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Modifying optical properties of phosphor-in-glass by varying phosphor size and content

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ABSTRACT

Phosphor-in-glass (PIG) has been attracting attention as a stable encapsulant for light-emitting diodes. However, the influence of the phosphor size and content on the morphology and optical properties of PIG must be further studied to achieve the desired color properties by understanding the relationship between the phosphor mixing conditions and the morphology. In this study, two different sizes of YAG:Ce^{3+} phosphors were used in different ratios and total amounts. The optical properties of the PIG samples were measured using an integrating sphere and UV-spectrometer, and cross-sectional scanning electron microscopy images were used to analyze the pore properties. The optical properties of PIG showed linear trends as functions of the pore and phosphor distributions, both of which affect the passage of light. This research shows that the desired color properties can be achieved in PIG by considering the phosphor mixing conditions and the related variations in the morphology.

1. Introduction

The market potential of white-light-emitting diodes (WLEDs) for efficient and environment-friendly lighting sources has been growing, and the use of high-power light-emitting diodes (LEDs) for even higher efficiencies has recently been gaining traction [1]. Currently, the most widely used method to obtain WLEDs is to use a blue LED as the light source with a yellow-light-emitting phosphor as a color-converting material [2]. However, as the LED power increases, commercially used organic encapsulants, such as resin or silicon, deteriorate and show yellowing and degradation because of the strong blue light and the accompanying heat from the package. This degradation reduces their long-term reliability and renders them undesirable as candidates for encapsulants in future high-power LEDs [3].

Attempts to overcome this problem include using various inorganic materials, such as phosphor ceramics [4], glass ceramics [5], and phosphor-in-glasses (PIGs) [6] with good thermal and chemical resistance to replace the commercially used organic encapsulants. Among these materials, PIG is attracting attention for its simple and easy color adjustment ability and ease of fabrication. Several studies have been conducted to achieve the desired optical properties of PIG by modifying the refractive index of the glass [7] as well as the phosphor size, content [8,9], or type [10] in order to improve the performance of PIG encapsulants.

Unlike conventional organic encapsulants, inherent pores exist within PIG encapsulants, which arise from their fabrication process. These pores affect PIG's optical properties owing to an increase in scattering events, even if all the phosphor properties remain the same [11], and the phosphor mixing conditions such as particle size and total contents can change the properties of these pores. However, few studies have been reported on the effect of mixing phosphors with different sizes on PIG properties, where significant differences in the morphology, optical properties, and the transmittance of PIG itself can occur. Since the combined effects of these properties can greatly change the output of the LED package, further studies on how they interact are necessary.

In this study, morphologies of several PIG samples were analyzed with respect to the phosphor size distribution and content to show how these parameters collectively affect the morphology and luminous properties of PIG plates and find the relationships between them. First, YAG:Ce^{3+} phosphors with two different size distributions were mixed with glass frits in different ratios, after which they were sintered. Because the difference in the mixing conditions affects the morphology and pore distribution of the PIG samples, causing their luminous properties, such as correlated color temperature (CCT), color rendering index (CRI), spectrum, and transmittance, to change, a proper understanding of how the phosphor mixing conditions affect the morphology and optical properties of PIG to strategize how to achieve the desired optical properties. By understanding how the phosphor mixing conditions affect the morphology, analyzing the difference caused by changing the mixing conditions enables prediction of the PIG pore

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properties and related trends in the optical properties in order to realize a certain color point.

2. Experimental procedure

Two YAG:Ce^{3+} phosphor powders, each with a peak wavelength of 550 nm but with different d_{50} values of approximately 3 μm and 12 μm (Force4 Co., Ltd., Korea), were used as yellow color-conversion materials. SiO_2-B_2O_3-ZnO-K_2O glass frits with a d_{50} of 15.2 μm (BASS Co., Ltd., Korea) were selected owing to its low glass transition temperature of $T_g = 436$ °C and its low glass softening temperature of $T_s = 610$ °C to prevent the used phosphor powders from deteriorating during the PIG sintering process. The sintering temperature was set to 630 °C, i.e., slightly above the T_s value to increase the wetting of the glass around the phosphor particles, thereby enhancing the densification of PIGs (Fig. 1).

Phosphor particles of different size distributions were mixed into the glass frits in different ratios to obtain a total amount of 3 wt% and 5 wt%. The d_{50} value of the glass frits were 15.2 μm while the d_{50} values of phosphors were 12.5 μm, which was named 12-μm phosphor, and 3.1 μm, which was named 3-μm phosphor. This is shown in further detail in Table 1. These mixed powders were numbered from 1 to 7 based on the phosphor mixing ratio, as described in Table 2.

The PIG mixing samples were prepared by mixing the glass frits and phosphors using a tubular mixer (Model T2F, Glen Mills Inc., USA) for 30 min and then compressing the mixture under 60 MPa in a 32-mm metal mold (Hantech, Inc., Korea). The pressed sample (green body) was then heated to 630 °C at a heating rate of 10 °C/min in a box furnace and sintered for 30 min in an air atmosphere. The sintered samples were allowed to cool naturally to room temperature inside the furnace. Finally, they were polished to a thickness of 500 μm using an auto polisher (METPOL-1 Fuzzypol, R&B, Inc., Korea) for further analysis.

The total transmittance of the prepared samples was measured using a UV–visible spectrometer (UV 2450, Shimadzu Corp., Japan); other luminous properties, such as the CCT, CRI, spectra, and luminous efficacy (lm/W), were measured using a spectroradiometer using an integrating sphere with a diameter of 50 cm (GS-1290-3 Spectroradiometer, Gamma Scientific, USA). Each PIG sample was held at a certain distance from a blue LED chip having a peak wavelength of 456 nm by a hollow reflector cup, which was placed between PIG and the LED chip. Finally, the PIG samples were cut down the middle into two halves, and the morphologies of the cross-sections were examined using a scanning electron microscope (SEM, S-4200, Hitachi, Japan). The SEM results were analyzed using image analysis software (Image-Pro Plus, Version 6.0, Media Cybernetics Inc., USA) to measure the pore cross-sectional area and porosity.

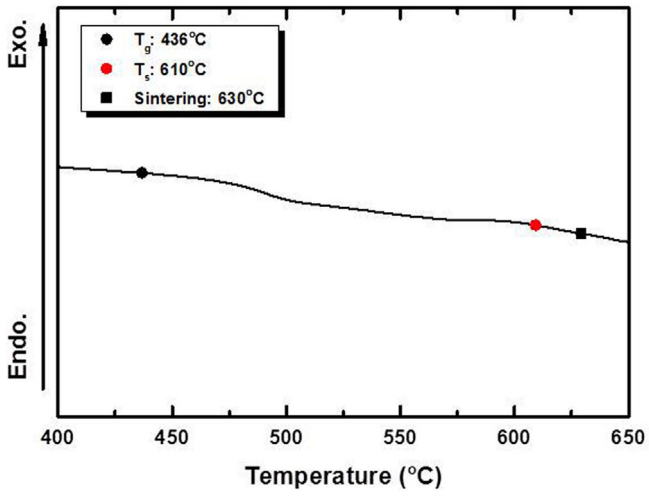

Fig. 1. Differential scanning calorimetry (DSC) thermal points (glass transition temperature (T_g), glass softening temperature (T_s), and sintering temperature of the glass frit).

Table 1
Particle size of the powders.

Powders	Particle size (μm)		
	d_{10}	d_{50}	d_{90}
Glass frit	2.3	15.2	45.6
3 μm phosphor	1.4	3.1	6.7
12 μm phosphor	9.5	12.5	19.1

3. Results

PIGs with 3-wt% YAG:Ce^{3+} showed higher transmittance than those with 5-wt% YAG:Ce^{3+} for both blue and yellow light, regardless of the mixing ratio (Fig. 2(a) and (b)). Furthermore, the transmittance of PIG at the same phosphor content increased linearly as the proportion of 12-μm phosphors in the total phosphor content increased for both blue and yellow light. The glass samples used as references showed significantly higher blue transmittance but a similar yellow transmittance to the 3 wt% sample with 100% 12-μm phosphor content.

The luminous intensities, however, showed different trends for the 3-wt% YAG:Ce^{3+} and 5-wt% YAG:Ce^{3+} samples (Fig. 3). Specifically, the blue light intensity of PIG with 3-wt% YAG:Ce^{3+} showed a dramatic increase in contrast with the yellow intensity with the same samples, which leveled off with the increasing content of 12-μm phosphors, whereas slight increases in both the blue and yellow light intensities were observed in PIG with 5-wt% as the 12-μm phosphor content increased.

As a result of these changes, the CCT and CRI values increasingly differed as the 12-μm YAG:Ce^{3+} phosphor ratio increased for both the 3-wt% and 5-wt% YAG:Ce^{3+} samples (Fig. 4). However, the CCT of each sample group showed significant differences, with the CCT of the 3-wt% YAG:Ce^{3+} samples showing a sharp increase and the CCT of the 5-wt% YAG:Ce^{3+} samples stabilized owing to the different trends in their blue and yellow intensities, as shown in Fig. 3(a) and (b).

The luminous efficacy showed different trends for the 3-wt% and 5-wt% PIG samples: the 3-wt% PIG samples leveled off as the larger phosphor particle content reached 70% (sample no. 5), whereas the 5-wt% PIG samples showed a constant increase under the same conditions (Fig. 5). These different trends were caused by the difference in transmittance and light intensity based on the variations in the phosphor size, amount of phosphor, and morphology related to the voids between the particles. The pore properties, therefore, are also an important factor in interpreting the data and phenomena.

The change in the phosphor content and particle size had a significant effect on the morphology of the PIG samples (Fig. 6). The changes in the morphology were examined by analyzing cross-sectional SEM images of each sample, and the glass matrix, phosphors, and pores were observed in all the PIG samples. The high porosity was observed in the PIG sample with only 3-μm phosphors at total phosphor contents of both 3 wt% and 5 wt%.

Table 2
Phosphor mixing ratios.

Sample no.	Phosphor mixing ratios (%)	
	d_{50}: 3 μm	: 12 μm
1	100	0
2	90	10
3	70	30
4	50	50
5	30	70
6	10	90
7	0	100