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铋掺杂铝硅酸盐玻璃的超宽带近红外发光性质

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摘 要：采用高温熔融法制备了组分为 $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3 (x = 5，10，15，20，摩尔比)的铋掺杂铝硅酸盐玻璃。研究了铋掺杂铝硅酸盐玻璃超宽带近红外发光性质，探讨了玻璃基质的光学碱度对铋离子宽带发光特性的影响。结果表明：在690 nm和808 nm的激发下，铋掺杂铝硅酸盐玻璃的红外荧光中心分别位于1 106 nm和1 294 nm；随光学碱度的增强，铋离子的红外发光强度减弱。并对铋离子超宽带发光的机理进行了探讨，认为其红外发光源于低价的 Bi^+和 Bi^{2+}。

关键词：光学性质；铋掺杂铝硅酸盐玻璃；红外发光；光学碱度
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ULTRA BROADBAND NEAR INFRARED EMISSION PROPERTIES OF BISMUTH DOPED Al_2O_3-MgO-SiO_2 GLASSES

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Abstract: The Bi-doped aluminosilicate glasses with molar composition of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–$1Bi_2O_3$ (x = 5, 10, 15, 20) were prepared by conventional melting-quenching technique. The broadband infrared (IR) luminescence properties of the glasses were studied. IR fluorescence centered at 1 106 nm and 1 294 nm was observed under 690 and 808 nm excitation, respectively. The influence of optical basicity of the glass host on broadband infrared fluorescence was investigated. The intensity of the IR fluorescence decreased with the increase of the optical basicity of glass host. It is revealed that the IR luminescence is due to low valence state bismuth ions Bi^+ and Bi^{2+}.

Key words: optical properties; bismuth doped aluminosilicate glass; infrared luminescence; optical basicity

Rare earth ion-doped fiber amplifiers (RDFA) have been extensively used in the long-distance optical communication. However, the gain bandwidths of traditional RDFA are too difficult to surpass 100 nm due to the nature of the inner shell transition of rare earth ions, which limits the transmission capacity of optical fiber communications. So many efforts, such as multiple amplifiers including different RDFA and multiwavelength pumping Raman fiber amplifiers (RFA), were done to extend the bandwidth of optical fiber amplifiers. However, these efforts have some disadvantages. Multiwavelength pumping FRAs have complicated system structures and require high power excitation sources. The hybrids of different amplifiers lead to serious signal loss for optical communication. Therefore, researchers are searching for novel materials with wider bandwidth as the gain medium of fiber amplifiers in order to realize amplification covering the 1.2–1.6 μm region in a single pumping source.

Bismuth doped glasses have attracted much attention since Fujimoto *et al.*[1] reported 1.3 μm optical amplification and broadband infrared(IR) emission from the bismuth-doped silica glasses excited by a single diode laser. The broadband infrared emissions from bismuth-doped germanate, silica, phosphate and borate glasses have been investigated.[2–6] However, the origins of broad IR fluorescence are not understood in the bismuth doped glasses, and several emission mechanisms were put forward. Fujimoto *et al.*[1] thought broadband near infrared emission was from Bi^{5+} because they didn't detect the electron spin resonance (ESR) signal. Qiu *et al.*[7] and Chi *et al.*[8] attrib

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uted it to lowvalence state bismuth ions. Dvoyrin *et al.*[9] 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. Compared with other glasses, aluminosilicate glasses have many advantages from the viewpoint of application as follows: (1) Aluminosilicate glass is suitable for the formation of glass fiber; (2) The softening point of aluminosilicate glasses is very high (about 900 ℃) and the low coefficient of thermal expansion; (3) Aluminosilicate glasses have good mechanical strength, chemical and thermal stability. In this work, the bismuth doped aluminosilicate glasses with compositions of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3 were prepared, and the origin of the broadband infrared luminescence was investigated.

1 Experimental procedure

1.1 Preparation of samples

High purity (99.99%, in mass) MgO, Al_2O_3, SiO_2 and Bi_2O_3 (all from Sinopharm Chemical Reagent Co., Ltd) were used as raw materials. The bismuth-doped SiO_2–Al_2O_3–MgO (SAM) glasses were prepared by the conventional melting-quenching technique. The molar compositions of the glasses were $50SiO_2$–xAl_2O_3–$(50–x)$·MgO–$1Bi_2O_3$ (x = 5, 10, 15, 20). Each 20 g batch was mixed homogenously in an agate mortar, and then melted at 1 600 ℃ in a platinum crucible for 2 h in air furnace.

1.2 Characterization

The IR emission spectra were measured on a ZOLIX SBP300 spectrophotometer under 690 nm and 808 nm excitation. The visible fluorescence emission measurements were carried out on F–7000 spectrophotometer under a 340 nm excitation. Absorption spectra were measured on a spectrophotometer (HITACHI U–4100).

2 Results and discussion

The absorption spectra of the glasses with compositions of $50SiO_2$–$20Al_2O_3$–$30MgO$–Bi_2O_3 and $50SiO_2$–$20Al_2O_3$–$30MgO$ are shown in Fig.1. Comparing with the glasses without doped bismuth ions, an absorption peak located at about 496 nm is obviously observed in glasses containing bismuth ions, which indicates that the absorption band should be from the transitions of bismuth ions. The strong absorption below 350 nm can be ascribed to the absorption edge of bismuth-doped glasses. The results are similar to those of bismuth doped aluminoborate glasses.[10]

The near IR fluorescence spectra of the glasses with compositions of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3 are shown in Fig.2. The IR emission peak located at about 1 261 nm is observed, and the corresponding FWHM is more than 200 nm. The broadband IR emission peaks

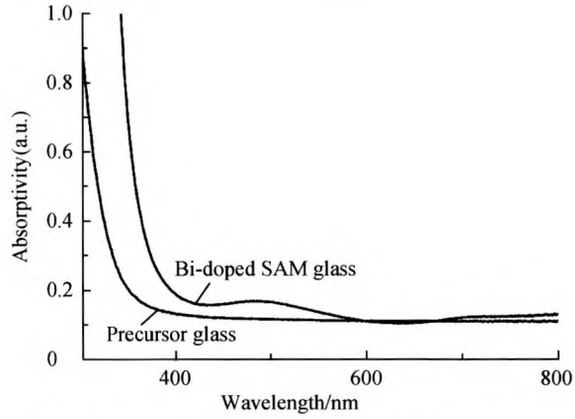

Fig.1 Absorption spectra of Bi-doped SAM glass and precursor glass

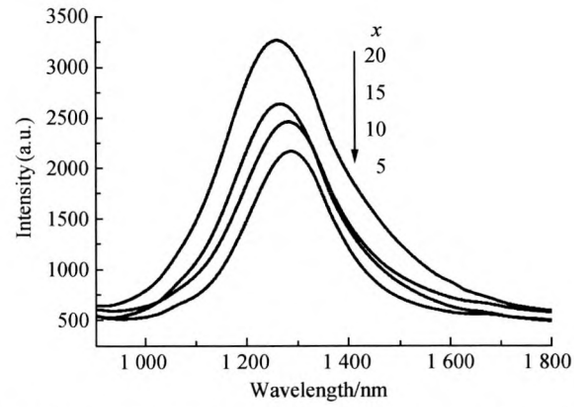

Fig.2 IR emission spectra of the glasses with compositions of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3

shift from 1 294 to 1 261 nm with increasing Al_2O_3 content from 5% to 20%, while the FWHM varies from 199 to 220 nm. The IR emission peaks variation with increase of Al_2O_3 content might be attributed to crystal field variation.[11] Just like some transition metal ions (*e.g.* Cr^{4+}, Ni^{2+}), the IR emission of bismuth ions is sensitive to crystal field because their electrons valence band is lack of shielding from surrounding crystal fields. The similar results were observed in bismuth doped germanate glasses.[12] The IR emission intensity increases with increasing Al_2O_3 content, which shows that addition of Al_2O_3 has an enhancing effect on the IR emission.

Figure 3 shows the fluorescence spectra of glasses with compositions of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3, excited at 340 nm. The emission peak appears at about 435 nm, which is the typical emissions of Bi^{3+} ions.[13]

There are a lot of investigations on the mechanism of IR luminescences in Bi-doped glasses. However, the relationship between the bismuth valent state and the broadband infrared luminescence is not clear at present. The IR luminescences are ascribed to Bi^{5+} and low valence states of Bi by different researchers. Up to now, there has been few report on the infrared luminescence from Bi^{5+}

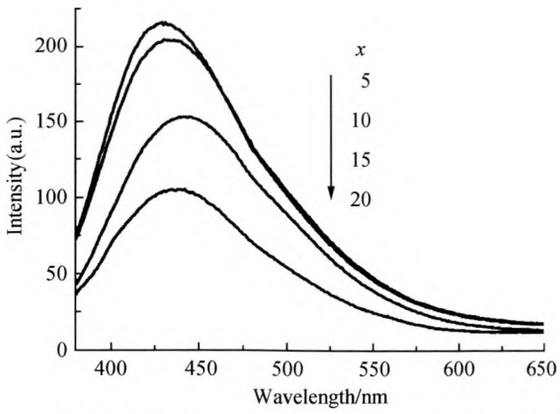

Fig.3 Visible fluorescence spectra of the glasses with compositions of $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3

besides Fujimoto *et al.*[1] In fact, Bi^{5+} ions usually exist in the host with high optical basicity, such as $NaBiO_3$, $LiBiO_3$ and $KBiO_3$, and are easily changed to Bi^{3+} due to decomposition, when they are heated above 300 ℃.[14–15] On the other hand, it is well known that Bi_2O_3 will be converted to BiO and Bi_2O at high temperature. In the present work, the aluminosilicate glasses with weak acidic were prepared at 1 600 ℃, thus Bi^{5+} is difficult to exist. Moreover, according to the optical basicity theory, the higher oxidation state of dopant is usually favorable in the glass with higher basicity. If the IR luminescence comes from Bi^{5+} ions, intensity of glasses should increase with increasing optical basicity. Figure 4 shows the relationship between optical basicity and the IR emission intensity in the $50SiO_2$–xAl_2O_3–$(50–x)$ MgO–Bi_2O_3 glasses. As shown in Fig.4, IR emission intensity of glasses decreases with increasing optical basicity in the bismuth doped $50SiO_2$–xAl_2O_3–$(50–x)$ MgO–Bi_2O_3 glass sample. So the IR fluorescence should be originated from low valence bismuth ions in the glasses investigated herein.

In order to identify further that which low valent bismuth ions contribute to the IR emission, more investigations were carried out. Figure 5 shows the luminescence

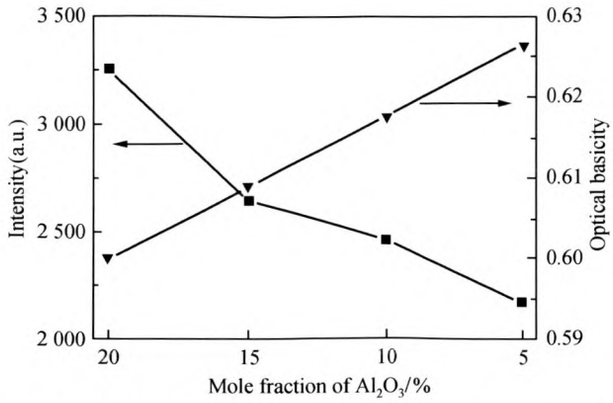

Fig.4 Relationship between optical basicity of glass host and infrared luminescence intensity in $50SiO_2$–xAl_2O_3–$(50–x)MgO$–Bi_2O_3 (x = 5, 10, 15, 20) glasses

spectra of $50SiO_2$–$5Al_2O_3$–$45MgO$–Bi_2O_3 glass under various pumping sources. Broad IR emissions at 1 106 nm and 1 294 nm are observed when the $50SiO_2$–$5Al_2O_3$–$45MgO$–Bi_2O_3 glass is pumped by 690 and 808 nm excitation, respectively. The corresponding FWHM of 1 106 and 1 294 nm emissions are 199 and 210 nm, respectively. Both emission peak position and corresponding FWHM of $50SiO_2$–$5Al_2O_3$–$45MgO$–Bi_2O_3 glass under 690 nm excitation differ from those of glass under 808 nm excitation. Such large differences indicate that the IR emission might be originated from two kinds of low valence bismuth ions. On the other hand, the IR luminescences cannot be ascribed to Bi^{3+} either.[16] Based on the above analysis, we suggest the IR broadband emission might arise from Bi^{+} and Bi^{2+} ions in the bismuth-doped aluminosilicate glasses investigated herein.

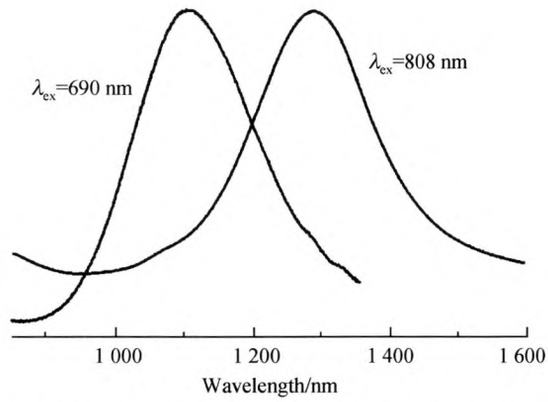

Fig.5 Infrared emission spectra of $50SiO_2$–$5Al_2O_3$–$45MgO$–Bi_2O_3 glass sample under 690 and 808 nm excitation

3 Conclusion

The IR fluorescence properties were investigated in bismuth-doped aluminosilicate glasses. The results show the IR fluorescence intensity depends on the glasses host optical basicity. The intensity of the IR fluorescence decreases with the increase of the host basicity. The origin of the broadband IR luminescence was investigated. On the base of the IR luminescence properties of glasses under various pumping sources, the IR luminescence centers might be from Bi^{+} and Bi^{2+} ions. The attractive properties of the Bi_2O_3-doped glasses make them useful for applications in optical communication.

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