Na₃Ce(PO₄)₂:Tb³⁺ and Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphors: a suitable selection for enhancing color quality and luminous flux of remote white light-emitting diodes

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Article Info

Keywords:

Article history:

Received Jul 25, 2019

Revised Mar 12, 2020

Accepted Apr 3, 2020

Color quality scale

Na₃Ce(PO₄)₂:Tb³⁺

Luminous flux

ABSTRACT

YAG:Ce3+ yellow phosphor, green Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn Remote phosphor structure

This study proposed the TRP, a remote phosphor structure that has 3 phosphor layers, to ehance the chromatic quality and lumen output for white light-emitting diodes devices (WLEDs). The arrangment of phosphor layers is $Na_3Ce(PO_4)_2:Tb^{3+}$ phosphor, and red Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor from bottom to top. Red Na(Mg2-xMnx)LiSi4O10F2:Mn phosphor is used for the red light component to boost color rendering index (CRI). The green layer Na₃Ce(PO₄)₂:Tb³⁺ phosphor is utilized for the green light component to produce higher luminous flux (LF). With the addition of red and green phosphor, the yellow YAG:Ce3+ concentration must decrease to maintain the 6000 K color temperature. The research results show that red phosphor Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn concentration is beneficial for CRI, while green phosphor Na₃Ce(PO₄)₂:Tb³⁺ is detrimental to CRI. Morever, CQS reaction with red and green phosphor is also studied, which show notable improvement when Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn concentration is from 10-14%, regardless of Na₃Ce(PO₄)₂:Tb³⁺. The luminous flux (LF) can also increase for more than 40% with the reduced light loss and added green phosphor. Research results are valuable references for producers to enhance the color quality and the light emission of WLEDs.

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INTRODUCTION 1.

White light-emitting diodes (WLEDs) with phosphor base is a potential lighting potential in view of small size, long lighting duration, minimal effort, and shading security [1-4]. The fabrication of white color in LEDs devices relied on color combination, in which the chip in the structure will emit a shade of blue that is ejected on the YAG:Ce³⁺ phosphor layer and blended with the chromatic radition from this source [5]. The LEDs lighting method is an important part in solid-state lighting application, however, an improvement in lighting emission proficiency and color performance can advance it even further [6]. For the most part, uninhibitedly scattered covering is the most widely recognized technique used to create white light. In this procedure, straightforward typified sap is joined with phosphor material and distributed on the structure. Despite the fact that this methodology permits good control over the density of material layer and diminishes a significant part of the cost, it doesn't create top notch WLEDs [7-9]. Subsequently, the conformal covering strategy can be utilized as an option. This strategy conveys hues consistently, bringing about rakish homogeneity of connected shading temperature (CCT) [9-13]. Be that as it may, the configuration that applied conformal coating is impacted by backscattering, which damage the emitted light. Past investigations have suggested the remote structure that seperates the phosphor film and the chip for this issue [14, 15]. Another notable solution is apply hemispherical shell made from polymer with phosphor interior can allow the extracted radiation to excel [16-18]. Moreover, a structure with gaps implanted at the base can support radiant profiency by reflecting light that emitted downward [19, 20]. Notwithstanding the structure of the bundle, the grouping of phosphor yield positive results on lighting capacity of the device. The re-assimilation event that occurs within the phosphor material unit arise when the phosphor constituent increases. Accordingly gadget radiant efficiency would be debased, particularly at lower CCTs [21]. Naturally, the solution would be enhancing the emission capacity of blue and yellow light sources and limiting the radiation impairment, which is the focus of this research. The triple-layer remote phosphor structure of WLEDs with color temperature of 6000 K is proposed in this study. TRP structure consists of three different phosphor layers with green layer Na₃Ce(PO₄)₂:Tb³⁺ phosphor between yellow YAG:Ce³⁺ phosphor and red Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor. The green phosphor layer adds green light to improve the luminous flux emitted while the red light component is supplemented by red phosphor to improve color quality. Research results show that, when there is a balance between the yellow, green, and red colors, the color quality can be maximized. Meanwhile, the luminous flux of WLEDs is not significantly reduced.

2. COMPUTATIONAL SIMULATION

The first idea of the study is to use the green light from $Na_3Ce(PO_4)_2:Tb^{3+}$ phosphor to enhance luminous flux. The second idea is to use the red phosphor $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2:Mn$ to enhance CRI and CQS with red phosphor particles. The LightTools program which relied on the Monte Carlo ray-tracing method [22] is the optical design software create RP-WLEDs with 6000 K CCT. The WLEDs 3-D model for optical replication of remote package WLEDs in the experiments was shown in Figure 1. The structure of this WLEDs is a reflector size 8 x 2.07 x 9.85 mm in bottom, side, and top. The phosphor materials are composed into layers with predetermined density of 0.08 mm. Below the layers of phosphor are the spaces to place the square blue light chips with the parameters of 1.14 mm base and 0.15 mm height. The lighting proficiency of the chip is 1.16 W at 455 nm amplitude. The concentration of phosphors particle changes continuously from 2% to 24% in the experiments to measure the results of quality indicators. An important notice is correlated color temperature values must be stabilized by controlling YAG:Ce³⁺ wt concentration to ensure the accuracy of the results.



Figure 1. (a) WLEDs, (b) Illustration of triple-layer remote phosphor configuration

3. RESULTS AND DISCUSSION

The content of Figure 2 demonstrate the variation of the CRI values, when the percentages of red phosphor and green phosphor in the structure rise from 2% to 20%. It can be seen that CRI continuously rises with the amount of $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$:Mn phosphor and reaches the highest value at 20% concentration. In contrast, the increase in green phosphor does not benefit CRI. As evidenced by the increase in green phosphor from 2% to 20%, CRI gradually decreased despite the increase of red phosphor

or the change of average correlated color temperature (ACCT). From the results of Figure 2, it obvious that the value of CRI increases if the amount of red light is enhance, which confirms the effectiveness of red layer Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor. When green concentration Na3Ce(PO4)2:Tb3+ phosphor increases, green light component prevails but is not beneficial for CRI. The conversion energy in the red phosphor layer decreases as the concentration of green phosphor increases. According to TRP structure, the order of material is green below red, which means the light must pass through the green layer first then to red phosphor. Therefore, green concentration $Na_3Ce(PO_4)_2$: Tb^{3+} phosphor should choose the smallest if the target is CRI. CRI is only one factor to evaluate color quality. It shows the ability to recognize the true colors of objects in the eyes of humans when light is shining on. Besides the true color of the object, the comfort of the viewer and the color coordinates are two important criteria that CRI does not evaluate. Therefore, color quality scale (CQS) can evaluate the synthesis of three elements: CRI, the pleasant of the viewer and the color coordinates for white light. Thus, when comparing between CRI and CQS, CQS value becomes more important and difficult to achieve. One question is how to improve the CQS value of WLEDs? Is it only necessary to increase the red light component as to improve the CRI? To find answers to these questions, COS values are also presented as shown in Figure 3. In general, CQS also increases with red Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor. However, unlike the CRI difference, the CQS difference is small when changing the concentration of the green layer $Na_3Ce(PO_4)_2$:Tb³⁺ phosphor. From the results shown in Figure 3, it is possible to confirm that both the green phosphor and the red phosphor increase CQS. The balance between 3 colors: yellow, green and red is the key to improving CQS. When the concentration of red phosphor or green phosphor increases, yellow phosphor concentration decreases to keep ACCT.





 $\begin{array}{l} Figure \ 2. \ CRI \ of \ TRP \ as \ a \ function \ of \ red \\ Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2: Mn \ phosphor \ and \ green \\ Na_3Ce(PO_4)_2: Tb^{3+} \ phosphor \end{array}$

Figure 3. CQS of TRP as a function of red $Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2:Mn$ phosphor and green $Na_3Ce(PO_4)_2:Tb^{3+}$ phosphor

The reduced yellow phosphor concentration means that the yellow light component decreases and this has two benefits. The first benefit is the better lumnious flux, which comes from the reduction of light loss due to back reflection to the chip. Another benefit is reducing the yellow light component. The final benefit is replacing the golden light element and the light red and light green composition. CQS control is the control of these 3 color components. CQS increases gradually when increasing green concentration Na₃Ce(PO₄)₂:Tb³⁺ phosphor from 2% to 10% and then gradually decreases. The highest CQS values in the case of 10% to 14% Na₃Ce(PO₄)₂:Tb³⁺. When the green phosphor concentration is low (2% to 10%), the yellow light component still dominates. The energy that transmits light is lost by later scattering, which leads to CQS not reaching its maximum. When the green level is between 10% and 14%, the green light component is enough for CQS to reach the highest level. However, when increasing the concentration of Na₃Ce(PO₄)₂:Tb³⁺, the excessive green light component causes a color imbalance in the 3 primary colors green, red and yellow. Therefore, the presence of Na₃Ce(PO₄)₂:Tb³⁺ phosphor should be restricted to achieve better results in CQS.

Controlling the color quality of remote phosphor structures is more complex than two conformal phosphor or in-cup phosphor structures. This control is even more difficult with WLEDs with higher ACCTs but the results show that the higher the ACCTs, the greater the CQS with the TRP structure. In addition to reducing the amount of scattered light, the TRP structure also helps increase scattered light inside WLEDs. This increase in scattering increases the mixing of light components, resulting in a high quality white light. However, does this increase in scattering process reduce the light transmission energy? This section is to demonstrate the mathematical equations employed in the calculation of blue radiation transmission

and mordified yellow light in double-layers remote structure. The results are to be studied for enhancement in LED productivity. Below is the equation for blue radiation transmission and mordified yellow light in singular WLED structure applying the remote configuration with the density of phosphor decribed as 2h:

$$PB_1 = PB_0 \times e^{-2\alpha_{B_1}h} \tag{1}$$

$$PY_{1} = \frac{1}{2} \frac{\beta_{1} \times PB_{0}}{\alpha_{B_{1}} - \alpha_{Y_{1}}} \left(e^{-2\alpha_{Y_{1}}h} - e^{-2\alpha_{B_{1}}h} \right)$$
(2)

The blue radiation transmission and mordified yellow light in dual-phosphor remote structure with the layers density prescribed as h can be concluded from the equations uderneath:

$$PB_2 = PB_0 \times e^{-2\alpha_{B2}h} \tag{3}$$

$$PY_2 = \frac{1}{2} \frac{\beta_2 \times PB_0}{\alpha_{B2} - \alpha_{Y2}} \left(e^{-2\alpha_{Y2}h} - e^{-2\alpha_{B2}h} \right)$$
(4)

The h depicts the phosphor layer density. The subscript "1" and "2" note the single layer and double-layer remote phosphor configurations. β is the conversion coefficient for blue light converting to yellow light. γ is the reflection coefficient of the yellow light. The intensities of blue light (PB) and yellow light (PY) are the light intensity from blue LED, indicated by PB0. α B; α Y are parameters describing the loss of transmitted energy in blue and yellow lights during their scattering process in the phosphor layer respectively. The luminous efficiency of pc-LEDs receives significant enhancement when the remote phosphor structure has multiple layers compared to the single layer structure:

$$\frac{(PB_2+PY_2)-(PB_1+PY_1)}{PB_1+PY_1} > 0$$
(5)

The scattering of $Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$ phosphor particles were analyzed by using the Mie-theory [23, 24]. In addition, the scattering cross section of circular particles Csca can be measured using the following equation with the Mie theory. The efficiency of light power transmission can be defined with Beer's law [25]:

$$I = I_0 \exp(-\mu_{ext}L) \tag{6}$$

The I_0 in this equation is the energy of incident light, *L* represents the density of phosphor layer (mm) and μ_{ext} is the extinction coefficient, which are measured by: $\mu_{ext} = N_r \cdot C_{ext}$, where N_r is as the number density distribution of particles (mm⁻³). C_{ext} (mm²) is the extinction cross-section of phosphor particles. Expression 5 demonstrates that the use of additional phosphor layer, in this case are the red Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor and green Na₃Ce(PO₄)₂:Tb³⁺ phosphor, increases the luminous flux of WLEDs. In order to keep ACCTs with the presece of red and green phosphor particles, the amount of yellow phosphor must adjust accordingly as described in Figure 4. Stable ACCTs in WLEDs is a mandatory requirement to conduct the experiments and to ensure the consistency of results. As observed from Figure 4, the yellow phosphor YAG:Ce³⁺ concentration must decrease to maintain the weight percentage between materials, which allows better management of back-scattering effect. A reduced yellow phosphor concentration also make the light transferred energy larger, according to Lambert-Beer's Law in (6). Therefore, the larger the concentration of Na₃Ce(PO₄)₂:Tb³⁺ or Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn is, the more the luminous flux emitted increases. However, this could be detrimental to CQS should the red or green component exceeds the approriate level and cause color imbalance, which results in lower CQS.

According to the results in Figure 5 which show the luminous flux in TRP WLEDs, the increase in green light component and back-scattered light reduction that come from $Na_3Ce(PO_4)_2$:Tb³⁺ helps luminous flux (LF) increase to more than 40%, regardless of the phosphor concentration in $Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2$:Mn. The obtained results are important references to help the manufacturer easily select the appropriate concentration of these two phosphor types. Specifically, to achieve CQS as LF in high value range, it is necessary to select $Na_3Ce(PO_4)_2$:Tb³⁺ concentration from 10% to 14%, and $Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2$:Mn concentration is 20%. Meanwhile, LF also increased slightly with $Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2$:Mn concentrations at 6000 K ACCT, LF almost unchanged in the range of 2-14% $Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2$:Mn. Then LF drops slightly when increasing green phosphor concentration to 20%.



 $\begin{array}{l} Figure \ 4. \ YAG:Ce^{3+} \ concentration \ varying \\ with \ Na(Mg_{2-x}Mn_X)LiSi_4O_{10}F_2:Mn \\ and \ Na_3Ce(PO_4)_2:Tb^{3+} \ concentration \\ for \ maintaining \ 600 \ K \ ACCT \end{array}$



Figure 5. Luminous flux of TRP as a function of red Na(Mg_{2-x}Mn_x)LiSi₄O₁₀F₂:Mn phosphor and green Na₃Ce(PO₄)₂:Tb³⁺ phosphor

4. CONCLUSIONS

TRP structure with two phosphor layers $Na_3Ce(PO_4)_2$:Tb³⁺ and $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$:Mn is proposed to enhance CRI, CQS and LF of WLEDs. The result presents that this structure not only improved color quality but also improved TRP structure. This is a new result that has not been available before. To achieve this, it is necessary to balance the yellow, green and red light in the phosphor layer through the concentration control of $Na_3Ce(PO_4)_2$:Tb³⁺ and $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$:Mn. Controlling the green layer $Na_3Ce(PO_4)_2$:Tb³⁺ phosphor is the control of green light components in WLEDs, resulting in luminous flux increasing. Moreover, the use of more phosphor layers is more beneficial for luminous flux than using one layer. Meanwhile, controlling the concentration of red $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$:Mn is controlling the red light component in WLEDs, resulting in increased CRI. The study results show that the balance of yellow, green and red colors, and reduced later scattering from the yellow YAG:Ce³⁺ layer will bring the highest color and luminous quality.

ACKNOWLEDGMENTS

This research is funded by Foundation for Science and Technology Development of Ton Duc Thang University (FOSTECT), website: http://fostect.tdt.edu.vn, under Grant FOSTECT.2017.BR.06.

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