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Co-DOPING GREEN-EMITTING $CaF_2:Ce^{3+},Tb^{3+}$ AND YELLOW-EMITTING PHOSPHOR PARTICLES FOR IMPROVING THE CCT DEVIATION AND LUMINOUS EFFICACY OF THE IN-CUP PHOSPHOR PACKAGING WLEDs

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In last few decades, Light emitting diodes (LEDs) with a series of excellence advantages is considered as the next generational light source. In this research, by co-doping the Green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor to yellow-emitting YAG:Ce phosphor compound of the 7000K and 8500 K in-cup packaging white LED lamps (WLEDs), an innovative solution for improving color uniformity and luminous efficiency is proposed, investigated, and demonstrated. By using Mie Theory with Mat Lab and Light Tool software, the obtained results show that the CCT Deviation and luminous efficacy of the 7000 K and 8500 K in-cup phosphor packaging WLEDs crucial are influenced by the Green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration. The results show that the green-emitting phosphor can beconsider as a potential practical solution for manufacturing the in-cup packaging phosphor WLEDs in the near future.

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1. Introduction

Light-emitting diodes (LEDs) is the modest type of solid-state lighting, which have the greatest advancement in the lighting industry in the last few decades [1–3]. LEDs is a solid-state light source which emits white light based on a blue die covered by the yellow or green-red phosphor. Such a light source has been intensively applied to general lighting and replaced most light sources in general lighting and even in special lighting (automobiles, transportation, communication, imaging, agriculture, and medicine) owing to its many advantages [4,5]. Generally, LEDs have the following advantages such as energy saving compared to other light sources, long lifetime (over 50,000 hours or more in theory), environment-friendly characteristics, wide range color temperatures (4500 K–12,000 K), wide operation temperature (−20 °C to 85 °C), and quick startup. From this point of view, LEDs have been considered as the fourth generation of light sources shortly [1-4]. Nowadays, the LEDs industry chain has three main categories: the upstream, the midstream, and the downstream. The upstream is the emitting layer, cladding layer, buffer layer, and reflector. The midstream is referred to as packaging. The downstream is connected with the product application in general purpose. In the midstream LEDs industry, the blue light from the blue LEDs chip should be convert into white light by packaging. Here, the LEDs packaging are considered as an essential step from LED chip to applications. Packaging not only can ensure better performanceof LED devices by enhancing reliability and optical characteristics but can also realize control and adjustment of the final optical performance [6-9]. There are many studies concentrate on improving the color uniformity, and the luminous efficacy of White LED lamps (WLEDs) by controlling the packaging process. In [10,11] the lighting properties of LEDs were significantly improved by using phosphors $Sr_1\text{-}xBaxSi_2O_2N_2:Eu^{2+}$(0x1)

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and by using β-SiAlON:Yb^{2+} phosphor. [9], or by varying phosphor materials and packaging structures[10], or by Red-Emitting Phosphor Li_2SrSiO_4:Eu^{3+}, Sm^{3+} [11], or by adding SiO_2 [12,13] to YAG:Ce phosphor compound of W-LEDs. The studies show the effect of method packaging and materials to the lighting performance of W-LEDs. From this point of view, research about the LEDs packaging and its materials is the important direction in LEDs industry.

Hollow micro-and nanostructures with their unique properties such as low density, high surface-to-volume ratio, low coefficients of thermal expansion, and low refractive index, have been applied in drug-delivery carriers, efficient catalysis, sensors, active-material encapsulation, photonic crystals, and so on [6,7]. Microstructure solid fluoride materials based on their properties (low-energy phonons, high ionicity, electron-acceptor behavior, high resistivity, and anionic conductivity) are used as potential optical applications. Among them, calcium fluoride (CaF_2) with low refractive index and the wide band gap is widely applied in optoelectronic devices. Moreover, the calcium fluoride (CaF_2) is well-known as the host for luminescent ions (Ce^{3+} and Tb^{3+}) due to its high transparency in a broad wavelength range, low refractive index, and low phonon energy as shown in Fig. 14 [8,9]. With significant advantages, green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor could be considered as a prospective approach in WLEDs lighting [10]. Nevertheless, there have not been many studies, which demonstrated green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor for enhancing the luminous flux and color quantity of the in-cup packaging WLEDs as yet. This research could fill a remaining gap.

For reaching the proposed problem, the paper can be divided into 3 main sections. In the first section, the physical model of the in-cup packaging WLEDs is built by the commercial software Light Tools 8.4, and the mathematical description of scattering, backscattering and reduced scattering process in the phosphor layer is presented. The second section investigated the influence of the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor' concentration on the correlated color temperature deviation (D-CCT) and the lumen output of the in-cup packaging WLEDs by the Mat lab and Light Tools software. Finally, some discussions and conclusions are proposed based on the research results. The research results showed that the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particle's concentration significantly influenced on the optical properties of the 7000K and 8500K in-cup packaging WLEDs.

2. Physical Model WLEDs and Mathematical Description

2.1. Physical Model WLEDs

To demonstrate the influence of the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor' concentration on the correlated color temperature deviation (D-CCT) and the lumen output of the in-cup packaging WLEDs, the physical model is necessary to build by Light Tools. In this section, the in-cup packaging 7000 K, 8500 K WLEDs is simulated by using the commercial Light Tools software based on the Monte Carlo ray-tracing method (Fig. 1). In this physical model of WLEDs, key parameters of the in-cup packaging WLEDs are defined as below:

1) The reflector: 8 mm bottom length, a 2.07 mm height, and a 9.85 mm length.

2) The in-cup phosphor layer: thickness of 0.08 mm covers the 9 LED chips.

3) The LED chip: 1.14 mm square base and a 0.15 mm height. The radiant flux of each blue chip is 1.16 W at wavelength 455 nm.

In this simulation, the concentration of the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particle was changed continuously from 0% to 1.8%. The optical properties of the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particles are details built by using the Light Tools 8.4 software. The refractive index of the green-emitting and yellow-emitting phosphors are set at 1.80 and 1.83, respectively. The average radius of the phosphor particles is 7.25 μm, and the refractive index of the silicone glue was chosen 1.5. The diffusional particle density is varied to fix the average CCT value. If the weight percentage of the diffusers is increased, the weight percentage of YAG:Ce phosphor is necessary to reduce to maintain the average CCT value 7000K and 8500 K.

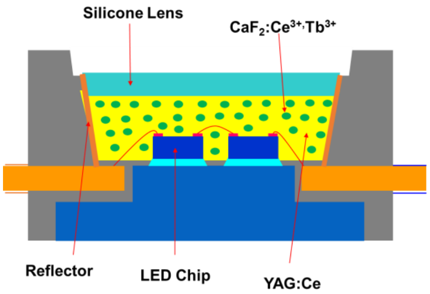

Fig. 1. The in-cup packaging WLEDs physical structure

2.2. Mathematical Description of Scattering Process

For more understanding the scattering process of the phosphor layer, the mathematical description is necessary to propose and demonstrate. In this section, applying Mie theory [21], the coefficients of the scattering process of the phosphor layer of the in-cup packaging WLEDs can be calculated as the below expressions:

1. The scattering coefficient $\mu_{sca}(\lambda)$:

$$\mu_{sca}(\lambda) = \int N(r) C_{sca}(\lambda, r) dr \tag{1}$$

Where $N(r)$ (mm^3) is the distribution densityof diffusional particles. $N(r)$ is composed of the diffusive particle number density $N_{dif}(r)$ and the phosphor particle number density $N_{phos}(r)$ can be presented as:

$$N(r) = N_{dif}(r) + N_{phos}(r) = K_N.[f_{dif}(r) + f_{phos}(r)] \tag{2}$$

Moreover, C_{sca} (mm^2) is the scattering cross sections. In Mie theory, C_{sca} can be obtained by the following expression:

$$C_{sca} = \frac{2\pi}{k^2} \sum_{0}^{\infty} (2n-1)(|a_n|^2 + |b_n|^2) \tag{3}$$

Here λ (nm) is the light wavelength, and r (µm) is the radius of diffusional particles.

2. The anisotropy factor $g(\lambda)$,

$$g(\lambda) = 2\pi \int \int_{-1}^{1} p(\theta, \lambda, r) f(r) \cos\theta d \cos\theta dr \tag{4}$$

Where $p(\theta,\lambda,r)$ is the phase function,

$f(r))$ is the size distribution function of the diffuser in the phosphor layer,

θ (°) is the scattering angle.

3. The reduced scattering coefficient $\delta_{sca}(\lambda)$:

$$\delta_{sca} = \mu_{sca}(1-g) \tag{5}$$

In these equations, $f(r)$ and $N(r)$ can be calculated by:

$$f(r) = f_{dif}(r) + f_{phos}(r) \tag{6}$$

Where $f_{dif}(r)$ and $f_{phos}(r)$ are the size distribution function data of the diffusor and phosphor particle. Here K_N is the number of the unit diffusor for one diffuser concentration and can be calculated by the following equation:

$$c = K_N \int M(r)dr \tag{7}$$

Where *M(r) is* the mass distribution of the unit diffuser and can be proposed by the below equation:

$$M(r) = \frac{4}{3}\pi r^3 [\rho_{dif} f_{dif}(r) + \rho_{phos} f_{phos}(r)] \tag{8}$$

Here $\rho_{diff}(r)$ and $\rho_{phos}(r)$ are the density of diffuser and phosphor crystal.
Where $k = 2\pi/\lambda$, and a_n and b_n are calculated by:

$$a_n(x,m) = \frac{\psi_n^{'}(mx)\psi_n(x) - \mathrm{m}\psi_n(mx)\psi_n^{'}(x)}{\psi_n^{'}(mx)\xi_n(x) - \mathrm{m}\psi_n(mx)\xi_n^{'}(x)} \tag{9}$$

$$b_n(x,m) = \frac{m\psi_n^{'}(mx)\psi_n(x) - \psi_n(mx)\psi_n^{'}(x)}{m\psi_n^{'}(mx)\xi_n(x) - \psi_n(mx)\xi_n^{'}(x)} \tag{10}$$

Where $x = k.r$, m is the refractive index, and $\psi_n(x)$ and $\xi_n(x)$ are the Riccati - Bessel function.
The below equation can express the phase function:

$$p(\theta,\lambda,r) = \frac{4\pi\beta(\theta,\lambda,r)}{k^2 C_{sca}(\lambda,r)} \tag{11}$$

Where $\beta(\theta,\lambda,r)$, $S_1(\theta)$ and $S_2(\theta)$ are calculated by below equations:

$$\beta(\theta,\lambda,r) = \frac{1}{2}[|S_1(\theta)|^2 + |S_2(\theta)|^2] \tag{12}$$

$$S_1 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \begin{bmatrix} a_n(x,m)\pi_n(\cos\theta) \\ +b_n(x,m)\tau_n(\cos\theta) \end{bmatrix} \tag{13}$$

$$S_2 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \begin{bmatrix} a_n(x,m)\tau_n(\cos\theta) \\ +b_n(x,m)\pi_n(\cos\theta) \end{bmatrix} \tag{14}$$

In equations (13) and (14), π_n and τ_n are the angular dependent functions [17-23].

3. Results and discussion

In Fig. 2, the scattering coefficient of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor at wavelengths of 453nm, 555nm crucial grew with increasing the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration. It means that the white-light quality can be enhanced by controlling the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor particle's concentration. The green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor has a great absorption ability for the blue light from LED. On the another hand, the reduced scattering coefficient of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor at wavelengths 453nm, 555nm are the same with each other in depending on the concentration (Fig 3). Itindicated that the scattering stability of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor showed the great uses for controlling the color quality of the in-cup packaging WLEDs. Fig. 5 showed the influence of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration on the angular scattering amplitudes of the in-cup packaging WLEDs at wavelengths 453nm, 555nm. From the figure, we can see the huge influence of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration on the angular scattering amplitudes. The angular scattering amplitudes at wavelengths 453nm are larger than at wavelengths 555nm. From the analysis the scattering process in the phosphor layer of the in-cup packaging WLEDs, the results indicated that the involvement of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor into the phosphor compounding could play a major role in controlling the optical properties of the in-cup packaging WLEDs.

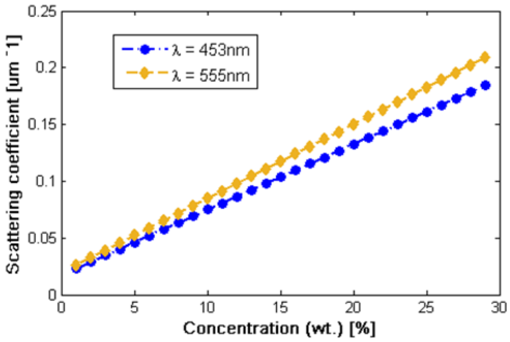

Fig. 2. The scattering coefficient of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor at wavelengths of 453nm, 555nm.

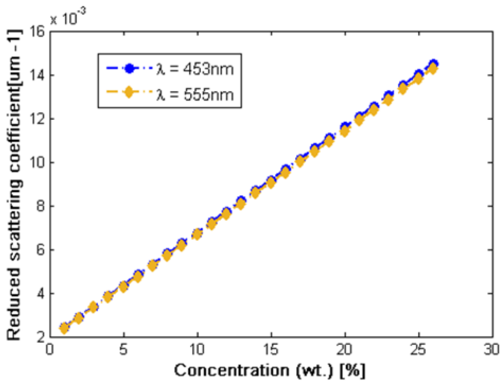

Fig. 3 The reduced scattering coefficient of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor at wavelengths of 453nm, 555nm.

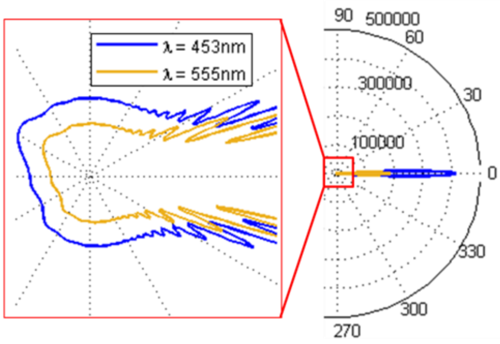

Fig. 4 The angular scattering amplitudes of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor at wavelengths of 453nm, 555nm.

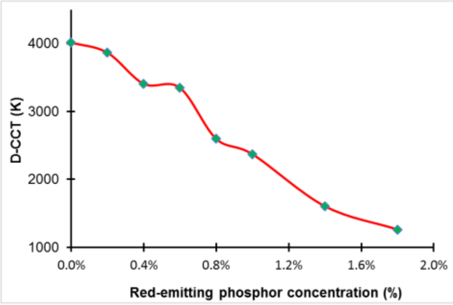

Fig. 5. The CCT deviation of the 7000 K in-cup packaging MCW-LEDs by adding the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particles

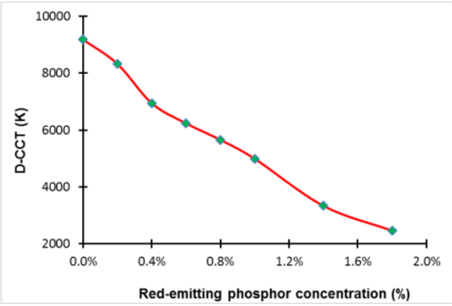

Fig. 6. The CCT deviation of the 8500 K in-cup packaging MCW-LEDs by adding the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particles

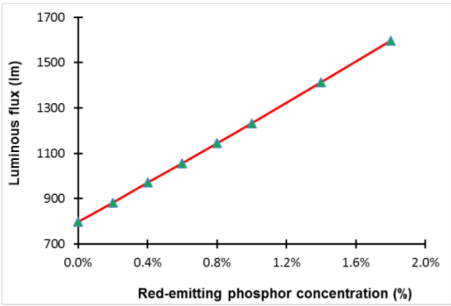

Fig. 7. The luminous flux of the 7000 K in-cup packaging MCW-LEDs by adding the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particles

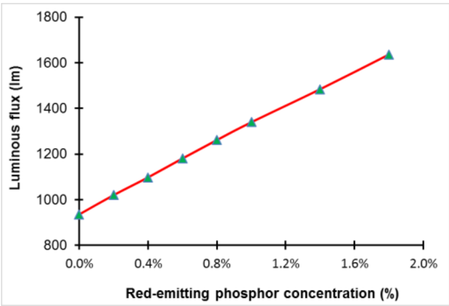

Fig. 8. The luminous flux of the 8500 K in-cup packaging MCW-LEDs by adding the green-emitting CaF_2:Ce^{3+},Tb^{3+} phosphor particles

In this section, we use the commercial program Light Tools 8.4 to investigate the effect of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration on the optical properties (D-CCT and luminous flux) of the 7000K and 8500K in-cup packaging WLEDs. The concentration of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor is increased from them 0% to 1,8 % continuously. Fig. 4 and 5 showed the D-CCT of the 7000K and 8500K in-cup packaging WLEDs on the increasing the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration, respectively. The D-CCT decreased from 4000K to 1250 K for the 7000K WLEDs cases, and from 9600K to 2100K for the 8500K WLEDs. In this situation, the D-CCT could be decreased more than 3 times. Furthermore, Fig. 6 and 7 showed the influence of particle concentration on luminous efficacy of the7000K and 8500K in-cup packaging WLEDs. These results indicated that the luminous flux crucially increased while the concentration of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor rose continuously from 0% to 1.8%. The luminous flux rose from 800 lm to 1600 lm in the 7000K WLEDs, and from 900 lm to 1700 lm in the 8500K WLEDs. The results provided that the luminous efficacy can enhance more than 2 times when we added the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor to the phosphor compounding. In this results, the scattered light of each particle in PC-LEDs is different, resulting in varying the optical properties of W-LEDs. In this situation, the CCT deviation can be reduced significantly in connected with the scattered blue light is enhanced enough inside. From the results, the involvement and the scattering process of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor could be playing an important role in enhancing the optical properties of the in-cup packaging WLEDs [17].

4. Conclusions

In this research, the influence of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor's concentration on the D-CCT and the luminous efficacy of the 7000K and 8500K in-cup packaging WLEDs was proposed and demonstrated totally. From results and theory analysis, some conclusions can be proposed:

1) CCT deviation can be decreased more than 3 times with rising concentration of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor particles.

2) The luminous efficacy had an increase more than 2 times in connecting with rising concentration of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor particles.

This study provided a potential technical implication for W-LEDs manufacturing and material development for WLEDs applications in thenear future. In the future work, the influence of both size and concentration of the green-emitting $CaF_2:Ce^{3+},Tb^{3+}$ phosphor particles on the optical properties of WLED with different packaging is necessary to propose and demonstrate.

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