Near infrared broadband emission of bismuth-doped aluminophosphate glass

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Abstract: Near infrared broadband emission characteristics of bismuth-doped aluminophosphate glass have been investigated. Broad infrared emissions peaking at 1210nm, 1173nm and 1300nm were observed when the glass was pumped by 405nm laser diode (LD), 514nm Ar^+ laser and 808nm LD, respectively. The full widths at half maximum (FWHMs) are 235nm, 207nm and 300nm for the emissions at 1210nm, 1173nm and 1300nm, respectively. Based on the energy matching conditions, it is suggested that the infrared emission may be ascribed to $^3P_1 \rightarrow {}^3P_0$ transition of Bi^+. The broadband infrared luminescent characteristics of the glasses indicate that they are promising for broadband optical fiber amplifiers and tunable lasers.

OCIS code: (300.2140) Emission, (160.2750) Glass and other amorphous materials

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#6310 - $15.00 US Received 13 January 2005; revised 21 February 2005; accepted 24 February 2005

1. Introduction

In the process of realizing super-high speed and super-large transmission capacity of optical communication, wavelength division multiplexing (WDM) technique is playing a key role because it can transmit multiple signals into a single optical fiber simultaneously. Novel optical fiber amplifiers with more broad band than existed EDFA, PDFA and TDFA amplifiers are indispensable for WDM systems to obtain much more transmission channels. There are two main working wavelengths in telecommunication windows: 1.55μm with lowest optical attenuation and 1.3μm with natural zero dispersion for silica fiber. Erbium-doped optical fiber amplifiers (EDFA) have been extensively utilized in WDM systems for the third telecommunication window (1.55μm) and ~80nm super-broad flat gain has been achieved [1]. However, there hasn't been any key breakthrough for optical amplification in the second window (1.3μm). Although praseodymium-doped optical fiber amplifiers (PDFA), especially praseodymium-doped ZBLAN optical fiber amplifier [2], have drawn much attention, the ZBLAN glass is weak both in chemical durability and mechanical strength and also difficult to connect PDFA to silica fiber by point-melting technique. To fully utilize the second window of the optical communication, two possible ways are now under consideration: 1) to investigate most suitable hosts for praseodymium ion, which have high quantum efficiency of Pr^{3+} and should be easily connected to silica fiber. 2) to search for new luminescent activators for 1.3μm telecommunication window.

Recently, Fujimoto discovered a new infrared broadband emission from bismuth-doped silica glasses and realized 1.3μm optical amplification with 0.8μm excitation [3,4], which provided a promising candidate for 1.3μm broadband optical fiber amplifiers and tunable lasers. Subsequently, bismuth-doped germanate glasses have also been developed and investigated [5].

It is well known that phosphate glasses are very attractive hosts for rare-earth ions, and have significant applications in optoelectronic fields. To the best of our knowledge, infrared emission of bismuth-doped aluminophosphate glasses hasn't been investigated up to now. In this letter, we synthesized bismuth-doped aluminophosphate glasses and observed infrared broadband emission centered at 1300nm with FWHM of 300nm under 808nm LD excitation. The lifetime is as long as 500μs, comparable to those of other transition metal ions (e.g. Ni^{2+}, Cr^{4+}) [6,7].

2. Experimental

A glass with the composition of $82P_2O_5$-$17Al_2O_3$-$1Bi_2O_3$ (PAB) in molar percentage was prepared by a conventional melting method. Analytical pure reagents of $NH_4H_2PO_4$, $Al(OH)_3$ and Bi_2O_3 were used as raw materials. The batch was melt in a corundum crucible in air at 1550℃ for 1h. The melts were poured onto a stainless steel plate. For comparison, a germanate glass with the composition of $96GeO_2$-$3Al_2O_3$-$1Bi_2O_3$ (GAB) was also prepared by melting the corresponding batch at 1550℃ for 1h. The obtained glass samples were transparent and bubble-free and were polished to 10mm×10mm×1mm size before optical measurements. Optical absorption spectra of the samples were measured on JASCO V-570 spectrophotometer. The infrared luminescence spectra were obtained on ZOLIX SBP300 spectrophotometer with InGaAs as detector in 850-1800nm with excitation of a 405nm LD, 514nm Ar^+ laser and 808nm LD. And the lifetime was obtained by exciting the sample with a modulated 808nm LD with a maximum power of 2W. The signals detected by an InGaAs photodetector were recorded by a storage digital oscilloscope (Tektronix TDS3052). All the measurements were taken at room temperature.

3. Results and discussion

The transmission spectra of PAB and GAB glasses are shown in Fig. 1. The two absorption peaks centered at 460nm and 700nm can be observed in the absorption spectrum of the PAB glass, while the absorption spectrum of the GAB glass shows three main peaks occurring at

#6310 - $15.00 US Received 13 January 2005; revised 21 February 2005; accepted 24 February 2005

500nm, 700nm, 800nm and a shoulder at 1000nm. There has been previous report about bismuth-doped silica glasses, in which three absorption peaks at 500nm, 700nm and 800nm were involved [3]. The strong absorption at 300nm could be considered to be the absorption edge of bismuth-doped glasses [8]. There is no apparent shift in the absorption peak at 700nm, while the peak at about 500nm shifts to 460nm in PAB glass from 500nm in GAB glass. Since no absorption peaks in the wavelength region of 450-1100nm are observed in the bismuth-undoped glasses investigated herein, the observed absorption bands can be assigned to electronic transition of bismuth ions.

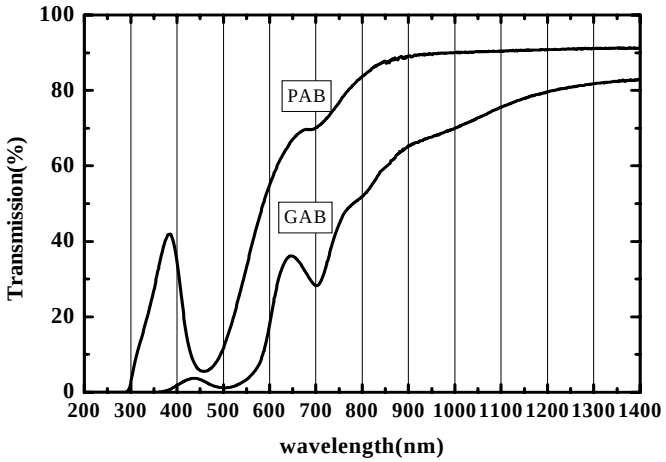

Fig. 1. Transmission spectra of PAB and GAB glasses

Figure 2 shows the luminescence specta of PAB glass under various pumping sources. Infrared emissions peaking at 1210nm, 1173nm, 1300nm and 1194nm were observed when the glass sample was excited by 405nm LD, 514nm Ar^+ laser, 808nm LD and 980nm LD, respectively. The corresponding FWHMs of 1210nm, 1173nm and 1300nm emissions are 235nm, 207nm and 300nm, respectively.

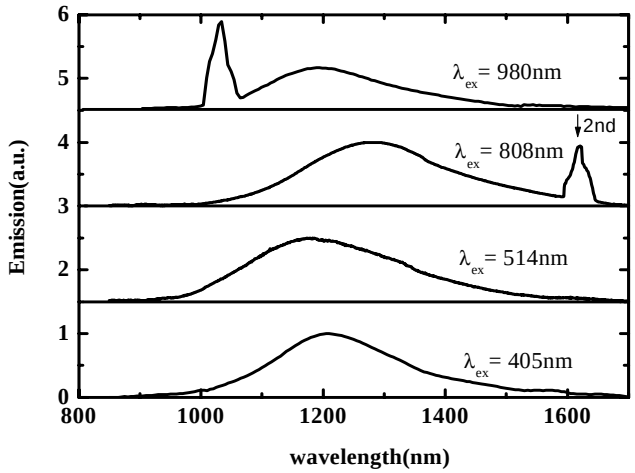

Fig. 2. Normalized emission spectra of PAB, when excited by 405nm LD, 514nm Ar^+ laser, 808nm LD and 980nm LD, respectively.

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The luminescent spectra of PAB and GAB glasses are shown in Fig. 3 when excited by 808nm LD. It could be observed that the infrared luminescent properties (emission peak, FWHM) of PAB glass are comparable to those of GAB glasses. We note that in aluminophosphate or germanate hosts the photoluminescence peak red-shifted about 50nm with respect to the silica hosts.

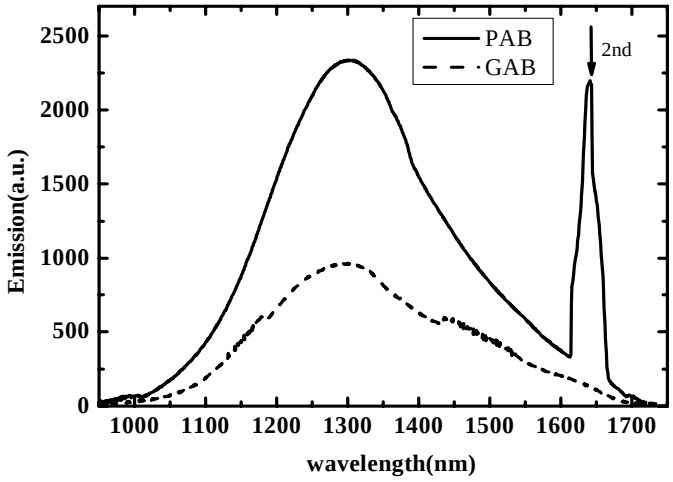

Fig. 3. Emission spectra of PAB and GAB glasses, when excited by 808nm LD.

It is not clear that which valent bismuth ion contributes to the infrared emission up to now. Not only the positions of both absorption and emission peaks of bismuth-doped aluminophosphate glass differ from those of previously reported Bi^{3+} or Bi^{2+} doped materials [9-13], but also the lifetime is almost two orders of those of Bi^{3+} or Bi^{2+} [10, 13]. Such large differences indicate that the infrared emission might not be originated from those valent bismuth ions. Fujimoto *et al* ascribed the absorption and emission bands of bismuth-doped silica glasses to the Bi^{5+} transitions between the ground state of $^1S_0$ and the excited states of $^3D_{3,2,1}$ and $^1D_2$. As Al^{3+} ions are doped in host and substitute for Si^{4+} sites, negative defect of $Al_{Si}^{'}$ will be formed and might be electrically compensated by the $Bi_{Si}^{\cdot}$ defect as Bi^{5+} in Si^{4+} site of the glass network. However, the weak acidic vitreous GeO_2 [14] as well as emission quenching with increasing alkaline earth metal oxide in borate glasses [15] seems that the upper oxidation state of dopant is not preferable based on the optical basicity theory proposed by J. A. Duffy [16]. Furthermore, at higher temperature, dissociation of Bi_2O_3 would occur. Bi_2O_3 may convert into the suboxide BiO or bismuth metal [14]. We did not observe apparent visible luminescence due to transitions of Bi^{3+} in the PAB glass when excited by ultraviolet light. Therefore, we suggest there are few Bi ions existing as Bi^{3+} and Bi^{5+} states in the glass though more detailed experiments should be carried out. We think that bismuth may exist as low valence state (Bi^+ or bismuth cluster) in the glasses investigated herein.

Based on energy matching conditions, we suggest tentatively that the infrared emission derives from monovalent bismuth ions. The simplified energy levels of Bi^+ are presented in Fig. 4. The ground configuration of Bi^+ ($6s^26p^2$) is split by spin-orbit coupling interaction into the ground state $^3P_0$ and the excited states $^1S_0$, $^1D_2$ and $^3P_{2,1}$. Although only two absorption bands at 460nm and 700nm occur in bismuth-doped aluminophosphate glass, additional 800nm absorption band in bismuth-doped silica glass and 800nm, 1000nm absorption bands in bismuth-doped germanate glass have also been reported. The above absorption bands centered at: 460, 700nm, 800nm and 1000nm could be ascribed to the transitions between the

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ground state $^3P_0$ and the excited states $^1S_0$, $^1D_2$ and $^3P_{2,1}$. It should also be mentioned that infrared emissions peaking differently can be observed in bismuth-doped silica glasses under 500nm, 700nm and 800nm pumping. Bismuth-doped aluminophosphate, silica and germanate glass systems show the near infrared emission due to $^3P_1 \rightarrow {}^3P_0$ transition under the above pumping sources excitation. After absorption the system reaches high vibrational levels of the excited states. Subsequently it relaxes non-radiatively to the lowest vibrational level of $^3P_1$ where emission $^3P_1 \rightarrow {}^3P_0$ occurs as a broad band.

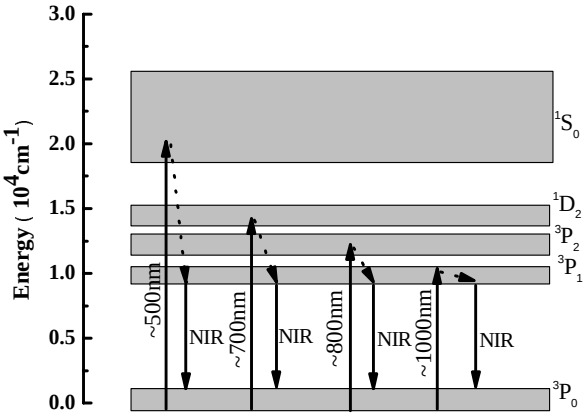

Fig.4. Energy level diagram for Bi^+, which is proposed based on energy matching conditions (NIR: near infrared emission).

Another possibility for the infrared emission has come into consideration: $^1S_0 \rightarrow {}^1D_2$. In this case, a two-photon absorption process should be involved based on energy matching conditions when excited by 808nm and 980nm. However, the log-log dependence of the infrared emission intensity on excitation power shown in Fig. 5 is roughly linear, showing that one incident photon is involved in this infrared emission. Since there is no confirmed evidence to prove the existence of Bi^+, spectrum might be an effective way to assume the mechanism of the unusual infrared emission from bismuth ions. More experiments should be carried out to clarify the mechanism of the infrared emission.

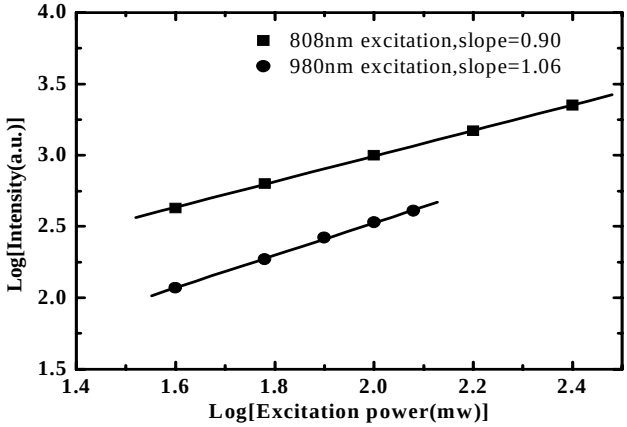

Fig. 5. Log-log plots of infrared emission intensity as a function of pump power at 808nm and 980nm

#6310 - $15.00 US Received 13 January 2005; revised 21 February 2005; accepted 24 February 2005

It is attractive that infrared emissions from PAB glass are acceptable with multiple wavelengths excitation and the emissions all cover the second telecommunication window. The broadband emission of 1300nm with FWHM of 300nm is of much more interest because it is the working wavelength of the second telecommunication window. Furthermore, the 1300nm broadband emission of bismuth ions covers the O, E, S, C and L bands (1260-1625nm), which shows that this material is also promising for ultrabroadband amplification. The 808nm-pumping scheme has offered a potential advantage of high power semiconductor lasers, which are most widely utilized in optical telecommunications and commercially available.

The fluorescence decay curve at 1300nm with 808nm LD excitation is shown in Fig. 6. The decay curve shows a good consistence with the first order exponential decay with the lifetime as long as 500μs.

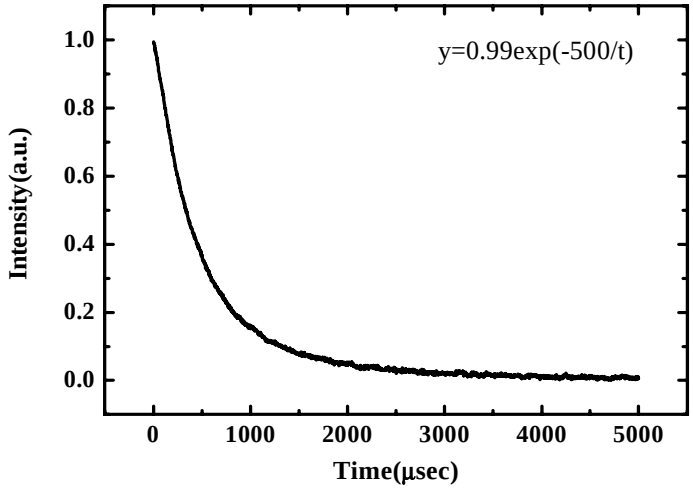

Fig.6. The emission decay curve of PAB, the monitoring wavelength is 1300nm under 808nm LD excitation.

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

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

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

$$\sigma = \frac{\lambda_0^2}{4\pi n^2 \tau_{21} \Delta\nu} \left(\frac{\ln 2}{\pi} \right)^{1/2} \tag{2}$$

where λ_0 is the band center wavelength and $\Delta\nu$ is the FWHM of the emission. We can obtain σ =1.0×10^{-20}cm^2, with λ_0 =1300nm, n=1.53, τ =500μs, and $\Delta\nu$ =1800cm^{-1} for the PAB glass, and σ =1.68 × 10^{-20}cm^2, with λ_0 =1300nm, n=1.60, τ =254.5μs, and

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$\Delta\nu$ =1922cm^{-1} for GAB glass. The product of the stimulated emission cross section and the lifetime, $\sigma\tau$, is an important parameter to characterize laser materials, because the laser threshold is proportional to $(\sigma\tau)^{-1}$. The $\sigma\tau$ products of the bismuth ions in the PAB glass and the GAB glass are 5.0×10^{-24}cm^{2}s and 4.28×10^{-24}cm^{2}s, respectively. The $\sigma\tau$ product of the glasses is about three times larger than that of Ti:Al_2O_3 ($\sigma\tau$ =1.4×10^{-24}cm^{2}s). It indicates that both bismuth-doped aluminophosphate glass and germanate glass are promising materials for optical amplification.

4. Conclusion

In summary, we have observed near infrared broadband emissions in bismuth-doped aluminophosphate glasses. This material possesses long lifetime even at room temperature and large product of the stimulated emission cross section and the lifetime. We ascribed the infrared emissions to $^3P_1 \rightarrow {}^3P_0$ transition of Bi^+ based on the observed absorption and luminescent spectra. Together with the possibility of multiple wavelengths excitation, the scheme of using 808nm LD as a pumping source suggests that this material might be a promising candidate for broadband fiber amplifiers and tunable lasers.

Acknowledgments

The authors would like to acknowledge the financial support provided by the National Natural Science Foundation of China under the number of 50125258 and Shanghai Science and Technology under the number of 04XD14018.

#6310 - $15.00 US Received 13 January 2005; revised 21 February 2005; accepted 24 February 2005