Eu²⁺-activated strontium-barium silicate: a positive solution for improving luminous efficacy and color uniformity of white light-emitting diodes

MY HANH NGUYEN THI¹, PHUNG TON THAT², NGUYEN DOAN QUOC ANH^{3,*}

¹Faculty of Mechanical Engineering, Industrial University of Ho Chi Minh City, Viet Nam

²Faculty of Electronics Technology, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam

³Faculty of Electrical and Electronics Engineering, Ton Duc Thang University, Ho Chi Minh City, Vietnam

In this research we have studied the lighting enhancement method by analyzing chromatic performance and luminous flux of light emitting diodes that produce white light. In order to achieve expected results, it is necessary to mix Eu²⁺-activated strontium-barium silicate (SrBaSiO₄:Eu²⁺) with its phosphor compounding, which has been demonstrated to have considerable influence on lighting performance. The results showed that with the gradually increasing concentration of yellow-green-emitting SrBaSiO₄:Eu²⁺ phosphor in LEDs devices, at 8500 K, the color homogeneity and the lighting output received a great improvement. The color quality scale, on the other hand, responded negatively to the increase in SrBaSiO₄:Eu²⁺. The impact of SrBaSiO₄:Eu²⁺ on optical properties of WLEDs was confirmed. The final step to optimize SrBaSiO₄:Eu²⁺ usage in lighting development is to figure out a suitable amount of particles and optimize their size.

Keywords: white light-emitting diodes; SrBaSiO₄:Eu²⁺; luminous efficacy; color uniformity; Mie-scattering theory

1. Introduction

In recent years, most studies in solid-lighting industry have been focusing on enhancing optical properties of LEDs configuration, a new lighting method with outstanding performance. The expected results have been achieved, in particular, the crucial quality aspects of white LED lamps, luminous flux, and color homogeneity were discussed and improved in the previous studies [1–5]. For instance, Anh et al. while studying the compound of SiO₂ particles and YAG:Ce³⁺ phosphor observed the potential of phosphor compound and applied it to enhance white light [6]. The white LED devices with multiple chips and phosphor compounding exhibited remarkable performance in comparison to the conventional ones. The most common method to combine SiO₂ and yellow YAG:Ce³⁺ phosphor is to bind the particles with silicone gel [7–13]. The phosphor compound absorbs blue light and discharges yellow light, which creates white light

during the fusing process of those two chromatic radiations. The light first diffuses within the phosphor compound, then passes through the phosphor particles. The yellow light from YAG:Ce³⁺ phosphor particles, when in contact with blue radiation, absorbs blue rays and weakens them [14–16], and thus, the yellow radiation becomes more intensive after each diffusing process of blue light. Therefore, white light at the center and near surface of LED devices normally has a shade of blue, and the color displayed at the angles further away from the center exhibits more yellow shade [17–19]. The color discrepancy between different zones of lighting devices can lead to deficiencies such as the yellow ring incident.

Therefore, many luminous flux and color quality enhancing methods have been studied, including configuration modification and phosphor adjustment. Won et al. [20] have proved the great impact of phosphor arrangement on light output and color quality scale (CQS) of lighting devices. They employed green (Ba,Sr)₂SiO₄:Eu²⁺ and red CaAlSiN₃:Eu²⁺ phosphors in the WLEDs

*E-mail: nguyendoanquocanh@tdtu.edu.vn

and calculated the effect of different phosphor parameters to obtain optimal efficiency [20]. In contrast, Oh's group has proposed the triple-phosphor layers WLEDs with three primary colors green, yellow, and red, that focused on light output and color rendering ability [21]. Zhang's team has used multi-chromatic phosphor to enhance the color rendering ability of light emitted from WLEDs [22]. Generally, although many different methods were applied in those studies, the primary objectives were light output and rendering index while the other crucial quality indicators, such as color uniformity, were neglected. In addition, those studies conducted experiments mainly on single chip packages, which is impractical considering that most WLEDs packages are multi-chip and have high correlated color temperature.

In this study, yellow-green SrBaSiO₄:Eu²⁺ particles have been applied in MCW-LEDs to support homogeneity of color and light output to achieve optimal results. SrBaSiO₄:Eu²⁺ particles are especially useful as they take part in the diffusion process of material particles. Due to this process, the participation of SrBaSiO₄:Eu²⁺ particles enhances the lighting quality and improves color uniformity. This manuscript consists of three parts: (1) MCW-LEDs fabrication process; (2) SrBaSiO₄:Eu²⁺ integration into the MCW-LEDs lighting configuration; (3) Calculating the emission spectra and the scattering of SrBaSiO₄:Eu²⁺ and discussing their impacts. The experimental results lead to a conclusion that if SrBaSiO₄:Eu²⁺ and YAG:Ce³⁺ phosphors are combined and added to WLEDs configuration at suitable concentration, the lighting performance can be enhanced greatly.

2. Preparation and simulation

2.1. Preparation of yellow-green SrBaSiO₄:Eu²⁺ phosphor

SrBaSiO₄:Eu²⁺ particles, with an emission peak of 2.36 eV and other remarkable traits such as high scattering effect and high thermal consistency, are known as a type of yellow-green phosphor and become more and more popular [23]. The elements which can directly influence

the luminescence properties of SrBaSiO₄:Eu²⁺ phosphor are their particle sizes and concentration. Its composition includes SrCO₃, BaCO₃, SiO₂, Eu₂O₃, NH₄Cl, and Eu²⁺ ion, all of which are used as raw materials as shown in Table 1 [24–26]. Moreover, SrBaSiO₄:Eu²⁺ is the primary material source for heavy duty and durable lighting devices. As a result, SrBaSiO₄:Eu²⁺ is the most widely used oxide phosphor material. On the whole, the fabrication process of SrBaSiO₄:Eu²⁺ is described as the follows:

Firstly, the materials are slurred in the water to be mixed together. Then they are ball-milled in the water into small particles. After drying in air, the materials are powdered. Secondly, this powder is fired in capped quartz tubes with CO at 1100 °C within an hour and powderized by dry milling. Then, 5.4 g NH₄Cl is added into this mixture and the constituents are mixed together by dry milling. Next, they are fired again in capped quartz tubes with CO at 1100 °C for an hour and powderized. Finally, the materials are washed in water for several times (pH ranges from 10 to 12) and dried after that.

2.2. Construction of MCW-LEDs

The MCW-LEDs model with flat silicone layer was created using LightTools 8.1.0 program and Monte Carlo method. The modeling process has been carried out in two steps: (1) the type of MCW-LEDs optical configuration and identification of components optical characteristics (2) SrBaSiO₄:Eu²⁺ concentration was constantly changed under careful monitoring to understand its influence on the optical performance of the MCW-LED. The optical performance of YAG:Ce³⁺ and SrBaSiO₄:Eu²⁺ in MCW-LED lamps was calculated and compared to other configurations to verify the attained results. Among them, two types of compounding: conformal and in-cup phosphor, which have average CCT of 8500 K, were applied as comparison targets. The MCW-LED with conformal phosphor coating and 8500 K CCT is presented in Fig. 1c. It is important to note that this lighting configuration does not have SrBaSiO₄:Eu²⁺ particles in the structure.

Table 1. Composition of yellow-green-emitting $\text{SrBaSiO}_4:\text{Eu}^{2+}$ phosphor.

Ingredient	Mole [%]	By weight [g]	Molar mass [g/mol]	Mole [mol]	Ions	Mole [mol]	Mole [%]
SrCO_3	31.28	145	147.63	0.982	Sr^{2+}	0.982	0.088
BaCO_3	31.79	197	197.34	0.998	Ba^{2+}	0.998	0.090
SiO_2	33.40	63	60.08	1.049	Si^{4+}	1.049	0.094
Eu_2O_3	0.32	3.5	351.926	0.01	O^{2-}	8.068	0.726
NH_4Cl	3.22	5.4	53.49	0.101	Eu^{2+}	0.02	0.002

The reflector with $8 \text{ mm} \times 2.07 \text{ mm} \times 9.85 \text{ mm}$ at bottom, height, and top respectively is placed in the structure to hold LED chips. The blue chip emits 1.16 W at 453 nm peak wavelength. The area of each square LED chip is 1.14 mm^2 and the height is 0.15 mm. Above the chips, there is a layer of phosphor compound with 0.08 mm thickness, created by the conformal coating.

Fig. 1c and Fig. 1d show two phosphor structures in two different geometries. In Fig. 1c, the phosphor compound is applied to the structure through conformal coating method. In the case of in-cup phosphor structure, a different method is used to mix the phosphor compound with the silicone lens. In both structures Mie-theory has been used to analyze the scattering of phosphor particles. In this research, the standard size of phosphor particles, $14.5 \text{ }\mu\text{m}$, has been applied in all experiments. Fig. 1e illustrates the spectral values measured from $\text{YAG}:\text{Ce}^{3+}$.

The $\text{SrBaSiO}_4:\text{Eu}^{2+}$, $\text{YAG}:\text{Ce}^{3+}$, and silicone gel are the materials used to create the phosphor layer of the WLEDs. The refractive index for the components in the phosphor layer is 1.85 for $\text{SrBaSiO}_4:\text{Eu}^{2+}$, 1.83 for $\text{YAG}:\text{Ce}^{3+}$, and 1.52 for silicone gel. The sizes of the components have been adjusted to fit the pre-determined parameters. After ensuring that the size and refractive index are correct, we proceeded to calculate the emission spectra of the conformal phosphor and presented them in Fig. 2. In Fig. 2a, the impact of $\text{SrBaSiO}_4:\text{Eu}^{2+}$ concentration from 0 % to 24 % on the emission spectra in conformal structure is demonstrated. In Fig. 2b, the emission spectra of in-cup phosphor configuration for $\text{SrBaSiO}_4:\text{Eu}^{2+}$ concentration changing from 0 % to 1.4 % are

shown. From the figures, it is certain that the light output in MCW-LEDs is enhanced with the addition of $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles.

3. Computation and discussion

Based on the Mie theory, the scattering coefficient μ_{sca} has been computed to verify the optical properties of phosphor compounding. The relationship of the scattering coefficient (SC) with the wavelength and $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles size is demonstrated in the formula below:

$$\mu_{\text{sca}}(\lambda) = \frac{c}{\bar{m}} \bar{C}_{\text{sca}}(\lambda) \quad (1)$$

$$\bar{C}_{\text{sca}}(\lambda) = \frac{\int C_{\text{sca},D}(\lambda) f(D) dD}{\int f(D) dD} \quad (2)$$

$$\bar{m} = \frac{\int m_i(D) f(D) dD}{\int f(D) dD} \quad (3)$$

$$C_{\text{sca}}(\lambda) = \frac{P_{\text{sca}}(\lambda)}{I_{\text{inc}}(\lambda)} \quad (4)$$

Here, $f(D)$ is the size distribution function, c is the phosphor concentration (g/cm^3), $C_{\text{sca},D}$ is the scattering cross-section of the phosphor having particle diameter D , while $\bar{C}_{\text{sca}}(\lambda)$ and $\bar{m}$ are the scattering cross-section and the particle mass of the phosphor integrated over $f(D)$, respectively. $P_{\text{sca}}(\lambda)$ and $I_{\text{inc}}(\lambda)$ are the power scattered by phosphor particles and the irradiance intensity, respectively.

In Fig. 3, the scattering coefficient (SC) measured from the material layer in each phosphor structure with $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles is

Fig. 1. Illustration of phosphor-converted MCW-LEDs doped with SrBaSiO₄:Eu²⁺: (a) the real MCW-LED and (b) its parameters; (c) conformal phosphor geometry (CPG) and (d) in-cup phosphor geometry (IPG); (e) the measured spectra of yellow-emitting YAG:Ce³⁺ phosphor.

recorded. It is easy to see that different concentrations of SrBaSiO₄:Eu²⁺ result in different SC values of the phosphors. This also confirms that the concentration and pre-stimulus of SrBaSiO₄:Eu²⁺ affect the color quality of both CPG and IPG structures. When the concentration of SrBaSiO₄:Eu²⁺ is increased, SC also tends to increase regardless of SrBaSiO₄:Eu²⁺ particle size. For the particle with the size of approximately 1 μm , SC increases more rapidly than in case of particles with larger size, leading to the development of color uniformity. Besides, when the size is approximately 7 μm , the SC value of the phosphor layer is more stable regardless of the SrBaSiO₄:Eu²⁺ concentration. This

is beneficial for color quality (CQS) of the LEDs. Hence, the SrBaSiO₄:Eu²⁺ size should be smaller than 7 μm if the target is CQS. Obviously, the SC value depends not only on the concentration but also the size of SrBaSiO₄:Eu²⁺, which is the reason why SrBaSiO₄:Eu²⁺ can be used for lumen output and chromatic performance improvement in LED devices.

It is crucial that some parameters remain constant during the experiments to ensure results accuracy. Hence, SrBaSiO₄:Eu²⁺ concentration change that can vary the average CCT of 8500 K in the lighting device must be adjusted. To address this issue, as the amount of SrBaSiO₄:Eu²⁺ particles

Fig. 2. Emission spectra of multiple phosphors for (a) CPG and (b) IPG.

increases, the yellow $\text{YAG}:\text{Ce}^{3+}$ particles must be reduced to keep CCT at 8500 K. The relation between the mass proportions of materials is demonstrated as follows:

$$\sum W_{pl} = W_{\text{yellowphosphor}} + W_{\text{silicone}} + W_{\text{yellow-greenphosphor}} = 100\% \quad (5)$$

W_{silicone} , $W_{\text{yellowphosphor}}$ and $W_{\text{yellow-greenphosphor}}$ are respectively: the amount of silicone gel, yellow $\text{YAG}:\text{Ce}^{3+}$ particles, and yellow-green $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles within MCW-LEDs.

The experiments on MCW-LEDs simulation showed that the angle-dependent color deviation responded positively to the increase in the amount of $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles, as shown in Fig. 4. In particular, the $\text{SrBaSiO}_4:\text{Eu}^{2+}$ particles contained in the MCW-LEDs structure can limit the color

Fig. 3. Scattering coefficients of phosphor compound at 453 nm as a function of concentration and size of $\text{SrBaSiO}_4:\text{Eu}^{2+}$ for (a) CPG and (b) IPG.

deviation. It can also be concluded that the chromatic distribution of MCW-LEDs in spatial region is more homogeneous when $\text{SrBaSiO}_4:\text{Eu}^{2+}$ is present in the structure.

In addition, there is a balance between the two performance factors and the optimization problem. Focusing on one quality indicator while neglecting other aspects can lead to poor overall performance at the end. However, it is also well known that optimal indices of CQS and luminous efficiency cannot be obtained simultaneously. Only one optical property can reach the highest index while the others undergo some reduction. Therefore, if the target is the highest CRI, a wide spectrum and single color light obtained at 555 nm wavelength must be optimized. In our research, we have considered the

(a)

(a)

(b)

(b)

Fig. 4. The CCT peak-valley deviation as a function of concentration and size of SrBaSiO₄:Eu²⁺ for (a) CPG and (b) IPG.

Fig. 5. Luminous efficacy as a function of concentration and size of SrBaSiO₄:Eu²⁺ for (a) CPG and (b) IPG.

connection between CQS, lumen output, and CCT P-V deviation, which can be observed in Fig. 5 and Fig. 6.

The results in Fig. 5 show that the light output of WLEDs also increases as the amount of SrBaSiO₄:Eu²⁺ rises. In addition, the luminous flux seems to keep increasing as long as the SrBaSiO₄:Eu²⁺ concentration is growing, however, the CQS is reduced. Therefore, choosing SrBaSiO₄:Eu²⁺ concentrations slightly lower than 6 % for CPG and 0.5 % for IPG could prevent the color quality from being deteriorated while maintaining a high lumen output index.

4. Conclusions

The purpose of this manuscript is to demonstrate how a yellow-green SrBaSiO₄:Eu²⁺ phosphor can improve the lighting performance of WLEDs configuration in both chromatic quality and light output. The color uniformity, according to the Mie-scattering theory, can be enhanced while ignoring the ACCT and phosphor setup, due to the enhanced scattered light in the WLED packages as the yellow-green SrBaSiO₄:Eu²⁺ phosphor is utilized. On the other hand, through the application of Monte Carlo simulation, the relation between luminous flux and SrBaSiO₄:Eu²⁺ concentration has been confirmed as the measured luminous flux also fluctuated when the SrBaSiO₄:Eu²⁺ concentration

Fig. 6. Color quality scale as a function of concentration and size of $\text{SrBaSiO}_4:\text{Eu}^{2+}$ for (a) CPG and (b) IPG.

varied. From these results, it can be concluded that $\text{SrBaSiO}_4:\text{Eu}^{2+}$ with suitable concentration is advantageous in producing high quality WLEDs or achieving certain demands imposed on the lighting device.

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