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Influence of optical basicity on broadband near infrared emission in bismuth doped aluminosilicate glasses

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ABSTRACT

The infrared luminescence with a full width at half maximum larger than 200 nm was observed in aluminosilicate glasses under an 808 nm LD excitation. The influence of optical basicity on broadband near infrared emission was investigated in bismuth doped aluminosilicate glasses. The intensity of the infrared fluorescence decreases with the increase in the optical basicity of the host glasses. On the base of the luminescence spectra, we thought the infrared emission might be attributed to low valence state of bismuth ions in the aluminosilicate glasses. The broadband infrared emission characteristics of the glasses suggest that they are promising candidate for broadband optical fiber amplifiers and tunable lasers.

1. Introduction

With the development of telecommunication technology, it is important to improve the transmission capacity of wavelength division multiplexing (WDM) technique. The transmission capacity of WDM systems depends on the bandwidth of fiber amplifier. However, traditional rare-earth ions doped fiber amplifiers are difficult to meet these requirements because the application bandwidths are too difficult to surpass 100 nm due to the f–f transitions of rare earth ions. So many researchers are looking for novel materials with wider bandwidth as the gain medium of fiber amplifiers. Bismuth doped materials have attracted much attention since Fujimoto and Nakatsuka [1] have reported 1.3 μm optical amplification and broadband infrared emission from the bismuth-doped silica glasses. Recently, the broadband infrared emission properties of bismuth-doped germanate, silica, phosphate and borate glasses have been investigated [2–7]. However, the origins of broad infrared emission are not understood in the bismuth doped glass systems, and several emission mechanisms were put forward. Fujimoto and Nakatsuka [1] thought broadband near infrared emission is from Bi^{5+} because they did not detect the electron spin resonance (ESR) signal. Qiu and co-workers [8,9] attributed it to low valence state bismuth ions. Dvoyrin et al. [10] considered that it is ascribed to the complexes of Bi^+ and $AlO^{4/2-}$.

It is well known that aluminosilicate glasses are very attractive hosts for rare earth ions, and have significant applications in optoelectronic fields. At present, there have been few reports about broadband near infrared emission of bismuth doped aluminosilicate glasses. Qiu and co-workers [11] have investigated infrared properties from bismuth-doped sodium aluminosilicate glasses. Ren et al. [12] have reported luminescence properties of bismuth-doped lime silicate glasses. In this paper, the bismuth doped aluminosilicate glasses with compositions of $60SiO_2–xAl_2O_3–(40–x)CaO–1Bi_2O_3$ ($x = 5$, 10, 15, 20) and $40CaO–xAl_2O_3–(60–x)SiO_2–1Bi_2O_3$ ($x = 0$, 1, 2, 5, 10, 15, 20, 25, 30) were prepared, and the influence of optical basicity on broadband infrared emission properties were investigated. On the base of the relationship between the luminescence properties and optical basicity, we thought the infrared emission might be from low valence state of bismuth ions.

2. Experimental

High purity CaO, Al_2O_3, SiO_2 and Bi_2O_3 were used as raw materials. The bismuth-doped aluminosilicate glasses were prepared by the conventional melting quenching technique. The compositions of the glasses are $40CaO–xAl_2O_3–(60–x)SiO_2–1Bi_2O_3$ ($x = 0$, 1, 2, 5, 10, 15, 20, 25, 30 mol%) and $60SiO_2–xAl_2O_3–(40–x)CaO–1Bi_2O_3$ ($x = 5$, 10, 15, 20 mol%), respectively. Each 10 g batch was mixed homogenously in an agate mortar, and then melted at 1600 °C in a platinum crucible for 2 h in air furnace.

The infrared fluorescence spectra were measured on a ZOLIX SBP300 spectrophotometer under an 808 nm excitation. The fluorescence lifetime measurements were carried out by exciting the samples with a modulated 808 nm LD, and the data were recorded using a storage digital oscilloscope (Tektronix TDS3052).

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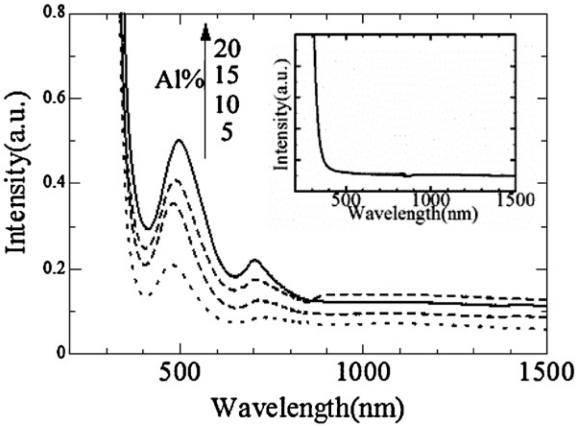

Fig. 1. Absorption spectra of the glasses with composition of $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$). Inset is absorption spectrum of the glass without bismuth ions doped.

3. Results and discussion

Absorption spectra of the glasses with composition of $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$ mol%) are shown in Fig. 1. Comparing with the glasses without bismuth ions doped (inset in Fig. 1), two absorption peaks located at about 500 nm and 700 nm was obviously observed in bismuth ions doped glasses, which indicated that the absorption band should be from the transitions of bismuth ions. The results are similar to those of bismuth doped germanate and phosphate glasses [6,13]. With the increasing of the Al_2O_3 concentration, the 700 nm absorption band shifts towards shorter wavelength, while the 500 nm absorption band shifts towards the longer wavelength. The reasons for the right-about shift of two absorption bands are not understood, which may be ascribed to crystal field variation caused by aluminum or alkaline ions [14].

Fig. 2 shows the near infrared fluorescence spectra of the glasses with compositions of $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$ mol%). The infrared emission peak located at about 1300 nm was observed, and the corresponding FWHM is more than 200 nm. No peak shift was observed with the variation of Al_2O_3 content, but the fluorescent intensity increased with the increase of Al_2O_3 content. Inset in Fig. 2 shows the relationship between fluorescence lifetimes and the Al_2O_3 content in the $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$ mol%) glasses. It can be seen that the infrared fluorescence lifetime decreases from 584us to 515us with the increasing of Al_2O_3 content. The coordination number of aluminum ion increases with increasing Al_2O_3 content in glasses [15]. When the Al_2O_3 concentration is higher than 5.0, the five- or six-coordinated Al^{3+} ions appear, and increase with the increasing of Al_2O_3 [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 Bi ions becomes stronger, and the fluorescent lifetime decreases. The similar results were reported in bismuth and aluminum co-doped germanium oxide glasses [13]. The 808 nm-pumping offer a potential advantage of using commercially available semiconductor lasers. Therefore the broad fluorescence at 1.3 μm with excitation source of 808 nm LD, as well as the long lifetime of the Bi doped glasses, provides a significant possibility to develop the tunable lasers and broadband fiber amplifiers.

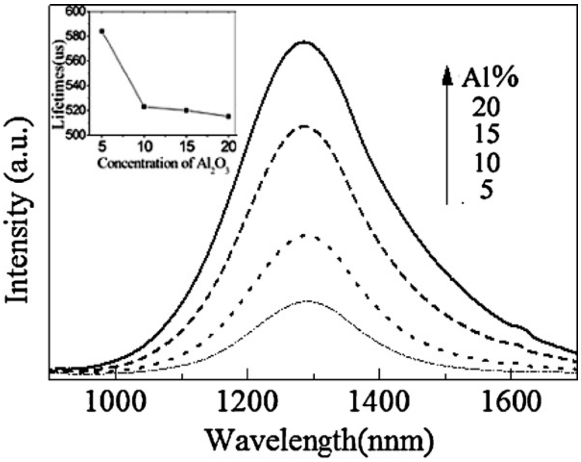

Fig. 2. Infrared fluorescence spectra of the glasses with compositions of $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$). Inset is lifetimes of the glasses.

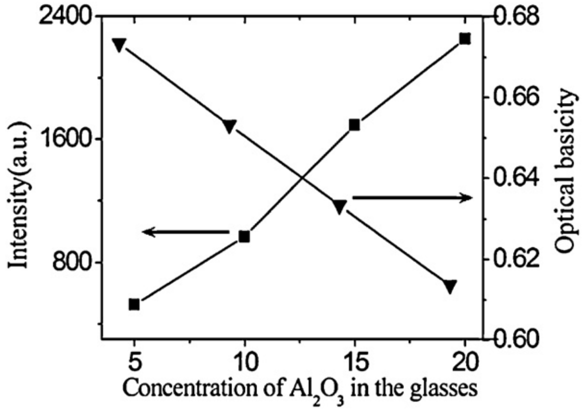

Fig. 3. Relationship between optical basicity and the infrared florescence intensity in $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$) glasses.

Though the broadband infrared emission has been reported in a series of bismuth-doped glasses [1–7], the origins of infrared emission are not understood at present. Fujimoto and Nakatsuka [1] ascribed the infrared emission 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 $^1D_2$. However, it is well known that Bi^{5+} ions usually exist in the host with high optical basicity, such as $NaBiO_3$, $LiBiO_3$ and $KBiO_3$, thus it is difficult to exist in aluminosilicate glasses for its weak acidic. The optical basicity of the $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ glasses were calculated from the empirical formula proposed by Duffy [16]:

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + X_3\Lambda_3 + X_4\Lambda_4 + \ldots + X_n\Lambda_n$$

where $X_1, X_2, X_3, \ldots, X_n$ denote equivalent mole fractions of each oxide in the overall glass systems, and $\Lambda_1, \Lambda_2, \Lambda_3, \ldots, \Lambda_n$ denote basicity of each oxide. Fig. 3 shows the relationship between optical basicity and the infrared emission intensity in the $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$ mol%) glasses. According to the optical basicity theory, the higher valence state of bismuth ions is usually favorable in the glass with higher basicity. If the infrared luminescence comes from Bi^{5+} ions, intensity of glasses should be increases with increasing of optical basicity. In fact, intensity of glasses decreases with increasing of optical basicity in the bismuth doped $60SiO_2$–xAl_2O_3–$(40-x)CaO$–$1Bi_2O_3$ ($x = 5, 10, 15, 20$ mol%) glasses, as shown in Fig. 3. So we think the infrared fluorescence should be originated from low valence bismuth ions in the glasses investigated herein.

In order to identify further that low valence bismuth ions really contribute to the infrared luminescence, more investigations were carried out. Fig. 4 shows the near infrared fluorescence spectra of the glasses with compositions of

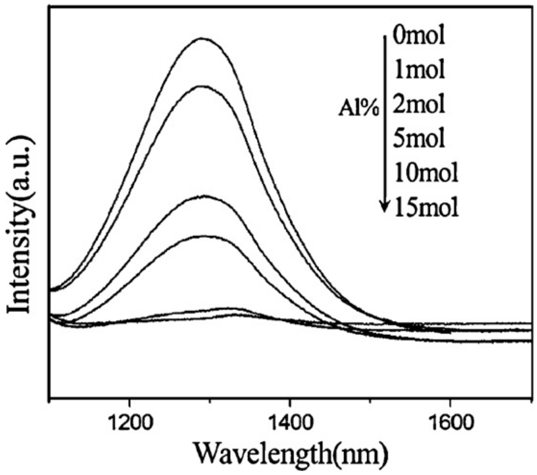

Fig. 4. Infrared fluorescence spectra of the glasses with compositions of 40CaO–xAl$_2$O$_3$–(60–x)SiO$_2$–1Bi$_2$O$_3$ (x = 0, 1, 2, 5, 10, 15, 20, 25, 30).

40CaO–xAl$_2$O$_3$–(60−x)SiO$_2$−1Bi$_2$O$_3$ (x = 0, 1, 2, 5, 10, 15, 20, 25, 30 mol%). The peak located at about 1.30 μm was also observed. In the present glass samples, it is considered that the optical basicity is proportion to the ratio of Al$_2$O$_3$/SiO$_2$. As shown in Fig. 4, the fluorescent intensity decreased with the increase of the ratio of Al$_2$O$_3$/SiO$_2$, which indicates that the infrared fluorescence should be indeed originated from low valence bismuth ions.

Meng et al. [6] thought that the infrared emission derives from monovalent bismuth ions. In the present glasses, not only both absorption and emission peaks are similar to the results reported by Meng, but also the lifetime is the almost same. Therefore, it is expected that Bi$^+$ is the infrared luminescence origin in the aluminosilicate glasses. On the other hand, infrared luminescences ranging from 1300 to 1700 nm wavelength region were observed from BiF, BiCl, BiBr and BiI [17], which are very similar to that from bismuth-doped aluminosilicate glasses investigated herein. Based on the above analysis, we suggested the infrared broadband emissions might arise from Bi$^+$ ions in the present glasses. But there is no direct evidence to prove monovalent bismuth ions existence, therefore, further investigations for the origin of the infrared fluorescence are necessary.

4. Conclusion

The infrared emission peak located at about 1300 nm was observed, and the corresponding FWHM is more than 200 nm. The intensity of the infrared fluorescence decreases with the increase in the optical basicity of the host glasses. On the base of the luminescence spectra, we thought the infrared luminescence centers might be from low valence state of bismuth ions in the aluminosilicate glasses. The attractive properties of the Bi$_2$O$_3$-doped glasses make them useful for applications in optical communication.

Acknowledgements

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