

Influence of alkali metal ions on thermal stability of Bi-activated NIR-emitting alkali-aluminoborosilicate glasses

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We study the influence of alkali oxides on the near-infrared (NIR)-emitting thermal stability of Bi-doped $R_2O-SiO_2-B_2O_3-Al_2O_3$ ($R = Li, Na, K$) glasses below T_g . Results show that undergoing heat treatment, remarkable luminescence quenching occurs for the glasses containing Na_2O and K_2O due to the formation of Bi metallic colloids, whereas the glass with Li_2O shows much better thermal stability. These changes can be understood by the tendency of modifier cations with lower mobility and higher tightness network to restrain the transport of Bi-related NIR-emitting centers. The results provide a scientific reference for composition design of Bi-doped optical fiber.

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With rapid development of global demand for fast information transfer and ultra-high data capacity networks, novel types of near-infrared (NIR)-emitting laser materials for super-broadband optical amplifiers are presently receiving significant attention. Since 2001^[1], especially in the recent decade, the reports of Bi-doped glasses with ultra-broad NIR emission have dramatically improved the development of Bi active luminescent materials owing to their promising applications in broadband optical amplification and tunable lasers^[2-8]. Significantly, fiber is one of the most important physical forms for the practical application of Bi-doped materials. Although the success of fabrication of Bi-doped fiber has been reported^[9-12], there is rarely systematic investigation about the effect of glass composition on the luminescence property change during the optical fiber preparation process.

Notably, it has been found that Bi-related NIR luminescence is very sensitive to thermal annealing processes and can even totally disappear for specific annealing processes^[13-17]. One significant reason for the instability of Bi-related NIR-emitting centers, such as Bi^+ and Bi^0 , is typically due to the relatively higher oxidation tendency of the low valent Bi ions^[13,14]. However, the instinct property of Bi-related ions or atom to agglomerate under heat treatment should be given a consideration, because they easily form the Bi metallic colloids in the host as heat-treatment temperature rises^[15-20], leading to NIR emission quenching.

In this work, we carefully investigate the effect of alkali oxides as network modifiers on the NIR-emission change of Bi-doped $R_2O-SiO_2-B_2O_3-Al_2O_3$ ($R = Li, Na, K$) glass during annealing processes. Remarkable

luminescence quenching is observed for glasses, of which network modifiers are Na_2O and K_2O , undergoing heat treatment below glass transition temperature (T_g). This is entirely different from traditional rare-earth ion doped glasses. The results may provide a scientific reference to the design of the fabrication process of Bi-doped optical fiber.

The glass samples with composition (in mol%) of $42.5SiO_2-12.5B_2O_3-25Al_2O_3-20R_2O-1Bi_2O_3$ ($R = Li, Na, K$) (simplified as SBAR in the below) were prepared by the conventional melt-quenching method. Higher purity SiO_2 , H_3BO_3 , Al_2O_3 , Bi_2O_3 , Li_2CO_3 , Na_2CO_3 , and K_2CO_3 were used as starting materials. Each 20 g batch was mixed homogeneously in an agate mortar and then melted in a corundum crucible for 1 h at 1550 °C in air atmosphere. Consequently, the melt was cast onto a stainless steel plate. The obtained glass samples were heat treated from 420 to 620 °C for 3 h with the heating rate of 2 °C/min in an electric furnace. The samples undergoing heat treatment were cut into a size of $10 \times 13 \times 2$ (mm) and polished for optical analysis.

The differential thermal analysis (DTA) was carried out by a DTG-60AH (SHIMADZU) at a heating rate of 10 °C/min. Absorption spectra were recorded by Hitachi U-4100 spectrophotometer. NIR luminescence spectra were performed by a ZOLIX SBP300 spectrophotometer with InGAs as detector at 800–1800 nm under excitation of 808 nm laser diode (LD) and the luminescence decay curves were recorded by a FLS980 fluorescence spectrophotometer (Edinburgh Instrument Ltd, UK). The morphology was determined by a transmission electron microscopy (TEM, JEM-2100). X-ray diffraction (XRD) patterns were characterized by

Bruker D8-Advance diffractometer using Cu K α as the incident radiation source. The density of glasses was determined by using the Archimedes method with water as an immersion fluid. All the measurements were carried out at room temperature.

According to the DTA tests, the T_g of SBAR glasses were estimated to be in the range of 620–640 °C. As a result, we chose 620 °C as the beginning heat-treatment

temperature to investigate the effect of annealing process on NIR emission initially. However, the treated SBAR and SBAN glasses became opaque and exhibited totally NIR-emitting quenching, which were entirely different from the traditional rare-earth ion doped glasses. In order to better understand the origin of this change and find the difference of alkali oxide component on the thermal stability of Bi-related NIR emission, the optical properties of SBAR glasses undergoing heat treatment near and below T_g were compared carefully.

Figure 1 presents the absorption spectra of the SBAR glasses undergoing heat treatment at the range of 420–620 °C and their corresponding images. It shows that SBAR glasses treated at 420 °C are light brown and have two main absorption bands centering at about 500 and 700 nm, assigned to the typical absorption peak of Bi NIR-emitting centers^[14,16,17]. However, the intensity of Bi-related absorption bands decreases significantly with the increase in treated temperature. After being heated at 620 °C, as stated above, all the SBAR glasses change markedly, especially the SBAN and SBAR glasses become deep brown and opaque. The detailed performances of SBAR glasses are presented as a representative of these glasses to elucidate the change of glass host during heat treatment. The inset of Fig. 1(c) shows the picture of undoped SBAR glass treated at the identical thermal-treatment condition, and it shows that the glass is transparent and there is no devitrification behavior in the glass matrix. However, with respect to the Bi-doped SBAR glasses, TEM picture (Fig. 2(a)) shows that some nanoparticles appear in the glass matrix after being heated at 520 °C, indicating that the darkening phenomenon of SBAR glasses may be due to the formation of Bi metallic colloids but not for the change in the glass matrix. XRD results of the samples (Fig. 2(b)) further confirm this assumption.

Figures 3(a)–(c) exhibit the NIR emission performance of SBAR glasses treated at different temperatures. Under excitation by 808 nm LD, the SBAR glasses emit broadband NIR emission from 900 to 1600 nm. The inset shows the dependence of normalized NIR luminescence intensity on the heat-treatment

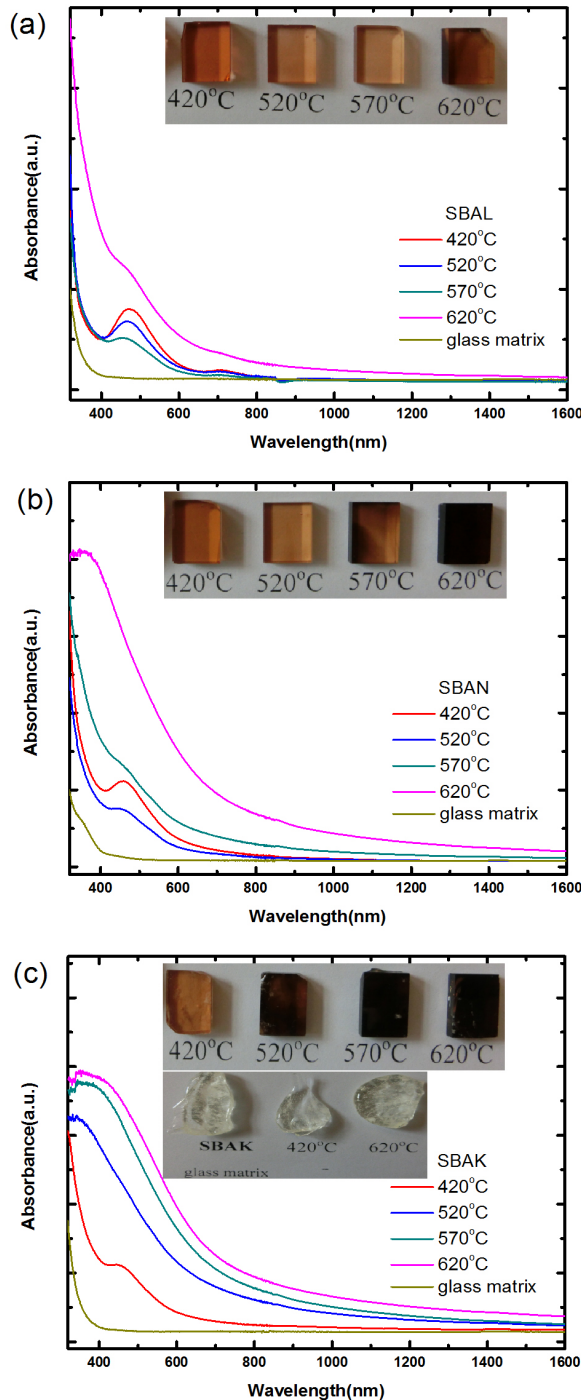


Fig. 1. Absorption spectra of the samples with SBAR glasses: (a) SBAL, (b) SBAN, and (c) SBAR. Insets show pictures of treated SBAR glasses and SBAR glass matrix before and after heat treatment.

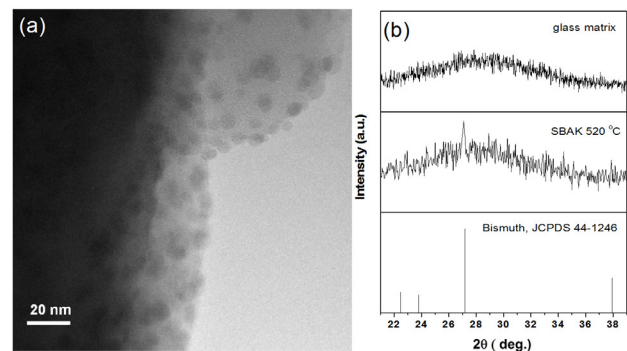


Fig. 2. (a) TEM photograph of Bi-doped SBAR. (b) XRD patterns of Bi-doped and undoped SBAR glasses treated at 520 °C.

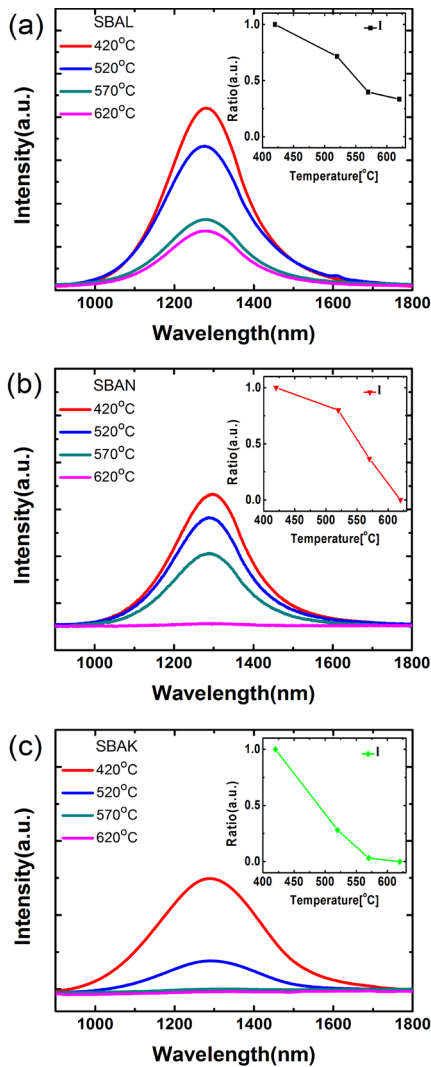


Fig. 3. NIR emission spectra of SBAR glasses undergoing heat treatment excited at 808 nm. Insets show the dependence of normalized emission intensity of SBAR glasses on the treated temperature.

temperature. It indicates that heat treatment also imposes significantly positive effect on NIR emission, which increases dramatically with the increase in the treated temperature as well as the radius of modifier cations. Similar to the results of absorption spectra, the SBAL glasses exhibit remarkably better NIR-emitting thermal stability compared with SBAN and SBAK glasses, of which the NIR luminescence are totally quenched under heat treatment at T_g (620 °C). The above results indicate that the SBAR glasses are very sensitive to heat treatment and the thermal stability of SBAR glasses decrease significantly with the increase in the radius of alkali metal ions.

The direct oxidation of low valent Bi-NIR-emitting centers are possibly one reason for the quenching or decrease in NIR emissions during heat treatment; however, in this work, we thought that thermally activated agglomerated behavior of Bi ion, leading to the decrease in Bi NIR-emitting center, is the main reason

for the NIR luminescence quenching of SBAR glasses. Because of the quenching temperature that darkening phenomenon occurred, which is much lower than T_g , where the direct oxidation behavior of Bi ions impossibly happened in the glass matrix. For Bi-doped glasses under heat treatment, the active Bi centers are supposed to easily capture the electrons released from the wrong bond during thermal activation, and then gradually aggregate into non-luminous Bi metallic colloids, resulting in the decrement of luminescence intensity and darkening phenomenon of the glass samples^[15–17,20]. From another view point, the behavior of forming Bi metallic colloids in the glass host during heat treatment can be considered as the process that Bi ions agglomerate together through thermal diffusion, in which melt viscosity plays an important role. However, according to the theory of the Vogel–Fulcher–Tammann equation and other reports^[21–23], it can infer that the viscosity of SBAR glass melts increase in the order of $Li^+–Na^+–K^+$. This means that there are some other critical mechanisms or factors determining the transformation of Bi-NIR-emitting centers in the glass matrix.

As for ion transport or diffusion performance in glass, it is the most widely studied phenomena in glass science, which can be considered as a thermally activated process^[24–26]. Some researchers have given a reasonable explanation for the transport ability of ions in different glass compositions^[24,27], such as that of alkaline earth ions in silicate glasses; however, the work on main group ions was rare. Although the migrating cations concerned are different, the NIR-emission quenching behavior of SBAR glasses during heat treatment, due to the thermal agglomeration of Bi ions in glass matrix, can also be understood according to the rules of ion mobility in glass.

Firstly, for component cations^[28–30], its self-diffusion or mobility can be related to the stabilization of site environments. Because the ion sites are fixed in the glass network, the migration parameters are determined by the activation energy for the jump between the adjacent sites, which are related to the distribution of site energies and the packing density of oxygen. In SBAR glasses, the alkali ions with smaller radius have a higher packing density of oxygen atoms and are preferentially to occupy the sites of lower energy with a concomitant higher activation barrier. This means that the migration of Bi ions around alkali ions needs lower activation energy to break the cation-oxygen bonds and overcome the lower interactions from neighbors when the cation radius of alkali oxide increases. This can lead to the significant thermal transport Bi ion in SBAR glass containing Na_2O and K_2O , resulting the remarkably emission quenching behavior when heated at high temperature.

On the other hand, the tightness structure of glasses is also one crucial factor determining the diffusion of cation ions^[24], especially below T_g . Namely, the loose network of glass is benefit for the transport of ions when

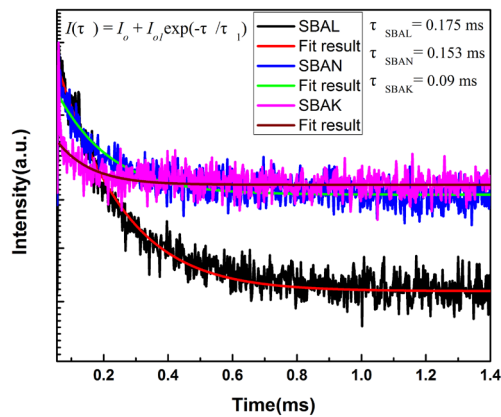


Fig. 4. Decay curves of SBAR glasses treated at 420 °C ($\lambda_{\text{ex}} = 808$ and $\lambda_{\text{em}} = 1300$ nm).

the glass network structure and ion sites are frozen below T_g . For SBAR glasses, the densities of the glass host are determined to be 2.533, 2.523, and 2.493 g/cm³ (± 0.004) when the cation oxides are Li₂O, Na₂O, and K₂O, respectively. Meanwhile, the mean cation-oxygen distances for Li⁺, Na⁺, and K⁺ in glass are about 0.196, 0.236, and 0.289 nm^[31], and the mole masses of these ions are about 7, 23, and 39 g/mol, respectively. This means that the volume density of alkali ions in glass increases in the order of Li⁺–Na⁺–K⁺, and the network of SBAR glass gets loosen with the increase in the radius of modifier cations. Figure 4 shows the decay curves of SBAR glasses, and also shows that the luminescence lifetime of the Bi-related NIR-emitting center (ascribed to Bi⁺ ions according to the previous work)^[32] in SBAR glasses decrease in the order of Li⁺–Na⁺–K⁺. This can also be ascribed to that glass structure around Bi-NIR-emitting centers becoming loose with increase in the radius of modifier cations, and enhancing the non-radiative relaxation of luminescence centers and reducing the luminescence lifetime consequently^[3]. Therefore, we find that the SBAR glasses with Na₂O and K₂O have much looser network structure, and the activated Bi distributed inside the glass network can easily migrate to form Bi metallic colloid through the floppy network at high temperature.

Based on the obtained results, it can be predicted that the capacity of modifier cations, Li⁺, with lower mobility and higher tightness network, can offer better thermal stability for Bi-activated NIR emission than the other two alkali ions. This result shows that the network modifiers of glasses are one crucial factor that determines the thermal stability of Bi-doped glasses. The performance of Bi-doped SBAR glasses should be useful for the guide for the composition design of Bi-doped optical fiber. However, remarkable thermal quenching of SBAR glasses occurring below T_g cannot present enough practical significance for the fiber-drawing process, and further work should be performed with concern about the thermal stability of Bi-doped glass near the softening point, which are in progress.

In conclusion, we study the effect of alkali oxide as network modifier on the NIR luminescence change of Bi-doped SBAR glasses under heat treatment below T_g . It shows that NIR-emission thermal stability of SBAR glasses increases in the order of K⁺–Na⁺–Li⁺, and that of SBAL glass is much better than other glasses. These phenomena are probably due to the smaller alkali cations as network modifier leads to the decrease in ion mobility and the enhancement of network tightness, which can restrain the thermal diffusion of Bi-related NIR-emitting centers in the glass matrix. These results can potentially provide a valuable reference for composition design and fabrication process of Bi-doped optical fiber.

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