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Red (SrCa)AlSiN$_3$: Eu^{2+} Nitride Phosphor Particle Size of Phosphor Converted Warm White LEDs

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Abstract

Red (SrCa)AlSiN$_3$: Eu^{2+} nitride phosphor with different particle sizes were characterized based on physical and luminescent properties, then packaged into Chip-On-Board (COB) Warm White Light Emitting Diode (LED) modules to investigate the influence of particle size on packaging parameters and optical output of the COB LED devices. The phosphor particle sizes investigated were 10µm, 12µm and 14µm, and experimental data indicates that the emission spectrum for the red phosphor with bigger particle size is slightly red-shifted compare with the red phosphor with smaller particle size. Besides that, COB LED modules packaged with smaller red phosphor particle required slightly lesser amounts of phosphor to achieve same value of Correlated Color Temperature (CCT) range from 3500K to 3600K, while enhancing the optical output power. The average lumen output and the average efficacy of COB LED devices packaged with 10µm phosphor had an increment of 5.07% and 9.55% respectively while 12µm phosphor had an increment of 5.14% and 9.79% respectively compared to the 14µm phosphor sample.

Keyword: *red nitride phosphor, phosphor particle size, packaging efficiency, light extraction efficacy, LED*

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1. Introduction

White Light Emitting Diode (LED) technology is currently replacing conventional white light sources in lighting applications due to their excellent properties of high luminous efficiencies, customizable spectrum output, low power consumption, good reliability, and long lifetimes [1]. General white LED lighting is categorized based on Correlated Color Temperature (CCT) into three general categories: Cool White (CW), with a CCT range of 2500K-4000K, Neutral White (NW) with a CCT range of 4000K-5000K and Warm White (WW) with a CCT range of 5000K-6500K [2].

Phosphor converted LED (pc-LED) utilizing a wavelength down converting yellow phosphor and blue GaInN/GaN LED chip light source is the most common method used in generating general illumination white light. This method has good conversion efficiencies and is easier to customize and manufacture compared to other methods of generating white light from LEDs [4]. In order to lower CCT values and obtain good Color Rendering Index (CRI) ratings via pc-LED, red phosphor is usually mixed with yellow phosphor to increase the red light spectrum of the generated white light [1, 3].

The optical performance in a pc-WW LED is directly influenced by phosphor conversion efficiency and amount of photon absorption loss inside the package. Emitted light of the pc-LED tends to follow a diffused pattern due to scattering and reflection of light by phosphor particles, with a significant portion of chip light source directed back towards the poorly reflective GaInN/GaN blue LED chip [5]. This significantly affects the Light Extraction Efficiency (LEE) of the pc-LED package and previous studies have reported that approximately 60% of the emitted light can remain trapped inside a poorly designed pc-LED package [6]. An influential factor of back scattering in a pc-LED package is the size of the phosphor particles [7]. LEE can be improved by optimizing the particle sizes of red phosphor. Other than that, the luminescence properties and total amount of red and yellow phosphors required to obtain the desired CCT range output of a pc-WW LED is also significantly influenced by the red phosphor particle size [8].

The first stage of this study investigates the correlation between phosphor luminescent properties and crystalline structure with red phosphor particle size. The physical properties (i.e., surface morphology images) and luminescence properties (i.e., excitation and emission spectra)

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of the red (SrCa)AlSiN3: Eu^{2+} nitride phosphors were experimentally determined. For the second part of this study, phosphor samples with different particle sizes were packaged into similar COB LED packages to examine their packaging efficiency and effects on the optical performance of the COB LED device.

2. Experiment Method

2.1. Red phosphor samples preparation and characterization

The separation of red $(SrCa)AlSiN_3$: Eu^{2+} phosphor particles into different size ranges with uniform size distribution was done through repetitive filtering with different sieve sizes. In this experiment, three red $(SrCa)AlSiN_3$: Eu^{2+} phosphor samples with different particle size distributions were filtered and labeled accordingly as Red-S, where S is the majority particle size within the phosphor sample. Scanning Electron Microscope (SEM) (Hitachi S-450) was employed to obtain the morphology image. The excitation and emission spectra of both phosphor samples were measured by a fluorescence spectrometer (SPEX fluoroMAX-2).

2.2. LED Samples Preparation

Fifteen COB pc-WW LED modules with similar blue LED InGaN semiconductor dice from Epistar Coordinate (peak wavelength 452.5nm; dominant wavelength 451.98nm), substrates and driving circuit configuration were fabricated with five units allocated for each phosphor sample. The total weight, concentration and weight ratio of yellow aluminate phosphor and red $(SrCa)AlSiN_3$: Eu^{2+} phosphor mixture on the LED modules were tuned with epoxy resin to generate warm white emission with the CCT range between 3500K to 3600K.

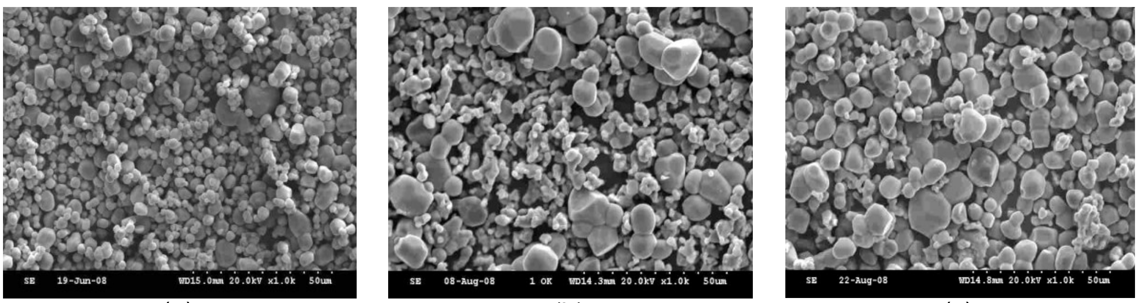
2.3. Optical Properties Measurement

Optical performance parameters of total luminous flux (lm), efficacy (lm/W) and CCT (K) were measured using the Thermal and Radiometric/Photometric Characterization LED (TERALED) system from Mentor Graphics. In this study, the driving current of LED modules was set at 0.7A and all measurements were carried out at room temperature.

3. Results and Discussion

3.1. Red Phosphor Samples Characterization

Figure 2(a), (b), and (c) illustrates the SEM surface morphology images of Red-10µm, Red-12µm and Red-14µm respectively. Variations in particles size were observed. Under the same visual magnification, the phosphor particles of Red-10µm are observed to be the smallest, followed by Red-12µm and Red-14µm.



(a) (b) (c)

Figure 2. SEM images of (a) Red-10µm, (b) Red-12µm and (c) Red-14µm phosphor samples

The excitation spectrum of the red $(SrCa)AlSiN_3$: Eu^{2+} phosphor samples is shown in Figure 3(a). These phosphor samples have a wide excitation band from 300nm to 550nm, which corresponds to the output emission spectrum of blue GaInN/GaN LED from 450nm to 470nm [9]. Figure 3(a) illustrates the excitation spectrum of phosphor samples where Red-10µm sample emits the highest excitation output intensity, followed by Red-12μm and Red-14μm samples. Figure 3(b) shows the emission spectrum of the phosphor samples at 455nm excitation. The peak emission wavelength of Red-10μm, Red-12μm, Red-14μm samples were 620nm, 624nm, and 629nm respectively. This comparison indicates samples with bigger phosphor particles tend to red shift their output spectrum.

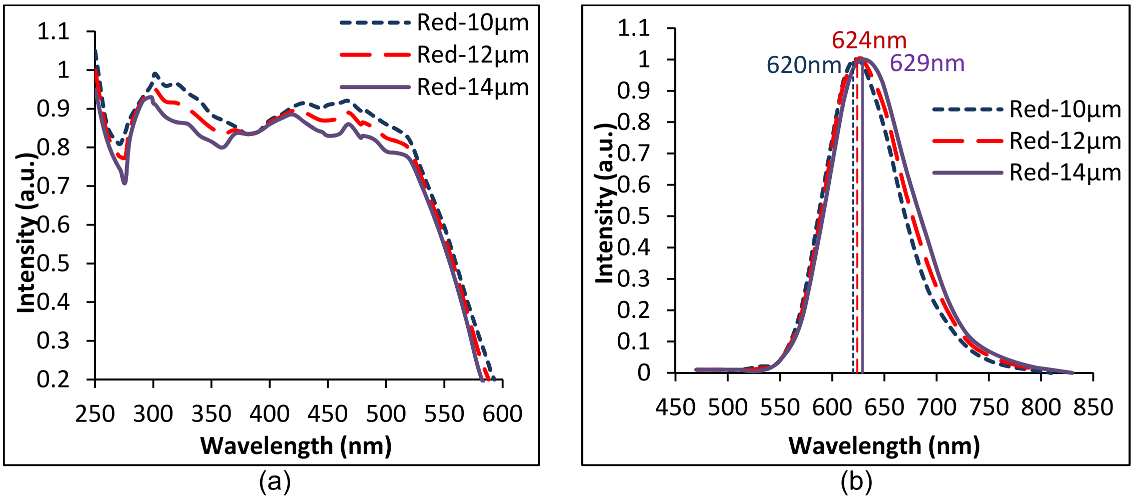


Figure 3. (a) Excitation spectrum and (b) Emission spectrum of Red-10μm and Red-12μm

The luminescent properties of red nitride (SrCa)AlSiN$_3$: Eu^{2+} phosphor is attributed to the electron transition between *4f^7* ground state to *4f^{6}5d^1* excited state of the free Eu^{2+} ion, as shown by the schematic illustration of a configurational coordinate model in Figure 4(a) [10]. The labelled black curves represent the energy level of the *4f^7* ground state and the *4f^{6}5d^1* excited state. The equilibrium positions of the two states are differ from each other because of the spatial distribution of the electron orbitals. The arrow from A to B indicates the excitation or optical absorption of blue (or violet) light, facilitating the transition from the *4f^7* configuration to the *4f^{6}5d^1* configuration. This inherent property of phosphor is shown by the broad excitation band from UV to blue region in Figure 3(a). Non-radiative relaxation then occurs from the position B to the equilibrium position C, followed by red light emission in the range of 600nm to 610nm from position C to D. Finally another non-radiative relaxation returns the electron from position D to A and ideally the cycle will repeat until the LED die source stops the emission of blue light for Eu^{2+} ion excitation [11].

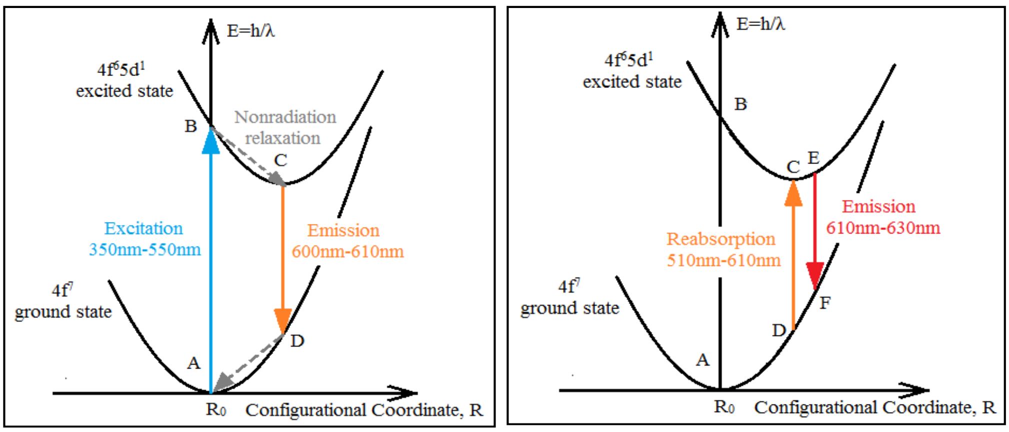


Figure 4. Schematic Illustration of (a) configurational coordinate model for excitation by blue light and (b) configurational coordinate model for the path from the re-absorption of the light

However, a number of electrons in ground state remain at D without falling back to A, due to the ambient thermal energy. Optical re-absorption can boost electrons from position D to C with a certain probability due to the wide absorption bandwitdth of phosphor**.** Figure 4(b) shows the schematic illustration of a configurational coordinate model for the energy level path for the re-absorption and emission of light by phosphor particles under the influence of thermal energy. The electrons at energy level C are excited from position D via photon re-absorption, and promoted to position E by thermal energy influences. The emission wavelength released from relaxation of level E to F is longer than relaxation from C to D as the differences between the energy levels is smaller; a photon with less energy is released and the cause the emission light red-shifted [11]. LED modules packaged with bigger red phosphor sample which causing more backscattering or trapping of light have higher probability of photon re-absorption in postion D [12]. Therefore, the light emitted by the LED modules packaged with bigger red phosphor sample has longer wavelength and more shifted to the red color. This explains the red-shift phenomenom occurred for bigger red phosphor sample as shown in Figure 3(b).

3.2. LED Samples Optical Properties

Table 1. LED Modules Packaging Parameter for Red-10μm, Red-12μm and Red-14μm

Packaging parameter	Red-10μm	Red-12μm	Red-14μm
Weight ratio Red-S phosphor : Yellow phosphor	1.2 : 1.0	1.7 : 1.0	2.0 : 1.0
Total phosphor weight	0.0940g	0.0950g	0.0960g
Phosphor concentration	8.5% phosphor 91.5% epoxy resin	8.5% phosphor 91.5% epoxy resin	8.5% phosphor 91.5% epoxy resin

The three of phosphor samples were packaged into fifteen LED modules according to the packaging parameter as tabulated in Table 1. To attain CCT range from 3500K to 3600K, the weight ratio of Red-10μm sample used is 1.2 times higher than the weight of yellow phosphor, while the Red-12μm and Red-14μm samples used were 1.7 and 2 times higher than the weight of yellow phosphor respectively. The total weight of Red 10μm sample and yellow phosphor required for phosphor packaging were 0.0010g lesser than the total weight of Red-12μm sample and yellow phosphor, and 0.0020g lesser than the total weight of Red-14μm sample and yellow phosphor. This indicates that red phosphor with finer particle size sample allows the usage of less phosphor while still achieving the required CCT ranges for a pc-WW LED package. This information is valuable for white pc-LED manufactures to reduce manufacturing costs by reducing phosphor amount used.

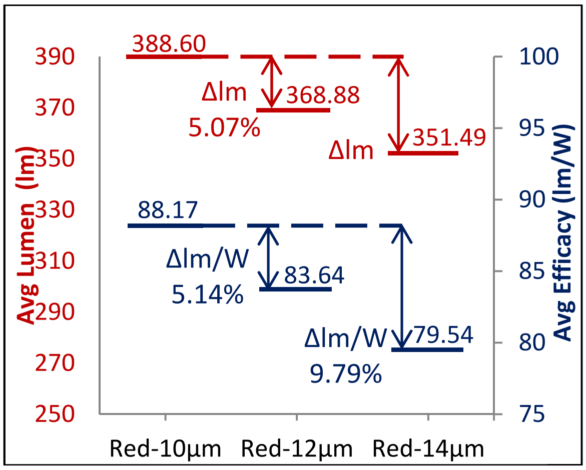


Figure 5. Optical Performance of LED Modules Packaged with Red-10μm, Red-12μm and Red-14μm

Figure 5 displays the measured optical performance of the fifteen COB LED modules installed with Red-10μm, Red-12μm and Red-14μm phosphor samples. The measured lumen outputs of these LED modules which driven at 0.7A direct current are 388.60lm for Red-10μm sample, 368.88lm for Red-12μm sample and 351.49lm for Red-14μm sample. Percentage calculations show that the Red-10μm sample is 5.07% and 9.55% higher than LED modules packaged with Red-12μm and Red-14μm samples respectively. The measurements also shows that the LED modules packaged with Red-10μm sample had the highest efficacy value at 88.17lm/W, while LED packaged with Red-12μm and Red-140μm samples were measured to be 83.64lm/W and 79.54lm/W, which is 5.14% and 9.79% lower than the efficacy value of Red-10μm sample. From these results, we conclude that a pc-WW LED packaged with finer red phosphor sample has a better LEE to generate WW light with higher brightness and efficacy.

Based on the Mie scattering theory, angular distribution and intensity distribution of light scattered by phosphor particles significantly depends on phosphor particles size. Mie scattering describes the elastic scattering of light by spheres with relative scattering particle size, $\alpha \geq 1$, where α is the ratio of particle size to wavelength of the incident light [13]. Red phosphor sample with bigger particle size have more backscattered light in a spread out pattern due to a larger surface area. This increases the trapping efficiency of COB LED modules the as more photons are either trapped or directed back towards the LED chip and reflector as shown in Figure 6 [12]. Besides that, these back-transmitted light may also recirculate between the phosphor and the reflector of the LED, causing the region where light circulate to have a relatively higher temperature [5]. High operating temperatures in LED devices not only accelerates the epoxy degradation, it also affects LEE of the COB LED modules.

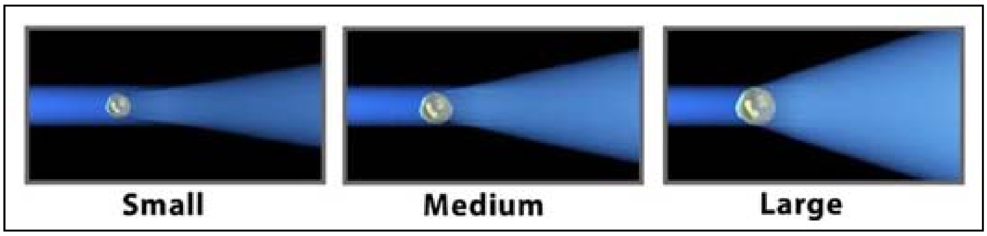


Figure 6. Scattering of Excitation Blue Light by a Small Size, Medium Size and Large Size Particle [14]

Apart from providing a less obstructive pathway for blue excitation light to radiate outwards, smaller phosphor samples also provide a higher surface to volume ratio for better light absorption and wavelength conversion in a phosphor layer. Therefore, the intensity of light emitted from a device with smaller phosphor particles is higher as observed in Figure 3(a)**,** allowing smaller phosphor sizes to obtain the same optical performance with less total amount of phosphor.

4. Conclusion

Red (SrCa)$AlSiN_3$: Eu^{2+} nitride phosphor with different particle sizes were characterized in terms of physical and luminescent properties. The effect of red phosphor particle sizes on light extraction efficiency and cost efficacy of COB LED modules packaged were also investigated in this paper. Measurements indicate that the emission spectrum of bigger phosphor sample was red shifted compared to smaller phosphor sample. Packaging efficiency for smaller phosphor particle sample in COB LED modules were also enhanced by the decrease of total phosphor weight. The average lumen output and the average efficacy of COB LED modules packaged with 10μm phosphor had an increment of 5.07% and 9.55% respectively while 12μm phosphor had an increment of 5.14% and 9.79% respectively compare with 14 μm phosphor. This is due to less back-scattering and absorption loss of the light within the LED package. This study concludes that the efficacy of a COB LED module was enhanced with the decrease of phosphor particle size.

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