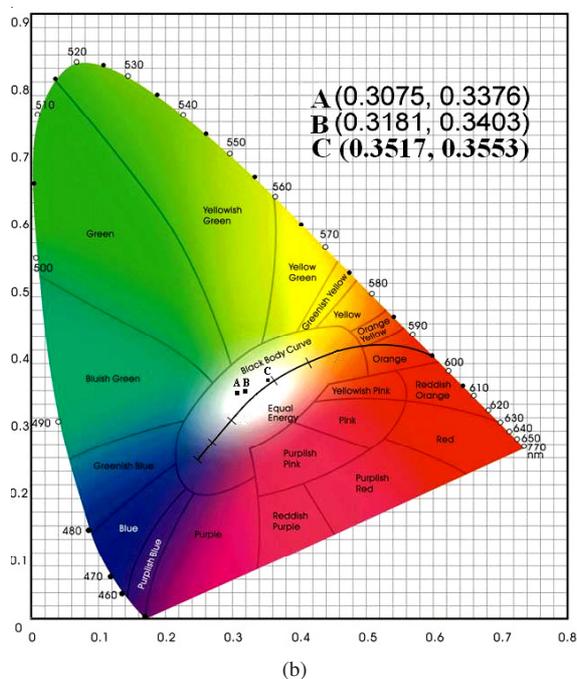
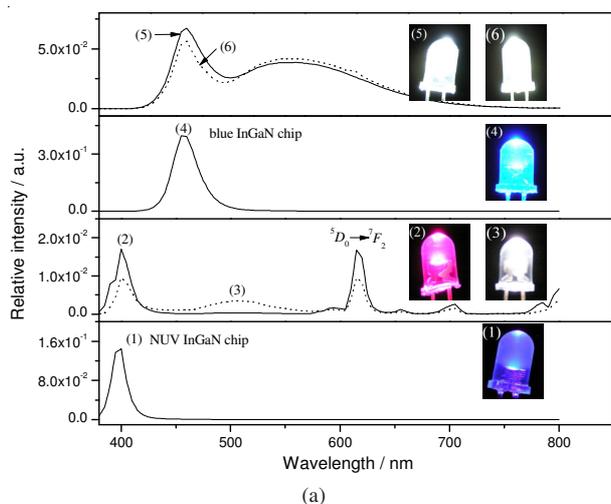


Fig. 3. (a) The emission spectra of the LEDs made from (1) the original NUV chip; (2) a NUV chip + $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$; (3) a NUV chip + $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ + green phosphor + blue phosphor; (4) the original blue chip; (5) a blue chip + $\text{YAG}:\text{Ce}^{3+}$; (6) a blue chip + $\text{YAG}:\text{Ce}^{3+}$ + $\text{Ca}_9\text{Eu}_2\text{W}_4\text{O}_{24}$ under excitation of 20 mA forward bias. (b) The corresponding CIE diagrams of the (A) WLED(5); (B) WLED(6); (C) WLED(3)

should be combined with near UV chips operating at *ca.* 395 nm better than the blue chips operating at *ca.* 460 nm. Fifth, the phosphors are not matched perfectly with the blue chips and the problem may be resolved by introducing other co-doped ions into the phosphor lattice to broaden the absorptions around 465 nm.

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