

Effect of various alkaline-earth metal oxides on the broadband infrared luminescence from bismuth-doped silicate glasses

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Abstract

We report on the effect of various alkaline-earth metal oxides on the broadband infrared luminescence covering 1000–1600 nm wavelength region from bismuth-doped silicate glasses. The full width at half maximum (FWHM) of the infrared luminescence and the fluorescent lifetime is more than 200 nm and 400 μ s, respectively. The fluorescent intensity decreases with increasing basicity of host glasses. Besides the broadband infrared luminescence, luminescence centered at 640 nm was also observed, which should be ascribed to Bi^{2+} rather than to the familiar Bi^{3+} . We suggest that the infrared luminescence should be assigned to the $X_2^2\Pi_{3/2} \rightarrow X_1^2\Pi_{1/2}$ transition of BiO molecules dispersed in the host glasses.

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1. Introduction

Dense-wavelength-division-multiplexing system (DWDM) can realize optical communication with large capacity and long distance transmission by effective use of bandwidth of optical fiber. DWDM system plays a significant role in the optical network. In the DWDM system, the transmission capacity depends on the bandwidth of optical fiber amplifiers. But the bandwidth of traditional rare-earth-doped optical fiber amplifiers cannot be more than 100 nm. Development of novel broadband optical fiber amplifiers has become a frontline subject now. Recently, Fujimoto et al. reported the broadband infrared luminescence covering 1000–1600 nm from a bismuth-doped silica glass and realized 1300 nm optical amplification at 808 nm excitation [1,2]. Subsequently, other

researchers reported broadband infrared luminescence from various bismuth-doped glasses [3–6]. But, the conclusions on which valence state of bismuth resulted in the broadband infrared luminescence are still controversial.

Here, we report on broadband infrared luminescence as well as visible emissions centered at 400 nm–640 nm from bismuth-doped silicate glasses. The effects of various alkaline-earth metal oxides on the infrared luminescence are discussed. The visible luminescence centered at about 640 nm has not been reported in bismuth-doped glasses with broad infrared luminescence, to the best of our knowledge, which should be ascribed to Bi^{2+} rather than to the familiar Bi^{3+} . The luminescence at 640 nm has a close relation with the infrared luminescence. We suggest that the infrared luminescence should be assigned to the BiO molecules dispersed in host glasses.

2. Experimental

The compositions of the bismuth-doped alkaline-earth metal silicate glasses and alkali metal silicate glasses are

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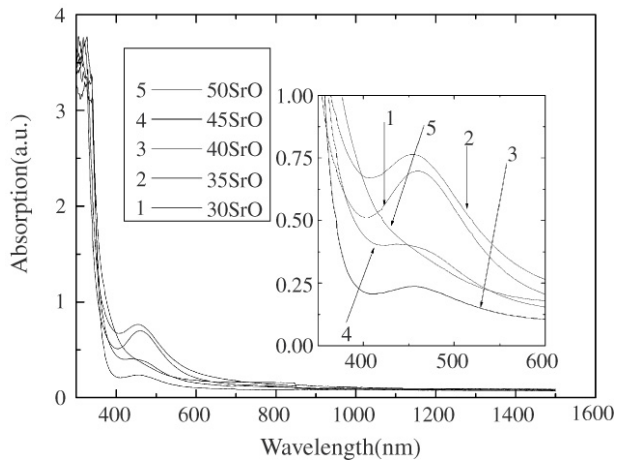


Fig. 1. Absorption spectra of $(95 - x) \text{SiO}_2 \cdot x\text{SrO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x = 30, 35, 40, 45, 50$, in mol%) glasses.

$(95 - x) \text{SiO}_2 \cdot x\text{RO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x = 30, 35, 40, 45, 50$, in mol%; $\text{R} = \text{Ca}, \text{Sr}, \text{Ba}$) and $65\text{SiO}_2 \cdot 30\text{R}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($\text{Li}, \text{Na}, \text{K}$), respectively. Raw materials were analytically pure CaCO_3 , SrCO_3 , BaCO_3 , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , $\text{Al}(\text{OH})_3$, SiO_2 , and Bi_2O_3 . The batches were mixed homogeneously in an agate mortar, and then melted in corundum crucibles at 1570°C for 1.5 h in air. Consequently, the melt was cast onto a graphite plate. The glass samples were then cut into the size of $10 \times 10 \times 2$ mm and polished for optical measurements.

Optical absorption spectra of the samples were measured on JASCO V-570 spectrophotometer. Emissions centered at about 1300 nm and 640 nm excited by 808 nm laser diode and 532 nm laser (the second harmonic of the YAG: Nd laser), respectively, were measured on ZOLIX SBP300 spectrofluorometer with an InGaAs detector. The fluorescence spectra centered at about 400 nm were measured on JASCO FP-65000 spectrofluorometer, excited by 280 nm ultraviolet light. The fluorescence lifetime measurements were carried out by exciting the samples with a modulated 808 nm LD. The signals detected by an InGaAs photodetector in TRIAX550 spectrofluorometer were recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were taken at room temperature.

3. Results

Fig. 1 shows the absorption spectra of $(95 - x) \text{SiO}_2 \cdot x\text{SrO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x = 30, 35, 40, 45, 50$, in mol%) glasses. Obviously there is an absorption peak at about 455 nm. The absorption peak becomes obscure with the increase in SrO content.

Fig. 2 shows the visible luminescence from alkali metal silicate glasses and alkaline-earth metal silicate glasses, excited by 280 nm ultraviolet light. All of the glasses show visible luminescence centered at about 400 nm that are the typical luminescence spectra of Bi^{3+} [7,8]. And with the increase in SrO content, the visible peak shifts from 408 to 438 nm.

Fig. 3 shows the fluorescent spectra of $(95 - x) \text{SiO}_2 \cdot x\text{SrO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x = 30, 35, 40, 45, 50$, in mol%) glasses, excited at 808 nm. The FWHM of the luminescence and

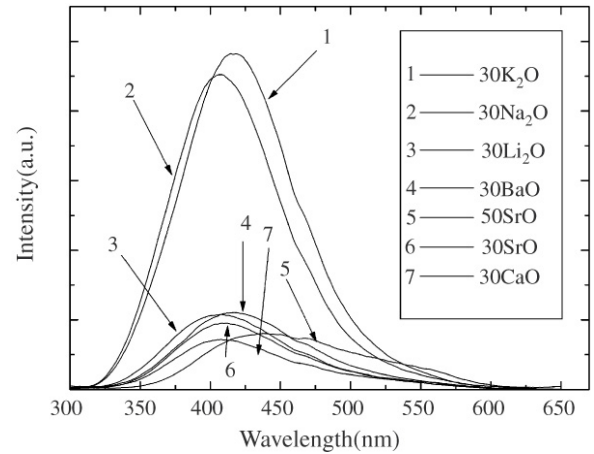


Fig. 2. Fluorescent spectra of $(95 - x) \text{SiO}_2 \cdot x(\text{RO or R}_2\text{O}) \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x\text{RO or R}_2\text{O} = 30\text{CaO}, 30\text{SrO}, 50\text{SrO}, 30\text{BaO}, 30\text{Li}_2\text{O}, 30\text{Na}_2\text{O}, 30\text{K}_2\text{O}$) glasses, excited by 280 nm ultraviolet light.

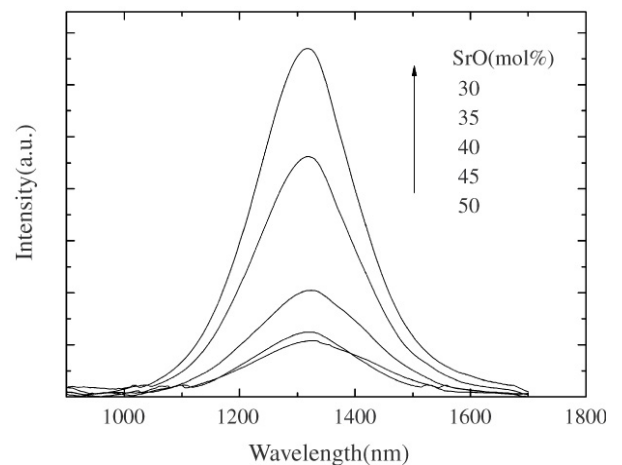


Fig. 3. Fluorescent spectra of $(95 - x) \text{SiO}_2 \cdot x\text{SrO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($x = 30, 35, 40, 45, 50$ in mol%) glasses, excited by 808 nm LD.

the fluorescence lifetime is more than 200 ns and 400 μs , respectively. The fluorescent intensity decreases with the increase in SrO content. Same phenomena were observed in bismuth-doped calcium silicate glass and barium silicate glasses. And the fluorescent intensity decreases with the increase in the alkaline-earth metal radius (see Fig. 4(b)). These indicate that the intensity of infrared luminescence decreases with the increase in the basicity of the host glass. In order to clarify the effect of basicity of the host glass on the infrared luminescence further, we also studied the infrared luminescence from glasses $65\text{SiO}_2 \cdot 30\text{R}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) with higher basicity. No infrared luminescence was observed when excited by 808 nm LD (see Fig. 4(b)). When 5% SrO is replaced by R_2O in $65\text{SiO}_2 \cdot 30\text{SrO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{Bi}_2\text{O}_3$ glass, the fluorescence intensity decreases sharply (see Fig. 4(b)), which indicates that alkali metal oxide has quenching effect on the infrared luminescence in the alkaline-earth metal silicate glasses. From the above analysis, it can be concluded that increase in basicity is harmful to the infrared luminescence from the bismuth-doped silicate glasses.

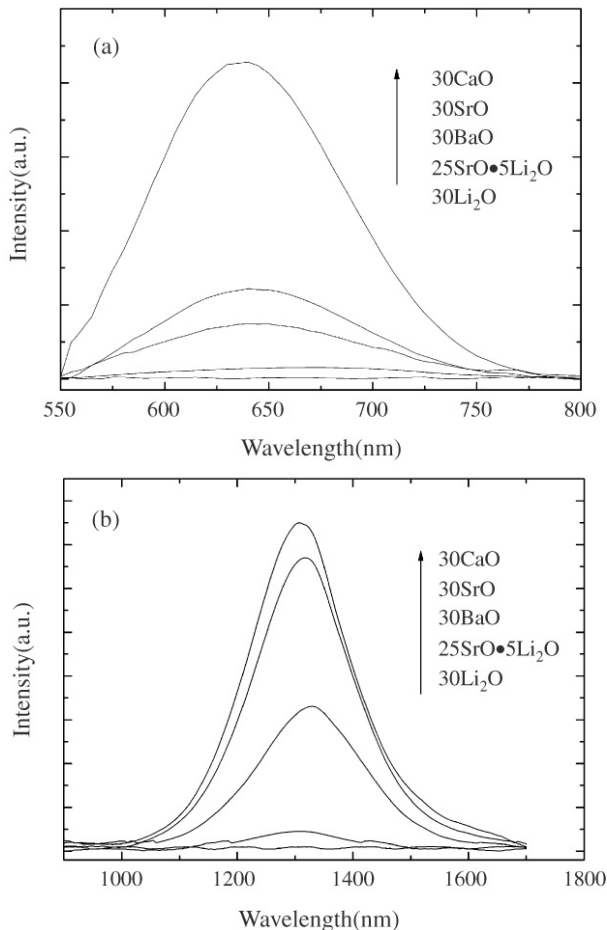


Fig. 4. (a) and (b) are the visible and infrared luminescent spectra of $65\text{SiO}_2\cdot 30\text{RO}\cdot 5\text{Al}_2\text{O}_3\cdot 2\text{Bi}_2\text{O}_3$ ($30\text{RO} = 30\text{CaO}, 30\text{SrO}, 30\text{BaO}, 25\text{SrO}\cdot 5\text{Li}_2\text{O}$ and $30\text{Li}_2\text{O}$) glasses, excited by 532 nm laser (the second harmonic of the YAG: Nd laser) and 808 nm LD, respectively.

Fig. 4(a) shows the visible luminescence centered at 640 nm, excited by 532 nm laser, which has not been reported in bismuth-doped glasses with broad infrared luminescence, to the best of our knowledge. From Figs. 4 and 5, we can find that the visible luminescence centered at about 640 nm and the infrared luminescence has the similar change tendency that both the emissions decrease with the increase in alkaline-earth metal ion radius and SrO content. Therefore, it is expected that both the emissions come from the same luminescent origins. These two emissions might come from bismuth with low valence states, since the increase in the host glass basicity favors the formation of high valence states of multivalent metal ions, according to the theory of Duffy and Ingram [9]. These two emissions might not come from Bi^{3+} ions, since both the emissions were not observed in the alkali metal silicate glasses in which Bi^{3+} ions exist. The visible luminescence centered at about 640 nm is similar to that from CaBPO_5 that has a luminescence peak at 628 nm as well as excitation peaks at 584 nm and was assigned to the luminescence of ${}^2P_{3/2} \rightarrow {}^2P_{1/2}$ of Bi^{2+} by Srivastava [10].

As shown in Fig. 4(b), the peak of infrared luminescence at 1315 nm is shifted to 1325 nm and 1305 nm, respectively, when BaO and CaO replace SrO. The shifts in the peak

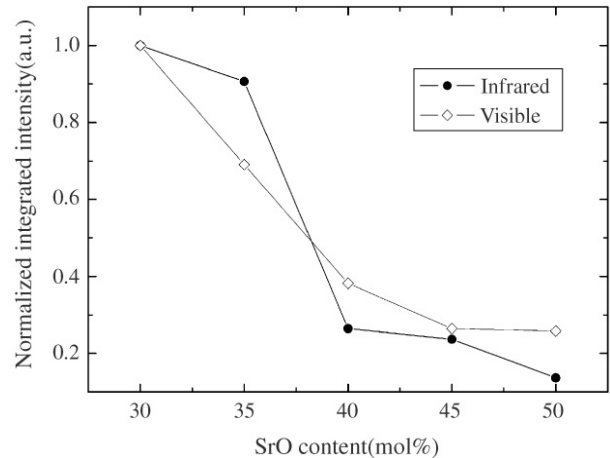


Fig. 5. Dependence of integrated intensity of the visible luminescence centered about 640 nm and the infrared luminescence, excited by 532 nm laser (the second harmonic of the YAG: Nd laser) and 808 nm LD, respectively, on SrO content.

position indicate that the infrared luminescence is susceptible to local chemical environment around the infrared luminescence origins. In fact, in bismuth-doped silicate glasses, the peak appears at 1250 nm [1], once the alkaline-earth metal oxides are added, it shifts to about 1300 nm. And, in bismuth-doped barium-aluminum-borate glasses [3], the peak position of the infrared luminescence excited at 808 nm is shifted from 1252 to 1300 nm with increasing BaO content from 20 to 40 mol%. But, significantly, the peak position remains at 1320 nm with variation of SrO content (see Fig. 3). We have also observed the same phenomena in bismuth-doped calcium silicate glasses and barium silicate glasses in which the peak remains at 1305 and 1325 nm, respectively. It can be explained as follows: in alkaline-earth metal silicate glasses, the first and the second shells around the infrared luminescence origins remain certain with variation of SrO content. The first and the second shells usually are consisted of oxygen and positive ions, respectively. We suggest that the second shell is exclusively of Sr^{2+} ions in bismuth-doped strontium silicate glasses, so the coordinate shell remains certain with variation of SrO content. Similar phenomena have been reported in erbium-doped alkaline-earth metal silicate glasses, in which the first and the second shell around Er^{3+} cannot be changed by alkaline-earth metal oxide content but can be changed by the species of alkaline-earth oxide since Er^{3+} are surrounded by alkaline-earth metal ions [11]. If the second shell consists of other ions, the peak position of the infrared luminescence should not be shifted by the change of the species of alkaline-earth metal oxide, similarly the first and the second shell around Er^{3+} is not changed by the content and species of alkaline-earth metal oxide in erbium-doped alkaline-earth metal phosphate glasses in which Er^{3+} ions selectively coordinate to $\text{P}=\text{O}$ [11].

4. Discussion

It is still unknown which valence state of bismuth results in the infrared luminescence. Fujimoto et al. think it is Bi^{5+} since no electron spin resonance signal was detected [1]. But others think it is bismuth with low valence state, since the silica

and germanium glasses are tiny acidic. Usually, the acidic host favors the formation of low valence state, based on the optical basicity theory of Duffy and Ingram [9]. Meng et al. suggest it is Bi^+ based on the different excitation wavelengths [3,4]. Peng et al. think it may be the bismuth clusters [6], since they observed the absorption peak at 515 nm, which was assigned to bismuth metal atom by Bishay [12].

From Section 3, we have known that increasing the host glass basicity results in the decrease of the infrared luminescence. Since increasing the host glass basicity favors the high valence state of multivalent metal ions, according to the theory of Duffy and Ingram [9], we think it is bismuth with low valence state that results in the infrared luminescence. In fact, Bi^{5+} ions often exist in hosts with higher basicity such as LiBiO_3 , NaBiO_3 , KBiO_3 and so on [13–15], and Bi^{5+} ions are easily reduced to Bi^{3+} due to decomposition, when they are heated above 300 °C. The infrared luminescence origins are not due to Bi^{3+} ions, since the typical luminescent spectra of Bi^{3+} were observed in alkali metal silicate glasses from which no infrared luminescence was observed. From Figs. 4 and 5, we find that the visible luminescence centered at about 640 nm and the infrared luminescence centered at 1320 nm may come from the same luminescent centers and the 640 nm luminescence might be assigned to divalent bismuth. Therefore we think that the infrared luminescence might come from the divalent bismuth. Fockele and Lohse et al. have reported infrared luminescence at 1358 nm of KF:Ti^0 and infrared luminescence at 1319 nm of $\text{BaF}_2:\text{Pb}^+-\text{Pb}^{2+}$ [16,17]. The FWHM of both the infrared luminescences is 284 nm. Bi^{2+} has the same electron configuration with Tl^0 and Pb^+ ($6s^26p^1$). Furthermore, Shestakov and Breidohr et al. have reported infrared luminescence ascribed to $X_2^2\Pi_{3/2} \rightarrow X_1^2\Pi_{1/2}$ transition of BiO molecules in gas phase [18]. The luminescence peak position appears at 1400 nm and the lifetime is $480 \pm 100 \mu\text{s}$ when excited by 800 nm light. The infrared luminescence from BiO molecules is so similar to that from the bismuth-doped alkaline-earth metal silicate glasses. All of these indicate that the infrared luminescence from bismuth-doped glasses should be ascribed to the $X_2^2\Pi_{3/2} \rightarrow X_1^2\Pi_{1/2}$ transition of BiO molecules dispersed in glass host. In fact, Bi_2O_3 can be partially converted into BiO , at high temperature [19].

5. Conclusion

Broadband infrared luminescence covering 1000–1600 nm was observed in bismuth-doped alkaline-earth metal silicate

glasses. The fluorescent lifetime at 1320 nm is about 400 μs . The peak position can be adjusted by the species of the alkaline-earth metal oxide in the glasses. Increasing the basicity of the glasses results in the decrease of the infrared luminescence. The luminescence centered at about 640 nm and the luminescence at 1320 nm may come from the same luminescence origins. We suggest that the infrared luminescence from bismuth-doped glasses should be ascribed to the $X_2^2\Pi_{3/2} \rightarrow X_1^2\Pi_{1/2}$ transition of BiO molecules dispersed in glass host.

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