Bismuth-activated luminescent materials for broadband optical amplifier in WDM system

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Abstract

New broadband near infrared luminescence covering the whole work windows (1260–1625 nm) of the current wavelength division multiplexing (WDM) system was found from bismuth-activated M2O–Al2O3–SiO2 (M = Li, Na) and Li2O–Ta2O5–SiO2 glasses at room temperature in the case of 808 nm-laser excitation. But the near infrared luminescence mechanism of the bismuth-activated glasses is not well understood up to now. The figure-of-merits of bandwidth and gain of the glasses are better than those of Er3+-doped silicate glasses and Ti3+ doped sapphire, implying they are the promising gain-medium candidates for the broadband amplifiers and the widely tunable laser sources.

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1. Introduction

As well known, expanding the gain bandwidth of the fiber amplifier is a key and promising way to achieve more efficient wavelength division multiplexing (WDM) transmission network with higher transmission capacity and faster transportation speed. However, there are still no efficient and broadband optical amplifiers that could cover all the optical windows of silica glass fiber. Even though the development of WDM technology based on the rare-earth ion-doped fiber amplifier (e.g. EDFA) has promoted the progress in the optical communication in past decades, rare-earth ion-doped fiber amplifier is hardly to realize this goal since the application bandwidths are difficult to surpass 100 nm because 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. This bandwidth limit can be easily overcome by transition-metal-ion-doped materials, e.g. Ni2+-doped zinc alumino-silicate glasses, which nowadays attract much more attention due to their excellent optical properties [1]. Recently, Fujimoto and Nakatsuka reported a bismuth-doped glass of 92SiO2·7.0Al2O3·1.0Bi2O3 (SAB, hereafter) with a novel infrared luminescence and realized its optical amplification at 1.3 μm with 0.8 μm excitation [2,3]. And consequently, we observed 1.3 μm emission with FWHM (full width at half maximum) larger than 300 nm in aluminum and bismuth codoped germanium oxide glasses with 808 nm excitation [4]. All the previous investigations have demonstrated that codoping of aluminum into bismuth-doped glasses is indispensable for the broadband infrared luminescence [2–4]. Since codoping of Bi
with Al into SiO₂ or GeO₂ glass can lead to the infrared luminescence, we suspect that the analogous results can be obtained when codoping of Bi with other foreign cations.

In this study, we report the broadband infrared luminescence covering the O band to L band (1260–1625 nm) from 10M₂O · 14Al₂O₃ · 75SiO₂ · 1.0Bi₂O₃ (M = Li, Na) and 10Li₂O · 14Ta₂O₅ · 75SiO₂ · 1.0Bi₂O₃ (in mol%) glasses with the FWHM larger than 250 nm and the fluorescent lifetime longer than 200 μs, study the glass composition effect on the luminescent properties of these glasses, and compare the bismuth-doped glasses including 94GeO₂ · 5.0Al₂O₃ · 1.0Bi₂O₃ glass with other laser materials activated by Er³⁺, Ni²⁺ or Ti³⁺. Experimental results demonstrate that bismuth-doped glasses have the potential applications in the broadband amplifiers and the widely tunable laser sources.

2. Experimental

High-purity reagents, Li₂CO₃, NaNO₃, Al(OH)₃, Ta₂O₅, SiO₂, GeO₂ and Bi₂O₃ were selected as raw materials. The compositions (in mol%) of the glass samples prepared in the present study were (1) 10Li₂O · 14Al₂O₃ · 75SiO₂ · 1.0Bi₂O₃ (LASB, hereafter), (2) 10Li₂O · 14Ta₂O₅ · 75SiO₂ · 1.0Bi₂O₃ (LTSB, hereafter), (3) 10Na₂O · 14Al₂O₃ · 75SiO₂ · 1.0Bi₂O₃ (NASB1, hereafter), (4) 5Na₂O · 10Al₂O₃ · 54SiO₂ · 1.0Bi₂O₃ (NASB2, hereafter) and (5) 94GeO₂ · 5.0Al₂O₃ · 1.0Bi₂O₃ (GAB, hereafter). Sixty grams batch for each sample was melted at 1400–1600 °C for 20 min ~ 2 h in air condition, and then quickly cast onto a stainless steel plate and finally annealed at 500–1600 °C for 1 h. NASB2 glass is colorless and other glasses are reddish brown or magenta. All the obtained glass samples were cut and polished into the appropriate shape and thickness for measurements.

The optical absorption spectra and the infrared luminescence spectra of the samples were measured using JASCO V-570 spectrophotometer and ZOLIX SBP300 spectrophotometer with InGaAs detector at the excitation of an 808 nm laser diode (LD), respectively. The emission and the excitation spectra in the UV–VIS range were recorded on a JASCO FP-6500 fluorescence UV–VIS spectrophotometer. And the fluorescence lifetime measurements were carried out by exciting the sample with a modulated 808 nm LD, the infrared fluorescence presents an ultra-broadband characteristic in all the glass samples in this study. The peaks lie at 1265 nm (FWHM = 318 nm), ~1300 nm (FWHM = 268 nm) and ~1300 nm (FWHM = 312 nm) for LASB, LTSB or GAB glasses, respectively (see Fig. 2).

In the transmission spectrum of NASB1 glass, there are also two noticeable absorption peaks at around 500, 700, 800 and 1000 nm can be found in GAB glass (see Fig. 1). The ESR technique is used to detect the unexpected impurities (e.g. transition metal Cr or Mn) and the oxygen-deficiency related defects in SiO₂- or GeO₂-based glasses doped with bismuth. However, no ESR signal could be detected in the glasses, which means that the absorptions are not from the impurities and defects [2,5,6]. Since there is also no any absorption in the aforementioned spectral regions for the glass samples without containing bismuth, the absorptions are therefore due to bismuth [2,4–7]. When pumped by the 808 nm LD, the infrared fluorescence presents an ultra-broadband characteristic in all the glass samples in this study. The peaks lie at 1265 nm (FWHM = 318 nm), ~1300 nm (FWHM = 268 nm) and ~1300 nm (FWHM = 312 nm) for LASB, LTSB or GAB glasses, respectively (see Fig. 2).

3. Results

Transmission spectra of LASB, LTSB and GAB glasses are illustrated in Fig. 1. Only the two peaks at around 500 and 700 nm can be noticeably detected in LASB and LTSB glasses while four absorption peaks at around 500, 700, 800 and 1000 nm can be found in GAB glass.
1310 nm was observed from NASB1 glass with a FWHM of 360 nm. However, similar near infrared fluorescence could not be detected in NASB2 glass. In NASB2 glass, only emission and excitation spectra attributed to Bi$^{3+}$ ions could be detected (see Fig. 3). As glass composition changes from SAB to LASB and NASB1, the glass optical basicity increases. Meanwhile, the strongest absorption peak shifts towards shorter wavelength from 500 nm for SAB glass to 488 nm for LASB glass and 480 nm for NASB1 glass, and the emission peak shifts towards longer wavelength from 1250 nm for SAB glass to 1265 nm for NASB1 glass and 1310 nm for NASB2 glass, respectively. As shown in Fig. 4, the fluorescent decay curve is close to the first-order exponential decay equation at the initial time, and however, after the period, the decay curves become more and more deviation with time. This phenomenon implies that a more complicated mechanism may contribute to the overall decay behaviors, rather than a simple exponential decay. Therefore, another more elaborate model of second-order exponential decay equation is employed to fit the fluorescence decay curves and better fitting results are achieved, implying that the decay process might consist of one fast process and one slow process (see Fig. 4). We suggest that the bismuth ions might occupy different sites in the glass matrix, which leads to the fluorescence decay deviations from the simple exponential decay equation [5–7].

**4. Discussion**

Luminescent properties of Bi$^{3+}$ or Bi$^{2+}$ doped crystals and glasses have been investigated for decades [8–14]. The ground state of the Bi$^{3+}$ ion is $^1S_0$, whereas the 6s6p excited states give rise to $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ in order of increasing energy. Because the $^1S_0 \rightarrow ^3P_0$ and $^1S_0 \rightarrow ^3P_2$ transitions are strongly forbidden, the Bi$^{3+}$ transitions between the $^1S_0$ ground state and the $^3P_1$ or $^1P_1$ excited state are usually observed. In general, the excitation peaks of Bi$^{3+}$ ion appear in the ultraviolet region, while the emission peak of Bi$^{3+}$ ion is not located in one characteristic spectral region but varies from the ultraviolet region into the red region with differing host lattice [8–12]. The fluorescent lifetime of Bi$^{3+}$ is no longer than 5 μs in crystals or glasses [8,9,12]. Contrary to Bi$^{3+}$-doped luminescent materials, Bi$^{2+}$-doped ones were paid little attention. To the best of our knowledge, only the luminescent properties of Bi$^{2+}$ doped crystals were reported. The Bi$^{2+}$ transition between the ground state of $^2P_{1/2}$ and the first excited state of $^2P_{3/2}$ is parity forbidden, but becomes allowed when $^2P_{1/2}$ and the excited states of $^2S_{1/2}$ and $^2P_{3/2}$ are mixed by the uneven crystal-field terms, whereas the transition between $^2P_{1/2}$ and $^2S_{1/2}$ is strongly allowed [13,14]. Therefore, three excitation peaks of Bi$^{2+}$ in SrB$_2$O$_7$:Bi$^{2+}$, corresponding to the transitions from $^2P_{1/2}$ to $^2P_{3/2}$ split into two by crystal-fields and to $^2S_{1/2}$ were observed at 575, 470 and <312 nm, and one emission peak due to $^2P_{3/2} \rightarrow ^2P_{1/2}$ was at about 586 nm [13]. And the fluorescent lifetime of SrB$_2$O$_7$: Bi$^{2+}$ was 10.6 μs at 300 K [13]. The luminescence in the near infrared region for Bi$^{3+}$ or Bi$^{2+}$ doped materials has not been reported up to now.

Compared with the aforementioned information on the Bi$^{3+}$ or Bi$^{2+}$ doped materials, the peak position in both absorption and emission spectra of LASB, LTSB, GAB...
and NASB1 glasses are greatly different from the previously reported Bi\textsuperscript{3+} or Bi\textsuperscript{2+} doped materials. Furthermore, the fluorescent lifetimes of these glasses are longer than 200 μs, which is one or two-order longer than those of the aforementioned Bi\textsuperscript{3+} or Bi\textsuperscript{2+} doped materials. Fujimoto et al. ascribed the absorption and the emission spectra of Bi and Al ions codoping SAB glasses to the Bi\textsuperscript{3+} transitions between the ground state of \textsuperscript{1}S\textsubscript{0} and the excited states of \textsuperscript{3}D\textsubscript{3,2,1} and \textsuperscript{1}D\textsubscript{2} [2]. However, at higher temperature, Bi\textsubscript{2}O\textsubscript{3} will readily dissociate into the suboxide BiO or even into bismuth metal [15,16]. We suspect that the broadband infrared luminescence with the lifetime longer than 200 μs in LASB, LTSB, GAB or NASB1 glasses might originate from the lower-valence bismuth rather than from the higher-valence unstable Bi\textsuperscript{5+} ions.

As well known, high-valent Bi\textsuperscript{5+} ion often exists in the compounds containing alkali oxides with higher basicity, e.g. NaBiO\textsubscript{3} or KBiO\textsubscript{3} [17,18]. The optical basicity calculated from the empirical formula proposed by Duffy [19,20] is 0.635 for the NASB2 glass, 0.538 for the NASB1 glass, 0.552 for LASB glass and 0.491 for SAB glass. According to the optical basicity theory [20], the upper oxidation state of dopant is usually favorable in the glass with higher basicity. Thus, the higher valent Bi\textsuperscript{5+} ions should be more preferred in the NASB2 glass than the NASB1, LASB and SAB glasses, since the NASB2 glass has the highest optical basicity value among them. If the infrared luminescence comes from Bi\textsuperscript{5+} ions, the infrared emission should also be observed from the NASB2 glass as well as from the NASB1 glass. However, no broad infrared emission but only the typical absorption and emission due to Bi\textsuperscript{3+} ions can be detected in the NASB2 glass with higher Na\textsubscript{2}O content at room temperature as indicated in Fig. 3. So the infrared luminescence is not from Bi\textsuperscript{5+} and Bi\textsuperscript{3+} ions.

At high temperature, Bi\textsubscript{2}O\textsubscript{3} can be partially converted into atomic bismuth metal [15,16]. If the resulting bismuth atoms have a chance to become aggregated, bismuth clusters like Bi\textsubscript{2} or Bi\textsubscript{4} might be formed. Bishay found a strong absorption band peaked at about 515 nm due to bismuth atoms in a γ-irradiated bismuth lead borate glass, which is similar to the ~510 nm absorption in LTSB or GAB glasses [15]. Ahmed and Nixon reported a fluorescence peak at about 13500 cm\textsuperscript{-1} (741 nm) in Bi\textsubscript{2}O\textsubscript{3}-containing argon matrix under the 19436 cm\textsuperscript{-1} (514 nm) excitation [21], which was similar to the case in SAB glass where a peak at 750 nm was observed at the 500 nm excitation [2]. Fink et al. found the emission in the spectral region of 7620 cm\textsuperscript{-1} (1312 nm)–7800 cm\textsuperscript{-1} (1282 nm) from Bi\textsubscript{2} in gas phase, but they did not present the lifetime data [22]. Recently, Fink and Shestakov et al. discovered the X\textsubscript{2}2\textsuperscript{\textsuperscript{I}3/2}→X\textsubscript{2}2\textsuperscript{\textsuperscript{I}1/2} emissions in 1.0–1.6 μm with radiative lifetime of 480 ± 100 μs and absorptions at ~500, 700, 800 and 1000 nm from BiO molecule in gas phase [22,23]. In view of the similarity in emission peak position, absorption peak positions and lifetime between BiO in gas phase, LASB, LTSB, GAB or NASB1 glasses, we propose that the infrared luminescence might be from BiO molecule dissolved in these bismuth-doped glasses. The more identified conclusion could not be made at this moment, because we cannot rule out the other possibility that the infrared luminescence origins from the bismuth cluster, e.g. Bi\textsubscript{2} or Bi\textsubscript{4}. Given that the infrared luminescence is really from BiO, the observed absorptions at ~500, 700, 800 and 1000 nm can be assigned to X\textsubscript{1}→(H, I), X\textsubscript{1}→A\textsubscript{2}, X\textsubscript{1}→A\textsubscript{1} and X\textsubscript{1}→X\textsubscript{2}, respectively, and the emission peak at 1300 nm can be to X\textsubscript{2}→X\textsubscript{1} [23].

The 1100–1600 nm region of telecommunication wavelength is divided into two low loss windows, viz. the second window centered around 1310 nm and the third window centered around 1550 nm by the strong 1400 nm absorption due to hydroxyl ions in silica fibers. Recently, Lucent Technologies succeeded in eliminating almost all water molecules from the silica glass fibers with a new ultrahigh purifying process to realize the ultra-low attenuation at around 1400 nm in silica fiber and provided a possibility for using more than 100 nm additional bandwidth for optical communication [24]. It is necessary to explore luminescent materials in the wavelength range covering the E + S bands in order to develop the fiber amplifier working around 1400 nm (E + S bands). However, there are only a few reports on such luminescent materials up to now. The LASB, LATB and GAB glasses show the super-wide luminescence with FWHM of about 300 nm covering not only the E + S bands but also the O (1260–1360 nm) band, even expanding into the C (1530–1565 nm)+L (1565–1625 nm) bands. These excellent properties make it possible to directly amplify the optical signal in the whole optical communication wavelength region only with a single fiber amplifier.

Stimulated emission cross-section (\(\sigma_{\text{em}}\)) estimated by Füchtbauer–Landenburg formula, \(\sigma_{\text{em}}\)×FWHM and \(\sigma_{\text{em}}\)×\(\tau\) are calculated in order to investigate whether the Bi-doped glasses have the advantages as gain-medium for the broadband amplifier over other laser materials. The values of \(\sigma_{\text{em}}\)×FWHM and \(\sigma_{\text{em}}\)×\(\tau\) are the important parameters to evaluate the figure-of-merits of bandwidth and gain of broadband amplifier, respectively [1,25]. The bigger the values, the better the bandwidth and gain properties of the optical amplifiers [1,25]. \(\sigma_{\text{em}}\)×FWHM and \(\sigma_{\text{em}}\)×\(\tau\) are about 0.96×10\textsuperscript{-20} cm\textsuperscript{2}, 305×10\textsuperscript{-20} cm\textsuperscript{2} nm and 4.4×10\textsuperscript{-24} cm\textsuperscript{2} s for LASB; 1.13×10\textsuperscript{-20} cm\textsuperscript{2}, 303×10\textsuperscript{-20} cm\textsuperscript{2} nm and 4.7×10\textsuperscript{-24} cm\textsuperscript{2} s for LTSB; 1.99×10\textsuperscript{-20} cm\textsuperscript{2}, 621×10\textsuperscript{-20} cm\textsuperscript{2} nm and 4.6×10\textsuperscript{-24} cm\textsuperscript{2} s for GAB. These parameters are bigger than the corresponding values for Er\textsuperscript{3+}-doped silicate glass (\(\sigma_{\text{em}}\) = 0.55×10\textsuperscript{-20} cm\textsuperscript{2}, \(\sigma_{\text{em}}\)×FWHM = 22×10\textsuperscript{-20} cm\textsuperscript{2} nm) and that for Ti\textsuperscript{3+} doped sapphire (\(\sigma_{\text{em}}\)×\(\tau\) = 1.4×10\textsuperscript{-24} cm\textsuperscript{2} s) but comparable to those for Nd\textsuperscript{3+}-doped ZnO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} glass (\(\sigma_{\text{em}}\) = 1.30×10\textsuperscript{-20} cm\textsuperscript{2}, \(\sigma_{\text{em}}\)×\(\tau\) = 3.1×10\textsuperscript{-24} cm\textsuperscript{2} s) [1,25]. Therefore, it can be suggested from the above comparisons that the bismuth-doped glasses are the promising host materials for the super-broadband amplifiers.
5. Conclusions

In summary, codoping tantalum instead of aluminum into bismuth-doped SiO$_2$-based glasses can also lead to the generation of the broadband near infrared luminescence. The near infrared luminescence mechanism remains unclear, and more works are needed to make it clarified in future. LASB, LTSB, NASB1 and GAB glasses exhibit the broadband luminescence with FWHM and lifetime more than 250 nm and 200 $\mu$s, respectively in the case of 808 nm-LD excitation at room temperature. The excellent optical properties possess these glasses as the promising gain-medium candidates for the broadband amplifiers and widely tunable laser sources.

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