Broadband infrared luminescence from Li$_2$O-Al$_2$O$_3$-ZnO-SiO$_2$ glasses doped with Bi$_2$O$_3$

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Abstract: The broadband emission in the 1.2–1.6μm region from Li$_2$O-Al$_2$O$_3$-ZnO-SiO$_2$ (LAZS) glass codoped with 0.01mol.%Cr$_2$O$_3$ and 1.0mol.%Bi$_2$O$_3$ when pumped by the 808nm laser at room temperature is not initiated from Cr$^{4+}$ ions, but from bismuth, which is remarkably different from the results reported by Batchelor et al. The broad ~1300nm emission from Bi$_2$O$_3$-containing LAZS glasses possesses a FWHM (Full Width at Half Maximum) more than 250nm and a fluorescent lifetime longer than 500μs when excited by the 808nm laser. These glasses might have the potential applications in the broadly tunable lasers and the broadband fiber amplifiers.

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References and links

1. Introduction

In order to develop broadband fiber amplifiers and broadly tunable laser sources for the efficient wavelength-division multiplexing system, it gradually becomes important to explore and synthesize new luminescent materials with larger FWHM emission in the telecommunication-wavelength region, especially at 1.3 and 1.55 μm. Considerable efforts have been devoted to rare-earth-ion-doped and transition-metal-ion-doped materials, and some interesting and promising results have therefore been achieved. For example, broad emissions in the region of 1.2~1.6 μm were observed from Cr$^{4+}$ or Ni$^{2+}$ doped glasses. Recently, Batchelor et al reported the enhancement of the Cr$^{4+}$ emission in aluminosilicate glasses through the Bi$_2$O$_3$ addition at room temperature. And they ascribed the broad emissions in 1000~1600nm region to the Cr$^{4+}$ ions at the excitations of 514nm or 800nm. However, our experimental results clearly indicate that the broad emissions should be assigned to bismuth ion rather than tetravalent chromium Cr$^{4+}$ ions. In this paper, we study the origin of the 1.2~1.6 μm broad emission in LAZS glasses codoped with Cr$_2$O$_3$ and Bi$_2$O$_3$, investigate the dependence of the fluorescence intensity and lifetime on the Bi$_2$O$_3$ concentration in the glasses and finally discuss the infrared broadband luminescence mechanism.

2. Experimental

The glass samples were prepared by the melting-quenching technique. Analytically-pure reagents Li$_2$CO$_3$, Al(OH)$_3$, ZnO, SiO$_2$, Cr$_2$O$_3$ and Bi$_2$O$_3$ were selected as the raw materials. 100g batch corresponding to the glass composition (in mol.%) of (18 – $y$)Li$_2$O·25.5Al$_2$O$_3$·5.5ZnO·51SiO$_2$·xCr$_2$O$_3$·yBi$_2$O$_3$ (x = 0, 0.01, 0.04 and y = 0, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0 respectively) was mixed homogenously in an agate mortar, and then melted at 1600°C in a platinum crucible for 2 hours in air. Consequently the melt was quickly cast onto a stainless steel plate and immediately pressed with another steel plate in order to prevent the glass samples from phase separation and devitrification. The samples were cut into the size of $10 \times 10 \times 2$mm$^3$ and polished for optical measurements.

The optical absorption spectra of the samples were measured using JASCO V-570 spectrophotometer and the infrared fluorescence spectra were collected using ZOLIX SBP300 spectrofluorometer with InGaAs detector at the excitations of 808nm (InGaAs laser diode with maximum power of 135mW) or 532nm (double frequency of the 1.064 μm laser of YAG: Nd with power of 50mW), respectively. The fluorescence lifetime measurements were carried out by exciting the sample with a modulated 808nm LD with power of 2W at maximum. The signal detected by an InGaAs photodetector in TRIAX550 spectrofluorometer was recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were taken at room temperature.

3. Results and discussion

There are three broad bands at about 350, 440 and 650nm in the spectrum of LAZS: 0.01 mol.% Cr$_2$O$_3$ (LAZSC) glass (see Fig. 1(b)). Since the blank glass sample shows no absorptions in these regions (see Fig. 1(a)), these absorption bands should be assigned to chromium ions. The former one is due to Cr$^{6+}$ ion and the latter two are due to Cr$^{3+}$ ions. In the absorption spectrum of LAZS: 1 mol.% Bi$_2$O$_3$ (LAZSB) glass shown as Fig. 1(c), there are two notable peaks at around 485 and 712nm attributed to bismuth, which are similar to those of bismuth doped SiO$_2$ and GeO$_2$ glasses (i.e., at 500 and 700nm) and to those of bismuth doped borate and phosphate glasses (i.e., at ~465 and 700nm). While adding 0.01 mol.% Cr$_2$O$_3$ into the LAZSB glass, the 485nm peak keeps almost un-shifted whereas the longer wavelength peak of 712nm becomes flattened due to the absorption overlap between bismuth and chromium ions as shown in Fig. 1(d). At the excitation of 808nm LD, the blank
sample and the LAZSC glass don’t give out any detectable fluorescence while LAZS: 0.01 mol.% Cr$_2$O$_3$, 1 mol.% Bi$_2$O$_3$ (LAZSCB) and LAZSB glasses exhibit broad emissions peaked at around 1300nm with a 1400nm shoulder in 1000–1600nm region at room temperature (see Fig. 2). That is sufficient to indicate that the 1300nm emission is not from Cr ions but from the luminescent centers correlated to the Bi$_2$O$_3$ addition, which is also the reason why Batchelor et al. couldn’t observe the Cr$^{4+}$ absorptions in LAZSCB glass. Interestingly, compared with the 1250nm emission observed in bismuth-doped silica glass at the excitation of 800nm, the strongest emission peak shifts to longer wavelength (i.e. 1300nm) in LAZSB glass, which demonstrates that the luminescent properties of Bi-doped glasses depend on the glass composition.
As the excitation source is changed into the 532nm laser, the strongest peak moves to the shorter wavelength of around 1200nm, implying the dependence of the infrared fluorescence on the excitation sources (see Fig. 2 (f)). Similar phenomena have also been observed in the bismuth doped silica glass \(^8\). Batchelor \textit{et al} assigned the emissions at \(\sim 750\) or \(\sim 1150\)nm to the \(\text{Cr}^{3+}\) or \(\text{Cr}^{4+}\) ions at high crystal-field sites in LAZSCB glass respectively in the case of 514nm excitation \(^4\). But in bismuth-doped silica glass without \(\text{Cr}_2\text{O}_3\) addition, the emissions at 750 and 1140nm were also observed at the 500nm excitation \(^8\). Even though the emission spectrum at the excitation of 514nm cannot be obtained due to the apparatus limits, the comparison between Batchelor’s and Fujimoto’s results and the observation of the \(\sim 1200\)nm emission in LAZSB glass support at least that the \(\sim 1150\)nm emission corresponding to the \(\text{Cr}^{3+}\) ions at high crystal-field sites in LAZSCB glass respectively in the case of 514nm excitation \(^4\) correlates to the \(\text{Bi}_2\text{O}_3\) addition.

![Figure 3](image-url)

**Figure 3.** Fluorescence decay curve of (a) LAZS: 1 mol.% \(\text{Bi}_2\text{O}_3\) (LAZSB) and (b) LAZS: 0.01 mol.% \(\text{Cr}_2\text{O}_3\), 1 mol.% \(\text{Bi}_2\text{O}_3\) (LAZSCB) when pumped by 808nm. It was measured by monitoring the emission of 1300nm at room temperature. The correlation coefficients for the fits by the first-order exponential decay equation (LAZSB: \(I=1.04941e^{-t/583}\); LAZSCB: \(I=1.0202e^{-t/530}\)) are 0.9668 for LAZSB and 0.9566 for LAZSCB; those by the second-order one (LAZSB: \(I=1.01865e^{-t/548}+0.03168e^{-t/26569}\); LAZSCB: \(I=0.94003e^{-t/514}+0.04921e^{-t/12129}\)) are 0.9966 for LAZSB and 0.9970 for LAZSCB. "○": fitting results by the first-order exponential decay equation; "●": fitting results by the second-order exponential decay equation.

Figure 3 shows the fluorescent decay curves of LAZS: 1 mol.% \(\text{Bi}_2\text{O}_3\) (LAZSB) and LAZS: 0.01 mol.% \(\text{Cr}_2\text{O}_3\), 1 mol.% \(\text{Bi}_2\text{O}_3\) (LAZSCB) glasses when pumped by 808nm LD at room temperature. The fluorescent lifetime is defined as the time when the fluorescent intensity decreases to the \(e^{-1}\)-fold of primary intensity. The measured fluorescent lifetime is about 583\(\mu\)s for the LAZSB glass and 530\(\mu\)s for the LAZSCB glass. The two decay curves show similar characteristics indicated as Fig. 3: at the initial time, the fluorescent decay curves are close to the first-order exponential decay equation; however, beyond the period, the decay curves become more and more deviation with time. This phenomenon indicates that a more complicated mechanism may contribute to the overall decay behaviors, rather than the simple exponential decay. Therefore a more elaborate model of second-order exponential decay equation is employed to fit the fluorescence decay curves and better fitting results are found, implying that the decay process might consist of one fast process and one slow process (see Fig. 3). The fluorescence decay deviations from the first order exponential decay equation might be due to that the bismuth ions occupy different sites in the disordered glass matrix.

Figure 4 shows the integrated fluorescent intensity and the lifetime as function of \(\text{Bi}_2\text{O}_3\) concentration in LAZS: \(x\) mol.% \(\text{Bi}_2\text{O}_3\) \((x = 0.5, 1.0, 1.5, 2.0, 3.0, 5.0)\) glasses. With increasing \(x\) value, the sample color turns gradually from pink, light mauve, to reddish-brown,
and the fluorescent intensity increases up to x=1.5, and then decreases, while the fluorescent peak keeps almost un-shifted. As the Bi$_2$O$_3$ content increases in the glass host, the interaction between activators increases which leads to the decrease of the fluorescent lifetime of LAZS: x mol.\% Bi$_2$O$_3$ (x = 0.5, 1.0, 1.5, 2.0, 3.0, 5.0) glasses as shown in Fig. 4 (However, the fluorescent intensities corresponding to x = 0.5 and 5.0 respectively are not strong enough for measurement of their lifetimes.). It can be determined from Fig. 4, the optimized Bi$_2$O$_3$ concentration is 1.5 mol.\%, corresponding to the lifetime of 521\mu s.

![Fig. 4. Integrated fluorescence intensity and lifetime of LAZS: x mol.\% Bi$_2$O$_3$ (x = 0.5, 1.0, 1.5, 2.0, 3.0, 5.0) glasses.](image)

Even though the broad infrared luminescence has been reported in a series of bismuth-doped glasses, the relation between the bismuth valent state and the broad infrared luminescence is not clear at present.\textsuperscript{7-10} Compared with the results on Bi$^{3+}$ or Bi$^{2+}$ doped luminescent materials previously reported in the literature, not only the positions of both absorption and emission peaks of LAZS: 1 mol.\% Bi$_2$O$_3$ glass differ from those of Bi$^{3+}$ or Bi$^{2+}$ doped materials, but also the lifetime is almost one or two order longer than those of the Bi$^{2+}$ or Bi$^{3+}$ doped materials.\textsuperscript{11-14} Such large differences rule out the possibility that the infrared luminescence comes from Bi$^{3+}$ or Bi$^{2+}$. Fujimoto et al attempted to assign the infrared luminescence to Bi$^{5+}$ ion.\textsuperscript{8} However, there is no direct and irrefutable proof to confirm the existence of unstable Bi$^{5+}$ ions in bismuth-doped silica glass (Bismuth trioxide Bi$_2$O$_3$ was selected as bismuth source.). Moreover, at higher temperature, Bi$_2$O$_3$ will dissociate and convert into BiO or even into bismuth metal.\textsuperscript{15} Meng et al. proposed that the observed absorptions and the near infrared emission were from Bi$^{+}$ ion.\textsuperscript{9,10} There are no efficient ways to distinguish the valence state of Bi ions in glasses.\textsuperscript{15} We tried to determine quantitatively the concentration of Bi ions in different valence states by EELS (Electron Energy Loss Spectrum), but found Bi-doped glass was destroyed due to the bombardment of electron beam during the measurement. We are doing further investigations to clarify the valence state and concentration of Bi ions.

Except for the two obvious absorption bands at 485nm and 712nm observed in LAZSB glass, the additional 800nm and 1000nm absorption bands have also been reported in bismuth-doped SiO$_2$- or GeO$_2$-based glasses.\textsuperscript{7,8} According to the results presented by Meng et al.\textsuperscript{9,10}, the absorption bands centered at ~500nm, ~700nm, ~800nm and 1000nm respectively should correspond to the transitions from the ground state of $^3P_0$ to the excited states, $^1S_0$, $^1D_2$, $^3P_2$ and $^3P_1$ respectively, and the ~1300nm emission is due to the transition of $^3P_1$ to $^3P_0$. The excited state of $^3P_1$ with longer lifetime in the magnitude of several hundred microseconds and the existence of the $^1S_0$ excited state above the $^3P_1$ level suggest that the excited state absorption (ESA) possibly appear from $^3P_1$ to $^1S_0$. If the ESA phenomenon is distinguished in
these bismuth-doped glasses, any potential amplification will be killed and these glasses will become useless even though they have the super-broad infrared luminescence. In the case of the 808nm-LD excitation, two photons are needed to lift one electron from $^3P_0$ up to $^1S_0$ in view of the energy matching condition. However, the log-log dependence of the infrared emission intensity on the pumping power for the 808nm excitation is nearly linear, which demonstrates only one incident photon is involved in the infrared emission and the ESA can be neglected in the bismuth-doped glasses. Furthermore, the 1.3μm optical amplification has been successfully realized in Bi-doped silica glass in the case of the 0.8μm excitation. In addition, as we know, the product between the stimulated emission cross-section ($\sigma_{em}$) estimated by Füchtbauer-Landenburg formula and the fluorescent lifetime $\tau$ is a very important parameter to evaluate the figure-of-merit of gain of the broadband optical amplifier. The bigger the product of $\sigma_{em}\times\tau$, the better the gain properties of optical amplifiers. The $\sigma_{em}\times\tau$ value is $5.65\times10^{-24}$cm$^2$·s for LAZSB, which is comparable to $5.0\times10^{-24}$cm$^2$·s for bismuth-doped phosphate glass, but about four times larger than $1.4\times10^{-24}$cm$^2$·s for Ti-doped sapphire, which indicates these bismuth-doped glasses are good candidates for the broadband optical amplification.

From Figs. 2(c), 2(d) and 2(e), another phenomenon can be easily noticed increasing Cr$_2$O$_3$ concentration can quench the 1300nm emission, which might be interpreted by three factors. First, increasing Cr$_2$O$_3$ concentration doesn't favor the forming of bismuth centers responsible for the infrared luminescence, which can be verified by the decrement of absorption coefficient in near infrared region as Cr$_2$O$_3$% increases from 0% for LAZSB glass to 0.01% for LAZSCB glass (see Figs. 1(c) and 1(d)). Second, upon the 808nm-LD excitation, part-pumping light is absorbed by Cr$^{3+}$ ion and consumed through non-radiation processes, since LAZSC glass cannot give out any light upon this excitation scheme. The third factor is described as follows. In the case of 808nm excitation, some pumping energy is absorbed by bismuth ions and excites their electrons up to the $^3P_2$ level. Some excited electrons of bismuth ions non-radiatively relax to the lower level of $^3P_1$ and hence give out the 1300nm emission. Some excited electrons at $^3P_2$ possibly lose their energy through cross relaxation by exciting the Cr$^{3+}$ ion to the $^1T_2$ state simultaneously ($^3P_2 + ^4A_2 \rightarrow ^1P_0 + ^1T_2$) in view of the partial overlap between the Cr$^{3+}$ absorption band peaked at 650nm due to $^4A_2 \rightarrow ^3T_2$ and the 800nm absorption band due to the Bi$^+$ transition of $^3P_0 \rightarrow ^3P_2$, and the $^4T_2$ electrons of Cr$^{3+}$ ions further lose their energy as mentioned above. With increasing Cr$_2$O$_3$ concentration, the energy transfer process from bismuth ions to Cr$^{3+}$ ions will be strengthened and therefore leads to the fluorescence lifetime reduction from 583μs for LAZSB to 530μs for LAZSCB (see Fig. 2 and Fig. 3).

4. Conclusions

In summary, the broad infrared luminescence in LAZS: 0.01 mol.% Cr$_2$O$_3$, 1 mol.% Bi$_2$O$_3$ glass is not initiated from Cr$^{4+}$ ions but from bismuth, which is different from those reported by Batchelor et al. The ~1300nm emission from LAZS: 1 mol.% Bi$_2$O$_3$ glass with FWHM of 280nm (see Fig. 2(e)) covers O, E, S, C and L bands (1260~1625nm) and provides one possibility to directly amplify the optical signals in the whole telecommunication wavelength region with single fiber amplifier simultaneously. The excitation scheme of the commercially available 808nm semiconductor laser as well as the fluorescent lifetime longer than 500μs provides a promising route for developing the high-power laser sources. The attractive properties of the Bi$_2$O$_3$-doped LAZS glasses make them useful for applications in optical communication.

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