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Research Article

Color Rendering Index Thermal Stability Improvement of Glass-Based Phosphor-Converted White Light-Emitting Diodes for Solid-State Lighting

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High color rendering index performance has been required for phosphor-converted warm-white light-emitting diodes (PC-WWLEDs) in lighting industry. The characteristics of low-temperature fabricated phosphor (yellow: Ce^{3+}:YAG, green: Tb^{3+}:YAG, and red: $CaAlClSiN_3:Eu^{2+}$) doped glass were presented for applications to high color rendering index warm-white-light-emitting diodes. Color coordinates $(x, y) = (0.36, 0.29)$, quantum yield (QY) = 55.6%, color rending index (CRI) = 85.3, and correlated color temperature (CCT) = 3923 K were characterized. Glass-based PC-WWLEDs was found able to maintain good thermal stability for long-time high-temperature operation. QY decay, CRI remenance, and chromaticity shift were also analyzed for glass- and silicone-based high-power PC-WLEDs by thermal aging at 150°C and 250°C for industrial test standard's aging time 1008 hours. Better than the silicone's, thermal stability of glass-based PC-WLEDs has been improved. The resulted high color rendering index (CRI) glass phosphor potentially can be used as a phosphor layer for high-performance and low-cost PC-WLEDs used in next-generation indoor solid-state lighting applications.

1. Introduction

For liquid crystal displays and outdoor lightings, white light-emitting diodes (WLEDs) have been extensively used as backlight source due to their eco-friendly features, compact size, and high reliability compared to conventional light sources, such as incandescent bulbs and fluorescent lamps [1–4]. The so-called "white light" emission can be typically generated by the mixture of three primary colors (red, green, and blue) or two complimentary colors (e.g., blue and yellow), based on the principle of additive color mixing [5–7]. Subjected to the physical structure of WLED modules, the strategy of realizing white light can be categorized into two major technologies: (1) combination of multiple LEDs and (2) phosphor-converted LEDs (PC-LEDs). In the first strategy of white light emission, two or three monochromatic LEDs are used to generate preferred white light. Dynamic color control is achievable by electronically adjusting the driving current of each LED individually. Its high quantum efficiency is also an advantage of the multiple LEDs technique without Stokes shift which is due to photonic energy downconversion [8, 9]. However, cost of multiple LEDs technique is much higher than other techniques, so multiple LEDs technique is only used in some special applications. Therefore, PC-LEDs technology dominates the market today because of significantly low cost, compact structure, and simple driving circuit, although the quantum efficiency of PC-LEDs is slightly lower than that of multiple LEDs. PC-LEDs are in a configuration with a short-wavelength-emitting LED as the excitation sources in the visible [10, 11] and/or UV [12, 13] spectral regimes, and a wavelength converter such as phosphor, which converts the light from excitation sources to generate white light. The correlated color temperature and color rendering property of the PC-LEDs can be determined upon the composition and concentration of the phosphor in the wavelength converters. Full development of phosphor materials significantly contributed to LED lightings. Yellow phosphors, such as broadband YAG phosphors, have been extensively studied on the integration with the complementary blue LEDs to form white light. However, color rendering

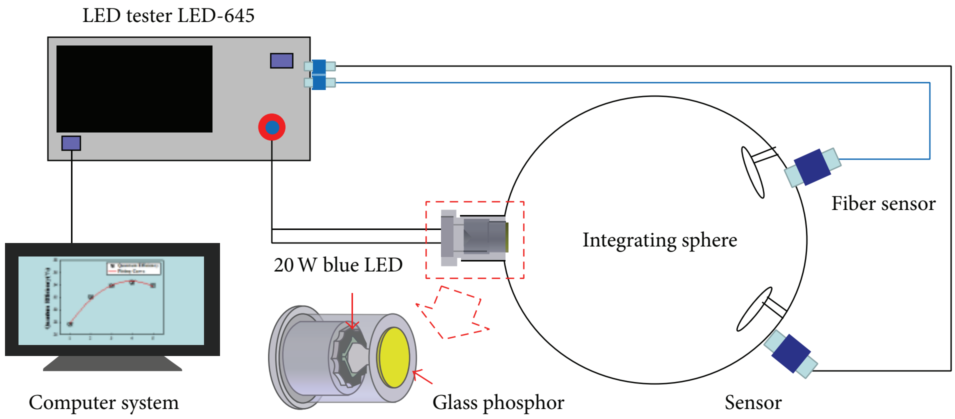


Figure 1: The test chamber schematic for optical measurement.

index (CRI) of the WLEDs is usually less than 70, which is not acceptable for general interior illumination and some special lighting including medical applications and architectural lighting. To achieve high color rendering properties, multi-phosphors such as red/yellow and orange/yellow have to be added into the color conversion layer. Multiphosphor-doped silicone as the color conversion layer of the high-CRI WLED has been fabricated to demonstrate the above purpose [14, 15], but the poor thermal stability of the silicone matrix weakens the superiority for high-luminance lighting applications, due to the lower glass transition temperature of silicone (150°C). In the previous works for yellow light emission to mix with blue light from LED, we have demonstrated novel glass-based phosphors with excellent thermal stability for the applications of high-power WLEDs [16], but the resulted CRI values were normally as low as 70s with single phosphor powder.

Remote phosphor was studied as an alternative technology for white light LED. Kuo et al. investigated patterned structure of remote phosphor for phosphor-converted white light LEDs [17]. This patterned structure was designed to reduce the angular-dependent correlated color temperature (CCT). Intematix Company reported polycarbonate-based remote phosphor layer around source LED [18], though glass-based remote phosphor product could be under development.

In this study, we fabricated a thermally stable multi-phosphor-doped glass (MPDG) for the goal. The results showed that the glass-based PC-WLEDs exhibited good thermal stability in lumen loss, chromaticity shift, CRI, and QE characteristics. Then we compared with the silicone-based high-power PC-WLEDs under thermal aging at lower temperature of 150°C, 250°C, 350°C, and 450°C. The results demonstrated that the thermal stability of glass-based PC-WLEDs outperformed the silicone-based PC-WLEDs. The novel development of glass-based PC-WLEDs is essentially critical to the application of LED modules in the area where absolute reliability is required and where silicone simply cannot stand the heat, humidity, or other deteriorating factors due to its low thermal stability. The multiphosphors layer of glass as an encapsulating material may be advanced for many applications where the LED modules with high reliability are required.

2. Experiment and Measurement

The glass matrix was composed of SiO_2, Na_2CO_3, Al_2O_3, and CaO to be mixed and then melt at 1300°C for 1 hour in a platinum crucible. The cooled cullet glass (SiO_2-Na_2O-Al_2O_3-CaO) was milled into powders and kept dried. Yellow ($Y_3Al_5O_{12}$:Ce^{3+}, YAG based), green ($Lu_3Al_5O_{12}$:Ce^{3+}, LuAG based), and red ($CaAlSiN_3$:Eu^{2+}, nitride based) phosphors of different ratio were uniformly mixed into the matrix glass powder followed by melting at 680°C for 6 hours, labeled as $Y_1G_0R_0$DG, $Y_1G_1R_1$DG, $Y_2G_1R_1$DG, $Y_1G_2R_1$DG, and $Y_1G_1R_2$DG according to the composition ratio among yellow/green/red phosphor in the glass phosphors. These glass phosphor samples were then polished to 0.5 mm of thickness after quenching down to room temperature. With 15 mm in diameter and 0.5 mm thick, the solidified glass phosphor circular disks were entirely covered over the LED and the reflective cup to form a WLED module. An integrating sphere equipped with an optical fiber and a CCD detector was employed to measure the optical spectra of the WLED module.

For thermal aging tests (its setup as shown in Figure 1), eleven phosphor disk samples from low-temperature glass CeYDG were aging at 150°C, 250°C, 350°C, and 450°C for 1008 hours. All the samples of MPDG ($Y_1G_1R_1$DG) with diameter, thickness, and chromaticity coordinates were 15 mm (±0.25), 0.5 mm (±0.025), and ($0.36 \pm 0.005, 0.29 \pm 0.005$), as shown in Table 1.

Thermal aging tests were measured periodically in order to characterize the degradation of phosphor materials on lumen, CIE, and CRI. The data of all samples were obtained through the LED-645 test system (Lightports). The quantum yield (QY) is one of the major parameters used as a selected

Table 1: High CRI sample counts of accelerated test.

Aging temperature (°C)	150	250	350	450
Sample quantity (pcs.)	11	11	11	11
Chromaticity coordinates	(0.35, 0.28)	(0.35, 0.28)	(0.35, 0.28)	(0.35, 0.28)
Diameter (mm)	15	15	15	15
Thickness (mm)	0.5	0.5	0.5	0.5

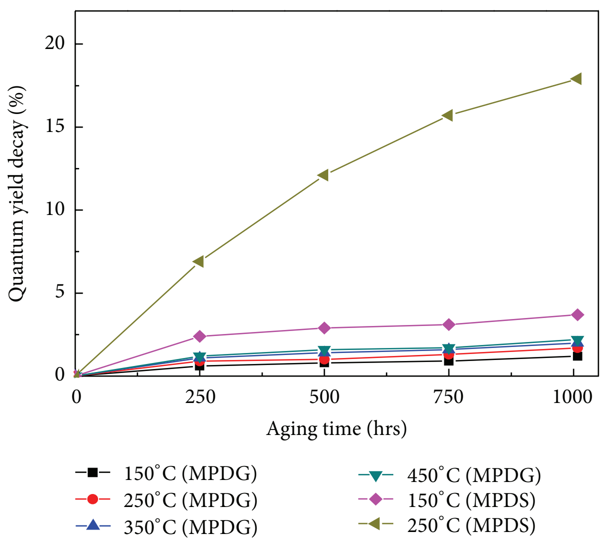


Figure 2: Quantum yield decay (%) versus aging time for PC-WLEDs of MPDG and MPDS samples at different temperatures.

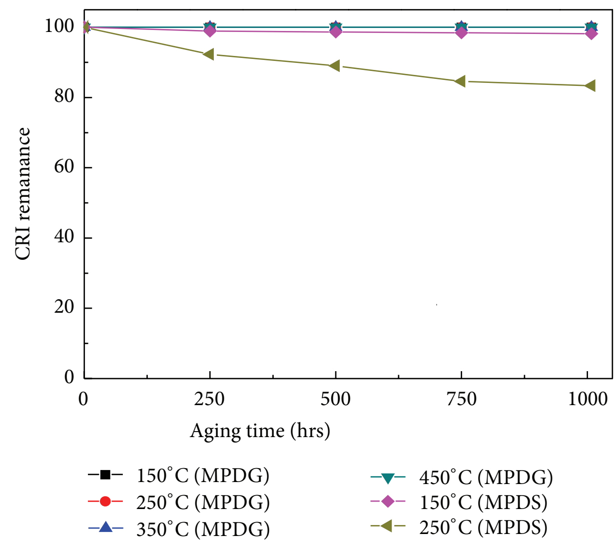


Figure 3: The CRI remanence versus aging time for PC-WLEDs of MPDG and MPDS samples at different temperatures.

criterion of luminescence materials in solid-state lighting applications, as shown in the following:

$$QY = \frac{N_{\text{erm}}}{N_{\text{Abs}}}, \quad (1)$$

where the QY of the wavelength converting materials is defined as the ratio of the number of photons emitted (N_{erm}) to the number of photons absorbed from the emission of the pumping light sources (N_{Abs}), where the number of photons in each wavelength, $N(\lambda)$ (cps/nm), can be obtained through dividing spectrum distribution $P(\lambda)$ (mW/nm) by photon energy $h\nu$ (J) [19].

CRI remanence is defined as the measured value of CRI after thermal degradation.

The chromaticity shift is defined as

$$\Delta E = \sqrt{\left(u'_f - u'_i\right)^2 + \left(v'_f - v'_i\right)^2 + \left(w'_f - w'_i\right)^2}, \quad (2)$$

where $u' = 4x/(3 - 2x + 12y)$, $v' = 9y/(3 - 2x + 12y)$ and $w' = 1 - u' - v'$. The u' and v' are the uniform chromaticity coordinates [20], the x and y are the chromaticity coordinates (CIE 1931), and the i and f are the chromaticity shift before and after test, respectively. A schematic diagram of the test chamber for optical measurements is shown in Figure 2. The test chamber consisted of a 5 W GaN blue-light LED, a heat sink, a removable phosphor layer, and an integral sphere. LED and phosphor layer were integrated together. This setup is to ensure the thermal aging effect on phosphor layer after thermal aging tests that can be obtained precisely. Lumen degradation, chromaticity shift, and CRI loss at the wavelength of 460 nm were recorded and compared before and after each thermal test.

3. Results and Discussion

Table 2 shows optical properties of the WLEDs utilizing MPDG. The color coordinates and color temperature of the WLED utilizing Y1G1R1DG are (0.358, 0.288; 3923 K) with high color rendering index up to 85 suitable for interior lighting.

3.1. Thermal Stability of High CRI Glass Phosphors. The thermal stability test results of both types of samples were carried out at 150°C, 250°C, 350°C, and 450°C for 1008 hours. Due to silicone material carbonized above 280°C, MPDS samples can merely be characterized under this temperature. Thus, MPDS can only be compared with MPDG below such critical temperature, while the characteristics of MPDG will be still presented at 350°C and 450°C.

3.1.1. Quantum Yield Decay. To investigate the reliability of the high CRI phosphor with the glass and silicone, QY decay was measured as a function of aging time after thermal aging

Table 2: Optical properties of MPDG based WLED.

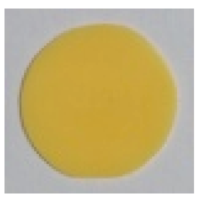
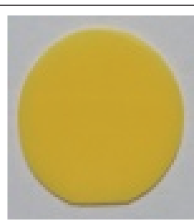
MPDG type	Top view	CIE (x, y)	CCT (K)	CRI	QY (%)
$Y_1G_0R_0DG$		(0.321, 0.325)	6043	68.58	68.36
$Y_1G_1R_1DG$		(0.358, 0.288)	3923	85.25	55.57
$Y_2G_1R_1DG$		(0.405, 0.363)	3248	73.96	59.40
$Y_1G_2R_1DG$		(0.375, 0.334)	3803	81.25	55.31
$Y_1G_1R_2DG$		(0.428, 0.302)	2182	70.16	47.24

Table 3: Characteristics of MPDG and MPDS based WLED samples accelerated thermal aging after 1008 hours.

Characteristics	Phosphor layer type	150°C	250°C	350°C	450°C
QY decay (%)	MPDG	1.2	1.7	2	2.2
	MPDS	3.7	17.9	N.A.	N.A.
CRI remanence	MPDG	100	100	100	100
	MPDS	98.2	83.4	N.A.	N.A.
CIE shift (10^{-3})	MPDG	3.5	4.2	4.6	5.5
	MPDS	10.1	151.8	N.A.	N.A.

at 150 and 250°C for MPDG and MPDS shown in Figure 2, at measurement period 250 hours. After 1080-hour aging, the QY losses of MPDG were 1.2%, 1.7%, 2%, and 2.2% at 150°C, 250°C, 350°C and 450°C, respectively. The QY losses of MPDS were 3.7 and 17.9 times higher than MPDG at 150°C and 250°C, respectively. MPDG samples maintained good thermal stability in QY characteristic.

3.1.2. Color Rendering Index Remanence. CRI remanence was measured as a function of aging time of the MPDG and MPDS after thermal aging at 150°C, 250°C, 350°C, and 450°C at measurement period 250 hours shown in Figure 3. After 250-hour aging, the CRI remanence of MPDS was 98.2% and 83.4% at 150°C and 250°C, respectively, while CRI attenuation was almost undetectable in the case of MPDG, indicating that

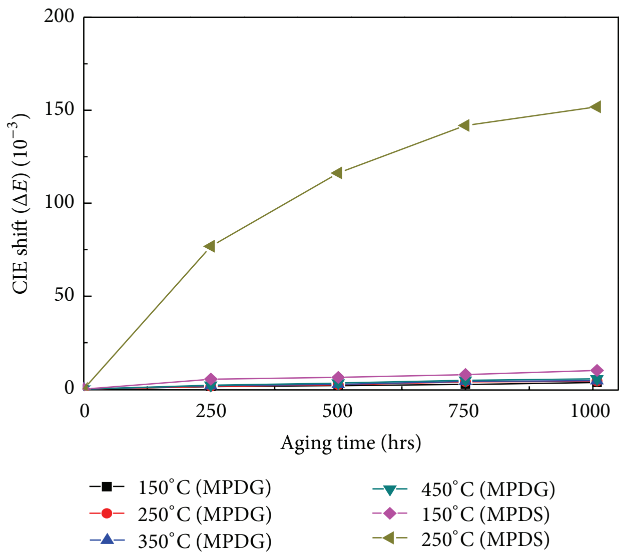


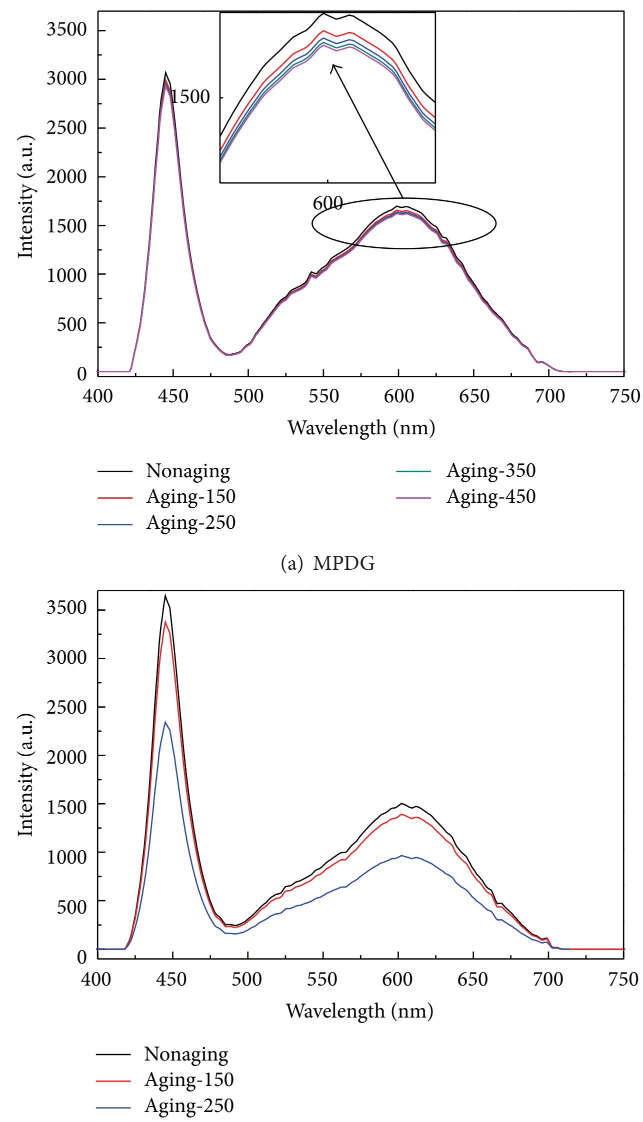
Figure 4: Chromaticity shift versus aging time for PC-WLEDs of MPDG and MPDS samples at different temperatures.

the MPDG samples maintained good thermal stability in CRI characteristic.

3.1.3. Chromaticity Shift. The chromaticity shift was measured as a function of aging time of the MPDG and MPDS after thermal aging at 150°C, 250°C, 350°C, and 450°C as shown in Figure 4 for period of 1080 hours. The chromaticity shifts of MPDG were 3.2, 4.2, 4.6, and 5.5 all in the order of 10^{-3} at 150°C, 250°C, 350°C, and 450°C, respectively. After 1008 hrs aging test, the chromaticity shifts of MPDS were 10.1×10^{-3} and 151.8×10^{-3} at 150°C and 250°C, respectively. The chromaticity of MPDG samples was thermally stable than MPDS's.

3.1.4. Emission Spectrum. The emission spectrum was measured, with integrating sphere spectrometer, as a function of aging time for the MPDG and MPDS after thermal aged at 150°C, 250°C, 350°C, and 450°C, (a) and (b), respectively, shown in Figure 5. After industrial test standard 1008-hour aging, better than MPDS's, all 4 samples of MPDG did not have significant intensity decay, as 2% and 3% at 150°C and 250°C, respectively, less than 7% and 35% of MPDS, respectively. This indicates that the MPDG sample maintained good thermal stability regarding spectrum.

In Table 3, for both MPDG and MPDS, the accelerated thermal aging test results of QY loss, CRI remanence, and CIE shift were summarized as regarding aging temperature at 150°C, 250°C, 350°C, and 450°C. Due to a higher T_g of glass matrix, it is also expected that internal strain is less in glass materials than in silicone under similar thermal stress owing to glass's lower thermal expansion coefficient. Since silicone matrix material tends to be carbonized by higher temperature aging [18], its thermal induced optical characteristic deterioration, such as CRI dropping, and so forth, will be prominent. These results showed that MPDG



(a) MPDG

(b) MPDS

Figure 5: Emission spectrum versus aging time for PC-WLEDs of MPDG and MPDS samples at different temperatures.

phosphor conversion layer is effective for long-time high-temperature operation, and high CRI potentially for use in highly efficient and high output power LEDs.

4. Conclusion

The highly thermal stable phosphor-doped glass material has been successfully developed with both higher CRI and QY than those made of silicone. CRI remanence and CIE shift in glass-based high-power PC-WLEDs outperformed silicone base under thermal aging at 150, 250, 350, and 450°C for industrial test standard 1008 hours. The results showed that the glass-based PC-WLEDs held better thermal stability in QY decay, CRI remanence, and chromaticity shift than the silicone-based PC-WLED, due to higher glass transition temperature (T_g) of glass material property. More thermally stable phosphor layer of glass encapsulation material may be beneficial for many applications where LED modules with high power and high reliability are demanded for the next-generation solid-state lighting industry.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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