The Impacts of Red-Emitting $Sr_WF_XB_YO_Z$:Eu^{2+}, Sm^{2+} Phosphor on Color Quality of Dual-Layer Phosphor Geometry

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Abstract. *When putting the features of remote phosphor structure in the comparison with these of conformal phosphor or in-cup phosphor, we recognize that remote phosphor structure is more outstanding than the others in term of luminous flux but its color quality is a drawback that needs to improve. To eliminate these disadvantages, the most crucial point is how the remote phosphor structure can make the color quality of WLEDs better. After many research conducted, we propose a dual-layer remote phosphor structure for the enhancement of the color rendering index (CRI) and color quality scale (CQS) for WLEDs, which is applied to three similar WLEDs packages with different color temperatures including 5600 K, 6600 K, and 7700 K. The principal idea is putting a red phosphoric layer* $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} *on the yellow phosphorus layer* YAG:Ce^{3+}*. The results show that* $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} *brings great benefits to increase CRI and CQS. Specifically, the greater the concentration of* $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}*, the better the CRI and CQS. However, the luminous flux has a tendency of dropping when the* $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} *concentration increases excessively. This can be demonstrated and explained based on the Mie dispersion theory as well as the Lambert-Beer law. The results of this article would be an important reference for producing WLEDs with higher color quality.*

Keywords

WLEDs, $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}***, Luminous Efficacy, Color Quality Scale.***

1. INTRODUCTION

Light-emitting diodes still exist some drawbacks despite have been through several stages of improvement. Therefore, the invention of phosphor converted white light emitting diodes (pc-WLEDs) is a remarkable turning point in the lighting market, making it deserve to become the fourth potential generation light source used to replace the conventional one [1]. Because of these outstanding features, white light-emitting diodes has become more and more popular in many different fields of our daily life such as landscape, street lighting, backlighting, etc. However, there are two problems which limit the benefit of phosphor converted white light emitting diodes that are the light extraction efficiency and the angular homogeneity of correlated color temperature of white LED [2]. Due to the constant rise of demand of the market and applications, further breakthroughs in luminous efficiency and color uniformity are essential [3]. The most common approach for white light generation is to combine the blue light with yellow light. Although this concept seems to be rather familiar, it cannot be denied that the structure of LEDs and the arrangement of phosphor layers play a significant role in determining the luminous efficiency, especially the angular homogeneity [4]-[8]. There are several common phosphor coating methods which are researched and selected carefully to so that the research can put the best results such as dispensing coating and conformal coating. Nevertheless, these structures do not provide high luminous flux due to the degradation in light conversion of phosphor material caused by yellow emitting phosphor directly contacts with the LED chip, leading to the temperature increase at the junction of the LED and phosphor layer. Therefore, reducing the outcome of heat would improve the phosphor performance and avoid the irreversible damage to the phosphor. Many previous studies have established that the remote phosphor structure in which phosphor is placed far from the heat source (LED chip) can reduce the effect of heating [9, 10]. With a sufficient large distance of phosphor and the LED chip, LEDs could limit the backscattering and circulation of light inside. This approach is an optimal solution to manage the heat of LED and thus can enhance the luminous efficiency as well as the color quality of LEDs [11]-[16]. Nonetheless, the remote phosphor structure is qualified enough for regular lighting but may not meet other requirements of many other illumination applications, which is probably the reason why the next generation of LED is needed creating. For further development, some novel structures of remote phosphor are proposed to minimize the backward scattering of the phosphor towards the chip and enrich the luminous efficiency. Another study showed that an inverted-cone-lens encapsulant and a surrounding ring remote phosphor layer can redirect the light from the LED chip to the surface of the LED and then reduce the loss caused by internal reflection inside LED [17]. A patterned remote phosphor structure with a clear region in the perimeter area without coating phosphor on the surface surrounding could achieve high uniformity of angular-dependent correlated color temperature and chromatic stability [18]. Moreover, the patterned sapphire substrate applied in the remote phosphor could deliver much better uniformity of the correlated color temperature in a far field pattern than a conventional pattern [19]-[24]. Remote phosphor with dual layer package is proposed to improve the light output of LEDs.

In this study, the effect of two phosphor layers, yellow $YAG:Ce^{3+}$ phosphor layer and red $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ phosphor layer, on the performance of pc-WLEDs in which the lumen effect and CCT uniformity was investigated and presented. The simulation is conducted via two steps, constructing dual-layer phosphor geometry at first, and then selecting the optimal concentration of $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ phosphor layer to obtain better lumen output and color quality. The simulation results show that $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ brings great benefits to increasing CRI and CQS. Specifically, the greater the concentration of $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ has, the higher CRI and CQS get. Consequently, the backscattered photons can extract as well as the overall light output and luminous efficacy can significantly increase. This study aims to find out how two phosphor layers affect to the final performance of a remote-phosphor white LED in terms of light output and color properties.

2. PREPARATION AND SIMULATION

2.1. Material preparation

The ingredient of $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ is listed in Tab. 1. From the composition of chemical compounds, which is referred to [21], the molar percentage of each element is calculated to obtain the formula of this mixed compound. Furthermore, the fabrication process of $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ is also described, specifically. First, Eu_2O_3 and Sm_2O_3 in particle form are dissolved in dilute nitric acid solution. Also, $Sr(NO_3)_2$ and H_3BO_3 are dissolved in warm water (90^0C). These 2 solutions are mixed together, then a 1 : 1 solution of acetone and ammonium hydroxide is added to this compound. Whole solution are stirred vigorously. After a while, a fine white precipitate will form and become a slurry. Keep this slurry at 80^0C for two hours, and then cool it down to room temperature. For the next step, filter and dry this precipitate in air and then blend it with SrF_2 and grind. The resultant is putting in an open quartz crucible and fired in air at 900^0C for approximately one hour. After that, it is cooled down again, then blended and grinded into fine particles. The firing process continues for two hours at 900^0C, this time in a flow of H_2 in N_2 gas through the same crucible. Finally, the resulted particle is cooled and re-grinded.

2.2. Simulation

The application of the LightTools 8.1.0 program and Mie-theory into this work makes WLEDs with dual-layer phosphor structure be easily simulated through analyzing the scattering of phosphor particles and the process of investigating the influence of $Sr_wF_xB_yO_z$:Eu^{2+} ,Sm^{2+} phosphor on the performance of the WLEDs at the high correlated temperature of 5600 K - 7700 K is supported. In order that the process of the in-cup phosphor configuration of WLEDs could perform smoothly, the $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} and YAG:Ce^{3+} phosphor compounding are mixed according to the Fig. 1. Consequently, the phosphor layer of WLEDs contains red $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphor, the yellow YAG:Ce^{3+} phosphor , and the silicone glue.

The constituents of simulated WLEDs expressed in the model are blue chips, a reflector cup, a phosphor layer, and a silicone layer. A reflector with a 2.07 mm depth, a bottom length of 8 mm and a length of 9.85 mm at its top surface is bonded with these chips. The radiant power of each nice blue chip is designed with 1.16 W, a peak wavelength of 453 nm. The refractive index of phosphor particle is set to be 1.85 and 1.83 for $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} and YAG:Ce^{3+} respectively. To maintain the average CCTs, the YAG:Ce^{3+} phosphor concentration need to change appropriately to the concentration of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}. Figure 2 shows the antipodal concentration change between the $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} red phosphorus and the yellow phosphorus YAG:Ce^{3+}. This change implies two meanings: one is the maintenance of average CCTs and the other is the influence of change on scattering and absorption in WLEDs. This inevitably affects the color quality and luminescence generated by WLEDs. The purpose of red phosphor grade is to increase the color quality. However, the reduction of luminous flux can occur.

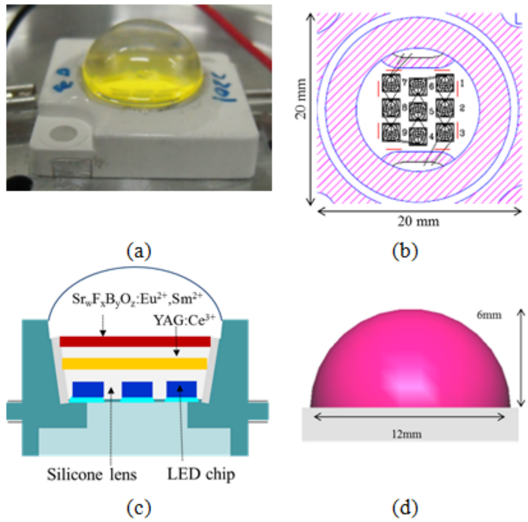

Fig. 1: Photograph of WLEDs structure: (a) Actual WLEDs, (b) Bonding diagram, (c) Illustration of pc-WLEDs model, (d) Simulation of WLEDs using LightTools commercial software.

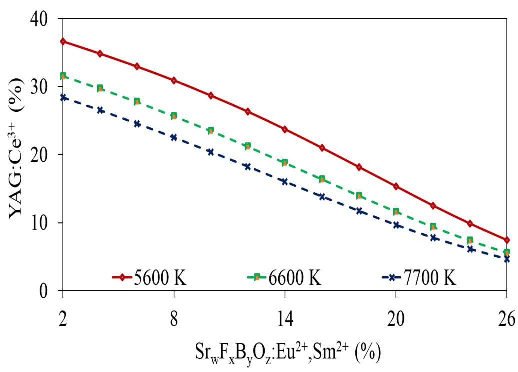

Fig. 2: The change of phosphor concentration for keeping the average CCTs.

Table 1. Composition of red-emitting $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphor.

Ingredient	Mole (%)	By weight (g)	Molar mass (g/mol)	Mole (mol)	Ions	Mole (mol)	Mole (%)
$Sr(NO_3)_2$	10.09	126.98	211.63	0.6	Sr^{2+}	0.6	2.4
SrF_2	5.43	40.58	125.62	0.32	F^-	0.646	2.6
H_3BO_3	84.12	309.2	61.83	5	B^{3+}	5	20.04
Eu_2O_3	0.25	5.28	351.93	0.015	O^{2-}	18.665	74.8
Sm_2O_3	0.11	2.09	348.72	0.006	Eu^{2+}	0.03	0.12
$Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}					Sm^{2+}	0.012	0.04

3. RESULTS AND DISCUSSION

As shown in Fig. 3, the color rendering index increased with $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphorus concentrations at all three CCTs due to the absorption of red phosphorus. When $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphor absorbs the blue light from the LED chip, the red phosphoric particles will transform the blue light into red light. Beside the blue light from the LED chip, $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} particles also absorb the yellow light. However, if compare these two absorptions, the blue light absorbed by the LED chip will be stronger due to the absorption properties of the material. Consequently, the component of red light in WLEDs increases with the addition of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}, resulting in a higher color rendering index (CRI). In the parameters selected of modern LEDs, the color rendering index is one of the important parameters. Obviously, the higher the color rendering index obtains, the higher the price of WLED is.

Nevertheless, $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} can be widely applied because of the low cost. As can be known, the color rendering index is just a factor that evaluates the color quality of WLEDs. A WLED can not be said to be good or bad although it has high color rendering index. In this study, the color quality scale (CQS) is proposed for estimating color quality of dual-layer phosphor geometry with red-emitting $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphor layer. CQS is an index defined by three factors: the color index as the first, the second is the viewer's preference, and lastly color coordinates. With these three important factors, CQS is almost a true overall color quality index regardless of color. Obviously, the using of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} can increase the color quality of white light of WLEDs with dual-layer

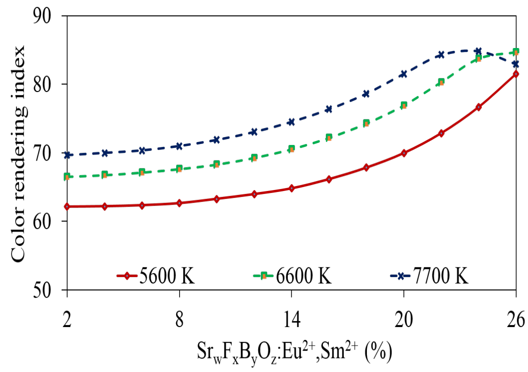

Fig. 3: The color rendering index of WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration.

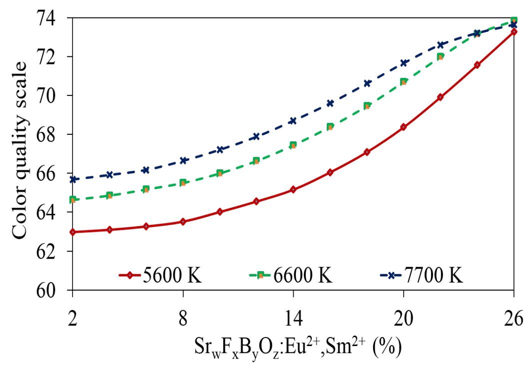

Fig. 4: The color quality scale of WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration.

phosphor geometry, as displayed in Fig. 4. With the aim of improving color quality, this is important for the turning point of the study. However, it cannot fail to mention the drawback of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} to the output flux. The scattering of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} phosphor particle was analyzed by using the Mie-theory. In addition, the scattering cross section Csca for spherical particles can be computed by the following expression through applying the Mie theory. The transmitted light power can be calculated through the Lambert-Beer law:

$$I = I_0 \exp\left(-\mu_{ext} L\right)$$

In this formula, I_0 is the incident light power, L is the phosphor layer thickness (mm) and μ_{ext} is known to be the extinction coefficient, which can be expressed as: $\mu_{\text{ext}} = N_r.C_{\text{ext}}$, where N_r is as the number density distribution of particles (mm^{-3}). C_{ext} (mm^2) is the extinction cross-section of phosphor particles.

According to Expression 1, when the phosphor content increases, the scattering in the phosphor layer will be higher, which leads to the weaker of the light transmission in the phosphor layer. In addition, scattering in WLEDs also increased. From these two reasons, it can be confirmed that the illumination is weakened by increasing the concentration of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}. To verify this point, $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentrations is allowed to be increased from 2% and the results is that the lumen decreased significantly at 26% in all average CCTs, see Fig. 5.

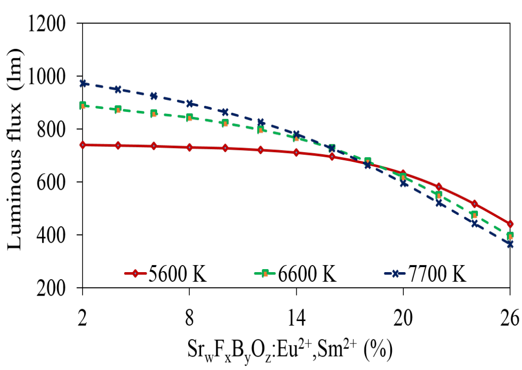

Fig. 5: The luminous flux of WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration.

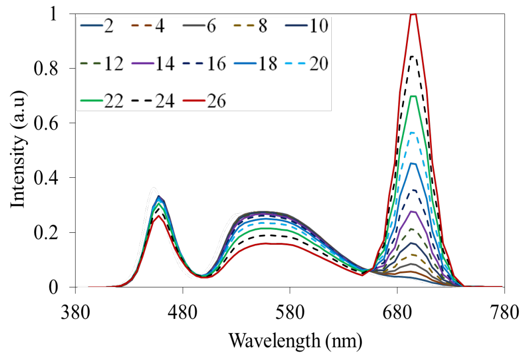

Fig. 6: The emission spectra of 5600 K WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration (2%÷26%).

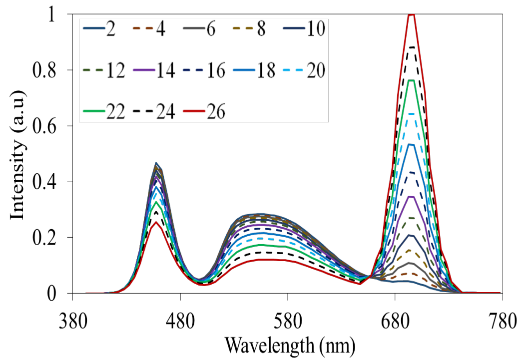

Fig. 7: The emission spectra of 6600 K WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration (2%÷ 26%)

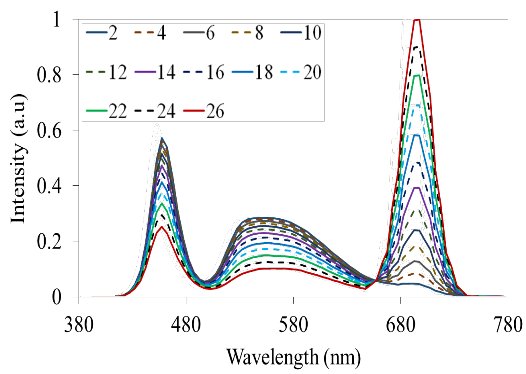

Fig. 8: The emission spectra of 7700 K WLEDs as a function of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} concentration (2%÷26%).

WLEDs with high color requirements can reduce the amount of light involved. White light is the combination of the spectral regions as shown in Fig. 6, Fig. 7 and Fig. 8. These represent the respective luminous flux at 5600 K, 6600 K and 7700 K. It is easy to see that the trend of the red light spectrum from 648 nm to 738 nm increases with the concentration of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}. However, this is not significant unless there is an increase in the spectrum of the two regions 420 nm - 480 nm and 500 nm - 640 nm. The enhancement of the spectrum leads to enhance scattered blue-light, resulting in increasing color quality and luminous flux. The higher the color temperature applies, the higher the emission spectra presents. Thus, the higher the color and luminosity will be. This is an important result when applying the $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+}. Mostly, it is very difficult to control the color quality of WLEDs. In summary, $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} plays an important role in improving the color quality of WLEDs even if low color temperature (5600 K) or high (7700 K).

4. CONCLUSION

This paper presents the effects of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} on CRI and CQS of dual-layer phosphor structure. Based on Mie's scattering theory and the Lambert-Beer law, the study has proven that $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} is the right choice for improving color quality. It can be applied for not only WLEDs with a low color temperature of 5600 K but also for higher color temperatures of 7700 K. This study has achieved a very difficult goal with the remote-phosphor structure - improving the color quality of white light. However, there is still some disadvantages to the emission of the flux. As the concentration of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} exceeded, the luminosity decreased sharply. Therefore, selecting a suitable concentration of $Sr_wF_xB_yO_z$:Eu^{2+}, Sm^{2+} becomes more important than ever, depending closely on the manufacturer's goal. The article also provided important information for reference in the production of dual-layer phosphor geometry with better quality.

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