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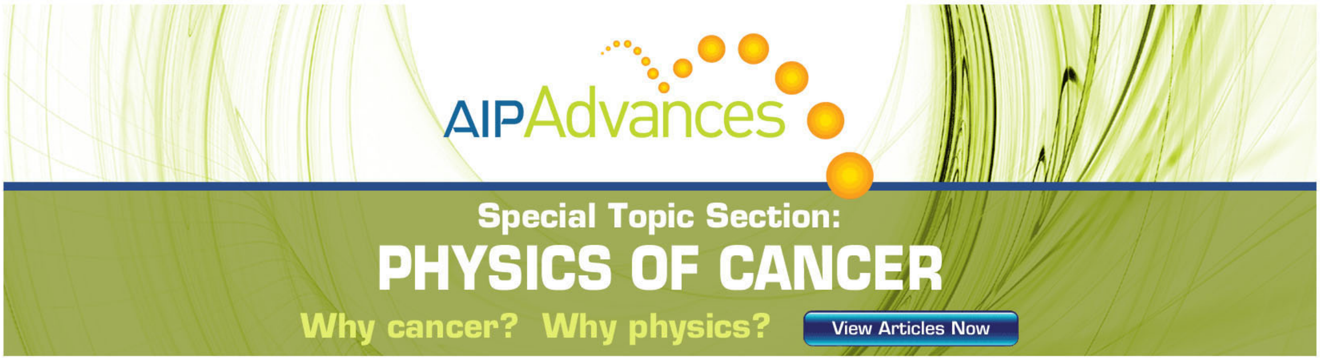

Reduction of light-scattering loss in silica glass by the structural relaxation of ''frozen-in'' density fluctuations

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Temperature dependences of light-scattering intensity in silica glasses were measured over a wide temperature range from 300 to 1 900 K. It was found that in OH-free silica glass, the diffusive density fluctuations are completely ''frozen-in'' at the glass transition temperature, while in OH-containing glass, OH gives rise to the structural relaxation of these ''frozen-in'' density fluctuations over 400 K below the glass transition temperature. This structural relaxation, expected to be caused by the introduction of some dopants with the same role of OH, can be used for reduction of the light-scattering loss in silica fibers. *© 1997 American Institute of Physics.* [S0003-6951(97)04726-8]

The minimum loss, which is primarily caused by light-scattering and multiphonon absorption, of the present silica fiber is 0.15 dB/km at 1.55 μm.[1] Since this value has been widely believed to be very close to the theoretical loss limit in silica glass,[2] new ultra-low-loss fiber materials have been researched extensively in multicomponent glasses.[3] However, to date, fibers superior to the silica based fiber have not been obtained. It is necessary for realizing ultra-low-loss fibers to reinvestigate the origin of light scattering in glass and then to develop an effective method of reducing the scattering.

According to the previous theories[4] of light scattering in glass, the scattering coefficient (turbidity) in single component glass can be expressed as

$$\alpha_T = \frac{8\pi^3}{3\lambda^4}\frac{n^8p^2}{\rho^2}\langle|\Delta\rho|^2\rangle V = \begin{cases} \dfrac{8\pi^3}{3\lambda^4} n^8p^2\beta_T(T)k_BT \quad (T>T_g) \\ \dfrac{8\pi^3}{3\lambda^4} n^8p^2[\beta_{T,\mathrm{rel}}(T_g)k_BT_g+\beta_{S,\infty}(T)k_BT] \quad (T<T_g), \end{cases} \tag{1}$$

where $\langle|\Delta\rho|^2\rangle$ is the mean-square amplitude of density fluctuations, λ the wavelength of incident light, p the photoelastic coefficient, n the refractive index, V the scattering volume, ρ the mean density, k_B is the Boltzmann constant, T_g the glass transition temperature, $\beta_T(T)$ the isothermal compressibility, $\beta_{T,\mathrm{rel}}(T_g)$ the relaxational component of β_T at T_g, and $\beta_{S,\infty}(T)$ the high-frequency limiting value of the adiabatic compressibility at temperature T. A contribution from the high-frequency shear modulus[5] is neglected here, since it is not so large. This equation has been often used for estimating optical loss in fibers.[6] The first term in the formula for $T<T_g$ describes the Rayleigh scattering due to static density inhomogeneity, and the second term the Brillouin scattering. This static density inhomogeneity is widely believed to be caused by freezing of density fluctuations at the glass transition temperature T_g. However, the present authors do not think it quite clear whether or not the diffusive density fluctuations are completely ''frozen-in'' below T_g. In this letter, the temperature dependence of light-scattering intensities in silica glass is reported, and behavior of the ''frozen-in'' density fluctuations is discussed.

Measurements of the scattered intensity of polarized light in silica glasses were carried out over a wide temperature range from 300 to 1 900 K, where cooling and heating rate was 100 K/h. The light source was a Spectra Physics 2065-6S Ar–ion laser with a linewidth of 10 MHz and jitter

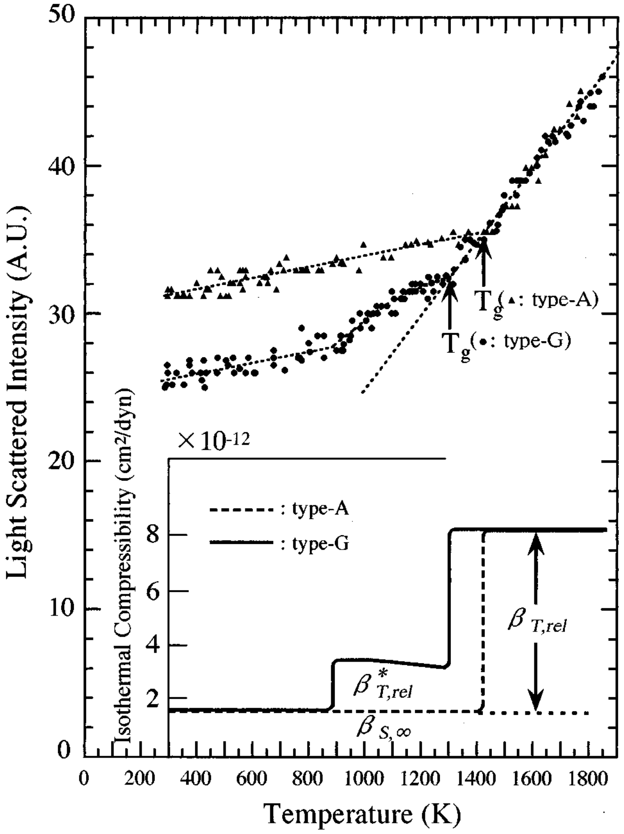

FIG. 1. Temperature dependences of VV scattered intensities and isothermal compressibilities of OH-free (type A) and OH-containing (type G) silica glasses. The latter has OH impurities of 1200 wt ppm. The measurements were carried out on both cooling and heating with the rate of 100 K/h.

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TABLE I. Different types of SiO_2 glass. These data were reported by Nippon Silica Glass Co. Ltd.

Type	Sample name	Method of manufacture	OH (wt ppm)	Refractive index (at 488 nm at R.T.)	Metal impurity (wt ppm)									
					Al	Ca	Cu	Fe	Na	K	Li	Mg	Mn	Ti
A	ED-C	VAD	<1	1.463 428	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B	ED-B	VAD	<10	1.463 295	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
C	ED-H	VAD	50	1.463 177	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
D	ED-A	VAD	100	1.463 241	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
E	ES	Flame hydrolysis of $SiCl_4$	700	⋯	0.1	0.1	0.01	0.05	0.05	0.05	0.05	<0.01	<0.01	<0.01
F	ES	Flame hydrolysis of $SiCl_4$	900	⋯	0.1	0.1	0.01	0.05	0.05	0.05	0.05	<0.01	<0.01	<0.01
G	ESL-2	Flame hydrolysis of $SiCl_4$	1200	1.463 092	0.1	0.1	0.01	0.05	0.05	0.05	0.05	<0.01	<0.01	<0.01

less than 2 MHz. The incident beam was transmitted through a sample and (VV) scattered intensities at a scattering angle of 90 °C, which are proportional to a_T, were measured. The scattered light was directly detected by a photomultiplier system, where a cold mirror, which reflects visible light and transmits infrared, and an ultranarrow bandpass filter with a bandwidth of 0.2 nm at 488 nm were used to eliminate the thermal radiation from the furnace.

Seven types of silica glasses with different OH concentrations, manufactured by Nippon Silica Glass Co. Ltd., were used. The method of manufacture, refractive indices, concentrations of OH, and metal impurities are tabulated in Table I. The density of all samples is 2.201 at room temperature. Five samples of each type of glasses were measured.

Temperature dependences of the scattered intensity in type-A and type-G are shown by triangles and circles, respectively, in the upper part of Fig. 1. Although T_g of silica glass cannot be determined by calorimetric or volume measurements, it can be clearly determined by the temperature dependence of the light-scattered intensity. T_g determined from this study is between the temperature where viscosity is 10^{13} P and the strain point, where viscosity is $10^{14.5}$ P, as tabulated in Table II. No hysteresis was observed within the experimental errors. The behaviors of the intensities below T_g are different form each other: in type G it decreases by a larger amount than that in type A, between T_g and 900 K.

According to Eq. (1), isothermal compressibility can be deduced from the derivatives of the temperature change of scattered intensities, if the term $n^8 p^2$ is almost constant against temperature. This term, which is approximately equal to $(n^2-1)^2$,[2] in silica glass is constant within 1% in the temperature range between 300 and 2 000 K, since maximum changes of n are only about 0.1%.[7] The dashed line and solid line in the lower part of Fig. 1 indicate the isothermal compressibilities in type A and type G, respectively, where their absolute values were deduced from the comparison between the intensities of the present samples and a standard sample. The relaxational part $\beta_{T,\mathrm{rel}}$ disappears rapidly at T_g in Type A. This fact indicates that the diffusive density fluctuations are frozen-in at T_g, that is, below T_g, structural relaxation time of the melt becomes so long that no structural rearrangement is possible during the experimental time scale. However, in the OH-containing type G, there exists another relaxational component $\beta^*_{T,\mathrm{rel}}$. Although a peculiar temperature dependence of $\beta^*_{T,\mathrm{rel}}$ cannot be explained explicitly so far, OH gives rise to the structural relaxation of ''frozen-in'' density fluctuations over 400 K below T_g, resulting in reducing the light-scattered intensity.

Figure 2 represents scattered intensities at 300 K and T_g against OH concentrations by circles and triangles, respectively. The intensity difference between these two temperatures is caused by two origins; the Brillouin scattering, which decreases with decreasing temperature, and structural relaxations. The latter is shown in Fig. 2 by hatching. The concentration of structural relaxation rapidly increases with increasing the OH concentration, especially at a concentration of less than 100 wt ppm.

To conclude, this study has revealed that in OH-free silica glass, the diffusive density fluctuations are completely ''frozen-in'' at T_g, while in OH-containing glass, OH gives rise to the structural relaxation of these ''frozen-in'' density

TABLE II. Glass transition temperature T_g of SiO_2 glass.

Type	T_g (K) Obtained from this study	T (K)[a] Where viscosity is 10^{13} P	Strain point (K)[a] Where viscosity is $10^{14.5}$ P
A	1430	⋯	⋯
B	1410	1470	1380
C	1370	1440	1330
D	1360	1420	1320
E	1310	≈1350	≈1240
F	1300	≈1350	≈1240
G	1300	1350	1240

[a] These data were reported by Nippon Silica Glass Co. Ltd.

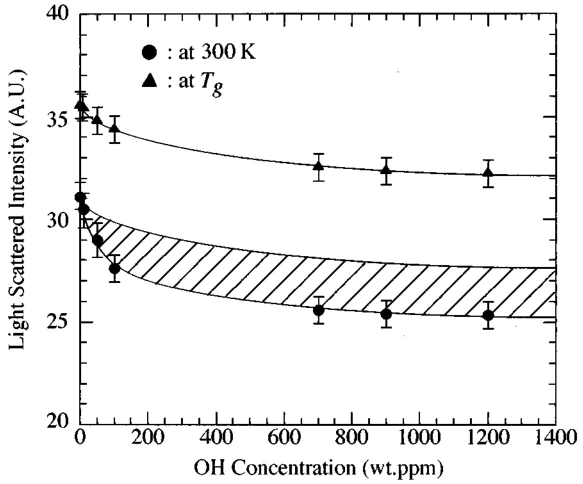

FIG. 2. Scattered intensity at 300 K and T_g against OH concentration. Hatching indicates the contribution of the structural relaxation of ''frozen-in'' density fluctuations.

fluctuations over 400 K below T_g. Tomozawa *et al.*[8] reported that the water diffusion in silica glass has a kinetic effect on the Si–O–Si bond angle. Presently observed structural relaxation of ''frozen-in'' density fluctuations of optical wavelength could be caused by the same effect of OH's, that is, OH ions diffuse and cut the network composed of SiO_4 tetrahedra. Both experiments have probably revealed the same effect of OH's from microscopic and macroscopic scales.

This result demands reconsideration of the previous estimate of light-scattered intensity, which was according to Eq. (1), in other glasses including multicomponent glasses. Furthermore, this result suggests a new and effective method for developing ultra-low-loss glasses: we can encourage the structural relaxations by introducing some dopants to reduce the light-scattering loss. Most applicable candidates are alkaline and alkaline earth ions. Lines[9] has already pointed out the importance of silica with small doping concentrations of alkaline ions (about 1 mol %) for low-loss fibers. However, taking into account the structural relaxation of the ''frozen-in'' density fluctuations, silica with smaller concentrations of impurities, 1/10–1/1000 of that pointed out by Lines, has a big possibility to be ultralow loss. Such a small concentration of impurities is of a great advantage, because any increase of loss due to concentration fluctuations and crystallization can be neglected.

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