Fabrication of transparent silica glass by powder sintering

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Received 24 February 2002; revised 11 April 2002; accepted 2 July 2002

Abstract

Transparent silica glasses were obtained by sintering a green compact (fabricated by slip-casting methods for high-purity silica glass powder) in diverse atmospheres. The relationships between sintering atmosphere and sintering temperature that result in transparent, sintered silica glass were shown. The results indicate that there are four forming phases for each sintering atmosphere and temperature: (1) nontransparent glass resulting from an overabundance of pores (2) crystal, such as cristobalite or $\beta$-quartz, (3) moganite, and (4) transparent glass. Optimum sintering temperature for fabricating transparent silica glass was above 1673 K in a high-vacuum ($10^{-4}$ Pa; $p$($O_2$) = $10^{-14}$) atmosphere. We investigate the fabrication of transparent and hydroxyl-free silica glass by a powder-sintered method. After studying the effect of sintering schedule on residual $[OH^2]$ concentration for transparent, sintered silica glasses, we sintered a green compact prepared by silica powders with a mean particle size of 1.6 $\mu$m, first heating it to 1523 K for dehydration and then to 1873 K for densification. This typical fabricated condition resulted in a transparent, sintered silica glass with $<1$ ppm [OH$^-$] concentration.

1. Introduction

Transparent silica glass is an important material with many desirable properties—low thermal expansion coefficient, low electrical conductivity, high chemical resistance, high UV transparency, etc. It is frequently used for high-efficiency lamps, crucibles for melting high-purity silicon, IC photo-mask substrate, and lens material for excimer stepper equipment. Many processes of the silica glasses have been used, for instance, melting, sol–gel [1] and VAD [2] methods etc. For example, the fabrication of transparent silica glass with complex shape using a melting method requires high temperatures of 2273–2573 K. The silica glass is heated over 2573 K by the oxygen–hydrogen gas burner again and shaped by skilled craftsmen. However, two major problems with this technique exist: the presence of hydroxyl in the silica glass and the high cost of producing transparent glass. Sintering method by slip casting in this paper we used is superior to the other processing in low energy cost. In the slip-casting technique, a plaster mold for shaping is cheap and easy to obtain large scale structure without skill and easy to obtain large scale structure.

In a previous study on sintering silica glass, devitrification problems resulting from crystallization of cristobalite or $\beta$-quartz arose in air atmosphere at temperatures over 1673 K [3,4]. Although the relationship between the several polymorphisms of silica and sintering temperature is well known, the effect of sintering atmosphere and temperature on the crystallization behavior of silica glass has not yet been described.

The purpose of this paper is to describe the fabrication of transparent and hydroxyl-free silica glass by sintering a green compact, which is fabricated using slip-casting methods for high-purity silica glass powder. We present the optimum conditions for fabricating transparent silica glass and hydroxyl-free silica glass, noting the effect of sintering atmosphere and silica powder particle size on densification of this glass.

2. Experimental procedure

The raw material was high-purity (6N) amorphous silica powder with mean particle sizes of 0.4 $\mu$m and impurities...
below 1 ppm (silica Ace-E, Nitto Chemical Industry Co., Ltd). The silica glass powder slurry was dispersed in distilled water in a 50:50 wt% ratio. Green compacts were prepared by pouring slips into the plastic frame of 10 £ 20 mm set on plaster molds and drying the slip. For the sintering atmosphere, the following conditions were set: (a) air (105 Pa: p(O2)¼2 £ 104 Pa), (b) water vapor/mixed argon (Ar) gas (103 Pa: p(O2)¼10 Pa), (c) dried Ar (10 Pa: p(O2)¼104 Pa), (d) dried & deoxidized Ar (101 Pa: p(O2)¼108 Pa), (e) low vacuum (102 Pa: p(O2)¼1010 Pa) and (f) high vacuum (104 Pa: p(O2)¼104 Pa). Here, oxygen partial pressure, p(O2), at above 1028 Pa was measured with a zirconia sensor, whereas below 1028 Pa, it was calculated from the degree of vacuum.

### 3. Results and discussion

#### 3.1. Effects of sintered atmosphere

Effect of sintering atmosphere and temperature on crystallization behavior of the green compact with a mean particle size of 0.4 mm were investigated. Fig. 1 shows the XRD patterns for the samples isothermally treated at 1673 K for 103 s at various sintering atmospheres.

![Fig. 1. XRD patterns for sintered bodies of silica glasses heated up to 1673 K with a heating rate at 17 K/min and holding time for 103 s. (a)–(f) shows sintering atmosphere (degree of vacuum, oxygen partial pressure, p(O2)). Oxygen partial pressure, p(O2) at above 1028 Pa, was measured with a zirconia sensor, whereas below 1028 Pa, it was calculated from the degree of vacuum.](image)

The crystal phase of sintered silica depends on oxygen partial pressure, p(O2), in the following; (a) p(O2)¼2 £ 104 Pa and (b) p(O2)¼10 Pa, β-quartz and cristobalite phase were observed. The results suggest that the crystallization of β-quartz and cristobalite were accelerated by the influence of oxygen and [OH2] on the surface of the raw powder [4]. The XRD patterns of (c) p(O2)¼1024 Pa and (d) p(O2)¼1028 Pa indicated the presence of moganite phase which is polymorph of silica mineral. According to JCPDS card (card No. 38-0360), the main peak values of 2θ angle for moganite are 19.935, 26.266, and 26.748, respectively. The results suggest that the main peaks in Fig. 1(c) and (d) are similar to that of moganite reported by Petrovic et al. [6] but distinct from cristobalite.

Fig. 2 shows the relationship between sintering atmosphere and temperature for sintered silica glass after a holding time of 103 s.

![Fig. 2. Effects of sintering atmosphere and temperature on the diagram, with holding time 10^3 s.](image)

Following Lambert–Beer equation [5]

\[ C = \left( \frac{1}{\alpha} \right) \log(T_a/T_b) \times M/10d \]  

where \( \alpha \) is the infrared absorption coefficient of water (8.6 l/mol £ mm) [5], \( t \) is the thickness of the sample (mm), \( T_a \) and \( T_b \) are the transmittance (%) at wavelengths of 2.6 and 2.73 μm, respectively, \( M \) is the molecular weight of water, and \( d \) is the specific gravity of the silica glass.

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Fig. 2 shows the relationship between sintering atmosphere and temperature for sintered silica glass after a holding time of 103 s based on XRD analysis. From this result, four forming phases emerge: (1) nontansparent glass resulting from an overabundance of pores, (2) crystal (cristobalite, β-quartz) production,
moganite, a polymorph of silica mineral, and (4) transparent glass. For sintering temperature below 1673 K, sintered bodies showed no densification. The temperature at which densification starts, based on measurement of relative density, was 1673 K. The results revealed that the transparency-forming region of sintered silica glass corresponds to a sintering temperature above 1673 K and high vacuum (10⁻⁴ Pa) atmospheric conditions. Fig. 3 shows the relationship between sintering temperature and time, in the fabrication of transparent sintered silica based on XRD analysis, for samples sintered in diverse atmospheres. The slant line in the figure shows starting time for crystallization. At sintering atmosphere (a) \( p(O_2) = 2 \times 10^4 \) Pa and (b) \( p(O_2) = 10 \) Pa, \( \beta \)-quartz and cristobalite phase was observed at all sintering times. On the other hand, at sintering atmosphere from (c) to (f), formation of the moganite phase was observed at each sintered temperature and time. From this result, we infer that the starting time for crystallization shifts to longer sintering time with decreasing \( p(O_2) \). Although the sintering mechanism for transparent silica glass are not clarify in this work, we may consider that it is related to evaporation of SiO2. According to the volatility diagram for the Si–O system [7], volatile species such as SiO and O2 are evaporated in accordance with the reaction SiO2 = [SiO] + 1/2[O2] from a sample surface at \( p(O_2) \) below 10⁻³ Pa during the isothermal treatment above 1673 K. The moganite phase \([Si_4O_{12}]^{3−}\) is formed as follows \([Si_4O_{18}]^{12−} \rightarrow [Si_4O_{12}]^{8−} + 2[SiO] \uparrow + 2[O_2] \uparrow\) where the structure of moganite [8–10] was found to be a three-dimensional framework with a distorted four-member ring of a corner-sharing SiO₄ tetrahedra. Moganite is unstable thermodynamically compared to \( \beta \)-quartz or cristobalite, and it decomposes and evaporates easily [6,10] \([Si_4O_{12}]^{12−} \rightarrow 4[SiO] \uparrow + 4[O_2] \uparrow\). Based on the assumption mentioned above the evaporation of moganite, it considered that the sintering behavior for transparent silica glasses involves evaporation of moganite, which prevents the glasses from crystallization during the sintering of the green compact prepared from silica powders.

### 3.2. Microstructure of sintered materials

Fig. 4 clarifies the relationship between the macroscopic transparency and microstructure of the sintered silica specimens, the figure showing the SEM micrographs of sintered bodies isothermally treated at 1673 K for \( 10^3 \) s at various sintering atmospheres. Fig. 5(A) shows a specimen sintered under an oxygen partial pressure of (a) \( p(O_2) = 2 \times 10^4 \) Pa; in it, the crystal phases of cristobalite and \( \beta \)-quartz with crystal size of 100 \( \mu m \) were confirmed by XRD patterns, and pores 10 \( \mu m \) in length were observed. In Fig. 4(B), under oxygen partial pressure from (c) \( p(O_2) = 10^{-8} \) Pa to (d) \( p(O_2) = 10^{-10} \) Pa, the crystal phase was moganite with a crystal size of about 10 \( \mu m \), with many pores inside the sample. In Fig. 4(C), under a low-vacuum condition (e) \( p(O_2) = 10^{-10} \) Pa, the glass state was confirmed by XRD patterns, and pores 10 \( \mu m \) in length were observed. In Fig. 4(D), high-vacuum condition (f) \( p(O_2) = 10^{-14} \) Pa, transparent silica glass formed, as evident from the XRD patterns, and no pores appeared. This result indicates that fabricating transparent, sintered silica glass requires a high-vacuum sintering atmosphere, (f) \( p(O_2) = 10^{-14} \) Pa.
3.3. Fabrication condition of hydroxyl-free and transparent sintered silica glass

To fabricate hydroxyl-free silica glass, we believed it was important to investigate optimum conditions such as densification of sintered body and heating pattern. Fig. 5 shows the effect of mean particle size of silica glass powder on relative density and linear shrinkage as a function of sintering temperature under a high-vacuum atmosphere \( (p(O_2) = 10^{-14} \text{ Pa}) \). The heating pattern for sintering was set to 17 K/min, and the samples were sintered at specified temperatures (1573, 1673, 1773, and 1873 K), and then furnace cooled. It was found that the sintered bodies were completely densified above 1773 K, with particle size of 0.4 and 1.6 \( \mu \text{m} \) for 1873 K. At 1873 K, with particle size of 4.9 \( \mu \text{m} \), densification of sintered bodies could not be obtained.

Fig. 6 shows the dependence of relative density and linear shrinkage on sintering time at 1673 K in a high-vacuum atmosphere \( (p(O_2) = 10^{-14} \text{ Pa}) \). The results revealed that densified sintered bodies could be obtained by heating for longer than 30 min at 1673 K, using the silica powder with particle sizes of 0.4 and 1.6 \( \mu \text{m} \).

Fig. 7 shows the heating pattern for three different temperatures and times. The dashed line in Fig. 7 shows the starting temperature for densification. Fig. 8 shows the IR transmittance spectra indicating the residual [OH\(^-\)] concentration using the heating patterns shown in Fig. 7. For Pattern 1, the residual [OH\(^-\)] concentration in the sintered transparent silica glass was 60 ppm, mainly because the sintered body was densified above 1673 K before removal of water. The results indicate that the holding temperature

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**Fig. 5.** Relationship between relative density and linear shrinkage as a function of sintering temperature under a high vacuum atmosphere, \( (p(O_2) = 10^{-14} \text{ Pa}) \) with three types of mean silica-glass-powder particle sizes.

**Fig. 6.** Relationship between relative density and linear shrinkage as a function of sintering time at 1673 K in a high-vacuum atmosphere \( (p(O_2) = 10^{-14} \text{ Pa}) \) with three types of mean silica-glass-powder particle sizes.

**Fig. 7.** Sintering heated pattern for the removal of [OH\(^-\)] concentration groups in the transparent silica glasses. Dashed line shows starting temperature for densification.

**Fig. 8.** IR transmittance spectra of sintered silica samples. Samples were 3 mm thick.
for sintering must be lower than 1673 K, based on the results in Figs. 5 and 6. At 1573 K, an isothermal treatment for $10^{4.26}$ s (Pattern 2), the residual [OH$^-$] concentration was 40 ppm. For Pattern 3, the residual [OH$^-$] concentration was removed by dehydration during sintering at 1523 K for $10^{4.03}$ s. The residual [OH$^-$] concentration for silica powder with mean particle size of 1.6 μm (Pattern 3) was lower compared to that with 0.4 μm mean particle size, as a result of a different packing structure and the specific surface area of green compacts involving [OH$^-$] content.

Transparent and hydroxyl-free sintered silica glass was successfully fabricated under the following conditions: a green compact prepared by silica powders with a mean particle size 1.6 μm sintered at 1523 K for dehydration and heated to 1873 K for densification.

4. Conclusions

To fabricate transparent and hydroxyl-free sintered silica glass, optimum fabrication conditions such as sintering atmosphere, temperature, and heating schedule were studied. The diagram describing the relationship between sintering atmosphere and temperature indicates the existence of four forming phases: (1) nontransparency glass resulting from an abundance of pores, (2) crystal (cristobalite, β-quartz), (3) moganite, a polymorph of silica mineral, and (4) transparent. It was found that the transparency-forming region of sintered silica glass corresponds to a sintering temperature above 1673 K and high-vacuum ($10^{-4}$ Pa) atmosphere conditions. Pores inside sintered bodies of transparent silica were observed during sintering under low-vacuum conditions ($10^{-2}$ Pa). In high-vacuum sintering conditions ($10^{-4}$ Pa), densified transparent silica glass was obtained without pores. To fabricate transparent and hydroxyl-free silica glass, we sintered a green compact using silica powders with a mean particle size 1.6 μm at 1523 K for dehydration and then heated to 1873 K for densification. These conditions resulted in a transparent sintered silica glass with <1 ppm [OH$^-$] concentration.

Acknowledgements

The authors are grateful to Dr Antoni P. Tomsia of Lawrence Berkeley National Laboratory, USA for many helpful discussions. This work was supported by the Regional Consortium Project through NEDO.

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