Origin of the discrepancy between photoluminescence brightness of TAG:Ce and electroluminescence brightness of TAG:Ce-based white LED expected from phosphor brightness

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A yellow-emitting $Tb_3Al_5O_{12}:Ce^{3+}$ (TAG:Ce) phosphor was coated on blue light-emitting diodes (LEDs) to obtain white LEDs (WLEDs). Since TAG:Ce showed 90% of the brightness of $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce), it was expected that TAG:Ce-based WLEDs showed 90% of brightness of YAG:Ce-based ones. However, the TAG:Ce-based WLED showed 74% of the brightness of YAG:Ce-based one. Considering the density and size of the phosphors, the higher density and larger size of TAG:Ce induced a great deal of sedimentation of TAG:Ce particles in an epoxy resin. It is believed that this is one of main reasons for the reduced optical power of the TAG:Ce-based WLED compared to that of the WLED expected from the brightness of TAG:Ce.

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White light-emitting diodes (WLEDs) have been spotlighted as a new concept of illumination, because LED lamps have the following advantages: high efficiency to convert electrical energy into light, reliability, and long operating lifetime [1]. Typical WLEDs are fabricated by combining a blue LED with a yellow-emitting phosphor. A commercial yellow-emitting phosphor is $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) [2–4]. However, the red spectral intensity of YAG:Ce is weak, and the Commission Internationale de l'Eclairage (CIE) color coordinates of YAG:Ce are in the greenish yellow region on the chromaticity diagram. Therefore, the color rendering property of YAG:Ce-based WLEDs (YAG-WLEDs) is not satisfactory for general illumination. To improve their color rendering property, some researchers introduced a red-emitting activator, substituting elements, or additional red-emitting phosphors, etc. [5–7]. Among these, the use of a $Tb_3Al_5O_{12}:Ce^{3+}$ (TAG:Ce) phosphor is appropriate for the application to phosphor-converted (pc) WLEDs. TAG:Ce shows broad yellow emission, and its color coordinates are in the yellow region [5]. In addition, the photoluminescence (PL) brightness of TAG:Ce is about 90% of that of YAG:Ce. However, when we fabricated WLEDs using TAG:Ce or YAG:Ce, TAG:Ce-based WLEDs (TAG-WLEDs) showed the relative electroluminescence (EL) brightness of 74% of YAG-WLEDs. In this Letter, we considered the causes on the difference between the measured EL brightness of fabricated TAG-WLED and the EL brightness of TAG-WLED expected from PL brightness of TAG:Ce. Since it is difficult to compare the PL brightness of TAG:Ce with the EL brightness of TAG-WLED directly, YAG:Ce and YAG-WLED were used as references.

The synthesis of TAG:Ce and YAG:Ce phosphors was performed by solid-state reaction method [6]. After the synthesis, each phosphor was mixed with an epoxy resin and coated on InGaN-based blue LEDs to fabricate WLEDs. There are several factors that must be considered, such as particle size, concentration, distribution, and encapsulated medium [8]. To compare effects of phosphors on the optical property of pc WLEDs, phosphor concentration, the encapsulated medium, and the shape of encapsulated medium were fixed. In the case of particle distribution, there are three types of distributions: dispersed, local, and remote, as shown in Fig. 1. We used the dispersed distribution. PL spectra of the phosphors were measured by DARSA PRO 5100 PL System (PSI, Korea), and the EL spectra of the WLEDs were analyzed by using the DARSA PRO 5100 PL system with an integrating sphere.

Figure 2(a) shows PL spectra of TAG:Ce and YAG:Ce phosphors. When we calculated relative PL brightness by integrating PL intensities of TAG:Ce and YAG:Ce from 480 to 750 nm employing visual spectral sensitivity, respectively [9], TAG:Ce showed the relative brightness of ~92% of YAG:Ce. Figure 2(b) shows the EL spectra of the TAG-WLED and the YAG-WLED. Although the amount of TAG:Ce coated on the blue LED was the same as that of YAG:Ce, the emission intensity of the yellow band of the TAG-WLED was much weaker than that of the YAG-WLED. The stronger blue band of the TAG-WLED means that TAG:Ce absorbed less blue light from the blue LED than YAG:Ce. When we compared EL brightness by integrating the EL intensity

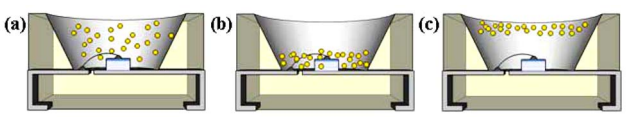

Fig. 1. (Color online) Schematic diagrams of particle distribution in transparent resin: (a) dispersed distribution, (b) local distribution, (c) remote distribution.

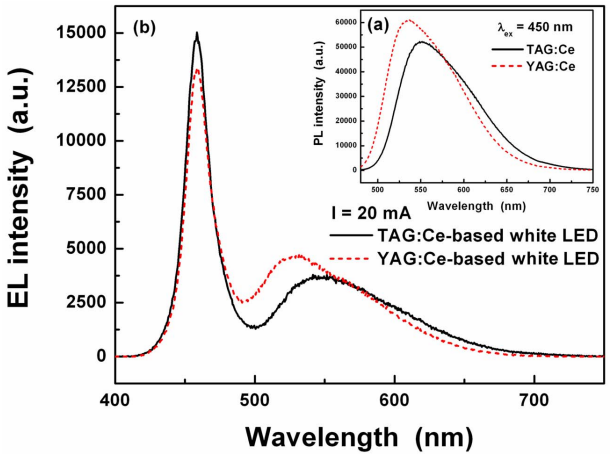

Fig. 2. (Color online) (a) PL spectra of TAG:Ce and YAG:Ce and (b) EL spectra of TAG-WLED and YAG-WLED.

of each WLED from 400 to 750 nm, employing visual spectral sensitivity, the TAG-WLED showed 74% of the brightness of the YAG-WLED. This means that another factor besides the luminescent property of TAG:Ce affected the optical property of the TAG-WLED. Although the same amounts of TAG:Ce and YAG:Ce were coated on the blue LED, the TAG-WLED showed cool white and the YAG-WLED showed natural white. This indicates that TAG:Ce did not efficiently convert blue light from the blue LED into yellow light. In this study, since other factors except the kinds of phosphor were the same, we considered phosphor distribution, which could be changed during the curing of epoxy in the WLED fabrication.

To investigate the distribution of phosphor particles in the TAG-WLEDs and the YAG-WLEDs, we observed cross-sectional images of those WLEDs using a scanning electron microscope (SEM) as shown in Figs. 3(a) and 3(b). The distribution of TAG:Ce particles was not homogeneous, and a lot of TAG:Ce particles were located on the bottom of the reflection cup. On the other hand, YAG:Ce particles were homogeneously dispersed in the reflection cup. To investigate the reason for the difference between the distribution of TAG:Ce and YAG:Ce particles, densities of TAG:Ce

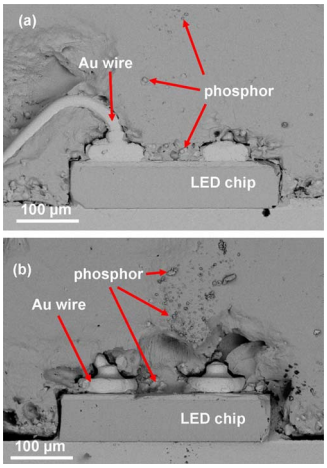

Fig. 3. (Color online) Cross-sectional SEM images of (a) TAG-WLED and (b) YAG-WLED.

and YAG:Ce were first looked into using AccuPyc 1330 (Micromeritics Instrument Corp.). The measured density of TAG:Ce was 6.085 g/cm^3, and that of YAG:Ce was 4.657 g/cm^3. Therefore, it is concluded that TAG:Ce particles settle down faster than YAG:Ce particles during the curing of the epoxy. To compare the sedimentation of TAG:Ce and YAG:Ce more accurately, gravitation and buoyancy should be considered. Because phosphor particles are in the epoxy, buoyant force is expressed by [10]

$$\vec{F}^{Buo} = -\rho_E V\vec{g}, \tag{1}$$

where ρ_E is the density of the epoxy, V is the volume of phosphor particles, and g is the acceleration of gravity. Then, total force that exerts to the sedimentation of TAG:Ce particles in the epoxy is given as

$$\vec{F}_T = M_T\vec{g} + \vec{F}_T^{Buo} = \rho_T V_T\vec{g} - \rho_E V_T\vec{g} = (\rho_T - \rho_E)V_T\vec{g}, \tag{2}$$

where F_T is the total force for TAG:Ce, ρ_T is density of TAG:Ce, M_T and V_T are the mean mass and the average volume of TAG:Ce particles, respectively. To get the mean mass and the average volume of the phosphors, distribution of particle size was measured. The measured and calculated data are summarized in Table 1. Similarly, the total force that is exerted on the sedimentation of YAG:Ce particles in the epoxy is given as

$$\vec{F}_Y = M_Y\vec{g} + \vec{F}_Y^{Buo} = (\rho_Y - \rho_E)V_Y\vec{g}. \tag{3}$$

where F_Y is the total force for YAG:Ce, ρ_Y is density of YAG:Ce, and M_Y and V_Y are the mean mass and the average volume of YAG:Ce particles, respectively. It is obvious that both ρ_T and ρ_Y are larger than ρ_E, because the direction of both F_T and F_Y is the same as that of gravity. Also, ρ_T is larger than ρ_Y, and V_T is larger than V_Y. Thus F_T is larger than F_Y, and faster sedimentation of TAG:Ce particles is expected.

To confirm the sedimentation of phosphor particles, the sedimentation characteristics of TAG:Ce and YAG:Ce were examined using Turbiscan LAB (Formulaction, France). The mixture of phosphor and epoxy in cylindrical tubes was placed in the instrument. Then the backscattering and transmission of light from a light source (λ=880 nm) were periodically measured along the tube height. Typical changes in delta transmission (ΔT, the difference between transmission at a certain time and transmission at an initial time) and delta backscattering (ΔBS, the difference between backscattering at a certain time and backscattering at an initial time) intensities over 7 h are presented in Fig. 4. In the case of YAG:Ce mix-

Table 1. Physical Properties of TAG:Ce and YAG:Ce

Phosphor	Density (g/cm^3)	Mean size (μm)	Average Particle Volume (μm^3)	Mean mass (ng)
TAG:Ce	6.085	21.4	5131.4	31.2
YAG:Ce	4.657	16.7	2395.1	11.2

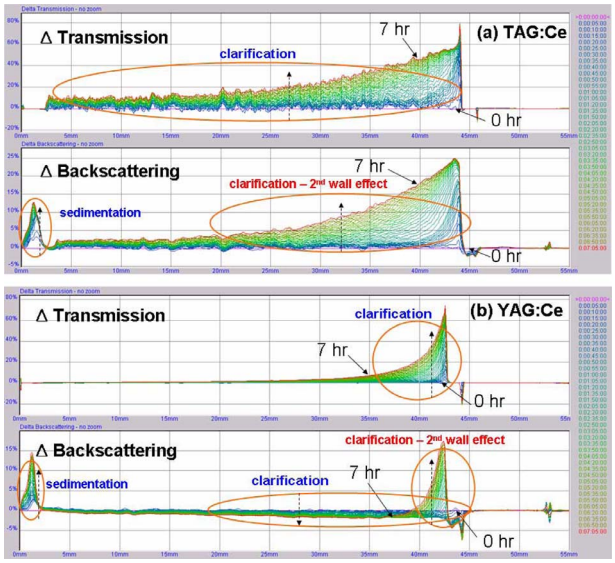

Fig. 4. (Color online) Sedimentation profiles (ΔT and ΔBS) of (a) TAG:Ce and (b) YAG:Ce in the epoxy.

ture, the increase in ΔT at the top of the tube indicates an increase in particle concentration at the bottom of the tube. Clearly, particles have migrated from the top to the bottom of the tube over a 7 h period spent in the measurement. In the case of the TAG:Ce mixture, ΔT increased significantly as time went by. ΔBS intensity decreased by the formation of clarification layer and then increased by reflection on the second wall of the tube (second-wall effect) in the YAG:Ce mixture, while it increased from the initial time by the second-wall effect owing to fast sedimentation in the TAG:Ce mixture. In addition, the change in transmittance versus time was calculated by the embedded software. The sedimentation rates were 17.5 μm/min for TAG:Ce and 3.7 μm/min for YAG:Ce. Consequently, when we coated TAG:Ce on the blue LED, the degree of dispersion of TAG:Ce was not maintained well, while that of YAG:Ce was maintained well during the fabrication of WLEDs.

Most light from the blue LED is emitted toward the top rather than the side. Thus it is believed that much sedimentation of TAG:Ce particles in the WLED induced less absorption of blue light and led to weaker white light compared with the YAG-WLED. In addition, when phosphor particles distribute locally, absorption of the light from the phosphor by the LED chip is large [11]. To reduce the sedimentation of TAG:Ce particles, the remote distribution was used as shown in Fig. 1(c). The TAG-WLED with remote distribution of TAG:Ce particles showed a relative EL brightness of 86% of the YAG-WLED. This indicates that the brightness of the TAG-WLED was improved by 12% owing to improved light conversion from blue to yellow and less yellow light absorption by LED chip.

In summary, the EL brightness of the TAG-WLED was much weaker than that of the TAG-WLED expected from the consideration of the PL brightness of TAG:Ce. Owing to the high density and large size of TAG:Ce, TAG:Ce particles settled down greatly during the curing of the epoxy. The sedimentation of TAG:Ce prevents it from converting blue into yellow light, and it is one of the main causes of lower brightness of the TAG-WLED than the expected brightness. The remote distribution for TAG:Ce in the WLED fabrication enhanced the brightness of TAG-WLEDs by 12%. The results in this study mean that phosphors that have high density and large particle size must be coated remotely to achieve bright pc WLEDs.

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