Dye-Bridged Hybrid Materials for Robust and High-Performance Wavelength Converter of White LEDs

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Abstract
Red and green dye-bridged hybrid materials (DBHs) are synthesized as organic wavelength converter to increase color rendering index and color temperature tunability of phosphor based white light-emitting diodes (LEDs). DBH based white LEDs show high performance and it is ensured to have long term thermal stability for solid-state lighting application.

1. Introduction
White light-emitting diodes (LEDs) are one of the main issues for the illumination and display because they have advanced properties on low energy consumption, long lifetime, reliability and wide application. In conventional white LEDs, white light is generated by combining a blue LED with a yellow phosphor as a wavelength converter [1]. But this yellow-blue combined white light has low color rendering index (CRI) and color tunability to be applied to room lighting or back lighting unit (BLU). Thus, there have been many studies to make red and green phosphors to generate white light with high CRI. But high cost and severe preparation condition restrict the usage of phosphors [2-4].

Upon this background, organic based fluorescent dye has merit on cost and optical properties to be used as a wavelength converter. The dye has broad absorption band to have high efficiency and it is easy to modify the structure to generate various luminescence, however, stability problem may limit further researches. Especially, to use the dye as a wavelength converter of white LEDs, the dye should be ensured the stability on the junction temperature of LEDs which rises to 120°C [5,6]. Thus, thermally stable dye as a wavelength converter is needed to fabricate high performance white LEDs with moderate cost.

In this study, red and green dye-bridged hybrid materials (DBHs) have been used as a wavelength converter of white LEDs. In contrast with the conventional mixture of a phosphor and encapsulant, the DBHs are a single component system of dyes and sol-gel based hybrid materials. It solves not only difficulty on dispersion of phosphor and encapsulant but also problem on thermal stability to be applied to white LED for solid-state lighting.

2. Experimental
DBHs have been synthesized which are one-body materials of the dye and sol-gel derived oligosiloxane to overcome limitation of the thermal stability of the dye. Each dye molecule is chemically bridged to oligosiloxane and it is seized by the siloxane network and restricted internal molecular rotation by the chemical structure.

2.1 Synthesis of dye-bridged hybrid materials (DBHs)
For the DBHs, dye-bridged alkoxysilanes have been synthesized through bridging alkoxysilanes with red and green dyes. These dye-bridged alkoxysilanes participate in sol-gel reaction with epoxy functional-alkoxysilane and diphenylsilanediol and they turn to dye-bridged oligosiloxane. Finally, this dye-bridged oligosiloxane becomes solid-state DBH through epoxy curing. The fabrication scheme is represented in **Figure 1**. We have followed references to synthesis DBHs [7-9].

2.2 Fabrication of DBH based white LEDs
We have fabricated two types of DBH based white LEDs. First one is inorganic/organic wavelength converter mixture that YAG phosphor is dispersed in red DBH (R-DBH) and dispensed on the blue LED chips. Second is red/green-DBH based white LED, which is consisted only with organic wavelength converter. We have demonstrated the photoluminescence and thermal stability after aging at 120°C for hundreds hours to ensure thermal stability.

Characteristics of the white LEDs such as color rendering index, color temperature, and color coordinates are measured using DARSA PRO 5100 PL System (PSI Trading Co., Ltd., Korea) and integrating sphere under a forward bias current of 10mA at room temperature.

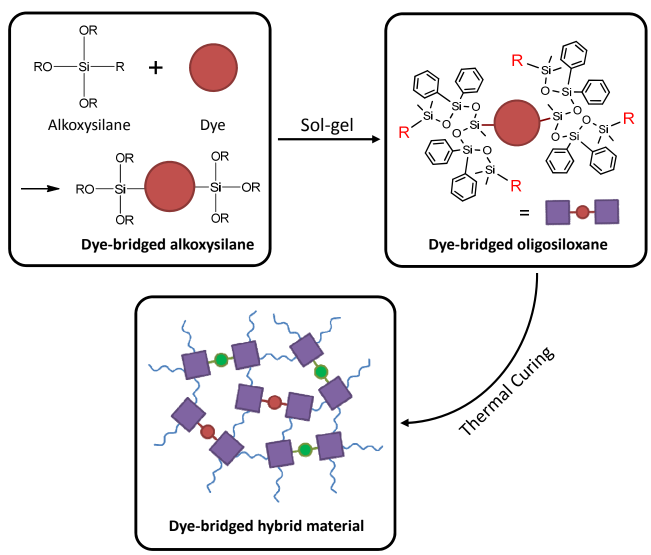

Figure 1. Synthetic scheme of dye-bridged alkosysilane, oligosiloxane and hybrid materials via sol-gel reaction and thermal curing [7]

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3. Results and Discussion

3.1 Characteristics of R-DBH/YAG based white LED

R-DBH has main absorption and emission at 498 nm and 662 nm, respectively. R-DBH has broad absorption band in the range of 350 nm to 600 nm, so it is matched with main emission of blue LED around 450 nm and it leads higher efficiency. To fabricate R-DBH and YAG phosphor based white LED, we controlled the ratio of R-DBH and YAG to find the white emission. The optimum emission is achieved when 5 wt% of YAG is dispersed in R-DBH. The dye concentration in R-DBH is 0.05 mM. When YAG is used alone, YAG based white LED has white point at (0.33, 0.346) on Commission Internationale de l'Eclairage (CIE) 1931 color space. R-DBH/YAG based white LED has white point at (0.369, 0.328) (**Figure 2**). Compare to white LED using YAG alone, its white emission is shifted to the red color. That means R-DBH/YAG based white LED has warm white. Comparing color temperature, color temperature of YAG based white LED is 5621K and that of R-DBH added one is 3923K. It is known that color temperature over 5000K is cool white and less than 4000K is warm white.

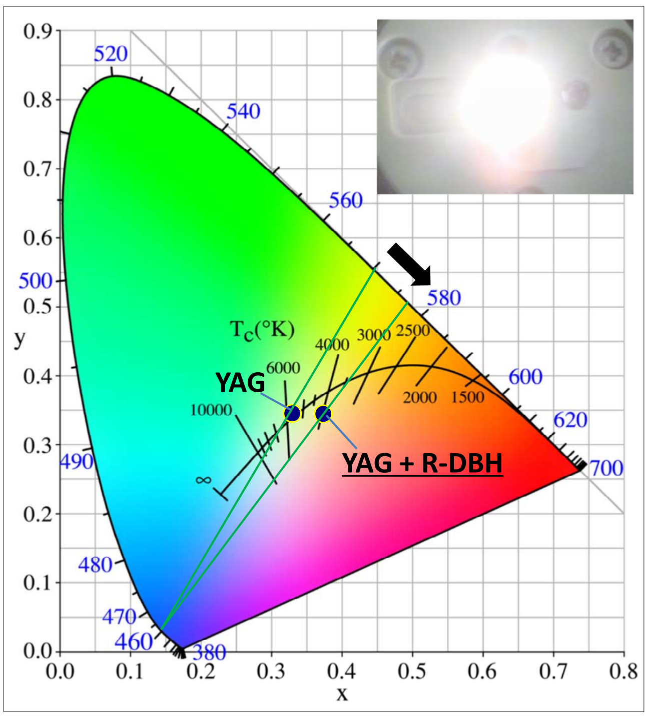

Figure 2. Commission Internationale de l'Eclairage (CIE) color coordinates of the white LEDs based on YAG and DBH mixture (Inset: Emission of YAG/R-DBH based white LED)

The R-DBH/YAG based white LED has suitable for room lighting that it has higher CRI of 86 compare to YAG based white LED, which has CRI value of 73. As presented in munsell code (**Figure 3**), index of R1 (7.5R) and R8 (10P) has been increased about 20 point. R1 and R8 represent light greyish red and light reddish purple. It means deficient red emission of YAG based white LED is filled by R-DBH. Also, R4 (2.5G), R5 (10BG) which are related to green emission are increased because emission of YAG and R-DBH overlapped and green emission is reinforced.

To the endurance of thermal stability of the R-DBH/YAG based LED, it was kept at 120°C in an air atmosphere for 1800 hrs. **Figure 4** shows that electroluminescence (EL) spectra of the fabricated white LEDs are almost unchanged during 1800 hrs before and after thermal aging. Before thermal aging, its color coordinate is (0.369, 0.328) and then it shifts to (0.365, 0.324) after thermal aging. The high thermal stability of DBH is because dye is covalent linked to the robust siloxane network, so dye is prevented from thermal decomposition.

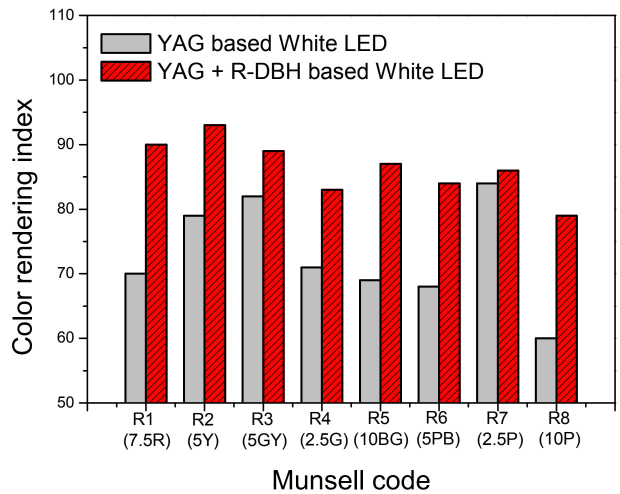

Figure 3. Color rendering index (CRI) comparison of R-DBH/YAG based white LED to YAG based white LED in Munsell code

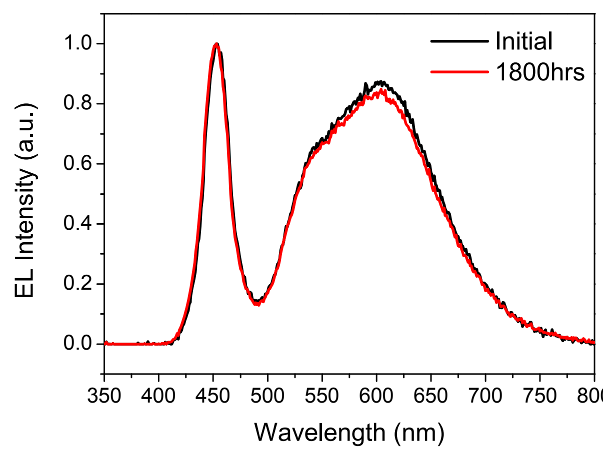

Figure 4. Electroluminescence spectra of R-DBH and YAG based white LED before and after thermal aging

To check the stability on forward current, the operation current has been increased from 5 mA to 80 mA (**Figure 5**). When the R-DBH/YAG based white LED is operated at 5 mA, it has color coordinate of (0.338, 0.281) and CRI is 86. After it is increased to 80 mA, the white LED shows CRI of 85 at (0.337, 0.274). We can conclude that wavelength converter consisted with R-DBH and

YAG has low photo-saturation and the white LED has high forward current stability.

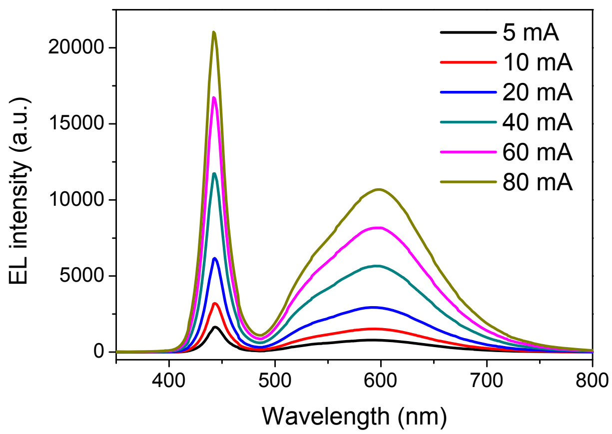

Figure 5. Forward current stability of R-DBH/YAG based white LED between 5 mA and 80 mA

3.2 Characteristics of R/G-DBH based white LED

Green DBH (G-DBH) is used as substance of YAG phosphor to exclude inorganic wavelength converter. G-DBH has the maximum photoluminescence at 528 nm when it is excited at 450 nm. G-DBH has deep green emission compare the YAG which has maximum photoluminescence at 560nm. Thus, it has advantage on expression of green color.

In the case of R/G-DBH based white LEDs, they have CRI up to 85 when it has color coordinate of (0.348, 0.334). It is much higher value compare to commercial white LED based on phosphor wavelength converter, which has the value of 64, because R/G-DBH has broader emission spectrum compare to that of inorganic phosphor. As presented in Munsell code (**Figure 6**), deficient red and green emission of phosphor based white LED is filled in R/G-DBH based white LED.

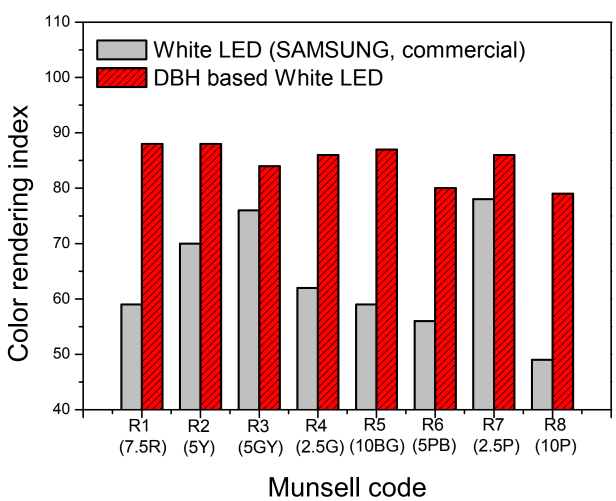

Figure 6. Color rendering index (CRI) comparison of R/G-DBH based white LED (sample C) to commercial white LED in Munsell code

Characteristics of white LED such as color coordinate, CRI and color temperature are simply controlled by controlling the ratio of red and green in DBH. The CRI is changed from 79 to 88 and color temperature is varied from 2668 K to 9727 K. So the DBH based white LEDs can be fabricated in purpose. Characteristics of various R/G-DBH based white LEDs are listed in **Table 1** and the position in color space is represented in **Figure 7**.

The R/G-DBH based white LEDs have large gamut that it has 133% larger color space compare to that of a typical CRT (NTSC 1987 space). The color coordinates of emission of R-DBH, G-DBH and blue LED are (0.705, 0.292), (0.265, 0.580) and (0.168, 0.016), respectively. Thus it can express wide color space to be used in display application.

Table 1. Characteristics of various R/G-DBH based white LEDs

	CIE (x, y)	R_a	T_c (K)
A	(0.417, 0.330)	88	2668
B	(0.377, 0.390)	82	4185
C	(0.348, 0.334)	85	4810
D	(0.301, 0.252)	79	9727
E	(0.331, 0.354)	81	5556

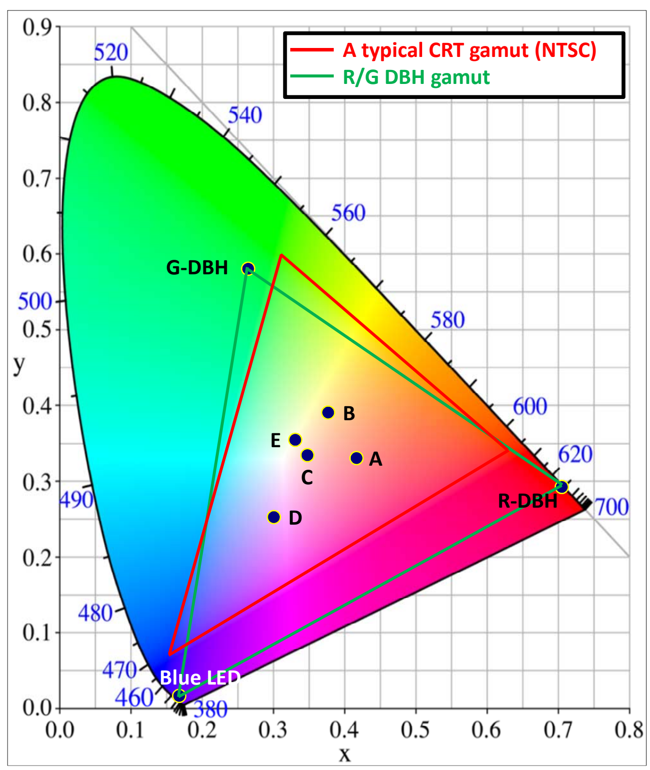

Figure 7. Color space and optical properties of various R/G-DBH based white LEDs

4. Conclusion

We have synthesized two types of dyes which are covalently bridged to epoxy functional-oligosiloxane. The CRI and color temperature of the DBH based white LED can be controlled by tuning the concentration of each dyes. Especially, this is the first report to ensure long term thermal stability of dye based white LEDs which might overcome the stability problem of the organic wavelength converter for application. We expect dye-bridged hybrid materials will provide a promising strategy to develop solid-state lighting technology.

5. Acknowledgements

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6. References

[1] S. Nakamura, G. Fasol, "The Blue Laser Diode: GaN Based Light Emitters and Lasers," Springer, Berlin (1996).

[2] R. J. Xie, N. Hirosaki, "Silicon-based oxynitride and nitride phosphors for white LEDs—A review," Science and Technology of Advanced Materials **8**, 588 (2007).

[3] R. J. Xie, N. Hirosaki, M. Mitomo, K. Sakuma, N. Kiumra, "Wavelength-tunable and thermally stable Li-α-sialon:Eu^{2+} oxynitride phosphors for white light-emitting diodes," Applied Physics Letters **89**, 241103 (2006).

[4] R. J. Xie, N. Hirosaki, N. Kiumra, K. Sakuma, M. Mitomo, "2-phosphor-converted white light-emitting diodes using oxynitride/nitride phosphors," Applied Physics Letters **90**, 191101 (2007).

[5] S. Chhajed, Y. Xi, Y. L. Li, Th. Gessmann, E. F. Schubert, "Influence of junction temperature on chromaticity and color-rendering properties of trichromatic white-light sources based on light-emitting diodes," Journal of Applied Physics **97**, 054506 (2005).

[6] Y. Xi, E. F. Schubert, "Junction–temperature measurement in GaN ultraviolet light-emitting diodes using diode forward voltage method," Applied Physics Letters **85**, 2163 (2004).

[7] S.Y Kwak, S.C Yang, N.R Kim, J.H. Kim, B.S. Bae, "Thermally Stable, Dye-Bridged Nanohybrid-Based White Light-Emitting Diodes," Advanced Materials **23** 5767 (2011).

[8] S.Y Kwak, N.R Kim, K. Lee, J. Yi, J.H. Kim, B.S. Bae, "Enhancement of Fluorescence and Lasing Properties of Covalent Bridged Fluorescent Dye in Organic-inorganic Hybrid Materials," Journal of Sol-gel Science and Technology **60** 137 (2011).

[9] S. Y. Kwak, S. C, Yang, N. R. Kim, J. H. Kim, B.S. Bae, "Sol-gel derived dye-bridged hybrid materials for white luminescence." Journal of Sol-Gel Science and Technology DOI: 10.1007/s10971-012-2676-z (2012).