Void-Engineering in Silica Glass for Ultralow Optical Scattering Loss

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Abstract *Optical loss of silica glass fiber remains a challenge. The main contributor to the optical attenuation is Rayleigh scattering. I review our recent findings on pressure-quenching to reduce optical loss, including experimental and modelling results.*

Introduction

Silica glass is composed of a single component, SiO_2. The technology is already well established to mass-produce homogeneous silica glass with extremely high purity by suppressing its structural defects and water content. In addition to such highly established techniques, various advantageous characteristics, such as extremely small thermal expansion coefficient of the order of 10^{-7} K^{-1} and a wide optical gap of 6 eV make silica glass irreplaceable as an optical material with negligible nonlinear optical effects. Silica glass having such excellent characteristics is currently used worldwide as a core material for optical communication fibers. Before the invention of low-loss optical fiber, information was transmitted by electric signals through electric cables, whose propagation loss was about 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 electric cables, so that the electric cable companies were forced to transform into optical communication cable companies. Fig.1 compares the values of transmission loss and the distance until the signal becomes 1/100, between generations. Only after 30 years, the loss of the optical fiber in the communication wavelength has been reduced down to 0.2 dB/km, and the transmission distance has dramatically increased. The world has been transformed into a telecommunication society of digital information, all 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 difficult due to the difficulty in making repeaters, may become widespread [2]. However, since 1980, the fiber loss seemed to hit the ceiling, and the world record of loss kept replaced by the order of 0.01 dB/km every 2-3 years [3]. Reducing optical fiber loss is still recognized as an important research issue, and a new breakthrough is desired.

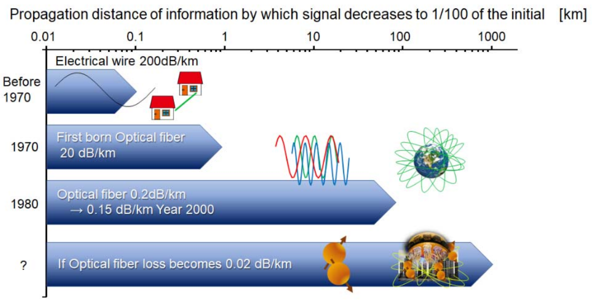

Fig. 1 Propagation distance of information by which signal decreases to 1/100, using each transmission line.

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

In silica glass, Rayleigh scattering loss accounts for more than 80% of the transmission loss. The other components such as structural mismatch and/or absorption are very small [4]. Therefore, it is important to find a method to suppress attenuation from Rayleigh scattering. Since Rayleigh scattering is caused by density fluctuations in the silica glass, a method of reducing the 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.) which lowers the viscosity so that the structure quickly reaches to a stable state. However, the former requires reducing the fiber-drawing speed, which is not realistic, considering the fiber-drawing speed is close to the speed of sound. In the latter case, density fluctuation can be improved but the composition fluctuations are stimulated simultaneously, and the scattering loss increases as a total. Therefore, it had been considered that there is no longer any way to significantly improve

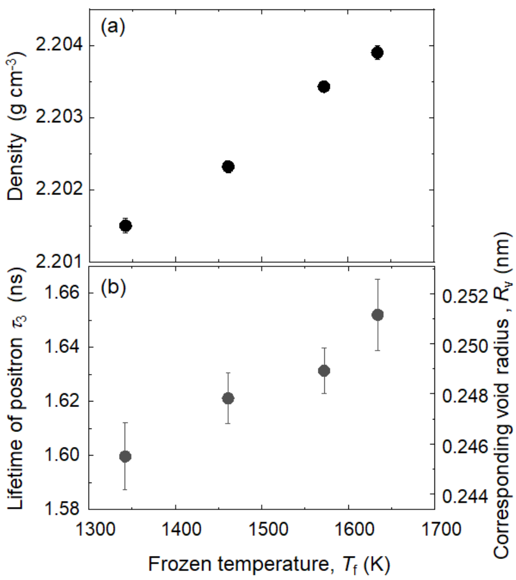

Fig. 2 (a) Density and (b) Lifetime of positron, τ_3 and corresponding void radius against fictive temperature in silica glass [6].

the loss [5].

We have proposed an alternative approach focused on the voids in the silica glass network structure (which is the "empty space" without atoms), measuring the void size using the Positron Annihilation Lifetime Spectroscopy (PALS) method. For details of the measurement method and calculating the void size using PALS, references [6]-[8] give good guidance. We prepared silica glass with various T_f, in the range of 1300 K to 1700 K, by rapid quenching. The density and the results of PALS measurements are shown in Fig. 2. When T_f is higher, the density of silica glass increases in this T_f region, as is well known (Fig.2(a)). Unexpectedly, the void radius R_v observed by PALS increased with the increase of T_f. That means, within this temperature range, the structural voids expand while the whole volume simultaneously decreases. Fig. 3 schematically shows the change of density and voids along with the temperature. The structural rearrangement by increasing temperature amplifies the densification of the originally dense parts, while making the coarse part hollower. Such change should correspond to the increase of the inhomogeneity of the density, so that it increases the density fluctuation. Thus, expansion of voids should be related strongly to the increase of Rayleigh scattering of silica glass. Thus, we assumed that the void measured by PALS behaves as scattering particles. With the assumption, the Rayleigh scattering coefficient is

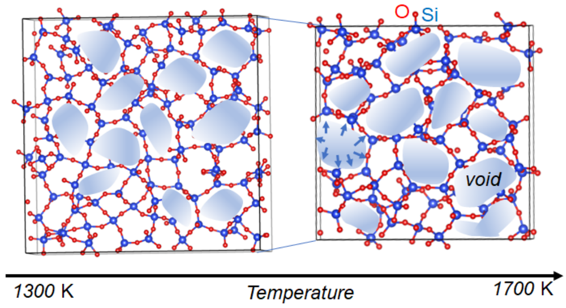

Fig. 3 Schematic picture of network and voids in silica glass with different frozen temperature T_f.

calculated using Mie theory of Eq (1) [9]. Here, R_v, N, n are the radius of the scattering particles, number density, and the refractive index, respectively.

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

When assuming N ~ 8 x 10^{20} cm^{-3}, the empirical equation of Rayleigh scattering coefficient α_R against T_g as Eq(2) [10].

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

is obtained. This value of N is in good agreement with the number density of voids of 1 × 10^{20} cm^{-3}, which was previously detected by the permeability of rare gas (Ar) in silica glass [11]. We also performed a calculation on the absolute value of loss using this assumption. Considering that scattering particles of a diameter of 0.5 nm (and the refractive index difference from the surroundings is 1.6), with number density of 5 × 10^{20} cm^{-3} exit, the light will be attenuated 3.7 × 10^{-2} times per km. That corresponds to the attenuation rate of 0.16 dB/km. This is in good agreement with the current loss values of optical fibers [3].

Reduction of Rayleigh scattering loss in silica glass

If we can assume voids as scattering particles, it may be possible to suppress the Rayleigh scattering coefficient by further reducing the size of the voids. With such an idea, we applied pressure onto silica glass to shrink the voids. Using a hot isostatic pressure machine (HIP), pressure was applied using Ar gas as a medium. The temperature was set to 2073K where glass is in the molten state. The compressed silica glass was obtained by following rapid quenching. PALS and Rayleigh scattering intensity measurements of these glasses were done. In Fig. 4, solid circles shows the void sizes of the obtained glasses are plotted on the horizontal axis, while the scattered light intensities are plotted on the left axis, and the Rayleigh scattering coefficients corresponding to them are plotted on the right axis. It was found that the higher the frozen pressure and the longer the pressure holding time, the smaller the void size and the more Rayleigh scattering is suppressed. ○ in Fig. 3 shows the glass obtained by changing frozen temperature, T_f, under ambient pressure. For example, silica glass with T_f of 1342K is used in semiconductor lithography equipment, and it is produced by extremely slow annealing over 100 hours or more to stabilize and homogenize the structure of the glass. However, even though the glass is annealed for such a long time, glass having a scattering coefficient of about 0.55 dB/km/μm^{-4} can only be obtained. Note that T_f of the fiber core is usually about 1700K due to fast fiber-drawing. In contrast, when pressure treatment is performed, the Rayleigh scattering coefficient can be significantly smaller, even when using the quenching process. Particularly, the Rayleigh scattering coefficient of the silica glass, which was prepared with a pressure of 200 MPa at 2073 K and kept for 4 hours, showed an extremely small value corresponding to a scattering coefficient of 0.34 dB/km/μm^{-4}. This

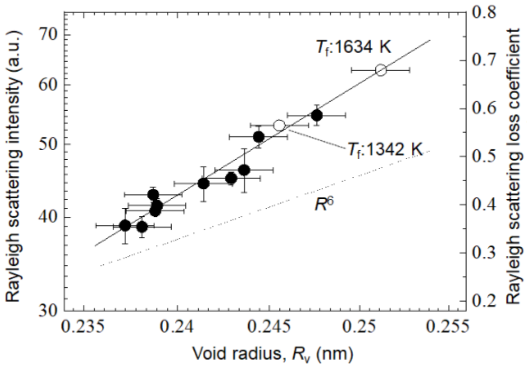

Fig. 4 The Rayleigh scattering intensity (left vertical axis) and the absolute value of the Rayleigh scattering loss (right vertical axis), are plotted against the void radius. The filled circles are for the samples made with the HIP machine. The broken line corresponds to the sixth power of the void radius (R_v). The closed circles are made with HIP, while the open circles represent the samples made

value is converted to the scattering loss of 0.07 dB/km at 1.55 μm, which is far below the reported world record of the optical loss of optical fiber, 0.1419 dB/km^4 [3].

Recently, we used molecular dynamics (MD) simulations to estimate how the density fluctuations in silica glass can be suppressed under conditions of varying pressures, including conditions beyond the experiments explained above [10]. In our calculation, two methods were attempted to obtain the scattering loss: 1. by estimating the scattering coefficient by assuming the void behaves as spherical scattering particles, and 2. by estimating the density fluctuation from parallel samples. In the former case, the scattering intensity monotonically decreases due to the increase in applied pressure, but this picture collapses when the void size becomes closer to that of the tetrahedra of Si-O. On the other hand, when the scattering intensity was calculated using the density fluctuations, the scattering intensity tends to decrease when the pressure increases from ambient to 4.0 GPa, then, above 4.0 GPa, it increases by increasing the pressure [13]. We are currently conducting experimental verification of the minimum of density fluctuation. Thus, suppression of loss by controlling its fictive *pressure* seems to have a bright future. However, there are some obstacles to overcome to form a fiber using higher-fictive-*pressure* glass. One challenge is that when this glass is heated under ambient pressure, it expands largely due to structural relaxation near 1070 K [14]. Moreover, if the glass is kept at a temperature close to 2400 K, the structure of glass will return to that of the current pressure. Thus, it seems necessary to clarify the glass structure of high fictive *pressure* and find methods to obtain the similar structure other than using the pressure.

Conclusions

I reviewed our recent findings on controlling void by using pressure-quenching as a new method to reduce the optical loss of silica glass. From both experiments and simulations, controlling fictive *pressure* seems promising. There is plenty of voids in silica glass by controling mere T_f. Now fictive pressure by void-engineering can be a new way to explore for realizing silica glass with small scattering. Toward the realization of ultra-low-loss silica glass fiber, the silica glass still has plenty of space left to research.

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