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Low temperature-elastic moduli, Debye temperature and internal dilational and shear frictions of fused quartz

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Longitudinal and transverse wave velocities, five kinds of elastic parameters (Young's, shear and bulk moduli, Lamé parameter, Poisson's ratio), Debye temperature, and dilational and shear internal frictions for fused quartz were simultaneously measured over the temperature range from 73 to 400 K, using the ultrasonic pulse wave with frequency of 7.7 MHz. Large increase in Young's and bulk moduli and small increase in shear modulus and Lamé parameter suggest enhancement of rigidity for K_l mode on heating. This would be explained by quasi-crystallization which is associated with a lateral motion of oxygen atoms and the resulting relief of macroscopic strains. The 99 and 137 K peaks and 360 K one in shear friction are probably related to dielectric loss peaks arising from Al^{3+}–Na^+ and Al^{3+}–K^+ substitutional–interstitial paired defects and to β_1/β_2-tridymite phase transition, respectively.

1. Introduction

The strength and various associated elastic moduli of glasses containing fused quartz change with progressive crystallization. The glasses have also various elastic after-effects, i.e. delayed elasticity [1] due to "anelasticity" [2]. Such an non-ideal elastic behaviour can be successfully detected by internal friction. Internal friction offers useful information about the various stages of incipient crystallization such as relief of strain, softening and embryo for nucleation [3], and phase transition [4] and dielectric relaxation [5].

Temperature dependence for the elastic moduli of fused quartz in the low temperature region has been reported by Marx and Sivertsen [6], by McSkimin [7], by Fine *et al.* [8], by Anderson ad Bömmel [9]. Internal friction effects have been observed by Marx and Sivertsen [6], by Fine *et al.* [8], by Anderson and Bömmel [9], and by Kosugi [10]. However, there are different opinions concerning the experimental results and theoretical explanations of the phenomena observed. In particular, no one has drawn a physical line between dilational and shear frictions for fused quartz. This discrepancy has generally been explained by the strong sensitivity of acoustic parameters to the quality of the sample preparation, and especially to certain kinds of impurities or grain boundaries.

However, three other causes may be added: first, low temperature deterioration [11, 12] of piezoelectricity in transducer materials such as PZT ($Pb(Zr_xTi_{1-x})O$) and $LiNbO_3$, which are epoxied onto the samples; second, failure to make different frequency measurements simultaneously; third, oversight of frequency dependence for internal friction effects. In the conventional method, these transducers are exposed to a cold temperature during measurement, and longitudinal and transverse waves with different frequencies are measured on separate runs. Since cold deterioration in piezoelectricity arrests the occurrence of friction peaks in the low temperature region, the conventional method is not necessarily suitable. Hypersonic or ultrasonic waves with frequencies over 10 MHz are not sensitive for evaluation of macroscopic strains [3] and dielectric relaxation peak arising from impurity defects [13]. Thus, it is necessary to reinvestigate all the elastic data reported to this day with respect to these points of view.

In a previous paper [3], five kinds of elastic parameters and dilational and shear internal frictions of fused quartz were simultaneously measured in terms of crystallization over the temperature range 298–1694 K. The dilational internal friction peaks were observed at 840 and 1110 K as α-quartz/β-quartz and β-quartz/β_2-tridymite phase transitions, respectively, and the shear at 390 and 1360 K peaks were regarded as β_1/β_2-tridymite and glass phase transitions, respectively.

Our next interest lies in simultaneously determining all the elastic moduli and both dilational and shear internal frictions of fused quartz in terms of atomic displacement in the low temperature region. In this study, we report temperature dependence of the longitudinal and transverse wave velocities, elastic (Young's, shear (C_{44} in the elastic constant matrix which is composed of six rows and six columns) and bulk) moduli, Lamé parameter, Poisson's ratio, Debye temperature, and dilational and shear internal frictions for fused quartz in the low temperature region between 73 and 400 K. (Strictly speaking,

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TABLE I Some properties of fused quartz used in this study

Density (Mg/m^3)	Softening point (K)	Strain point (K)	Viscosity (pa/s)	Impurity (p.p.m.)					Dielectric coefficient at 1 kHz
				Al	Fe	Na	K	OH	
2.2199	1933	1363	4.0×10^{11}	8	0.4	0.8	0.8	200	3.58

because Lamé constants ($= C_{12}$) are a function of temperature, "Lamé parameter" is used in place of "Lamé constant" in this study.) As far as we know, no research has been carried out previously on low-temperature, simultaneous measurement of all the parameters of fused quartz using both longitudinal and transverse waves with the same frequency. Simultaneous measurement can enable us to evaluate the effects of all the parameters for elasticity [3]. In addition, a precise temperature dependence of Debye temperature for quartz in the low temperature region has not reported for acoustic and thermal measurements until now, because of deficiency of both longitudinal and transverse wave velocities and excess specific heat, respectively.

2. Experimental procedure

Some of the properties of the fused quartz (Toshiba Ceramics, T-1030) used in this study are listed in Table I. Longitudinal and transverse wave velocities, all elastic moduli and internal frictions were accurately measured by means of an ultrasonic pulse method with zero cross time detection. The experimental procedure is minutely described in previous papers [3, 14]. The specimen was in the form of a short rod fastened to the waveguide of fused quartz with threads of pitch 1.75 mm, to eliminate the generation of spurious signals by mode coversion at the sides [15, 16], using a domed cap nut of copper. The specimens, which were vertically mounted in cryostat with a liquid nitrogen cooling system under vacuum of 0.2 MPa, were measured from 73 K up to 400 K at a heating rate of approximately 2 K min^{-1}. The temperature was first lowered to 73 K by decompressing the pressure over liquid nitrogen. The transducer and the specimen were jointed to both sides of the waveguide by water-free glycerine grease (Sonicoat). Because trailing pulses are generated when a longitudinal sound wave is propagating into a rod, both accurate longitudinal and transverse velocities are simultaneously determined by means of mode conversion in one run [15, 16, 17], even if there is a temperature gradient, and the resulting velocity gradient occurs through the waveguide between the room temperature and the cooled sides. In order to avoid propagation loss due to the high frequency of ultrasonic waves, a longitudinal wave generation piezoelectric transducer with the frequency of 7.7 MHz was used. Since the ratio of α ($= 3.5$ mm), the radius of the specimen, to λ ($= 0.78$ mm), the wavelength, α/λ ($= 4.5$ at 298 K), is greater than 2.5, the measured pulse wave velocity approaches the bulk velocity in an infinite elastic medium without interference of either longitudinal or transverse waves [18]. This high ratio can enable us to distinguish a physical meaning between pure mode III shear, defined as shear modulus and mixed mode II–mode III shear designated as the Lamé parameter [12]. Increasing and decreasing rates in the internal friction at low temperature were calculated using the ratio of logarithmic echo amplitude of the ultrasonic wave at the given temperature to the lowest one [17].

An atomic volume at room temperature was measured by X-ray diffraction method using CuK_α. The temperature dependent volume is calculated using a thermal coefficient ($0.5 \times 10^{-6}\ K^{-1}$ [19]) of quartz.

3. Results and discussion

3.1. Temperature dependence of elastic moduli and Debye temperature

The longitudinal and transverse wave velocities as a function of temperature are shown in Fig. 1. Both velocities increase substantially with increasing temperature, in contrast to those of other crystalline solids. This suggests either atomic displacement or flow of the chilled amorphous phases.

According to previous papers [10, 17, 20, 21, 22], Young's, shear and bulk moduli, Lamé parameter and Poisson's ratio were calculated using longitudinal and transverse wave velocities. These results are presented in Figs 2 and 3, respectively. In comparison with the Young's (7.3 GPa) and shear (3.1 GPa) moduli reported by Spinner [23] and Carnevale *et al.* [24], respectively, the room-temperature values in Fig. 2 are consistent with their data within the error limits. All parameters increase as temperature increases from 73 to 400 K, accompanied by enhancement of rigidity. This would be explained by near-neighbour replacement of atoms, i.e. quasi-crystallization in glassy phases on heating, although the increase in Young's modulus is interpreted in a qualitative way as being analogous to the case of rubber stretching [25, 26].

When any modulus M is considered as a function of volume V and temperature T, $M = M(V, T)$, the sign of dM/dT of fused quartz is governed by the sign of $(dM/dT)_V$ [27], because of its small expansion coefficient and negligible pressure effect [3]. The positive dM/dT suggests a progressive transition to an open tetrahedrally coordinated structure.

In contrast to the relatively large dM/dT in Young's (9.6×10^{-3} GPa K^{-1}) and bulk moduli (1.4×10^{-2} GPa K^{-1}), dM/dT in shear modulus (1.4×10^{-3} GPa K^{-1}) and the Lamé parameter (1.5×10^{-3} GPa K^{-1}) is extremely small. This suggests that

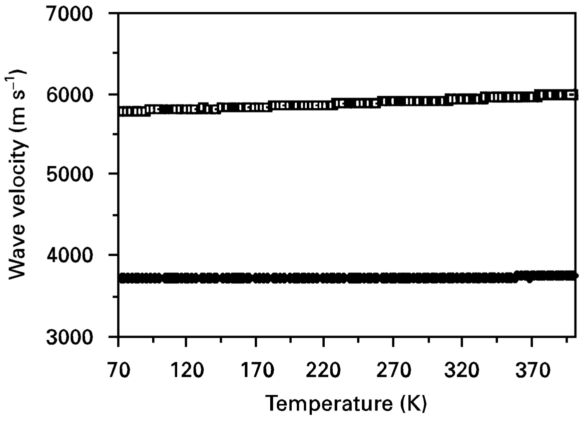

Figure 1 Temperature dependence of longitudinal (□) and transverse(◆) wave velocities of fused quartz.

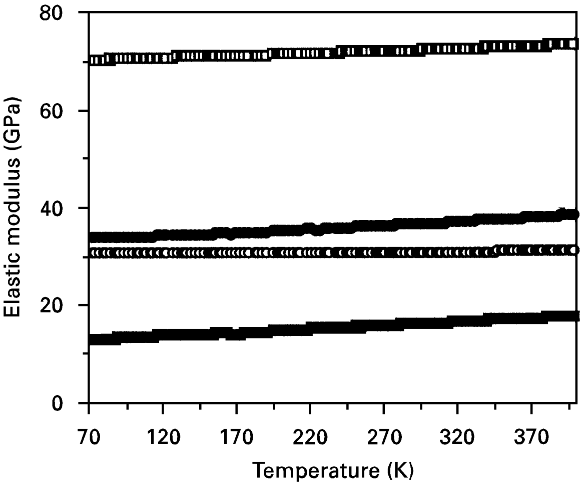

Figure 2 Young's (□), shear (○) and bulk (●) moduli and Lamé parameter (■) of fused quartz as a function of temperature.

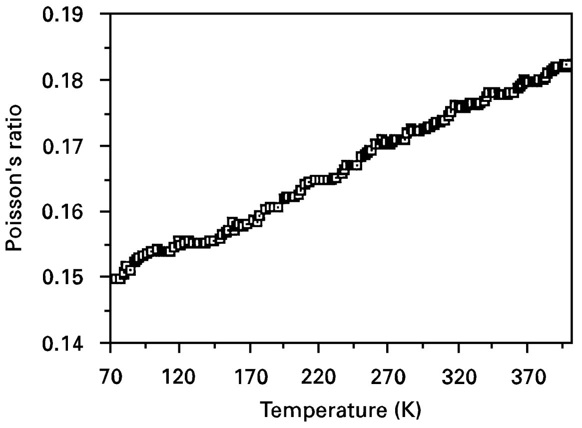

Figure 3 Poisson's ratio of fused quartz as a function of temperature.

enhancement of rigidity for K_{I} mode by heating is larger than that for K_{II} and K_{III} modes, as deduced from the definition for C_{44} and C_{12} in the elastic constant matrix. Paradoxically speaking, shear stress promotes α-quartz amorphization [28]. The qausi-crystallization seems to be associated with a result of a small variation in Si–O–Si bond angles [29] or the lateral motion of the oxygen atom [9]. In other words, the qausi-crystallization is connected to an interlocking of two parts of the random glassy network [30].

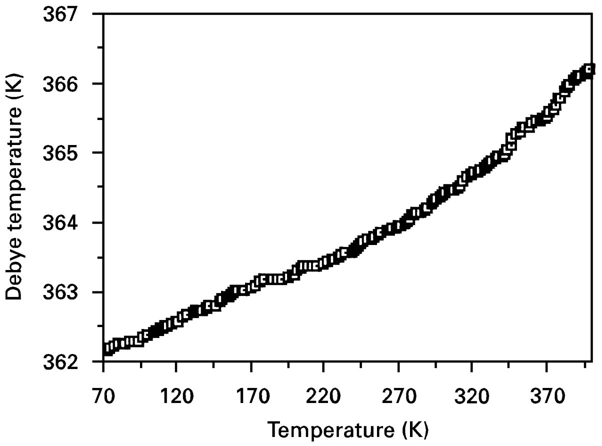

Figure 4 Temperature dependence for Debye temperature of fused quartz.

Behaviour in Poisson's ratio increases as temperature increases, in accordance with other crystal solids [17, 22]. This indicates an activation of shear mode for deformation [17, 21, 22].

Ultrasonic wave velocity measurements relate to the long wavelength acoustic phonons, which are the only modes to be excited to any extent at liquid helium temperatures. If a coupling of the phonons with a thermally activated relaxation process occurs [9], it will induce a change in Debye temperature. Next, we calculated the elastic Debye temperature of the quartz with an atomic volume of 113.01×10^{-30} m^3 at room temperature, using longitudinal and transverse wave velocities [12]. The temperature dependence is presented in Fig. 4, showing a gradual increase without any anomalies. Increase in Debye temperature, i.e. increase in the maximum frequency allowed, indicates decrease in effective ionic distance among Si and O atoms. This suggests a progressive transition from disordered network to regularly repeating structure, accompanied by a change in Si–O–Si bond angle or the lateral motion of the oxygen atom [9]. Although it is reported that there is a discrepancy for temperature dependence of Debye temperature between quartz and vitreous silica [31], we could not find such a discrepancy; our data resemble those for vitreous silica. This agreement would be attributed to low-temperature simultaneous determination of longitudinal and transverse wave velocities with the same frequency.

3.2. Temperature dependence of internal friction

In propagation of an acoustic wave which is mainly phonon velocity, acoustic energy generally decreases by absorption and scattering. The acoustic scattering effect plays an important part in the propagation for the fused quartz during heating. Internal friction curves for longitudinal and transverse waves are shown in Fig. 5, as a function of temperature. The dilational friction increases gradually up to 280 K and

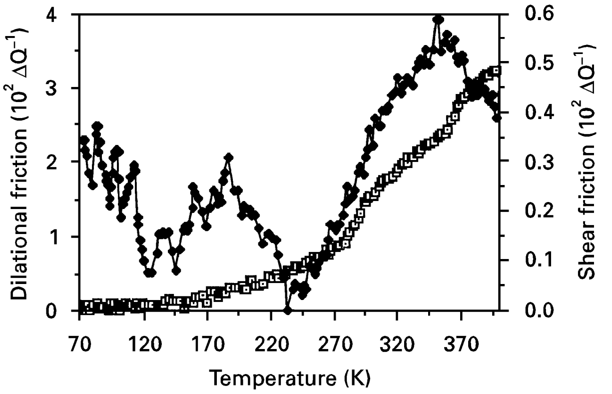

Figure 5 Temperature dependence of internal friction for longitudinal and shear waves of fused quartz. ☐ dilational friction; ◆ shear friction.

then begins to rise remarkably, and lastly again rises up at 360 K, with increasing temperature. While the shear friction shows seven peaks at 99, 113, 137, 160 and 360 K. Based on previous papers [3, 12, 18], the increase from 280 K in dilational friction is associated with the relief of macroscopic elastic strain in the random glass network matrix deriving from the motion of dislocation. The rapid increase from 360 K in dilational friction corresponds to a 360 K peak in shear friction, described later.

The small 99 and 137 K peaks in shear friction may be connected to the dielectric loss peaks observed by Park and Nowick [32], who hypothesized that the two 100 and 138 K peaks are due to some substitutional–interstitial (s–i) paired defects [33]. Stevels and Volger [34] have attributed the 95 and 140 K peaks to the presence of Al^{3+}–Na^{+} and Al^{3+}–K^{+} s–i pairs, respectively. Martin [5] has also found that the 100 and 135 K peaks are associated with the presence of the Al hole centre from a study of the acoustic loss spectra of a series of 5 MHz fifth overtone AT-cut resonator blank. These Al^{3+}–X^{+} defects are responsible for the acoustic loss peak [5]. For this reason, the interstitial alkali ions X^{+} in synthetic quartz serve as the charge compensators, because the substitutional aluminium ions present in all quartz requires charge compensation. Since, indeed, the sample used in this study contains Al, Na and K elements, as presented in Table I, there is a possibility that these impurities or hole centres are related to shear frictions. Thus shear friction provides a sensitive convenient probe for determining the impurities such as Al, Na and K ions in fused quartz. However, the attribution of many peaks is not necessarily conclusive at the present time. In a subsequent paper, their origins will be invesigated by changing the concentration of impurities.

The broad 360 K peak in shear friction is probably due to the transition of β_1/β_2-tridymite phase associating atomic rearrangement of amorphous colonies [35]. Examples of atomic rearrangement have been reported in previous papers [3, 12]. On the other hand, we can not assign clear origins for the 113 and 160 K peaks which were also observed by Kosugi [10]. Since chlorine and hydroxyl are equally effective in breaking Si–O–Si bonds [36], these unknown peaks might be associated with an existence of such broken bonds.

Vacher *et al.* [37] have measured the attenuation of longitudinal and transverse waves with frequencies ranging between 200 MHz and 35 GHz on the same sample of vitreous silica in the temperature region from 10 to 300 K, and observed only a strong broad peak between 50 and 130 K. In order to investigate the interaction between the ultrasonic wave and thermal phonons in amorphous quartz, usage of high frequency over 200 MHz is desirable under the condition $\omega\tau_{th} \gg 1$ [38], where ω is the angular frequency of the sound wave and τ_{th} the lifetime of the thermal phonons. However, such high frequency is not suitable to investigate relief of macroscopic strains and dielectric relaxation arising from s–i paired defects. Missing of many acoustic peaks in study of Vacher *et al.* [37] is this case. Strakna and Savage [39] have also found only a broad peak in shear and longitudinal ultrasonic attenuation measurement of SiO_2 glass, using a frequency of 21.5 MHz. However, their quartz crystal transducer was exposed to a cold temperature during measurement. In addition, from monotonous increase in Debye temperature of Fig. 4, all internal friction peaks observed in this study are not coupled with thermal phonons in the temperature region of interest.

As reported in previous studies of ceramics [17, 20], metals [21, 22] and polymer [14], the physical properties of dilational friction are different from those of shear friction; the former corresponds to superplasticity, recrystallization and a second-order normal-superconducting phase transition accompanied by relief of strain, and the latter is caused by phase transformation, solute solubility, softening of the precipitate or glassy phases at grain boundaries, diffusion of ions and glass transition. A common point for origins of dilational friction is motion of dislocation along grain boundaries or variation of potential energy between atoms, while that for origins of shear friction is atomic rearrangement in crystalline and amorphous structure. In ordinary studies, indeed, the physical meanings of both frictions have been confused.

From the above mentioned results and discussion, it is clear that the fused quartz has rare thermal characteristics which we can not find in any other solids [17, 20–22]. This could arise from the fact that the structure of the SiO_2 network permits a wide variety of possible imperfections [40].

4. Conclusions

Characteristic elastic and damping behaviours in the low temperature range 73–400 K for fused quartz have been investigated in terms of quasi-crystallization associated with atomic displacement. Young's and bulk moduli increase effectively and shear modulus and Lamé parameter increase generously as temperature increases, suggesting enhancement of rigidity for K_I mode on heating. This would be explained by qausi-crystallization which is associated with the small variation in Si–O–Si bond angles or the lateral motion of the oxygen atoms and the resulting relief of macroscopic strains. The 99, 137 and 360 K peaks in shear friction are probably related to the Al^{3+}–Na^{+} and Al^{3+}–K^{+} substitutional–interstitial paired defects, and to β_1/β_2-tridymite phase transition, respectively. All internal friction peaks observed are not coupled with thermal phonons.

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