Bismuth-doped glasses have attracted considerable attention as materials for broadband amplifiers and tunable lasers that cover all telecommunication wavelengths from 1 100 to 1 600 nm since ultra-broadband, near-infrared (NIR) fluorescence and the relevant optical amplification have been reported by Fujimoto et al.\cite{1,2}. The spectroscopic properties of Bi-doped glasses have been widely investigated in various glass hosts, such as silicate\cite{3−9}, phosphate\cite{10,11}, germanate\cite{12−15}, bismuthate\cite{16}, and chalcogenide glasses\cite{17,18}. The full-width at half-maximum (FWHM) of the NIR luminescence band was reported to reach up to 600 nm in a Bi-doped chalcogenide glass. The FWHM can even reach 850 nm at cryogenic temperature\cite{17}, and the decay time of NIR emission reaches up to 1 275 μs in a Bi-doped aluminogermanate glass\cite{15}.

Compared with other host glasses, silicate glasses are more remarkable in terms of compatibility with commercial silica fiber networks. Alkali or alkaline earth oxides are commonly used in silicate glass hosts as network modifiers, but they increase the optical basicity of glasses, which is reported to be harmful to NIR emissions of Bi-doped glasses\cite{8}. Compared with the M-O bond-strengths of alkali- and alkali earth-based glasses, La-O bonds are stronger, because of the high field-strength of La³⁺ ions. Lanthanum aluminosilicate (LAS) glasses exhibit high glass transition temperatures that range from 800 to 900 °C and are virtually independent of the composition\cite{19}. Excellent physical properties and lower optical basicity make LAS glasses potential hosts for bismuth doping.

To our knowledge, no research on Bi-doped LAS (La₂O₃-Al₂O₃-SiO₂) system glasses has been performed. In this letter, we select the composition of 65SiO₂-20Al₂O₃-15La₂O₃ (in mole%) as the host of bismuth doping. The composition has been chosen based on the glass forming region in a previous work\cite{20}. The influence of Bi₂O₃ content and temperature on the spectroscopic properties of bismuth ions in La₂O₃-Al₂O₃-SiO₂ glass is also investigated.

The analytical-grade reagents of SiO₂, Al(OH)₃, La₂O₃, and Bi₂O₃ were used as starting materials. Glass compositions (in mol%) of 65SiO₂-20Al₂O₃-(15-x)La₂O₃-xBi₂O₃ (x = 0.5, 1.0, 2.0, 3.0, and 4.0 mol%) were studied and named as xBi-LAS, where x = 0.5 to 4.0 mol%. The mixed 40-g batches were melted in silica ceramic crucibles at 1 600 °C at room temperature for 3 h. The glass melt was poured on the pre-heated steel mold and annealed at 700 °C for 200 min. The color of the glass samples changed from pink to brownish red as the of Bi₂O₃ doping level increased. Considering the volatilizing losses of bismuth during the melting process, the real bismuth content was measured using inductively coupled plasma atomic emission spectroscopy. Bi₂O₃ concentrations in 0.5, 1.0, 2.0, 3.0, and 4.0Bi-LAS were 0.40, 0.63, 1.28, 1.83 and 2.58 mol%, respectively.

The glasses were cut and polished to a 10×25×3-(mm) size for optical measurements. The optical absorption spectrum was measured by a Lambda spectrophotometer (900UV/VIS/NIR, Perkin-Elmer, USA). The fluorescence spectra and fluorescence decay were obtained using a steady state spectrometer (FLSP920, Edinburgh, England). A xenon lamp was used as the pumping source. Liquid helium was used to achieve low temperatures.

Figure 1 shows the absorption spectrum of 0.5Bi-LAS glass ranging from 300 to 1 600 nm with a sample thickness of 3 mm. The absorption spectrum consists of five peaks. Peaks at approximately 500 and 700 nm and a shoulder at 800 nm are similar, as reported in other bismuth-doped glasses\cite{1,13}. An ultra-broad absorption band exists, ranging from 850 to 1 400 nm with an absorption peak at approximately 1 100 nm. A weak absorption band at approximately 1 420 nm can be observed in Fig. 1. This has also been observed in previous stud-
ies on Bi-doped fibers\textsuperscript{[21,22]}. The absorption spectra are similar in glasses with different Bi$_2$O$_3$ doping levels.

The absorption cross sections $\sigma_{\text{abs}}$ at 500 and 700 nm, which are the primary absorption bands of bismuth ions\textsuperscript{[1]}, are calculated using

$$\sigma_{\text{abs}} = \frac{2.303 \log(I_0/I)}{NL}, \quad (1)$$

where $I_0$ is the initial incidence intensity, $I$ is the transmitted intensity, $N$ is the bismuth ion concentration, and $L$ is the sample thickness. We used $L=0.3 \text{ cm}$, and calculated $N$ as $N = \frac{\rho \omega}{M_{\text{Bi}_2O_3}} \frac{\text{mol}}{\text{cm}^3}$, where $\rho$ is the density of glass, $\omega$ is the mass percentage of Bi$_2$O$_3$, and $M_{\text{Bi}_2O_3}$ is the molar mass of Bi$_2$O$_3$. The $\sigma_{\text{abs}}$ of the Bi-LAS samples reaches $8.31 \times 10^{-21} \text{ cm}^2$ at 500 nm.

The inset of Fig. 1 shows the concentration dependencies of the absorption cross sections ($\sigma_{\text{abs}}$) at 500 and 700 nm. The $\sigma_{\text{abs}}$ increases as the Bi$_2$O$_3$ content increases. When the Bi$_2$O$_3$ content is less than 2 mol% (e.g., 3.0 Bi-LAS), the $\sigma_{\text{abs}}$ at 500 nm and the content follow a linear trend. The slope of the line decreases as the Bi$_2$O$_3$ content increases. Moreover, $\sigma_{\text{abs}}$ at 700 nm and the Bi$_2$O$_3$ content both increase as the slope decreases. This phenomenon occurs because less active bismuth centers form when the Bi$_2$O$_3$ doping level is larger than a certain limit.

Figures 2(a) and (b) show the emission spectra of bismuth-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses with various bismuth doping levels under the 500 and 700-nm excitations, respectively. These figures also show a substantial increase in NIR luminescent intensity with increasing Bi$_2$O$_3$ content up to 1.83 mol% in 3.0 Bi-LAS. The intensity reduction in high bismuth doping levels likely results from concentration quenching. In addition, the peak wavelengths and asymmetry of emission bands gradually increase as the Bi$_2$O$_3$ contents increase under the 500 and 700-nm excitations.

Figure 3 shows the FWHM and peak wavelength of the emission spectra as a function of Bi$_2$O$_3$ content. The red-shift of the emission peaks with increasing Bi$_2$O$_3$ content, as observed in Fig. 2, is visualized in Fig. 3. The FWHM also increases along with the increase in bismuth doping level (Fig. 3), even when the emission intensity decreases in 4.0Bi-LAS glass.

To investigate the emission properties for high bismuth doping levels, the emission bands of 4.0Bi-LAS under the 500 and 700-nm excitations were deconvoluted to Gaussians, as shown in Figs. 4(a) and (b), respectively. The two emission bands are deconvoluted to 2 Gaussians with a determination coefficient $R^2 > 0.999$. The emission spectrum under the 500-nm excitation consists of two emission bands at 1 160 (peak 1) and 1 320 nm (peak 2). The emission spectrum excited at 700 nm is deconvoluted to 2 peaks positioned at 1 100 (peak 1) and 1 300 nm (peak 2). Similar Gaussian fitting results have been observed in other Bi-doped materials\textsuperscript{[5,23]}. The emission spectra Gaussian fitting results of other Bi-LAS glass samples are roughly the same as those shown in Fig. 4. Table 1 shows the ratio of Gaussian peaks, which are calculated by dividing the integrated area of peak 2 with the integrated area of peak 1 in all Bi-LAS glasses. The ratios increased from 0.49 to 1.95 under the 500-nm excitation and from 0.37 to 1.22 under the 700-nm excitation as the Bi$_2$O$_3$ content increased from 0.40% to 2.58%. The different concentration dependencies of the Gaussian peaks cause the red-shifting and broadening of the emission bands in Fig 3. Similarly, the asymmetric...
Table 1. Integrated Areas of Deconvoluted Gaussian Peaks under the 500- and 700-nm Excitations for Various Bi$_2$O$_3$ Contents

<table>
<thead>
<tr>
<th>Bi$_2$O$_3$ Content (mol%)</th>
<th>Integrated Area 500-nm-excitation</th>
<th>Integrated Area 700-nm-excitation</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak1 ($\times 10^7$)</td>
<td>Peak2 ($\times 10^7$)</td>
<td>Peak1 ($\times 10^7$)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.43</td>
<td>0.21</td>
<td>0.49</td>
</tr>
<tr>
<td>1</td>
<td>1.03</td>
<td>0.96</td>
<td>0.93</td>
</tr>
<tr>
<td>2</td>
<td>1.68</td>
<td>2.65</td>
<td>1.58</td>
</tr>
<tr>
<td>3</td>
<td>2.53</td>
<td>4.00</td>
<td>1.58</td>
</tr>
<tr>
<td>4</td>
<td>1.39</td>
<td>2.71</td>
<td>1.95</td>
</tr>
</tbody>
</table>

emission bands at higher bismuth doping levels resulted from the increased contribution of peak 2 to the emission band. Furthermore, the different concentration dependence indicates that two emission centers may exist. One is responsible for the emission band at around 1100 nm and the other is responsible for the emission band at 1300 nm. The different locations of the emission bands under various exciting wavelengths can be ascribed to the different proportions of the emission peaks.

We used X-ray photoelectron spectroscopy (XPS) to explore the valence states of active Bi ions in Bi-LAS glasses. Figures 5(a–c) show the XPS peaks of Bi(4$f_{5/2}$, 4$f_{7/2}$) on 1.0 and 2.0Bi-LAS glasses and Bi$_2$O$_3$ powders, respectively. The red dashed curves of Figs. 5(a) and (b) indicate the Bi(4$f_{5/2}$, 4$f_{7/2}$) peaks, and are the fitting curves of the measured results. The main Bi(4$f_{5/2}$, 4$f_{7/2}$) peaks of both 1.0 and 2.0Bi-LAS glasses are at 163.8 and 158.5 eV, respectively. No significant shifts are observed in the XPS spectra of 1.0 and 2.0Bi-LAS glasses. Therefore, the Bi$_2$O$_3$ doping level does not affect the valence state of Bi ions in Bi-LAS glasses. Compared with the XPS spectrum of Bi$_2$O$_3$ powders in Fig. 5(c), the Bi(4$f_{5/2}$, 4$f_{7/2}$) peaks of Bi-LAS glasses in Figs. 5(a) and (b), which are 164.1 and 158.8 eV respectively, shift to a lower energy at 0.3 eV. The energy shift proves the existence of Bi ions with valence states lower than +3 in bismuth-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses, given that the valence state of the target ion becomes higher with increasing bonding energy

The NIR emissions of bismuth-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses is associated with two centers with low valence state species of Bi. The contributions of low valence state Bi, such as Bi$^+$ or Bi$^0$, to NIR emission have been reported in some bismuth-doped materials. Following the hypothesis of Wu et al. for NIR emissions in Bi-doped glass preforms and fibers, we ascribed the NIR emission of Bi-LAS glasses to both Bi$^+$ and Bi$^0$. The hypothesis is also supported by Wang’s investigation on bismuth-doped phosphate glasses. The schematic energy level diagrams for Bi$^+$ and Bi$^0$ are shown in Fig. 6. The absorption peaks identified in Fig. 1 are roughly matched to the proposed energy levels of Bi$^0$ and Bi$^+$. The emission at approximately 1100 nm matches well with the transition from (1)$^2$D$_{3/2}$ to $^4$S$_{3/2}$ of Bi$^0$. 

Fig. 4. Emission spectra deconvoluted into Gaussians of 4.0Bi-LAS glass excited at (a) 500 and (b) 700 nm.

Fig. 5. X-ray photoelectron spectroscopy peaks of Bi(4$f_{5/2}$, 4$f_{7/2}$) in (a) 1.0 and (b) 2.0Bi-LAS glasses and (c) Bi$_2$O$_3$ powders.
The emission band at approximately 1300 nm can be attributed to the $^3P_1 \rightarrow ^3P_0$ transition of Bi$^+$. Figure 7 shows the decay curves of bismuth-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses in various doping levels excited at 500 nm. The inset plots the $1/e$ lifetime of each sample, detected at 1150 nm, as a function of the Bi$_2$O$_3$ content. In Fig. 7, the lifetimes of the Bi-LAS samples decrease from 420 to 230 µs as the Bi$_2$O$_3$ content increases, indicating the occurrence of concentration quenching. The inset shows that the lifetime quickly decreases at low Bi$_2$O$_3$ contents (in 0.5, 1.0, and 2.0Bi-LAS). The lifetime then changes slightly as the Bi$_2$O$_3$ content increased. The decay curves and the $1/e$ lifetime of the 1100-nm emission under 700-nm excitation follow a similar concentration dependence (Fig. 7).

The influence of temperature on NIR emissions and decay properties was investigated at series temperatures ranging from 9 to 350 K on a 2.0Bi-LAS glass sample with 1-mm thickness. Figure 8 shows the temperature-dependent emission spectra (a) and the decay curves of the 1170-nm emission (b) of the 2.0Bi-LAS sample excited at 500 nm. The inset of Fig. 8(b) plots the $1/e$ lifetime as a function of temperature. When the temperature increases from 9 to 350 K, the peak wavelengths and the FWHMs of emission bands remain constant at approximately 1170 and 220 nm, respectively. Figures 8(a) and (b) show that the shapes of emission spectra and decay curves are approximately unchanged as the temperature varies. The inset of Fig. 8(b) shows that the lifetime of 2.0Bi-LAS is approximately 460 µs, and remains almost constant when the temperature increased from 9 to 350 K. The observation is similar to previous findings on Bi-doped LAS glass[23] and Bi-doped germanate glass[9]. The nearly-independent lifetime shows that the non-radiative decay process does not significantly occur until 350 K, and that NIR emissions have strong resistance to thermal quenching.

In conclusion, the impact of doping levels and temperature on the spectroscopic properties of Bi$_2$O$_3$-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses are investigated. The absorption cross section, $\sigma_{abs}$, increases as the Bi$_2$O$_3$ content increases. The absorption cross section reaches $8.31 \times 10^{-21}$ cm$^2$ at the 500-nm excitation when the Bi$_2$O$_3$ content is 2.58 mol%. The emission intensity reaches a maximum value when the Bi$_2$O$_3$ content is 1.83 mol%. The emission peaks are at 1190 and 1117 nm, and the FWHM data are 330 and 228 nm at the 500 and 700-nm excitations, respectively. Two NIR emission centers, Bi$^0$ and Bi$^+$, are responsible for the NIR emission bands of Bi$_2$O$_3$-doped La$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses. The different concentration dependencies of emission centers are the most likely causes of the red shift and the broadening of emission bands as bismuth content increases. In addition, the fluorescent lifetime decreases from 420 to 230 µs as the Bi$_2$O$_3$ content increases from 0.40 % to 2.58% (in mol%).
Low temperature spectroscopic results show that the fluorescent lifetime of Bi-LAS glass is almost constant from 9 to 350 K. The nearly-independent lifetime suggests that the NIR emission of Bi in the system has strong resistance to thermal quenching.

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References