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$SrSi_2O_2N_2:Eu^{2+}$ green emitting phosphor and the effects on the lighting performance for high-quality WLEDs

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$SrSi_2O_2N_2:Eu^{2+}$ phosphor, with green emission, broad excitation band, and great stability against temperature changing, is prepared and used for improving the optical performances of white light. The concentration of this green phosphor is adjusted to analyze the effects on color quality and luminous power. In some cases, the particle size of the phosphor is also taken into consideration. Results demonstrates that low concentration and the large particle size of $SrSi_2O_2N_2:Eu^{2+}$ could be used for WLEDs requiring high flux at low CCT of 3000 K. Meanwhile, to achieve high flux for WLED having CCT ≥ 4000 K, the greater concentration and small particle size seem to be better choices. The color uniformity is in the same trend as the WLED luminescence power, low CCT favors low $SrSi_2O_2N_2:Eu^{2+}$ concentration, while higher CCTs prefer higher concentration. The color rendering characteristics show enhancement with smaller amount of $SrSi_2O_2N_2:Eu^{2+}$ (5 wt%) accompanied by bigger particle size, regardless of CCTs. The $SrSi_2O_2N_2:Eu^{2+}$ can be a potential luminescent phosphor for WLED development, and its size and concentration must be chosen appropriately.

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Keywords: Green phosphor, $SrSi_2O_2N_2:Eu^{2+}$, Luminescence power, Color indices

1. Introduction

In order to widen the application scale of white light emitting diodes using down-conversion phosphor materials (PCWLED), figuring out the desirable phosphor has been in high demand [1-3]. The currently using phosphor $YAG:Ce^{3+}$ can yield high luminescence power for WLED, yet the color uniformity is not sufficient as essential green and red components are absent [4-6]. Thus, combining the green or red phosphor with the yellow phosphor could promote wide-band mixing color to the white light emission and, as a result, may satisfy the color quality at an adequate level.

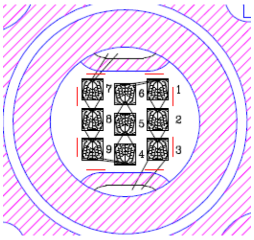
The phosphor that is regarded as good a conversion phosphor type should have broad excitation band to cover the near-UV or blue light wavelength (from ~380 nm to ~470 nm) to effectively absorb lights from LED chips and emit them in visible wavelength band [7-9]. Additionally, it is desirable for the phosphor to has emission in a part of red region, so that the color rendering could be benefitted [10-15]. Considering these points, the oxynitrides phosphor type could be a good choice to become the host matrix for doping rare-earth ion, contributing to getting the broadband excitation of the phosphor [16]. The ion Eu^{2+} has been investigated and reported to be an excellent ion in terms of broadband emission that can shift to red region, depending on the host matrix [17-19].

The green emitting oxynitride phosphor, $SrSi_2O_2N_2:Eu^{2+}$, is used this paper for the investigation on lighting-efficiency enhancement of WLED packages [20-22]. The selected green phosphor presents wide excitation band, good color consistency and thermal stability, making it an appropriate phosphor type for solid state lighting solution. The influences of this oxynitride green phosphor are examined via the performances of color uniformity and rendering factors, along with the luminous intensity [23]. The color concentration of the phosphor plays the key role in those examination. In some cases, the particle size of the used phosphor is investigated [24]. The study recognizes that the optical features of the WLED are dependent on not only the concentration but also the particle size of the phosphor as well as the preset color correlated temperature (CCT) of the WLED. Suggestions on determining suitable doping amount and particle size of $SrSi_2O_2N_2:Eu^{2+}$ phosphor to optimize certain lighting properties are also included in the discussion part of the paper.

2. Preparation of the phosphor and WLED package

To synthesize desired green phosphor $SrSi_2O_2N_2:Eu^{2+}$, a two-step solid state reacting process is applied. The raw chemical ingredients of the phosphor composition include $SrCO_3$, SiO_2, α-Si_3N_4, and Eu_2O_3, all of which having the purity percentage of $\geq$ 99.9%. The first step of the synthetic process consists of well mixing $SrCO_3$, SiO_2, and Eu_2O_3, and then heating the mixture at 1250 ^oC for 3h under the reducing atmospheric condition [25-27]. The attained product is $Sr_2SiO_4:Eu^{2+}$. Subsequently, in the second step, α-Si_3N_4 is blended with $Sr_2SiO_4:Eu^{2+}$ and followingly fired for 6h in the same atmospheric environment. The temperature for the second heating process is set at 1450 ^{o}C. As soon as the heating time is over, the product of $SrSi_2O_2N_2:Eu^{2+}$ is obtained.

The WLED used in this study is produced with blue chip (460 nm), $YAG:Ce^{3+}$ phosphor, and $SrSi_2O_2N_2:Eu^{2+}$ phosphor. The structural illustrations for the WLED package are shown in Fig. 1. The LED chips were wire bonded and fixed to the lead frame, see Fig. 1 (a). The phosphor layers were formed by mixing the phosphor powders with silicone resin and curing at 150 ^{o}C for 1.5 hours. These phosphor films were placed above the LED chip with an arrangement demonstrated in Fig. 1 (b). The $YAG:Ce^{3+}$ is the closest layer to the chip surface. The 3D simulation of the fabricated WLED package was created with the LightTools software, as shown in Fig. 1 (c).



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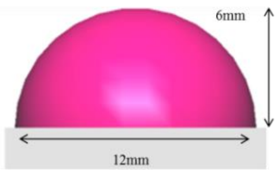

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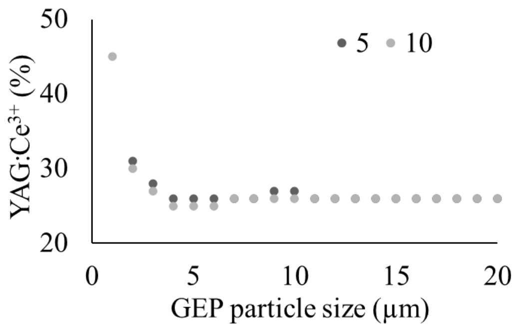
Fig. 1. WLED structural illustration: (a) LED chip packet; (b) cross-section of the LED package; (c) 3D simulation model (color online)

3. Results and discussion

When adding the green phosphor $SrSi_2O_2N_2:Eu^{2+}$ to the phosphor layer, the change in concentration of the yellow phosphor can be observed in Fig. 2. Particularly, Fig. 2 (a), (b), and (c) describes this change in WLED configurations having the CCTs of 3000 K, 4000 K, and 5000 K, respectively. At all CCTs, comparing the $YAG:Ce^{3+}$ concentration when green phosphor (GEP) $SrSi_2O_2N_2:Eu^{2+}$ concentrations are at 5 wt% and 10 wt%, it shows that the higher GEP concentration (10 wt%) results in the lower $YAG:Ce^{3+}$ concentration. In other words, the increase in $SrSi_2O_2N_2:Eu^{2+}$ dosage induces the decrease in $YAG:Ce^{3+}$ amount. This reduced concentration of yellow phosphor $YAG:Ce^{3+}$ has significant impacts on the lighting properties of the WLED. It contributes to maintaining the CCT values and performing better scattering pattern while limiting the backscattering and light trapping effects. Thus, the color conversion and light transmission in the WLED could gradually increase.



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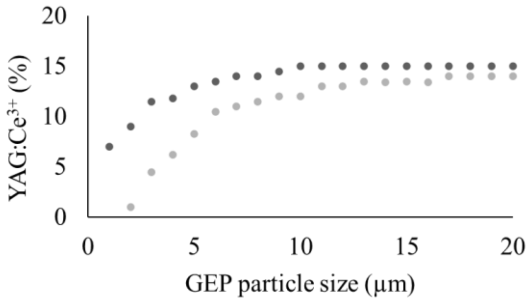

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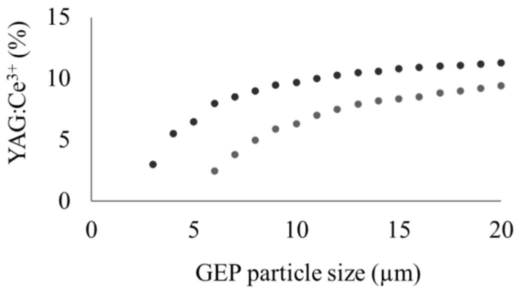

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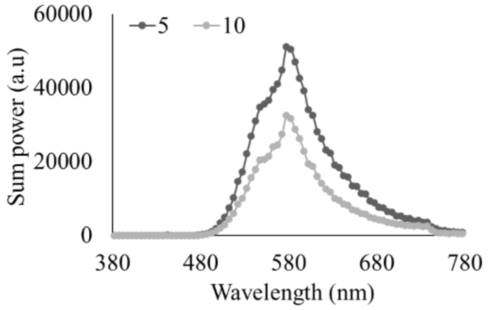
Fig. 2. Changing the concentration of phosphor to preserve the average CCT: (a) 3000 K; (b) 4000 K; (c) 5000 K

The emission power of the WLED could get certain benefits from the addition of the $SrSi_2O_2N_2:Eu^{2+}$ phosphor, as depicted in Fig. 3. The most noticeable effect is the enhanced green emission spectra at all three CCTs of the WLED. Moreover, when the CCT > 3000 K, the blue emission is stimulated by the green phosphor, see Fig. 3 (b) and (c). The increase in two blue and green wavelength regions implies the improved conversion and transmission efficiencies of the blue light from the LED chips. The enhancement of the green emission also the provides essential green-light proportion for color blending procedure, resulting in a more uniform color performance. From these results, the utilization of $SrSi_2O_2N_2:Eu^{2+}$ green phosphor is expected to yield enhancement in both color properties and luminous intensity of the total WLED package.



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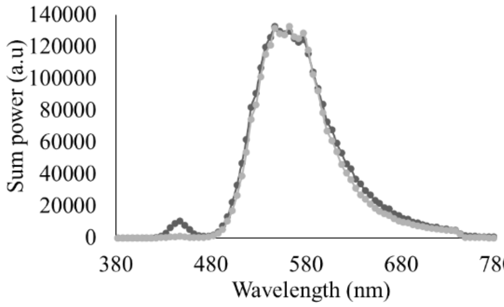

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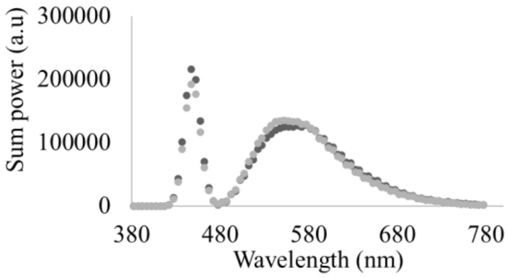
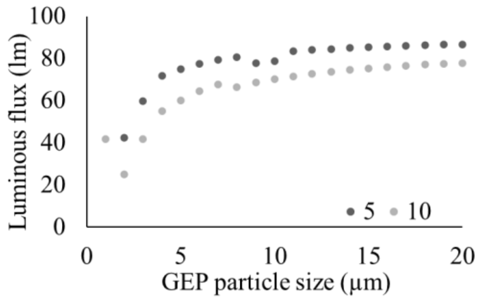


(c)

Fig. 3. The emission power of WLEDs with the adjusted concentration of $SrSi_2O_2N_2:Eu^{2+}$: (a) 3000 K; (b) 4000 K; (c) 5000 K

The luminous flux (LF) of the WLED applying green phosphor $SrSi_2O_2N_2:Eu^{2+}$ is presented in Fig. 4, in which the GEP's concentration and particle size and the package's CCT values all have influences on the performance of LF. Generally, at the lowest predetermined CCT (3000 K), it requires lower amount of the GEP to yield stronger LF than at higher predetermined CCTs (4000 K and 5000 K). Meanwhile, the LF increases with larger GEP particle size at 3000 K and 4000 K but decreases as the CCT increases to 5000 K. The scattering and CCT factors that depend on the concentration and particle size of the phosphor could be the reasons for this LF performance. The higher concentration of the phosphor results in more significant scattering pattern and narrower spatial distribution between the phosphor particles. Therefore, the light will be scattered more and then backscattered along the LED surfaces and eventually absorbed by the chips. Consequently, the emission energy loss is initiated by this re-absorption phenomenon, causing the light output to be degraded. On the other hand, the larger size of the phosphor particle is more beneficial to the LF than the smaller particle as it limits the backscattered lights to reduce the loss by re-absorption. In addition, the increasing size of phosphor particles also shorten the distance between the phosphor grains. Besides, high CCT usually needs higher phosphor concentration to get sufficient scattering events for light generation. Thus, large particle size and lower amount of the green phosphor could be ideal for the LF enhancement at low CCT. In contrast, at high CCT, high phosphor concentration should be used in company with small particle size to avoid a large amount of light loss by backscattering and reabsorption.



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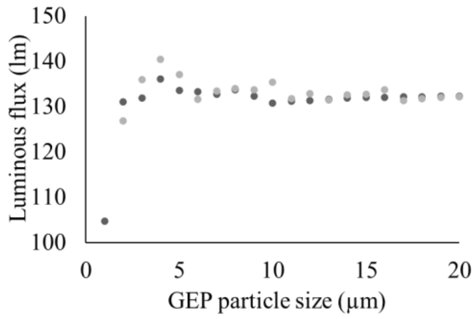

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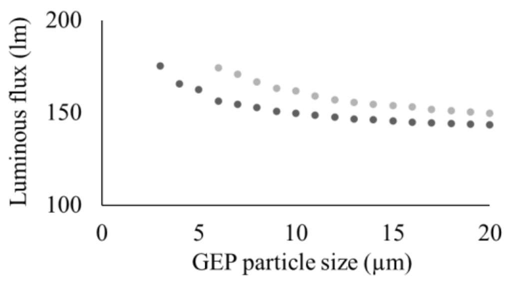

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Fig. 4. The luminescence intensity of WLEDs with the adjusted concentration of $SrSi_2O_2N_2:Eu^{2+}$: (a) 3000 K; (b) 4000 K; (c) 5000 K

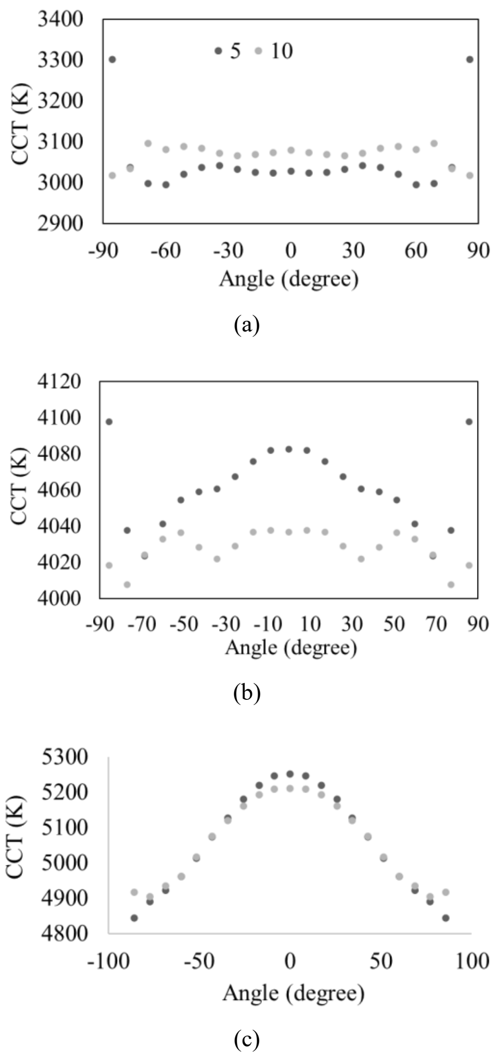


Fig. 5. The CCT of WLEDs with the adjusted concentration of $SrSi_2O_2N_2:Eu^{2+}$: (a) 3000 K; (b) 4000 K; (c) 5000 K

The light scattering enhancement is significantly advantageous to the color distribution of white light or the color consistency of white light output. Referring Fig. 5, the larger amount of $SrSi_2O_2N_2:Eu^{2+}$ offers better consistence of the angular color temperature (ACT) property. The ACT of the 3000-K WLED package seems to be favored by the low concentration of green phosphor (5 wt%), in Fig. 5 (a). For the greater predetermined CCTs, the greater $SrSi_2O_2N_2:Eu^{2+}$ concentration is required to suppress the CCT variation. As demonstrated, higher CCT needs higher concentration of phosphor concentration to present more efficient scattering events. More lights scattered will leads to more lights scattered backward and blended before escaping from the LED. These improved features of light propagation process lead to less differences among color wavelength, in other words, more uniform color distribution in the white-light emission. Moreover, the higher concentration of green phosphor stimulates the LF when the CCT > 3000 K, as discussed. Using $SrSi_2O_2N_2:Eu^{2+}$ with high concentration, therefore, could manage to get strong LF and adequate spatial chromatic uniformity of white light emission.

The color reproduction efficiency is another factor required for the high-performance WLED devices. Assessing the color rendering properties could be useful to the determine the color reproducing quality of the white light. The color quality scale and color rendering index, abbreviated as CQS and CRI, respectively, have been the popular parameters for this type of assessment. The CRI, however, has been realized to give inaccurate evaluating results because it allows the light source that is either blue-spectral dominant or red-spectral dominant to exhibit high value. This means these high-CRI light sources perform low color uniformity and may discomfort the human eyes. Then, the CQS has been introduced to improve the disadvantages of CRI. It is proved to be more powerful than the CRI due to the larger amount of color samples for chromatic reproduction and more assessing elements. The CQS assigns the CRI, the coordination of color gamut, and the preference of human eyes to evaluate the color reproducing accuracy. Hence, it could be more desirable to have a light source with intense LF and good CQS.

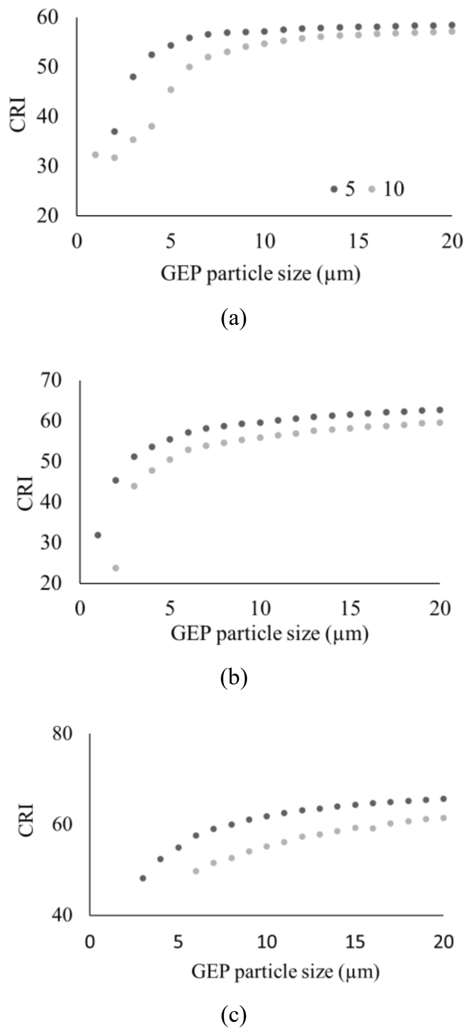
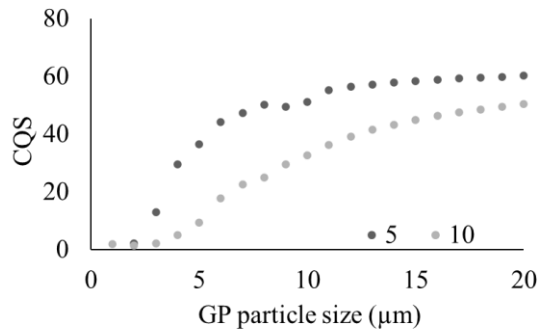


Fig. 6. The CRIs of WLEDs with the adjusted concentration of $SrSi_2O_2N_2:Eu^{2+}$: (a) 3000 K; (b) 4000 K; (c) 5000 K



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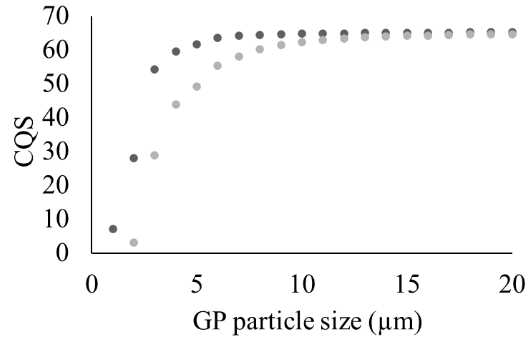

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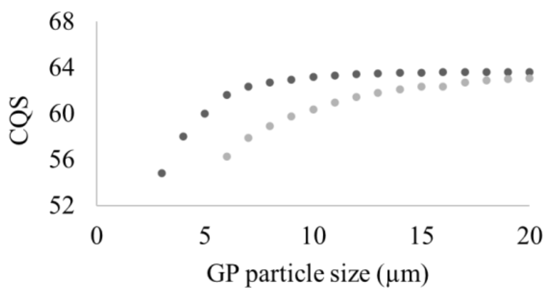

(c)

Fig. 7. The values of CQS of WLEDs with the adjusted concentration of $SrSi_2O_2N_2:Eu^{2+}$: (a) 3000 K; (b) 4000 K; (c) 5000 K

The CRI and CQS results with different concentrations and particle sizes of green phosphor $SrSi_2O_2N_2:Eu^{2+}$ are presented in Figs. 6 and 7, respectively. Overall, the smaller amount and bigger particle size of the green phosphor are advantageous to both CRI and CQS. The highest CRI and CQS of WLEDs with 5wt% of $SrSi_2O_2N_2:Eu^{2+}$ are realized in the range of 60 – 65, which could be sufficient for general lighting applications. The scattering events inside the WLED along with the $SrSi_2O_2N_2:Eu^{2+}$ addition can demonstrate the observed results. The green phosphor when added to the phosphor layer probably reduces the yellow phosphor concentration and improves the scattering efficiency. Hence, the yellow and blue lights scatter more and are absorbed by the phosphor after being scattered backward to the chips. Note that the green phosphor absorbs more blue light than yellow light, therefore, the blue light conversion to green light is more considerable than the yellow one. Then, the essential green component is provided to produce white light. This is why having the green phosphor in the package could improve the CRI and CQS. As the concentration of $SrSi_2O_2N_2:Eu^{2+}$ increases to 10wt%, the color rendering factors decrease because the scattering events are redundant. As a result, the produced green light amount becomes excessive, causing the light to move to the greenish area. The redundant scattering is also resulted from the small particle size as greater phosphor concentration should be applied to initiate good scattering of lights. Hence, the green $SrSi_2O_2N_2:Eu^{2+}$ phosphor is potential for WLED lighting improvements, but it requires careful selection of concentration and particle size regarding the CCT values. Also, it essential to realize that good color consistency and color rendition might slightly lower the intensity of luminous flux, and the priority of optical properties should be determined depending on which field the WLED is applied.

4. Conclusions

In this study, the phosphor material with green emission $SrSi_2O_2N_2:Eu^{2+}$ is applied in the phosphor package of WLED model. The application of this green phosphor is to investigate the improvement in lighting performance of the white light. The results display that the green phosphor have certain influences on the color properties and luminous flux of the WLED. It also exhibits the connection between the white-light characteristics and the concentration and particle size of $SrSi_2O_2N_2:Eu^{2+}$. The presence of $SrSi_2O_2N_2:Eu^{2+}$ green phosphor encourages the scattered lights to increase the efficiency in color conversion and light output. The low concentration and increasing particle size can yield better color rendition (CRI and CQS) and stronger flux of white light emission. This is because the scattering pattern is sufficient for light color mixing, light absorption and conversion. Meanwhile, larger surface of the phosphor particle allows the light to easily transmit through the phosphor layer and then escape from the WLED. When heightening the $SrSi_2O_2N_2:Eu^{2+}$ concentration, the scattering is too much, leading to the imbalance in color reproduction as the green light is excessive. The significant color uniformity could be attained with higher the concentration of $SrSi_2O_2N_2:Eu^{2+}$, in the case of CCT > 3000 K. With the WLED having CCT of 3000 K, smaller amount of green phosphor is required to reduce the color variations. Referring the collected findings, the green phosphor $SrSi_2O_2N_2:Eu^{2+}$ can be a promising material for WLED production and development if its concentration and the particle size are appropriately utilized, after considering the CCT values for the prepared WLED.

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