Investigations on bismuth and aluminum co-doped germanium oxide glasses for ultra-broadband optical amplification

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Abstract

The broadband luminescence covering 1.2–1.6 \( \mu \text{m} \) was observed from bismuth and aluminum co-doped germanium oxide glasses pumped by 808 nm laser at room temperature. The spectroscopic properties of GeO\(_2\):Bi,Al glasses strongly depend on the glass compositions and the pumping sources. To a certain extent, the Al\(^{3+}\) ions play as dispersing reagent for the infrared-emission centers in the GeO\(_2\):Bi,Al glasses. The broad infrared luminescence with a full width at half maximum larger than 200 nm and a lifetime longer than 200 \( \mu \text{s} \) possesses these glasses with the potential applications in broadly tunable laser sources and ultra-broadband fiber amplifiers in optical communication field.

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1. Introduction

The demand for the information transportation system with much higher transmission capacity and much faster bit rates results in the extraordinarily increasing utilization of the wavelength division multiplexing (WDM) system in the telecommunication field [1]. To achieve the more efficient WDM transmission network, one of attractive approaches is to increase the transmission-channel number through broadening the gain bandwidth of the laser sources and the fiber amplifiers. Therefore, exploration of new broadband luminescent materials especially covering the 1.2–1.6 \( \mu \text{m} \) region and possessing much larger full width at half maximum (FWHM) becomes a key step to further develop the broadband fiber amplifiers and the broadly tunable laser sources. In the past years, more studies have been performed on the rare earth ion, e.g., Er\(^{3+}\), Tm\(^{3+}\) or Pr\(^{3+}\), doped materials [2,3]. However, the work bandwidths of such materials hardly surpass 100 nm since the emissions in near infrared region are mainly initiated from the forbidden f–f transitions between the inner-shell 4f orbits of the rare earth ions. On the contrary, the broad emissions with FWHM larger than 100 nm can be easily achieved with transition-metal-ion-doped materials, because the emissions originate from the d–d transitions of transition-metal ions [4–6]. For example, broadband emission in 1.2–1.6 \( \mu \text{m} \) was observed with FWHM wider than 200 nm from Cr\(^{4+}\)- or Ni\(^{2+}\)-doped glasses [5,6]. Recently, Fujimoto and Nakatsuka reported a novel infrared luminescence from bismuth-doped silicate glass and realized its optical amplification...
at 1.3 μm with 0.8 μm excitation [7,8]. Subsequently, our group also observed the 1.3 μm emission with FWHM more than 300 nm in aluminum and bismuth co-doped germanium oxide glasses pumped by the 808 nm laser diode [9]. All the previous works have clearly demonstrated that co-doping of aluminum into bismuth-doped glasses is indispensable for the occurrence of the broadband infrared luminescence [7,9]. However, it is still unknown up to now what role the aluminum ion plays in the generation of infrared luminescence. In addition, no systematic investigations have been carried out on the effect of the principle glass composition on luminescent properties of GeO$_2$:Bi,Al glasses.

In this work, we firstly investigate the effects of the bismuth or aluminum concentrations and the pumping sources on the luminescent properties of GeO$_2$:Bi,Al glasses, and then study the possible role of aluminum in infrared luminescence of GeO$_2$:Bi,Al glasses and finally discuss the luminescent mechanism.

2. Experimental

The compositions of the glass samples prepared in this study are \((100 - x - y)\)GeO$_2$·\(x\)Bi$_2$O$_3$·\(y\)Al$_2$O$_3$ where \(x = 0, 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0\) and \(y = 0, 1, 2, 3, 4, 5, 6, 8\), respectively. Twenty grams batch for each sample was prepared from commercial powders of high-purity GeO$_2$ (99.999%), analytic reagent Al(OH)$_3$ and Bi$_2$O$_3$ by mixing homogeneously in an agate mortar. Each batch was melted at 1540°C in a high-pure alumina crucible for 20 min in air, and then quickly cast onto a stainless steel plate and finally annealed at 600°C for 2 h. All the prepared and selected glass samples were transparent and bubble-free through the inspection by an optical microscope. The glass specimens were cut and polished into the appropriate shape and thickness for measurements.

All the samples were confirmed to be amorphous by X-ray diffraction (XRD) patterns recorded on a Bruker D4 X-ray diffractometer at 40 kV/20 mA with CuKα1 (\(λ = 1.5405 \) Å) as a radiation source. Absorption spectra were recorded with JASCO V-570 spectrophotometer from 400 to 1500 nm using the sample with a thickness of approximately 1 mm. Infrared emission spectra were measured using ZOLIX SBP300 spectrophotometer with InGaAs as detector in 850–1800 nm. A 50 mW double frequency YAG: Nd laser with 532 nm wavelength, a 50 mW He–Ne laser with 632.8 nm wavelength and a 135 mW InGaAs semiconductor laser diode with 808 nm wavelength were chosen as the excitation sources. Lifetime measurements were carried out by exciting the sample with a modulated 808 nm laser diode with a maximum power of 2 W. The signal detected by an InGaAs photodetector in TRIAX550 was recorded using a Tektronix TDS3052 storage digital oscilloscope.

X-band ESR spectra in the case of \(γ = 9.82 \) GHz were obtained with a Bruker model ER200D-SRC spectrometer under microwave power of 20 MW. The polished glass sample hardness was measured using a HXD-1000 microhardness instrument under an applied load of 100 g. The refractive index was measured on the prism minimum deviation method. All the above measurements were taken at room temperature. Differential thermal analysis (DTA) curve was measured with a CRY-Z Differential Thermal Analyzer at a heating rate of 10 °C min$^{-1}$ using aluminum oxide ceramic pans.

3. Results

3.1. Effect of bismuth concentration

Figs. 1 and 2 show the absorption and fluorescent spectra of \((97 - x)\)GeO$_2$·\(x\)Bi$_2$O$_3$·\(3\)Al$_2$O$_3$ \((x = 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0)\) glasses. As can be seen from Fig. 1, there are four absorption peaks at about 500, 700, 800 and 1000 nm, respectively. With the bismuth concentration increasing, the peak of the 500 nm band shifts towards shorter wavelength from about 560 nm gradually to 500 nm while the peak of the 700 nm band shifts towards the reverse direction. Furthermore, with increasing \(x\) value, the fluorescent intensity monotonically increases until \(x = 0.5\), and then decreases, showing that the critical dopant concentration is about 0.5 mol%.

![Fig. 1. Absorption spectra of (97 − x)GeO$_2$·3Al$_2$O$_3$·xBi$_2$O$_3$ (x = 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0) glasses.](image-url)
3.2. Effect of aluminum concentration

Fig. 3 illustrates the fluorescent spectra of \((99 - y)\text{GeO}_2 \cdot x\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3 (x = 1.0, 3.0, 5.0, 8.0)\) pumped by 808 nm laser. As \(y\) value increasing, the fluorescent intensity continuously increases until \(y = 5.0\), and then decreases as shown in Figs. 3 and 4. Meanwhile, the emission peak shifts from 1320 nm \((y = 1.0)\), 1300 nm \((y = 3.0)\), 1300 nm \((y = 5.0)\) to 1286 nm \((y = 8.0)\). Obviously, the influence of \(\text{Al}_2\text{O}_3\) addition on the fluorescent peak position seems slighter than that of the \(\text{Bi}_2\text{O}_3\) addition.

3.3. Effect of pumping sources

Fig. 5 presents the normalized fluorescent spectra of 96\text{GeO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3 by different excitation sources: (a) 532 nm, (b) 632.8 nm and (c) 808 nm. With pumping-source variation from 532 nm to 632.8 nm and 808 nm, the strongest emission peak shifts towards longer wavelength, viz. 1247 nm \((\text{FWHM} = 295 \text{ nm})\) to 1300 nm \((\text{FWHM} = 281 \text{ nm})\), and the shoulder peak at around 1170 nm vanishes gradually, indicating the fluorescence dependence on the pumping source. Similar result was also found in bismuth doped silicate glasses [7].

The fluorescence dependence on the excitation sources provides the possibility to optimize the pumping routes for the optical amplifications.

3.4. Thermal, mechanical and optical properties of 94.5\text{GeO}_2 \cdot 5\text{Al}_2\text{O}_3 \cdot 0.5\text{Bi}_2\text{O}_3 glass

Based on the studies on Sections 3.1 and 3.2, the glass sample with optimized composition of 94.5\text{GeO}_2 \cdot 5\text{Al}_2\text{O}_3 \cdot 0.5\text{Bi}_2\text{O}_3 (GAB) was prepared. The DTA data of GAB glass show that the glass transition temperature \(T_g\), the crystallization onset temperature \(T_x\) and the
maximum crystallization temperature \( T_c \) are 651, 757 and 779 °C, respectively. Glass thermal stability roughly characterized by the parameter \( \Delta T = T_c - T_g \) can be considered to be better if \( \Delta T > 100 \) °C [10]. The GAB glass is stable against devitrification due to its larger \( \Delta T \) value up to 106 °C.

Vicker’s hardness of GAB glass was measured to be 274 kg mm\(^{-2}\), a little bigger than 264 kg mm\(^{-2}\) for the 91GeO\(_2\):8Al\(_2\)O\(_3\):1Bi\(_2\)O\(_3\) glass. The hardness decrement partially reflects that the glass network becomes looser as Al\(_2\)O\(_3\) concentration increases.

The absorption cross-section \((\sigma_{abs})\) at 808 nm for GAB glass was calculated to be \(1.61 \times 10^{-20}\) cm\(^2\). The stimulated emission cross-section \((\sigma_{em})\) at 1280 nm was estimated to be \(1.55 \times 10^{-20}\) cm\(^2\) by Füchtbauer–Landenburg equation: 

\[
\sigma_{em} = \frac{\lambda}{n \cdot CN} \cdot \frac{\tau_{rad}}{g(\lambda)}
\]

where \(\lambda\) is wavelength, \(g(\lambda)\) is the normalized spontaneous emission shape function, \(n\) is the host refractive index, \(CN\) is light velocity, \(\Delta \lambda\) is the FWHM of emission and \(\tau_{rad}\) is the emission lifetime [11]. In this work, \(\Delta \lambda = 322\) nm, \(\tau_{rad} = 273\) µs and \(n = 1.6166\), respectively for GAB glass.

4. Discussion

4.1. Absorption and emission spectra

As can be seen from the absorption and emission spectra of the series of \((97-x)\)GeO\(_2\):xBi\(_2\)O\(_3\):3Al\(_2\)O\(_3\) \((x = 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0)\) glasses (see Figs. 1 and 2), the strongest emission lies at \(~1100\) nm with a shoulder peak at about 1254 nm and the strongest absorption lies at about 560 nm with a shoulder peak at about 510 nm when \(x = 0.01\). Along with increasing the \(x\) value to 0.05, the 1254 nm emission and the 510 nm absorption becomes the strongest whereas the 1100 nm emission and the 560 nm absorption becomes a shoulder. As \(x\) value further increases to 1.0, the \(~1300\) nm emission turns into the strongest with appearance of another new shoulder peak at 1450 nm except the 1100 nm shoulder, meanwhile the strongest absorption moves to \(~500\) nm. We propose that at least four emission centers, e.g., 1100, 1254, 1300 or 1450 nm emission centers, exist in these glasses, which might be the reason why the fluorescence decay curve of 96GeO\(_2\):3Al\(_2\)O\(_3\):1Bi\(_2\)O\(_3\) is not just a simple exponential decay (see Fig. 6). Previously, we considered the fluorescence decay to obey the first-order exponential equation [9]. But as we redraw the figure with the intensity in natural logarithm against decay time, the divergence between the fluorescence decay curve and the first-order exponential equation clearly protrudes in the latter stage even though the decay curve is consistent with the first-order exponential equation in the initial stage. At lower bismuth concentration, the 1100-nm emission center is preferred; while at higher bismuth concentration, the other centers can be favored to form, which results in the shape changes in both absorption and emission spectra.

4.2. The role of aluminum in the infrared luminescence

The coordination number of aluminum ion increases with increasing Al\(_2\)O\(_3\) content in Al\(_2\)O\(_3\):SiO\(_2\) glass [12]. As a small amount of Al\(_2\)O\(_3\) is built into the Al\(_2\)O\(_3\):SiO\(_2\) glass, Al\(^{3+}\) ions will be mainly in the four-fold coordination [12–17]. In view of the much more structural resemblance between glassy SiO\(_2\) and GeO\(_2\), the [AlO\(_4\)]\(^{-}\) tetrahedrons will be more favorable in GeO\(_2\)-based glasses because the ion radius of Ge\(^{4+}\) (\(R_{Ge}^{4+}\)(CN = 4) = 0.39 Å where CN is the coordination number) matches that of Al\(^{3+}\) (\(R_{Al}^{3+}\)(CN = 4) = 0.39 Å) better than that of Si\(^{4+}\) (\(R_{Si}^{4+}\)(CN = 4) = 0.26 Å) [18]. When the Al\(_2\)O\(_3\) concentration is as lower as \(y < 4.0\), the formed [AlO\(_4\)]\(^{-}\) tetrahedrons coupled with [GeO\(_4\)] tetrahedrons will surround the bismuth-related infrared-emission centers and enlarge the center-to-center spacing in the bonding association of Al–O–Bi, which is similar to the dispersing of the Nd\(^{3+}\) ions by Al\(^{3+}\) ions in Nd\(^{3+}\) and Al\(^{3+}\) co-doped silica glasses [12–15]. Consequently, the interaction between these emission centers will be weakened and the energy loss due to non-radiation transitions will be reduced. Therefore the fluorescent intensity and lifetime increases as indicated in Fig. 4. However, when the Al\(_2\)O\(_3\) concentration becomes as higher as 5.0 < \(y < 8.0\), the five- or six-coordinated Al\(^{3+}\) ions, coexisting with four-coordinated ones, appear and increase [12,15]. The five- or six-coordinated Al\(^{3+}\) ions play as the glass network modifiers and could not efficiently disperse the infrared-emission centers. Thus, the interaction between the
infrared-emission centers becomes stronger, and the fluorescence intensity and lifetime decreases as shown in Fig. 4.

In the preparation process of GeO$_2$:Bi,Al glass, we observed that the glass molten becomes more easily poured out of the alumina crucibles with increasing the Al$_2$O$_3$ concentration, which might be attributed to the increasing non-bridging oxygen ions with increasing network modifiers of five- or six-coordinated Al$^{3+}$ ions. When $y$ is up to 10, no transparent glass could be obtained.

4.3. Where does the broad infrared luminescence come from?

In the past decades, luminescent properties of Bi$^{3+}$ or Bi$^{2+}$ doped crystals and glasses have been investigated [19–24]. The Bi$^{3+}$ transitions between the ground state ($^1$S$_0$) and the excited states ($^3$P$_1$ and $^1$P$_1$ mixed by the spin–orbit coupling) are usually observed [19]. The absorption (or excitation) peaks of Bi$^{3+}$ in both crystals and glasses appear in the ultraviolet region, while the emission peaks of Bi$^{3+}$ occurs in the ultraviolet, green, or even red wavelength region corresponding to the variation of host materials [19–22]. But no infrared luminescence from Bi$^{3+}$ and no fluorescent lifetime of Bi$^{3+}$ longer than 5 µs in crystals or glasses have been reported up to now [19,22]. Contrary to Bi$^{3+}$-doped luminescent materials, Bi$^{2+}$-doped ones were paid little attentions.

To the best of our knowledge, only the luminescent properties of Bi$^{2+}$ in crystals were reported. The Bi$^{2+}$ transition between the ground state of $^2$P$_{1/2}$ and the first excited state of $^2$P$_{3/2}$ is parity forbidden, but becomes allowed when $^2$P$_{1/2}$ and the excited states of $^2$S$_{1/2}$ and $^2$P$_{3/2}$ are mixed by the uneven crystal-field terms, whereas the transition between $^2$P$_{1/2}$ and $^2$S$_{1/2}$ is strongly allowed [13,14]. Therefore, three excitation peaks of Bi$^{2+}$ in SrB$_4$O$_7$ corresponding to the transitions from $^3$P$_{1/2}$ to $^2$P$_{3/2}$ split into two by crystal fields and to $^2$S$_{1/2}$ were observed at 575, 470 and <312 nm, and one emission peak of $^2$P$_{3/2}$ → $^2$P$_{1/2}$ was at 586 nm [23]. And the fluorescent lifetime of SrB$_4$O$_7$:Bi$^{2+}$ was 10.6 µs at 300 K [23].

Compared with the information on the Bi$^{3+}$ or Bi$^{2+}$ doped materials mentioned above, the absorption and emission peak-positions of GeO$_2$:Bi,Al glasses are greatly different from the Bi$^{3+}$ or Bi$^{2+}$ doped materials. Four absorption peaks of GeO$_2$:Bi,Al glasses cover the large wavelength region from visible to infrared, and their emission peaks lie in the infrared region. Furthermore the fluorescent lifetimes of GeO$_2$:Bi,Al glasses are more than 200 µs, which are one order or two order longer than those of the aforementioned Bi$^{2+}$ or Bi$^{3+}$ doped materials. Fujimoto et al. ascribed the absorption and the emission spectra of Bi and Al ions co-doping silicate glasses to the Bi$^{5+}$ transitions between the ground state of $^1$S$_0$ and the excited states of $^3$D$_{3,2,1}$ and $^1$D$_2$ [7]. But as well known, Bi$^{5+}$ ions are confirmed to exist in compounds containing alkali oxides with higher basicity, e.g., in NaBiO$_3$ or KBiO$_3$, which are absent in GeO$_2$:Bi,Al glasses [25,26]. Moreover, at higher temperature, Bi$_2$O$_3$ will readily dissociate into the black suboxide BiO or into bismuth metal [27]. ESR measurement is employed to detect the paramagnetic centers like Bi$^{2+}$ ions. Unfortunately no signal could be detected, which is similar to Ref. [7].

Dong and Zhu studied the optical properties of the surface-modified Bi$_2$O$_3$ nanoparticles in the size range of 5–13 nm [28]. One exciton-absorption peak at 484 nm and the absorption band gap of ~376 nm (~3.3 eV) were reported for both orange and wine-red Bi$_2$O$_3$ nanoparticles, which was very close to the absorption peak of ~500 nm and the absorption edge of ~375 nm in GeO$_2$:Bi,Al glasses [9]. But no infrared luminescence was investigated in such Bi$_2$O$_3$ nanoparticles. As examined by the X-ray diffractometer, no obvious signals indicate the existence of Bi$_2$O$_3$ phase in the GeO$_2$:Bi,Al glasses. Therefore there are two possibilities. One is that the infrared luminescence is not from Bi$_2$O$_3$ nanoparticles. The other is that the infrared luminescence is from the Bi$_2$O$_3$ nanoparticles, but the amount of Bi$_2$O$_3$ is too small to be detected by the X-ray diffractometer. If the infrared luminescence comes from the Bi$_2$O$_3$ nanoparticles indeed, it should not be arising from the direct transitions from conduction band to valence band since the band gap energy of Bi$_2$O$_3$ is about 3.3 eV [28]. It might be from recombinations between the defect levels in the band gap or from the defect levels to the valence band. In order to identify what types of bismuth really contribute to the infrared luminescence, more investigations should be carried out even though the spectral features of the GeO$_2$:Bi,Al glasses are similar to those of the SiO$_2$: Al, Bi glasses.

4.4. Figure-of-merits of bandwidth and gain

As well known, the products of $\sigma_{em} \times$ FWHM and $\sigma_{em} \times \tau$ are the important parameters to evaluate the figure-of-merit of bandwidth and gain of broadband amplifier, respectively [6,29]. The bigger the products, the better the bandwidth and gain properties of the amplifiers. The parameters of $\sigma_{em} \times$ FWHM and $\sigma_{em} \times \tau$ for the GAB glass are about $499 \times 10^{-20}$ cm$^2$ nm and $4.23 \times 10^{-24}$ cm$^2$ s, respectively, which are bigger than that for Er$^{3+}$-doped silicate glass ($\sigma_{em} \times$ FWHM = $22 \times 10^{-20}$ cm$^2$ nm) [29], that for Cr-doped forsterite ($\sigma_{em} \times \tau = 2.85 \times 10^{-24}$ cm$^2$ s) [11] and that for Ti-doped sapphire ($\sigma_{em} \times \tau = 1.4 \times 10^{-24}$ cm$^2$ s) [6]. Therefore, it can be suggested from the above comparison that the Bi- and Al-co-doped germanium oxide glass might be the promising host material for the super-broadband amplifiers.
5. Conclusions

The broad near infrared emission, which was greatly different from those Bi$^{3+}$- or Bi$^{2+}$-doped materials previously reported in the literatures, was observed in the spectral region of 1.2–1.6 $\mu$m from GeO$_2$:Bi,Al glasses at room temperature in the case of 808 nm excitation. The luminescent properties of GeO$_2$:Bi,Al glasses depend on the glass compositions. The Al$^{3+}$ ions play as dispersing role for the infrared-emission centers in GeO$_2$:Bi,Al glasses. The broad infrared luminescence with FWHM more than 200 nm and lifetime longer than 200 µs covers the O (1260–1360 nm), E (1360–1460 nm) and S (1460–1530 nm) bands and even extends into C (1530–1565 nm) and L (1565–1625 nm) bands, implying that these glasses might be very useful for the applications in the high power or broadly tunable laser sources and the wide-band optical amplifiers.

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