Infrared superbroadband emission of Bi ion doped germanium–aluminum–sodium glass

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Abstract

The $96GeO–(3-\chi)Al_2O_3–\chi Na_2O–1NaBiO_3$ ($\chi = 0$, 0.5, 1.5 molar percent designated as A1, A2 and A3) and $96GeO–(3.5-\psi)Al_2O_3–\psi Na_2O–0.5Bi_2O_3$ ($\psi = 0.5$, 1, 2 molar percent designated as B1, B2 and B3) glasses were prepared by conventional melting method with the measurement of their DTA curve, fluorescence decay curve, transmission, absorption and emission spectra. The near infrared super-broadband emission characteristics of the A1, A2, B1 and B2 glasses peak at $\sim$1220 nm were observed when pumped by an 800 nm laser diode. The stimulated emission cross section (σ_p) was obtained from the emission spectra. The result indicated that the introduction of Bi^{5+} in $NaBiO_3$ into raw materials could increase the emission intensity of the obtained glasses by 5.6 times than that of Bi^{3+} in Bi_2O_3, and the FWHM ($\Delta\lambda$) and emission lifetime (τ) at 1220 nm increased from 195 nm to 275 nm, and 280 μs to 434 μs. Meanwhile, it was found that the absorption edges were blue-shifted from 486 to 447 nm by comparing those of A1 and B1. The absorption edges were considered to be ascribed to the charge transfer from Bi^{3+} $6s^2$ to Bi^{5+} $6s^0$. Therefore we could conclude that the content of Bi^{5+} ions in A1 was more than that in B1 glasses. It could be deduced from the emission and absorption spectra that the stronger emission intensity and wider FWHM were due to the higher concentration of Bi^{5+} ion in glass. In particular, the increase of Na_2O content was in proportion to the thermal stability and the value of $\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$ of glasses.
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1. Introduction

Information traffic in telecommunication networks has been under rapid development in the latest decade due to the discovery of erbium-doped fiber amplifiers (EDFA) and the popularization of wavelength-division multiplexing (WDM) technique. Among the major two working wavelengths for optical communication are 1.55 μm of EDFA working wavelength, the lowest loss wavelength of silica fiber, and 1.3 μm, the zero dispersion for silica fiber. EDFA utilization in the third telecommunication window (1.5 μm) has received extensive efforts of research [1–4] which gener-

ated a $\sim$80 nm broadband flat gain. On the contrary, no outstanding breakthroughs in the second telecommunication window (1.3 μm) have been made yet. Although the Raman fiber amplifier [5–8] have drawn much attention, however the efficiency of the Raman fiber remains low (at best 5%). Therefore, an alternative luminescent activator to maximally utilize the second telecommunication window is keenly desired.

Recently, Fujimoto [9,10] has discovered a broadband emission around 1.3 μm from bismuth-doped silica glass (BIQG) with 800 nm excitation. Much subsequent research has developed glasses with bismuth doped in different host media [11–15], which are also obtained over 200 nm full width at half maximum (FWHM) at around 1.3 μm. However, Fujimoto [9] suggested that the broadband emission of Bi originated from the transitions between the ground

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state of $^1S_0$ and the excited states of $^3D_{1,2,3}$ and $^1D_2$ from Bi^{5+} but Meng [13] attributed it to the transition of Bi^+ between $^3P_1$ and $^3P_0$. Yet neither of them has been supported by confirmative proofs.

In this work, we chose to dope separately Bi^{5+} in $NaBiO_3$ and Bi^{3+} in Bi_2O_3 into the same host media so as to compare the outcomes of their emission properties and to illuminate which valence of doped Bi brought about a superbroadband emission. In bismuth and aluminum–codoped germanium oxide glasses, the adoption of Al_2O_3 is indispensable to broaden the Bi emission wavelength and the replacement of germanium from silica can greatly enhance the transmittance of glasses and reduce the melting temperature [15]. As a result of the Bi^{5+} introduced from $NaBiO_3$ compound, and in order to keep the same chemical compositions of the host glasses for the dopants of $NaBiO_3$ and Bi_2O_3, we integrated Na_2O, a common glass modifier, into the GeO_2–Al_2O_3 glass system. Analysis of the effect of modifiers such as Na_2O on the fluorescence behavior of Bi ion is thus necessary to provide a guide for a new host with strong and broad emission.

2. Experimental

The $96GeO$–$(3-\chi)Al_2O_3$–χNa_2O–$1NaBiO_3$ ($\chi = 0$, 0.5, 1.5 molar percent, designated as A1, A2 and A3, respectively) and $96GeO$–$(3.5-\psi)Al_2O_3$–ψNa_2O–$0.5Bi_2O_3$ ($\psi = 0.5$, 1, 2 molar percent, designated as B1, B2, B3, respectively) glasses were prepared by the conventional melting method. Na_2O was introduced in the form of Na_2CO_3. GeO_2, Al_2O_3 and Bi_2O_3 were introduced directly from their oxide compounds. All the raw materials were of analytical purity. The batches of 30 g were mixed in an Al_2O_3 crucible under air atmosphere and then sintered at 1580 °C for 40 min. Subsequently the glass melts were poured onto a preheated stainless steel plate. Each glass was annealed at 450 °C for 4 h and cooled into room temperature. Finally, all the glasses were cut into a size of 10 mm × 10 mm × 1 mm and well polished for optical measurements.

The differential thermal analysis on the powders with a 20 mg weight was performed between 50 °C and 900 °C in flowing dry air with a 10 °C/min increase, using a CRY-2 thermal analyzer. The transmission spectra and the infrared luminescence spectra of the samples were measured by a PerkinElmer lambda950 UV/VIS spectrometer (the percentage of the error around 1200 nm is 0.15%) and a TRIAX 550 florescence spectrometer with an excitation of 800 nm laser diode. The fluorescence decay curves of these glasses were recoded by a Tektronix TDS 1012 digital storage oscilloscope. All measurements were taken at room temperature.

3. Results and discussion

3.1. Thermal analysis

Glass transition temperature (T_g), crystallization onset temperature (T_x) and crystallization temperature (T_c) are important parameters of glasses, where the thermal stability of glass can be approximately defined as the quantity of $T_x - T_g$. Fig. 1 illustrates the respective DTA curves of A1, A2, B1 and B2 glasses, represented by the T_g, T_x and T_c temperatures respectively. T_g of A1, A2, A3, B1 and B2 is about 454, 462, 461 and 466 °C, their T_x is about 743, 761, 746, 761 °C, and their T_c is 874, 803, 879 and 893 °C, respectively. The magnitude of $T_x - T_g$ of A1, A2, B1 and B2 is 289, 299, 285 and 295. These results indicated slight increase of T_g, T_x and T_c temperatures in both groups of glasses (A and B) occurred with the accentuating concentration of Na_2O. ($T_x - T_g$) was also in direct proportion to the concentration of Na_2O. The introduction of Na_2O can therefore strengthen the thermal stability of glass.

3.2. Transmission and absorption spectra

The transmission spectra of A1, A2, A3, B1, B2 and B3 are shown in Fig. 2. Glass A1 consists of four main absorption peaks at 370, 500, 700 and 800 nm in the range of 300–1700 nm. On the other hand, Glasses A2, A3, B1, B2 and B3 showed no full four peaks. In the A3 curve there is only one peak at 530 nm and the B3 curve does not contain any obvious peaks.

At the expected working wavelength of the Bi doped broadband glasses (1000–1600 nm), it can be obviously observed from Fig. 2 that with the increasing concentration of Na_2O (from A1 to A3 and from B1 to B3) the transmittance rate reduces slightly (from about 87% to 84% and 86% to 83%, respectively).

Mizoguchi et al. [16] reported that the absorption edges of films shifted from 3.0 eV (414 nm) to 2.1 eV (592 nm) as Bi^{3+} changed into Bi^{5+} gradually. The absorption edges, which were below 3.0 eV (above 414 nm), were ascribed to the charge transfer transitions from Bi^{3+} $6s^2$ to Bi^{5+} $6s^0$. Therefore, the concentration of Bi^{5+} ions in glasses could be reflected from their change of absorption edges. In order to compare the effect of Bi_2O_3 and $NaBiO_3$ chemical compositions on the absorption edge of the glasses, the
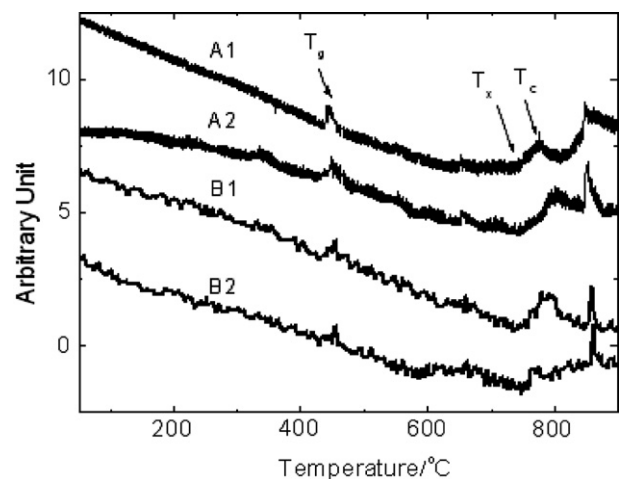

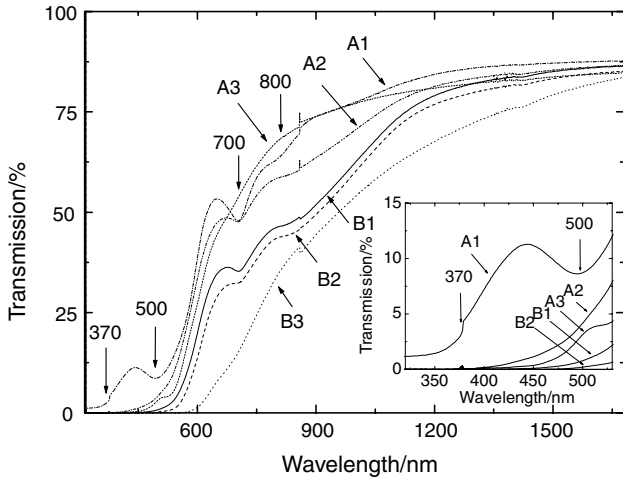
Fig. 1. DTA curves of glasses.

Fig. 2. Transmission spectra of glasses.

absorption spectra of A1 and B1 were shown in Fig. 3. It could be seen from Fig. 3 that the absorption edges of A1 and B1 glasses were 486 and 447 nm, and were blue-shifted obviously, indicating that the A1 glass possesses a much higher concentration of Bi^{5+} ions than B1 glass does. The blue-shifted phenomena were also found by comparing the absorption edges of the other glasses doped with Bi_2O_3 and $NaBiO_3$ as raw materials in the same molar ratio of Bi.

3.3. Emission spectra and fluorescence decay curve

Fig. 4 shows the emission spectra of the glasses peak at 1220 nm, when pumped by an 800 nm laser dioxide. As can be seen, the sample A1 possesses the strongest emission intensity and the widest FWHM. The intensity of A1 at 1220 nm is 5.6 times of that of B1, and the intensity of A2 is also stronger than that of B2. The FWHM of A1, A2, B1 and B2 at 1220 nm is about 275, 182, 195 and 161 nm, respectively. The A3 and B3 glasses however exhibit no characteristic of a wide FWHM. Therefore, the Bi^{5+} dopant directly integrated into raw materials gained advantages over the Bi^{3+} dopant both in intensity and FWHM. The intensity and FWHM was also found to reduce with the increase of Na_2O content in both A and B groups.
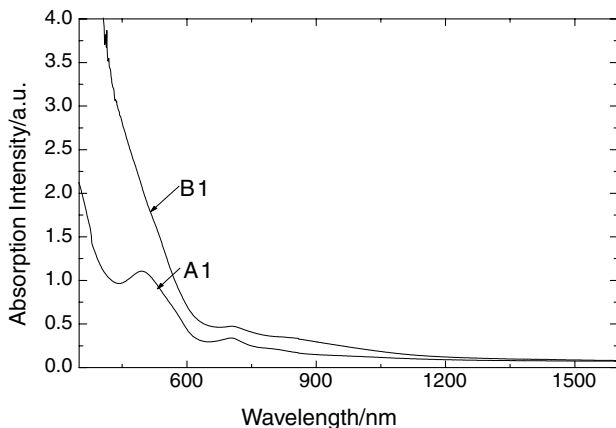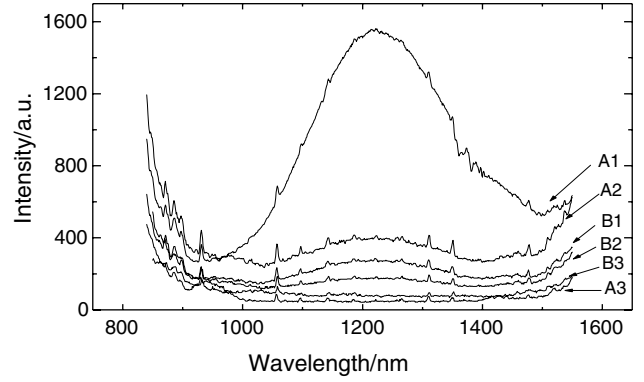

Fig. 3. Absorption spectra of A1 and B1.

Fig. 4. Emission spectra of glasses when pumped by an 800 LD.

The florescence decay curves of A1 and A2 at 1220 nm with an 800 nm laser diode (LD) excitation are shown in Fig. 5. These decay curves are in good agreement with the first order exponential decay with the lifetime as long as 434 and 330 μs. The lifetime of 1220 nm emission thus reduced as the Na_2O content in the glasses increased. Take the absorption spectra into consideration, it was clear that, the higher the concentration of Bi^{5+} ions, the stronger the emission intensity, longer lifetime, and broader FWHM. Therefore, It was suggested that the wide emission band of Bi doped germanium–aluminum–sodium glass was ascribed to the fluorescence of Bi^{5+} ion.

The stimulated emission cross section σ_p as a function of wavelength to a first approximation coincides with the spontaneous emission spectrum [13] which is expressed by the following formula:

$$\sigma_p(\lambda) = \frac{\lambda^2 g(\lambda)}{8\pi n^2 \tau} \tag{1}$$

where $g(\lambda)$, λ, n and τ are the normalized spontaneous emission shape function, the emission wavelength, the host refractive index and the emission lifetime, respectively. By assuming a Gaussian-shaped emission band, the stimulated emission cross section σ_p at the band center can be estimated by the following formula [13]:

$$\sigma_p = \frac{\lambda_c^4}{4\pi n^2 \tau c \Delta\lambda} \left(\frac{\ln 2}{\pi}\right)^{1/2} \tag{2}$$
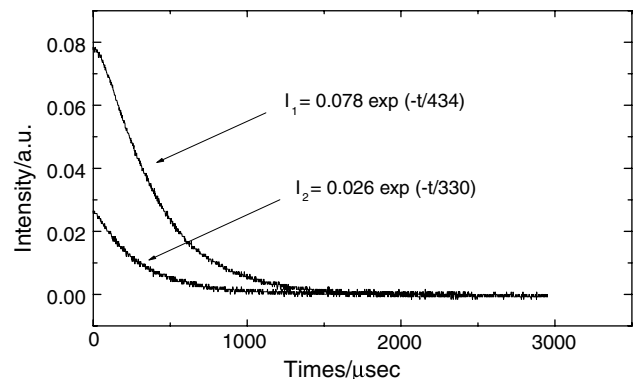

Fig. 5. The fluorescence decay curve of A1 and A2 at 1220 nm with an 800 nm LD excitation.

Table 1
The emission property parameters (n, λ_c, $\Delta\lambda$, τ, σ_p) of glasses at 1220 nm

Samples	n	λ_c/nm	$\Delta\lambda$/nm	τ/μs	$\sigma_p/10^{-22}$ cm
A1: $96GeO–3Al_2O_3–0Na_2O–1NaBiO_3$	1.62	1220	275	434	0.88
A2: $96GeO–2.5Al_2O_3–0.5Na_2O–1NaBiO_3$	1.62	1220	182	330	1.75
B1: $96GeO–3Al_2O_3–0.5Na_2O–0.5Bi_2O_3$	1.62	1220	195	280	1.93
B2: $96GeO–2.5Al_2O_3–1Na_2O–0.5Bi_2O_3$	1.62	1220	161	242	2.7
PAB, Ref. [13]	1.53	1300	300	500	1.0
GAB, Ref. [13]	1.60	1300	320	254.5	1.68

Table 2
The value of $\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$ of glasses samples

Samples	A1	A2	B1	B2	GTB [14]	Ti^{3+}:Al_2O_3 [14]	Er^{3+}:SiO_2 [19]
$\sigma_p \times \tau/10^{-24}$ cm^2 s	3.8	5.8	5.4	6.5	3.53	1.4	–
$\sigma_p \times \Delta\lambda/10^{-20}$ cm^2 nm	242	319	376	435	639	–	22

where λ_c, c, $\Delta\lambda$ are the center wavelength of the band, the velocity of light and the FWHM of the emission, respectively. The emission property parameters (n, λ_c, $\Delta\lambda$, τ, σ_p) at 1220 nm are shown in Table 1.

We could deduce from Table 1 that the stimulated emission cross section σ_p expanded as the content of Na_2O increased. The value of σ_p in Group A was smaller than that in Group B and all the values of σ_p except A1 were larger in comparison to PAB and GBA in Ref. [13].

$\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$ are very important parameters in optical amplifiers in that, the laser threshold is in direct proportion to $(\sigma_p \times \tau)^{-1}$ [17] and a bigger product of $\sigma_p \times \Delta\lambda$ will induce better gain bandwidth properties of optical amplifiers [18]. The values of $\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$ for glass samples (Table 2) indicated that $\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$ of samples prepared in this work were larger than those of Ti^{3+}:Al_2O_3 [14] and Er^{3+}:SiO_2 [19]. Therefore, the $NaBiO_3$ doped germanium–aluminum–sodium glass and Bi_2O_3 doped germanium–aluminum–sodium glass are promising materials for optical amplifier covering the O to L bands in optical communication.

4. Conclusion

In sum, the introduction of Bi^{5+} in $NaBiO_3$ into raw materials could increase the emission intensity of the obtained glass at the center 1220 nm by 5.6 times than that of Bi^{3+} in Bi_2O_3, and the FWHM and emission lifetime at 1220 nm increased from 195 nm to 275 nm, and 280 μs to 434 μs, respectively. The absorption edge of the glass was blue-shifted by comparing those of the glasses, which make use of $NaBiO_3$ and Bi_2O_3 as raw materials, respectively. Taking the emission and absorption spectra together into consideration, we could infer that it should be Bi^{5+} ions that bring about the superbroadband emission property of the germanium–aluminum–sodium glasses. Concomitant with the increasing concentration of Na_2O are the accentuation of glass thermal stability as well as the value of $\sigma_p \times \tau$ and $\sigma_p \times \Delta\lambda$, and the decline of glass transmittance rate, the emission intensity, FWHM and emission lifetime.

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