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Internal friction and relaxation mechanism of F-doped SiO_2 glasses

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Abstract

The internal friction and the Young's moduli of pure SiO_2, SiO_2–4 mol% F and –8 mol% F glasses were measured in the temperature range of 1.6–250 K. The temperature dependencies of the internal friction were not different except for their peak values, which showed differences of a few percent at 35 K. In contrast, the Young's moduli of F-doped SiO_2 glasses were 7.5% (–4 mol% F) and 15% (–8 mol% F) less than that of pure SiO_2 glass, respectively. Both temperature dependencies were analyzed on the basis of Debye relaxation by the distributed double-well potential model.

Keywords: Internal friction; Young's modulus; SiO_2 glass; Fluorine

1. Introduction

SiO_2 glass is one of the materials for studying complex systems in which many scientists have recently shown a strong interest. We have been measuring both the low-temperature dependencies of the internal friction and the Young's moduli of Ge-doped, O-excessive and O-deficient SiO_2 glasses [1,2]. Analysis using the thermal relaxation model with a double-well potential has succeeded in providing an explanation of these phenomena [3]. With this model, the internal friction is attributed to the lateral motion of the bridging oxygen atoms across the Si–O–Si bridge.

It is well-known that the incorporation of fluorine reduces the optical refractive index of SiO_2 glass. Fluorine-doped SiO_2 glass possesses many advantages as the cladding glass of an optical waveguide, and is expected to have a transmission higher than that made by Ge-doped glass. Fluorine doped in the glass has the formation of an SiO_3F tetrahedron substituted by an oxygen atom at its corner. Dumas et al. reported that a $945\,cm^{-1}$ Raman band corresponds to a ν (Si–F) stretching vibration of an SiO_3F tetrahedron, in which the fluorine atom is only bonded to one Si atom [4].

In the present paper, we report the low-temperature measurements of the internal friction and the Young's moduli of fluorine-doped SiO_2 glasses,

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and try to explain both phenomena by the double-well potential model which has succeeded in the analysis of Ge-doped SiO_2 glasses [3].

2. Experiment and specimens

The experimental method applied to the measurements of the internal friction and the Young's modulus is a composite oscillator type with a quartz of $50 \times 3.5 \times 3.5\,mm^3$, which produces longitudinal waves [5]. This method has only one oscillational frequency of 51 kHz but the capability of high resolution suitable for measurements of small changes of internal friction. Glass specimens were obtained as follows. SiO_2 soot rods were obtained from $SiCl_4$ by the vapor-phase axial deposition (VAD) method, and then the rods were heat treated at a high temperature in an atmosphere of SF_4 and He gases. These rods were sintered at a temperature of 1500°C, and SiO_2–4 mol% F and –8 mol% F glasses were obtained. Pure SiO_2 glass which was obtained by the direct method was prepared and used as the standard of SiO_2 glasses.

3. Analysis

The observed relaxation peak around 35 K is considered to be a superposition of widely distributed Debye-type mechanical relaxation peaks. For the analyses the internal friction is expressed as [3,6]

$$\pi Q^{-1} = \sum_i \frac{A_i}{T}\frac{1}{\Delta_i^m}\int_0^{\Delta_i^m} \frac{\omega\tau}{1+(\omega\tau)^2}\,\mathrm{sech}^2\left(\frac{\Delta}{2k_BT}\right)d\Delta. \tag{1}$$

where Q is the quality factor, A_i is the magnitude of contribution from ith Debye relaxation, T is the temperature, ω is the angular frequency of sound, Δ is the asymmetric energy of the double-well potential, and Δ_i^m is the maximum value of the distribution of the asymmetry energy for the i's potential. τ is the relaxation time in the asymmetric potential and given by, $\tau = \tau_0 \exp(U_i/k_BT)\mathrm{sech}(\Delta/k_BT)$, where U_i is the barrier height of the ith potential and τ_0 is a constant.

The change of the Young's modulus, δE, due to the relaxation is expressed as

$$-\left(\frac{\delta E}{E_0}\right) = \sum_i \frac{A_i}{T}\frac{1}{\Delta_i^m}\int_0^{\Delta_i^m} \frac{1}{1+(\omega\tau)^2}\,\mathrm{sech}^2\left(\frac{\Delta}{2k_BT}\right)d\Delta. \tag{2}$$

Eqs. (1) and (2) are fitted to the internal friction and the Young's modulus data by the Monte Carlo method, and 50 sets of parameters (U_i, A_i, Δ_i^m) are determined. A series of U_i values are chosen for the fitted curves to be smooth.

To determine the potential distribution uniquely, any functional form for the distribution was not assumed. Firstly the fitting of internal friction was made under the condition of a symmetric potential ($\Delta_i^m = 0$ for all i's), and the modulus change is calculated by using the determined A_i values. Secondly, both the asymmetry parameter Δ_i^m's and the relaxation strength A_i's are used as the fitting parameters, and the internal friction and the elastic modulus change are fitted simultaneously. When the parameters A_i's are determined, the density of relaxation strength, $P(U_i) = (A_{i+1} + A_i)/2(U_{i+1} - U_i)$, is calculated.

4. Discussion

The internal frictions of three types of SiO_2 glasses were measured in the temperature range of 1.6–250 K. The results are shown in Fig. 1, in which the symbols O, + and X show those of pure SiO_2, SiO_2–4 mol% F and –8 mol% F glasses. At low temperatures below 5 K, the internal friction is almost independent of temperature, which is thought to be due to the TLS relaxation [7]. In order to compare the values of the internal friction of the glasses, they are normalized in Fig. 1 by those at 2 K, which are 1.49×10^{-3} (pure SiO_2), 1.41×10^{-3} (–4 mol% F), and 1.63×10^{-3} (–8 mol% F). These values of three glasses are not very different except for their peaks, which show a few % point differences at 35 K. In Fig. 2, the Young's moduli of the three kinds of glasses are shown, in which the symbols O, + and X show the values of pure SiO_2, SiO_2–4 mol% F and –8 mol% F glasses

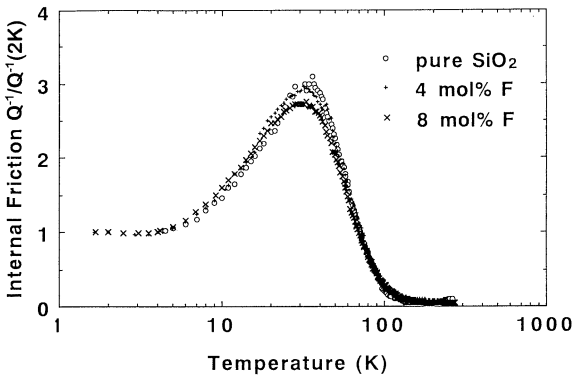

Fig. 1. Internal friction normalized at 2 K of pure SiO_2, SiO_2–4 mol% F and –8 mol% F glasses.

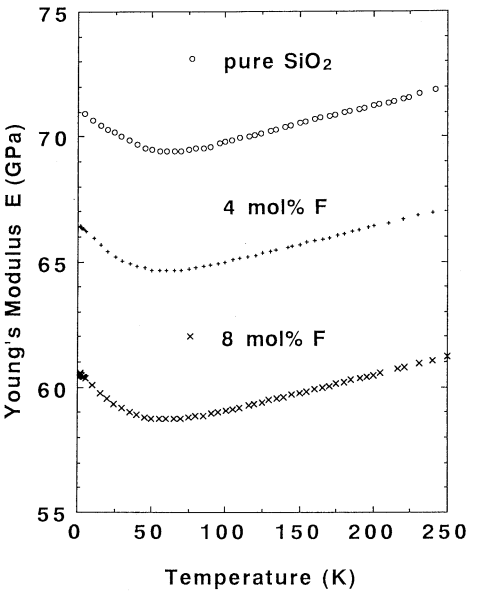

Fig. 2. Young's moduli of pure SiO_2, SiO_2–4 mol% F and –8 mol% F glasses.

in the temperature range of 1.6–250 K. In contrast to the internal friction, the Young's moduli of fluorine-doped SiO_2 glasses are 7.5% (–4 mol% F) and 15% (–8 mol% F) less than that of pure SiO_2 glass, respectively. The thermal relaxation theory shows internal friction $\pi Q^{-1} \propto n/E$, where n is the number of particles (bridging oxygen atoms) moving in a double-well potential and E is Young's modulus

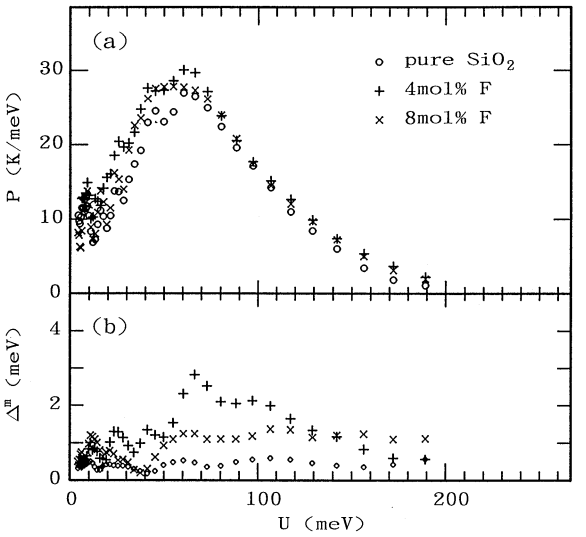

Fig. 3. Determined relaxation strength density P (a), and asymmetry parameter Δ^m (b).

[6]. With the increment of the fluorine content, the values of n and E decrease in the same manner, which, it is thought, cancels the change of πQ^{-1}. When an oxygen atom moves by the applied force over the potential height from one site to the equivalent site, it is difficult to jump directly across the Si–Si bond line in a plane. It is supposed that an oxygen atom can move around the Si–Si line smoothly. Kaneta suggested that an oxygen impurity atom in an Si crystal exists at a bridging oxygen site and turns round the Si–Si axis [8].

The experimental data of πQ^{-1} and Young's modulus have satisfactorily been fitted to Eqs. (1) and (2), respectively, and the relaxation strength A_i and the asymmetry parameter Δ^m were determined, and the relaxation density P was calculated. The results are shown in Fig. 3. It can be seen that the oxygen atoms with the activation energy of about 60 meV are largely contributed to the relaxation phenomena. The effect of the fluorine atoms on the density P is not clearly seen in the present analysis. It is noted that the present model can reproduce the πQ^{-1} and the Young's modulus simultaneously, then this relaxation model can explain the mechanical dynamics of SiO_2 glasses very well.

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