Matrix effect on absorption and infrared fluorescence properties of Bi ions in oxide glasses

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Abstract

Absorption and fluorescence spectra of Bi ions in multi-component oxide glasses melted in air were measured. Absorption bands in the range of 400–1000 nm and fluorescence bands at round 1210 nm were only detected in the silicate, borosilicate, borate, and germanate glasses with or without a small amount of alkali or alkaline-earth oxides. The relative IR fluorescence intensity increased with decreasing basicity of matrix glasses and with adding the Al_2O_3. The compositional dependence of the relative IR fluorescence intensity and the IR fluorescence mechanism are discussed in terms of redox reaction and energy diagram of bismuth-related species in oxide glasses.
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1. Introduction

As capacity and performance of optical telecommunication system advances, the WDM system, which is made full use of optical telecommunication window between 1260 and 1675 nm of silica fiber, has been required. Cr^{4+} or Ni^{2+} doped glasses have been researched for new fiber amplifiers instead of EDFA because the fluorescence bands of these glasses could cover the optical telecommunication window of silica fiber [1,2]. However, Cr^{4+} or Ni^{2+} in glasses cannot emit the IR fluorescence at room temperature, so that these glasses need to cool down near the liquid nitrogen temperature or to crystallize the local structure surrounding Cr^{4+} or Ni^{2+} [1–5].

On the other hand, Fujimoto et al. [6,7] discovered that IR fluorescence of aluminosilicate glasses containing with the Bi_2O_3. This IR fluorescence shows broad bands around 1200 nm at room temperature without any crystalline phases. However, the origin of broad IR fluorescence and compositional dependence of its intensity are not understood.

The purpose of this work is to investigate the effect of composition on absorption and fluorescence properties of Bi ions in silicate, borosilicate, borate, and germanate glasses melted in air. The compositional dependence of the relative fluorescence intensity of Bi ions in the infrared region is discussed in terms of matrix glass basicity. The mechanism of IR fluorescence from bismuth-related species in oxide glasses is also discussed in terms of those energy diagrams.

2. Experimental procedure

Alkali or alkaline-earth silicate, borate, and geramanate and alkali and alkaline-earth free borosilicate glasses were

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Table 1
Glass matrix compositions

System	Glass composition (mol%)	
Silicate	$20Na_2O$–xAl_2O_3–$(80 - x)SiO_2$	$x = 0, 10$
	$40Na_2O$–xAl_2O_3–$(60 - x)SiO_2$	$x = 0, 10$
	$40CaO$–$10Al_2O_3$–$50SiO_2$	
	$40BaO$–xAl_2O_3–$(60 - x)SiO_2$	$x = 0, 10$
Borosilicate	$20B_2O_3$–$80SiO_2$	
	$5Al_2O_3$–xB_2O_3–$(95 - x)SiO_2$	$x = 5, 10, 15, 20$
Borate	$20CaO$–xAl_2O_3–$(80 - x)B_2O_3$	$x = 5, 10$
	$20BaO$–xAl_2O_3–$(80 - x)B_2O_3$	$x = 0, 10$
	$30BaO$–xAl_2O_3–$(70 - x)B_2O_3$	$x = 0, 10$
	$40BaO$–xAl_2O_3–$(60 - x)B_2O_3$	$x = 0, 10$
Germanate	$5Na_2O$–xAl_2O_3–$(95 - x)GeO_2$	$x = 0, 5$
	$30Na_2O$–xAl_2O_3–$(70 - x)GeO_2$	$x = 0, 5$
	$5RO$–$5Al_2O_3$–$90GeO_2$	$R = Ca, Sr, Ba$
	$10CaO$–$5Al_2O_3$–$85GeO_2$	
	$10BaO$–$10Al_2O_3$–$80GeO_2$	
	$30BaO$–xAl_2O_3–$(70 - x)GeO_2$	$x = 0, 5$

investigated for all matrices. Fujimoto et al. [7] reported that IR fluorescence intensity of Bi ions in silica glass increased with adding the Al_2O_3. Therefore, effect of Al_2O_3 on the absorption and fluorescence properties of Bi ions in these oxide glasses also investigated. The matrix compositions are listed in Table 1. Taking concentration quenching into account, each matrix glass was doped with 0.8 mol% Bi_2O_3. Twenty grams of starting materials mixed with 0.8 mol% Bi_2O_3 were melted in a platinum crucible at 1200–1650 °C for 1–3 h under air. Each glass melt was poured into a stainless-steel mold expect borosilicate which was cooled down to room temperature in a platinum crucible, and subsequently annealed near the glass transition temperature. Annealed samples were cut approximately 20 mm × 10 mm × 2 mm and polished for measurements.

Absorption spectra were measured at room temperature using a spectrophotometer (Model U-3500, HITACHI, Tokyo, Japan) in the range of 300–1500 nm. Fluorescence spectra were measured at room temperature using a monochromator (Model TRIAX 320, Horiba Jobin-Yvon, Tokyo, Japan) with Ge detector (Model J16 Series, Judson Technologies, PA, USA) and lock-in amplifier (Model SR830, Stanford Research Systems, CA, USA) in the range of 900–1550 nm. The samples were excited at 800 nm with 540 mW using a cw-Ti:sapphire laser (Model 3900S, Spectra Physics, CA, USA).

3. Results

Figs. 1 and 2 show absorption and fluorescence spectra of representative samples. A detailed account of the results is given below.

3.1. Silicate glasses

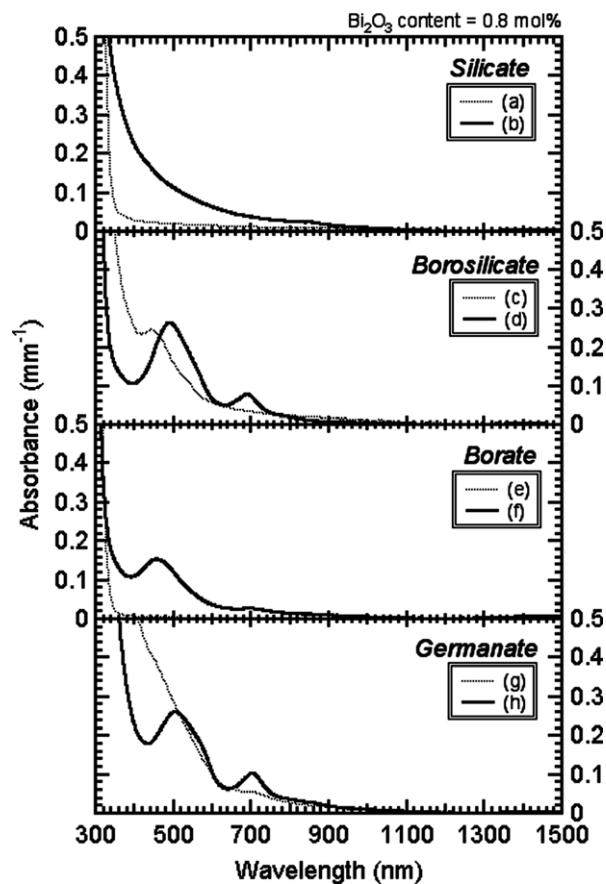The absorption and fluorescence spectra of Bi ions in the binary alkali or alkaline earth silicate glasses were mea-

Fig. 1. Absorption spectra of Bi ions in representative glasses: (a) $20Na_2O$–$80SiO_2$, (b) $20Na_2O$–$10Al_2O_3$–$70SiO_2$, (c) $20B_2O_3$–$80SiO_2$, (d) $5Al_2O_3$–$15B_2O_3$–$80SiO_2$, (e) $20BaO$–$10Al_2O_3$–$70B_2O_3$, (f) $20CaO$–$10Al_2O_3$–$70B_2O_3$, (g) $5Na_2O$–$5Al_2O_3$–$90GeO_2$, (h) $5CaO$–$5Al_2O_3$–$90GeO_2$.

sured. Any absorption and fluorescence bands were not detected in the $20Na_2O$–$80SiO_2$ (refer to Figs. 1(a) and 2(a)), $40Na_2O$–$60SiO_2$, and $40BaO$–$60SiO_2$ glass samples. Effect of Al_2O_3 addition on the absorption and fluorescence properties in silicate glasses was investigated. Though any particular absorption bands were not detected, the very weak fluorescence bands were detected in $20Na_2O$–$10Al_2O_3$–$70SiO_2$ (refer to Figs. 1(b) and 2(b)), $40CaO$–$10Al_2O_3$–$50SiO_2$, and $40BaO$–$10Al_2O_3$–$50SiO_2$. However, any absorption and fluorescence bands could not be observed in the $40Na_2O$–$10Al_2O_3$–$50SiO_2$ glass sample.

3.2. Borosilicate glasses

Bi ions in $20B_2O_3$–$80SiO_2$ glass show a broad absorption band located at around 440 nm and a narrow fluorescence band around 1400 nm as shown in Figs. 1(c) and 2(c). Effect of Al_2O_3 addition on the absorption and fluorescence properties of Bi ions in $5Al_2O_3$–xB_2O_3–$(95 - x)SiO_2$ ($x = 5, 10, 15, 20$) glasses was investigated. The absorption and fluorescence spectral profiles of Bi ions changed with adding the Al_2O_3: the absorption spectrum has three peaks occurring at about 500, 700, and 800 nm and the fluores-
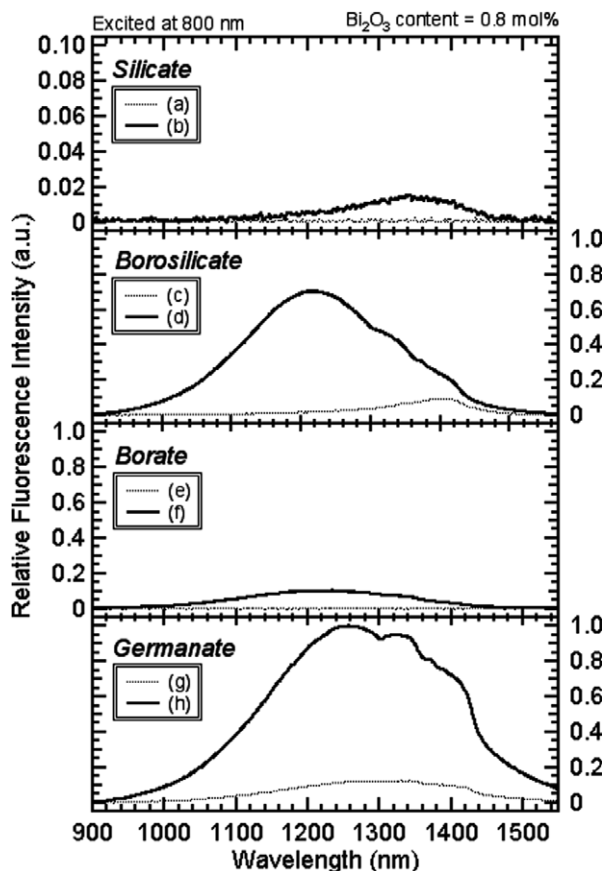
Fig. 2. Fluorescence spectra of Bi ions in representative glasses: (a) $20Na_2O–80SiO_2$, (b) $20Na_2O–10Al_2O_3–70SiO_2$, (c) $20B_2O_3–80SiO_2$, (d) $5Al_2O_3–15B_2O_3–80SiO_2$, (e) $20BaO–10Al_2O_3–70B_2O_3$, (f) $20CaO–10Al_2O_3–70B_2O_3$, (g) $5Na_2O–5Al_2O_3–90GeO_2$, (h) $5CaO–5Al_2O_3–90GeO_2$. The vertical axis for spectra (a) and (b) is expanded.

cence spectrum show a broad band located at around 1200 nm in $5Al_2O_3–15B_2O_3–80SiO_2$ glass (refer to Figs. 1(d) and 2(d)). The relative fluorescence intensity of Bi ions increased with decreasing B_2O_3 content in alumino-borosilicate glasses.

3.3. Borate glasses

The absorption and fluorescence spectra of Bi ions in the $BaO–Al_2O_3–B_2O_3$ glass systems were measured. Any absorption and fluorescence bands were not detected in both binary $xBaO–(100 − x)B_2O_3$ and Al_2O_3 containing $xBaO–10Al_2O_3–(90 − x)B_2O_3$ ($x = 20, 30, 40$) glass samples. Bi ions in $20BaO–10Al_2O_3–70B_2O_3$ glass does not show any absorption and fluorescence bands as shown in Figs. 1(e) and 2(e), whereas Bi ions in $20CaO–10Al_2O_3–70B_2O_3$ glass exhibits the absorption bands at around 460 and 700 nm and the weak broad fluorescence band located at around 1200 nm, as shown in Figs. 1(f) and 2(f).

3.4. Germanate glasses

The $5Na_2O–95GeO_2$ glass sample shows the absorption bands at around 500 and 700 nm and the weak broad fluo-

rescence band located at around 1200 nm. The relative fluorescence intensity is increased with adding Al_2O_3 in $5Na_2O–5Al_2O_3–90GeO_2$ glass, compared with that of $5Na_2O–95GeO_2$ glass. On the other hand, the $30Na_2O–70GeO_2$ and $30Na_2O–5Al_2O_3–65GeO_2$ glass samples do not show any absorption and fluorescence bands. The relative fluorescence intensity of Bi ions increased with decreasing ionic radius of alkaline earth ion in $5RO–5Al_2O_3–90GeO_2$ (R = Ca, Sr, Ba) glasses. The $5CaO–5Al_2O_3–90GeO_2$ glass sample shows the highest relative fluorescence intensity in this study as shown in Fig. 2(h).

4. Discussion

The absorption and fluorescence properties of Bi ions depend on the matrix glass compositions. The relative fluorescence intensity shows a tendency to increase with increasing the absorption bands in the range of 400–1100 nm. Both the absorbance and the relative fluorescence intensity indicate as higher as smaller amount of alkali or alkaline earth with their smaller ionic radius in the Bi-doped glass samples. This result implies that the valency state of Bi ions varies with glass compositions. The compositional dependence of the relative fluorescence intensity is discussed in terms of the valency state of Bi ions. The relationship between the relative fluorescence intensity and glass basicity was considered because the parameters affecting a redox reaction such as melting temperature, oxygen partial pressure in the furnace atmosphere, and total Bi ion concentration were fixed in this study. A basicity parameter, B, is used to express the oxygen ion activity of multi-component matrix glass quantitatively. The B proposed by Morinaga et al. [8] is calculated from glass composition in terms of Coulomb force between the cation and oxygen ion using their ionic radii and valences.

Fig. 3 shows the relationship between the relative fluorescence intensity at peak wavelength and basicity parameter, B, in Bi-doped silicate, borosilicate, borate, and germanate glass samples. The errors for the fluorescence
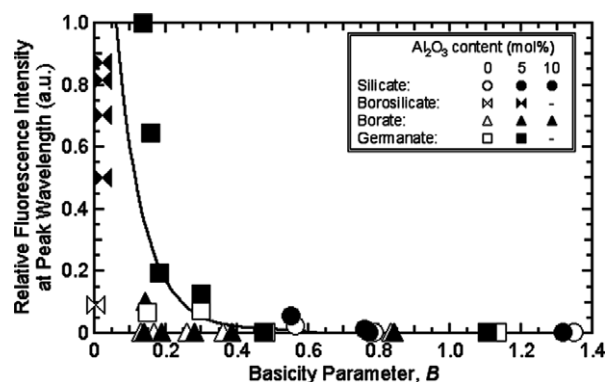

Fig. 3. Relationship between the relative fluorescence intensity at peak wavelength of Bi ions and basicity parameter, B, in oxide glasses. The errors for the relative fluorescence intensity were within 8% for all the glasses. Line is drawn as guide for the eye.

intensity of Bi ions were within 8% for all the glasses. The relative fluorescence intensity at peak wavelength increases with decreasing B below 0.4 and adding the Al_2O_3 in Bi-doped glass samples. In contrast, any IR fluorescence cannot be observed and the addition of Al_2O_3 has no effect on the improvement of the IR fluorescence intensity above 0.4 of B in Bi-doped glass samples. Therefore, we find the design of matrix glass composition that the required condition for emitting the IR fluorescence from Bi ions is B for matrix glass below 0.4 and the addition of Al_2O_3.

Generally, Bi ions exist in oxide glasses as trivalent. However Bi^{3+} cannot emit the IR fluorescence [9]. Fujimoto et al. [6,7] reported that the origin of IR fluorescence would be Bi^{5+}. According to our results, higher valency state Bi^{5+} would be impossible to form such reducing conditions: low basicity of matrix composition and high melting temperature. In contrast, Meng et al. [10] estimated the IR fluorescence derives from Bi^+ on the basis of energy matching conditions. However the existence of Bi^+ and the authority of theoretical energy diagram for Bi^+ is not clear. Therefore, the origin of IR fluorescence is discussed in terms of energy levels for lower valency states of Bi species. Fig. 4 shows the estimated energy diagram of Bi doped oxide glass samples in this study with those of Bi metal, BiO radicals, and Bi^{3+} as comparison. The each energy level is calculated by absorption and fluorescence peak wavelength in $5Al_2O_3$–$15B_2O_3$–$80SiO_2 + 0.8\ Bi_2O_3$ glass samples as shown 1(d) and 2(d): it is assume that all fluorescence transitions would occur between excited and ground states. The energy diagrams of Bi metal, BiO radicals, and Bi^{3+} were cited by the previous works [9,11,12]. As shown in Fig. 4, the measured energy diagram (a) would be consistent with that for BiO radicals (c). Consequently, these results support the hypothesis that the origin of IR fluorescence would be BiO-radical-like species in Bi-doped oxide glasses.

Next, we will discuss the effect of adding Al_2O_3 on the absorption and fluorescence properties of Bi ions in oxide glasses. The formation of BiO-radical-like species needs lower basicity of matrix glass. Bi ions would be easy to form clusters in lower basicity of matrix glass because of higher degree of polymerization. To add Al_2O_3 into lower basicity of matrix glasses, Bi ions would be selectively incorporated into certain Al^{3+} sites. Therefore, the concentration of BiO-radical-like species would increase with increasing Al_2O_3 content because Bi ions clusters would be decomposed.

As mentioned above, the origin of IR fluorescence in Bi-doped oxide glasses was discussed in terms of energy levels for lower valency states of Bi species. However, there is room for further investigation concerning X-ray absorption fine structure measurements of valency state of Bi in order to reveal the detailed mechanism [13].

5. Conclusion

The effect of composition on absorption and fluorescence properties of Bi ions in silicate, borosilicate, borate, and germanate glasses melted in air was investigated. The relative fluorescence intensity shows a tendency to increase with increasing the absorption bands in the range of 400–1100 nm. We find the design of matrix glass composition that the required condition for emitting the IR fluorescence from Bi ions is basicity parameter, B, for matrix glass below 0.4 and the addition of Al_2O_3. The $5CaO$–$5Al_2O_3$–$90GeO_2$ glass sample shows the highest relative fluorescence intensity in this study. The measured energy diagram for Bi ions in oxide glasses would be consistent with that for BiO radicals. This similarity supports the hypothesis that the origin of IR fluorescence would be BiO-radical-like species in Bi-doped oxide glasses.

Fig. 4. Energy diagrams of Bi: (a) measured data in this study, (b) Bi metal, (c) BiO radicals, and (d) Bi_2O_3.

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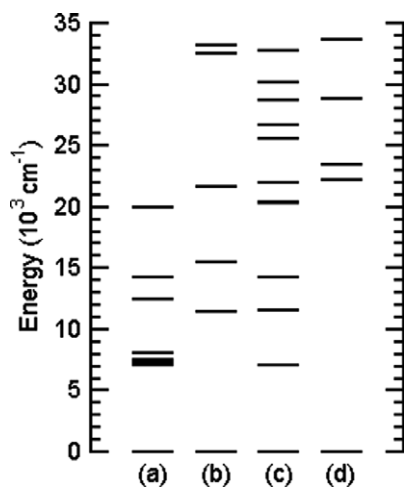[5] T. Suzuki, Y. Ohishi, in: Proc. XX ICG in Kyoto (2004) sr007H00122DIS.pdf.

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