Fabrication and photoluminescence of monolithic silica glass doped with alumina nanoparticles using SiO$_2$-PVA nanocomposite

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Al$_2$O$_3$ nanoparticle doped SiO$_2$-PVA nanocomposites were prepared using fumed silica, fumed alumina, and poly(vinyl alcohol) (PVA). Nanocomposites containing from 0 to 6 mol % Al$_2$O$_3$ were heat-treated in air at 1100 to 1300°C to obtain monolithic, transparent silica glass. The 0.6 mol % Al$_2$O$_3$ doped nanocomposite was sintered at 1200°C, a higher temperature than was required for the non-doped nanocomposite. The obtained Al$_2$O$_3$ doped silica glass exhibited characteristic blue photoluminescence (PL) on UV excitation. The effects of the Al$_2$O$_3$ nanoparticles on the sintering temperature and the PL characteristics of the sintered silica glass are discussed in terms of the morphology and structure of the sintered glass.

Key-words : Fumed silica, Fumed alumina, Composite, Silica glass, Sintering, Fluorescence

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As the water in the sample evaporated during the drying process, the suspension gradually consolidated to form a wet gel, eventually generating a solid Al$_2$O$_3$ doped SiO$_2$-PVA nano-composite. The monolithic silica glass was finally obtained by sintering this nanocomposite at 1100–1300°C for various periods of time in air. The sintered samples were examined by X-ray diffraction (XRD; MultiFlex, Rigaku, Japan) and their morphologies were observed using transmission electron microscopy (TEM; JEM-1300NEF, JEOL, Japan) in conjunction with electron energy-loss spectroscopy (EELS). The PL characteristics of the sintered glasses were evaluated by means of a fluorescence spectrophotometer (F-4500, Hitachi, Japan) with a Xenon lamp source. The Vickers hardness (Hv) values of the samples were measured using a hardness testing apparatus (MVK-H1, Mitutoyo, Japan). The structure of each Al$_2$O$_3$ doped silica glass was analyzed with Fourier transform infrared spectroscopy (FT-IR; FTIR-8400, Shimadzu, Japan) applying the KBr pellet method.

### Table 1. Effects of temperature and holding time on the sintering behavior of SiO$_2$-PVA nanocomposites doped with 0, 0.6 and 1.2 mol% Al$_2$O$_3$ (○ = transparent, △ = opaque, ■ = crystalline. The symbols -,- and --- indicate materials expected to be transparent, opaque and crystalline.)

<table>
<thead>
<tr>
<th>Al$_2$O$_3$ amount (mol%)</th>
<th>Temperature (°C)</th>
<th>0.5</th>
<th>3</th>
<th>6</th>
<th>8</th>
<th>9</th>
<th>12</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1100</td>
<td>○</td>
<td>○</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>(Non-doped)</td>
<td>1200</td>
<td>■</td>
<td>■</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.6</td>
<td>1100</td>
<td>--</td>
<td>△</td>
<td>-</td>
<td>-</td>
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<td>△</td>
<td>△</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>--</td>
<td>△</td>
<td>○</td>
<td>○</td>
<td>△</td>
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<tr>
<td></td>
<td>1300</td>
<td>■</td>
<td>■</td>
<td>-</td>
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<tr>
<td>1.2</td>
<td>1200</td>
<td>--</td>
<td>△</td>
<td>△</td>
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<td>■</td>
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<tr>
<td></td>
<td>1300</td>
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</table>

The amount of Al$_2$O$_3$ in the SiO$_2$-PVA nano-composite was found to affect the sintering temperature of the material. Table 1 summarizes the effects of temperature and hold time on the sintering process. In the case of the non-doped SiO$_2$-PVA nanocomposite, transparent silica glass was obtained by sintering at 1100°C for 3–18 h. In contrast, complete densification of the 0.6 mol% Al$_2$O$_3$ doped nanocomposite was not achieved at 1100°C even after more than 18 h, while transparent glass was obtained after sintering at 1200°C for 6–9 h. At 1300°C, a cristobalite phase was precipitated in the sintered body. In the case of the nanocomposite containing 1.2 mol% Al$_2$O$_3$, transparent glass did not result from any of the heat-treatment temperatures over the range of 1100–1300°C. With nanocomposites containing over 1.2 mol% Al$_2$O$_3$ (results not shown), sintering of the nanocomposite was not accomplished by heat-treatment within the range of 1100–1300°C. These results indicate that the required sintering temperature of the nanocomposites increases with the concentration of the Al$_2$O$_3$ nanoparticles. Thus, transparent and monolithic silica glass doped with Al$_2$O$_3$ can be fabricated over the limited Al$_2$O$_3$ content range of 0–0.6 mol%.

The optimal sintering conditions for the 0.6 mol% Al$_2$O$_3$ doped nanocomposite were determined to be 1200°C for 6 h in air. Figure 2 presents photographic images of the 0.6 mol% Al$_2$O$_3$ doped SiO$_2$-PVA nano-composite and the Al$_2$O$_3$ doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air.

![Photographic images of the 0.6 mol% Al$_2$O$_3$ doped SiO$_2$-PVA nanocomposite (left) and the Al$_2$O$_3$ doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air (right).](image1)

![XRD pattern of the 0.6 mol% Al$_2$O$_3$-doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air.](image2)
mol %). To confirm the Al2O3 in the sintered silica glass, the morphology of the Al2O3 doped silica glass was observed by means of TEM and EELS, as shown in Fig. 4. In the TEM image, particles 10–30 nm in size can be observed in the glass matrix. These nanoparticle sizes are comparable to those of the initial fumed alumina (mean diameter of 13 nm). In addition, the EELS elemental mapping for Al shows that these nanoparticles contained Al ions. Based on the results of previous study on the preparation of crystalline Al2O3-doped silica glasses,3) α-alumina may be present in the sintered glass. In fact, XRD data from the present study indicated that fumed alumina heat-treated at 1200°C consisted α-alumina (data not shown). These results suggest that crystalline Al2O3 nanoparticles were dispersed in the silica glass matrix even after sintering at 1200°C.

The dispersion state of the Al2O3 nanoparticles in the silica matrix was further confirmed by measurement of the Vickers hardness of the glass. It has been reported that crystal particles dispersed in a glass matrix improve the fracture toughness of the glass, because these particles suppress crack propagation.15) Therefore, it was anticipated that the mechanical strength of the sintered glass would be improved by the Al2O3 nanoparticles, assuming homogeneous dispersion in the silica matrix. In fact, the Vickers hardness (Hv) value of the glass was found to be 797, which was slightly higher than that of the non-doped silica glass (Hv = 777). This increase in the hardness of the glass indicates that the Al2O3 nanoparticles were dispersed throughout the whole silica glass matrix.

The Al2O3 nanoparticle doped silica glass demonstrated PL characteristics under UV irradiation, and Fig. 5 presents the photoluminescence excitation (PLE) and PL spectra of the glass. Blue PL was observed upon UV excitation, as shown in the inset photograph, and is attributed to the broad emission band located at approximately 480 nm. In the excitation spectrum, a broad band is located in the vicinity of 250 nm. In contrast, sintered silica glass without Al2O3 nanoparticles showed no PL during UV excitation (data not shown). These results indicate that the addition of Al2O3 nanoparticles to the silica glass resulted in the PL characteristics of the sintered glass.

4. Discussion

The effect of Al2O3 nanoparticles on the sintering conditions of the SiO2–PVA nanocomposite and the PL characteristics of the sintered glass is discussed in terms of the morphology and structure of the doped glass. The addition of Al2O3 nanoparticles resulted in an increment in the sintering temperature. According to a previous study on the sintering of amorphous SiO2 particles,16) sintering occurs due to the viscous flow of these particles at high temperatures. Thus, the sintering behavior of SiO2 is related to its viscosity at a given temperature. In the case of sintering of an SiO2–Al2O3 composite (Si:Al = 1:3.68, molar ratio),17) the viscosity of the SiO2 at 1000°C was found to increase by the addition of Al2O3, since the viscous flow of Al2O3 particles does not proceed at this temperature. In the present study, therefore, it is presumed that the rigid Al2O3 nanoparticles inhibited sintering of the SiO2 nanoparticles by increasing the viscosity of the nanocomposite at the heat treatment temperature. Consequently, the sintering temperature of the nanocomposite increased by the addition of Al2O3 nanoparticles.

The addition of Al2O3 nanoparticles also caused the sintered silica glass to exhibit PL. According to prior work concerning the PL characteristics of Al2O3 doped silica glass,3) OH groups present on Al2O3 and SiO2 contribute to the PL emission of the material. To elucidate the effect of OH groups in sintered glass on the PL characteristics, the structure of the Al2O3 doped silica glass was evaluated by means of FT-IR measurements. Figure 6 shows the FT-IR spectra of Al2O3 doped silica glass, non-doped...
silica glass, fumed silica and fumed alumina. In the spectra of the fumed silica and fumed alumina, broad absorption peaks are observed at approximately 3450 cm⁻¹, attributed to the stretching vibrations of Si–OH and Al–OH groups. It has been previously reported in the literature that the surface Si–OH density of fumed silica is approximately 2.5 Si–OH/nm². In the spectrum of the non-doped sintered silica glass, the intensity of the Si–OH peak is reduced compared to that in the fumed silica spectrum. The result suggests that the condensation reaction of the Si–OH groups (2Si–OH → Si–O–Si + H₂O) progressed concomitantly with the sintering of the particles above 1000°C. Additionally, there is no discernible peak from the Si–OH groups even after sintering at 1200°C for 6 h. Furthermore, it is assumed that the blue PL is due to the presence of defects related to the Al–OH and Si–OH groups at the interfaces between the Al₂O₃ nanoparticles and the silica glass matrix, although the mechanism by which the PL arises has not yet been determined.

The PL spectra of the as-received fumed alumina (the starting material) and fumed alumina heat-treated at 1200°C for 6 h in air were examined in order to confirm the effect of Al₂O₃ on the PL characteristics of the material. As a result, no characteristic emission band was observed in the spectra of either of these fumed alumina samples. In addition, the PL spectra of the as-received fumed silica (the starting material) and heat-treated fumed silica also did not exhibit characteristic emission bands. Therefore, it is assumed that the blue PL is due to the presence of defects related to the Al–OH and Si–OH groups at the interfaces between Al₂O₃ nanoparticles and the silica glass matrix, although the mechanism by which the PL arises has not yet been determined. More detailed investigations of the interfaces between the Al₂O₃ nanoparticles and the silica matrix should be further performed in future to determine the origin of the PL of the Al₂O₃ nanoparticle-doped silica glass.

5. Conclusions

The 0.6 mol% Al₂O₃ nanoparticle-doped nanocomposite was found to require sintering at 1200°C. TEM, EELS, and Vickers hardness analyses showed that the Al₂O₃ nanoparticles were dispersed in the silica matrix. It is considered that the Al₂O₃ nanoparticles inhibited the sintering of the SiO₂ nanoparticles, resulting in an increase in the required sintering temperature. The resulting material exhibited broad PL emission around 480 nm under UV excitation, presumably because of defects involving Si–OH or Al–OH groups. The method presented herein is considered to be an attractive technique for the fabrication of nanoparticle-doped silica glass.

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References