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Influence of light scattering on luminous efficacy in Ce:YAG glass-ceramic phosphor

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The luminous efficacy of Ce:$Y_3Al_5O_{12}$ (YAG) glass-ceramic (GC) phosphor increased with the increasing crystal size of precipitated Ce:YAG, while the light scattering coefficient decreased. This increase in luminous efficacy can be attributed to the decrease in light scattering loss owing to the decrease in light scattering coefficient with increasing Ce:YAG crystal size. According to Mie scattering theory, the reason for the decrease in the light scattering coefficient is the decrease in light scattering cross-section per unit volume with increasing Ce:YAG crystal size.

Key-words : Ce:YAG, Glass-ceramic, Phosphor, Light scatterin

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1. Introduction

The white light emitting diode (LED) is seen as the next-generation solid state lighting and is rapidly becoming common in daily life. To date, we have developed Ce:$Y_3Al_5O_{12}$ (YAG) glass-ceramic (GC) phosphor for white LEDs using a glass-ceramic process.[1)–2)] Since Ce:YAG micro crystals are precipitated in the glass-matrix phase, good stability at high temperature and high humidity can be expected compared with conventional white LEDs, in which phosphors are embedded in a resin matrix.[3)]

In Ce:YAG–GC, Ce^{3+} ions, incorporated in the *Y* sites of the precipitated Ce:YAG micro crystals, emit yellow fluorescent light when they are optically excited by a blue LED. White light emission can be obtained by mixing the exciting blue light and the fluorescent yellow light. In the emission process of Ce:YAG–GC, light scattering generally occurs at the phase boundary between the precipitated Ce:YAG micro crystals and the glass-matrix phase due to the difference in refractive index. Since the light scattering changes the direction of both the exciting blue light and the fluorescent yellow light, this directly affects the luminous efficacy of Ce:YAG–GC phosphor.

In this study, the interdependence between Ce:YAG particle size, luminous efficacy, and the light scattering coefficient were investigated in order to improve the luminous efficacy of Ce:YAG–GC phosphor. Since the luminous efficacy should be affected by the light scattering, as mentioned above, an understanding of light scattering phenomena is critical for the development of Ce:YAG–GC phosphor with higher luminous efficacy.

2. Experimental

The glass composition of Ce:YAG–GC is 42.5 mol% SiO_2, 20 mol% Y_2O_3, 34 mol% Al_2O_3, 3 mol% Li_2O, and 0.5 mol% Ce_2O_3. The mixed raw materials were melted in a platinum crucible at 1650°C for 2 h. Then, the molten melt was cast into a carbon mold followed by annealing. The glass obtained was crystallized using four kinds of heat treatment: 1380°C 9 h, 1440°C 9 h, 1440°C 36 h, and 1440°C 72 h. Plate-shaped samples with a thickness of 0.4 mm were prepared for all of the following measurements. The samples were polished with a diamond slurry containing 3 μm diamond particles, to obtain a mirror surface.

An electron probe micro analyzer, EPMA (JEOL Ltd., JXA–8900) was used to obtain a back scattered electron image of the Ce:YAG–GC, where precipitated Ce:YAG crystals can be clearly distinguished from the glass-matrix phase. The back scattered electron images were analyzed using image-processing software (MITANI Corporation, WinROOF) to obtain the average geometric cross-section, *A*, and the area ratio of Ce:YAG crystals. The average particle size of the Ce:YAG crystals was calculated from the geometric cross-section, *A*. The area ratio was employed as the number density, *D*,[4)] of the Ce:YAG crystals.

All of the spectral power distributions, $P(\lambda)$, were measured in an integrating sphere with a 10-inch diameter (Labsphere Inc., LMS–100), which was connected to a CCD detector (Ocean Optics, USB2000) with a 400-μm core optical fiber. The current for exciting the blue LED was fixed at 20 mA. A standard halogen lamp (Labsphere, SCL–600, 450 lm) was used for the calibration of this measurement system. Total luminous flux, Φ_v, of the luminescence was calculated from the measured spectral power distribution, $P(\lambda)$, using

$$\Phi_v = K_m \int_{380\,nm}^{780\,nm} V(\lambda)P(\lambda)d\lambda \quad (1)$$

where $V(\lambda)$ is the relative eye sensitivity and K_m is the maximum luminous efficacy at 555 nm, 683 lm/W. Then, the luminous efficacy, η, was obtained by dividing total luminous flux, Φ_v, by the electrical power on the blue LED.

The light scattering coefficient, μ, was derived from Lambert-Beer's law:

$$\mu = -\frac{\log T}{d} \quad (2)$$

where *T* is the transmittance and *d* is the thickness of Ce:YAG–GC plate. Transmittance, *T*, was measured by a spectrophotom-

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eter (Shimadzu, UV3100–PC).

The refractive index, n, of Ce:YAG crystals and the glass-matrix phase was derived from the following equation:

$$n = (\sqrt{r} + 1)/(1 - \sqrt{r}) \quad (3)$$

where r is the reflectance at 550 nm that was measured by the reflective film thickness monitor (Photal, FE–3000).

3. Theory

The light scattering phenomenon of one spherical particle is explained by the Mie theory when the particle size is almost the same or larger than that of the wavelength of visible light. The basis for applying the Mie theory was a publication by G. Mie[5] in 1908, and a detailed description was presented by H. C. van de Hulst.[6] According to the Mie theory, light scattering efficiency, Q, is explained by the following equations as a function of ρ when the ratio of n_1/n_0 is less than two:

$$Q = 2 - \frac{4}{\rho}\sin\rho + \frac{4}{\rho^2}(1 - \cos\rho) \quad (4)$$

$$\rho = 2x\left(\frac{n_1}{n_0} - 1\right), \qquad x = \frac{2\pi a n_0}{\lambda} \quad (5)$$

where n_0 and n_1 are the refractive indices of medium and scatterer, respectively, and a is the radius of scatterer, and λ is the wavelength of the incident light.

Light scattering cross-section for one particle, σ, is explained by

$$\sigma = Q \times A \quad (6)$$

where A is the geometric cross-section of one scatterer.

The calculated light scattering coefficient, μ_s, is explained by

$$\mu_s = \sigma \times D \quad (7)$$

where D is the scatterer number density.

4. Results

4.1 Luminous efficacy, η, and light scattering coefficient, μ, of Ce:YAG–GC

Back scattered electron images of Ce:YAG–GC are shown in **Fig. 1**. Precipitated Ce:YAG particle sizes increased from (a) to (d) with increasing heat-treatment temperature or holding time.

Table 1 shows geometric cross-section, A, particle size, and area ratio of Ce:YAG crystals, which were derived using image-processing software. The geometric cross-section, A, and the particle size increased from (a) to (d), while the area ratio showed little change, remaining at almost a constant value.

Emission spectra of these samples with a thickness of 0.4 mm are shown in **Fig. 2**. The sharp emission band around 460 nm is due to the transmitted blue light from the exciting blue LED, and the broad emission band around 550 nm is due to the fluorescent yellow light from the Ce^{3+} ions in the YAG crystals. Both emission intensities increased with increasing heat treatment temperature or holding time, from (a) to (d). The Ce:YAG particle size dependencies of luminous efficacy, η, and light scattering coefficient, μ, are shown in **Fig. 3**. The luminous efficacy, η,

Table 1. Geometric Cross-Section, Particle Size, and Area Ratio of Ce:YAG Crystals for Each Heat-Treatment Condition

Heat-treatment condition	Geometric cross-section, A ($\times 10^{-12}$ m^2)	Particle size (μm)	Area ratio (%)
(a) 1380°C-9 h	144	14	30
(b) 1440°C-9 h	247	18	34
(c) 1440°C-36 h	485	25	32
(d)1440°C-72 h	688	30	32

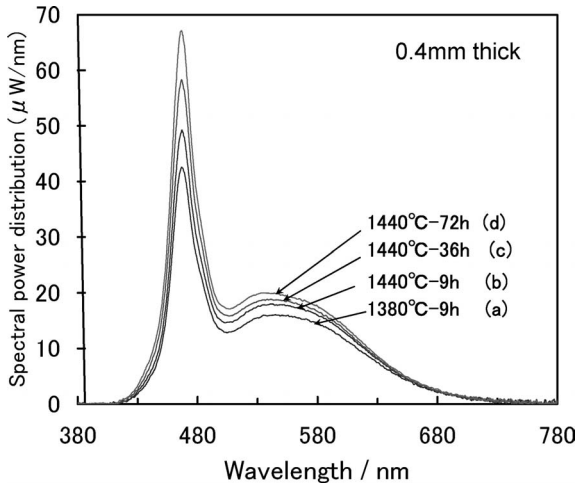

Fig. 2. Emission spectra of Ce:YAG–GC with a thickness of 0.4 mm.

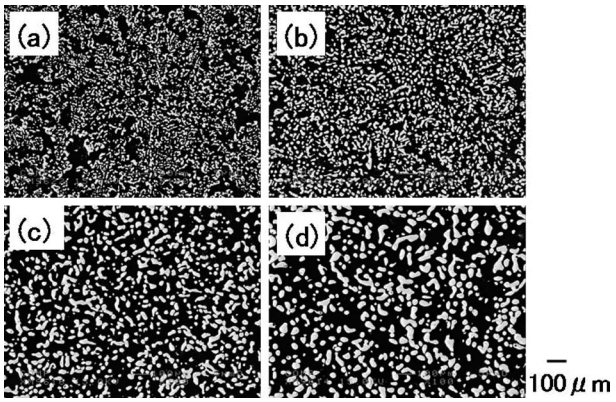

Fig. 1. Back scattered electron images of Ce:YAG–GC, heat-treated with the following heat-treatment profiles: (a) 1380°C 9 h, (b) 1440°C 9 h, (c) 1440°C 36 h, (d) 1440°C 72 h.

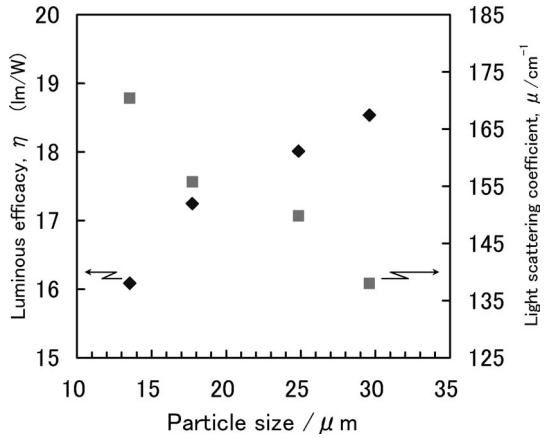

Fig. 3. Luminous efficacy, η, and light scattering coefficient, μ, of Ce:YAG–GC with Ce:YAG particle size.

increased with increasing Ce:YAG particle size while the light scattering coefficient, μ, decreased. The relationship between η and μ is shown in **Fig. 4**, where an approximately linear relationship was observed.

4.2 Light scattering efficiency, Q, and calculated light scattering coefficient, μ_s

The light scattering efficiency, Q, of Ce:YAG–GC was plotted and indicated by square marks on the theoretical value shown by a solid line in **Fig. 5**. In the process of calculation for Q, 380 nm and 780 nm were used as the incident light, λ, for each Ce:YAG particle radius, a. The refractive indices of the glass-matrix phase as a medium, n_0, and the Ce:YAG crystals as scatterers, n_1, were fixed at 1.641 and 1.800, respectively. Q showed almost a constant value of 2.

Figure 6 shows the interdependence between the particle size of the light scattering cross-section, σ, the scatterer number density, D, and the calculated light scattering coefficient, μ_s. Relative values were plotted against the standard values at a particle size of 14 μm. The value of σ increased with increasing Ce:YAG particle size, while D decreased. As a result, the light scattering coefficient, μ_s, calculated as the product of σ and D, decreased with increasing Ce:YAG particle size.

4.3 Comparison of the light scattering coefficients between the observed and calculated values

In **Fig. 7**, the observed light scattering coefficients, μ, are com-

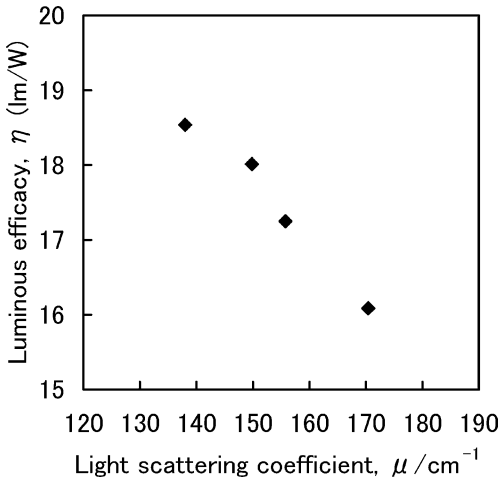

Fig. 4. Relationship between luminous efficacy, η, and light scattering coefficient, μ.

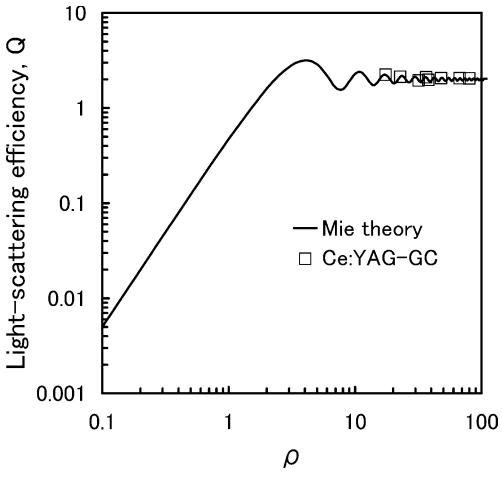

Fig. 5. Light scattering efficiency, Q. Solid line: theoretical curve based on Mie scattering; open squares: experimental plots of Ce:YAG–GC for typical values of wavelength.

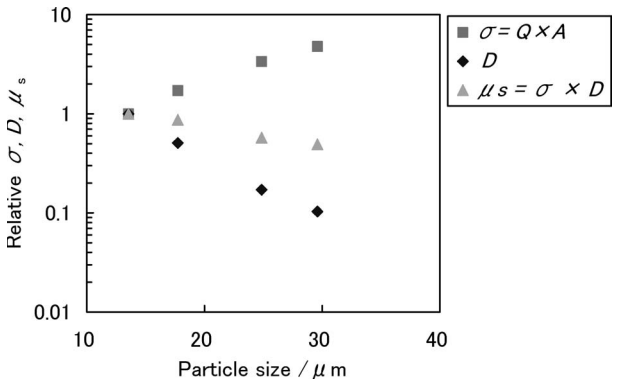

Fig. 6. Calculated relative light scattering cross-section, σ, number density of scatterer, D, and light scattering coefficient, μ_s, with Ce:YAG particle size.

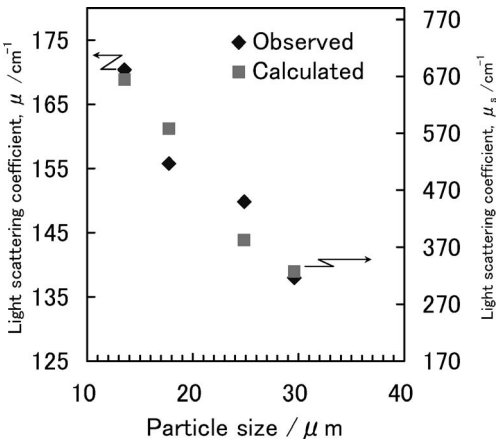

Fig. 7. Comparison between the observed light scattering coefficient, μ, and calculated light scattering coefficient, μ_s, with Ce:YAG particle size.

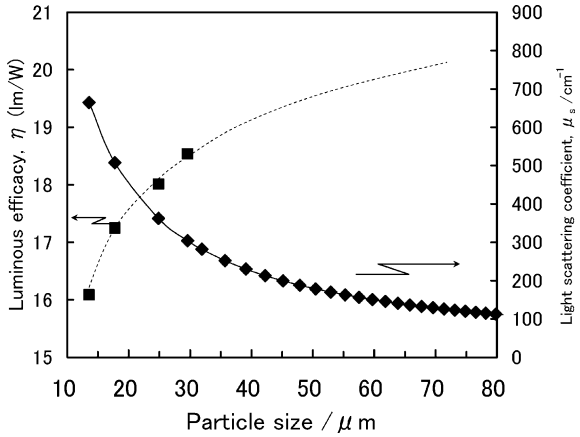

Fig. 8. Luminous efficacy, η, and calculated light scattering coefficient, μ_s, with Ce:YAG particle size.

pared with the calculated light scattering coefficients, μ_s. Although the actual values are different, the same tendency was confirmed in that the light scattering coefficients decreased with increasing Ce:YAG particle size.

Figure 8 shows the dependencies of the luminous efficacy, η, and the calculated light scattering coefficient, μ_s, on the Ce:YAG particle size. The luminous efficacy, η, of Ce:YAG–GC increased with increasing Ce:YAG particle size, while the calculated light scattering coefficient, μ_s, decreased.

5. Discussion

5.1 Influence of light scattering on luminous efficacy

The luminous efficacy, η, of Ce:YAG–GC increased with increasing Ce:YAG particle size, while the light scattering coefficient, μ, decreased, as shown in Fig. 3. Generally, a decrease in light scattering coefficient reduces light scattering loss. Therefore, the increase in luminous efficacy, η, in Ce:YAG–GC can be attributed to the decrease in light scattering loss due to the decreasing light scattering coefficient, μ, with increasing Ce:YAG particle size.

The theoretical light scattering coefficient, μ_s, generally showed a good agreement with the observed value, μ. Therefore, it seems appropriate that the light scattering phenomena of Ce:YAG–GC be explained by the Mie theory. For the differences in actual values between μ and μ_s, several reasons can be considered. One reason for the differences may be due to the nonspherical shape of the Ce:YAG crystals, because the Mie theory is generally applicable to spherical particles. Another reason might be an overestimation of transmittance for the Ce:YG–GC samples, resulting in a small light scattering coefficient. Also, since Ce:YAG–GC is translucent and exhibits very low transmittance less than 1%, some measurement error might be included.

The reason for the decrease in the light scattering coefficient, μ, with increasing Ce:YAG particle size, was considered on the basis of Mie theory. The light scattering efficiency, Q, of Ce:YAG–GC showed almost a constant value, 2, as shown in Fig. 5. This result suggests that one Ce:YAG particle scatters the incident light in twice the area of its geometric cross section, A. Since A increases with increasing Ce:YAG particle size, it is consistent that the light scattering cross section, $\sigma = Q\ (const. = 2) \times A$, also increases.

On the other hand, the number density, D, of the scatterers (Ce:YAG crystals) decreased with increasing Ce:YAG particle size. The area ratio of Ce:YAG crystals exhibited little change as shown in Table 1; therefore, the volume fraction of Ce:YAG crystals also must change in the same manner. In the small volume fraction change, it is consistent that the scatterer number density should decrease with increasing scatterer particle size.

Because the light scattering coefficient, μ_s, can be calculated as the product of σ and D, the decrease in μ_s is attributed to the decrease in the scatterer number density, D, rather than the increase in the light scattering cross section, σ, with increasing Ce:YAG particle size.

5.2 Estimation of the change in luminous efficacy from the calculated light scattering coefficient

The relation between the luminous efficacy, η, and the light scattering coefficient, μ, is almost proportional, as shown in Fig. 4. Therefore, the possible change in luminous efficacy of Ce:YAG–GC can be estimated for larger particle sizes by the tendency of the calculated light scattering coefficient, μ_s as shown in Fig. 8. In the small Ce:YAG particle-size region, the influence of light scattering coefficient, μ_s on the luminous efficacy, η, is much larger than that in large particle-size region. From this consideration, it is suggested that the size of the Ce:YAG crystals has already been optimally adjusted for higher luminous efficacy.

6. Conclusion

This study evaluated the influence of light scattering on the luminous efficacy of Ce:YAG–GC phosphor. The luminous efficacy of Ce:YAG–GC phosphor increased with increasing Ce:YAG crystal size while the light scattering coefficient decreased. The reason for the increase in luminous efficacy can be attributed to the decrease in light scattering loss due to the decreasing light scattering coefficient, μ, with increasing Ce:YAG particle size.

From the calculated light scattering coefficient it appears that the size of Ce:YAG crystals has already been optimally adjusted for higher luminous efficacy.

References

1) S. Tanabe, S. Fujita, A. Sakamoto and S. Yamamoto, *Ceram. Trans*., 173, 19 (2006).
2) S. Fujita, A. Sakamoto and S. Tanabe, *IEEE J. Sel. Top. Quantum Electron*., 14, 1387 (2008).
3) S. Fujita, S. Yoshihara, A. Sakamoto, S. Yamamoto and S. Tanabe, "Fifth Int'l Conf. on Solid-State Lighting," Proc. SPIE, San Diego, Aug. 3 (2005) pp. 594111-1–594111-7.
4) Y. Seimiya, *Res. Bul. Meisei Univ. Fac. Sci. Eng*., 42, 21–24 (2006).
5) G. Mie, *Ann. Phys*. 25, 377 (1908).
6) H. C. van de Hulst, "Light Scattering by Small Particles", Wiley New York (1957).