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Terbium-activated heavy scintillating glasses

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Abstract

Tb-activated scintillating glasses with high Ln_2O_3 (Ln=Gd, Y, Lu) concentration up to 40mol% have been prepared. The effects of Ln^{3+} ions on the density, thermal properties, transmission and luminescence properties under both UV and X-ray excitation have been investigated. The glasses containing Gd_2O_3 or Lu_2O_3 exhibit a high density of more than 6.0g/cm^3. Energy transfer from Gd^{3+} to Tb^{3+} takes place in Gd-containing glass and as a result the Gd-containing glass shows a light yield 2.5 times higher than the Y-or Lu-containing glass. The Effect of the substitution of fluorine for oxygen on the optical properties was also investigated.

1. Introduction

Glasses actived with rare earth ions are promising alternatives to single crystals and ceramic scintillators for applications in high energy physics, in X-CT for industrial and medical areas. The main advantages of the glasses scintillators lie in the possibility of being produced with low cost and being easily manufactured to desired size and shape, such as fibers. Among the properties required for most of the applications, for an example, for X-CT application, the density of the scintillators is very important because the high density could result in an increased X-ray absorption across section, thus significantly increasing the image signal-to-noise. However, the density of the existing glass scintillators is low below 4 g/cm^3 [1, 2]. Although the density of the glasses can be easily increased to more than 6.0 g/cm^3, which is desirable for most applications, by the introduction of some heavy components such as PbO, Bi_2O_3, this is often accompanied by a dramatic decrease in the luminescence response of rare earth ions.

Introduction of heavy metal oxides Gd_2O_3, Y_2O_3, Lu_2O_3 can be expected to increase the density of the glasses. Moreover these oxides are main host components of some commercial scintillators such as Gd_2SiO_5:Ce, Lu_2SiO_5:Ce singles and $(Y, Gd)_2O_3$: Eu, Gd_2O_2S:Tb ceramics [3-6]. However, to the present authors' knowledge, effects of these oxides at high concentration of more than 30mol% in glasses on the scintillating properties have not been reported. In this work, we report on terbium-actived dense scintillating glasses which contain high concentrations of Ln_2O_3 (Ln=Gd, Y, Lu) up to 40mol%. Effects of Ln^{3+} ions on the scintillating properties under X-ray excitation have been investigated. Furthermore, fluorine is introduced to the glasses and the effect of fluorine on the scintillating properties has been studied.

2. Experimental

Glasses with mole compositions $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) and $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$28Ln_2O_3$-$10GdF_3$-$2Tb_2O_3$ were prepared using the following procedure. Reagent-grade SiO_2, H_3BO_3, $NH_4H_2PO_4$, Ga_2O_3, Gd_2O_3, Y_2O_3, Lu_2O_3 and GdF_3 were used as starting materials. 50g batches were placed in platinum crucibles and melted under an air atmosphere at 1520 - 1550°C for 3 h. The melts were poured into preheated stainless-steel plate and pressed into plates 4mm thickness. The glasses were cut and polished to 2mm thickness for various spectroscopic measurements. Density was measured by Archimedes' method using distilled water as an immersion liquid. Thermal properties were measured by differential thermal analysis (DTA) at a heating rate of 10°C/min. Ultraviolet/visible transmission spectra were recorded on a spectrometer. Luminescence under UV excitation using Xe lamp as excitation source was recorded by a JASCO LP-750 spectrometer. Luminescence under X-ray excitation was measured using an X-ray tube with Cu anode operated at 50kV and 30mA. Emission in the range of 300-700nm was collected and spectral sensitivity of the detection system was corrected. Light yield of the samples was estimated relative to that of a $Bi_4G_3O_{12}$ crystal. All the above measurements were performed at room temperature.

3. Results

3.1. Effects of Ln^{3+} ions on the physical properties

Density and refractive index of the $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses are listed in Table 1. As expected the density increases in the order of Y_2O_3 <Gd_2O_3 <Lu_2O_3. It is worth noting that the glass containing Gd_2O_3 or Lu_2O_3 exhibits a density of more than 6.0 g/cm^3, which meets basically the requirement for the practical applications in high energy physics and medical field. The refractive index (nd) of these glasses is very high, up to 1.83 for Gd-containing glass.

The thermal properties of the above glasses based on DTA results are shown in Fig. 1. Tg decreases from 780℃ to 760℃ and (Tx-Tg) decrease from 195℃ to 140℃ with the increase of ionic radius of Ln^{3+} ions. The difference of (Tx-Tg) are usually used to judge the stability of a glass against to crystallization, the higher the difference, more stable the glass. Therefore, the glass containing Lu exhibits the highest stability.

3.2. Effects of Ln^{3+} ions on the optical properties (Ln=Gd, Y, Lu)

Figure 2 shows the transmission spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses together with those of Tb-free glasses for comparison. There exist two weak absorption peaks at 375nm and 480nm in all Tb-doped glasses and an extra peak at 313nm only in Gd-containing glasses. The former two peaks are due to f-f transition of Tb^{3+} and latter one to that of Gd^{3+}. The Tb-doped glasses show the almost same transmission regardless of the kind of Ln^{3+} ions, but they obviously have a broad absorption band ranging from the absorption edges to 580nm in comparison with Tb-free glasses, indicating the broad absorption originates from terbium ions.

Figure 3 shows the luminescence spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses when excited with 276nm light. All observed emission peaks are attributable to the $^5D_4$-^7F_J transition of Tb^{3+}. The Gd-containing glass has a luminescent response at least a factor of 2 higher than the Y or Lu-containing one. Almost the same results have been observed under X-ray excitation as shown in Fig. 4. From the emission peaks, the light yield was estimated relative to BGO single crystal and the results were shown in Fig. 5. The Gd-containing glass exhibits higher light yield 2.5 times that of Y- or Lu-containing one. From the decay curves obtained by monitoring the intensity of the strongest emission peak at 545nm, the decay time for all the glasses investigated above was estimated. It was shown that the decay time did not change too much with the kind of Ln^{3+} and had a value around 1.8ms.

Dependence of the light yield on terbium concentration for the Gd-containing glasses is shown in Fig. 6. It can be seen that the light yield increases slightly with the increase in the terbium concentration.

Figure 7 shows the excitation spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses for the Tb^{3+} emission at 545nm. Same excitation bands are observed for the Y- and Lu-containing glasses. The broad band peaking at 260nm is due to the $4f^8$-$4f^7 5d^1$ transition of Tb^{3+} and the remaining bands at longer wavelength to the 4f-4f transitions of Tb^{3+}. For the Gd-containing glass, however, there exist extra two sharp and strong excitation bands at 276nm and 313nm. These two bands can be attributed to Gd^{3+} ion as they are identical with the $^8S_{2/7} \rightarrow {}^6I_J$ and $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transitions of Gd^{3+} ion, respectively.

3.3. Effect of fluorine on the optical properties

To investigate the effect of fluorine on the properties, 10mol% of Gd_2O_3 in the $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Gd_2O_3$-$2Tb_2O_3$ glass was replaced with GdF_3. Emission spectra under UV excitation indicated that the introduction of fluorine resulted in an increase in emission intensity, and similar result is also obtained under x-ray excitation as shown in Fig. 8. Transmission curves before and after the introduction of fluorine is shown in Fig. 9. It is obvious that the broad absorption becomes weaker significantly after the introduction of fluorine.

4. Discussion

Terbium in a glass exists mainly as Tb^{3+}, usually being accompanied by a small amount of Tb^{4+}. The ratio of these two ions depends on the melting atmosphere and the compositions of the host. Tb^{3+} ion emits fluorescence, but Tb^{4+} does not. The Tb^{3+} gives several sharp absorption peaks due to f-f transition in the visible region while Tb^{4+} has a broad absorption from ultraviolet to visible region peaking at 320-370nm due to the charge transfer transition [7]. It is therefore reasonable to assign the observed broad absorption in the present Tb-doped glasses (Fig. 3) to Tb^{4+} ions. Almost the same transmission for Gd-, Y- and Lu-containing glasses implies that the ratio of Tb^{3+}/Tb^{4+} is almost equal in these glasses, i.e. the same Tb^{3+} concentration.

Improvement of the transmission after the introduction of fluorine indicates the fluorine-containing glass has a lower concentration of Tb^{4+} and hence a higher concentration of Tb^{3+}. This is consistent with fact that the fluorine favors the lower oxidation states of ions.

Appearance of excitation bands of Gd^{3+} in the excitation spectra of Tb^{3+} indicates that energy transfer from Gd^{3+} to Tb^{3+} takes place in Gd_2O_3-containing glass. This must be responsible for the much stronger luminescence response under either UV or X-ray excitation in Gd-containing glass than that in Y- or Lu-containing glass. To investigate the optimum concentration of Gd^{3+} ion for energy transfer to Tb^{3+}, the substitution of

Lu_2O_3 for Gd_2O_3 was made in the $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-(38-x)Lu_2O_3-xGd_2O_3-$2Tb_2O_3$ glasses and emission spectra under the X-ray excitation were shown in Fig. 10. In addition to the emission peaks at longer wavelength beyond 350nm due to Tb^{3+} ions, emission peak due to the transmission of $^6P_{7/2}$ level → $^8S_{7/2}$ level of Gd^{3+} ions is also observed. The intensity of Tb^{3+} emission increases with the increase of Gd^{3+} concentration, but the intensity of Gd^{3+} emission decreases significantly and even disappears at high concentration more than 16mol%. The enhanced emission of Tb^{3+} ions with the increase of Gd^{3+} concentration could be explained by the following energy transfer process from Gd^{3+} to Tb^{3+}. At low Gd^{3+} concentration, excited Gd^{3+} ions return to ground state by two routs; one is by transferring its energy to Tb^{3+} and the other by radiative decay from $^6P_{7/2}$ level to $^8S_{7/2}$ level. At higher Gd^{3+} concentration, however, besides the energy transfer from Gd^{3+} to Tb^{3+}, the energy transfer between Gd^{3+} ions becomes more probable than the radiative decay of the Gd^{3+} ions. Energy migrates among Gd^{3+} ions and finally is trapped by Tb^{3+}, hence resulting in a decrease in Gd^{3+} emission and an increase in Tb^{3+} emission.

Figure 8 reveals that fluorine is effective in improving the light yield. This is most likely due to the higher Tb^{3+} concentration in the fluorine-containing glass as discussed above. The dependence of light yield on the terbium concentration (Fig.6) supports this speculation.

5. Conclusions

Tb-activated scintillating glasses containing high Ln_2O_3 concentration (Ln=Gd, Y, Lu) have been studied. The glasses are very heavy, having density up to 6.0g/cm^3 for Gd_2O_3-containing glass and 6.6g/cm^3 for Lu_2O_3-containing glass. Due to the energy transfer from Gd^{3+} to Tb^{3+}, the Gd-containing glass shows a light yield 2.5 times higher than the Y or Lu-containing glass. Part substitution of fluorine for oxygen is effective in improving the light yield.

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Figure Captions

Fig. 1. Tg and (Tx-Tg) of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses.

Fig. 2. Transmission spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses, (a) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$40Gd_2O_3$ glass and (b) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$40Lu_2O_3$ glass

Fig. 3. Emission spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses when excited with 276nm.

Fig. 4. Emission spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses under X-ray excitation.

Fig. 5. Light yield of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses under X-ray excitation.

Fig. 6. Dependence of the light yield on the terbium concentration for $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$(40\text{-}x)Gd_2O_3$-xTb_2O_3 glasses

Fig. 7. Excitation spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ (Ln=Gd, Y, Lu) glasses for the Tb^{3+} emission at 545nm.

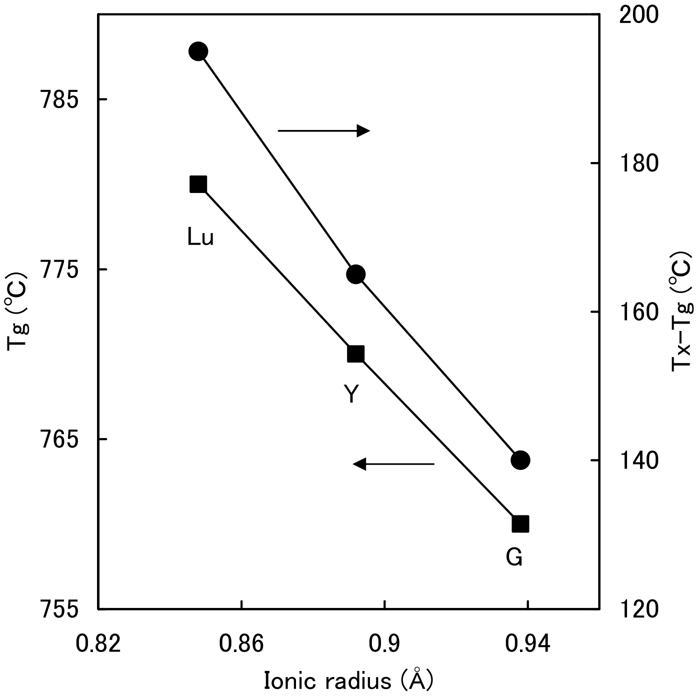
Fig. 8. Emission spectra of (a) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Gd_2O_3$-$2Tb_2O_3$ glass and (b) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$28Gd_2O_3$-$10GdF_3$-$2Tb_2O_3$ glass under x-ray excitation.

Fig. 9. Transmission spectra of (a) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Gd_2O_3$-$2Tb_2O_3$ glass and (b) $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$28Gd_2O_3$-$10GdF_3$-$2Tb_2O_3$ glass.

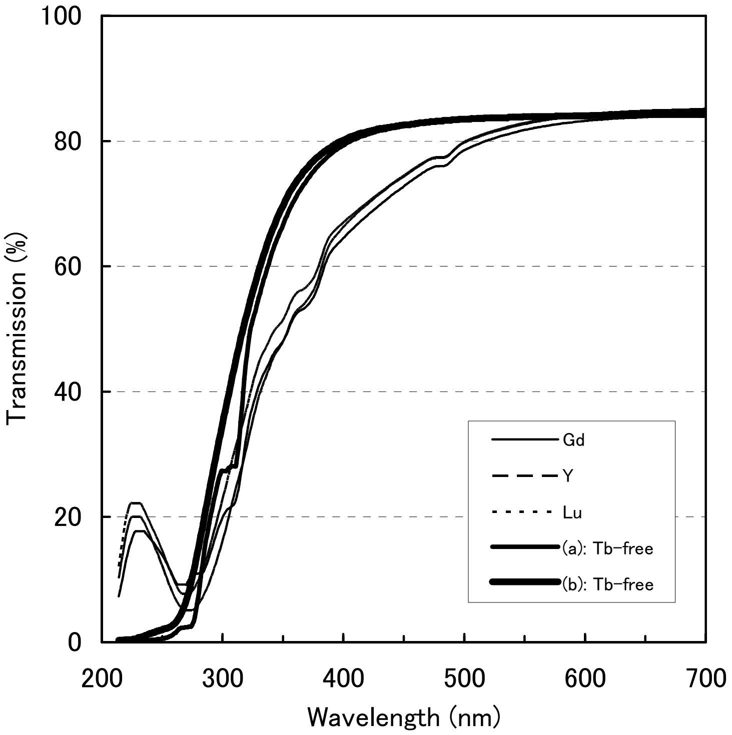
Fig. 10. Emission spectra of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-(38-x) Lu_2O_3-xGd_2O_3-$2Tb_2O_3$ glasses under x-ray excitation.

Table 1. Density and refractive index of $15SiO_2$-$25B_2O_3$-$5P_2O_5$-$15Ga_2O_3$-$38Ln_2O_3$-$2Tb_2O_3$ glasses (Ln=Gd, Y, Lu).

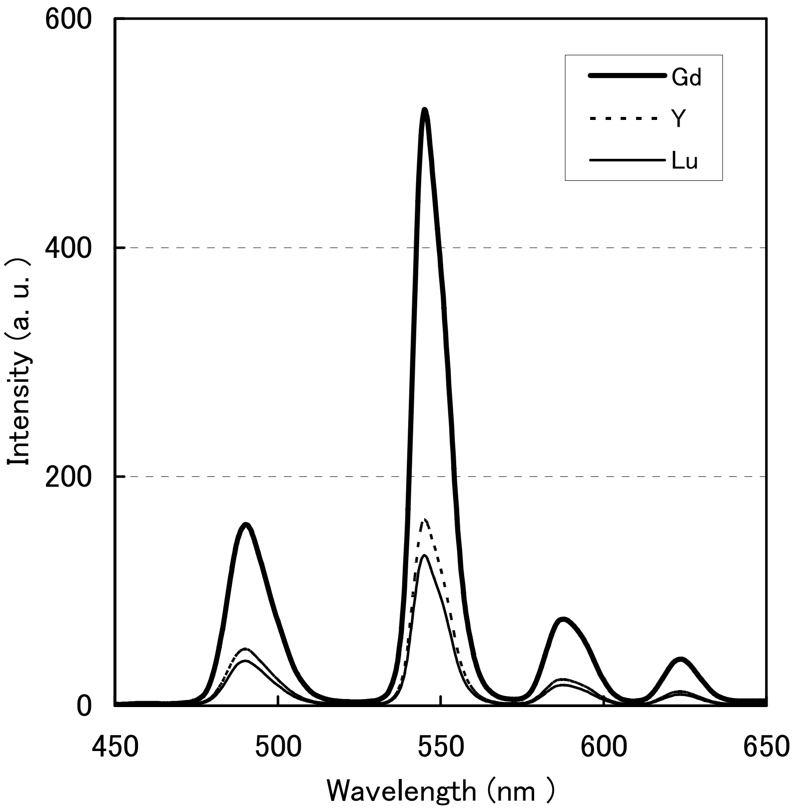
Ln	Density (g/cm^3)	Refractive index (nd)
Y	4.52	1.793
Gd	5.96	1.832
Lu	6.56	1.796

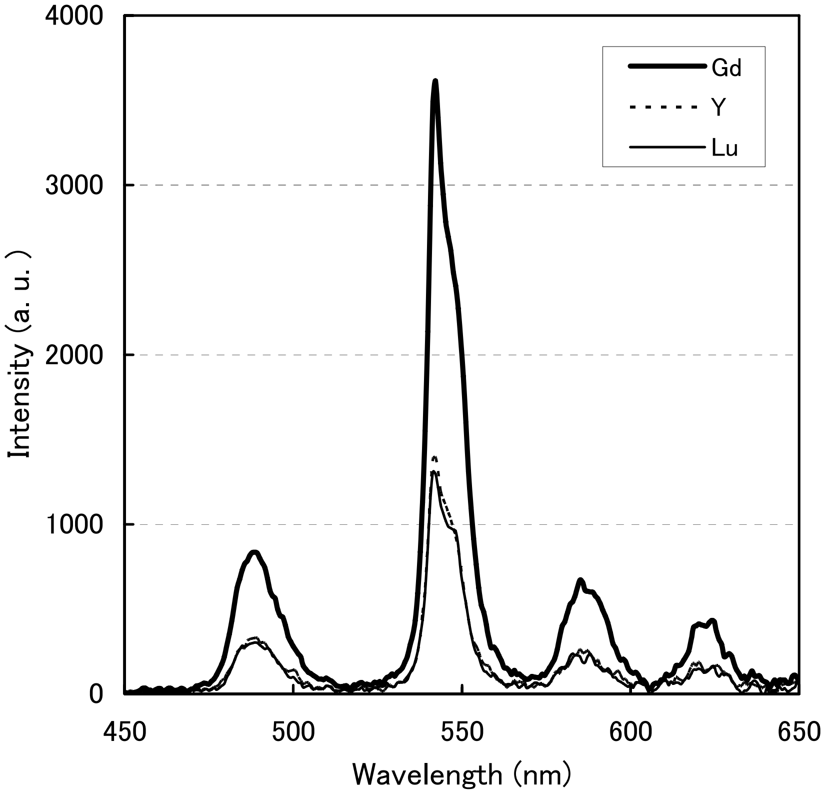


Tg (°C)
Tx−Tg (°C)
Ionic radius (Å)
785
775
765
755
200
180
160
140
120
0.82
0.86
0.9
0.94
Lu
Y
G

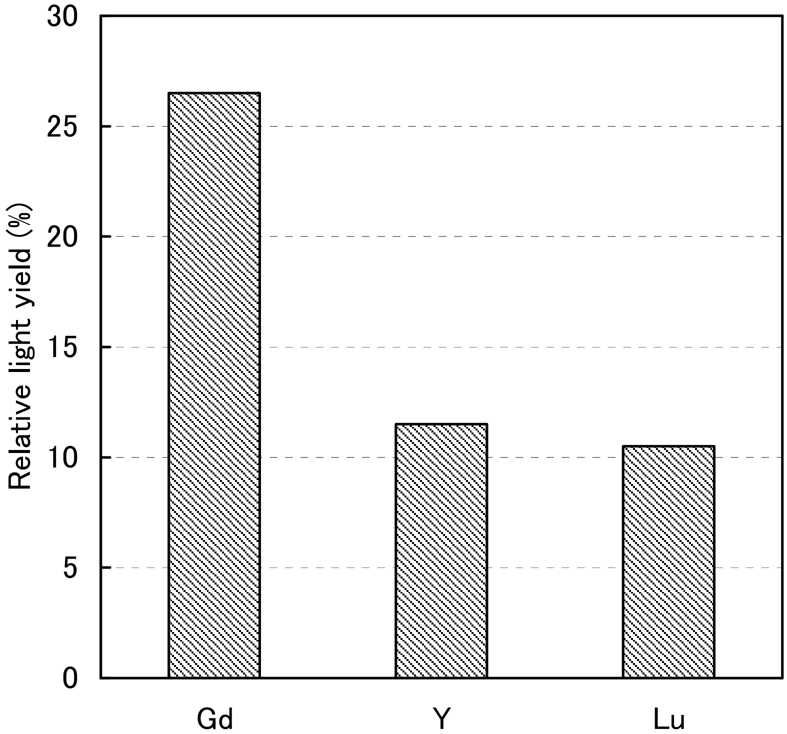


100
80
60
40
20
0
200
300
400
500
600
700
Transmission (%)
Wavelength (nm)
Gd
Y
Lu
(a): Tb-free
(b): Tb-free

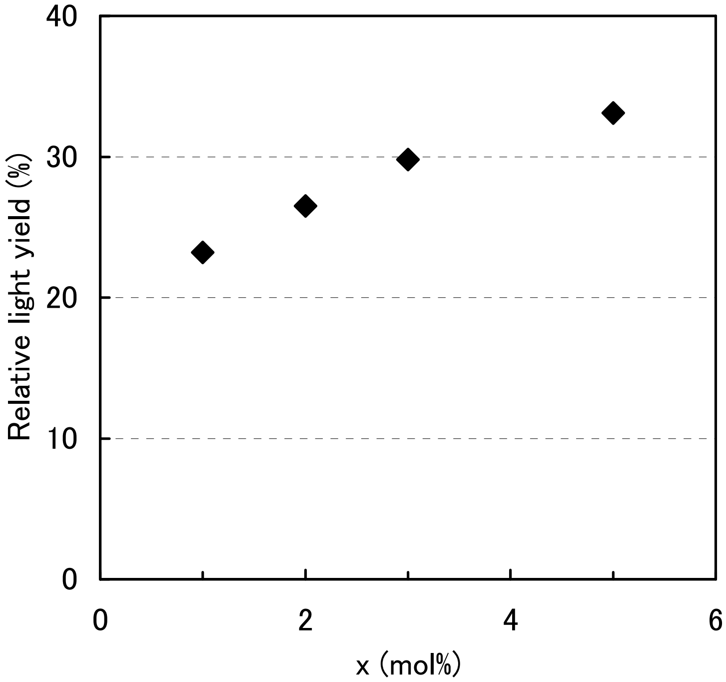

600
400
200
0
Intensity (a. u.)
450
500
550
600
650
Wavelength (nm)
Gd
Y
Lu



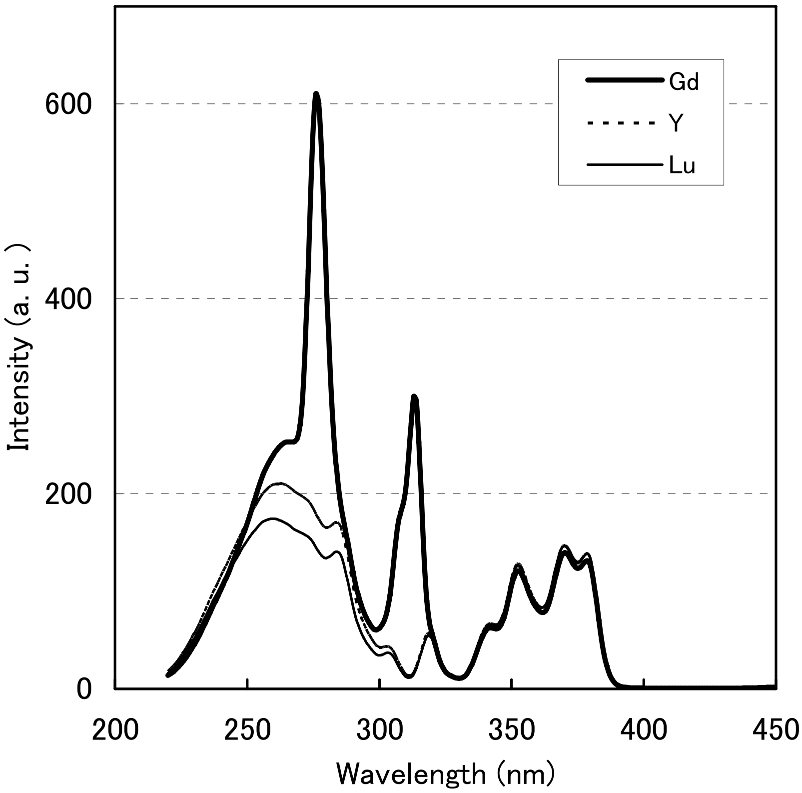
4000
3000
2000
1000
0
Intensity (a. u.)
450
500
550
600
650
Wavelength (nm)
Gd
Y
Lu



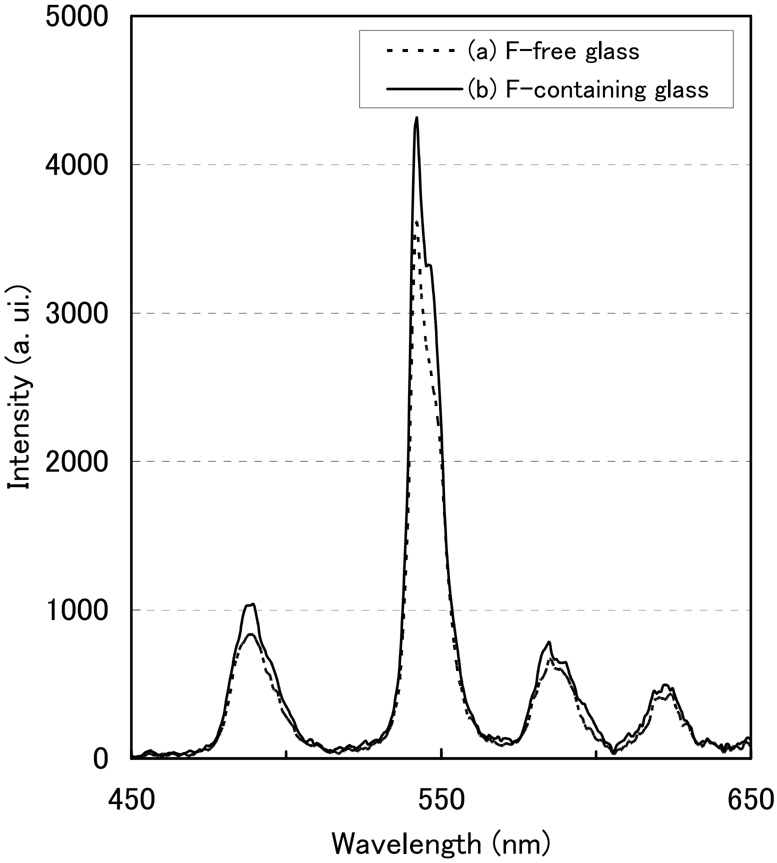
Relative light yield (%)
30
25
20
15
10
5
0
Gd
Y
Lu



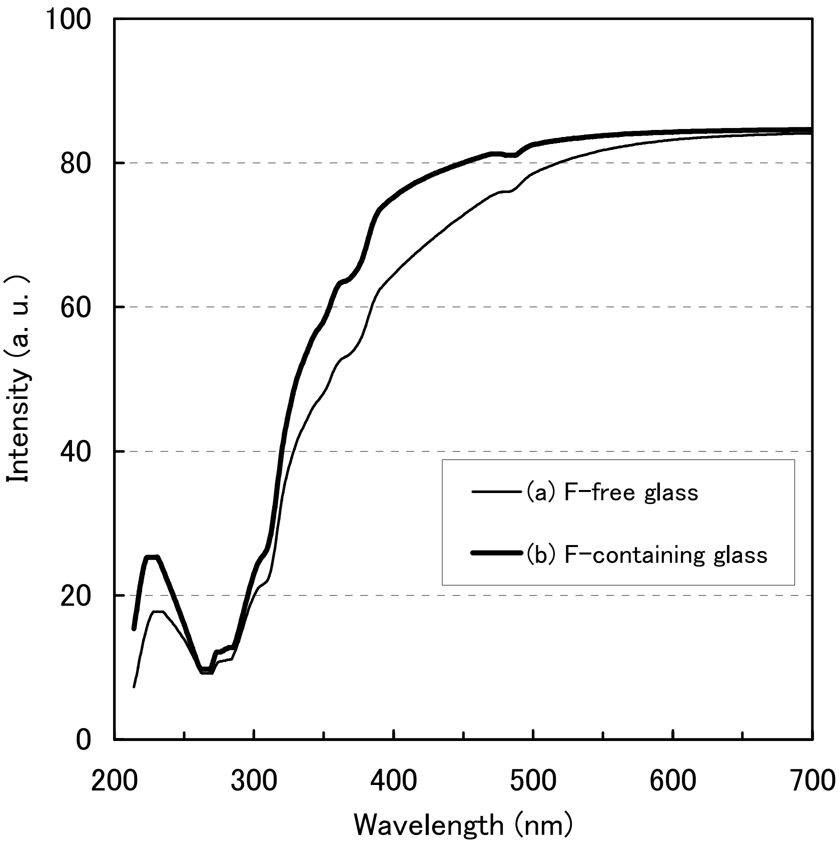
40
30
20
10
0
0
2
4
6
Relative light yield (%)
x (mol%)



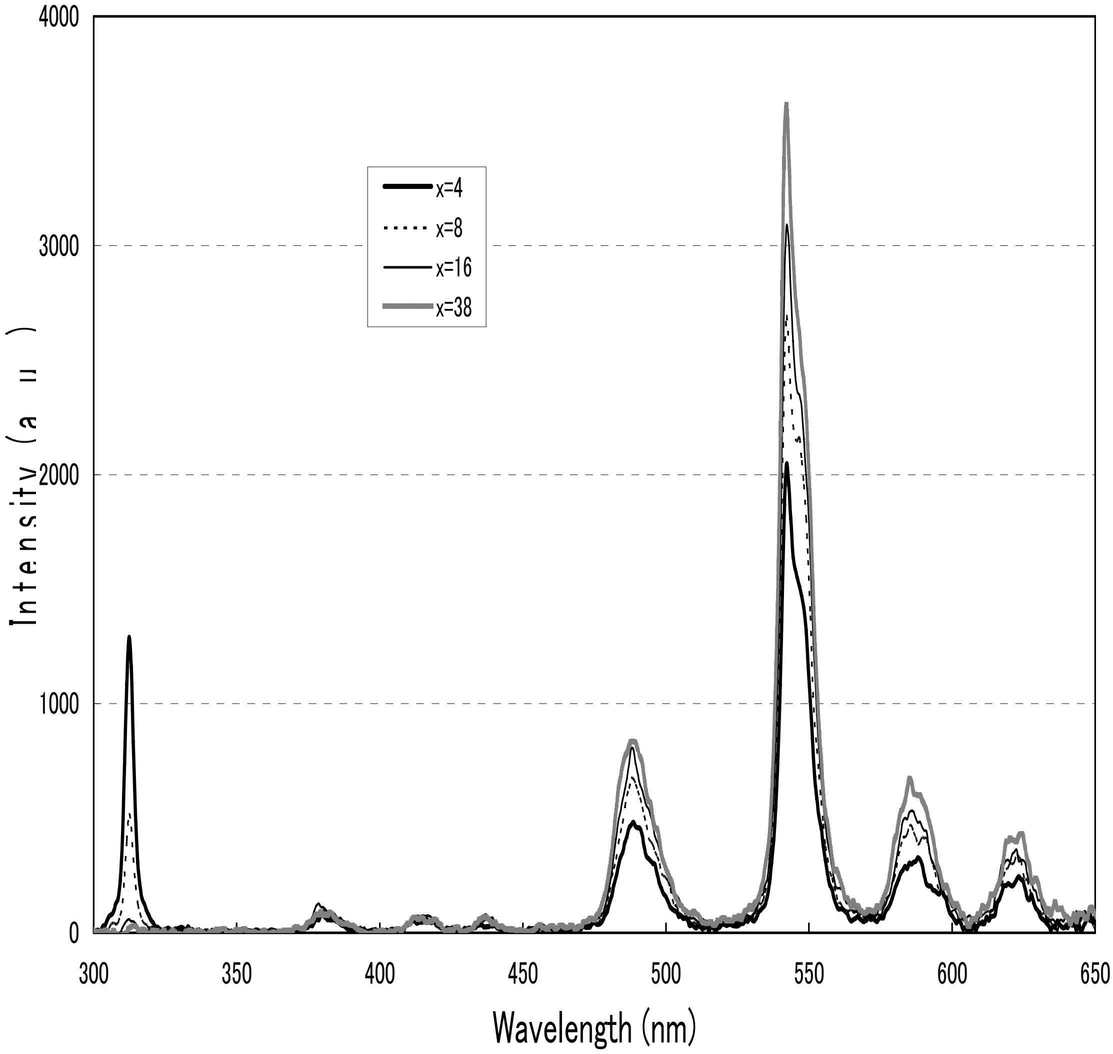
Gd
Y
Lu
600
400
200
0
Intensity (a. u.)
200
250
300
350
400
450
Wavelength (nm)



5000
4000
3000
2000
1000
0
Intensity (a. ui.)
450
550
650
Wavelength (nm)
(a) F-free glass
(b) F-containing glass



100
80
60
40
20
0
200
300
400
500
600
700
Wavelength (nm)
Intensity (a. u.)
(a) F-free glass
(b) F-containing glass



x=4
x=8
x=16
x=38
Intensity (a u)
Wavelength (nm)
0
1000
2000
3000
4000
300
350
400
450
500
550
600
650