Enhancement of photoluminescence of glass phosphor by nanoimprint of moth-eye structure

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We demonstrated that a moth-eye surface pattern on the luminous inorganic glass could enhance the photoluminescence (PL) intensity notably. A moth-eye pattern of a square array of cones at pitch of 250 nm was fabricated on Eu³⁺-doped MgF₂–MgO–BaO–B₂O₃ glass by thermal nanoimprinting at 520°C. A simulation with rigorous coupled-wave analysis demonstrated that the surface structure could reduce the surface reflectance in the optical input for the excitation wavelength λ of 405 nm, i.e., −1.1% for p-polarized light, 10.6% for s-polarized light, and 4.1% for non-polarized light in total of a half round angle for the irradiation from a surface light source. The angularly dependent PL of the excitation angle on the nanoimprinted glass was measured by an excitation of UV laser diode (λ = 405 nm). The enhancements of ~8% for p-polarized light and ~9% for s-polarized light were observed at the incident angle = 5°.

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Highly efficient phosphors have been strongly required for practical applications of solid-state lightings such as white LEDs (WLEDs), displays, and wavelength converters for solar cells. For instance, most WLEDs have been obtained by combing blue LEDs and yellow phosphors such as Ce-doped Y₂Al₅O₁₂ (YAG:Ce), where the crystal powders are dispersed into a resin matrix. Recently, the demand for higher power WLEDs has been increasing; therefore, the low thermal conductivity and degradation of resin by the heat are becoming a problem. To overcome this, transparent inorganic phosphors comprising transparent ceramics, glass-ceramics, and glasses have been proposed. Transparent ceramics, glass-ceramics, and nanocrystals such as rare earth (RE) -doped YAG and fluoride nanocrystals have received much attention because of their excellent transparency and photoluminescence (PL) properties. Highly efficient PL in glasses has been also reported. Recently, Shinozaki et al. proposed that the new oxyfluoride glasses of Eu³⁺-doped BaF₂–Al₂O₃–B₂O₃ system exhibit highly efficient red PL of Eu³⁺ up to the quantum yield of 97%. These transparent phosphors generally have high refractive index; e.g., the refractive index of YAG is ~1.82. This leads to a high optical reflectance at the surface, which impedes the efficient-incoupling of the excitation light into the phosphor and outcoupling of the emission light out of the phosphor.

Nanostructuring on the surface of the phosphor is a sensible way of reducing in- and out-coupling loss. Anti-reflective moth-eye structures have been used to reduce the reflection loss and investigated for transmitting, refracting, and light emitting devices. For instance, it has been proposed that the total internal reflection in LED chips could be reduced by growing a light-emitting GaN layer on moth-eye patterned sapphire substrate (MPSS) with sub-micrometer scales structure as a substrate for the GaN thin film. It has also been pointed out that the moth-eye structure allows the extraction of light output from a smaller angle because of the diffraction effect. Recently, Kondo et al. proposed that LEDs with an MPSS could enhance the transmittance of blue light at the GaN/sapphire interface and exhibit a 1.89 times higher light output compared to LEDs on flat sapphire substrates. Cho et al. made a moth-eye patterned polymer thin film containing YAG:Ce powders on an LED chip to reduce the reflection loss at the LED surface, resulting in the PL intensity increased up to 13.9%. Moth-eye structures on silica glasses and transparent ceramics have also been studied, especially for the realms of lenses and lasers, for the reduction of reflection losses and enhancement of the laser damage thresholds. Conventionally, surface nanopatterns on ceramics have been produced by resist patterning on the surface by using electron beam lithography followed by dry etching. Thermal nanoimprinting would be an effective way of surface nanopatterning in terms of production rate and reproducibility. By using molds made of thermally stable materials such as SiC and C, nanoimprinting at high temperatures has been demonstrated for inorganic glasses to achieve reduced reflectance, polarization-independent diffraction, polarization splitting, and phase control.

In this work, we fabricated a moth-eye pattern on a glass phosphor using the thermal nanoimprint technique for the first time, and the impact on PL intensity was proposed with both experimental and simulation approaches. We developed an Eu³⁺-doped oxyfluoride glass that is highly luminous and possesses thermal properties suitable for thermal nanoimprinting. It is known that Eu³⁺ ions in glasses exhibit sharp PL spectra because of f–f transition by the excitation of near-UV light. The sharp PL peak allows for easy comparison of the experimental results and simulated optical transmission; therefore, the present glass is a
suitable model for investigating the impact of the nanopattern on PL intensity. A significant enhancement in PL intensity by nanoimprinting on the surface of a glass phosphor is firstly demonstrated in this study.

Glass phosphors of 2.9Eu₂O₃–33.0BaO–18.9MgF₂–18.9MgO–26.3B₂O₃ (in mol %) (EuBMBF glass) were investigated in this work. Highly pure (at least 99.99%) powders of Eu₂O₃, BaCO₃, MgF₂, MgO, and B₂O₃ were well mixed. The batch, 20 g, was placed in a platinum crucible and melted at 1100°C for 20 min in air in an electric furnace. The melts were poured onto an iron plate and press-quenched into a thickness about 3 mm by another iron plate. The obtained glasses were polished to a thickness of 2.5 mm and mirror-finished using CeO₂ powders. The glasses were cut into 10 × 10 mm² square for nanoimprinting. Differential thermal analysis (DTA) of glass was carried out to determine its glass transition (Tg), crystallization onset (Tc), and crystallization peak (Tm) temperatures. The refractive index (n) of the glass at a wavelength of λ = 632.8 nm (He–Ne laser) at room temperature was measured with a prism coupler (Meticon Model 2010).

A SiC mold plate of 25 × 25 × 2 mm³ with two-dimensional 250 nm, periodic sinusoidal cone patterns (moth-eye) with a height of 130 nm in 6 × 6 mm² area was fabricated by the same process as reported in another paper. The moth-eye pattern was imprinted on the polished glass by a pressing machine (GMP-311V, Toshiba machine Co., Ltd.) with carbon-coated molds. The optically flat SiC mold and patterned SiC were set onto upper and lower sides, respectively. Nanoimprinting was carried out at 520°C for 120 s in vacuum. Applied force onto samples was 2 kN (~20 MPa), and then the glass was pressed into 1.42 mm thick (hereafter “nanoimprinted sample”). For the reference, a glass was pressed by optically flat SiC molds in the same condition, and then pressed into 2.38 mm with flat surfaces both side (hereafter “flat sample”). The surface of the nanoimprinted sample with an area of 2 μm² was observed with an atomic force microscope (MultiMode8, Bruker).

The PL spectra were measured with controlled incident (θin) and emission (θem) angles at room temperature. A laser diode (LD) with λ = 405 nm was used as the excitation source. We measured the PL intensity, I, as functions of λ and θem(θin, θem), where λ is the wavelength of emission light. The linearly polarized output from the LD was incident on the nanoimprinted surface of the sample (spot diameter = 2 mm). The PL spectra were collected from the opposite side by a fiber-coupled CCD spectrometer at a fixed angle of θin = 0° while θem was varied in the z-x plane [see Fig. 1(a)].

The structure model used for all simulations was 130 nm high and had a squarely arranged sinusoidal cone period of 250 nm [see Fig. 1(a)]. Rigorous coupled-wave analysis (RCWA) was carried out with DiffractionsMOD (RSoft Design Group, Inc., USA). The transmission of the glass (n₁ = 1.61) with the surface structure, T, and that of the flat sample as a reference, Tref, were simulated as a function of θin. The wavelength of λ = 405 nm as the optical input light was used for the simulation.

The thermal properties and refractive index n₁ of the glass are Tg = 473°C, Tc = 532°C, and n₁ = 1.614. Brewster’s angle (θB) for the flat sample was calculated as θB = 57° with the following equations:

\[
\theta_B = \arctan(n_1/n_0)
\]

where n₀ is the refractive index of air. Thermal nanoimprinting requires a low viscosity, usually lower than that at glass transition temperature. To avoid crystallization, thermal nanoimprinting should be carried out below Tc. Distinct nanoimprinting patterns were obtained on the glass surface by pressing at 520°C. The AFM image of the nanoimprinted sample surface clearly shows the moth-eye pattern [Fig. 1(b)]. The pitch and height of the pattern were 250 and about 100 nm, respectively.

The simulated transmittance of the nanoimprinted sample, T(θin), and that of the flat sample, Tref(θin), are plotted in Fig. 2(a). The transmittance increases because of the pattern, e.g.,
The value for non-polarized light was given in the normal incidence, indicating that the pattern works as an anti-reflection structure. $T_{em}(\theta_m = 57^\circ)$ is unity for p-polarized light, corresponding to the Brewster’s angle. $T(\theta_m = 57^\circ)$ for p-polarized light is less than unity, implying that the moth-eye pattern affected the Brewster condition. For the s-polarized light, $T(\theta_m)$ was larger than $T_{em}(\theta_m)$ for all the $\theta_m$ calculated. The enhancement in transmittance in total of a half round angle by the surface structure for the irradiation from a large surface light source, $\eta_T,$ was calculated from the following equation:

$$\eta_T = \frac{\int_0^\alpha 2\pi T(\theta_m) \sin(\theta_m) d\theta_m - \int_0^\alpha 2\pi T_{em}(\theta_m) \sin(\theta_m) d\theta_m}{\int_0^\alpha 2\pi T_{em}(\theta_m) \sin(\theta_m) d\theta_m}.$$

(2)

The simulated enhancements by the surface pattern are $-1.1\%$ for p-polarized light, $10.6\%$ for s-polarized light, and $4.1\%$ for non-polarized light. The value for non-polarized light was given by average of the values of transmittance for p- and s-polarized lights. The disturbance of Brewster condition decreases the transmittance in p-polarized light; in contrast, the pattern significantly enhances it in s-polarized light. $T(\theta_m)$ drops at $\theta_m = 38^\circ$, which corresponds to the $\theta_m$ where the peak appears in $R(\theta_m = 613 \text{ nm}, \theta_m)$ [see Fig. 2(b)]. The transmittance attributed to a diffraction of $(-1, 0)$ is also shown in Fig. 2(a). For the nanoimprinted model, both transmittances of p- and s-polarized lights have a peak at $\theta_m = 38^\circ$, and they decrease after the peak.

Figure 3 shows $R(\lambda_m, \theta_m)$ collected at a fixed angle of $\theta_m = 0^\circ$ by irradiating s-polarized light. The sharp peaks at $\lambda_m = 590, 613, 655,$ and $700 \text{ nm}$ are assigned to the $\bar{3}D_0 \rightarrow \bar{3}F_1, \bar{3}F_2, \bar{3}F_3$, and $\bar{3}F_4$ transitions, respectively. The peak intensities of the PL spectra were measured by changing $\theta_m$. In Fig. 2(b), we plotted the intensity of the main peak at $\lambda_m = 613 \text{ nm}$ ($\bar{3}D_0 \rightarrow \bar{3}F_2$ transition) as a function of $\theta_m$ [$R(\lambda_m = 613 \text{ nm}, \theta_m)$] at $\theta_m = 0^\circ$. PL intensities are normalized by their thickness and the PL intensity of $I_{em}(\lambda_m = 613 \text{ nm}, \theta_m = 5^\circ)$ for the nanoimprinted sample, the PL intensity of s-polarized component is higher than those from the flat sample until higher angles. A peak is observed at $\theta_m \sim 38^\circ$ in both the p- and s-polarized lights, and is particularly large in s-polarized light. The experimental enhanced angle of PL is coincident with the simulated enhanced angle of the transmittance. At $\theta_m = 5^\circ$, the enhancement of PL intensity was $9\%$ for s-polarized light and $0\%$ for p-polarized light irradiations. The increase of transmittance for s-polarization is $4\%$ from Fig. 2(a); therefore, the increase of transmittance should have a notable impact on the increase of the PL intensity. The enhancement in emission by the surface structure, $\eta_{PL},$ was calculated from the following equation:

$$\eta_{PL} = \frac{\int_0^\alpha 2\pi I_{em}(\lambda_m, \theta_m) \sin(\theta_m) d\theta_m - \int_0^\alpha 2\pi I_{em}(\lambda_m, \theta_m) \sin(\theta_m) d\theta_m}{\int_0^\alpha 2\pi I_{em}(\lambda_m, \theta_m) \sin(\theta_m) d\theta_m}. \tag{3}$$

The experimental enhancements by the surface pattern are $10.6\%$ for p-polarized light, $17.0\%$ for s-polarized light, and $13.8\%$ for average of s- and p-polarized lights. The reduction of transmission loss by the anti-reflection structure and diffraction effect increase the optical input intensity of the excitation light, resulting in enhancement of PL intensity. It also indicates that the optimal $\theta_m$ would be tunable with controlling the pitch and arrangement of the cones. Until now, we just accounted for effect of transmittance. The impact of the effect for optical output, absorbance, quantum yield, optical path such as thickness and shape, and optical loss from sample edge because of the critical angle should be considered in the future.

In summary, the impact of moth-eye surface pattern on the PL properties was investigated for a Eu$^{3+}$-doped MgF$_2$–MgO–BaO–B$_2$O$_3$ glass phosphor. A moth-eye pattern of approximately 100 nm in height having squarely arranged cones of 250 nm in pitch was fabricated by thermal nanoimprinting at 520°C. The RCWA simulation indicates that the transmittance in incident light ($\lambda = 405 \text{ nm}$) increased with the use of the moth-eye pattern. From the simulation, the transmittance for the incident light ($\lambda = 405 \text{ nm}$) is enhanced by the pattern, i.e., $-1.1\%$ for p-polarized light, $10.6\%$ for s-polarized light, and $4.1\%$ for non-polarized light. The experimentally obtained enhancements of PL intensities in the nanoimprinted sample are $0\%$ for p-polarized light and $9\%$ for s-polarized light compared to that of the flat sample. It is worth pointing out that as the decrease in reflection at the interface is more notable when the refractive index contrast is higher, this technique would be more effective for the glasses with a higher refractive index.

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