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Brillouin-scattering studies of $K_2Si_4O_9$ glass and melt up to 1000 °C

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The Brillouin-scattering technique has been used with glass plate samples and with glass sandwich assemblies to measure the acoustic velocities of $K_2Si_4O_9$ glass as a function of temperature up to 1000 °C. Results differ from those of the sodium silicate glass reported earlier in that the turning points of the velocity versus temperature curves for the potassium silicate glass are found not only at the strain point (466 °C) but also at the softening point (720 °C). Combined with the results of the 90° platelet- and 180° back-scattering geometry measurements, the refractive index n and equation of state of the glass and melt as a function of temperature were also determined.

Recently we used a sapphire/glass/sapphire-sandwich assembly to perform Brillouin-scattering experiments on a sodium silicate glass.[1] We measured the velocities of longitudinal and shear modes as functions of temperature up to 1000 °C and found that the trend of velocity versus temperature changes at the strain point (494 °C) but not at the softening point (720 °C). Combined with the results of 90°- and 180°-scattering geometry measurements, the refractive index n of the glass as a function of temperature was also determined. This technique provides a method not only to determine precisely strain and softening points for glasses, but also to study continuously the property changes of glasses and melts at various temperatures.

Interest in amorphous $K_2Si_4O_9$ stems from various practical and theoretical considerations. This composition has low glass-transition and melting temperatures and is difficult to crystallize. It provides a simplified model for SiO-rich glasses and liquids and many of its properties are well known. At 592 °C and atmospheric pressure (0.1 MPa), the low-pressure $K_2Si_4O_9$ phases exhibit an inversion similar to the α-β quartz, and its melt at 770 °C is more dense than its solid phase.[2] Furthermore, in its high-pressure phase there are five- and six-coordinated Si atoms,[3–5] and this coordinated configuration can be quenched in its glass from 1.9 GPa and 1200 °C.[6] The $K_2Si_4O_9$ glass used was synthesized at Institut de Physique du Globe, Paris, France.[7] The present paper reports our Brillouin-scattering studies on the glass at atmospheric pressure and high temperatures at the University of Hawaii.

Four experimental runs were performed on $K_2Si_4O_9$ glass samples. In the first two runs, the spectra of glass plate samples were measured in both our 90°- (or platelet- as defined by Zouboulis and Grimsditch[8]) and 180°-scattering geometries up to 735 °C. A turning point was found at 466 °C, and abnormal increases in values of both V_s and V_p were observed at 720 °C. Hence the strain and softening points were determined to be at those temperatures. In the third run, the sapphire-glass-sapphire sandwich assembly was used, and in the fourth run we replaced the two sapphire plates by cubic zirconia plates. Good agreement for all of the velocities (V_s, V_p, and nV_p) was found in both sandwich assemblies up to 1000 °C.

The measured velocities V_s, V_p, and nV_p for the $K_2Si_4O_9$ glass at various temperatures are shown in Fig. 1, and the calculated values of refractive index n, density ratio ρ/ρ_0 (assuming the electronic polarizability is constant as assumed previously by Xu and Manghnani), and bulk modulus K_s are shown versus temperature in Fig. 2. As in the case of the sodium silicate glass,[1] there is no hysteresis and the changes in the glass are reversible even when the glass is heated beyond the softening point. Unlike the earlier results with the sodium silicate glass, the turning points in the curve of velocity versus temperature for the $K_2Si_4O_9$ glass have been found at not only its strain point (466 °C), but also at its softening point (720 °C) for the velocity of longitudinal mode (V_p). The values of these properties and their temperature dependences are listed in Table I.

For comparison, the viscosity η at various temperatures has been determined by using a glass sample from the same batch as the Brillouin specimen. We have $\log_{10}\eta = 1.49 + 2875.74/(T - 512.16)$, where η and T are taken as poise and kelvin.[9] Thus the strain point ($\eta = 10^{14.5}$ P) and softening point ($\eta = 10^{7.5}$ P) can be determined as 460 °C and 718 °C, in good agreement with the temperatures (466 °C and 720 °C) determined from our Brillouin-scattering measurements. As a comparison with these values, we have extrapolated the viscosity versus temperature data listed in *The Handbook of Glass Physical Properties*[10] and calculated strain and softening points as ~449 °C and ~683 °C, respectively. The calculated refractive η (1.4838) is in good agreement (less than 1%) with previous results (Table I).

Velocities behave similarly over the temperature range examined, increasing with temperature up to 466 °C and

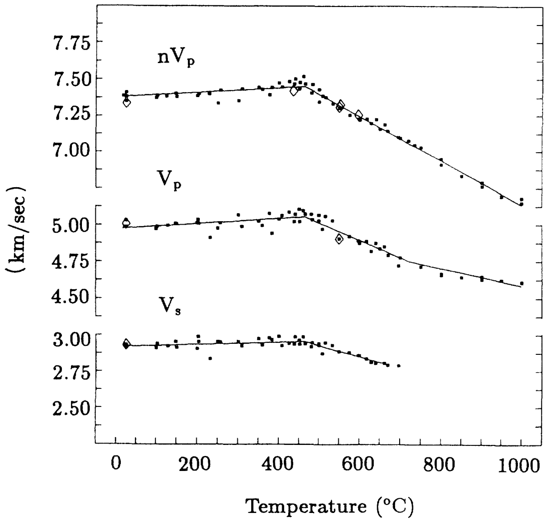

FIG. 1. Acoustic velocities V_s, V_p, and nV_p as functions of temperature in $K_2Si_4O_9$ glass. Solid squares represent observed data for the heating cycle; the open diamonds represent cooling. The solid lines are the best-fit curves calculated with the parameters listed in Table I.

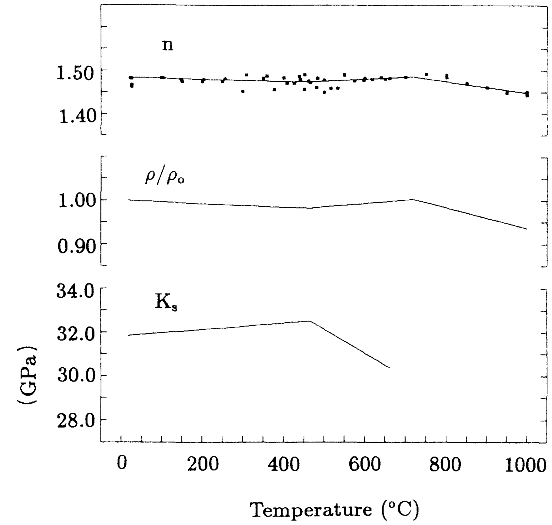

FIG. 2. Calculated values for refractive index n, density ratio ρ/ρ_0, and adiabatic bulk modulus K_s as functions of temperature in the $K_sSi_4O_9$ glass.

then decreasing with increasing temperature. The refractive index n and the density ratio ρ/ρ_0 decrease slightly at first from room temperature to the strain point (466 °C), then decrease again. Between 466 °C and 720 °C, the glass appears to undergo a subtle increase in density that was not seen in earlier thermal expansion measurements.[12] From the equation of state thus determined, the average volume thermal expansion coefficient β can be easily determined (Table I).

Following the relationship

$$K_s=\rho(V_p^2-\tfrac{4}{3}V_s^2)\ ,$$

the adiabatic bulk modulus K_s of the glass can be determined as 31.83 GPa at 25 °C where the Archimedean density ρ_0 at room temperature (2.381 ± 0.001) is in good agreement with the values given by Manghnani.[13] Temperature dependences ($\partial K_s/\partial T$) are 1.48×10^{-3} below 466 °C and 1.10×10^{-2} above 4.66 °C; $\partial K_s/\partial T$ is larger than the only available reported data[13] of 0.6×10^{-3} below 200 °C. Above 720 °C, K_s can no longer be determined, because the Brillouin-scattering signal of the shear mode becomes too weak to detect.

The parameters listed in Table I in solid state (below 466 °C) are almost an order smaller than those in the melt states (above 720 °C), and the state between the two temperatures seems a transition zone.

The bulk modulus of a liquid can be split into a

TABLE I. Experimental results and a comparison with reported data for $K_2Si_4O_9$ glass. An asterisk indicates thermal expansion ($=\beta$).

	Units	Values	T dependences			Earlier reported data
		at 25 °C	below 466 °C	between 466 and 720 °C	above 720 °C	
V_s	(km/s)	2.9182	7.851×10^{-5}	-78.11×10^{-5}		V_s: 2.881[a] (at 25 °C)
V_p	(km/s)	4.9721	11.86×10^{-5}	-118.8×10^{-5}	-59.89×10^{-5}	V_p: 4.935[a] (at 25 °C)
nV_p	(km/s)	7.3781	15.12×10^{-5}	-152.6×10^{-5}	-152.6×10^{-5}	
n		1.4838	-2.196×10^{-5}	4.459×10^{-5}	-13.29×10^{-5}	n: 1.495,[b] 1.4924,[c] 1.4937[d] (at 25 °C)
K_s	(GPa)	31.83	1.482×10^{-3}	-11.03×10^{-3}		K_s: 31.62[a] (at 25 °C); $\partial K_s/\partial T$: 60×10^{-5} ($T<200$ °C)[a]
V/V_0			4.061×10^{-5}*	-8.884×10^{-5}*	25.91×10^{-5}*	β: 3.5×10^{-5} ($T<200$ °C)[d]; 3.34×10^{-5} ($T<200$ °C)[a]; 1×10^{-5} ($T<400$ °C)[e]

[a] Reference 12.

[b] Reference 2.

[c] Reference 10.

[d] Reference 11.

[e] Reference 13.

configurational and a vibrational part.[14] For silicate liquids, available data generally do not show a significant influence of the configurational state on vibrational properties. For instance, this is the case for the vibrational heat capacity.[15] With Brillouin spectroscopy, we determine directly elastic properties at very high frequencies, i.e., their vibrational part only. The possibility of direct measurements thus allows us to detect a dependence of these properties on the configurational state through the change in the slope of the curves at the glass transition. As could be expected, the existence of temperature-induced configurational changes in the liquid results in a greater vibrational compressibility. We obtained similar results for a window glass, with the exception of the second kink shown by the curve of Fig. 1 at 720 °C, which was not observed. Comparison of the data for window glass and K_2SiO_4 thus shows subtle differences in compression mechanisms that depend specifically on chemical composition.

Low-temperature extrapolation of ultrasonic measurements[16] yields a relaxed speed of sound of 1970 m/s for K_2SiO_4 liquid at 1000 K, which compares with the value of 500 m/s obtained in this study for the glass V_p. The difference between these numbers represents the configurational speed of sound, which is thus three times greater than the vibrational part. As such, it is not significantly affected by the slight dependence of vibrational properties on the configurational state. The compression mechanisms of silicate melts have important geophysical consequences since they determine the density at pressure. The present data show how they are essentially determined by configurational factors. More data are thus needed to understand the way they depend on chemical composition.

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