Understanding and Controlling Chromaticity Shift in LED Devices

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Abstract

Chromaticity shift in light-emitting diode (LED) devices arises from multiple mechanisms, and at least five different chromaticity shift modes (CSMs) have been identified to date. This paper focuses on the impacts of irreversible phosphor degradation as a cause of chromaticity shifts in LED devices. The nitride phosphors used to produce warm white LEDs are especially vulnerable to degradation due to thermal and chemical effects such as reactions with oxygen and water. As a result, LED devices utilizing these phosphors were found to undergo either a green shift or, less commonly, a red shift depending on the phosphor mix in the LED devices. These types of chromaticity shifts are classified as CSM-2 (green shift) and CSM-5 (red shift). This paper provides an overview of the kinetic processes responsible for green and red chromaticity shifts along with examples from accelerated stress testing of 6” downlights. Both CSMs appear to proceed through analogous mechanisms that are initiated at the surface of the phosphor. A green shift is produced by the surface oxidation of the nitride phosphor that changes the emission profile to lower wavelengths. As the surface oxidation reaction proceeds, reactant limitations slow the rate and bulk oxidation processes become more prevalent. We found that a red chromaticity shift arises from quenching of the green phosphor, also possibly due to surface reactions of oxygen, which shift the emission chromaticity in the red direction. In conclusion, we discuss the implications of these findings on projecting chromaticity.

1. Background

With the recent gains in luminous efficacy of solid-state (SSL) devices, the chromaticity shift of these devices is attracting more attention as a potential failure mode. Compared to luminous flux maintenance, much less is known about the causes of chromaticity changes, and there are no accepted methods for projecting chromaticity over time.

Fortunately, within the last 3 years, a better understanding of the causes of chromaticity shifts in SSL devices has emerged, including the realization that chromaticity changes often proceed in an orderly fashion and are often dominated by the behavior of the light-emitting diodes (LEDs). In addition, device optical components such as lenses, reflectors, and power electronics can potentially have an impact [1-12]. To date, various mechanisms that cause chromaticity shifts have been proposed including discoloration of polymeric materials used in LED packaging [1, 2], delamination of the phosphor from the LED die [2, 3], and chemical changes in the phosphor that produce a shift in emission peaks [13]. However, the kinetics of these processes have not been fully determined. Such information could help in projecting chromaticity shifts and ultimately in designing SSL products that achieve acceptable chromaticity stability during intended life.

Although chromaticity is often expressed as the distance, as measured by $\Delta u'v'$, between the current chromaticity point and the original chromaticity point, $\Delta u'v'$ only provides information on the magnitude of the shift, not the direction. A significant amount of information about the causes of chromaticity shift can be gleaned by looking at the direction of the shift, which can be gauged from changes in the individual chromaticity coordinates (i.e., $\Delta u'$ and $\Delta v'$) and an examination of the spectral power distribution (SPD) [11].

As shown in **Figure 1**, white light from LEDs can be produced by combining a blue-emitting LED (e.g., 450 nm) with a phosphor that emits at a nominally yellow wavelength (e.g., cerium-doped yttrium aluminum garnet (YAG:Ce) phosphors). The relative amounts of blue emissions and yellow phosphor emissions produced by the white LED determines the initial chromaticity point, and any chromaticity point on the blue-yellow line can be achieved by changing the relative amounts of blue and yellow emissions. An increase in blue emissions (or a decrease in yellow emissions) produces a shift from the original chromaticity point toward the blue direction, and an increase in yellow emissions (or a decrease in blue emissions) produces a yellow shift. Hence, a natural linkage exists between blue and yellow chromaticity shifts.

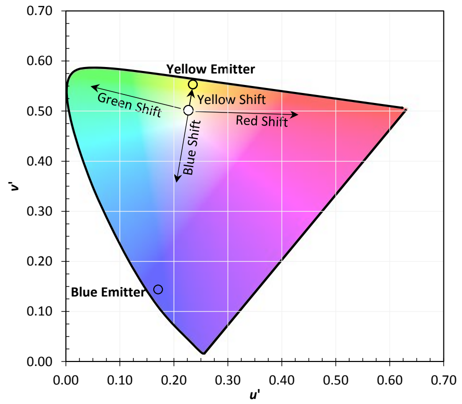

Figure 1: Chromaticity shift directions for LED devices shown using the CIE 1976 color space. The initial chromaticity point is the white circle and the chromaticity points of the blue and yellow emitters are also shown.

Similarly, chromaticity shifts can also occur in the green and red directions. However, these shifts are not caused by a simple change in the relative intensity of the primary sources, but must also involve a change in emission wavelength of the primary emitters. For multicomponent phosphors, such a spectral change may be difficult to see because emissions occur over a broad wavelength range. Consequently, a deeper analysis of the SPD is required to understand the spectral changes responsible for the chromaticity shift [11]. In this way, red and green shifts have some similarity in that they often involve spectral changes in the phosphor.

To date, four chromaticity shift modes (CSMs) have already been identified in SSL devices such as LEDs, lamps, and luminaires [11] and a fifth CSM is reported here. These CSMs can be characterized by the direction of the shift during steady state, as shown in **Table 1**. Several potential mechanisms of chromaticity shifts have been identified [1-13], and **Table 2** provides a summary of some of these mechanisms.

Table 1. Common CSMs of LED devices and direction of chromaticity shift during steady state.

CSM Mode	Shift Direction	Change in u'	Change in v'
1	Blue	Decrease	Decrease
2	Green	Decrease	Minimal to positive change
3	Yellow	Smaller increase	Larger increase
4	Yellow then Blue	Decrease	Decrease
5	Red	Increase	Minimal to positive change

Table 2. Summary of possible mechanisms of chromaticity shift in LEDs.

Shift Direction	Possible Causes
Blue	• Reduction in phosphor quantum efficiency due to heat or photon flux • Cracks in the phosphor binder [2, 3] • Swelling of the phosphor binder [12] • Oxidation of LED package sidewalls [1, 2]
Green	• Phosphor oxidation [10, 13] • Reduction of red emissions from direct emitting LEDs or red phosphors [10]
Yellow	• Phosphor-binder separation from die [2, 3] • Increase in phosphor quantum efficiency • Increased blue photon absorption by encapsulants, lenses, or reflectors. [9, 10]
Red	• Reduction of green emissions from phosphor • Increase in relative amounts of red emissions from direct-emitting LEDs

This paper examines the changes in u' and v' that occur during chromaticity shifts, especially those involving phosphors (i.e., green and red shifts). By examining the chromaticity shifts attributable to the phosphor, and the associated SPD changes, researchers can gain new insights into some of the kinetic processes responsible for phosphor-related chromaticity shifts, and this information may be useful in projecting long-term chromaticity. In examining spectral changes in phosphors, we identified a fifth CSM; in this paper, we also present evidence of this new CSM.

2. Experimental

The devices under test (DUTs) examined in this study consisted of different 6” downlight products containing mid-power LEDs (MP-LEDs) as the light source. The experimental methods used on the DUTs in this study included wet high-temperature operational lifetime testing (WHTOL) methods described previously [10, 12]. An accelerating stress environment of 75˚C and 75% relative humidity (7575) was used throughout for WHTOL testing. The power supplied to each DUT consisted of a duty cycle with the power applied to the luminaires for 1 hour followed by the power turned off for 1 hour.

The photometric properties of each DUT were measured after every 250 hours of exposure using a 1.65-meter integrating sphere. The luminaires were mounted on the side of the sphere and the 2π test geometry was used throughout. The integrating sphere was calibrated using a forward radiant flux standard (Labsphere FFS-100-1000) traceable to standards from the National Institute of Standards and Technology (NIST),

The DUTs consisted of 6” downlight products taken from two different manufacturers and are identified as DUT-A and DUT-B herein. Although different manufacturers made the two products, they both used poly methylmethacrylate (PMMA) lenses, which are known to be stable in the 7575 test conditions [4, 9, 10]. Therefore, contributions to chromaticity shifts from optical elements are expected to be minimal. DUT-A contained a frosted lens and an optical cavity to ensure light uniformity. DUT-B is an indirect luminaire in which light from the LEDs is projected on the dome of a mixing chamber and then exits the luminaire. Additional characteristics of the two products is given in **Table 3**.

Table 3. General characteristics of the LED luminaires examined in this study.

	Power (W)	# LEDs	# Samples
DUT-A	15 W	156	5 + control
DUT-B	11 W	32	4 + control

3. Results

3.1. *DUT-A: Green Shift in LED Luminaires*

A green chromaticity shift can arise from a change in the phosphor emission wavelengths, and CSM-2 behavior have been observed in most LED package types. This type of shift is potentially prevalent in packages containing warm white nitride phosphors because these phosphors are known to change chemically in the presence of heat and moisture [13-15]. The rate of this change appears to be sensitive to the amount of oxygen and water present in the ambient environment and significant shifts to lower phosphor emission wavelengths have been reported previously [12-15].

During testing in 75/75, the 6” downlight products DUT-A exhibited CSM-2 behavior, and the change in *u′* and *v*′, as measured by Δ*u*′ and Δ*v′*, for this product is shown in **Figure 1a** and **Figure 1b**. In general, the chromaticity shifted rapidly and the 7575 test was terminated after 3,000 hours for all samples. At this point, the chromaticity shift, as measured by Δu′v′, exceeded the EnergyStar maximum allowed value of 0.007 and the devices can be considered parametric failures.

The *u′* coordinate of DUT-A decreases in a nearly linear fashion after a short induction period of approximately 250 hours. A least squares fit of the data yields a linear equation, and a summary of the statistical properties of this fit is given in **Table 4**. The correlation coefficient (R^2) of this least squares fit was high and the sum of the squares of the errors (SSE) was low. The fit was statistically significant using both the *p*-test and the F-test.

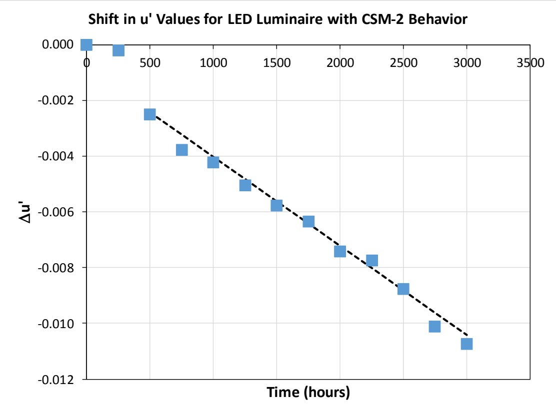

Figure 1a. Change in the average *u′* chromaticity coordinate for a population of five DUT-A devices as a function of exposure time in 7575. The dotted line indicates the least squares fit to the data between 500 and 3000 hours.

Table 4. Statistical parameters of the linear fit (500-3,000 hours) of the average *u’* coordinate of the DUT-A population.

Statistic	Value
Least Squares Fit	$\Delta u' = (-3.17x10^{-6})t - 1.04x10^{-3}$
SSE	5.9×10^{-7}

The *v’* component of chromaticity shift rose quickly toward an asymptotic value that is reached after 1,000 hours of exposure. At this point, the value of *v′* plateaued. The vastly different behaviors of the u′ and *v′* components suggests that different processes are active. Due to the rapid rise and then plateauing of the *v′* component, the process involved in this shift may also be responsible for the induction period found in *u′*.

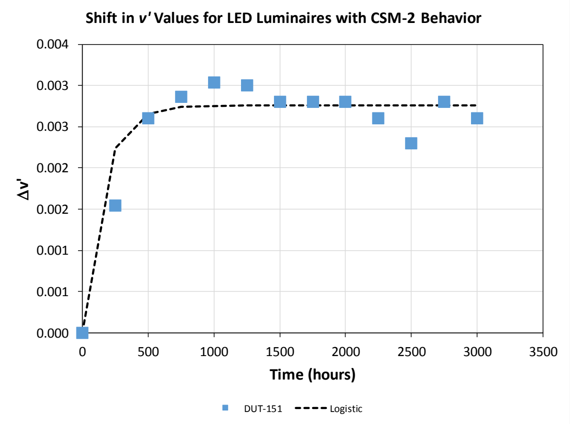

Figure 1b. Change in the average *v′* chromaticity coordinate for a population of five DUT-A devices as a function of exposure time in 7575. The dotted line gives a least squares fit of the data assuming a bounded exponential model.

Due to this behavior, a bounded exponential model was the best fit to the data, and this model can be applied over the full data set including the first 250 hours. A least squares fit of the data to a bounded exponential function and other statistical properties of this fit is given in **Table 5**. The fit produced by this process had a low SSE and can be judged to have minimal autocorrelation of the residuals using the Durbin-Watson test.

Table 5. Statistic parameters of the bounded exponential model (0-3,000 hours) of the average v’ coordinate of the DUT-A population.

Statistic	Value
Least Squares Fit	$\Delta v' = (2.76x10^{-3})(1 - e^{(6.68x10-3)t})$
SSE	$9.11x10^{-7}$

The SPD observed for DUT-A is shown in **Figure 2a,** both for the initial measurement and after 3,000 hours of 7575 exposure. The same spectra normalized to the phosphor emission maximum is shown in **Figure 2b**. In examining the normalized spectra, the relative changes in the phosphor emissions become readily apparent. The normalized SPD intensity increases over the wavelength range of 500 nm to 600 nm and decreases above 600 nm.

This shift has previously been shown to rise from a change in the lattice coordinate sites around the emitter dopant and can be directly tied to chemical changes in the phosphor [13].

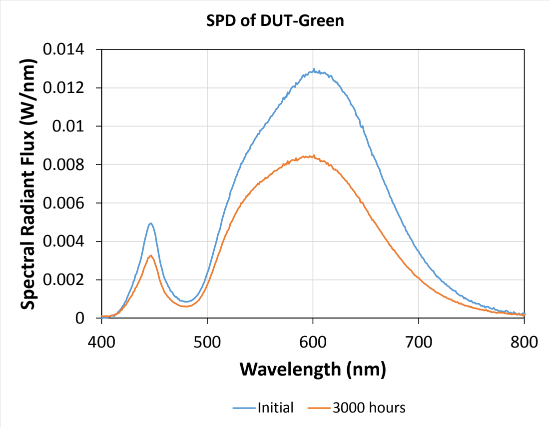

Figure 2a. SPD of DUT-A equipped with warm white MP-LEDs as initially recorded and following 3,000 hours of 7575 exposure.

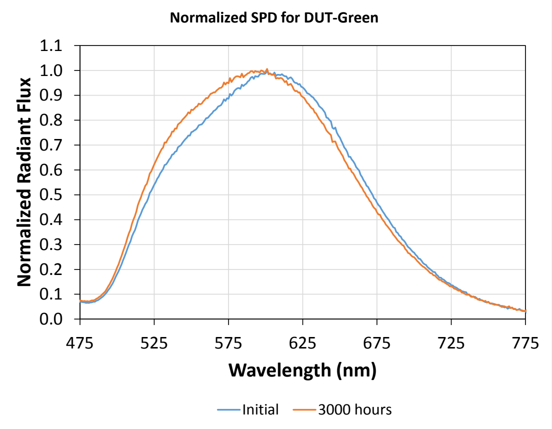

Figure 2b. SPD normalized to the phosphor emission maximum for both the initial measurement of DUT-A and following 3,000 hours of 7575.

Information on the rate of the spectral changes of the phosphor emissions can be determined by calculating the centroid wavelength ($\bar{\lambda}$) of the phosphor emission spectrum using the following equation.

$$\bar{\lambda} = \frac{\int_a^b \lambda \Phi(\lambda) d\lambda}{\int_a^b \Phi(\lambda) d\lambda}$$

Where *a* and *b* are the limits of the integration (480 nm and 800 nm for the phosphor peak), λ is the wavelength, and Φ(λ) is the spectral radiant flux at each wavelength. The centroid wavelength was calculated for one device in the DUT-A population after each 500 hours of exposure to 7575, and the results are shown in **Figure 3**. The centroid wavelength decreases, as expected for a green chromaticity shift, and this shift is linear in time with exposure to 7575.

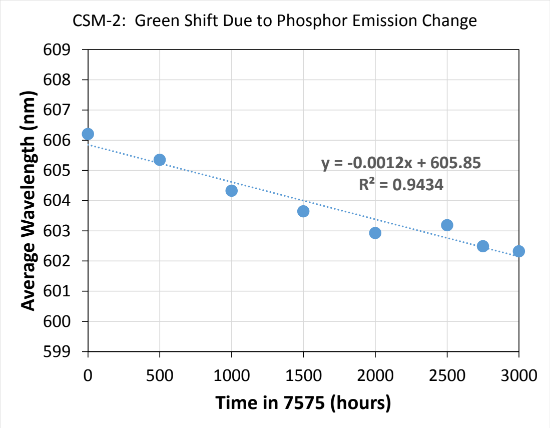

Figure 3. Change in the centroid wavelength of the phosphor peak during exposure to 7575.

3.2. DUT-B: Red Shift in LED Luminaires

A red chromaticity shift can also arise from a change in the phosphor properties, but this CSM is less common than CSM-2. The 6” downlight product DUT-B provides an example of this type of shift, and plots of the change in the *u′* and *v′* chromaticity coordinates, as measured by $\Delta u'$ and $\Delta v'$, are shown in **Figure 4a** and **Figure 4b**, respectively. The *u′* coordinate increases in a linear fashion after an induction period of approximately 2,000 hours. The *v′* coordinate also changes in a roughly linear fashion. The rate of chromaticity shift in 7575 was much slower than observed for DUT-A so testing continued for 7,000 hours. At that point, testing was terminated since $\Delta u'v'$ exceeded the EnergyStar maximum threshold and the devices can be considered to have failed parametrically for excessive chromaticity shift.

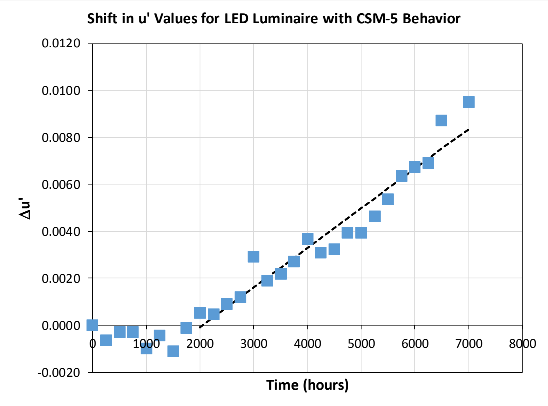

Figure 4a. Change in the *u′* chromaticity coordinate for DUT-B as a function of exposure time in 7575. The dotted line shows the least squares fit for 2,000 to 7,000 hours.

The *u′* coordinate of DUT-B increases in a linear fashion after the induction period. A least squares fit of the data yields a linear equation, and a summary of the statistical properties of this fit is given in **Table 6**. The linear equation shows a strong dependence of the chromaticity shift with time over the range of 2,000 to 7,000 hours. The correlation coefficient (R^2) of fit was high and the SSE was low. The fit was statistically significant using both the *p*-test and F-test.

Table 6. Statistic parameters of the linear fit (2,000-7,000 hours) of the average *u’* coordinate of the DUT-B population.

Statistic	Value
Least Squares Fit	$\Delta u' = (1.69\text{x}10^{-6})\text{t} - 3.45\text{x}10^{-3}$
SSE	$8.67 \text{ x } 10^{-6}$

As shown in **Figure 4b**, the *v′* coordinate of DUT-B also increases in roughly linear fashion after an induction period. A least squares fit of the *v′* data for DUT-B yields a linear equation and a summary of the statistical properties of this fit is given in **Table 7**. As found with the *u′* behavior of DUT-B, the linear equation shows a strong dependence of the chromaticity shift from 2,000 to 7,000 hours. The correlation coefficient (R^2) of this least squares fit was high and the SSE was low. The fit was statistically significant using both the *p*-test and F-test. A closer examination of Figures 4a and 4b suggests the possibility of a second red shift mechanism appearing after 4,000 hours, and additional study is required to investigate this effect further.

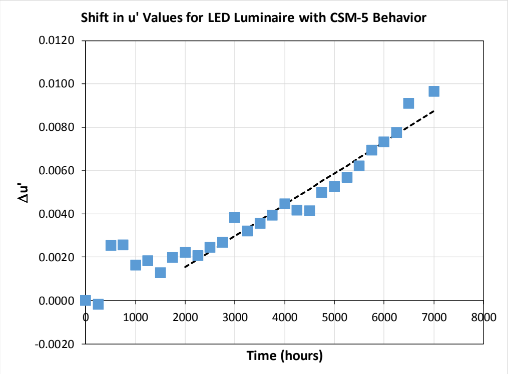

Figure 4b. Change in the *v′* chromaticity coordinate for DUT-B as a function of exposure time in 7575.

Table 7. Statistic parameters of the linear fit (2,000-7,000 hours) of the average *v’* coordinate of the DUT-B population.

Statistic	Value
Least Squares Fit	$\Delta u' = (1.44\text{x}10^{-6})\text{t} - 1.35\text{x}10^{-3}$
SSE	$5.71 \text{ x } 10^{-6}$

The SPD observed for DUT-B is shown in **Figure 5a** for the initial measurement, after 4,000 hours of exposure to 7575, and a measurement after termination of the experiment after 7,000 hours of 7575 exposure. The same spectra normalized to the phosphor emission maximum is shown in **Figure 5b**. In contrast to the findings for DUT-A, the SPD intensity for DUT-B decreased over the wavelength range of 475 nm to 600 nm. The SPD also remained relative constant above 600 nm and no new peaks appear in this region of the spectrum. This finding indicates that the observed red shift is due to a loss of a portion of the green emissions, relative to the starting point, and not to the emergence of new red emitters. Because a reduction in green emissions relative to red produces a red shift, the observed spectral changes are consistent with the observed red shift found in the chromaticity coordinates.

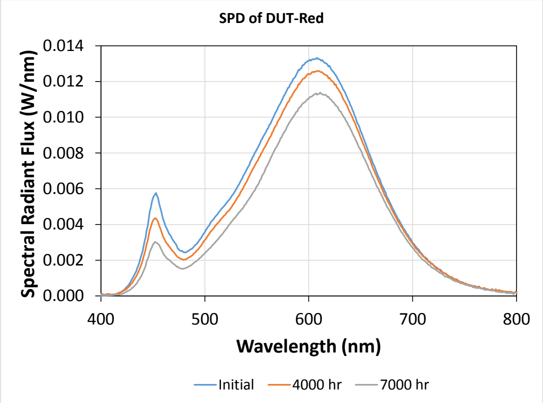

Figure 5a. SPD of DUT-B equipped with warm white MP-LEDs as initially recorded and following 4,000 and 7,000 hours of exposure to 7575.

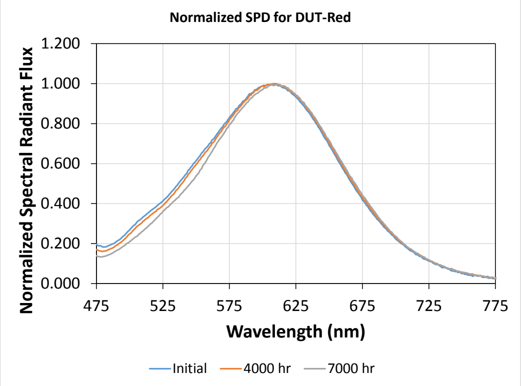

Figure 5b. SPD normalized to the phosphor emission maximum for both the initial measurement of DUT-B and following 4,000 and 7,000 hours of exposure to 7575.

Additional information on the rate of the spectral changes in phosphor emissions can be obtained by calculating the centroid wavelength of the phosphor emission spectrum from DUT-B. The centroid wavelength was calculated after each 1,000 hours of exposure to 7575; the results are shown in **Figure 6**. The centroid wavelength increased, consistent with proportionately more spectral content shifting to the red direction. Although the cause of this loss of green emissions is not yet known, a loss of quantum efficiency of the phosphor, possibly due to quenching, is thought to be the likely reason.

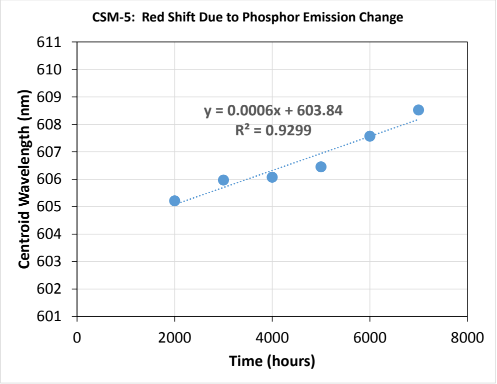

Figure 6. Change in the centroid wavelength of the phosphor peak of DUT-B during exposure to 7575.

4. Discussion

The chromaticity shift in LED devices appears to occur consistently and principally in directions that roughly correlate to the major colors, red, green, blue, and yellow. The major white LED structure (i.e., pcLEDs) utilizes emission from both a blue LED and a broadband phosphor to produce white light. Since the average emission wavelength of the phosphor is typically in the yellow to orange spectral regions, a change in relative emissions from the phosphor or the blue LED causes a chromaticity shift along the blue-yellow line. In contrast, changing the emission properties of the phosphor can produce a chromaticity shift in the green or red directions, as shown here. Because the processes involved in shifting chromaticity in the blue-yellow directions are fundamentally different from those in the green-red directions, the spectral behavior for these shifts, not surprisingly, are also different.

The underlying causes for the green and red chromaticity shifts reported here can be broadly assigned to chemical changes in the phosphor. This finding is consistent with previous studies showing that a change in the emission wavelength of Eu-doped silicon nitride phosphors in air can be attributed to a change in the crystal field around Eu emitter centers and oxidation of Eu ions [13-15]. Such changes produced a systematic shift in phosphor emissions to lower wavelength, as found here, or a quenching of the fluorescence process. Wavelength shifts of phosphor emissions have also been observed for warm white LEDs experiencing prolonged exposure to WHTOL tests [10, 12].

This phosphor oxidation reaction can be written simplistically as the kinetic expression

$$P + A \rightarrow P^*$$

where P represents the original state of the phosphor, A represents the oxidizing species such as water, and P* represents the oxidative state of the phosphor after exposure to air. The change from P to P* arises from either a change in the crystal field around the rare-Earth dopant or oxidation of the rare-Earth dopant itself [13 – 15]. The reaction can be followed spectroscopically because both P and P* emit light, albeit at different wavelengths. A change in the relative populations of P and P* will change the emission profile of the phosphor, which will alter the SPD. Because properties such as u', v', and CCT are calculated from the SPD, any changes in the spectral emissions of the phosphor will also be reflected in these parameters.

The changes in DUT-A produced a linear decrease in $\Delta u'$ after a short incubation period. In contrast, $\Delta v'$ for DUT-A initially increased rapidly and then began to slow down and approach an asymptote. The different behavior of the two chromaticity coordinates suggests that there are different chemical processes responsible for the observed u' and v' behavior, although both chromaticity coordinates may be initially reflecting the same stimuli during the observed incubation period.

The behavior found for the v' chromaticity coordinate for DUT-A is typical of a resource-limited chemical reaction in which the reaction rate slows down because of declining concentrations of reactants or loss of reaction sites. Our least squares analysis provided a good fit for the $\Delta v'$ curve with a bounded exponential model, consistent with a resource-limited kinetic process. It is perhaps significant that a bounded exponential was a better fit to the observed $\Delta v'$ data than a logistic function which has an S-shape. Bounded logistic behavior suggests that the chemical reaction is already occurring at experimental time 0 and is suggestive of a chemical reaction (e.g., annealing processes or completion of curing reactions) that started during product manufacturing. A logistic shape to the $\Delta v'$ is indicative of a process that starts after experimental time 0 and generates the end products at an initially slow rate and then the rate increases exponentially. It is possible that the incubation period found in the $\Delta u'$ coordinate may be best reflected in the $\Delta v'$ profile since the $\Delta u'$ value is strongly influenced by the shift produced by the phosphor oxidation reaction after 250 hours.

Using X-ray photoelectron spectroscopy, Yeh *et al.* demonstrated that the concentration of the oxidized form of Europium, Eu^{3+}, is higher at the surface of nitride phosphor particles than in the bulk [13]. This finding suggests that oxidation processes can occur more rapidly at the surface than in the bulk. Yeh *et al.* also demonstrated that the bulk concentration of Eu^{3+} increases under the influence of a high temperature anneal, suggesting that a diffusion process plays a role in the oxidation of the bulk [13]. Based on these results, the oxidation of the Eu-doped phosphor likely involves three main chemically processes: (1) transport of the oxidizing species to the surface of the phosphor, (2) diffusion of the oxidizing species to the reactant, and (3) oxidative reaction of the Eu-dopant and the surrounding ligand field. The transport process is virtually instantaneous since the silicone binder is highly permeable to water [16].

Surface diffusion of the oxidizing species is rapid, and combined with the favorable kinetics of the phosphor oxidation reaction, this reaction can be expected to proceed quickly. However, once the surface concentration of Eu^{2+} becomes depleted, the surface oxidation reaction becomes resource-limited and the rate decreases. Additional oxidation can occur but is controlled by diffusion processes into the bulk of the phosphor.

If the concentration of reactant species on the phosphor is given by [P] and the concentration of the oxidized species is given by [P*], then the above kinetic process can be expressed mathematically as

$$\frac{d[P*]}{dt} = k[A][P]$$

where k is a constant. Because the concentration of the oxidizing species (i.e., [A]) is very large, it can also be considered a constant and the formation of the oxidized phosphor states (i.e., P*) responsible for the green chromaticity shift will increase until the readily accessible reaction sites drop below a critical level. As the oxidation reaction proceeds, the value of [P] will decline, the formation rate of the oxidized phosphor species eventually becomes resource-limited, and the rate of the green CSM-2 chromaticity shift slows.

After the incubation period, the rate of the green chromaticity shift found in this study remains more or less constant until at least $\Delta u'v' = 0.010$, which is above the typical threshold for a parametric failure for color shift. Prolonged WHTOL tests of LEDs have shown that a green shift can occur at a linear rate for an extended period beyond that observed here and produce chromaticity shifts, as measured by $\Delta u'v'$, well above the allowable maximum value of 0.007 [10, 12]. This process was found to be irreversible indicative of some degradation in the phosphor. In at least one of these studies, the slope of $\Delta u'v'$ slows after extended exposure [12]. This indicates that the reaction is continuing to proceed, albeit at a lower rate, even when significant chromaticity shifts have already occurred.

The kinetic process responsible for the chromaticity shift in DUT-A is analogous to the Deal-Grove kinetic model that is widely used to describe the growth of an oxide on silicon and other materials [17]. The Deal-Grove model consists of three main steps:

a) Diffusion of the oxidizing species from the ambient gas to the surface of the material;
b) Diffusion of the oxidizing species through the existing oxide layer to the interface between the oxidized and unoxidized substrate;
c) Reaction of the oxidizing species with the surface.

The diffusion reaction (step a) is generally fast and does not usually play a role in controlling the reaction rate. The reaction step (step c) occurs rapidly at the surface, especially when the oxidizing species is present in abundance. This reaction occurs at the surface of the oxide-material substrate and proceeds at a linear rate for an extended period. As the oxide layer grows on the surface of the material, the surface reaction sites are consumed and the oxidizing species must diffuse through the oxidized material to reach new reaction sites (step b), slowing the reaction rate. Diffusion of the oxidizing species through the oxide layer depends on $(Dt)^{0.5}$ where D is the Fick's diffusion coefficient and t is time. Hence, the reaction can be shown to exhibit a constant linear rate over a long period followed by a slower reaction rate that depends on the square root of time.

For DUT-A, the oxidation of the rare-Earth doped silicon nitride phosphor increased spectral emissions between 500 nm and 600 nm and decreased emissions above 600 nm. In contrast, the chromaticity shift observed for DUT-B resulted from a decrease in emissions from 500 to 600 nm, but no accompanying increase above 600 nm. From the SPD data presented in Figure 5, we conclude that the red chromaticity shift observed for DUT-B products is due to a reduction in green emission that causes the chromaticity to shift in the red direction. The exact mechanism of this reduction is unknown and likely depends highly on the chemistry of the chosen green phosphor as this type of chromaticity shift is not often observed. From the available data, we infer that the green phosphor used in DUT-B is susceptible to oxygen-induced quenching reactions that lower emissions at these wavelengths and produce the red shift. Although red chromaticity shifts (i.e., CSM-5) are rare, this type of shift has been reported in air for some chip-scale packages [18] and on at least one PAR38 lamp with HP-LEDs [11].

The exposure of the DUT-B devices to 7,000 hours of 75/75 was sufficient to cause a chromaticity shift that exceeds EnergyStar guidance. Consequently, these devices can be considered parametric failures. The red chromaticity shift found in DUT-B exhibited high linearity after the first 2,000 hours until the end of the experiment. Based on this finding, we believe a kinetic reaction similar to that described above may also be responsible for the loss of green emissions and the resulting red chromaticity shift. This reaction involves the transport and adsorption of oxidizing species on the surface of the phosphor. The oxidizing species then react with the lattice and/or the dopant. However, instead of producing a green shift, as found with DUT-A, this reaction partially quenches at least some of the green phosphor emissions producing the net red shift found in DUT-B. This reaction is likely irreversible and also produces degradation of the phosphor.

4. Conclusions

The stability of phosphors used in pcLED devices plays a major role in chromaticity maintenance. Changes in the emission properties of the phosphor can move the chromaticity point in either the green or red directions. At least two major chromaticity shift modes can be attributed to irreversible changes in the phosphors used in pcLED products.

A green shift, termed CSM-2, is produced by the oxidation of a rare-Earth containing silicon nitride phosphor and can be identified by the characteristic shift of the phosphor emission peak to lower wavelengths. This oxidation process occurs spontaneously on the surface of the phosphor and has a major impact on the observed SPD for the LED device. Consequently, the chromaticity point will shift with the value of u' decreasing while the value of v' changes little. For the chromaticity shift range, generally of interest in lighting ($\Delta u'v' \leq 0.007$), this shift occurs at a constant, linear rate. However, at longer operational times, the oxidation reaction becomes resource-limited and the reaction rate slows down. By extrapolating the linear behavior that was demonstrated here for CSM-2, we can project the time required for the LED device to shift by a certain level.

A red shift, termed CSM-5, can be attributed to the quenching of some phosphors, possibly by absorbed oxygen or water, resulting in a net shift of the chromaticity point in the red direction. This process was also found to proceed at a linear rate, which facilitates the projection of the time before an undesired level of chromaticity shift occurs.

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