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Void Engineering in Silica Glass for Ultralow Optical Scattering Loss

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Abstract *Optical losses in silica glass fibers remain a challenge in their applications. The main contributor to optical attenuation is Rayleigh scattering. This review discusses the recent studies and findings on voids in silica glass and their effects on the optical loss. Through experimental studies of pressure-quenching on glass at the melting temperature, void size shrunk, and the optical loss was reduced to approximately half of that of conventional optical fibers at 0.2 GPa. Our modeling results predicted that further reduction was expected, credited to the optimization of the glass network, called topological pruning, under high compressive pressures of up to 4 GPa.*

Introduction

Silica glass comprises a single SiO_2 component. The technology to mass-produce homogeneous silica glass with extremely high purity by suppressing its structural defects and water content has already been established. In addition to such well-established techniques, various advantageous characteristics, such as an extremely small thermal expansion coefficient on the order of 10^{-7} K^{-1}, a wide optical gap of 6 eV, and negligible nonlinear effects render silica glass irreplaceable as an optical material. Silica glass is currently used worldwide as a core material for optical communication fibers. Before the invention of the low-loss optical fibers, information was transmitted by electrical signals through electrical cables whose propagation loss was approximately 200 dB/km. When the optical fiber appeared in 1970, the first propagation loss of light was 20 dB/km [1] but it was an order of magnitude lower than that of electrical cables. Therefore, the electrical cable companies were forced to convert into optical communication cable companies. Fig.1 compares the values of transmission loss and the distance until the signal became 1/100 over the years. It was only after 30 years that the loss of the optical fiber in the communication wavelength was reduced to 0.2 dB/km, and the transmission distance increased dramatically. Thus, the world had transformed into a society of digital telecommunication carried over optical fibers. If the loss is further reduced by one more order of magnitude, the use of expensive optical amplifiers can be reduced, and quantum communication, which is currently challenging due to the difficulties involved in making repeaters, may become widespread [2]. However, since 1980, the fiber loss reached a prolonged downshift in which, the world record of fiber loss decreased by an order of 0.01 dB/km every 2–3 years [3]. Hence, reducing optical fiber loss is still recognized as an important research issue, and a new breakthrough is required.

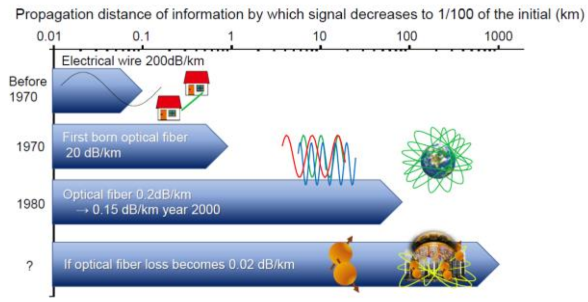

Fig. 1 Propagation distance of information by which signal decreases to 1/100 using each transmission line.

Structural voids in silica glass and their relation to Rayleigh scattering loss

In silica glass, Rayleigh scattering loss accounts for more than 80% of transmission loss. Other components, such as structural mismatch and/or absorption, are very small [4]. Therefore, it is important to develop a method to suppress the attenuation from Rayleigh scattering. Because Rayleigh scattering is caused by density fluctuations in silica glass, a method for reducing density fluctuations by lowering the fictive temperature T_f of the glass has been the primary means of reducing loss. However, to lower T_f, only two methods are possible: 1. freezing the glass into a stable structure by annealing the glass for a long period of time, or 2. adding a component (such as fluorine, hydroxyl group, alkali ion, etc.) that lowers the viscosity so that the structure quickly reaches a stable state.

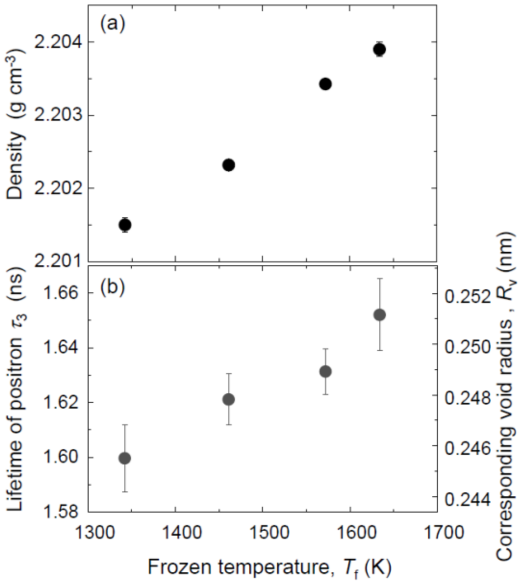

Fig. 2 Experimental results [6]. (a) Density and (b) Lifetime of positron τ_3, and corresponding void radius against fictive temperature in silica glass. Reproduced from M. Ono, K. Hara, M. Fujinami and S. Ito: Appl. Phys. Lett. 101 (2012) 164103., with the permission of AIP Publishing.

However, the former requires reducing the fiber-drawing speed, which is not realistic, considering that the fiber-drawing speed is close to the speed of sound. In the latter case, the density fluctuations can be improved but the composition fluctuations are stimulated simultaneously, and the scattering loss increases ultimately. Therefore, it has been considered that there remains no other way to significantly reduce the loss [5].

We proposed an alternative approach focused on the voids in the silica glass network structure (which is the "empty space" without atoms) that involved measuring the void size using the positron annihilation lifetime spectroscopy (PALS) method. References [6]–[8] provide details on the measurement method and calculation of the void size using PALS. Furthermore, we prepared silica glass with various T_f values in the range of 1300–1700 K by rapid quenching. The density and the results of the PALS measurements are shown in Fig. 2. As T_f increased, the density of silica glass increased in this region, as demonstrated in Fig.2(a). Unexpectedly, the void radius R_v observed by PALS increased with an increase in T_f. This means that, within this temperature range, the structural voids expand, while the entire volume decreases simultaneously. Fig. 3 schematically shows the changes in density and voids with temperature. Structural rearrangements occurred by increasing the temperature and this amplified the densification of the originally dense parts, while making the coarse part hollower. Such a

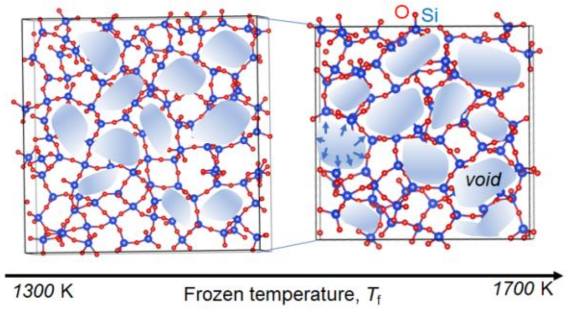

Fig. 3 Schematic picture of network and voids in silica glass with different frozen temperature T_f.

change corresponds to an increase in the inhomogeneity of the density, which increased the density fluctuation. Thus, the expansion of voids was strongly related to increase in the Rayleigh scattering of silica glass. Therefore, we assumed that the voids measured by PALS behaved as scattering particles; the Rayleigh scattering coefficient was calculated using Eq (1) [9]. Herein, R, N, and n are the radius of the scattering particles, number density, and refractive index, respectively.

$$\alpha_R = \frac{2}{3}\pi^5 N \left(\frac{n^2-1}{n^2+2}\right)^2 \frac{(2R)^6}{\lambda^4} \qquad (1)$$

To examine whether R in Eq (1) represents the void size R_v observed by PALS, we plotted $(2R_v)^6$ against T_f in Fig. 4. The plot was well fitted by a linear function of T_f with a slope of 6.4 × 10^{-6} [nm^6/K]. Substituting $(2R)^6$ in Eq (1) by 6.4 × 10^{-6} T_f led to the empirical equation [10] of the Rayleigh scattering coefficient α_R in terms of T_f as stated in

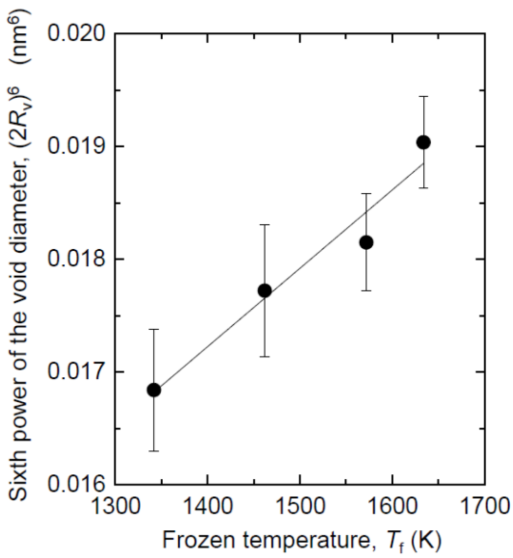

Fig. 4 Experimental results [6]. $(2R_v)^6$ plotted against T_f, where R_v is the PALS-measured void radius and T_f is the frozen temperature of the glass. $(2R_v)^6$ is found to have linear dependency to T_f with the slope of 6.4 x 10^{-6} [nm^6/K]. Reproduced from M. Ono, K. Hara, M. Fujinami and S. Ito: Appl. Phys. Lett. 101 (2012) 164103., with the permission of AIP Publishing.

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Eq (2):

$$\alpha_R = 4.0 \times 10^{-4} T_f \quad (2)$$

When N was assumed to be 8×10^{20} cm^{-3} in Eq (1), this value of N corresponded with the value for the density of voids of 1×10^{20} cm^{-3}, which was previously detected by the permeability of rare gas (Ar) in silica glass [11]. The volume of the voids that contributes to Rayleigh scattering corresponds to about 5 % of the total volume. We also calculated the absolute value of loss using the assumption that voids behave like scattering particles, considering that scattering particles with a diameter of 0.5 nm, refractive index difference from the surroundings of 1.6, and a density of 5×10^{20} cm^{-3} allow light attenuation at 3.7×10^{-2} times per km. This corresponds to an attenuation rate of 0.16 dB/km and current losses in the optical fibers [3].

Reduction of Rayleigh scattering loss in silica glass

If voids can be assumed as scattering particles, it may be possible to suppress the Rayleigh scattering coefficient by further reducing the size of the voids. However, even if pressure induces the shrinkage of the void, the scattering coefficient will not change if the reduction in the void size is proportional to the shrinkage of the network structure because the density fluctuation does not change. Fluctuation decreases only if the voids shrink selectively due to pressure. Previously, we calculated the distribution of the relative void volume against the void radius under compression [12] (Fig. 5). It was shown that for SiO_2, compressive strain reduced the size of larger voids selectively or disintegrated the voids into smaller ones. As a result, the distribution of voids became narrower. Such a narrow distribution implies that the glass consists of smaller density fluctuations that lead to reduced Rayleigh scattering. This prediction was supported by pressure-dependent modulus experiments and void simulations by Guerette [13] under pressure at high temperatures. In addition, a decrease in the distribution of the refractive index $\Delta n/n$ with an increase in the refractive index n in hot-compressed silica glass [14] indicated that the glass had a smaller structural fluctuation. With this prospect, we applied pressure onto silica glass to shrink the voids. Using a hot isostatic pressure machine (HIP), pressure was applied using Ar gas as the medium. The temperature was set to 2073 K, where the glass was in a molten state. Compressed silica glass was obtained by rapid quenching. The PALS and Rayleigh scattering intensity measurements of these glass were performed [15]. In Fig. 6 (a), the solid circles show the void sizes of the obtained glass plotted against the applied pressure. Fig. 6 (b) shows the scattered light intensities for each quenching pressure. It was found that the higher the frozen pressure and longer the pressure holding time, the smaller the void size and more Rayleigh scattering is suppressed. In Fig.7, the Rayleigh scattering intensity data are summarized with the void radius as the horizontal axis. Additionally, it shows the glass obtained by changing the frozen temperature, T_f, under ambient pressure. For example, silica glass with a T_f of 1342 K was used in a semiconductor lithography equipment and was produced by extremely slow annealing over 100 h or more to

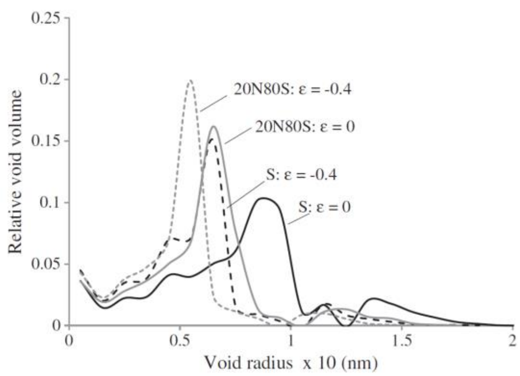

Fig. 5 Calculation results [12]. Void distribution under compression at strains of 0 and 0.4 for SiO_2 (denoted as S) and $20Na_2O$-$80SiO_2$ (in mol denoted as 20N80S) glass. Copyright permission from © 1969, Elsevier.

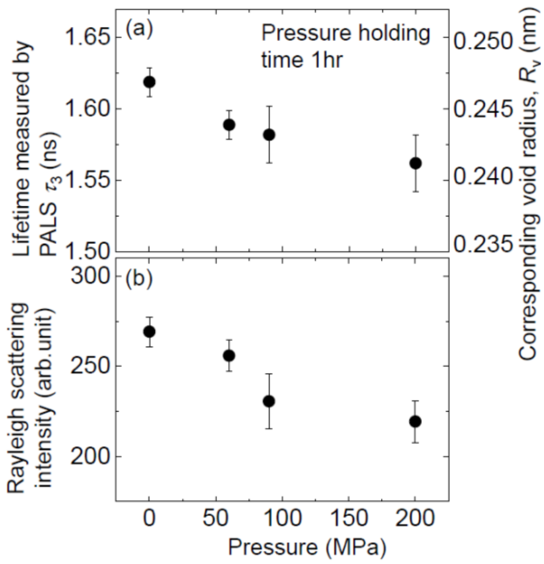

Fig. 6 Experimental results [15]. (a) Pressure dependence of the third lifetime component τ_3 (left vertical axis), and the corresponding void radius R_v (right vertical axis), calculated using the Tao-Eldrup model. (b) The Rayleigh scattering intensity plotted against the applied pressure [15].

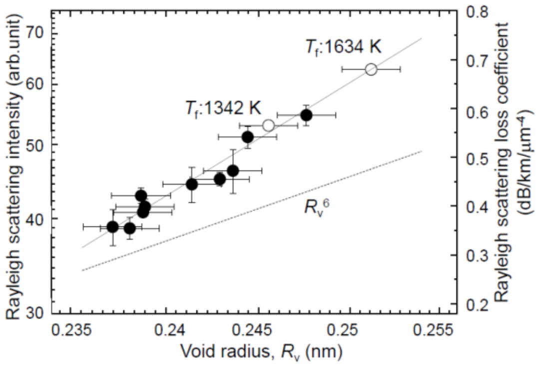

Fig. 7 Experimental results [15]. Rayleigh scattering intensity (left vertical axis) and the absolute value of the Rayleigh scattering loss (right vertical axis), are plotted against the void radius. The filled circles are for the samples synthesized with the HIP machine. The broken line corresponds to the sixth power of the void radius (R_v). The closed circles are made with HIP, while the open circles represent the samples fabricated without the HIP machine.

stabilize and homogenize the structure of the glass. However, even though the glass was annealed for such a long time, glass having a scattering coefficient of about 0.55 dB/km/μm^{-4} could only be obtained. Note that *the* T_f of the fiber core is usually approximately 1700 K due to fast fiber drawing. In contrast, when pressure treatment is carried out, the Rayleigh scattering coefficients are reduced significantly, even when using the quenching process. In particular, the Rayleigh scattering coefficient of the silica glass, which was prepared at a pressure of 200 MPa at 2073 K and kept for 4 h, showed an extremely small value corresponding to a scattering coefficient of 0.34 dB/km/μm^{-4}. This value was converted to a scattering loss of 0.07 dB/km at 1.55 μm, which was far below the reported world record of optical loss of glass fiber of 0.1419 dB/km^4 [3].

Molecular dynamic simulations for estimation of scattering loss by varying pressures

As shown in the previous section, Rayleigh scattering was observed to decrease with increasing pressures of up to 0.2 Gpa. The loss

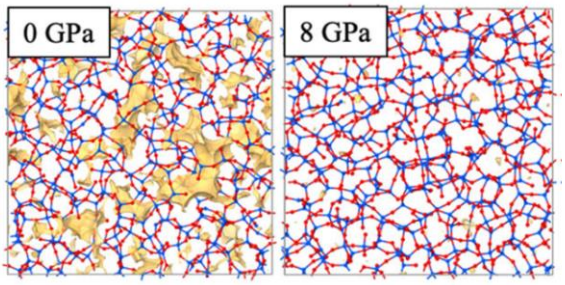

Fig. 8 Calculation results [17]. Pressure effects on voids in silica glass. Morphologies of voids in three silica glass samples pressure-quenched at 0 and 8 GPa, respectively, and released at 0 GPa. The yellow regions are isosurfaces with a minimum distance of 0.1 nm from the atom surfaces (red: oxygen, blue: silicon).

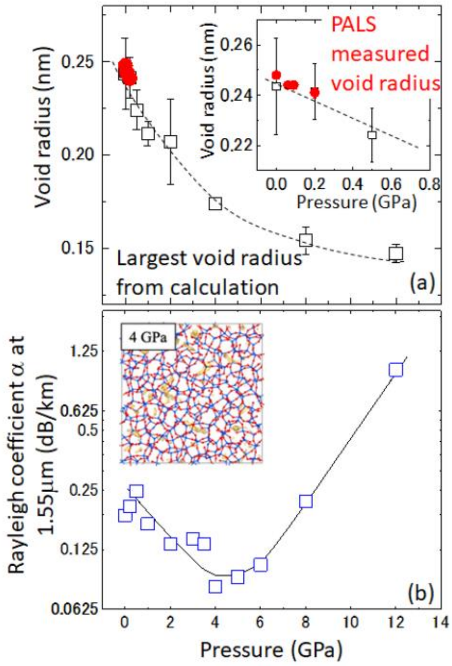

Fig. 9 Calculation results [17]. (a) Pressure dependence of the largest void radius from calculation (black) compared to the PALS- measured ones (red, data same as Fig.5 (b)). Voids continue decreasing due to pressure. Insert is the expansion of the small pressure region. (b) Calculated Rayleigh scattering coefficient at 1.55 μm, α, against quenching pressure. From density fluctuation, α is predicted to reduce up to the pressure of 4 GPa, but start to increase under higher pressure. Inset is the network picture of 4 GPa quenched glass. Voids are few but exist. Note that the absolute value of α deviates from experimental one [15]. The minimum loss by calculation was 0.08 dB/km at 4.0 GPa.

is expected to decrease further at higher pressures. However, the application of a high hydrostatic pressures at 2073 K is limited. Pressure application is possible by using a solid pressure medium, but the pressure is not perfectly hydrostatic, and the anisotropy tends to cause crystallization, especially at temperatures higher than 1000 K [16]. Experimental examinations of the optimized pressure and temperature require considerable cost and time. Thus, we used molecular dynamic (MD) simulations to estimate how the density fluctuations in silica glass changed under conditions of varying pressures at the melting temperature [17], including conditions beyond the experiments [15]. Fig.8 shows how the voids (yellow part) in silica glass disappeared due to high pressures. The void radius showed a continuous decrease with increasing pressure, as shown in Fig.9 (a). In our calculations, two methods were applied onto the same glass model to obtain the scattering loss: 1. estimating the scattering coefficient by assuming that the void behaves as a spherical scattering particle, and 2. estimating the density fluctuation using the coordination of the atoms. In the former case, the scattering intensity monotonically decreased due to an increase in applied pressure, but this image collapsed when the void size approximated that of the tetrahedra of Si-O. Moreover, when the scattering intensity was calculated using the density fluctuations, the scattering intensity tended to decrease when the pressure increased from ambient to 4.0 GPa, then above 4.0 GPa, it increased by increasing the pressure (Fig.8 (b)) [17]. The mechanism of the change in density fluctuation was explained as follows: At lower pressure, small ring structures, such as three-membered rings are pruned to rearrange into larger rings by connecting with close-by voids in densification process. Such rearrangement induced homogenization in glass network structure. While, at pressure higher than 4.0 GPa, densification led to increase of coordination number of Si and significant rebound of small rings, which increased the density fluctuation.

Thus, the suppression of loss by controlling the fictive *pressure* seems to have potential. However, there are some obstacles to the formation of a fiber using a high-fictive-*pressure* glass. One challenge is that when this glass is heated under ambient pressure, it expands largely due to structural relaxation at approximately 1070 K [18]. Moreover, if the glass is kept at a temperature close to 2400 K, the structure of the glass returns to that of the current pressure. Thus, it seems necessary to clarify the glass structure of high fictive *pressure* and find methods to obtain a structure similar to that of pressure.

Conclusions

A series of past findings that were co-authored by the author were reviewed herein based on observing and controlling voids in silica glass structures to suppress optical loss, as introduced in Ref.19. The voids were observed using positron annihilation spectroscopy, which is useful for evaluating relatively large-sized voids. Such voids are expected to behave as scattering particles and are responsible for the Rayleigh loss. To suppress the loss, the size of the voids was reduced by pressure-quenching at the melting temperature. Pressure up to 0.2 GPa was applied, and the loss was largely suppressed. Computational estimation was performed to examine the effect of higher pressure. The results showed that pressures up to 4 GPa suppressed the optical loss even further. The loss reduction is attributed to the topological pruning of the network. However, a pressure greater than 4 GPa leads to degradation of the loss. From both the experiments and simulations, controlling the fictive *pressure* seems promising. A large number of voids in the silica glass remain by merely controlling T_f. Currently, void engineering by controlling pressure can be a new way to explore the realization of silica glass with small scattering. Significant research remains to be conducted toward the realization of ultra-low-loss silica glass fibers.

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