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Improved color properties of light emitting diodes with red phosphors and quantum dots

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This paper is dedicated to Prof Wolfgang Kiefer on the occasion of his 80th Birthday

This paper presents the effect of red color-conversion materials on the emitting spectrum of typical light emitting diodes (LEDs) for general lighting applications. Conventional LEDs consist of blue LED chips and yellow phosphors lacking deep red in their emitting spectra. Addition of red phosphors or red quantum dots may improve the color-rendering properties of white LEDs. Either the $K_2SiF_6:Mn^{4+}$(KSF) red phosphor or red CdSe/ZnS quantum dot was included in the white LED made by using blue LEDs and YAG($Y_3Al_5O_{12}:Ce^{3+}$) green phosphors. Inclusion of red emitting materials enhanced the color rendering index(CRI) significantly, especially the R9 index associated with the strong red. In addition, it was found that the improved white LEDs could be used to enhance the color gamut of liquid crystal displays.

Keywords: Light emitting diode, Phosphor, Quantum dot, Color rendering index, Color gamut

1 Introduction

White light emitting diodes (LEDs) have become one of the main streams of lighting technologies. The birth of commercial blue LEDs in 1990s opened a new way to generate white light based on a new form factor. The most conventional structure of white LEDs consists of blue LED chips (wavelength near 450 nm) and yellow phosphors such as YAG($Y_3Al_5O_{12}:Ce^{3+}$) [1]. There have been tremendous efforts on the improvement of light efficiency of LED resulting in at least comparable to or even larger efficiency than conventional light sources such as fluorescent lamps [2]. The first main application of white LEDs was the light source in the backlight unit for liquid crystal displays(LCDs) [3]. The adoption of white LEDs in LCD realized an ultra-slim form factor and a lower power consumption. The subsequent application field of white LEDs was general lightings [4].

One of the most important properties of general lighting is its color rendering property, which is related to the color appearance of objects illuminated under a certain light source and quantified in terms of color rendering index (CRI). The emitting spectrum of white LEDs lacks deep red component, which makes their CRI be lower than 80 in general. One of the ways to improve CRI of white LEDs is to use a mixture of green and red phosphors instead of using a yellow phosphor [5-7]. The $K_2SiF_6:Mn^{4+}$(KSF) red phosphor is one of the candidate materials for solid-state lighting [8-9]. The other way is to apply red quantum dots (QDs) to the white LEDs [10-14].

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QDs are nano-sized semiconductors and have arisen as a new color-conversion material for lighting and display applications [15]. Especially, the sharp spectral feature is a great advantage for enhancing color gamut of displays [16]. The emitting wavelength of QDs can be easily tuned in terms of their size due to the quantum confinement effect. On the other hand, QDs have been adopted in other applications such as a bio-marker, plant growth, etc. In this study, a systematic comparison of two color-conversion materials, i.e., red phosphors and red QDs has been carried out. Especially, we focused on the color rendering properties and their improvement of white LEDs in terms of these two materials.

2 Experiments

White LEDs were fabricated by using typical blue LED chips (IWS-L5056-UB-K3) with an emitting area of approximately 5.4×5.0 mm^2 and typical YAG yellow phosphors (x = 0.421±0.0005, y = 0.560±0.005). For fabricating high-CRI white LEDs, the green YAG phosphor (x = 0.363±0.003, y = 0.579±0.003, particle size : 23.0±2.0 μm) was mixed with either the red phosphor or the red QD. The KSF red phosphor (x = 0.695±0.003, y = 0.305±.003, Particle size : 25.0±3.0 μm) or the red CdSe/ZnS QD was mixed with the green phosphor in a photo-polymer (NOA63, Norland Co.). The mixture was hardened under a UV lamp at the wavelength of 365~370 nm (30 W, Skycares). The emitting spectrum and the color coordinates were measured by using a spectroradiometer (PR670, Photo-Research Co.) and the CRI was measured by using an illuminance meter (Spic-200, Everfine). Table 1 shows the masses of each component included in the two kinds of white LED. Total 10 LEDs were fabricated under the same conditions. Each LED was aged for at least 20 min. and then measured for five times. All the measured values reported in this study are averages from the multiple measurements for all LEDs. As to the CRI, the 15 CRI values from R1 to R15 were measured.

Table 1. Masses of all components included in the two kinds of white LED

blue LED + (red, green) phosphors			blue LED + green phosphor + red QD		
material	component	mass (g)	material	component	mass (g)
photo-polymer	NOA63	1.0247	photo-polymer	NOA63	1.0115
green phosphor	$Y_3Al_5O_{12}:Ce^{3+}$	0.2282	green phosphor	$Y_3Al_5O_{12}:Ce^{3+}$	0.2252
red phosphor	$K_2SiF_6:Mn^{4+}$	0.2034	red QD	CdSe/ZnS	0.0280

3 Result and Discussion

Figure 1 shows the emitting spectra of four kinds of LED: (a) LED(blue)+YAG(green)+KSF(red), (b) LED (blue) + YAG (green) + CdSe (red), (c) LED (blue) + YAG (green), and (d) LED (blue) + YAG (yellow). The four spectra were normalized with respect to the height of the blue peak. The corresponding color coordinates on the CIE1931 chromaticity diagram are shown in Fig. 2.

When only the green phosphor is coated on the blue LED, the spectrum consists of a blue peak near 450 nm and a broad peak centered near 530 nm resulting in greenish light (x = 0.307, y = 0.442). When the green phosphor is replaced by yellow phosphor, the broad peak in the green-yellow region shifts to the longer wavelength range which moves the color coordinates toward the white point (x = 0.335, y = 0.346). This is close to the white point of the equal-energy condition (x = 0.333, y = 0.333). However, the spectrum of the ‘LED (blue)+ YAG(yellow)’ combination lacks of deep red component which is the reason for the low CRI of this kind of white LED.

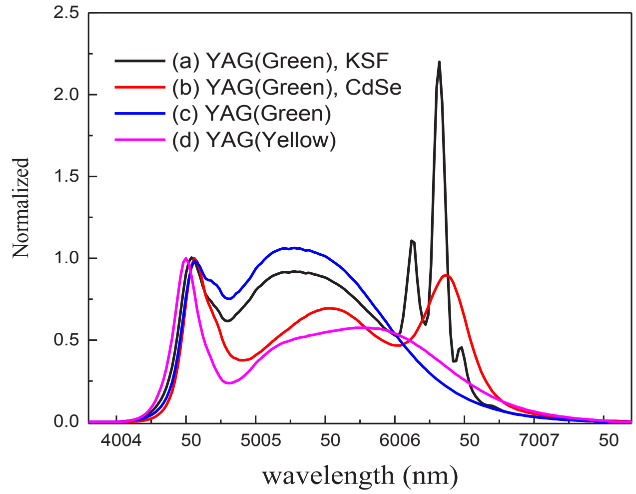


Fig 1. The emitting spectra of four kinds of LED: (a) LED(blue)+YAG(green)+KSF(red), (b) LED (blue) +YAG(green) +CdSe(red), (c) LED(blue) + YAG(green), and (d) LED(blue)+YAG(yellow).

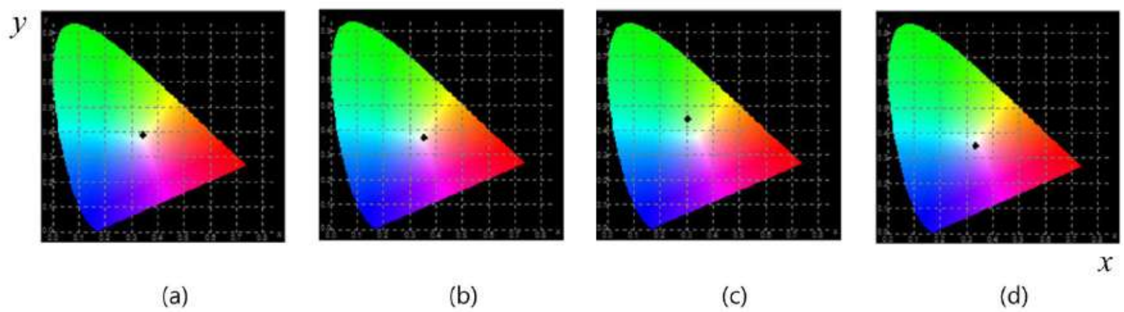


Fig 2. The color coordinates of four kinds of LED on the CIE1931 chromaticity diagram: (a) LED(blue)+YAG(green)+ KSF(red), (b) LED(blue)+YAG(green)+CdSe(red), (c) LED(blue)+YAG(green), and (d) LED(blue)+YAG(yellow).

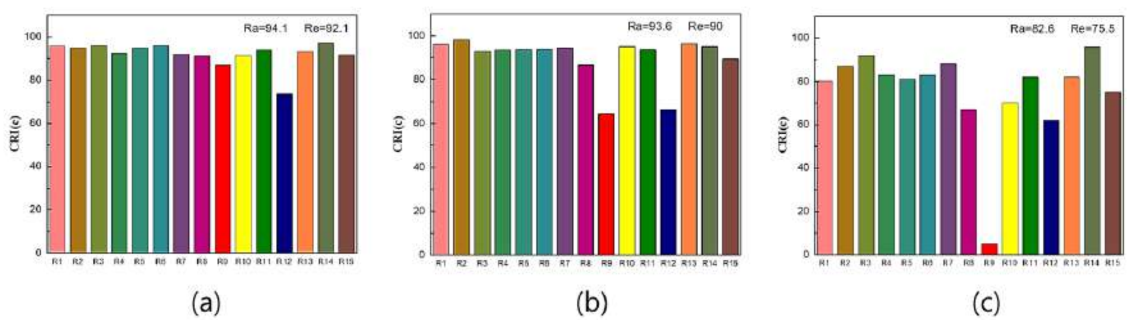


Fig 3. The CRI of three types of white LED: (a) LED (blue)+ YAG(green) + KSF(red), (b) LED(blue) + YAG(green) + CdSe(red), and (c) LED(blue) + YAG (yellow). The two average CRI values (Ra and Re) are also shown.

The addition of the KSF red phosphor increases the red component significantly. In general, the red spectrum from the KSF phosphor consists of five peaks among which three peaks are strong in the wavelength range of 610~630 nm. The Mn^{4+} activator is excited via $^4A_2 \rightarrow ^4T_2$ by blue photons and exhibits the strongest peak near 630 nm due to the $^4E_g \rightarrow ^4A_{2g}$ transition [5,8-9]. This transition corresponds to the dipole-forbidden transition but becomes allowed due to the coupling of the MnF_6^{2-} octahedra and vibrational modes. In the case of QD-based white LED shown in Fig 1, a relatively narrow peak near 640 nm, which is added to the broad green peak, is observed. As a result of enhanced color conversion into strong red, the color coordinates shifted slightly to the yellow-red region as shown in Fig 2, and the correlated color temperature decreased accordingly. The enhancement of the red component in terms of the two color-conversion materials is expected to improve the color rendering properties of white LED.

Figure 3 shows the measured CRI values for 15 test color samples of three white LEDs: (a) LED (blue) + YAG(green) + KSF(red), (b) LED(blue) + YAG(green) + CdSe(red), and (c) LED(blue) + YAG(yellow). It also includes the average CRI Ra for R1~R8 and Re for R1~R15. It means that Ra is a general CRI for 8 test samples while Re is an extended version including R9~R15 in addition to R1~R8. Table 2 shows the Ra and Re values of the three types of white LED. The CRI of the conventional white LED (type (c)) is not high, Ra is 82.6 and Re is even lower than 80. This is mainly because the R9, the CRI for strong red, is very low (less than 10) due to the insufficient red component in the emitting spectrum. R9 is important in many applications, such as textiles, photography, and other related area where, for example, skin tones of human need to be reproduced faithfully.

Table 2. Ra and Re values of three white LEDs.

White LED	Ra	Re
YAG(green)+KSF(red)	94.1	92.1
YAG(green)+CdSe(red)	93.6	90
YAG(yellow)	82.6	75.5

Figure 3 and Table 2 clearly show that the R9 is substantially improved by adding either red phosphor or red QD to the green phosphor. The R9 is more than 85 and 65 for the 'YAG(green)+KSF(red)' and 'YAG(green)+CdSe(red)' combination, respectively. This improvement contributes to the increase of Ra and Re of both LEDs. This is mainly due to the enhancement of red component in the visible range.

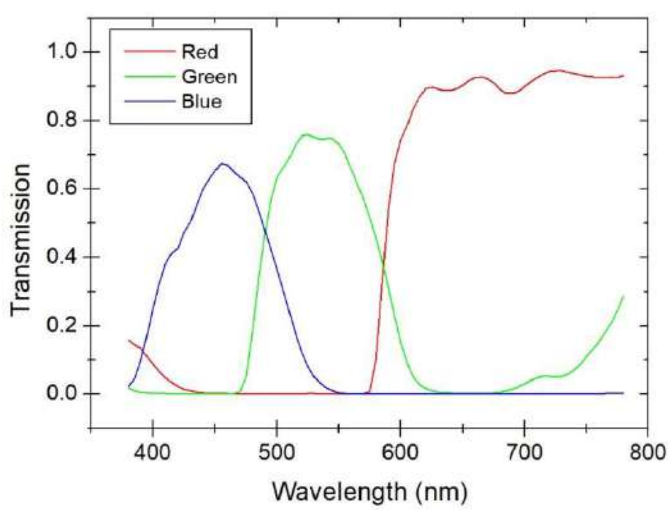
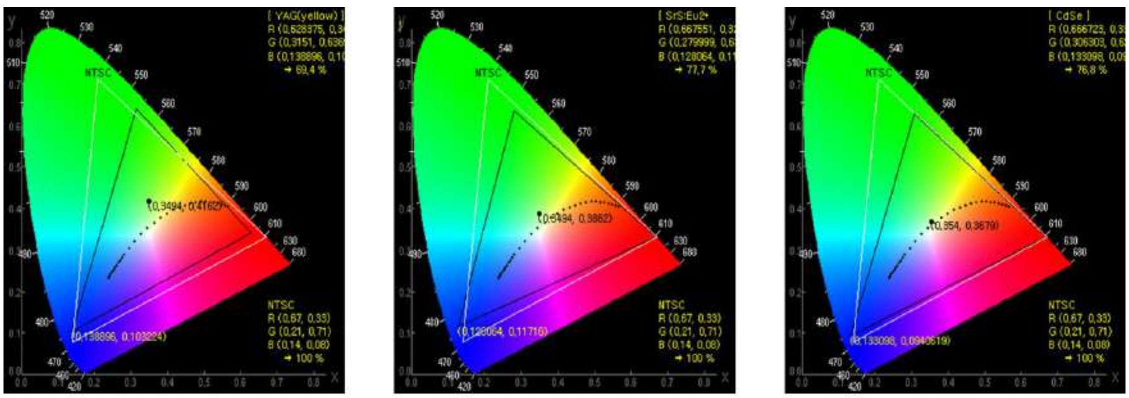


Fig 4. Typical transmission spectra of LCD panels which were used to obtain the color gamut for each white LED.

Another possible advantage of applying red color-conversion materials in conventional white LEDs is the color gamut of displays. Especially, the color properties of white LEDs adopted in backlight units for LCDs may be improved. Figure 4 shows typical transmission spectra of LCD panels. The measured emitting spectra were multiplied with these three transmission curves to obtain the spectra of primary colors of LCD, which were, then, multiplied with the color matching functions to derive the tristimulus values and color coordinates. The area of the obtained triangle on the chromaticity diagram was compared to the NTSC(National Television System Committee) standard to calculate the color gamut in %.



(a) (b) (c)

Fig 5. The color gamut of three types of white LED : (a) LED(blue) + YAG(yellow), (b) LED(blue) + YAG(green) +KSF(red), and (c) LED(blue) + YAG(green) + CdSe(red). The white solid lines denote the NTSC standard (100%) while the black solid lines show the calculation results for the color gamut of three types of white LED lighting.

Figure 5 shows the calculation results for the color gamut. The white solid lines denote the NTSC standard (regarded as 100%) while the black solid lines show the calculation results for the color gamut of three types of white LED lighting assuming that they are included in the LCD backlight unit. The color gamut of the conventional white LED with the yellow phosphor was 69.4%, slightly less than 70%. The color gamut was 77.7% and 76.8% for the 'YAG(green) + KSF(red)' and 'YAG(green) + CdSe(red)' combination, respectively. These values are slightly higher than that obtained from the LCD adopting typical white LEDs. The relatively sharp spectral feature of the red component shifts the color coordinate of the red color toward the monochromatic line on the chromaticity diagram, extending the area of the color gamut.

The present result suggests two possible improvements by adopting red color-conversion materials in conventional white LEDs: (1) the CRI of white LED lightings can be greatly increased, especially R9 corresponding to the strong red, and (2) the color gamut of LCDs may be improved to a moderately good value. Regarding the latter aspect, it is necessary to reduce the half widths of green and red peaks for further improvement. One promising approach is to combine both green and red QDs, which is the current method adopted in the premium LCD TV's, called QLED TV. In this context, it seems better to suggest more discussions about the former, i.e., the lighting technology suggested in this study.

First, applying the red phosphor and the red QD to the conventional white LEDs exhibit comparable performances to each other from the viewpoint of color rendering properties. The formation of relatively sharp red peaks in the low-wavelength range enhanced the R9 significantly contributing to the overall CRI values. However, the Table 1 clearly shows that the required amount of the red QDs is much smaller than that of the red KSF phosphors. The mean diameter of phosphor particles is about 25 μm while that of red QDs is only a few nm. It means that the number density of QDs in one LED is substantially larger than that of phosphor particles in one white LED. Large number of QD particles induce multiple scattering in the encapsulant resulting in more efficient color conversion in spite of much smaller amount. This seems to be the reason for the much smaller amount of QDs used in the LED to obtain comparable color properties to those of LEDs with red phosphors being adopted. This result also indicates that the red QD may be a cost-effective choice for the development of high-CRI white lightings.

Second, the reason for the slightly worse CRI values of the QD-based white LED than those of the phosphor-based white LED may be due to the insufficient broadness of the red peak located near 640 nm. The half width of the emission peak of QDs is mainly determined in terms of the size distribution of QDs. For display applications, sharper spectral feature is desirable, thus strict control for the size distribution of QDs is required to achieve high color purity. On the other hand, for illumination applications, wider size distribution of QDs may be necessary to secure good color-rendering properties. This can easily be achieved during the growth of colloidal QDs.

Finally, the location of QDs is adjacent to the hot LED chips in the present design, which may deteriorate the long-term thermal stability and thus lifespan of QD-based white LEDs. Other designs such as QD caps or QD films may be combined with the conventional LED lighting to secure remote distance between the LED chips and QDs. One of our previous studies revealed that appropriate adoption of QD films in the conventional high-power LED lighting could improve CRI substantially [17]. Studies on the QD caps are under progress which, we hope, to report in near future.

4 Conclusion

The results of this paper show that both red phosphors and QDs can be adopted in conventional white LEDs to substantially improve their color-rendering properties. The KSF-adopted white LED exhibits a general CRI Ra higher than 94 and an extended CRI Re higher than 92. The CdSe/ZnS QDs also showed Ra > 93 and Re > 90. These are mainly due to the formation of large peaks in the red regions and the resulting increase of R9, the individual CRI related to the strong red. These spectral modifications also form a favorable condition for improving the color gamut of LCD when these white LEDs are included in the backlight unit. Considering the thermal load on the QDs near the hot LED chips, additional QD designs such as QD caps or QD films may be incorporated in the conventional white LEDs for realizing high-CRI and long-term stability.

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References

1. Schubert E F, Kim J K, Luo H, Xi J-Q, Solid-state lighting—a benevolent technology, *Rep Prog Phys*, 69(2006)3069-3099.
2. Zhmakin A I, Enhancement of light extraction from light emitting diodes, *Phys Rep*, 498(2011)189-241.
3. Ko J-H, Recent research trends in the development of new light sources for the backlight unit of liquid crystal display, *Asian J Phys,* 14(2005)231-237.
4. Krames M R, Shchekin O B, Mueller-Mach R, Mueller G O, Zhou L, Harbers G, Craford M G, Status and Future of High-Power Light-Emitting Diodes for Solid-State Lighting, *J Disp Tech*, 3(2007)160-175.
5. Lin C C, Meijerink A, Liu R-S, Critical Red Components for Next-Generation White LEDs, *J Phys Chem Lett*, 7(2016)495-503.
6. Wu W-L, Fang M-H, Zhou W, Lesniewski T, Mahlik S, Grinberg M, Brik M G, Sheu H-S, Cheng B-M, Wang J, Liu R-S, High Color Rendering Index of $Rb_2GeF_6:Mn^{4+}$ for Light-Emitting Diodes, *Chem Mater*, 29(2017)935-939.

7. Luo D, Wang L, Or S W, Zhang H, Xie R-J, Realizing superior white LEDs with both high R9 and luminous efficacy by using dual red phosphors, *RSC Adv*, 7(2017)25964-25968.
8. Kim M, Park W B, Bang B, Kim C H, Sohn K-S, Radiative and non-radiative decay rate of K_2SiF_6:Mn^{4+} phosphors, *J Mater Chem C*, 3(2015)5484-5489.
9. Jeong D Y, Ju J, Kim D H, Optimized Photoluminescence of K_2SiF_6:Mn^{4+} Phosphors for LED Solid-state Lighting, *New Phys: Sae Mulli*, 66(2016)311-316.
10. Nizamoglu S, Erdem T, Sun X W, Demir H V, Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering, *Opt Lett*, 35(2010)3372-3374.
11. Denault K A, Mikhailovsky A A, Brinkley S, Baars S P D, Seshadri R, Improving color rendition in solid state white lighting through the use of quantum dots, *J Mater Chem C*, 1(2013)1461-1466.
12. Jo D -Y, Yang H, Spectral broadening of Cu–In–Zn–S quantum dot color converters for high color rendering white lighting device, *J Lumin*, 166(2015)227-232.
13. Chung S-R, Chen S-S, Wang K-W, Siao C-B, Promotion of solid-state lighting for ZnCdSe quantum dot modified-YAG-based white light emitting diodes, *RSC Adv*, 6(2016)51989-51996.
14. Yoon H C, Oh J H, Lee S, Park J B, Do Y R, Circadian-tunable Perovskite Quantum Dot-based Down-Converted Multi-Package White LED with a Color Fidelity Index over 90, *Sci Rep*, 7(2017)2808; doi.org/10.1038/s41598-017-03063-7.
15. Shirasaki Y, Supran G J, Bawendi M G, Bulović V, Emergence of colloidal quantum-dot light-emitting technologies, *Nat Photon*, 7(2013)13-23.
16. Kim S J, Jang H W, Lee J-G, Ko J-H, Ko Y W, Kim Y, Study on Improvements in the Emission Properties of Quantum-Dot Film-Based Backlights, *New Phys: Sae Mulli*, 69(2019)861-866.
17. S C Hong, J Baek, H Lee, G J Lee, J -G Lee, J -H Ko, Y W Ko, Y Kim, T Park, Study on the Improvement of the Color Rendering Index of White LEDs by Using red Quantum dots, *New Phys: Sae Mulli*, 70(2020)698-704.

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