

YAG glass-ceramic phosphor for white LED (II): Luminescence characteristics

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ABSTRACT

Optical properties of the Ce:YAG glass-ceramic (GC) phosphor for the white LED were investigated. Concentration dependence of fluorescence intensity of Ce³⁺:5d→4f transition in the GC showed a maximum at 0.5mol%Ce₂O₃. Quantum efficiency (QE) of Ce³⁺ fluorescence in the GC materials, the color coordinate and luminous flux of electroluminescence of LED composite were evaluated with an integrating sphere. QE increased with increasing ceramming temperature of the as-made glass. The color coordinates (x,y) of the composite were increased with increasing thickness of the GC mounted on a blue LED chip. The effect of Gd₂O₃ substitution on the optical properties of the GC materials was also investigated. The excitation and emission wavelength shifted to longer side up to Gd/(Y+Gd)=0.40 in molar composition. As a result, the color coordinate locus of the LED with various thickness of the GdYAG-GC shifted to closer to the Planckian locus for the blackbody radiation. These results were explained by partial substitution of Gd³⁺ ions in the precipitated YAG micro-crystals, leading to the increase of lattice constant of unit cell, which was confirmed by X-ray diffraction.

Keywords: white LED, phosphors, YAG, glass-ceramic, Cerium, garnet, Gadolinium

1. INTRODUCTION

With development of high-brightness LEDs, the solid-state lighting technology is getting more and more opportunities in practical stage.¹⁾ The wavelength-converting phosphors in combination with InGaN blue LED are important materials for one-type of white LEDs, because they have less critical issues for applications than other types. For example, the RGB 3-chip LED requires complex control of electronics in order to guarantee a defined color over operating time.²⁾ Among several phosphor-converting white LEDs, YAG-based one originally developed by Nichia has the best performance in terms of efficiency.³⁾ Since the phosphor works by the 5d→4f transition of Ce³⁺ ion (Fig.1), the luminescence spectrum is very broad compared with 4f-4f transitions of most rare-earth ions. In the part I of our papers in this proceeding,⁴⁾ we have shown the development and excellent material properties of YAG-based glass ceramics phosphor. The glass ceramics (GC) show yellow fluorescence due to the Ce³⁺: 5d→4f transition by 460nm excitation, as the powder phosphor of Ce:YAG does. Various advantages of the glass ceramic (GC) phosphor over the powder phosphors for white LEDs have been shown⁴⁾. These glass ceramic materials are expected to be used especially for high power applications because of their excellent physical properties. In order to further improve and optimize the optical properties and luminescence efficiency, it is important to investigate the relationship between preparation condition, microstructures of the GC, and optical properties. In this study, optical properties of the YAG-GC were investigated with different compositions and the effect of Gd₂O₃ substitution of Y₂O₃ was also investigated. Also variations of luminescence spectra, color coordinates of composite white LED were evaluated with an integrating sphere.

It is recognized that one disadvantage of YAG-based white LED for illuminating source is its high correlated color temperature, CCT, typically higher than 6000K; only “cool white” can be obtained. In order to decrease the CCT of a white light source and to obtain “warm white”, it is necessary to move the color coordinate to right-side in the chromaticity diagram by changing the spectral shape in the visible range; increasing the intensity of red component and decreasing that of blue component. Such a method can be realized by increasing the powder content of YAG phosphor in typical YAG-based white LED packages. However, in our materials, it was easily realized simply by changing thickness of GC plate in the composite LED.

2. EXPERIMENTAL

Ce³⁺-doped glasses in SiO₂-Al₂O₃-Y₂O₃ and SiO₂-Al₂O₃-Y₂O₃-Gd₂O₃ systems were prepared by melting a mixture of raw materials in a platinum crucible at 1500°C ~1650°C for 5h in an electric furnace. The obtained glass was crystallized at temperatures ranging from Tx to Tx+120°C for the prescribed time of period, where Tx is a typical ceramming temperature in this study.

A crystalline phase in the glass-ceramic was identified by XRD measurement and the lattice constant was estimated from the Miller index of diffraction peaks, diffraction angles and wavelength of X-ray.

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

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

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

For the calibrated luminescence spectra of all the samples, the color coordinates (x, y) of CIE-1931 chromaticity diagram were obtained with the Irrad-C software of Ocean Optics.

3. RESULTS AND DISCUSSION

3.1. Concentration dependence of emission intensity of Ce³⁺ in glass ceramics

Ce₂O₃ concentration dependence of emission intensity at 540nm in the YAG-GC is shown in Fig.2. It shows a maximum at 0.5mol% Ce₂O₃. This value is lower than that of Ce:YAG powder phosphor. In this study, the Ce₂O₃ concentration of the samples is fixed to be 0.5mol%.

3.2. Electroluminescence spectra of composite LED

Variation of electroluminescence spectra of composite LED with different GC thickness is shown in Fig.3. The 465nm band is due to the emission of the blue LED and broad emission band around 550nm is due to the fluorescence of the GC excited by the blue LED. The latter spectrum is almost the same as that of the Ce:YAG powder phosphor.

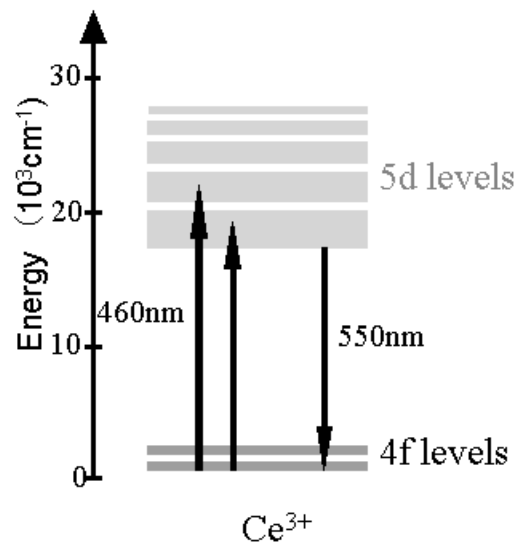


Fig.1. Energy level diagram of Ce³⁺ ion.

It can be seen that the intensity of the blue LED decreased with increasing GC thickness. On the other hand, that of the yellow emission band increases and saturates at around 1mm thickness.

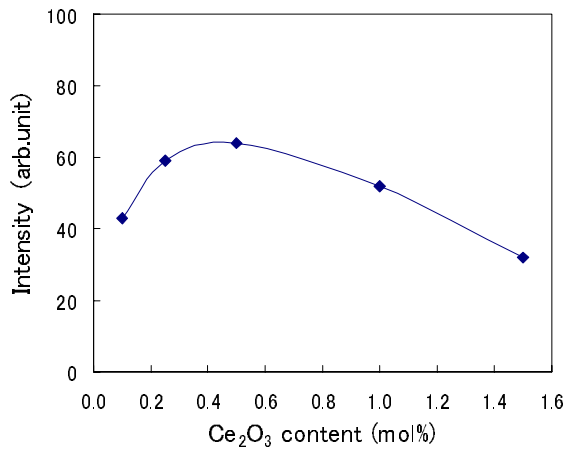


Fig.2. Ce-concentration dependence of emission Intensity of the YAG-GC.

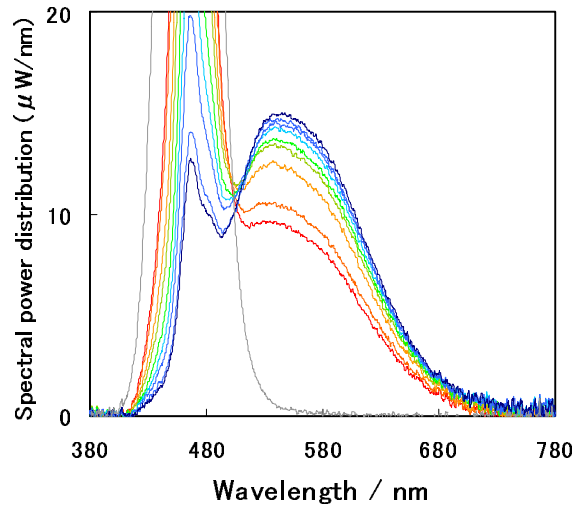


Fig.3. Variation of spectral power distribution of composite LED with different GC thickness.

3.3. Quantum efficiency of GC

The quantum efficiency of Ce^{3+} emission in GC materials was evaluated by the following procedure. The spectral power distribution and total radiant flux of a blue LED, which is used for the excitation source of GC are measured in the integrating sphere. The abscissa of distribution spectra is converted to wavenumber (cm^{-1}) for accurate deconvolution of widely broadened spectra. By dividing the $P(\nu)$ (mW/cm^{-1}) in the distribution spectra (ordinate) with photon energy, $h\nu$ (J) at each wavenumber, the spectral distribution of number of photons per second $N(\nu)(cps/cm^{-1})$ can be obtained. Those of LED composite are also measured, where a GC plate is mounted on the blue LED chip. The obtained spectrum can be deconvoluted into two components; transmitted blue light from excitation LED and fluorescence from the GC plate as shown in Fig.4. By subtracting the $P(\nu)$ spectrum of the blue LED and blue component of LED composite, the absorbed photon number, N_{abs} can be estimated by integrating the distribution with wavenumber. The emitted photon number, N_{em} can also be evaluated by integrating the fluorescence component of the LED composite. The quantum efficiency QE is defined by

$$QE = N_{em} / N_{abs} \quad (2)$$

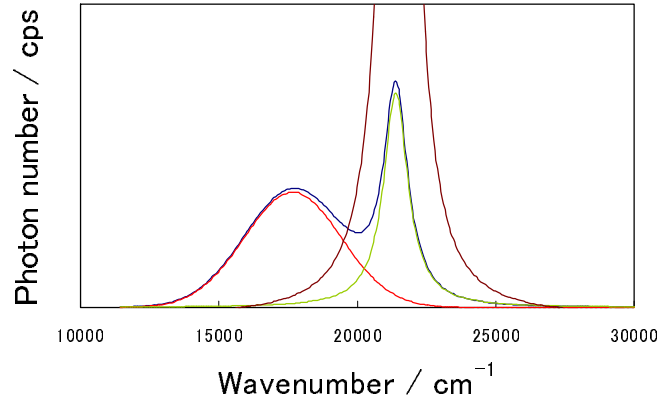


Fig.4. Deconvolution of electroluminescence spectrum of composite white LED.

Fig.5 show the thickness dependence of evaluated QE of a YAG-GC cerammed at temperature of Tx. Although the obtained spectra change with GC thickness as shown in Fig.3, the η calculated is almost constant at about 28% independent of GC thickness. The apparent QE shows small value at thickness less than 0.4mm. This is probably due to the effect of reflection at the GC surface, which results in overestimation of the absorbed photon numbers. The effect of surface reflection can be negligible with samples with enough thickness.

Fig.6 show the ceramming temperature, Tcr dependence of the QE of the YAG-GC materials with different thickness. As shown in Fig.5, the QE is almost independent of GC thickness from 0.4mm to 0.6mm. The QE increases with

increasing ceramming temperature. This result is probably due to the decrease of concentration of some defect in microcrystals with increase of crystalline size after crystal growth. The QE of the GC is nearly 40% at $T_{cr}=T_x+120^\circ\text{C}$

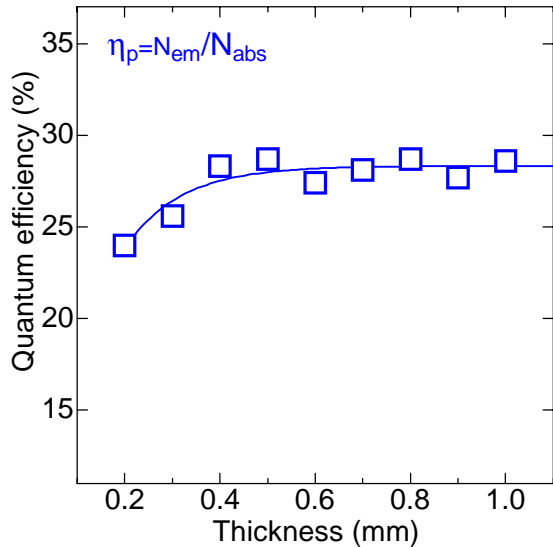


Fig.5. Thickness dependence of apparent quantum efficiency of GC($T_{cr}=T_x$)

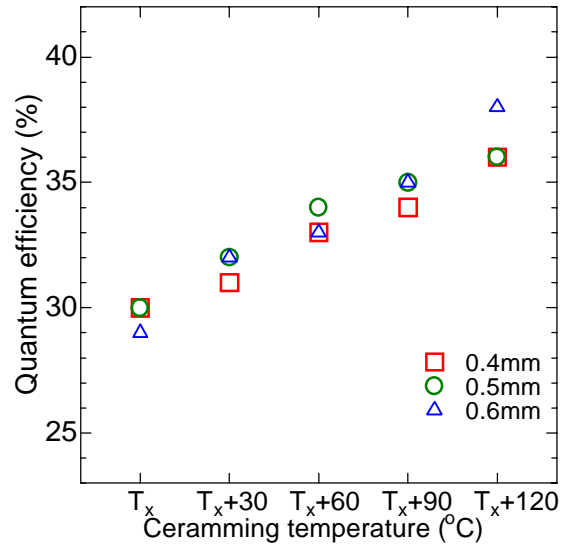


Fig.6. Ceramming temperature dependence of quantum efficiency of GC with different thickness

3.4. Effect of Gd substitution

In order to investigate the possibility of improvement of spectral characteristics, the GC materials, the composition of which contains Gd_2O_3 with various contents were prepared. In the glass composition, 40% of Y_2O_3 was substituted with Gd_2O_3 at maximum. Fig.7 shows the excitation and emission spectra of the YAG-GC and GdYAG-GC materials. In the composition of the GdYAG-GC sample, the molar ratio of $\text{Gd}/(\text{Y}+\text{Gd})=0.40$. We can see that both excitation and emission bands shift to longer side by Gd substitution. This result is consistent with the tendency of wavelength shifts for the powder phosphors of $(\text{Y}_{3-x}\text{Gd}_x)\text{Al}_5\text{O}_{12}$.

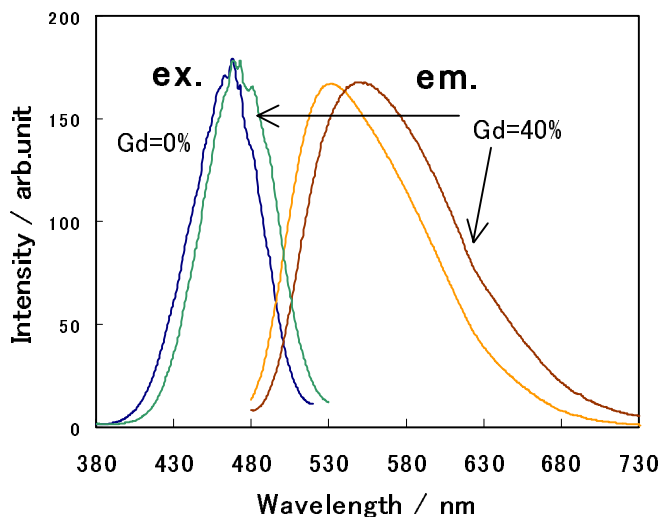


Fig.7. Excitation and emission spectra of YAG-GC and GdYAG-GC.

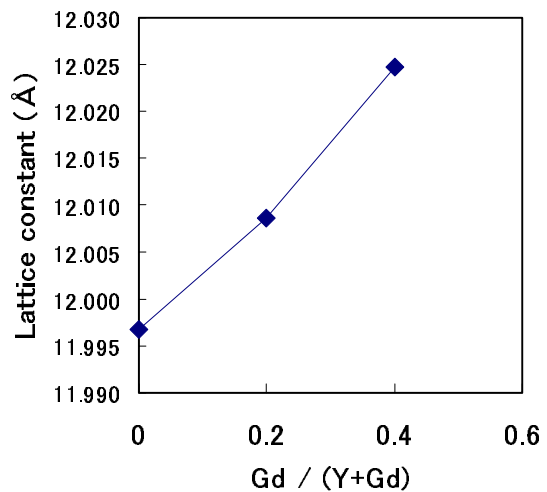


Fig.8. Gd content dependence of lattice constant of garnet micro-crystals in GCs.

Fig. 8 shows the compositional dependence of the lattice constant of garnet microcrystals estimated by XRD. For the YAG-GC, where $Gd/(Y+Gd)$ is zero, the value of the lattice constant is slightly smaller than that of the pure $Y_3Al_5O_{12}$ crystal ($a_0=12.009\text{\AA}$). With increasing Gd content, the lattice constant increases up to 12.025\AA at $Gd/(Y+Gd)=0.40$. Since the ionic radius of Gd^{3+} (1.05\AA) is larger than that of Y^{3+} (1.02\AA for eight-fold coordination), the partial substitution of Y-site with Gd^{3+} ions in the garnet microcrystals in the GdYAG-GC materials must be a reason for the increase of lattice size.

Fig.9 shows the compositional dependence of the emission peak wavelength. It increases monotonically with increasing Gd content. With Gd substitution of Y-site of YAG structure, the ligand fields of doped Ce^{3+} ions are expanded resulting in the energy change of 5d-orbital. Red shift of emission wavelength is probably related to the increase of 10Dq splitting of 5d-orbitals, leading to the decrease of energy difference between 5d and the ground 4f levels. For the GdYAG-GC with $Gd/(Y+Gd)=0.40$, the peak wavelength was 554nm , which is shorter than that of the powder phosphor of $Y_{1.8}Gd_{1.2}Al_5O_{12}$. This result indicates that $Gd/(Y+Gd)$ in the microcrystals are smaller than that of the batch composition of mother glass. Therefore, some amount of Gd^{3+} exists in the silicate glass matrix. Further increase of Gd^{3+} fraction in the crystalline phase would shift the emission wavelength to still longer side.

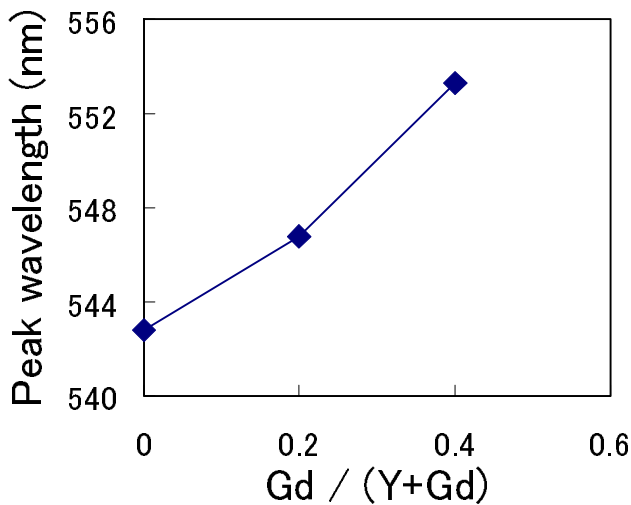


Fig.9. Gd content dependence of peak wavelength Of emission spectra of GdYAG-GC.

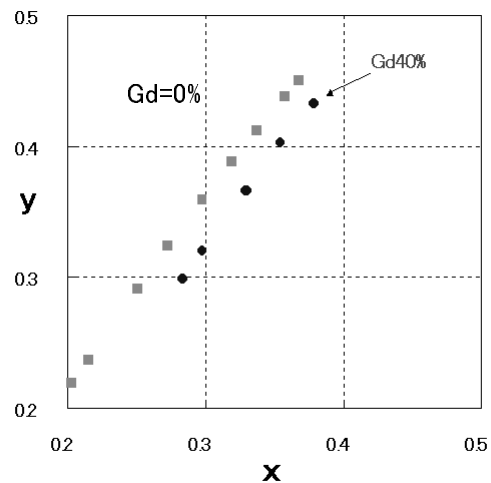


Fig.10. Variation of color coordinates of composite LED with YAG- and GdYAG-GC.

3.5. Variation of color coordinates of composite LED

Fig.10 shows the variation of color coordinates (x,y) of composite LEDs with different thickness of GC for YAG and GdYAG. Both x and y increase with increasing thickness and a typical white color was obtained with thickness ranging from 0.4mm to 0.8mm . This tendency can be explained the spectral change observed in Fig.3, where the intensity of 460nm band is decreased and that of 550nm band is increased with increasing GC thickness. While the value of y is much larger than x for the YAG-GC, both values are more similar for the GdYAG-GC. This tendency is consistent with the wavelength shift of GdYAG-GC to longer side, observed in Fig.6.

It is recognized that one disadvantage of YAG-based white LED for illuminating source is its high correlated color temperature, CCT, typically higher than 6000K ; only “cool white” can be obtained. In order to decrease the CCT of a white light source and to obtain “warm white”, it is necessary to move the color coordinate to right-side in the chromaticity diagram by changing the spectral shape in the visible range; increasing the intensity of red component and decreasing that of blue component. Such a spectral modification cannot sufficiently be realized by increasing the powder content of YAG phosphor in typical YAG-based white LED packages. However, in our materials, it can be realized simply by changing thickness of GC and its composition. For realization of a warm white LED, development of GC phosphor material with orange emission is expected.

4. CONCLUSIONS

Optical properties of Ce³⁺-doped YAG glass ceramics were investigated with an integrating sphere. The quantum efficiency of Ce³⁺ emission in the GC was estimated to be about 30%, which was improved by increasing ceramming temperature of mother glass. Peak shift of emission wavelength to longer side was observed for the samples with larger Gd₂O₃ content. The increase of lattice constant of the garnet microcrystals were confirmed, which results in the energy change of 5d orbital of doped Ce³⁺ ions in the Y-site of YAG. The color coordinate of the composite LED was widely varied simply by changing the thickness of GC plate. The Gd-substituted GC materials can realize color coordinates closer to “warm white”. It is expected that this newly developed glass-ceramic phosphor is a promising candidate for the realization of simple and compact white LED devices, especially for high-power applications.

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