The elastic moduli of tellurite glasses

S. HART

Ceramics, Glass and Phase Studies Division, National Physical Research Laboratory, Council for Scientific and Industrial Research, PO Box 395, Pretoria, South Africa

The elastic moduli of two tellurite glasses have been measured as functions of both temperature and pressure. The results indicate that these glasses are normal in their behaviour and this contrasts with the anomalous behaviour of silica-based glasses. The coordination number seems to be the parameter which decides the elastic characteristics of glasses.

1. Introduction

In 1924 Bridgman [1] made the remarkable discovery that the bulk modulus of pyrex glass decreased with pressure and noted that this was the first observation of such a phenomenon. This means that the higher the pressure the easier the glass becomes to compress, which is the inverse of common experience. In further studies [2-4]it became apparent that such behaviour was common to a number of glassy materials (notably silica-based) but not to all and that such abnormal behaviour could be changed to normal by the imposition of very high pressure. With the advent of high precision ultrasonic techniques, the study of the elastic behaviour of glasses has been revived and the results on a number of compositions have been reported [5-8].

Tellurium oxide has been shown to form glass [9] in melts containing up to 90 wt % TeO₂ with no other network formers and since tellurium is thought to be six-fold coordinated with oxygen in contrast to the tetrahedral bonding in SiO₂, it was thought of interest to examine the pressure and temperature variation of the elastic constants of two such tellurite glasses to establish which elastic anomalies, if any, would be present. Such glasses are typically of high density, have a high refractive

index (>2), good infrared transmission to $5 \,\mu m$ and high dielectric constants [9].

2. Experimental details

Two glasses were formed by melting the appropriate oxides in alumina crucibles followed by a quenching process. Glass A had a wt % composition of 50 TeO₂, 20 PbO and 30 WO₃ and Glass B 75 TeO₂, 21 PbO and 4 La₂O₃. The samples were light yellow in colour (perhaps from impurities in the TeO₂ [9]) and were free from visible imperfections. Specimens, approximately 1 cm² × 1 cm long cylinders, were cut with a diamond wire saw, then lapped and polished to give opposite faces plane and parallel to 0.01 mm for the ultrasound propagation. Densities were determined by the Archimedes method.

X cut and Y cut quartz transducers were bonded to the specimens using a 1:1 mixture of glycerine and pthalic anhydride. These were used with a commercial Panametrics system and the pulse echo overlap technique to measure the elastic moduli. The values were obtained at ambient conditions, at lower temperatures (to -50° C), using alcohol freezing mixtures and at high pressures (to 1.5 GPa), using a piston-cylinder apparatus and a method described previously [10].

T.	A	В	LI	Ε	I	Thermoelastic	properties c	of tellurite	glasses
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Sample	P (kg m ⁻³)	L (GPa)	G (GPa)	$\frac{\mathrm{d}L}{\mathrm{d}P}$	$\frac{\mathrm{d}G}{\mathrm{d}P}$	$\frac{\mathrm{d}L}{\mathrm{d}T}$ (GPa K ⁻¹)	$\frac{\mathrm{d}G}{\mathrm{d}T}$ (GPa K ⁻¹)
Glass A	6680	67.1	21.3	9.84	2.17	-0.014	- 0.0065
Glass B	6145	56.7	18.0	9.53	2.10	-0.0165	- 0.0068

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Figure 1 The pressure variation of the longitudinal elastic modulus for two tellurite glasses.

3. Results and discussion

The experimental results are shown in Figs. 1 to 4 and are summarized in Table I where L is the longitudinal and G the shear modulus.

The other moduli, bulk (B), Young's (E) and Poisson's ratio (σ) may be derived from these results by the usual equations for isotropic media, i.e.

$$B = \frac{3L - 4G}{3} \tag{1a}$$

$$E = \frac{3LG - 4G^2}{L - G} \tag{1b}$$

$$\sigma = \frac{L - 2G}{2L - 2G}.$$
 (1c)

The thermal expansion coefficients are rela-

Figure 3 The temperature variation of the longitudinal elastic modulus for two tellurite glasses.

tively small but have not been accurately determined. Over the restricted temperature range used, the corrections for length changes are negligible and the temperature variations are uncorrected. However, over the large pressure range the volume of the sample will change significantly and must be allowed for. The primary measurement is a frequency f, the inverse transit time through the sample, and a modulus M is then given by

$$M = 4\rho l^2 f^2 \tag{2}$$

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where ρ is the density and *l* the length.

It is usual practice to plot the natural modulus, $\rho_0 W^2 = 4\rho_0 l_0^2 f^2$, against pressure, where the subscript 0 denotes the ambient value. On differentiating the Equation 2 the true variation of M



Figure 2 The pressure variation of the shear elastic modulus for two tellurite glasses.



Figure 4 The temperature variation of the shear elastic modulus for two tellurite glasses.

TABLE II Second pressure derivatives of elastic moduli

Sample	$\frac{\mathrm{d}^2 L}{\mathrm{d}P^2}$ (GPa ⁻¹)	$\frac{\mathrm{d}^2 G}{\mathrm{d} P^2}$ (GPa ⁻¹)	$\frac{\mathrm{d}^2 B}{\mathrm{d} P^2}$ (GPa ⁻¹)
Glass A	- 0.38	- 0.24	- 0.06
Glass B	- 0.48	- 0.21	- 0.2

with respect to pressure at P = 0 is given by

 $\frac{\mathrm{d}M}{\mathrm{d}P} = \frac{\mathrm{d}}{\mathrm{d}P}(\rho_0 W^2) + \frac{M}{3B_\mathrm{T}} \tag{3}$

where $B_{\rm T}$ is the isothermal bulk modulus. The first term is the slope of the experimentally derived graph and the second term is the correction for length change with pressure. For correction purposes the difference between the adiabatic $B_{\rm S}$ and $B_{\rm T}$, typically less than 1%, can be ignored. The pressure derivatives in Table I have been calculated in this way.

The variation of the natural modulus with pressure shows curvature in all cases and is slightly concave to the pressure axis. The second derivative of a modulus with pressure can be corrected in the same way as outlined above by further differentiation of the modulus equation and is given by (at P = 0).

$$\frac{d^{2}M}{dP^{2}} = \frac{d^{2}(\rho_{0}W^{2})}{dP^{2}} + \frac{2}{3B_{T}}\frac{d(\rho_{0}W^{2})}{dP} + \frac{M}{9B_{T}^{2}} - \frac{M}{3B_{T}^{2}}\frac{dB_{T}}{dP}$$
(4)

and the corrected values are given in Table II.

The scatter of results leads to estimates of accuracy of 3% for the first derivatives but over 10% for the second derivatives and the values given in Table II should be read essentially to give "order-of-magnitude" information.

A comparison of the pressure and temperature variation of the bulk and shear moduli of the tellurite glasses with an "abnormal" glass, vitreous silica, and a normal glass, fluorozirconate, is given in Table III. It is at once apparent from the presented data that the tellurite glasses studied are "normal" in their behaviour and, as with all crystalline material, they stiffen with pressure increase and weaken with temperature increase.

Anomalous behaviour appears [12] to correlate well with low Poisson's ratio and low coordination number, e.g. the tetrahedrally bonded glasses SiO_2 and BeF_2 . The high value of Poisson's ratio together with the six-fold coordination of the tellurite glasses and normal elastic behaviour fits this pattern well.

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TABLE III Pressure and temperature derivatives of the shear, G, and bulk, B, moduli

				and the second		
Material	$\frac{\mathrm{d}B}{\mathrm{d}T}$ (GPa K ⁻¹)	$\frac{\mathrm{d}G}{\mathrm{d}T}$ (GPa K ⁻¹)	$\frac{\mathrm{d}B}{\mathrm{d}P}$	$\frac{\mathrm{d}G}{\mathrm{d}P}$	σ	
Silica [11] Fluorozirconate [12] Glass A Present Glass B Results	0.0118 - 0.0109 - 0.0074 - 0.0056	0.0043 - 0.0104 - 0.0068 - 0.0065	- 6.3 9.19 6.73 6.94	$-3.1 \\ 1.27 \\ 2.10 \\ 2.17$	0.17 0.29 0.27 0.27	