27Al NMR structural study on aluminum coordination state in bismuth doped silica glass

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Abstract

The aluminum coordination state in bismuth doped silica glass, which has new broad infrared emission at 1.3 μm regions, was investigated by using 27Al NMR, and it is demonstrated that 6-fold coordinated aluminum ions with corundum structure are dominant in bismuth doped silica glass until Bi2O3 concentrations of 1.0 mol% with Al2O3. The aluminum ion efficiently affects the creation of a Bi luminescent center at an intensity of Bi2O3 (1.0 mol%)-Al2O3 (2.3 mol%)-SiO2 (96.7 mol%); the sample is three orders of magnitude larger than the Bi2O3 (1.0 mol%)-SiO2 (99.0 mol%) sample. Aluminum ions with corundum structure in silica glass have a very important role for the configuration of peculiar Bi luminescent centers.

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1. Introduction

Infrared fluorescence materials are widely used as laser media, for example, Nd:YAG, Er doped silica fiber. The existence of fluorescence in infrared regions has many advantages because there are many type of optics, and we can use semiconductor lasers or flash lamps for their excitation and can also obtain frequency doubled beams with non-linear crystal in visible regions; therefore, the light sources are very useful for scientific research and industrial uses.

Fujimoto and Nakatsuka discovered a new infrared fluorescence from bismuth doped silica glass (BiSG) [1]. A wide fluorescence exists between 1000 and 1600 nm, and the absorption is in the visible region. Since this silica glass based material has luminescence around 1.3 μm of zero-disperssion wavelength, it can be used as core material of an optical fiber amplifier for telecommunications at a range of 1.3 μm. They also demonstrated optical amplification at 1.3 μm with 0.8 μm excitation [2]. Therefore, BiSG is expected to be a promising substitute for Pr3+:ZBLAN fiber amplifiers or Raman amplifiers in 1.3 μm regions.

The spectroscopic properties of BiSG are different from previously reported Bi luminescent material [1] because previous Bi-doped glasses or crystals with low Bi2O3 concentration showed that fluorescences exist in the visible region (400–600 nm) and absorptions in the ultraviolet region. The lifetimes (~4 μs) are much shorter than BiSG at room temperature. It is reported that these types of luminescences originated from Bi3+ ion in the media [3–5]. BiSG is also different from Bi2O3 rich type glass whose Bi2O3 concentration is from 18.7 to 42.5 mol% [6] because the glass has no absorption at the visible region. Therefore, determining the luminescent mechanism, which is still unclear, is not only interesting for condensed matter physics but also for such optical applications as lasers or amplifiers.

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Aluminum ions are needed to generate BiSG luminescence [1]. Aluminum is expected to have a special role in the formation of Bi luminescent centers. Therefore, discovering the aluminum status in BiSG, especially the aluminum coordination state (ACS), will help us understand the unknown luminescent center. ACS can be investigated by using $^{27}$Al NMR [7,8].

In this paper, we investigate ACS in BiSG by $^{27}$Al NMR and showed the Bi$_2$O$_3$ or Al$_2$O$_3$ concentration dependence to ACS in BiSG. After that, we discuss the behavior of aluminum ions in BiSG.

2. Experimental

BiSG samples were prepared as follows. Bismuth-oxide (Bi$_2$O$_3$; 99.9%), aluminum-oxide (Al$_2$O$_3$; 99.99%), and silica powder (SiO$_2$; 99.8%) were mixed and kneaded in a mortar. The mixture compound was put in an alumina crucible and sintered at 1750 °C in air.

The sample composition was decided as follows:

1. The Bi$_2$O$_3$ to Al$_2$O$_3$ ratio was kept at 3/7, and the Bi$_2$O$_3$ concentration varied from 0.1, 0.3, 0.5, 1.0, and 3.0 mol%. These samples are called A1–A5, respectively.
2. Bi$_2$O$_3$ concentration was fixed at 1.0 mol%, and Al$_2$O$_3$ concentration varied from 1.0, 2.3, and 5.0 mol%. These samples are called B1–B3, respectively.

All samples showed a reddish-brown color. We also made two reference glasses; one was an Al$_2$O$_3$ (2.3 mol%)-SiO$_2$ (97.7 mol%) glass (C1) that was compared with ACS in all the BiSG samples, and the other was a Bi$_2$O$_3$ (1.0 mol%)-SiO$_2$ (99.0 mol%) sample (C2) that was compared with the fluorescence intensity of BiSG (A4). C1 and C2 were colorless and dark brown, respectively. These samples are listed in Table 1.

$^{27}$Al NMR spectra were obtained on a JEOL JNM-GSX-400 nuclear magnetic resonance spectrometer. We selected two aluminum-oxide crystals ($\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$) as standard materials with which we compared the ACS in all the BiSG samples. $^{27}$Al chemical shifts were measured relative to Al($\text{H}_2\text{O}$)$_6^{3+}$.

X-ray diffraction (XRD) data of the glass samples were also measured to check any existing crystallization, for example, undissolved alumina, mullite or crystbalite, because the crystallization influences $^{27}$Al NMR spectra of the samples. The measurements of XRD data were carried out by RIGAKU RINT2500 X-ray diffractometer.

3. Results

3.1. $^{27}$Al NMR spectra from A1 to A5

Fig. 1 shows the $^{27}$Al NMR spectra of dependance on Bi$_2$O$_3$ concentrations while retaining the Bi$_2$O$_3$ to Al$_2$O$_3$...
ratio at 3/7; these spectra were normalized at peak intensity. The peaks at 70 and −40 ppm were derived from spinning sidebands. An α-Al₂O₃ peak with a corundum structure exists at 15 ppm. The peaks of ²⁷Al NMR from A1 to A3 also exist at 15 ppm, which are the same as α-Al₂O₃. The A4 peak is still dominated by the 15 ppm peak, but a peak around 50 ppm begins to emerge, and then a peak of 56.4 ppm becomes dominant in A5. These peaks are listed in Table 2.

3.2. ²⁷Al NMR spectra from B1 to B3

Fig. 2 shows the ²⁷Al NMR spectra of dependence on Al₂O₃ concentrations with 1.0 mol% of Bi₂O₃ concentration, and these spectra are normalized at peak intensity. All three spectra are dominated at the 15 ppm peak, the same as α-Al₂O₃, but each sample also shows a weak peak at 50 ppm, and peak intensity increases with increasing Al₂O₃ concentration. These peaks are listed in Table 2.

3.3. Comparisons of A4 with C1 in ²⁷Al NMR spectra

Sample A4, which includes Al₂O₃ of 2.3 mol%, has a 50 ppm peak in the ²⁷Al NMR spectrum, while sample C1, which has the same amount of Al₂O₃ without Bi₂O₃, shows no signal around 50 ppm; therefore, Bi ion affects ACS over 1.0 mol% of Bi₂O₃ concentration.

3.4. Comparisons of A4 with C2 in fluorescence intensities

The C2 sample has no aluminum and did not show peculiar glassy wetting. On the other hand, all the BiSG with Al₂O₃ have glassy wetting. C2 has little fluorescence that can be considered a Bi luminescent center, and the intensity was three orders of magnitude smaller than sample A4. All the BiSG samples have peculiar Bi luminescence, and all the intensities of the BiSG samples were also increased by two or three orders of magnitude larger than C2.

3.5. X-ray diffraction data

Fig. 3 shows the XRD data on α-Al₂O₃ (alumina), B3 sample and pure silica with the range between 10 and 80 degree in 2θ. We did not recognize the peak due to any kind of crystallization, especially undissolved alumina.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical shift [ppm]</th>
<th>Coordination number</th>
<th>Crystal system</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>15.1</td>
<td>6-fold</td>
<td>Amorphous</td>
</tr>
<tr>
<td>A2</td>
<td>14.8</td>
<td>6-fold</td>
<td>Amorphous</td>
</tr>
<tr>
<td>A3</td>
<td>15.1</td>
<td>6-fold</td>
<td>Amorphous</td>
</tr>
<tr>
<td>A4, B2</td>
<td>15.1 (50.0)</td>
<td>6-fold (4-fold)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>A5</td>
<td>56.4</td>
<td>4-fold</td>
<td>Amorphous</td>
</tr>
<tr>
<td>B1</td>
<td>15.0 (50.0)</td>
<td>6-fold (4-fold)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>B3</td>
<td>14.9 (50.0)</td>
<td>6-fold (4-fold)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>C1</td>
<td>15.2</td>
<td>6-fold</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Ref1 (α-Al₂O₃)</td>
<td>15.1</td>
<td>6-fold</td>
<td>Corundum structure, Dₑₑ₃ (R3c), trigonal system a₀ = 5.350 Å, α = 55°9'</td>
</tr>
<tr>
<td>Ref2 (γ-Al₂O₃)</td>
<td>8.3</td>
<td>6-fold</td>
<td>Spinel structure, D₁₉₄ (I4/amd), tetragonal system a₀ = 5.75 Å, e₀ = 9.42 Å</td>
</tr>
</tbody>
</table>

The values given in parentheses are for second peaks.
even in B3 which has the maximum rate of alumina with corundum peak, and we can see only a halo pattern. We measured XRD pattern on Nd$_2$O$_3$ (3 wt%; 0.55 mol%)–SiO$_2$ (97 wt%; 99.45 mol%) system, and confirmed the peaks due to undissolved Nd$_2$O$_3$ only at 0.55 mol% [9]. It is thought that the 5 mol% of alumina is enough quantity for XRD detection if there is undissolved alumina in the sample. We have also got same data for A1–A5, B1, B2, and C1, therefore, we conclude that all our samples are in amorphous phase.

4. Discussion

It is well-known that chemical shift in $^{27}$Al NMR spectrum is strongly affected by the local coordination of aluminum ions [7,8], and aluminum-27 is 100% isotropic abundance; therefore, $^{27}$Al NMR spectrum reflects the local structures of all the aluminum ions in the samples. The increment of the aluminum coordination number moves the chemical shift toward the lower part in ppm (higher magnetic field) [8]. The $^{27}$Al NMR peaks of well-known crystal structures, such as α-Al$_2$O$_3$ and γ-Al$_2$O$_3$, were 15.1 and the two peaks of 8.3 and 70.4 ppm, respectively (Table 2). α-Al$_2$O$_3$ is a corundum structure, and γ-Al$_2$O$_3$ is a spinel structure with two coordination states of 4- and 6-fold. The 8.3 ppm peak of γ-Al$_2$O$_3$ is due to 6-fold coordination, and 70.4 ppm is due to a 4-fold coordination state. Although α-Al$_2$O$_3$ also configures the 6-fold coordination, the corundum structure is more distorted than the 6-fold coordination in γ-Al$_2$O$_3$ [10,11], shifting the peak to a higher chemical shift in ppm (lower magnetic field). Therefore, the ACS in BiSGs, which has 15 ppm peaks, is considered a distorted 6-fold corundum structure.

Let us consider the following four points with respect to experimental results: (a) roles of aluminum ions, (b) ACS in BiSG at low aluminum concentration, (c) bismuth concentration dependence for ACS in BiSG, and (d) aluminum concentration dependence for ACS in BiSG.

4.1. Roles of aluminum ions

Two facts must be considered. First, as already described in Section 3.4, aluminum ions effectively help construct the Bi luminescent center because, if there is aluminum in BiSG, the luminescent intensity is drastically increased. The fluorescence enhancement effect is probably generated by some coupling effect between Bi and Al, and so both atoms should be close together. Second, Al$_2$O$_3$ assists Bi ions to get into the silica glass network because C2 has no glassy wetting. Therefore, the aluminum ion has two roles in BiSG: assisting the configuration of the peculiar luminescent center of Bi ion with some coupling effect, and increasing compatibility with the silica network.

4.2. ACS in BiSG at low aluminum concentration

The C1 spectrum peak corresponds to a 6-fold coordinated state of corundum structure. Therefore, at least, the aluminum ions in silica glass configure the 6-fold coordinated state of corundum structure up to 2.3 mol% of Al$_2$O$_3$ without Bi$_2$O$_3$. This is also supported by the work of Mysen et al. [12], who concluded that the aluminum ions in silica glass function as a network modifier rather than a network former up to 6.1 mol% Al$_2$O$_3$ concentration in measurements of Raman spectra.

4.3. Bismuth concentration dependence for ACS in BiSG

The main peaks in the spectra of samples A1–A4 also correspond to a 6-fold coordinated state of the corundum structure. A small amount of peak at 50 ppm appears in sample A4, because Bi$_2$O$_3$ concentration affects the configuration of the 50 ppm peak, and then the 56.4 ppm peak is dominant in sample A5. Peaks around 50 ppm in samples A4 and A5 are due to a distorted 4-fold coordination state [8].

When Bi$_2$O$_3$ concentration is over 1.0 mol% in BiSG, the aluminum coordination state is gradually shifted to 4-fold; after concentration reaches 3.0 mol%, ACS is mainly dominated by a distorted 4-fold coordination state. On the other hand, if Bi$_2$O$_3$ concentration is under 0.5 mol%, the $^{27}$Al NMR spectra show that the 6-fold aluminum coordination of corundum structure is dominant and without obvious 4-fold coordination. This implies that the ACS of the corundum structure efficiently affects the configuration of the peculiar Bi luminescent center.

4.4. Aluminum concentration dependence for ACS in BiSG

The $^{27}$Al NMR spectra of B1–B3 show that the 50 ppm peak increased with increasing Al$_2$O$_3$ concentration for the following two reasons:

(1) Increments of Al$_2$O$_3$ concentration independently affect increases of the 4-fold coordination state.
Increments of different types of Al ion coupling with Bi ion, which is not a corundum structure, affect increases of the 4-fold coordination state.

Risbud et al. [13] reported that the corundum structure retains at 6.1 mol% of the Al2O3 concentration in SiO2–Al2O3 glass, but the obvious peak of corundum structure is distinguished at 9.4 mol% of Al2O3 concentrations. There are many types of aluminum coordination states (4-, 5-, and 6-fold) in the sample [13,14], and the same phenomenon occurs in B1–B3.

A comparison of A3 with B1 implies that some bismuth ions over 0.5 mol% couple with aluminum ions that do not have corundum structure. Bi2O3 concentration also changes the aluminum coordination state from 6-fold to 5- or 4-fold coordination structure, and the effect of Bi2O3 is stronger than Al2O3.

The above discussion implies that there are, at least, two types of Bi ion with Al ion local structures. One is the Bi ion set close to 6-fold coordination aluminum, like α-Al2O3. This type of Bi ion contributes peculiar Bi luminescence, which is verified by the 27Al NMR results of samples A1–A3. Another is Bi ion set close to 4- or 5-fold coordination aluminum, and in this experiment it is unclear whether this type of Bi ion contributes Bi luminescence.

The valence state of Bi ions in BiSG was checked by electron spin resonance. Since there was no signal due to unpaired electrons, the valence state is Bi3+ or Bi5+ [1]. The coordination number and effective ionic radius for Bi3+ ion are 5, 6, 8 and 0.96, 1.03, 1.17 Å, and for Bi5+ ion they are 6 and 0.76 Å, respectively [15]. If the peculiar Bi luminescent center is close to 6-fold coordination of aluminum and has similar local coordination structure to the neighboring aluminum ion, a Bi3+ ion is more suitable than a Bi5+ ion because the coordination number and ionic radius of Bi3+ is closer than Bi5+. It is also suggested that the possible valence state of Bi luminescent center is Bi5+ by analyzing the fluorescence spectra and lifetime [1].

5. Conclusions

Aluminum ions efficiently affect the creation of a Bi luminescent center and can naturally behave as 6-fold corundum structure in silica glass up to 2.3 mol%. ACS in BiSG is divided into three parts with respect to Bi2O3 concentration: (1) ACS with corundum structure below 0.5 mol%, (2) ACS with corundum structure and 4-fold coordination structure between 0.5 and 3.0 mol%, and (3) ACS with 4-fold coordination structure above 3.0 mol%. Since aluminum ions only have 6-fold corundum structure below Bi2O3 concentrations of 0.5 mol% with peculiar Bi luminescence, we conclude that aluminum ions with 6-fold corundum structure in silica glass have a crucial role for the configuration of peculiar Bi luminescent center.

References