Pressure and Temperature Dependence of the Elastic Moduli of a Low-Expansion Lithium Aluminum Silicate Glass-Ceramic

KWANG YUL KIM and ARTHUR L. RUOFF

A THERMODYNAMIC pressure gage based on simultaneous measurements of specimen length and ultrasonic transit time under high pressure was developed by Ruoff *et al.*[1] Particular attention was given to a commercial glass-ceramic material* as a possible gage medium[2] because it has a near-zero thermal expansion coefficient at zero pressure and room temperature. In such a case the isothermal and adiabatic bulk moduli, B^T and B^s, are equal, a situation particularly advantageous for the gage. The relation between B^T and B^s is

$$B^s/B^T = 1+[(\beta^2 B^s T)/(\rho C_P)] = 1+\Delta \tag{1}$$

where β is the volume thermal expansion coefficient, T the absolute temperature, ρ the density, and C_P the specific heat at constant pressure. The supplier gives values of $\beta = 1.3\times10^{-8}/°K$ at $T = 298°K$, $C_P = 0.23$ cal/g°K, and $\rho = 2.504$ g/cm^3.

From these data and the measured B^s, Δ is found to be 0.13×10^{-8}. Therefore, the behavior of the elastic moduli at high pressures and temperatures was investigated. The pressure derivative of the thermal expansion coefficient at constant temperature, $(\partial\beta/\partial P)_T$, can be obtained from

$$(\partial\beta/\partial P)_T = -(\partial\kappa^T/\partial T)_P \tag{2}$$

where κ^T ($=1/B^T$) is the isothermal compressibility.

A pulse interferometer technique described elsewhere[3] was used to measure the transit times from which the velocities were calculated. Argon was the pressurizing medium, and the pressure was measured using a Heise gage with an accuracy of ±5 bars up to 4 kbars. The maraging-steel pressure vessel was placed inside a constant-temperature chamber.† Liquid nitrogen was the cooling agent, and the temperature was read by a Cu-Constantan thermocouple within ±1°K. The system for control of pressure and temperature is described in detail elsewhere.[4] The faces of the samples, which were nominally 2.5 cm long, were polished parallel to $\pm5\times10^{-5}$ cm. The lengths were measured using a lightwave micrometer.‡

Table I. Summary of Data for Low-Expansion Glass-Ceramics

Modulus	M_0 (kbars)	a	b (kbar^{-1})
C_{11}^s	1112±0.41	−16.92±0.48	−1.49±0.15
C_{44}	367.8±0.03	− 2.67±0.04	0.01±0.008
B^s	621.5±0.39	−13.36±0.46	−1.51±0.11

Transducers (10-MHz X-cut) were bonded to the specimens with glycerin. A nonaqueous grease,§ salol, and 910 cement‖ were used below, at, and above room temperature, respectively, for bonding the AC-cut crystal. The longitudinal and shear moduli, C_{11}^s and C_{44}, were calculated from the standard equations.[5] In terms of C_{11}^s and C_{44}, $B^s = C_{11}^s - {}^4/_3 C_{44}$[6]; s denotes the adiabatic value. Here $M(P,T)$ represents any elastic modulus as a function of pressure and temperature, and M is a quadratic expansion in terms of pressure:

$$M(P,T_0) = M_0(T_0) + a(T_0)P + b(T_0)P^2 \tag{3}$$

Similarly, the compressibility, $\kappa^T(P,T)$, is expanded in terms of temperature:

$$\kappa^T(P_0,T) = 1/(B^T(P_0,T)) = \kappa_0{}^T(P_0) + c(P_0)(T-273.2) + d(P_0)(T-273.2)^2 \tag{4}$$

Then,

$$\beta(P,T_0) = \beta(P_0,T_0) + \int_{P_0}^{P} \frac{\partial\beta}{\partial P}\Big)_{T_0} dP$$

$$\simeq \beta(P_0,T_0) - \int_{P_0}^{P} \frac{\partial\kappa^T}{\partial T}\Big)_{P_0} dP \tag{5}$$

Equation (5) was integrated numerically up to 4 kbars, using Eq. (4). Typical values at $P_0 = 2$ kbars and $T = 220°$ to 340°K are $\kappa_0{}^T(P_0) = (1.744\pm0.002)\times10^{-3}$/kbar, $c(P_0) = (-1.891\pm0.069)\times10^{-6}$/kbar °K, and $d(P_0) = (6.30\pm1.75)\times10^{-9}$/kbar (°K)^2. Hence, $(\partial\beta/\partial P)_T = -1.891\times10^{-6}$/kbar °K at $T = 273.2°K$.

Table I summarizes the moduli data for the glass-ceramic at $T_0 = 298°K$. Both a and c are negative, i.e. the glass-ceramic becomes softer with increasing pressure and stiffer with rising temperature, as is typical of noncrystalline glass materials.[7-10] This anomalous behavior is phenomenologically related to the small coefficient of thermal expansion, as explained by Anderson and Dienes[11,12] for vitreous silica.

The quite large β at several kilobars pressure contrasts with the very small β at atmospheric pressure, i.e. $\beta = 1.3\times10^{-8}/°K$ at 1 bar vs $\beta = 6.3\times10^{-6}/°K$ at 4 kbars and 298°K. The usefulness of the glass-ceramic as a reference length (essentially independent of temperature)[2] is diminished at high pressures.

These data suggest a macroscopic elastic instability (of B) when the pressure exceeds 16.3±0.5 kbars, assuming that the quadratic representation is exact. (Similarly, C_{11} is predicted to be zero at 22.2±0.5 kbars.) In other words, permanent densification should occur if the modulus is unstable. Such permanent densification is fairly common in silica glasses, as shown by Cohen and Roy.[13] To check this prediction, the lengths of specimens were determined at atmospheric pressure after they had been subjected to pressures of 15, 20, 25, and 30 kbars. The lengths were unchanged within experimental error (<0.01%). The apparent absence of permanent densification in this material suggests that B'''_0 is not negligible but rather is positive and large.

Since the pressure derivative of the bulk modulus in glass, B'_0, is commonly negative, it would be useful to investigate B''_0 and the possibility of macroscopic elastic instability in glasses to determine whether these properties are related to the permanent densification which occurs.

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The writers are with the Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853.

*CER-VIT, Owens-Illinois, Toledo, OH, is a lithium aluminum silicate consisting of a crystalline phase and a glass phase. The crystallite size is less than the wavelength of light, and the material is ≈75% crystalline. Further details have not been made available by the supplier.

†MK 6300, Delta Design, Inc., San Diego, CA.

‡The Van Keuren Co., Watertown, MA.

§Nonaq Stopcock Grease, Fisher Scientific Co., Fairlawn. NJ.

‖Eastman Kodak Co., Rochester, NY.

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