Fabrication and photoluminescence of monolithic silica glass doped with alumina nanoparticles using SiO₂-PVA nanocomposite

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Al₂O₃ nanoparticle doped SiO₂-PVA nanocomposites were prepared using fumed silica, fumed alumina, and poly(vinyl alcohol) (PVA). Nanocomposites containing from 0 to 6 mol % Al₂O₃ were heat-treated in air at 1100 to 1300°C to obtain monolithic, transparent silica glass. The 0.6 mol % Al₂O₃ doped nanocomposite was sintered at 1200°C, a higher temperature than was required for the non-doped nanocomposite. The obtained Al₂O₃ doped silica glass exhibited characteristic blue photoluminescence (PL) on UV excitation. The effects of the Al₂O₃ 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.

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1. Introduction

Glasses doped with crystalline particles have received intense research interest owing to their outstanding properties, including transparency, good formability and unique optical and electrical characteristics. Among the various oxide glasses, silica glass is considered to be one of the most promising materials for matrix applications, because it exhibits high thermal stability and superior transparency in the vacuum-ultraviolet to near-infrared region of the spectrum. A sol-gel method has been used to fabricate silica glasses doped with various nanoparticles, and this technique allows controls over both the concentration and dispersion state of the dopants as a means of obtaining desirable properties in the glass. For instance, silica glasses doped with SnO₂,¹⁾ TiO₂,²⁾ ZnO²⁾ or Al₂O₃^{3),4)} have been prepared using the sol-gel method. Glasses doped with Al₂O₃ particles are of interest in the field of functional optical materials, because these show a strong photoluminescence (PL) band in the range of 400–600 nm upon UV excitation.³⁾ However, there have been no reports of monolithic silica glass doped with Al₂O₃ nanoparticles and so there is room for further investigation of the preparation process with respect to the fabrication of large and monolithic silica glass on the centimeter scale.

The fabrication of large and monolithic glasses has been performed using a particulate sol-gel process in which SiO₂ particles are employed as the starting material.⁵⁾ In fact, silica glass rods, tubes and plates with sizes on the order of several tens of centimeters have been made by sintering SiO₂ nanoparticles.^{6–10)} Despite this, there have been few reports concerning the fabrication of monolithic silica glasses doped with crystalline nanoparticles using the conventional particulate sol-gel process. In previous work, monolithic silica glass doped with metal ions or

nanoparticles was obtained using a newly developed fabrication process employing an SiO₂-poly(vinyl alcohol) (PVA) nanocomposite as the silica glass precursor.^{11),12)} The SiO₂-PVA nanocomposite is prepared from fumed silica and PVA via an SiO₂-PVA suspension and is then sintered in air to fabricate a monolithic silica glass at the relatively low temperature of 1100°C. In contrast, the conventional particulate sol-gel process requires sintering above 1300°C in an inert atmosphere. As previously reported, this lower sintering temperature allowed us to fabricate monolithic silica glass doped with various metal nanoparticles or rare-earth ions, including Au nanoparticles¹³⁾ and Tb ions.¹⁴⁾

In the present study, we further examined the preparation of monolithic silica glass doped with Al₂O₃ nanoparticles using the SiO₂-PVA nanocomposite. The effects of Al₂O₃ nanoparticles addition on the sintering conditions and the PL characteristics of the glass are discussed in terms of the morphology and structure of the sintered glass. This paper reports the fabrication of transparent and monolithic silica glasses doped with Al₂O₃ nanoparticles and exhibiting PL characteristics.

2. Experimental

The preparation procedure of the Al₂O₃ nanoparticle doped silica glass is shown in **Fig. 1**. An Al₂O₃ doped SiO₂ suspension (8 wt. %) was initially prepared from fumed silica (mean diameter of 7 nm, Aerosil300, Nippon Aerosil, Japan) and fumed alumina (γ -alumina, mean diameter of 13 nm, AluC, Nippon Aerosil, Japan) dispersed in water by ultra-sonication. The concentration of the Al₂O₃ in the SiO₂ was varied from 0.02 to 6 mol %. An 8 wt. % solution of PVA (degree of polymerization 1500–1800, degree of hydrolysis 78–82 mol %, Wako Pure Chemical, Japan) was prepared and added into the Al₂O₃ doped SiO₂ suspension followed by mixing with a magnetic stirrer for 12 h at room temperature, resulted in the formation of a homogeneous suspension. The obtained suspension was poured into a container and subsequently dried at 30°C for one week under atmospheric

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Fig. 1. Preparation procedure for the Al₂O₃ doped silica glass.

Table 1. Effects of temperature and holding time on the sintering behavior of SiO₂-PVA nanocomposites doped with 0, 0.6 and 1.2 mol % Al₂O₃ (○ = transparent, △ = opaque, ■ = crystalline. The symbols -, -- and --- indicate materials expected to be transparent, opaque and crystalline.)

Al ₂ O ₃ amount (mol %)	Temperature (°C)	Holding time (h)						
		0.5	3	6	8	9	12	18
0 (Non-doped)	1100		○	○	-	-	○	○
	1200		■	■	---	---	---	---
0.6	1100	--	--	△	--	--	△	△
	1200	--	△	○	○	■	■	---
	1300	■	---	---	---	---	---	---
1.2	1200	--	--	△	△	■	■	---
	1300	■	---	---	---	---	---	---

pressure. As the water in the sample evaporated during the drying process, the suspension gradually consolidated to form a wet gel, eventually generating a solid Al₂O₃ doped SiO₂-PVA nanocomposite. 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 Al₂O₃ doped silica glass was analyzed with Fourier transform infrared spectroscopy (FT-IR; FTIR-8400, Shimadzu, Japan) applying the KBr pellet method.

3. Results

The amount of Al₂O₃ in the SiO₂-PVA nanocomposite 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 SiO₂-PVA nanocomposite, transparent silica glass was obtained by sintering

Fig. 2. Photographic images of the 0.6 mol % Al₂O₃ doped SiO₂-PVA nanocomposite (left) and the Al₂O₃ doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air (right).

Fig. 3. XRD pattern of the 0.6 mol % Al₂O₃-doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air.

at 1100°C for 3–18 h. In contrast, complete densification of the 0.6 mol % Al₂O₃ 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 cristbalite phase was precipitated in the sintered body. In the case of the nanocomposite containing 1.2 mol % Al₂O₃, however, 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 % Al₂O₃ (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 Al₂O₃ nanoparticles. Thus, transparent and monolithic silica glass doped with Al₂O₃ can be fabricated over the limited Al₂O₃ content range of 0–0.6 mol %. The optimal sintering conditions for the 0.6 mol % Al₂O₃ doped nanocomposite were determined to be 1200°C for 6 h in air. **Figure 2** presents photographic images of the 0.6 mol % Al₂O₃ doped SiO₂-PVA nanocomposite and the resulting sintered silica glass. Subsequent to these trials, detailed evaluations of the 0.6 mol % Al₂O₃-doped silica glass were carried out.

Figure 3 shows the XRD pattern of the 0.6 mol % Al₂O₃ doped silica glass. The diffraction pattern is broad due to the silica glass matrix and does not exhibit any characteristic peaks of crystalline Al₂O₃ because of the low Al₂O₃ concentration (0.6

Fig. 4. (a) TEM image (bright field) and (b) EELS elemental mapping for aluminum in the 0.6 mol % Al₂O₃ doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air. The arrows indicate Al₂O₃ nanoparticles.

Fig. 5. PLE (broken line) and PL (solid line) spectra of the 0.6 mol % Al₂O₃ doped silica glass obtained by sintering the nanocomposite at 1200°C for 6 h in air. Inset photograph shows the glass sample under a UV lamp at a wavelength of 254 nm.

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.

Fig. 6. FT-IR spectra of (a) 0.6 mol % Al₂O₃ doped silica glass sintered at 1200°C for 6 h in air, (b) non-doped silica glass sintered at 1100°C for 3 h in air, (c) as-received fumed silica and (d) as-received fumed alumina.

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-OH¹⁸⁾ and Al-OH groups.^{19),20)} It has been previously reported in the literature²¹⁾ that the surface Si-OH density of fumed silica is approximately 2.5 Si-OH/nm^2 . 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 ($2\text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$) progressed concomitantly with the sintering of the particles above 1000°C .²²⁾ The spectrum of Al_2O_3 doped silica glass, in contrast, shows that considerable Si-OH or Al-OH groups remained in the sintered glass even after sintering at 1200°C for 6 h. Additionally, there is no discernible peak from the Si-O-Al stretching vibration in the region of $600\text{--}700\text{ cm}^{-1}$.²³⁾ In the case of the Al_2O_3 nanoparticles doped silica glass, therefore, it is assumed that considerable Al-OH and Si-OH groups were present at the interfaces between the Al_2O_3 nanoparticles and silica glass matrix even after sintering.

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 Al_2O_3 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 Al_2O_3 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 Al_2O_3 nanoparticles and the silica matrix should be further performed in future to determine the origin of the PL of the Al_2O_3 nanoparticle doped silica glass.

5. Conclusions

The $0.6\text{ mol}\%$ Al_2O_3 nanoparticle-doped nanocomposite was found to require sintering at 1200°C . TEM, EELS, and Vickers hardness analyses showed that the Al_2O_3 nanoparticles were dispersed in the silica matrix. It is considered that the Al_2O_3 nanoparticles inhibited the sintering of the SiO_2 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 con-

sidered to be an attractive technique for the fabrication of nanoparticle doped silica glass.

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