Inhomogeneous Broadening, Luminescence Origin and Optical Amplification in Bismuth-Doped Glass

Jinjun Ren,[†] Guoping Dong,[†] Shiqing Xu,[‡] Renqiang Bao,[‡] and Jianrong Qiu[§]*

Graduate School of the Chinese Academy of Sciences, Beijing 100080, PR China, and Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, PR China, College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China, and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, PR China

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Absorption and luminescence spectra and optical amplification in bismuth-doped germanate silicate glass were investigated. Two kinds of bismuth ion valence states could exist in the glass. One is Bi^{2+}, which has shown red luminescence, another might be Bi^{+}, which is the active center for infrared luminescence. The infrared luminescence excited at 700, 800, and 980 nm should be ascribed to the electronic transition $^3P_1 \rightarrow {}^3P_0$ of Bi^{+} ions in three distinct sites. The shifting, broadening, and multiple configuration of the luminescence could be due to the randomly disorder of local environment and multiple sites of the active centers. In this glass, obvious optical amplification was realized at 1300 nm wavelength when excited at 808 and 980 nm, respectively.

Introduction

Recently, bismuth-doped glasses have received much attention due to their ultra broadband luminescence covering wavelength region from 900 to 1700 nm, excited at 800 nm.[1−3] Ultra broadband optical amplification and continuous wavelength lasing action at 1300 nm were realized, excited at 800 and 1064 nm, respectively.[4,5] Recently, Bi-doped glass optical fiber laser was also reported.[6] But the luminescence origin is still unclear.[1−3] Additionally, optical amplification excited at 980 nm has not been reported, though there are many reports about the luminescence excited at 980 nm.[2,3,7]

In this paper, optical amplification at 1300 nm is demonstrated with excitation at 808 nm and 980 nm wavelength, respectively. Dependence of the visible and infrared luminescence on excitation wavelength from 400 to 980 nm is also investigated. The luminescence origin is proposed.

Experimental Section

Glass was fabricated with analar grade $Al(OH)_3$, Bi_2O_3, $Mg(OH)_2{\cdot}4MgCO_3{\cdot}5H_2O$, SiO_2 and 6 N GeO_2 chemicals in the composition $50SiO_2{\cdot}30GeO_2{\cdot}15MgO{\cdot}5Al_2O_3{\cdot}Bi_2O_3$ (mol %). A 20 g batch was mixed homogenously in an agate mortar and melt in a corundum crucible at 1680 °C for 90 min in air. Consequently, the melt was cast onto a graphite plate. The glass was then cut into $7 \times 7 \times 2$ mm^3 dimensions and polished for optical measurements.

The optical absorption spectra of the glasses were measured on a JASCO V-570 spectrophotometer. The luminescence spectra were measured on HORIBA JOBINYVON Fluorolog spectrophotometer, excited with laser diodes at 940 and 980 nm wavelengths and a xenon lamp at wavelength between 400 and 800 nm. Optical amplification configuration is the same with Figure 1 in ref 8, except that the filter and an InGaAs detector were replaced by a sp350i spectrometer. The fluorescence lifetime measurements were carried out by exciting the samples with a modulated LD at 940 nm and a xenon lamp at 500 nm, respectively. The signals detected by an InGaAs photodetector in TRIAX550 spectrofluorometer were recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were carried out at room temperature.

Results and Discussion

Absorption spectrum of the glass is shown in Figure 1. To observe the absorption band obviously, the wavelength region between 650 and 1250 nm is put in the insert. We have observed four absorption bands centered at 500, 700, 800, and 990 nm. Because no absorption band could be observed in the glasses without bismuth, these absorption bands have been ascribed to Bi-related sites.[1,7] But the origin of these absorption bands was unclear, because there were several kinds of bismuth valence states in the glasses. We will discuss the origin of the four absorption bands later.

Figure 2 shows the optical amplification at 1300 nm and the dependence of luminescence spectra on excitation wavelength. The luminescence peaks linearly shift from 1131 to 1289 nm and the full width at half maximum (FWHM) increases from 217 to 325 nm, with increments in the excitation wavelength from 700 to 800 nm. Such red shifting and broadening of the luminescence is due to the inhomogeneous broadening of optical transitions. In glasses, crystalline periodicity does not occur. The random disorder of the local environment around active ions leads to the continuous distribution of the minimum of excited energy, and a linear shift of the luminescence bands with decrement in the excitation energy.[9]

However, when excited at 980 and 940 nm, the luminescence bands have shown a blue shift to about 1130 nm (see Figure 2b) and the luminescence spectra can be fitted into three Gaussian peaks centered at about 1130, 1300, and 1420 nm.

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* Corresponding author. Tel: +86-0571-88925079. E-mail address: renjinjunsiom@163.com.

[†] Chinese Academy of Sciences.

[‡] China Jiliang University.

[§] Zhejiang University.

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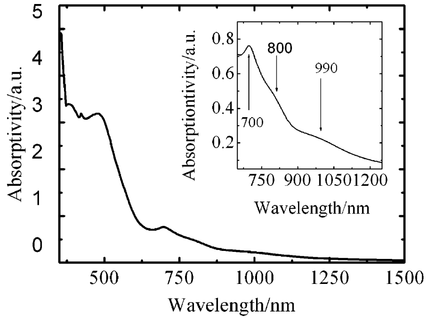

Figure 1. Absorption spectrum of glasses. The wavelength region between 650 and 1250 nm wavelength is put in the insert.

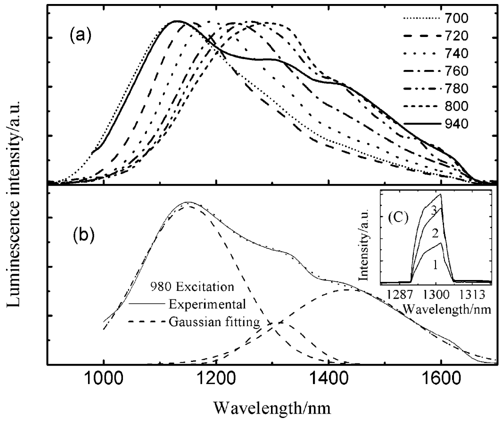

Figure 2. Luminescence spectra excited at wavelength between 700 and 980 nm. (a) Luminescence spectra excited between 700 and 940 nm. (b) Luminescence spectra excited at 980 nm. The dashed line is Gaussian fitting peak. (c) Optical amplification curve: curve 1 presents the probe beam without pumping; curve 2 and 3 present the amplified signal beam pumped at 808 and 980 nm, respectively.

The FWHM is 439 nm. The fluorescence lifetimes at 1130, 1300, and 1420 nm are 250, 200, and 200 μs, respectively, with 940 nm excitation. The blue shift and the multiple configuration of the luminescence cannot be ascribed to the randomly disorder around the active centers. Such three Gaussian peaks might be ascribed to the active centers in distinct sites or different electron transitions of the active centers in the same sites. In $50SiO_2\cdot30GeO_2\cdot15MgO\cdot5Al_2O_3\cdot Bi_2O_3$ (mol %) glass, the active centers might locate at distinct sites coupled by $[SiO_4]$, $[GeO_n]$, $[AlO_n]$, and $[MgO_m]$ groups, where the subscripts denote the coordinate numbers. If there are several excited levels responsible for the infrared luminescence, the glass components will have little effect on the number of the absorption bands, the luminescence configuration and the fitting Gaussian peaks. However, earlier researches have found that glass components have dominating effects on the FWHM, the configurations, and the number of the absorption bands.[1,7] Therefore, it is more reasonable to ascribe these Gaussian peaks to the same electron transition of the active centers in distinct sites than to different electron transitions (see Figure 3). The shifting and broadening of the infrared luminescence should be ascribed to the randomly disorder around the active centers as well as the multiple sites of the active centers.

The Gaussian peaks at 1130 nm excited at 940 and 980 nm should arise from the electron transition between the same levels with the luminescence excited at 700 nm, because they arise at the same position. The former arise from the excitation of the higher vibration levels of the ground level to the lowest vibration levels of the excited level; however, the latter arise from the excitation of the lowest vibration levels of the ground level to the higher vibration levels of the excited level. Similarly, the Gaussian peak at 1300 nm has the same origin with the luminescence excited at 800 nm and arises from the excitation of the higher vibration levels of the ground level to the lowest vibration level of the excited level. However, the Gaussian peak at 1420 nm arises from the excitation at 980 nm from the low vibration levels of the ground level to the higher vibration levels of the excited level (see Figure 3). The luminescence centered at 1130, 1286, and 1420 nm, excited at 700, 800, and 980 nm, should arise from the active centers at distinct sites.

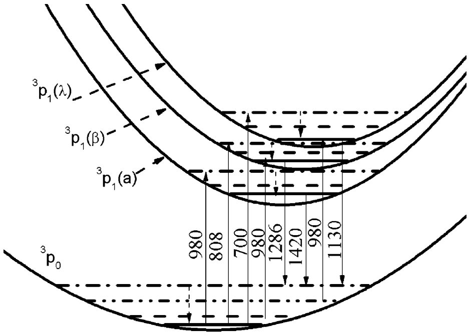

Figure 3. Configurational coordinate diagram for active centers (Bi^+). α, β, and λ represent the active centers coupled by $[RO_n]$ (R = Mg. Al, Si, or Ge), respectively; the horizontal lines represent the vibration levels. The solid arrows denote electron radiative transition, and the dot arrow represents the nonradiative transition.

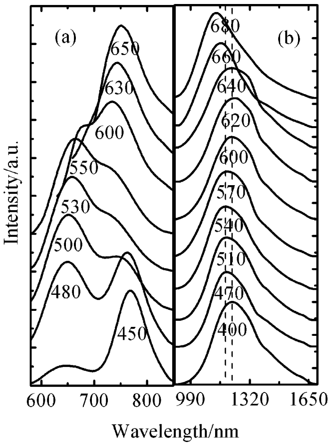

Figure 4. Visible and infrared luminescence spectra excited between 400 and 680 nm. (a) is the visible luminescence spectra, excited between 450 and 650 nm; (b) is the infrared luminescence spectra excited between 400 and 680 nm.

Optical amplification at 1300 nm was realized, when excited with diode lasers at 808 and 980 nm, respectively (see Figure 2c). The excitation power is 0.97 W at 808 nm and 3 W at 980 nm. The optical net gain is 1.70 and 1.82, excited at 808 and 980 nm, respectively. The optical gain is much higher than that (1.19) of bismuth-doped silicate glasses.[5] Fujimoto et al. has found that germanium oxide was more promotive of the generation of peculiar active centers than silicon oxide and sharply increased the absorption coefficient, luminescence intensity and the quantum yield.[10] Our glass sample contains 30 mol% GeO_2. We think the higher gain of our glasses sample is ascribed to the effect of germanium oxide on the luminescence.

Figure 4a shows the visible luminescence spectra excited at wavelength range from 400 to 650 nm. The luminescence consists of two bands centered between 650 and 760 nm, respectively, when excited within this region. The luminescence possesses a FWHM of about 190 nm and covers the wavelength range from 560 to 760 nm. The luminescence lifetime at 750 nm excited at 500 nm is 14.6 μs. Similar luminescence was reported and ascribed to Bi^{2+} by Blasse, Hamstra, and Srivastava et al.[11−13] The red luminescence is the characteristic spectra of Bi^{2+}. Luminescence from Bi^{2+}-activated SrB_4O_7, $M^{2+}SO_4$, and $M^{2+}PO_5$ ($M^{2+} = Ba^{2+}$, Sr^{2+}, and Ca^{2+}) has the maximum at wavelengths from 585 to 638 nm, excited at wavelengths between 413 and 622 nm.[11−13] Such red luminescence and the absorption bands arise from the electron transition between the first excited level $^2P_{3/2}$ and ground level $^2P_{1/2}$ of Bi^{2+}. Because the absorption band centered at about 500 nm and the red luminescence from the glass are almost the same with the absorption and luminescence from Bi^{2+} activated crystals, they should also be ascribed to the electron transition $^2P_{1/2} \rightarrow {}^2P_{3/2}$ and $^2P_{3/2} \rightarrow {}^2P_{1/2}$, respectively, of Bi^{2+}. The multiple configurations of the visible luminescence are consistent with the infrared luminescence, which might arise from Bi^{2+} in distinct sites. Because the red luminescence arises from the electron transition between the first excited level and the ground level of Bi^{2+}, the absorption bands centered at 700, 800, and 980 nm, and the corresponding infrared luminescence, which even have lower energy, should arise from other bismuth ions except Bi^{2+}.

Figure 4b shows the infrared luminescence spectra, excited at wavelength range from 400 to 700 nm. When excited at 680 nm, the infrared luminescence peaks at about 1130 nm, having the same origin with the infrared luminescence excited at 700 nm. But excited at 400, 600, 620, and 640 nm, the luminescence remains at 1220 nm. This infrared luminescence does not shift with the excitation wavelength, which is different with the luminescence excited between 700 and 800 nm. This indicates that they may have different luminescence mechanism. It should be noted that these luminescence peaks are between those excited at 740 and 760 nm (see Figure 2a). From Figure 4a it is found that when excited at 450, 600, 630, and 650 nm, the glass has shown visible luminescence just peaking between 740 and 760 nm. Therefore, the infrared luminescence, excited at 400, 600, 620, and 640 nm, actually arises from the excitation by the visible luminescence from the Bi^{2+} excited at these wavelength regions. Excited at 660 nm, the luminescence peaks at 1156 nm, which peaks between the luminescence excited at 680 nm (peaks at 1130 nm) and 640 nm (peaks at 1220 nm). The luminescence blue shifts with the increment in excitation wavelength from 640 to 660 nm. Such blue shift of the peak positions is extraordinary, because it does not arise from the usual inhomogeneous broadening of electron transition resulted by the randomly disorder around the active centers. The luminescence spectrum excited at 660 nm may be the superposition of two emission bands, one (peaking at 1130 nm) directly excited at 660 nm and the other (peaking at 1220 nm) excited by the 740 nm visible luminescence excited at 660 nm. When excited at 470, 510, 540 and 570 nm, the maxima of the infrared luminescence remain at about 1190 nm between the peak positions of the luminescence excited at 660 and 640 nm (see Figure 4b). Similarly, the luminescence actually arises from the excitation by the visible luminescence centered at about 650 nm from Bi^{2+} excited at these wavelength regions (See Figure 4a). From above it is found that the infrared luminescence could not be directly excited when the excitation wavelength is below 640 nm, because such an absorption band arises from Bi^{2+} ions, not from the infrared active centers. But in previous reports, the absorption band centered at 500 nm was ascribed to the infrared active centers and the infrared luminescence excited at wavelength below 640 nm was considered as arising from the direct excitation of active centers.[2] This clarification of the infrared luminescence origin is valuable for the clarification of the infrared luminescence mechanism and the selection of excitation wavelength to obtain good optical properties.

The infrared luminescence mechanism is still unclear. Bismuth always has several kinds of valence states simultaneously existing in glasses and crystals.[14,15] Murata et al. and we found that the concentration of the infrared luminescent centers and the infrared luminescence intensity decreased with the increment in the basicity of the glasses.[3,16,17] On the basis of the optical basicity of Duffy (higher basicity favors higher valence states of multivalent metal ions),[18] we think that the infrared luminescence should be ascribed to the bismuth in low valence states such as Bi^{2+} and Bi^{+} ions.[3,16] Bi^{2+} has been considered preclusive, on the basis of the above analysis. It is well-known that Bi_2O_3 will be partially converted into BiO and Bi_2O, at high temperature. Pb^0, isoelectronic with Bi^+, also shows similar infrared luminescence with long fluorescence lifetime (3.2 ms at room temperature).[19] Therefore, we think the infrared luminescence most probably arises from Bi^+ and should be ascribed to the electronic transition $^3P_1 \rightarrow {}^3P_0$ of Bi^+ ions (see Figure 3). Because the $^3P_1 \rightarrow {}^3P_0$ transition is forbidden, the infrared fluorescence lifetime of bismuth-doped glass is as long as several hundred microseconds[1,2] and the absorption intensity is weak.

Conclusions

In summary, we have reported the optical amplification, with luminescence dependence on excitation wavelength and luminescence origin in bismuth-doped glass. There should be two kinds of bismuth ion valence states besides Bi^{2+} in the glass. Bi^{2+} has shown red luminescence, and another bismuth ion has shown the infrared luminescence. The absorption bands centered at 700, 800, and 980 nm should be ascribed to the active centers of infrared luminescence, but the absorption band centered at 500 nm should be ascribed to Bi^{2+}.

Excited between 680 and 800 nm, the luminescence peak red shifts from 1130 to 1286 nm with increments in the excitation wavelength. For excitation wavelengths between 650 and 660 nm, the infrared luminescence can be both directly excited at this wavelength and secondarily excited by the 760 nm visible luminescence from Bi^{2+} excited at this wavelength region. When the excitation wavelength is below 640 nm, the infrared luminescence cannot be directly excited because this absorption band arises from Bi^{2+}, not from the infrared active centers, but could be excited by the visible luminescence from Bi^{2+} excited within this wavelength region. Such visible luminescence arises from $^2P_{1/2} \rightarrow {}^2P_{3/2}$ of Bi^{2+}. The infrared luminescence excited at 700, 800, and 980 nm should be ascribed to the electronic transition $^3P_1 \rightarrow {}^3P_0$ of Bi^+ ions in distinct sites. The net optical gain at 1300 nm is 1.70 and 1.82 when pumped with diode lasers at 808 and 980 nm, respectively. The obvious net optical gains at 1300 nm indicate that this glass may be the promising gain medium for optical amplifiers operating at the second optical communication window.

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