The Application of Mg$_2$TiO$_4$:Mn$^{4+}$ and NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and Double Convex Structure in Improving Optical Performance of Phosphor-in-Glass Based White Light-Emitting Diodes

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Abstract. Improving lighting performance of WLEDs, especially the color quality, has always been a priority in lighting researches. Recently, the conventional remote phosphor configuration is unable to fulfill the needs of modern lighting market, particularly the high color expression demand, has inspired the search for a novel manufacturing procedure. In this study, based on the results from previous studies, the struggles in enhancing lighting performances are pointed out, and a solution, the dual-layer remote phosphor, is proposed from our conducted experiments. Through experiments with NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and Mg$_2$TiO$_4$:Mn$^{4+}$ phosphors, the dual-layer phosphor is proven to be effective in improving lighting properties such as color rendering index (CRI) and color quality scale (CQS). The research method involves structuring and experimenting the phosphor configuration of the yellow phosphor YAG:Ce$^{3+}$ layer with a green NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ or a red Mg$_2$TiO$_4$:Mn$^{4+}$ phosphor layer whose phosphor concentrations are varied. The results show that the red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ particles benefit the CRI and CQS because the values of CRI and CQS increase with red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ concentration. On the other hand, the green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ is inferior in improving CRI and CQS but exhibits better luminous flux. Despite being useful in enhancing lighting performance, the phosphor concentration must be kept below a certain level, which will be mentioned in the article, to prevent damages. These results are verified using
**Mie scattering theory** and Lambert-Beer’s law and can be utilized in producing WLEDs with high lighting quality.

**Keywords**
WLEDs, lumen output, color quality, NaYF₄:Er³⁺, Yb³⁺, Mg₂TiO₄:Mn⁴⁺, Mie-scattering theory.

1. Introduction
The phosphor converted white light emitting diodes (pc-WLEDs) have received increasing attention in recent time and been gradually replacing the other lighting solutions [1]. Along with the perks of high durability and small size that allow them to last longer, work better, and require less maintenance, WLEDs also consume less energy and do not use mercury, comparing to the traditional lighting sources. In other words, they are energy-efficient and earth-friendly. Thus, they are so highly valued and encouraged in modern lighting industry is understandable and undeniable. As the application of WLEDs began to expand from the initial usage to street lighting, back lighting or landscape lighting, the demand for better lighting quality also increases. While there are many aspects to evaluate the performance of a WLED, the light extraction efficiency and the angular homogeneity are arguably the elements that need significant changes for better WLED quality [2]. So, to address these issues effectively, researchers have been focusing on bettering the luminous flux and color quality [3]. The most common method to fabricate white light is to mix the blue light from the LED chip with red light components from the red phosphor and the yellow light from yellow phosphor; however, the arrangement of components in a WLED is also crucial to the generated white light as it can influence the luminous efficacy and color rendering index [4]-[8]. Therefore, many researches devote attention to this aspect, and the results are dispersed coating method and conformal coating method [9, 10]. These approaches have brought certain positive effects, for example, dispersed coating allows the control over the phosphor layers thickness with low expense while conformal coating supports color uniformity. However, these methods are not optimal, and the white light yielded from them is not high-quality. This is due to the heat generated at the joint between LED and phosphor layers that probably damages the quality of light output. To solve this problem, the remote phosphor structure, which separates the LED chips and phosphor by creating a gap between them, is proposed and proved to be the best solution in managing heating effect. This solution can eliminate the light loss from backscattering and inner circulation, thus, leading to enhanced luminous efficiency and color quality [11]-[16]. However, the idea of using remote phosphor structure is only sufficient for simple lighting tasks; for more advanced occasions, the production of WLED needs more alterations to boost the luminous efficiency and other lighting properties even higher. Considering the results from previous studies, we can see that there are many structures proposed to answer this need. For example, one research suggested using an inverted cone lens encapsulant with remote phosphor layer circling the lens can limit light loss by guiding the light from the chip directly to the LED surface [17]. In another instance, the patterned configuration that only has phosphor layer at the center area with the non-phosphor surrounding edge can achieve better color angular uniformity and stability [18]. Many research findings suggested using patterned sapphire substrate to replace conventional pattern can yield much better results in the far field pattern, in terms of color uniformity. These suggestions all aim to improve the lighting performance of WLED and focus primarily on color uniformity and light energy converted. However, they only work with single-chip WLEDs at low color temperatures. Therefore, a study that focuses on multi-chip WLED at high color temperatures packaged with multi-phosphor layer configuration is essential to the enhancement of lighting performance of high-quality WLED. Also, the experimental results are collected and compared to ensure the accuracy and to guide the manufacturers to the optimal manufacturing solution.

In this research paper, two dual-layer phosphor structures are used, the first one includes...
red phosphor $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ and yellow phosphor YAG:$\text{Ce}^{3+}$, the second one is comprised of green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$ and yellow phosphor YAG:$\text{Ce}^{3+}$. The chemical compositions of the phosphors and their synthesizing processes are introduced in details. The correlated color temperature throughout all experiments is kept at the intended level, and the purpose is to verify the effectiveness of green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$ and red phosphor $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ in promoting CRI and CQS. The research results show green phosphor and red phosphor have significant effects on the enhancement of their experimented optical aspects. This research provides an appropriate and effective method to enhance the lighting properties of WLED for manufacturers. They can decide the configuration suitable for their WLED requirements while monitoring the concentration of phosphor to prevent unwanted damages.

2. Phosphor preparation and WLED simulation

Red phosphor $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ and green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$ are the two types of phosphor employed throughout the experiments in this research. The chemical compositions of red phosphor $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ and green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$ are shown in Tab. 1 and Tab. 2, in turn. The red phosphor $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ exhibits a deep red color at 1.885 eV emission peak. The green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$ emits green color at 550 nm. The following are the chemical compositions of the phosphors and their producing processes.

To create phosphor used in experiments, researchers must ensure to follow the requirements of each step to produce the best quality for phosphors and avoid contamination. The red $\text{Mg}_2\text{TiO}_4\cdot\text{Mn}^{4+}$ phosphor has a 4-step manufacturing procedure: mixing, drying, firing, and re-firing. First, mix all the ingredients in water or methanol evenly to make the uniform slurry. Then leave the mixture in the air until it dries, and gently grind it into powder after that. After that, place the powder in open quartz boats at 1300°C for an hour, the finished product will be integrated into a solid form before being powdered again by grinding or milling. Finally, fire that powder in open quartz boats at 570°C, with O$_2$, for 16 hours.

There are 3 steps in the fabrication of green phosphor $\text{NaYF}_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$: mixing, drying, firing. First, mix Na$_2$SiF$_6$ with (Y,YB,Er)F$_3$ that has reached solid form using aqueous nitrate solution and HF solution. Next, leave the mixture to dry before going to the next step. In the firing process, place the mixture in capped Pt crucibles and fire for 2 hours in Ar atmosphere at 630°C. The NaYF$_4$ lattice will be formed once the Na$_2$SiF$_6$ decomposes and NaF fluxes out.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mole %</th>
<th>By weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{YF}_3$</td>
<td>57</td>
<td>100</td>
</tr>
<tr>
<td>$\text{YbF}_3$</td>
<td>39</td>
<td>107.9</td>
</tr>
<tr>
<td>$\text{ErF}_3$</td>
<td>4</td>
<td>10.8</td>
</tr>
<tr>
<td>Na$_2$SiF$_6$</td>
<td>100</td>
<td>226.2</td>
</tr>
</tbody>
</table>

Tab. 2: Chemical composition of green phosphor NaYF$_4\cdot\text{Er}^{3+},\text{Yb}^{3+}$.
Figure 1 shows the two phosphor configurations applied in this research, Fig. 1(a) and Fig. 1(b) are the green-yellow dual-layer phosphor configuration (GYC) with the green phosphor layer placed on the yellow phosphor layer and the red-yellow dual-layer phosphor configuration (RYC) with the red phosphor layer placed on the yellow phosphor layer, respectively. The blue chips are at the bottom of the model and below the two phosphor layers in both phosphor structures. By adjusting the green and red light components in both structures, the suitable setting to improve the color and optical quality of WLEDs will be revealed. The concentration of green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ are also closely monitored.

Figure 2 illustrates the adjustments of yellow phosphor to the fluctuation of green phosphor in GYC structure and red phosphor in RYC structure. In particular, when the concentrations of red or green phosphor increase from 2% to 20% wt, the yellow phosphor concentration must decrease. The purpose of changing the concentration of yellow phosphor YAG:Ce$^{3+}$ is to maintain the correlated color temperature at the average level and to ensure the consistency of the research. On the other hand, the changes in green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ concentrations directly affect the color quality and lumen output of WLEDs, which allows the lighting performance to be easily controlled.

In Fig. 3, we can observe the changes in the emission spectrum when the green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ or red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ is in the composition. In Fig. 3(a), which expresses the emission spectrum of RYC structure, there are three regions in which the intensity rises with the concentration of phosphor: 420 nm - 480 nm, 500 nm - 640 nm, and 648 nm - 738 nm. The growth in spectrum intensity within these regions stimulates the emitted blue light and leads to better color uniformity. In Fig. 3(b), the spectrum intensity of WLED with green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ also rises at 420 nm - 480 nm and 500 nm - 640 nm wavelengths, but remains the same in the wavelength region of 648 nm - 738 nm. The spectral enhancement of GYC structure in these wavelength regions also boosts blue-light scattering and luminous flux. As can be seen from Fig. 3, the spectral intensity is proportional to the color temperature of WLED, which leads to better light output. However, the color quality is in inverse ratio to the light output, therefore, in WLEDs that have high chromatic demand, the luminosity can be slightly decreased.

3. Results and analysis

The color rendering index (CRI) indicates the WLED ability of depicting a color when there are energy flows through, and therefore CRI becomes an important criterion for WLED. To fully evaluate GYC and RYC color rendering index, the CRI of both GYC and RYC structures are measured and displayed in Fig. 4. In
Fig. 3: Emission spectra of RYC (a) and GYC (b).

Fig. 4: The color rendering index as a function of the concentration of Mg$_2$TiO$_4$:Mn$^{4+}$ and NaYF$_4$:Er$^{3+}$, Yb$^{3+}$.

Fig. 4(a), which shows the effect of red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ on color rendering index, CRI increases when red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ concentration moves from 2% - 20% wt.

This result occurs based on the absorption characteristic of red light particles in the red phosphor layer. Particularly, these particles transform the blue light emitted from LED chip into red light and increase the CRI. Through observation, we can see that the yellow light from YAG:Ce$^{3+}$ phosphor is consumed by red light particles as well; however, the amount is less significant to the absorbed blue light. With these two absorption processes, the red light in WLEDs definitely increases when using red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$, so the color rendering index gets benefits from this result. The CRI of GYC structure presented in Fig. 4(b) shows the opposite trend to RYC structure. The diagram suggests that CRI will decline if there is green phosphor NaYF$_4$:Er$^{3+}$, Yb$^{3+}$ in WLED.

Additionally, the more the green phosphor concentration increases the lower the CRI becomes, and this leads to the lowest CRI appearing at 20% green phosphor concentration and damaging the truthfulness of colors from WLED. This reduction is caused by the disproportion between the three colors constituting white light: blue, yellow, and green when the additional green light component from the green phosphor NaYF$_4$:Er$^{3+}$, Yb$^{3+}$ appears. From the content of Fig. 4, it can be concluded that red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ is suitable for WLED with high CRI demand for its ability to balance the color components and low cost.

However, the limitation of CRI accessible aspects is a drawback when comparing it to other quality indicators. Therefore, evaluating WLED performance solely with CRI is not sufficient as there are more elements contributing to the
value of WLED. So, to assess the color quality more thoroughly, a more diverse indicator is needed, and the color quality scale (CQS), which includes color rendering index, preference of viewer, and color coordinate, can fully respond to this requirement. Accordingly, the color quality scales (CQS) in GYC and RYC structures are calculated and can be viewed in Fig. 5. The CQS in RYC structure presented in Fig. 5(a) shows a strong increase when the concentration of red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ rises. This result and the CRI increase in Fig. 4 verify the high color quality of WLED with the presence of red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$. In Fig. 5(b), the CQS in GYC also experiences reduction when the green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ concentration increases. These results can be applied to the manufacturing of dual phosphor layer WLEDs that aim for the color quality scale.

This section presents mathematical equations used to measure the parameters in the research. The following equation is to compute the transmitted blue light and converted yellow light that are used to study for lighting performance development. In single phosphor layer WLED, with the phosphor layer thickness expressed as $2h$, the formula for transmitted blue light and converted yellow light is as follow:

$$PB_1 = PB_0 \times e^{-2\alpha_B h}$$

(1)

$$PY_1 = \frac{1}{2} \frac{\beta_1}{\alpha_B - \alpha_Y} PB_0 \left( e^{-2\alpha_Y h} - e^{-2\alpha_B h} \right)$$

(2)

In dual phosphor layer package with the phosphor layer thickness of $h$, the transmitted blue light and converted yellow light are calculated with the formula below:

$$PB_2 = PB_0 \times e^{-2\alpha_B h}$$

(3)

$$PY_2 = \frac{1}{2} \frac{\beta_2}{\alpha_B - \alpha_Y} PB_0 \left( e^{-2\alpha_Y h} - e^{-2\alpha_B h} \right)$$

(4)

The thickness of phosphor layer is represented by $h$. The subscripts “1” and “2” indicate the structure single layer and dual-layer remote phosphor. $B$ is the conversion coefficient from blue light to yellow light. $(PB)$, $(PY)$, and $PB_0$ in turns, are blue light intensity, yellow light intensity, and the light intensity from blue LED. $\alpha_B$; $\alpha_Y$ are the light loss from the scattering processes in the phosphor layers of blue light and yellow light.

The dual layer phosphor structure results in higher lighting efficiency, compared to that of single layer structure:

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

(5)

The Mie scattering theory is employed to calculate the scattering of the phosphor particles. $Csca$, which is the spherical particles’ scattering cross section, is based on the application of Mie theory [3, 4]. The transmitted light power is measured using the Lambert-Beer law [5]:

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

(6)

Here, the incident light power is indicated by $I_0$, the phosphor layer thickness (mm) is $L$ and $\mu_{ext}$
is the extinction coefficient. The value of extinction coefficient $\mu_{\text{ext}}$ is measured by the following equation: $\mu_{\text{ext}} = N_r \cdot C_{\text{ext}}$. In which, $N_r$ is the number density distribution of particles (mm$^{-3}$). $C_{\text{ext}}$ (mm$^2$) is the extinction cross-section of phosphor particles.

Figure 6: The light output of WLEDs with NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ (a) and Mg$_2$TiO$_4$:Mn$^{4+}$ (b).

Equation (5) shows that dual-layer remote phosphor structure benefits the WLED luminous efficiency resulting in better light output. The detailed luminous efficiencies of both GYC and RYC are presented in Fig. 6. As can be seen, the increase of green phosphor can enhance the light output of WLED, on the other hand, when red phosphor concentration increases, the light output gradually declines. In particular, Fig. 6(a) shows the luminous efficiency of WLED rises with the presence of green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and reaches the highest index when the green phosphor concentration is at 20% wt. On the contrary, Fig. 6(b) shows that when the concentration of red phosphor rises from 2%-20% wt, the luminous efficiency decreases in all ACCTs. This reaction is due to red phosphor that is directly proportional to the extinction coefficient while being inversely proportional to emitted light energy. Despite being disadvantageous to luminous efficiency, red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ greatly contributes to the higher light output in dual-layer remote phosphor structure, compared to that in single-layer phosphor structure. Simultaneously, Mg$_2$TiO$_4$:Mn$^{4+}$ phosphor possesses a more remarkable color quality, therefore, using red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$ still has more benefits.

4. Conclusions

We set up two dual-layer phosphor structures, GYC with the green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ and RYC with the red phosphor Mg$_2$TiO$_4$:Mn$^{4+}$, and observe their influences on the development of WLED lighting performance. The results from experiments confirm that the addition of green phosphor NaYF$_4$:Er$^{3+}$,Yb$^{3+}$ enhances the luminous efficiency, and Mg$_2$TiO$_4$:Mn$^{4+}$ can increase the CRI and CQS values, which can also be applied for WLED with color temperature higher than 8500 K. The remote phosphor structures are simulated in dual-layer remote phosphor WLEDs with measurements based on and verified by the Mie scattering theory and the Lambert-Beer law. Besides the positive effects, the green phosphor and red phosphor could potentially damage the color quality and luminous flux of WLED if their concentrations are too high. The coverage of the research and comparison between different aspects of WLED ensure the reliability of the conclusions, therefore, the manufacturers can rely on the content in this research to create a WLED that matches their needs.
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