Infrared broadband emission of bismuth-doped barium-aluminum-borate glasses

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Abstract: We report near infrared broadband emission of bismuth-doped barium-aluminum-borate glasses. The broadband emission covers 1.3μm window in optical telecommunication systems. And it possesses wide full width at half maximum (FWHM) of ~200nm and long lifetime as long as 350μs. The luminescent properties are quite sensitive to glass compositions and excitation wavelengths. Based on energy matching conditions, we suggest that the infrared emission may be ascribed to ${}^3P_1 \rightarrow {}^3P_0$ transition of Bi^+. The broad infrared emission characteristics of this material indicate that it might be a promising candidate for broadband optical fiber amplifiers and tunable lasers.

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

References and links

1. G. Blasse and A. Bril, "Investigations on Bi^{3+}-activated phosphors," J. Chem. Phys. **48**, 217-222 (1968)
2. M. J. Weber and R. R. Monchamp, "Luminescence of $Bi_4Ge_3O_{12}$: spectral and decay properties," J. Appl. Phys. **44**, 5495-5499 (1973)
3. R. B. Lauer, "Photoluminescence in $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$," Appl. Phys. Lett. **17**, 178-179 (1970)
4. G. Blasse, "Unusual bismuth luminescence in strontium tetraborate (SrB_4O_7: Bi)," J. Phys. Chem. Solids **55**, 171-174 (1994)
5. A. M. Strivastava, "Luminescence of divalent bismuth in $M^{2+}BPO_5$ ($M^{2+}=Ba^{2+}$, Sr^{2+} and Ca^{2+})," J. Lumin. **78**, 239-243 (1998)
6. S. Parke and R. S. Webb, "The optical properties of thallium, lead and bismuth in oxide glasses," J. Phys. Chem. Solids **34**, 85-95 (1973)
7. G. Blasse and A. Bril, "Study of energy transfer from Sb^{3+}, Bi^{3+}, Ce^{3+} to Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}," J. Chem. Phys. **47**, 1920-1926 (1967)
8. M. Wang, X. Fan and G. Xiong, "Luminescence of Bi^{3+} ions and energy transfer from Bi^{3+} ions to Eu^{3+} ions in silica glasses prepared by the sol-gel process," J. Phys. Chem. Solids **56**, 859 (1995)
9. C. H. Kim, H. L. Park and S. Mho, "Photoluminescence of Eu^{3+} and Bi^{3+} in $Na_3YSi_3O_9$," Solid State Commun. **101**, 109 (1997)
10. Y. Fujimoto and M. Nakatsuka, "Infrared luminescence from bismuth-doped silica glass," Jpn. J. App. Phys. **40**, L279-L281 (2001)
11. Y. Fujimoto and M. Nakatsuka, "Optical amplification in bismuth-doped silica glass," App. Phys. Lett. **82**, 3325-3326 (2003)
12. M. Peng, J. Qiu, D. Chen, X. Meng, L. Yang, X. Jiang and C. Zhu, "Bismuth- and aluminum co-doped germanium oxide glasses for super-broadband optical amplification," Opt. Lett. **29**, 1998-2000 (2004)
13. X. Meng, Photon Craft Project, Shanghai Institute of Optics and Fine Mechanics, Graduate School of Chinese Academy of Sciences and Japan Science and Technology Agency, Shanghai 201800, China, and M. Peng, J. Qiu, D. Chen, X. Jiang and C. Zhu are preparing a manuscript to be called "Infrared broadband emission of bismuth-doped borosilicate glasses."
14. X. Meng, Photon Craft Project, Shanghai Institute of Optics and Fine Mechanics, Graduate School of Chinese Academy of Sciences and Japan Science and Technology Agency, Shanghai 201800, China, and M. Peng, J. Qiu, D. Chen, X. Jiang and C. Zhu are preparing a manuscript to be called "Effect of sodium oxide on infrared broadband emission of bismuth-doped borosilicate glasses."
15. K. Nagasawa, Y. Hoshi and Y. Ohki, "Effect of Oxygen Content on Defect Formation in Pure-Silica Core Fibers," Jpn. J. Appl. Phys. **26**, L554-L557 (1987)
16. A. Diaz, Douglas. A. Keszler, "Red, green, and blue Eu^{2+} luminescence in solid-state borates: A structure-property relationship," Mater. Res. Bull. **31**, 147-151 (1996)

#6311 - $15.00 US Received 13 January 2005; revised 21 February 2005; accepted 24 February 2005

17. G. Blasse, Luminescence of Inorganic Solids (Academy, New York, 1978), 463
18. M. B. Volf, Chemical approach to glass, Vol. **7** of Glass Science and Technology Series (Elsevier, New York, 1984) 406-410, 465– 469
19. J. A. Duffy, "Redox equilibria of glass," J. Non-Cryst. Solids **196**, 45-50 (1996)

1. Introduction

Bismuth ion, as a luminescent activator with applications in lasers and a sensitizer for some rare earth ions (e.g. Eu^{3+}, Ho^{3+}), has been investigated in the past decades [1-9]. The previously investigated luminescence of bismuth ions appears usually in visible wavelength regions, such as orange-red emission of Bi^{2+} [4,5], blue or green emission of Bi^{3+} [1-3,6].

Recently, Fujimoto reported a novel infrared emission centered at 1250nm with 800nm excitation from bismuth-doped silica glasses and realized 1.3μm optical amplification under 0.8μm excitation [10,11], which have drawn much attention because of their potential applications in optical fiber amplifiers and tunable lasers. Subsequently, relevant researches have been carried out on bismuth-doped germanate and borosilicate glasses [12-14].

Alkaline earth borate glass is of much interest due to their applications in optoelectronic fields. To the best of our knowledge, broadband infrared luminescent properties of bismuth-doped barium-aluminum-borate glasses have not been investigated up to now. In this work, we synthesized barium-aluminum-borate glasses doped with bismuth ion and investigated their luminescent properties. Absorption spectra, luminescent spectra and fluorescence decay properties of bismuth-doped barium-aluminum-borate glasses with various BaO concentrations have been presented.

2. Experimental

Glasses with compositions of (95-x) B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40) and 70B_2O_3-25BaO-5Al_2O_3-yBi_2O_3 (in mol%, y=0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5) were prepared by a conventional melting method. Analytical pure reagents of H_3BO_3, Ba_2CO_3, $Al(OH)_3$ and Bi_2O_3 were used as raw materials. The batches were melt in corundum crucibles in air at 1550℃ for 20 min. The melts were poured onto a stainless steel plate. 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 luminescent spectra were obtained on ZOLIX SBP300 spectrophotometer with InGaAs as detector in 850-1800nm with excitation of 532nm Nd:YAG laser and 808nm laser diode (LD). And the lifetimes were 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 through a storage digital oscilloscope (Tektronix TDS3052). All the measurements were taken at room temperature.

3. Results

The absorption spectra at room temperature (RT) of (95-x) B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40) are shown in Fig. 1. In order to observe the changes obviously, the absorption spectra in the region 350-600nm and 640-800nm are presented in inserts, respectively. It can be observed that the two absorption peaks centered at 465nm and 700nm become obscure with increasing BaO concentration. When the BaO concentration is above 25mol%, the 700nm absorption peaks can't be observed. The strong absorption at 300nm can be considered to be the absorption edge of bismuth-doped glasses [15]. There have been reports on bismuth-doped silica glasses in which absorption spectra were composed of three peaks occurring at 500nm, 700nm and 800nm, while in bismuth-doped germanate glasses additive 1000nm absorption shoulder peak was also observed except for the above three peaks [10,12]. Since no absorption peaks in the wavelength region of 450nm-1100nm are observed in the bismuth-undoped glasses, the observed absorption peaks can be assigned to electronic transitions of bismuth ions.

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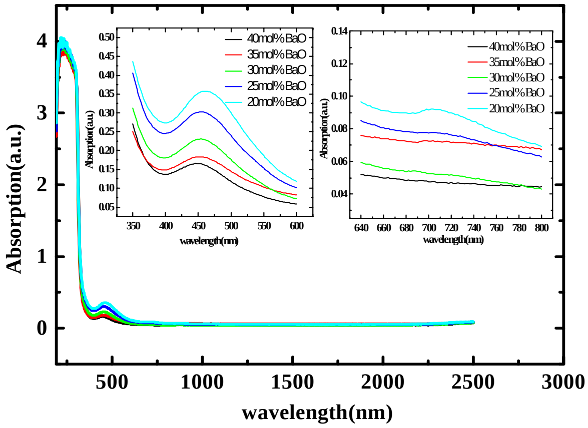

Fig. 1. Absorption spectra of (95-x)B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40)

Figure 2 presents the luminescent spectra of (95-x) B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40) when excited by 808nm LD. The results show that the peak position of the broadband infrared emission shifts from 1252nm to 1300nm with increasing BaO concentration from 20mol% to 40mol%. There have been several reports about emission peak variation with alkali or alkaline earth concentration in some glasses [16,17]. G. Blasse ascribed this shift to crystal field variation caused by alkaline earth ions [17]. The phenomenon investigated herein might be assigned to the same reason. We have discovered that in bismuth-doped borosilicate glasses, small amount of sodium oxide makes emission peak shift from 1210nm to 1340nm, which shows that alkali or alkaline earth oxides have an obvious effect on the infrared emission of bismuth ions [14]. Just like some transition metal ions (e.g. Cr^{4+}, Ni^{2+}), the infrared emission of bismuth ions is sensitive to crystal field because their valent electrons lack of shielding from surrounding crystal fields. Therefore, obvious variations occur in the luminescent spectra when the glass composition is modified.

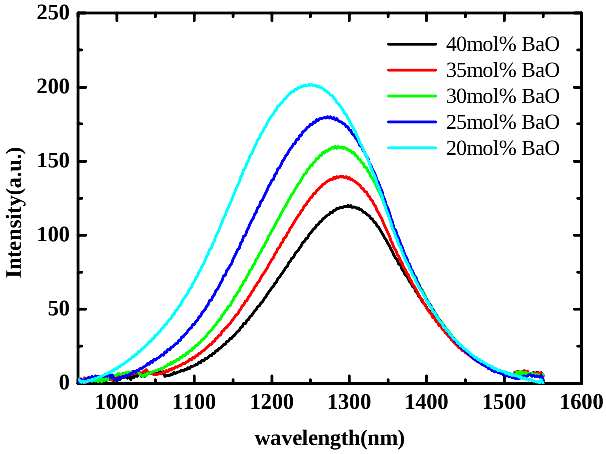

Fig. 2. Fluorescence spectra of (95-x)B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40) when excited by 808nm LD

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Figure 3 shows the dependence of peak position and FWHM on BaO concentration in (95-x) B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40) glass systems with 808nm LD excitation. The peak position shifts monotonically to longer wavelength with increasing BaO concentration, while the FWHMs vary from 230nm to 194nm, but is still much wider than those of rare earth ions (e.g. Pr^{3+}, Dy^{3+}).

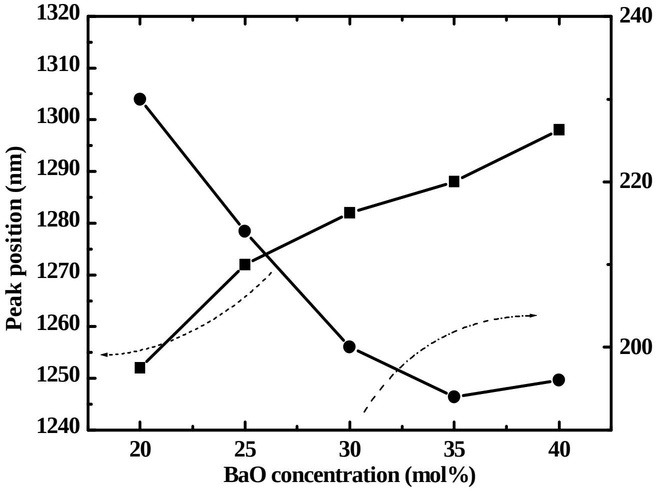

Fig. 3. Peak position and FWHM of the fluorescence of (95-x)B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40), λ_{ex}=808nm.

Figure 4 shows the dependence of integrated intensity and lifetime on BaO concentration for the above glass systems with 808nm LD excitation. The integrated intensity decreases monotonically with further addition of BaO, which shows that addition of alkaline earth oxides have a quenching effect on the infrared emission. The lifetime decreases from 370μs to 275μs with increasing BaO concentration, which is comparable to those of Cr^{4+}, Ni^{2+}.

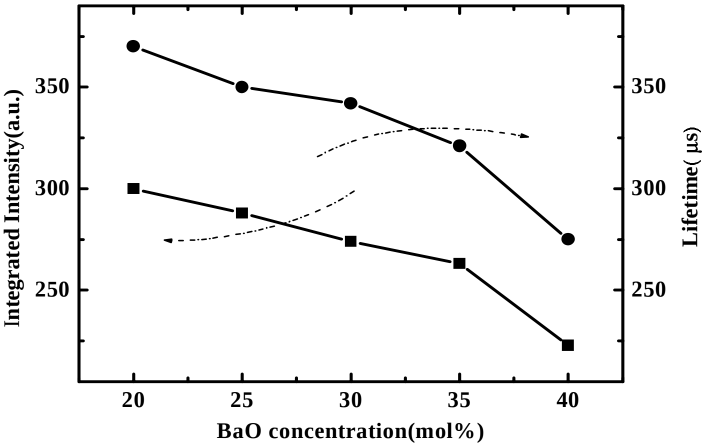

Fig. 4. Integrated intensity and lifetime of the fluorescence of (95-x)B_2O_3-xBaO-5Al_2O_3-2Bi_2O_3 (in mol%, x=20, 25, 30, 35, 40), λ_{ex}=808nm.

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Figure 5 shows the integrated intensity and FWHM of the 1272nm fluorescence of bismuth-doped $70B_2O_3$-25BaO-$5Al_2O_3$ glasses as a function of Bi_2O_3 concentration (mol%) with 808nm LD excitation. An obvious phenomenon is that at low dopant concentration (Bi_2O_3<1.0mol%) the infrared emission can't be observed. The integrated intensity reaches maximum with 2mol% Bi_2O_3. The FWHM varies from 204nm to 242nm with different Bi_2O_3 concentration.

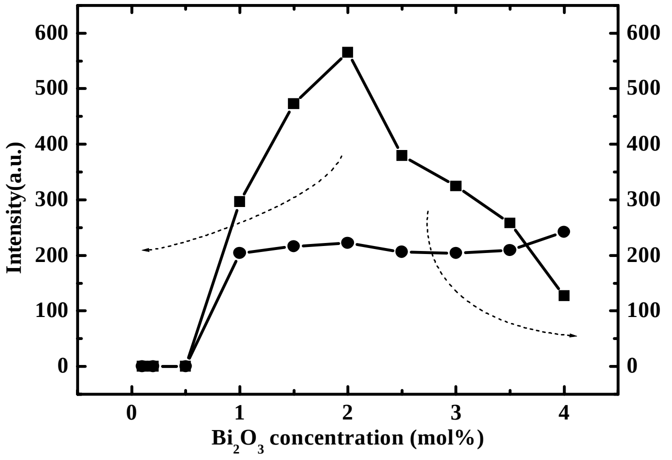

Fig. 5. Integrated intensity and FWHM of the 1272nm fluorescence of bismuth-doped $70B_2O_3$-25BaO-$5Al_2O_3$ glasses as a function of Bi_2O_3 concentration (mol%),λ_{ex}=808nm.

Figure 6 shows the lifetime of the 1272nm fluorescence of bismuth-doped $70B_2O_3$-25BaO-$5Al_2O_3$ glasses as a function of Bi_2O_3 concentration (mol%) with 808nm LD excitation. It shows that the lifetime can reach as long as 350μs.

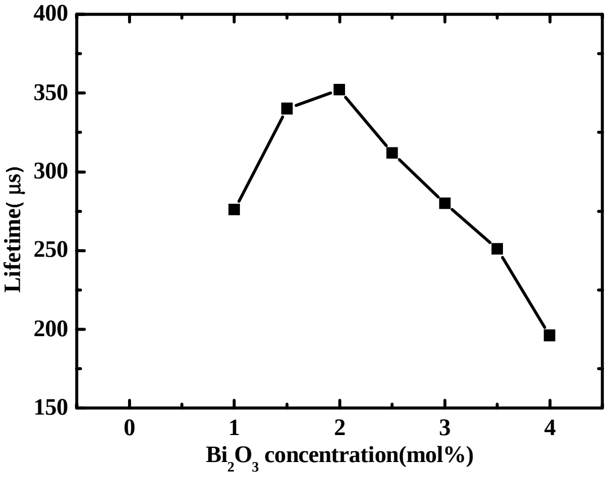

Fig. 6. The lifetime of the 1272nm fluorescence of bismuth-doped $70B_2O_3$-25BaO-$5Al_2O_3$ glass as a function of Bi_2O_3 concentration (mol%),λ_{ex}=808nm.

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The fluorescence spectra of $75B_2O_3$-20BaO-$5Al_2O_3$-$2Bi_2O_3$ under 532nm and 808nm excitation are shown in Fig. 7. Broad infrared emissions peaking at 1148nm and 1272nm are observed when the glass is pumped by 532nm Nd:YAG laser and 808nm LD respectively. The FWHMs are 244nm and 230nm for the emissions at 1148nm and 1272nm, respectively.

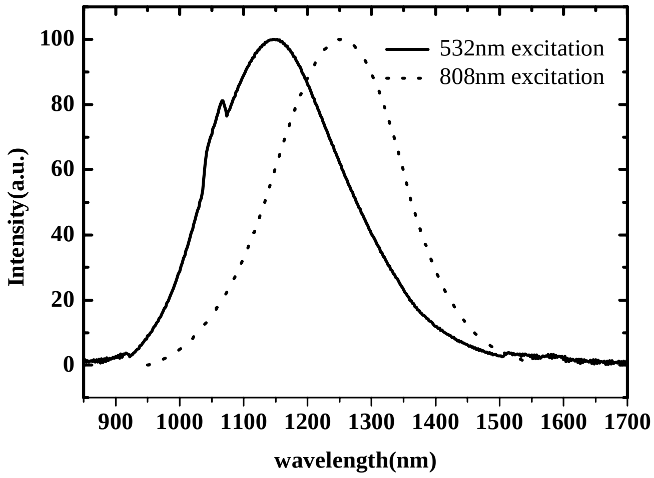

Fig. 7. The fluorescence spectra of $75B_2O_3$-20BaO-$5Al_2O_3$-$2Bi_2O_3$, the excitation wavelengths are 532nm Nd:YAG laser and 808nm LD excitation.

4. Discussion

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 barium-aluminum-borate glasses differ from those of previously reported Bi^{3+} or Bi^{2+} doped materials [1,2-5], but also the lifetime is almost two orders larger than those of Bi^{3+} or Bi^{2+} [2, 5]. Such large differences indicate that the infrared emission might not be originated from Bi^{3+} or Bi^{2+}. 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 $Bi_{Si}^{\bullet}$ defect as Bi^{5+} in Si^{4+} site of the glass network. However, the weak acidic vitreous GeO_2 [18] as well as emission quenching with increasing alkaline earth metal oxide in barium-aluminum-borate glasses seems that the upper oxidation state of dopant is not preferable based on the optical basicity theory proposed by J. A. Duffy [19]. Furthermore, at higher temperature, dissociation of Bi_2O_3 would occur. Bi_2O_3 may convert into the suboxide BiO or bismuth metal [18]. We think that bismuth may exist as low valence state (Bi^+ or bismuth cluster) in the glasses investigated herein.

We suggest tentatively that the infrared emission derives from monovalent bismuth ions based on the energy matching conditions. The simplified energy levels of Bi^+ are presented in Fig. 8. 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 465nm and 700nm occur in bismuth-doped barium-aluminum-borate glasses, additional 800nm absorption band in bismuth-doped silica glasses and 800nm, 1000nm absorption bands in bismuth-doped germanate glasses have been reported. The above absorption bands centered at: 465nm, 700nm, 800nm and 1000nm could be ascribed to the transitions between the 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 barium-aluminum-

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borate glasses, 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 in a broad band.

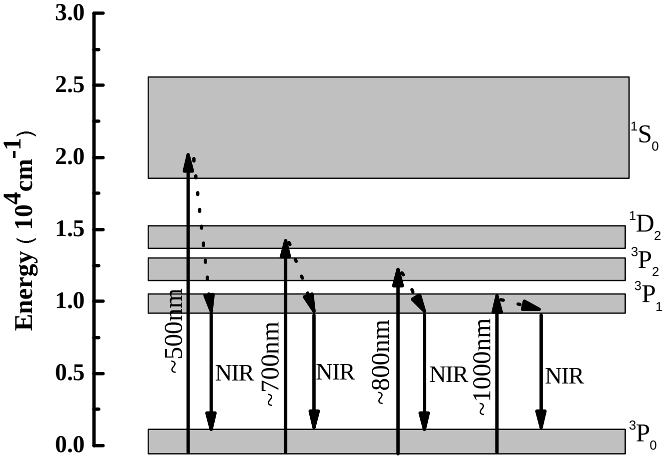

Fig. 8. Energy level diagram for Bi^+, which is proposed based on energy matching conditions (NIR: near infrared emission).

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. However, the non-quadratic log-log dependence of the infrared emission intensity on excitation power for 808nm excitation rejects this speculation. 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.

The above results show that one can optimize the fluorescence intensity, lifetime and FWHM by adjusting the glass composition for fabrication of glasses suitable for optical fiber amplifiers. In addition, as shown in Fig. 7, the emission peak position depends strongly on the excitation wavelength. Such phenomenon has also been observed by Fujimoto *et al.*[10]. The red-shift in the emission peak with increasing excitation wavelength may be ascribed to the Bi ion transition nature and energy transfer among Bi ions in a different structural states. The observed absorption peaks are broad and overlap with each other. When excited by a light with shorter wavelength (e.g. 532nm), the transition probability from excited state with higher energy level increases, thus would result in the emission of shorter wavelength. In addition, the energy transfer among Bi ions would also cause the red-shift of the emission in the Bi high doping glass samples. We are carrying out time-resolved spectrum of the glasses under various excitations to clarify the mechanism of the phenomenon.

5. Conclusion

In conclusion, bismuth-doped barium-aluminum-borate glasses were synthesized and their spectral properties were investigated. Broad infrared emission with long lifetime has been achieved. The infrared emission is quite sensitive to glass compositions and excitation wavelengths. Based on the energy matching conditions, we suggest that the infrared emission may be ascribed to $^3P_1 \rightarrow {}^3P_0$ transition of Bi^+. The infrared broadband emission characteristics

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of bismuth-doped barium-aluminum-borate glasses indicate that they might be promising for potential applications in broadband optical fiber amplifiers and tunable lasers.

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