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THERMOELASTIC PROPERTIES OF ULE® TITANIUM SILICATE GLASS *

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The elastic moduli, and their temperature and pressure derivatives, for ULE titanium silicate glass, have been measured by the ultrasonic pulse superposition technique. From the extrapolated 0 K values of the elastic moduli and their pressure derivatives, the elastic 0 K Debye temperature and Grüneisen constant have been evaluated, and compared with the thermally measured values. The same anomalies in the dynamic properties as found in other glasses, i.e. positive temperature and negative pressure derivatives, are also found for ULE glass. The correlation between the changes in the bulk modulus and additive in silica-rich glasses is discussed.

1. Introduction

The production of glasses with essentially a zero thermal expansion coefficient [1,2], is one of the most exciting developments in glass technology in recent years. Such a glass, ULE® titanium silicate glass, Corning code 7971, has a nominal composition of 7.4 wt% TiO_2, the balance being fused silica, and can be described by the formula $Ti_{0.06}Si_{0.94}O_2$.

The anomalous dynamical properties of glasses are well known [3]. Also, the thermal expansion of a solid can be correlated with its elastic properties [4–6]. Thus, there should be some interest in investigating the elastic properties of ULE glass. Such an investigation may elucidate, whether, in line with other glasses, the dynamical properties of ULE glass are anomalous, how the thermal expansion deduced from elastic data compares with the one measured thermally, and the effect of the addition of TiO_2 on the change in the properties of pure fused silica. In this work, the elastic moduli, their pressure and temperature derivatives for ULE glass were measured.

2. Experimental

Blanks of annealed ULE glass were purchased from the Corning Glass Works. They were sawn to size, and opposite faces were hand-lapped plane and parallel, so

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that specimens of cube shape, 14 mm on edge, were obtained. The elastic moduli and their pressure and temperature derivatives were determined by measuring the velocity of ultrasound for longitudinal and shear waves, as well as its variation with pressure and temperature. The sound waves were generated by X- and Y-cut crystalline quartz transducers, operating at their fundamental frequency of 15 MHz, bonded to the sample by benzophenone. For the pressure measurements, the specimens were placed in a pressure bomb, connected to a gas pressure generator, while for the temperature measurements, the samples were placed inside a sealed cell under dry nitrogen, where the temperature could be varied between room temperature and 0°C.

The absolute values of the sound velocity were measured by the pulse-echo technique, utilizing the unrectified signal [7]. The variation of the sound velocity with pressure and temperature, from which the pressure and temperature derivatives are evaluated, was determined by the pulse superposition method [8], modulating the repetition rate and utilizing phase-sensitive detection [9]. Thus, the elastic moduli and their pressure and temperature derivatives at room temperature may be determined.

3. Results

In table 1, the travel times, velocities and the values of the corresponding elastic moduli for longitudinal and shear waves are presented, while table 2 shows the values of the different second-order elastic moduli, c_{11}, c_{44}, the bulk modulus B, the shear modulus G and Young's modulus E, together with values furnished by Corning. In table 3, the values of the temperature derivatives of the elastic moduli are shown. Since the thermal expansion of the material is negligible, the adiabatic and isothermal constants are essentially equal.

In fig. 1, the results of $\rho_0 W^2$ as a function of the applied hydrostatic pressure for longitudinal and shear waves are shown. Here ρ_0 is the zero pressure density and W the natural velocity [10]. The dots are the experimental data, all normalized to a temperature of 293 K, while the straight lines are a least-squares fit to the data. From the slopes of the lines, the pressure derivatives of $\rho_0 W^2$ at zero pressure $(\rho_0 W^2)'_{P=0}$ for longitudinal and shear waves may now be determined. From the lat-

Table 1
Values of the travel times and corresponding elastic moduli for longitudinal and shear waves.

Mode	Travel time (μs)	Path length (cm)	Sound velocity (10^3 m/s)	Elastic modulus (10^{10} N/m^2)
longitudinal	5.28	2.9436	5.58	6.84
shear	7.47	2.6756	3.58	2.82

Table 2
Values of the second-order elastic moduli at 293 K (units are 10^{10} N/m^2).

	c_{11}	c_{44}	B	G	E
this work	6.84	2.81	3.09	2.81	6.47
Corning results	7.27	2.86	3.49	2.86	6.78

Table 3
Temperature derivatives of the elastic moduli at 293 K (units are 10^{-4} K^{-1}).

$1/c_{11}\ \partial c_{11}/\partial T$	$1/c_{44}\ \partial c_{44}/\partial T$	$1/B\ \partial B/\partial T$	$1/G\ \partial G/\partial T$
2.41	1.78	3.17	1.78

Table 4
Values of $(\rho_0 W^2)'_{P=0}$ and the pressure derivatives of the elastic moduli.

$(\rho_0 W^2)'_{P=0}$		$\partial c_{11}/\partial P$	$\partial c_{44}/\partial P$	$\partial B/\partial P$
longitudinal	shear			
−11.86	−3.80	−11.12	−3.50	−8.20

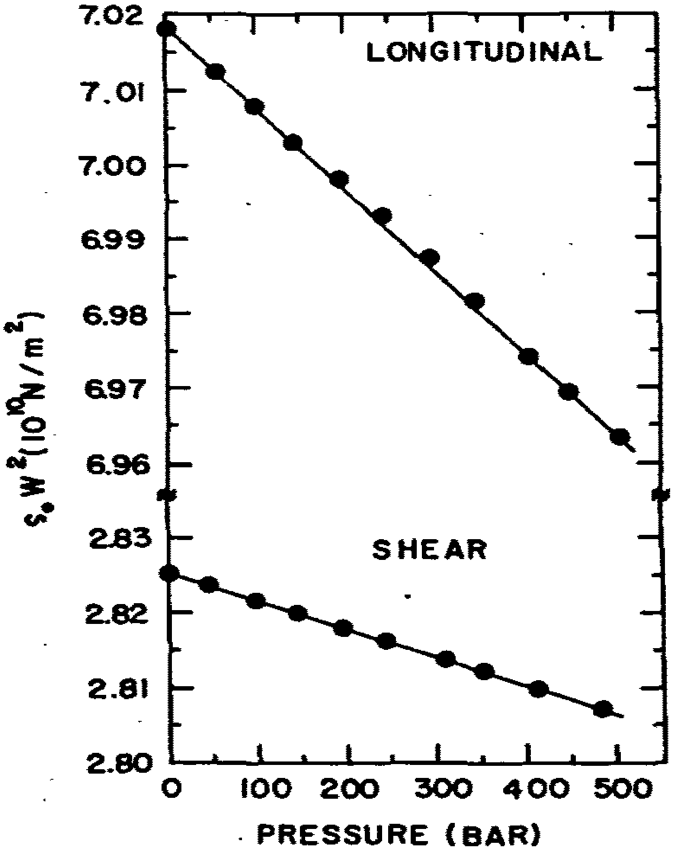

Fig. 1. $(\rho_0 W^2)'_{P=0}$ as a function of pressure.

ter quantities, the pressure derivatives $=\partial c_{11}/\partial P$, $\partial c_{44}/\partial P$ and $\partial B/\partial P$ may now be evaluated, and are shown in table 4. The negative value of $\partial B/\partial P$ is noteworthy.

4. Discussion

The anomalous dynamical properties of glasses — i.e. excess heat capacity [11–12], negative thermal expansion coefficient and the discrepancy between thermal and elastic Grüneisen constants [13–15], and positive temperature and negative pressure derivatives of the elastic moduli [15–17] — are well known. The characteristic behaviour of these properties in ULE glass is now discussed.

In fig. 2, the values of the Debye temperature, θ_D, deduced from the measured heat capacity, as a function of temperature are plotted. Also shown in fig. 2 is the 0 K value of θ_D, computed from the extrapolated values of the elastic moduli, which is 453 K. As can be seen, the thermal θ_D varies strongly with temperature in the range 300–1000 K. Unfortunately, experimental data for the specific heat of ULE glass at low temperatures are not available, and thus, a direct comparison between the thermal and elastic θ_D cannot be made.

The thermal expansion and the elastic properties of the solid may be correlated via the Grüneisen constant γ [4–6]. In fig. 3, the dots represent the values of γ deduced from the thermal expansion measurements on the one hand [2,18], while the line depicts the values calculated from the pressure derivatives [6]. The parameters entering this calculation are shown in table 5. As can be seen, the thermal γ is essentially zero in the range 100–1000 K, while the elastic γ is also constant in the

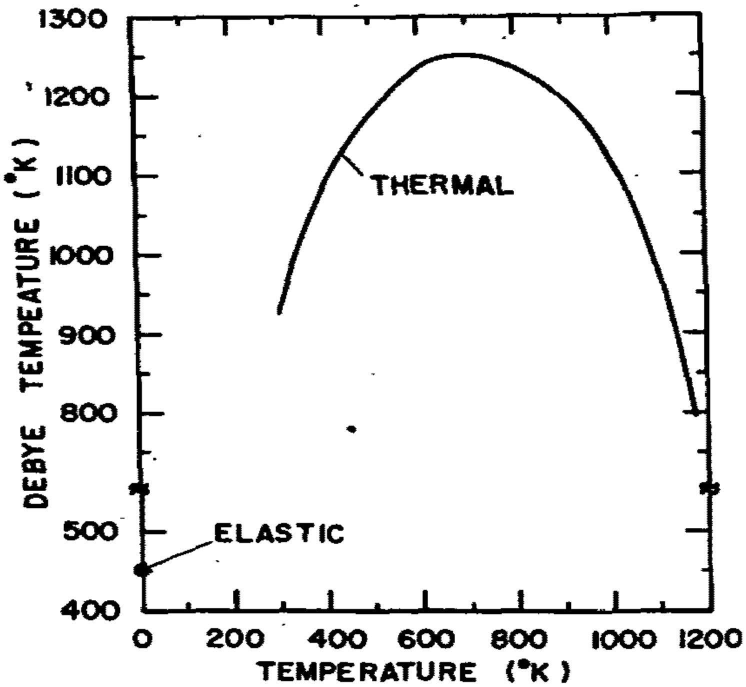

Fig. 2. Elastic and thermal Debye temperature as a function of temperature.

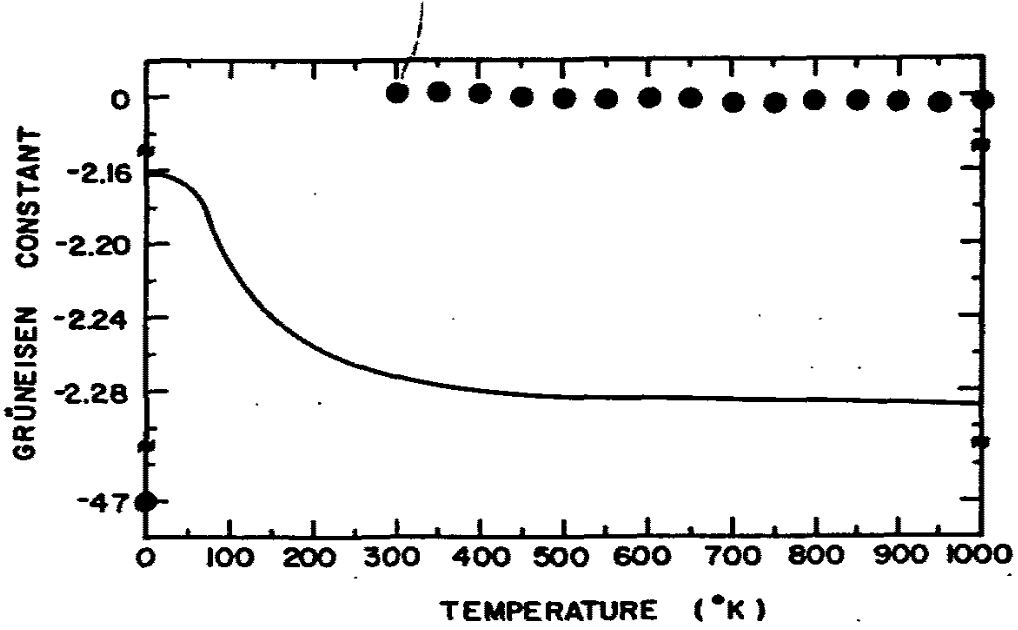

Fig. 3. Elastic and thermal Grüneisen constant as a function of temperature.

above range, but equals –2.26, which is in line with the value found for the elastic γ in other glasses [13–15]. The negative sign of the elastic γ is in qualitative agreement with the fact that the thermal expansion coefficient of ULE glass is either zero or negative, with a tendency to become more strongly negative at low temperatures [2,18]. On the other hand, there is an appreciable discrepancy between the magnitudes of the thermal and elastic γ. This is really not surprising, as the calculation of the elastic γ assumes that the heat capacity follows a Debye model, which is not valid in the case of glasses.

The anomalous properties of glasses mentioned above, i.e. positive temperature and negative pressure derivatives of the elastic moduli [15–17], also occur in ULE glass. Furthermore, the thermal γ becomes large and negative (≈–47) at very low temperature [18], as is the case for pure fused silica.

The composition of ULE glass, as well as that of a number of other glasses, contains a large fraction of fused silica. It should therefore be instructive to try and treat them as dilute alloys of fused silica, treating the additive as a defect in the host matrix. Several calculations of the effect of inclusion of point defects have been pub-

Table 5
Parameters entering into the calculation of the Grüneisen constant from the pressure derivatives.

Quantity	Unit	Value
density	kg/m^3	2205
molecular weight	kg/mol	0.06286
c_{11}(0 K)	10^{10} N/m^2	6.36
c_{44}(0 K)	10^{10} N/m^2	2.66

Table 6
Experimental and calculated values of $(\Delta B/B)/(\Delta V/V)$ in various silica-rich glasses.

	Additives (wt%)	$(\Delta B/B)/(\Delta V/V)$	
		experimental	calculated
Vycor	$96SiO_2, 3B_2O_3, 1N_2O{-}K_2O$	39.4	0.39
ULE	$92.6SiO_2, 7.4TiO_2$	−2.48	0.39
Pyrex	$80.6SiO_2, 13B_2O_3, 4Na_2O,$ $2Al_2O_3$	2.15	0.39

lished [19–21]. Applying a sphere-in-hole model to the glass [21], the change in the bulk modulus ΔB is related to the change in volume ΔV by

$$\frac{\Delta B/B}{\Delta V/V} = \frac{3B(B'G - BG')\,[3B + 4G - B(B'G - BG')]}{(3B + 4G)\,[(3B + 4G)(BG' - G) + 4G(B'G - BG')]}, \tag{1}$$

where the primes denote pressure derivatives, and all quantities on the right-hand side refer to pure fused silica. Associating V with the average volume per molecule, and denoting the molecular weight of SiO_2 by M, that of the additives by M_1, M_2, etc. the density deviation of the glass from that of fused silica by $\Delta\rho$, and the weight fraction of fused silica by w, that of the additives by w_1, w_2, etc. one obtains

$$\frac{\Delta V}{V} = 1 - \frac{1}{w}\left(1 - \frac{\Delta\rho}{\rho}\right)\left[1 - \frac{M}{w}\left(\frac{w_2}{M_1} + \frac{w_2}{M_2} + \dots\right)\right]. \tag{2}$$

Hence, the measured values of $(\Delta B/B)/(\Delta V/V)$ for various silica-rich glasses may be compared with the value computed from the right-hand side of eq. (1), the data being shown in table 6. As can be seen, the measured and calculated values disagree grossly, even their signs being opposite. It is thus obvious that a general thermodynamic model, based on strain energy considerations cannot account for the changes in the elastic moduli between pure fused silica and the silica-rich glasses.

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