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PRESSURE AND TEMPERATURE STUDIES OF GLASS PROPERTIES RELATED TO VIBRATIONAL SPECTRA

By

MURLI H. MANGHNANI

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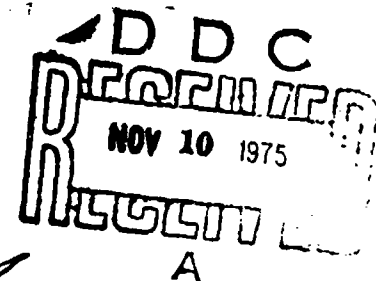
FINAL REPORT

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PRESSURE AND TEMPERATURE STUDIES OF GLASS PROPERTIES
RELATED TO VIBRATIONAL SPECTRA

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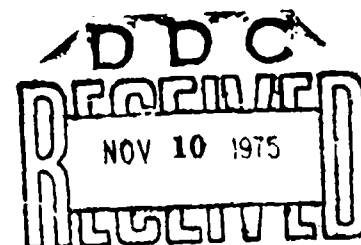
FINAL REPORT

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George V. Woodland
Date: 1 December 1974

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SECTION I
ULTRASONIC ATTENUATION IN ALKALI SILICATE
GLASSES BETWEEN 80 and 300°K

Introduction

The acoustic loss spectra for almost all glasses having tetrahedral structure exhibit very interesting features at low temperatures [1-8]. For instance, a large attenuation peak is observed for fused silica at 48°K. Anderson and Bommel [1] suggested that the observed attenuation in the low temperature region is related to the transverse motion of oxygen atoms in the Si-O-Si bridge. The oxygen atom can assume any of two or more equivalent positions around the straight angle. The displaced oxygen atom requires a small activation energy (1340 cal/mole) to return to its original position, thereby causing ultrasonic loss. Based on the same structural concept but assuming longitudinal rather than transverse motion of the oxygen atom in the Si-O-Si bridge, Strakana [2,3] developed a theory to explain the loss peaks for SiO_2 , GeO_2 , B_2O_3 , and As_2O_3 glasses. Although both of the theories offer a good explanation for acoustic loss they do not explain any of the other anomalous properties of fused silica such as negative thermal expansion, positive temperature derivatives of elastic moduli, negative pressure derivatives of elastic moduli, and excess specific heat. Moreover, neither theory is compatible with the X-ray data on oxygen angle distribution [9]. Recently, Vukceovich [9] has developed a new 'two minima potential' model to explain most

of the anomalous properties of fused silica including anomalous acoustical properties, the model being in agreement with the X-ray data. According to this model, the vitreous network has a tendency to assume certain values of the Si-O-Si angle. These angles are grouped around two crystalline phases, namely α and β phases, separated by a potential barrier. The activation energy required for a rotation from α to β phase is very close to the activation energy calculated for dielectric and acoustic loss. The Vukceovich theory thus offers very good explanation for the relaxation mechanism.

A review of the work on glasses shows that not much attenuation work has been done in alkali silicate glasses at ultrasonic frequencies. The results of ultrasonic attenuation at 30 MHz in M_2O-SiO_2 glasses (where M is lithium, sodium, or potassium) are presented here in the temperature range of 80 to 300°K. Three relaxation mechanisms are possible for alkali silicate glasses-- the low temperature structural relaxation involving a small activation energy caused by oxygen atom vibration in the Si-O-Si bridge [1,2], the alkali ion-migration-type relaxation occurring at relatively higher temperature [4,10,11,15], and the relaxation caused by phase transformation near the phase transition temperature, T_g [12,15]. However, in the present temperature range and frequency, only structural relaxation and some part of the alkali-migration is observed.

Experimental Methods

Alkali silicate glasses, synthesized at the National Bureau

of Standards, Washington, D. C., and fused silica (Corning Glass Works code 7940) were used in this study. Table 1 contains the chemical composition of the glasses along with their annealing temperatures. Right circular cylinders of 1.9-cm diameter and ~ 1.2 -cm length were cored, and the end faces of these specimens were polished so that they were parallel to within 1 part in 10^4 and flat to $\pm 1/2$ wavelength of sodium light.

A modified pulse-echo-overlap method developed by Chung et al. [13] was used for measuring ultrasonic attenuation at low temperatures. The block diagram of the experimental setup is shown in Figure 1. This method is essentially a pulse-echo method with a few variations in the velocity measuring technique. In this method, the pulse repetition frequency is divided by 100 or 1000, and the RF pulse generator is triggered at the divided frequency. However, the oscilloscope is triggered externally by the repetition rate generator so that a cycle-for-cycle match of all echoes is observed. Selective intensification of a pair of echoes is effected with a two-channel 'strobe' delay generator contained within the attenuation recorder (Matec model 2470) and with output to the Z-axis of the scope. These strobes simultaneously open two gates within the attenuation recorder so as to select the video forms of the same two echoes from the echo train. Following peak detection, the logarithmic difference of the two echoes is measured and displayed on the X-Y recorder. In practice, attenuation measurements have an accuracy of 1% and a resolution of 0.2 db. The method allows a continuous

Table 1. Chemical composition, density and annealing temperature of the alkali silicate glasses. Also included are data for fused silica (CGW 7940) [1, 3, 8]

Glass	Composition Mole %		Density	Annealing Temp. °C
	H ₂ O	SiO ₂		
CGW 7940 (fused silica)	0	100	2.207	1020
<u>Li₂O-SiO₂ Glasses</u>				
K-199	20	80	2.282	
K-154	25	75	2.306	
K-171	28	72	2.322	
K-163	30	70	2.331	
K-162	35	65	2.348	
K-197	35	65	2.349	
<u>Na₂O - SiO₂ Glasses</u>				
K-110	10	90	2.288	575
K-111	15	85	2.336	540
K-112	20	80	2.383	520
K-113	25	75	2.431	510
K-114	30	70	2.474	495
K-115	35	65	2.495	475
K-116	40	60	2.520	450
<u>K₂O - SiO₂ Glasses</u>				
K-196	15	85	2.337	
K-194	20	80	2.380	
K-192	25	75	2.422	

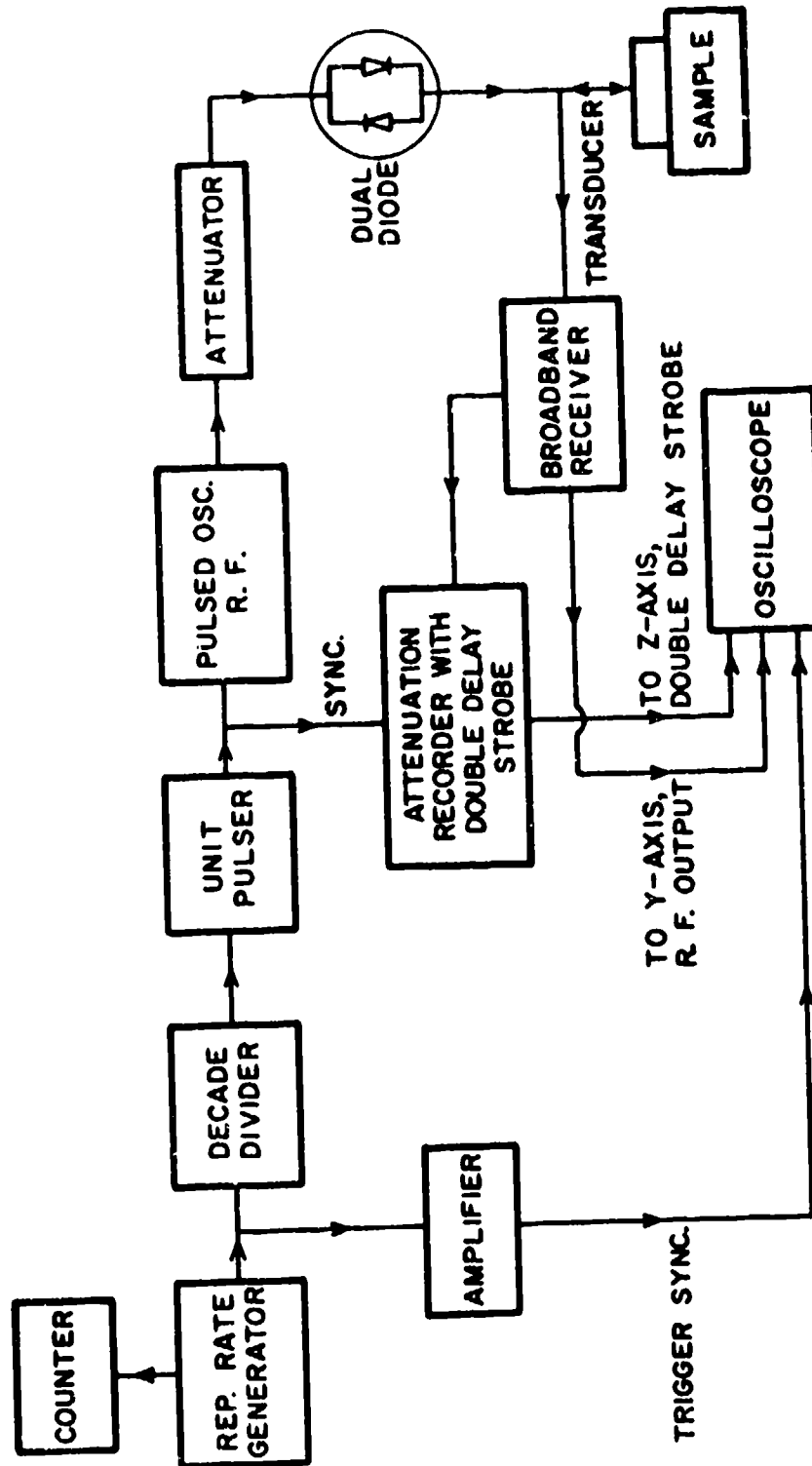


Fig. 1. Electronics setup used in ultrasonic velocity and attenuation measurements (from reference [14]).

monitoring of the attenuation as a function of temperature, and resolving any relaxational phenomena within the absorption spectra.

Twenty MHz, X- and Y-cut, 6-mm diameter, quartz transducers were bonded to the specimen with either Nonaq (Fisher Scientific Co.) or DC 200 silicon fluid (Dow Corning) having viscosity of 12,500 cs.

Results and Discussion

The composition dependence of 30 MHz longitudinal, α_p , and shear attenuation, α_s , was investigated in 17 alkali silicate glasses at room temperature. Of these, seven were $\text{Li}_2\text{O}-\text{SiO}_2$, seven $\text{Na}_2\text{O}-\text{SiO}_2$, and three $\text{K}_2\text{O}-\text{SiO}_2$ glasses. The results of attenuation versus the M_2O content, listed in Table 2 and plotted in Figure 2, show that both the α_p and α_s generally increase with the M_2O content. As compared with the nearly linear composition-dependence of α_p , the α_s varies curvilinearly with composition, the concavity of the curves being toward the composition-axis. Among the glasses studied, the $\text{Na}_2\text{O}-\text{SiO}_2$ glasses have highest α_p and α_s values. For given M_2O content, α_p value increases in the order of $\text{Na} > \text{K} > \text{Li}$ glasses, whereas the α_s value increases in the order of $\text{Na} > \text{Li} > \text{K}$ glasses (Fig. 2). The best-fit equations relating the linear dependence of α_p and quadratic dependence of α_s to the M_2O content, M , respectively, for the three types of alkali silicate glasses are listed in Table 3.

Table 2. Composition Dependence of 30 MHz Longitudinal and Shear Attenuation in Alkali Silicate Glasses

Glass No.	Composition, Mole %		Attenuation, db/cm		$\frac{\alpha_s}{\alpha_p}$
	H ₂ O	SiO ₂	Longitudinal (α_p)	Shear (α_s)	
<u>Li₂O-SiO₂ glasses</u>					
K-199	20	80	3.50	6.97	1.99
K-154	25	75	4.03	7.60	1.89
K-171A	28	72	4.82	8.95	1.86
K-163	30	70	5.11	9.12	1.78
K-170	32	68	5.06	10.18	2.01
K-162	35	65	5.37	11.01	2.05
K-197	35	65	5.36	10.90	2.03
<u>Na₂O-SiO₂ glasses</u>					
K-110	10	90	2.60	5.40	2.08
K-111	15	85	3.70	7.61	2.06
K-112	20	80	4.31	9.22	2.14
K-113	25	75	5.12	11.95	2.33
K-114	30	70	6.12	14.89	2.43
K-115	35	65	7.05	17.75	2.52
K-116	40	60	7.90	20.21	2.56
<u>K₂O-SiO₂ glasses</u>					
K-196	15	85	2.51	5.35	2.13
K-194	20	80	3.27	7.09	2.17
K-192	25	75	3.88	8.90	2.29

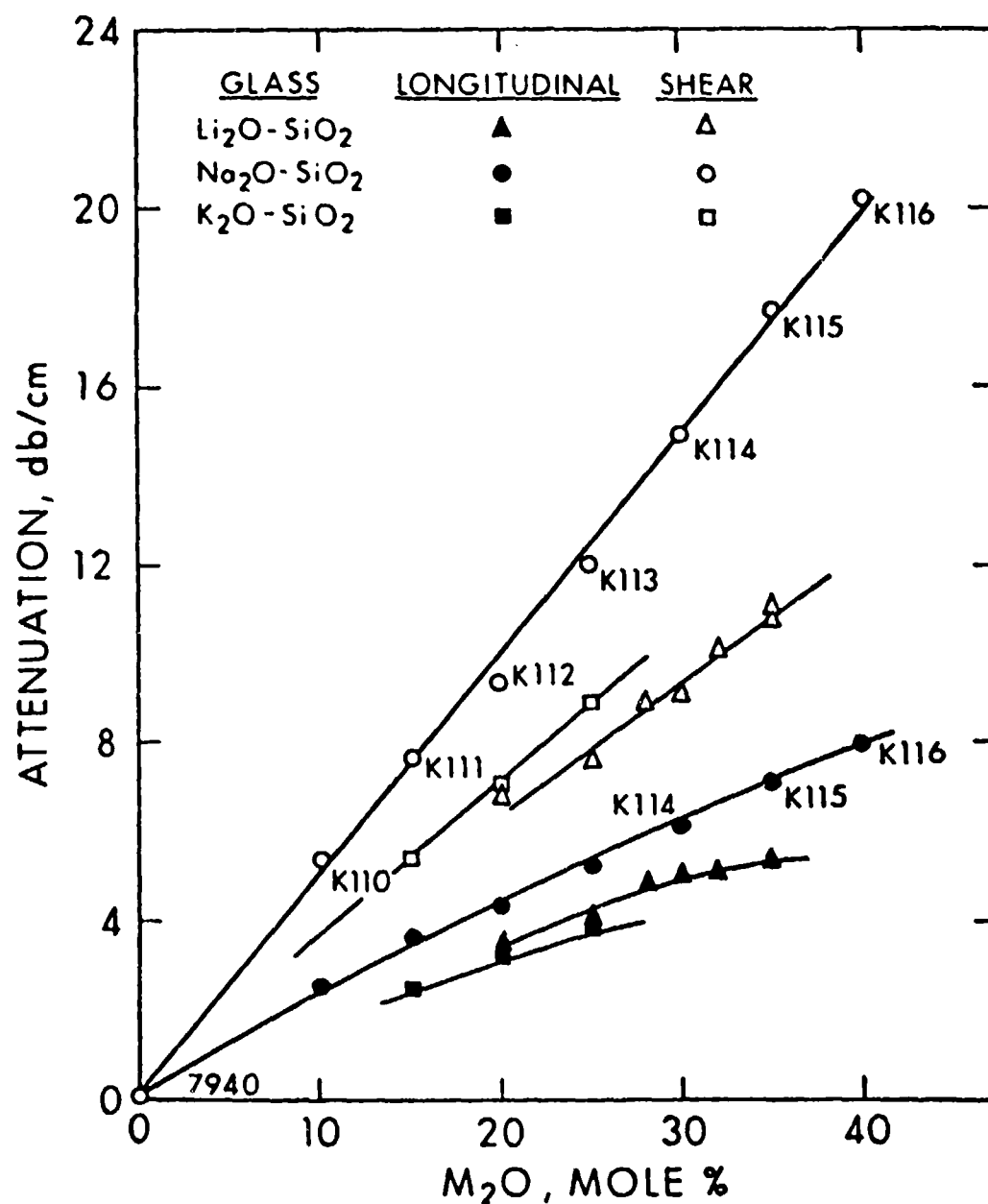


Fig. 2. Composition dependence of ultrasonic attenuation of longitudinal and shear waves in alkali silicate glasses at room temperature.

Table 3. Results of the analyses of data in Table 2, expressed as $\alpha_p = A + BM$ and $\alpha_s = C + DM + EM^2$, where M is mole % M_2O . Units of α_p and α_s coefficients A and C: db/cm; B and D: db/cm mole %; and E: db/cm (mole %) ²

Glass Type	Best-Fit Values		Correlation Coefficient	Best-Fit Values			Standard Deviation
	A	B		C	D	E	
Li_2O-SiO_2	1.040	0.127	0.969	6.350	-0.116	0.0071	0.26
Na_2O-SiO_2	0.898	0.174	0.998	1.845	0.314	0.0038	0.32
K_2O-SiO_2	0.480	0.137	0.998	0.550	0.299	0.0014	0

For the alkali silicate glasses investigated, the ratio α_s/α_p ranges between 2 and 2.6, being ~ 2 for $\text{Li}_2\text{O}-\text{SiO}_2$ containing 10 mole % Li_2O , slightly decreasing and then increasing with increasing M; for the $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ glasses, the ratio monotonically increases from ~ 2.1 (for 15 mole % K_2O) to ~ 2.6 (for 40 mole % K_2O).

The frequency (f) dependence of α_p was studied in the 10 to 90 MHz range for the 10 alkali silicate glasses in which M_2O content varies from 15 to 40 mole %. Results are given in Table 4. The relationship between α_p and f for the three alkali silicate glasses, containing 25 mole % M_2O , is shown in Figure 3A. Figure 3B is a similar α_p versus f plot for the three types of alkali silicate glasses for which the frequency dependence of α_p was studied in the maximum frequency range.

As can be seen in Figure 3, relationship between α_p and f is linear, within experimental errors, for all the glass compositions studied. By assuming an exponential relationship of α_p to f (as was commonly found), $\alpha_p = kf^{\chi}$, where k and χ are constants, we calculated χ to be ~ 1 (1.00 ± 0.09) for all the glass compositions. This then excludes any possibility of Akhieser-type phonon-phonon interaction loss, which would have yielded values of $\chi \gg 1$. The attenuation α_p was also found to be independent of the power of the ultrasonic generator (within receiver linearity), which shows that the attenuation is not hysteresis-type loss.

The temperature dependence of α_p and α_s at 30 MHz, investigated in the range of 80 to 300°K for seven lithium and three

Table 4. Frequency dependence of longitudinal attenuation (α_p) in alkali silicate glasses; k and χ are the best-fit values for the assumed relation $\alpha_p = k f^\chi$

Glass No. and Composition*	α_p , db/cm						k db. sec/cm	χ
	10	30	Frequency, Mhz		90	110		
			50	70				
<u>Li₂O-SiO₂ glasses</u>								
K-199 (20)	1.30	3.50	6.17	8.60	11.90	14.43	-0.917	1.011
K-154 (25)	1.79	4.03	6.80	10.31			-0.651	0.882
K-163 (30)	1.99	5.11	8.75	12.79			-0.662	0.948
K-162 (35)	2.05	5.37	9.11	12.71			-0.636	0.941
<u>Na₂O-SiO₂ glasses</u>								
K-113 (25)	1.75	5.12	9.07	13.23	16.35		-0.794	1.03
K-115 (35)	2.54	7.05	11.75				-0.546	0.948
K-116 (40)	3.0	7.90	13.2				-0.441	0.914
<u>K₂O-SiO₂ glasses</u>								
K-196 (15)	83	2.51	4.45	6.63	9.53	11.49	-1.207	1.105
K-194 (20)	1.01	3.27	5.72	8.46			-1.087	1.088
K-192 (25)	1.24	3.88	6.63				-0.948	1.041

* H₂O content of glass is given in parentheses.

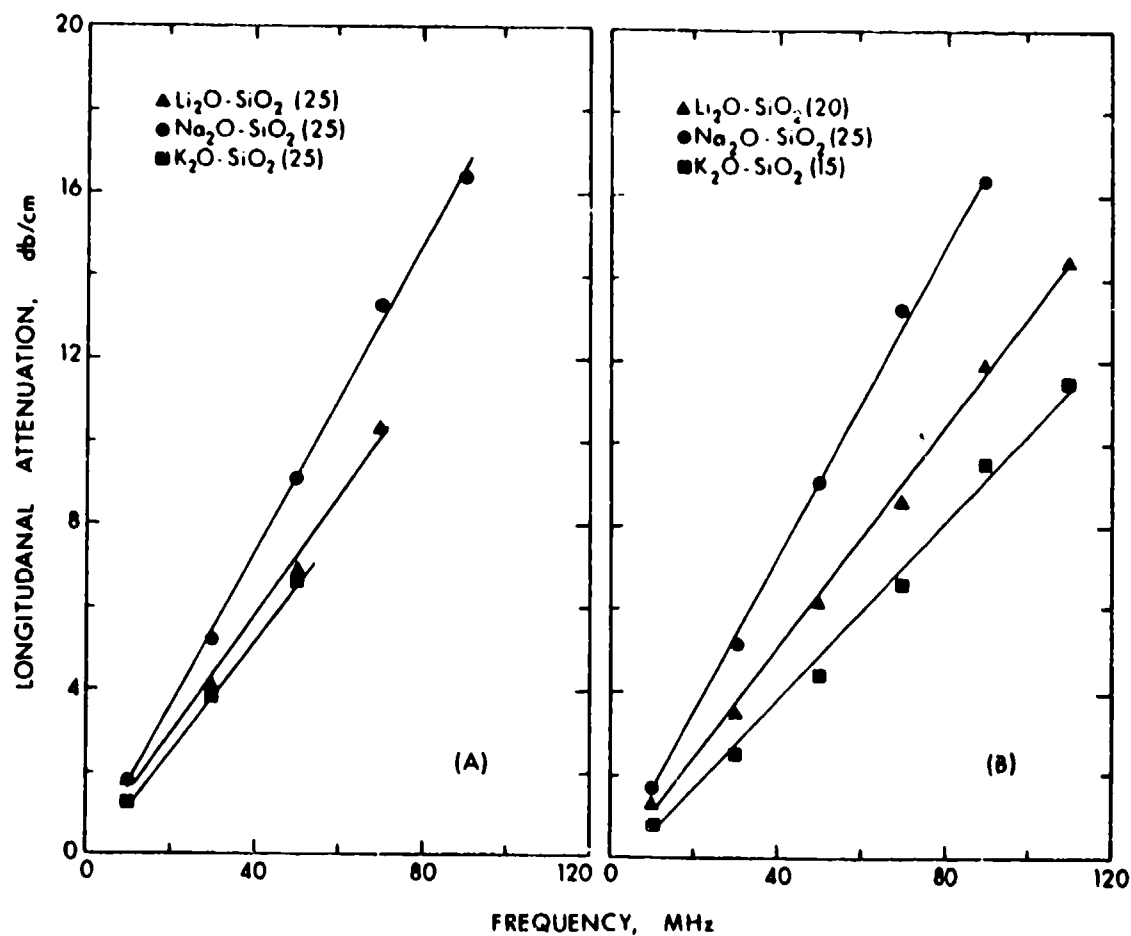


Fig. 3. Frequency dependence of longitudinal wave attenuation in alkali silicate glasses at room temperature.
 (A): alkali silicate glasses containing 25 mole % M_2O ;
 (B): the three types of alkali silicate glasses for which frequency dependence of α_p has been examined in maximum frequency range.

potassium silicate glasses, are presented in Figures 4-7. Similar data for seven sodium silicate glasses were reported in an earlier paper [14] and are reproduced in Figure 8. One of the important findings of the previous study of $\text{Na}_2\text{O-SiO}_2$ glasses [14] was the broadening of the low-temperature attenuation peak (observed at $\sim 47^\circ\text{K}$ in fused silica) with increasing Na_2O content, which was explained as being caused by either thermal broadening [1], or a wider distribution of activation energies, or superposition of the high-temperature alkali ion relaxation, the latter possibility existing at least for the low-silica glasses. The other important finding was the shift of peak attenuation temperature toward higher temperature with increasing Na_2O content (see Fig. 8). In view of this and the limited temperature range (80 to 300°K) of previous and present studies, the low-temperature attenuation peaks below 80°K could not be observed for the low-alkali glasses. In the study of $\text{Na}_2\text{O-SiO}_2$ glasses [14], the attenuation peak above 80°K was observed for only those which contained 20 or higher mole % Na_2O (Fig. 8). In the present study of the lithium silicate glasses, the corresponding low-temperature attenuation peak is not observed for any of the glasses (Fig. 4); the attenuation peaks presumably occur between 47 and 80°K , more so near 47°K , which is outside the temperature range of our study. In Figure 5, showing temperature dependence of α_p for the three potassium silicate glasses, we observe an attenuation peak at $\sim 103^\circ\text{K}$ for the K 192 glass which contains 25 mole % K_2O . The temperature dependences of α_s for

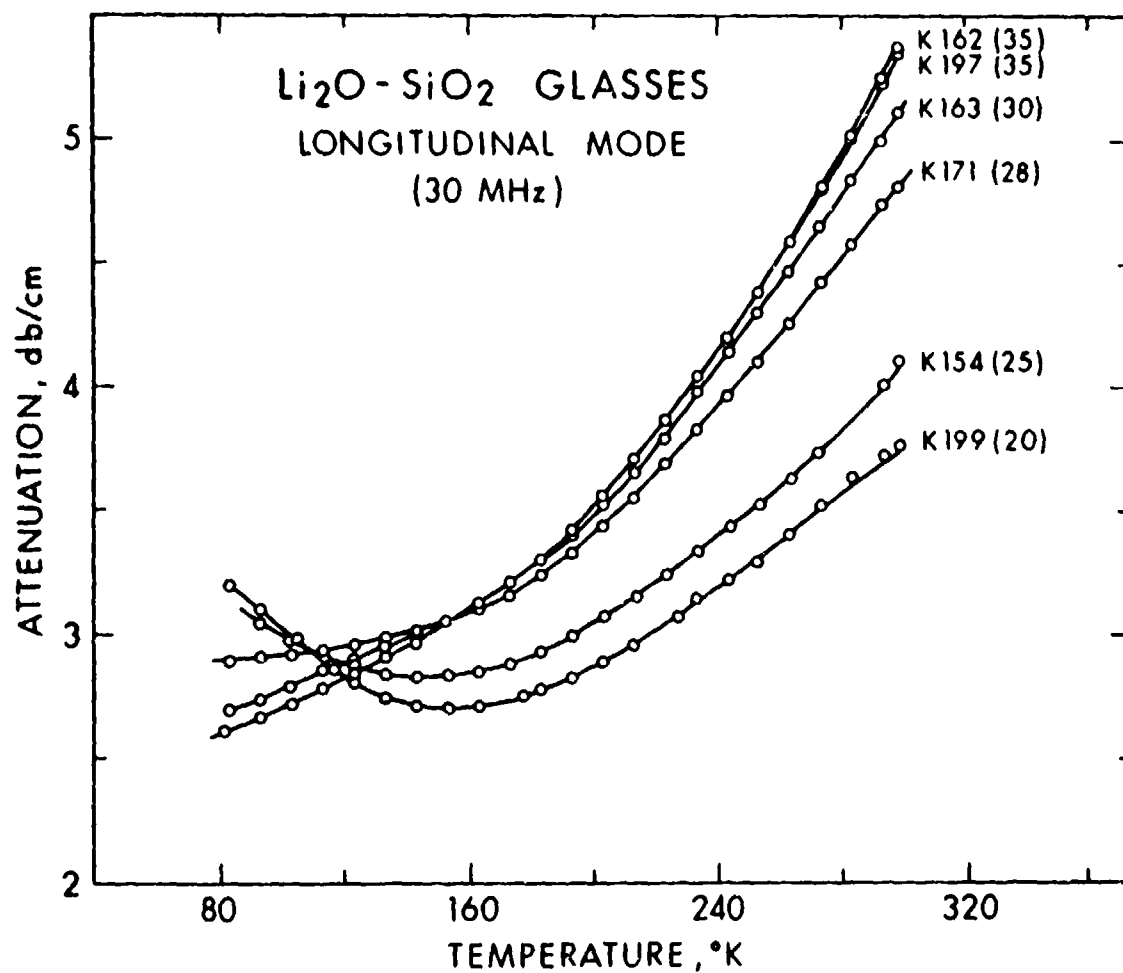


Fig. 4. Temperature dependence of longitudinal wave attenuation in Li₂O-SiO₂ glasses.

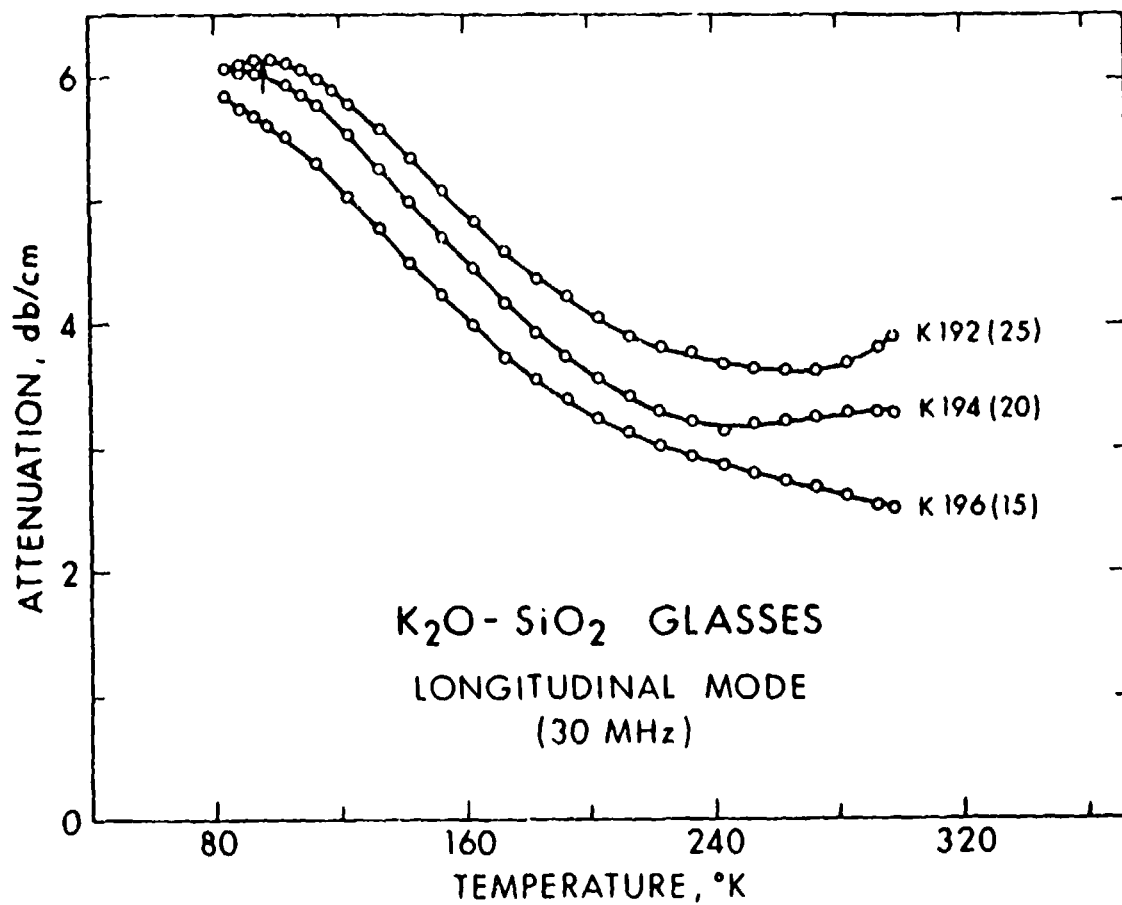


Fig. 5. Temperature dependence of longitudinal wave attenuation in K₂O-SiO₂ glasses.

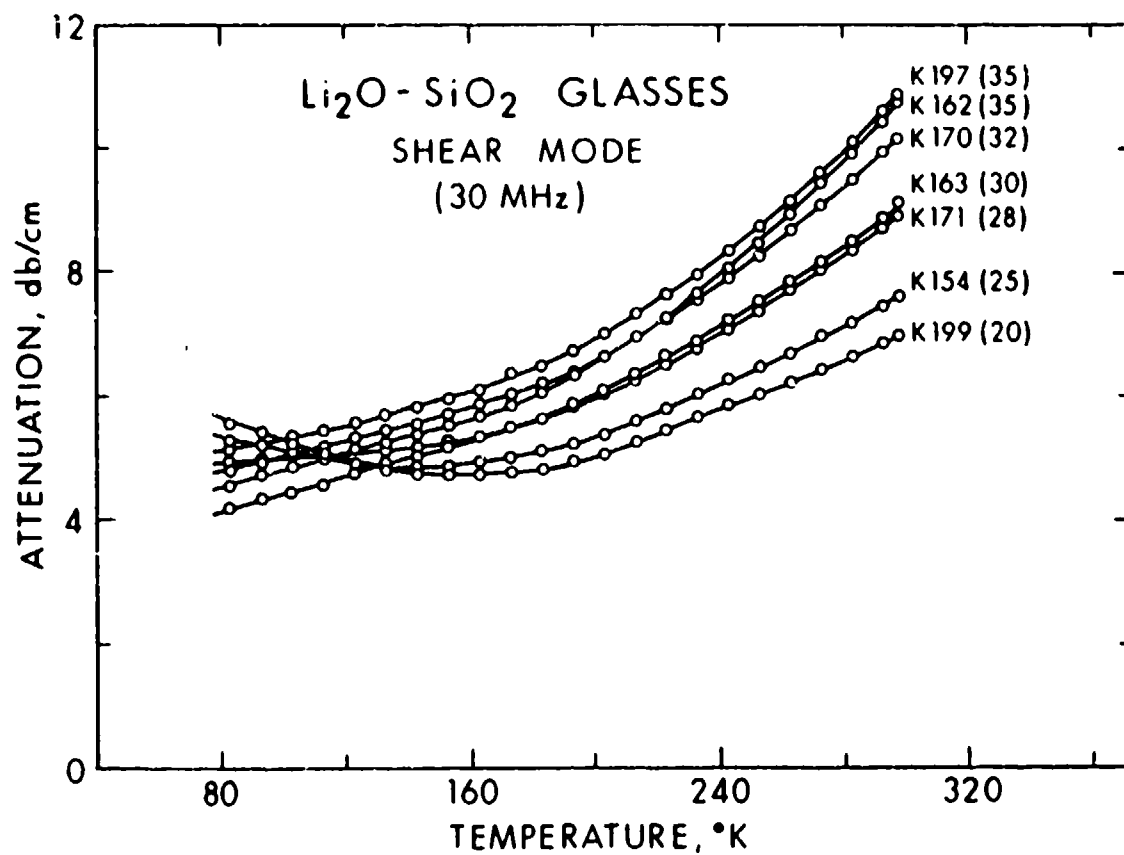


Fig. 6. Temperature dependence of shear wave attenuation in Li₂O-SiO₂ glasses.

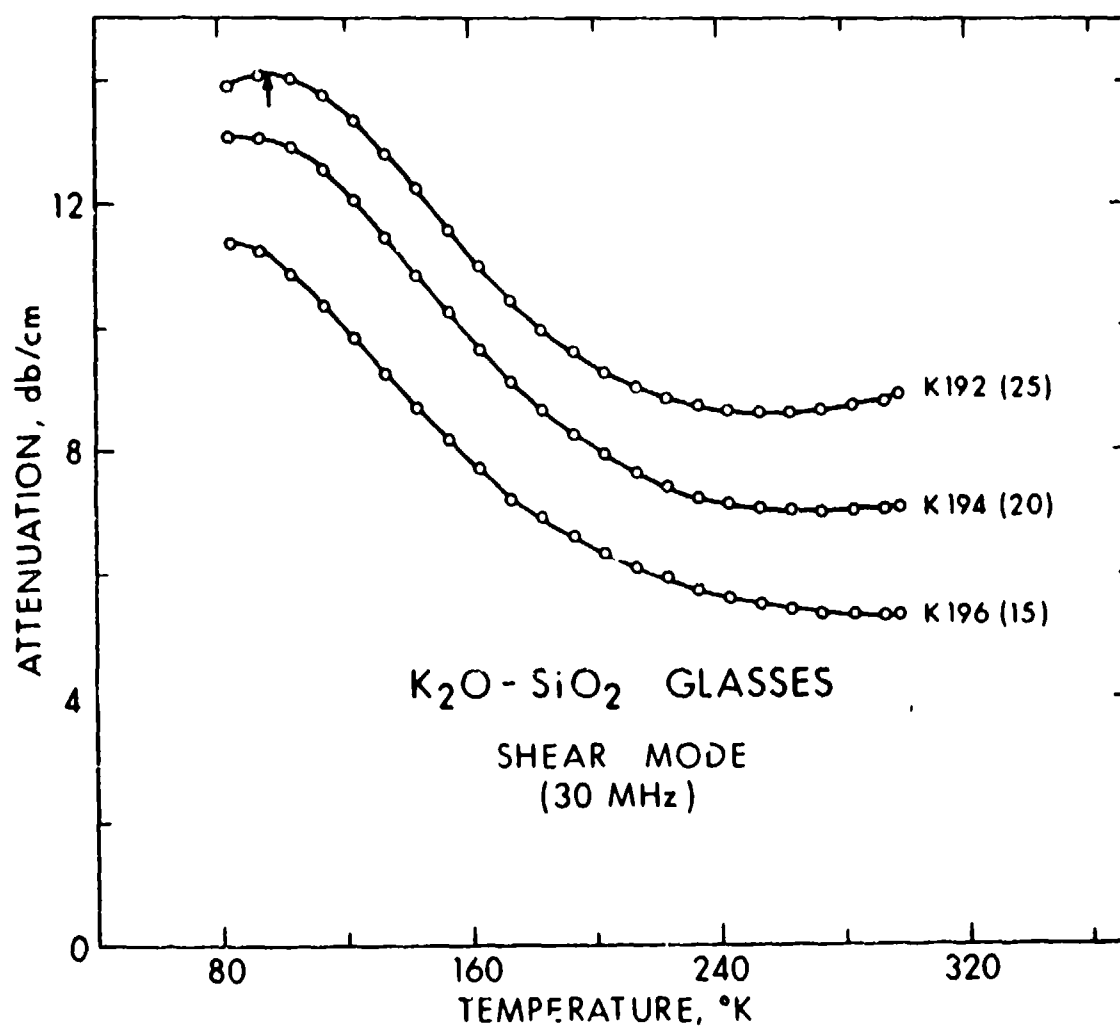


Fig. 7. Temperature dependence of shear wave attenuation in K_2O-SiO_2 glasses.

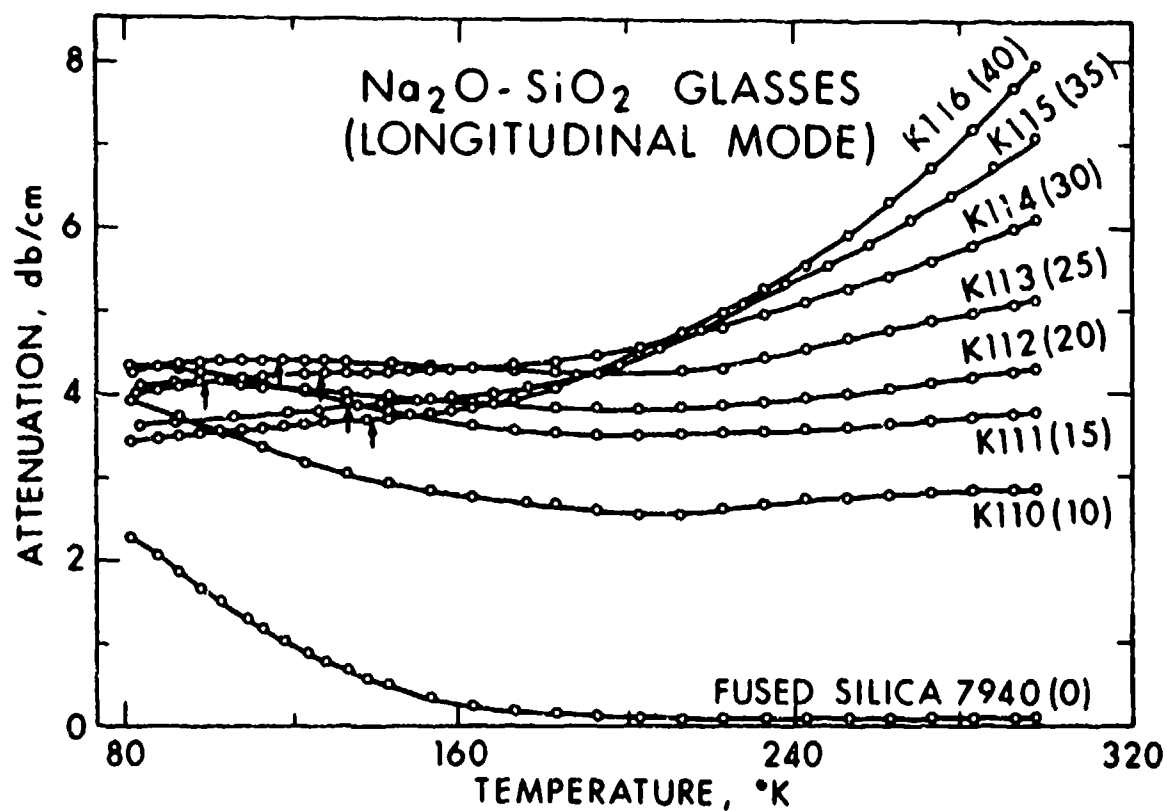


Fig. 8. Temperature dependence of longitudinal wave attenuation for $\text{Na}_2\text{O}-\text{SiO}_2$ glasses; the values in parentheses denote mole % Na_2O .

these glasses (Figs. 6 and 7) follow the same trends as their temperature dependence of α_p (Figs. 4 and 5). A comparison of the trends in the α_p versus temperature curves for the K_2O-SiO_2 glasses (Fig. 5) indicates that the attenuation peak for the K 194 (20 mole % K_2O) and K 196 (15 mole % K_2O) glasses would be observed at temperatures below 80°K.

In order to examine the low-temperature structural relaxation, it would be of interest to find if the attenuation peak in K_2O-SiO_2 glasses shifts in a trend similar to that in Na_2O-SiO_2 glasses, by extrapolating the attenuation versus temperature curves. Because of the broadening of the peak, there is significant uncertainty in predicting the peak attenuation temperatures in this manner, especially for the low alkali glasses, as was the case for the glasses K 110 and K 111 (Fig. 8) [14]. Nonetheless, an examination of Figures 4 and 6 indicates a strong support for our previous finding that the peak attenuation temperature does shift toward higher temperature with increasing alkali content. This point may be further tested by conducting experiments in the 50 to 80°K range.

In order to examine the low-temperature structural relaxation mechanism present in fused silica and also in alkali silicate glasses, it would be of interest to compute, from the frequency dependence of peak sound attenuation temperature, the most probable activation energies for different alkali concentrations. As attenuation data at different frequencies are not yet available, no attempt can be made to calculate the activation

energies. However, from the shift of the peaks to higher temperatures, it is suggested that in some systematic fashion the activation energy is increasing with increasing alkali content.

Although the high temperature alkali relaxation seems to obscure the low temperature side of the attenuation curve, at least for low-silica glasses, it is clearly indicated by the magnitude of the attenuation curves that the magnitude of the peak attenuation (see Figs. 4, 6 and 8), and thus the relaxation strength, decreases with increasing alkali concentration. However, this behavior is not observed in potassium silicate glasses (Figs. 5 and 7), which could be because of a relatively slower decrease of K ion relaxation strength with temperature. Phenomenologically, the attenuation process can be interpreted on the basis of a structural model in which the alkali molecule modifies the existing Si-O-Si bridge. This modification may result in the formation of a weaker Si-O-M bond or an unbridged Si-O bond. The former type of modification would impede the movement of the oxygen atoms, and since the movement of the oxygen atom is assumed to be the cause of attenuation, this would result in a decrease in attenuation accompanied by an increase in the activation energy. The latter structure would, however, make no contribution to the attenuation α . In other words, loosening of the structure occurs with the addition of alkali ions. This is compatible with the internal friction data at low frequencies [10].

Figure 9 shows the temperature dependence of longitudinal attenuation in the three types of alkali silicate glasses containing 25 mole % M_2O . It appears that the effect of alkali ions on the peak attenuation temperature is increasing in order of $Li > K > Na$. No comments can be made on the intensity of structural relaxation peak as it is hard to resolve from alkali ion relaxation contribution.

At 30 MHz, one would expect to observe alkali ion relaxation as temperature-dependence of longitudinal and shear attenuation increases with increasing alkali content. The effect of composition on the internal friction at much lower frequencies for Na_2O-SiO_2 system, studied by Forry [10], shows an increase in intensity and decrease in peak temperature as the Na_2O content increases. In light of this and our results (Figs. 4-5 and 9), it may be concluded that the high temperature attenuation peak would shift toward lower temperature, accompanied by a decrease in the activation energy, with increasing alkali content. A similar shift in the high temperature relaxation is also observed for the Na_2O-GeO_2 system [12]. However, because of the limited temperature data, no comparative study on the strength of alkali ion relaxation can be made. It is desirable to investigate further the composition dependence of alkali ion relaxation at high temperatures and low frequencies in the alkali silicate glasses.

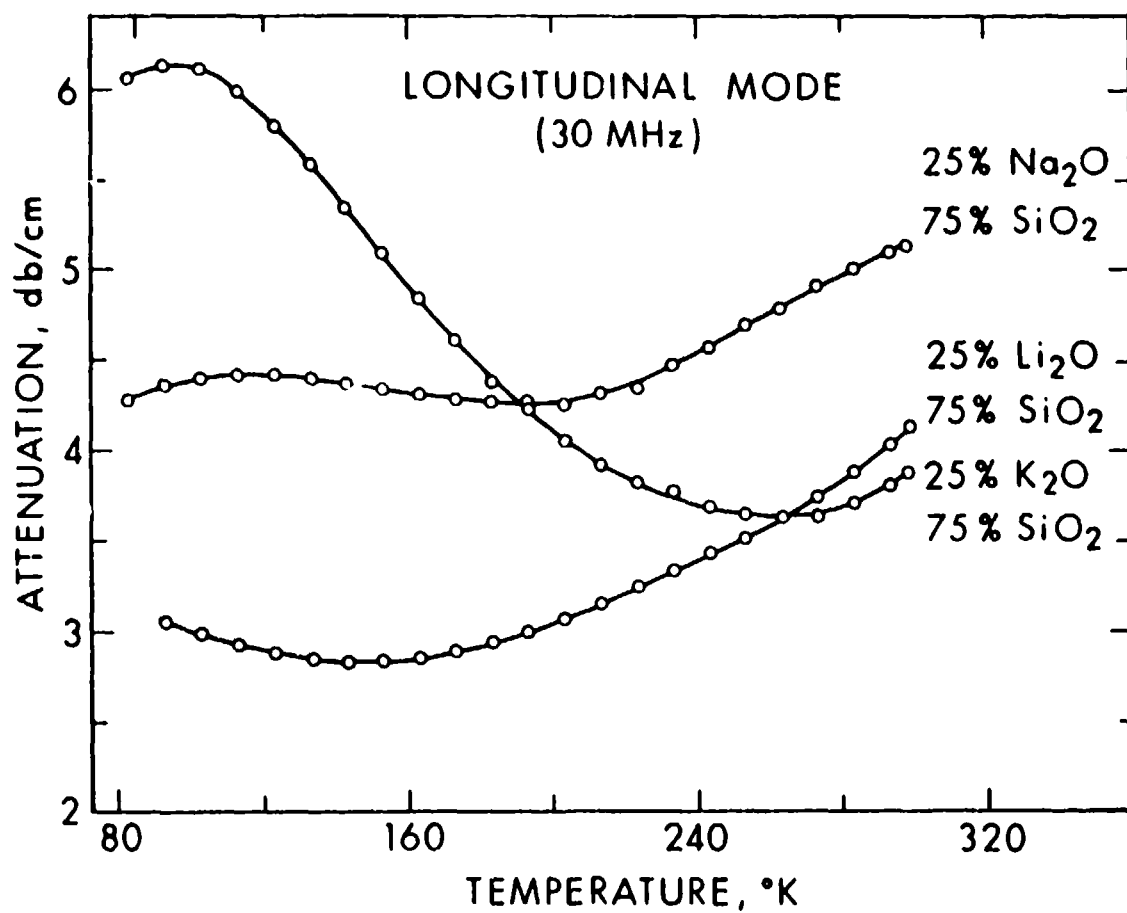


Fig. 9. Temperature dependence of longitudinal wave attenuation for the alkali silicate glasses containing 25 mole % M₂O.

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SECTION II

ELASTICITY OF ALKALI SILICATE GLASSES

The elastic parameters of the 21 glasses in the systems $\text{Li}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-SiO}_2$, and $\text{K}_2\text{O-SiO}_2$ with systematic compositional variation (M_2O content varying from 10 to 55 mole %) have been investigated both at ambient pressure and temperature as well as to 5 kbar and to 300°C . The results are given in Table 1. In a given $\text{M}_2\text{O-SiO}_2$ glass system, the elastic properties can be related to the M_2O content or $\text{SiO}_2/\text{M}_2\text{O}$ ratio. The composition-dependence of the moduli is shown in Figures 1 through 3. The $\text{Li}_2\text{O-SiO}_2$ glasses behave differently from the $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$ glasses in that the addition of M_2O causes an increase in Young's and shear moduli in the former and a decrease in the latter. The bulk modulus, however, increases in all three cases. It appears that Li_2O does not weaken the silica structure, in contrast to the role of Na_2O and K_2O .

Figures 4 and 5 show the relationships between dK/dP , $d\mu/dT$, dK/dT , and composition. The present results confirm the earlier findings that the anomalous behavior of silica-based glasses (decrease of moduli with pressure) can be quantitatively related to the SiO_2 content. Figure 6 shows a relationship between $(d \ln \mu/dP)$ versus Poisson's for the alkali silicate glasses, which compares well with the other tetrahedrally coordinated glasses like SiO_2 , GeO_2 , and BeF_2 [1].

Table 1 Elastic parameters of the alkali silicate glasses at ambient conditions, and their pressure and temperature derivatives

Glass #	Composition (mole %)	ρ (gm/cm ³)	V_p (km/sec)	V_s (km/sec)	K (kb)	ν (kb)	Z (kb)	γ	β (mb ⁻¹)	$(\frac{dK}{dP})^\dagger$	$(\frac{d\nu}{dP})^\dagger$	$(\frac{d\beta}{dP})^\dagger$	$(\frac{d\gamma}{dT})^\ddagger$ (kb/deg)	$(\frac{d\beta}{dT})^\ddagger$ (kb/deg)
<u>Li₂O-SiO₂ Glasses</u>														
K199	20.0	2.282	6.033	3.724	408.8	316.4	754.5	.192	2.44	0.51	-1.20	.018 (-0.015)	.034 (-0.038)	
K194	25.0	2.306	6.105	3.727	432.2	320.3	770.6	.203	2.31	1.39	-0.660	-0.551 (-0.055)	-.084 (-0.091)	
K171A	29.0	2.322	6.149	3.722	449.2	321.6	778.9	.211	2.23	2.94	-0.194	.014 (-0.005)	-.129 (-0.132)	
K171B	28.0	2.322	6.149	3.720	449.6	321.3	778.5	.211	2.22	3.59	-0.153	-.052 (-0.065)	-.079 (-0.079)	
K198	28.0	2.322	6.153	3.720	450.4	321.4	778.9	.212	2.22	3.42	-0.173	-.043 (-0.058)	-.084 (-0.083)	
K163	30.0	2.331	6.176	3.715	460.2	321.8	782.9	.216	2.17	3.22	0.183	-.067 (-0.094)	-.089 (-0.097)	
K170	32.0	2.341	6.224	3.706	478.1	321.5	788.0	.225	2.09	3.96	0.384	-.112 (-0.125)	-.022 (-0.106)	
K162	35.0	2.346	6.302	3.708	497.6	326.4	803.4	.231	2.01	4.82	0.523	-.075 (-0.101)	-.112 (-0.120)	
K197	35.0	2.349	6.294	3.736	493.4	327.9	805.3	.228	2.03	5.34	0.551	-.136 (-0.159)	-.112 (-0.117)	
<u>Na₂O-SiO₂ Glasses</u>														
K110	10.0	2.288	5.565	3.478	339.5	276.8	652.9	.180	2.94	-2.16	-1.93	.063 (-0.063)	.004 (-0.004)	
K111	15.0	2.336	5.457	3.355	345.1	262.9	629.0	.196	2.90	-0.22	-1.15	.030 (-0.030)	-.021 (-0.021)	
K112	20.0	2.383	5.392	3.251	354.6	251.8	610.8	.213	2.82	1.55	-0.46	-.017 (-0.017)	-.041 (-0.041)	
K113	25.0	2.431	5.347	3.159	371.6	242.6	597.7	.232	2.69	3.18	0.06	-.060 (-0.060)	-.058 (-0.058)	
K114	30.0	2.474	5.348	3.101	390.3	238.0	593.3	.247	2.56	4.11	0.39	-.097 (-0.098)	-.077 (-0.076)	
K115	35.0	2.495	5.361	3.038	410.2	230.2	581.8	.264	2.43	4.51	0.57	-.122 (-0.133)	-.107 (-0.106)	
K116	40.0	2.520	5.401	2.993	434.1	225.8	577.3	.278	2.30	5.83	0.84	-.182 (-0.182)	-.108 (-0.108)	
<u>K₂O-SiO₂ Glasses</u>														
K196	15.0	2.337	5.065	3.042	311.3	216.2	526.7	.218	3.22	1.41	-0.982	.041 (-0.039)	-.005 (-0.004)	
K194	20.0	2.380	4.935	2.881	316.2	197.5	490.4	.242	3.16	3.35	-0.247	.006 (-0.006)	-.019 (-0.019)	
K192	25.0	2.422	4.846	2.759	323.1	184.3	464.5	.260	3.10	4.13	-0.195	-.024 (-0.026)	-.034 (-0.034)	

ρ = density; V_p = compressional wave velocity; V_s = shear wave velocity; K = bulk modulus; ν = shear modulus; E = Young's modulus; γ = Poisson's ratio; β = compressibility.

†: Values determined at 25°C.

††: Values shown were determined in the 25-100°C interval; values shown in parentheses were determined in the 25-200°C interval.

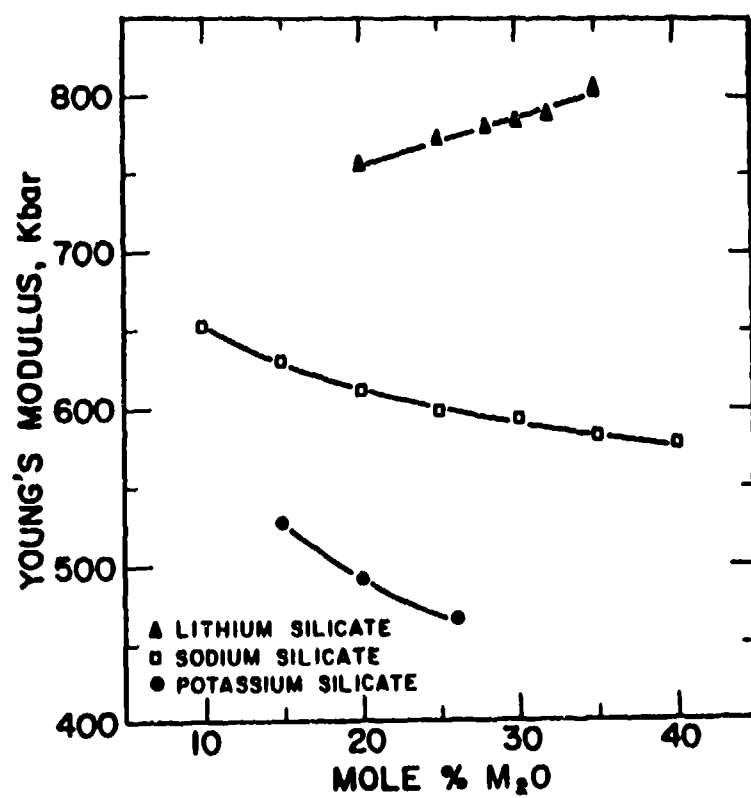


Fig. 1. Young's modulus versus mole % M_2O in alkali silicate glasses.

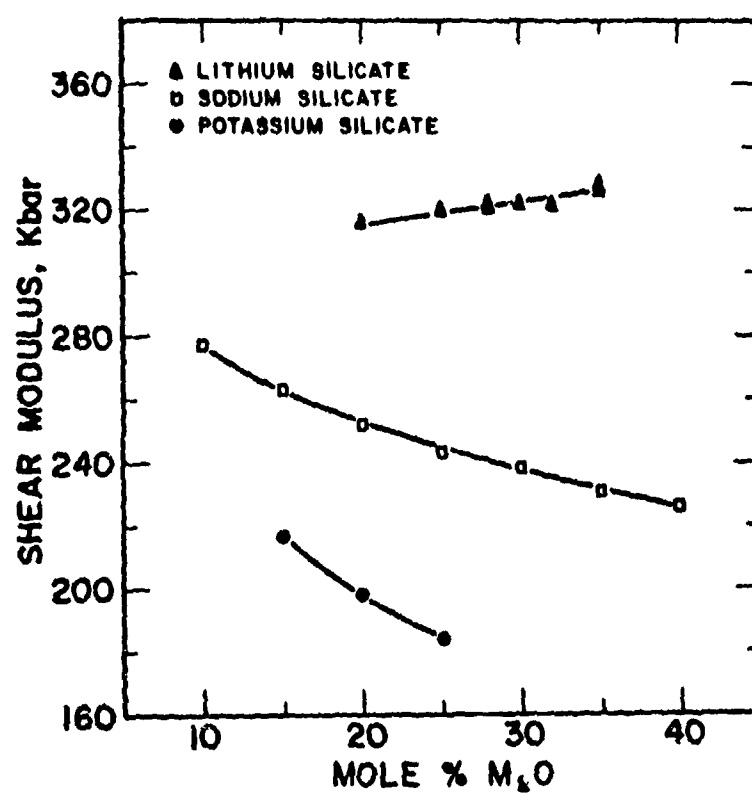


Fig. 2. Shear modulus versus mole % M_2O in alkali silicate glasses.

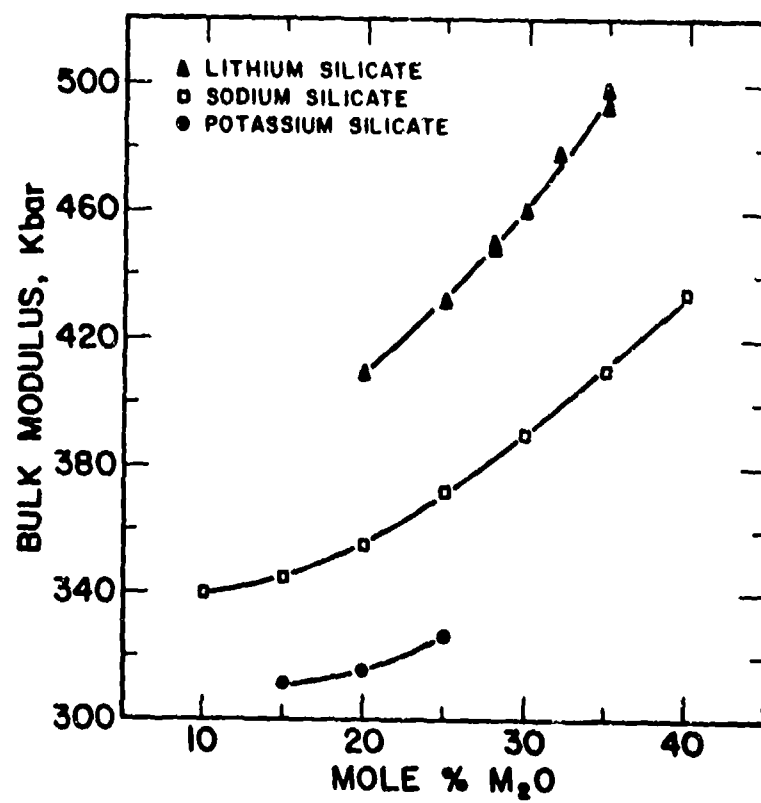


Fig. 3. Bulk modulus versus mole % M_2O in alkali silicate glasses.

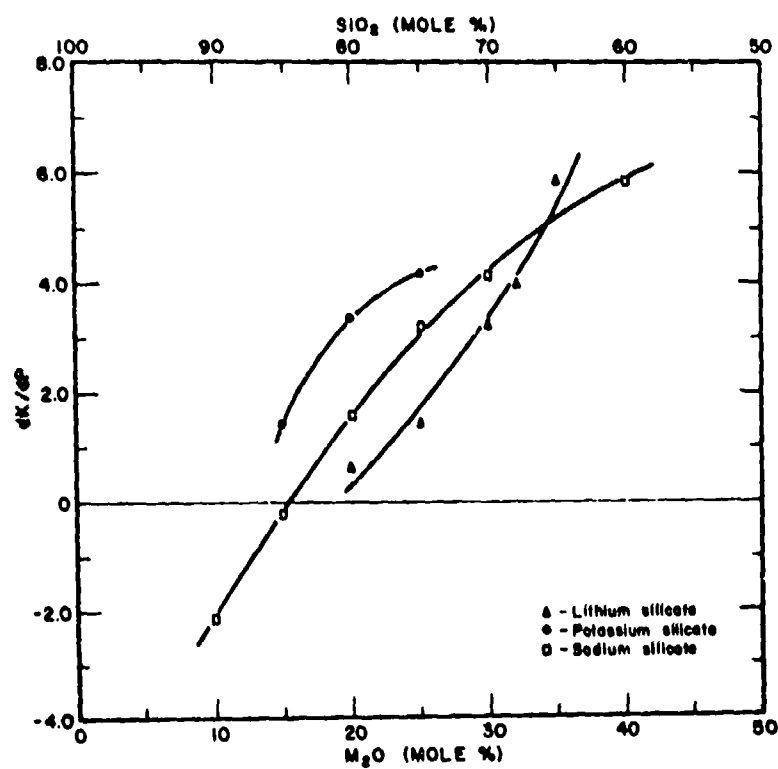


Fig. 4. dK/dP versus mole % M_2O in several M_2O-SiO_2 glasses.

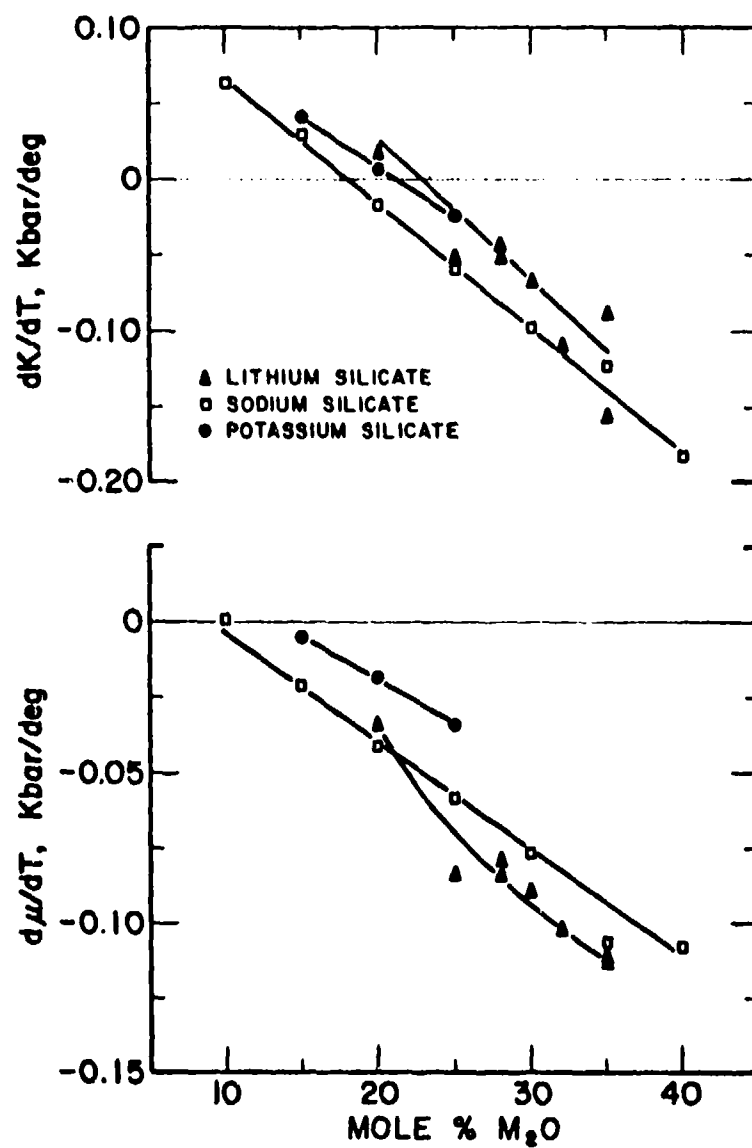


Fig. 5. dK/dT and $d\mu/dT$ versus mole % M_2O in several M_2O-SiO_2 glasses.

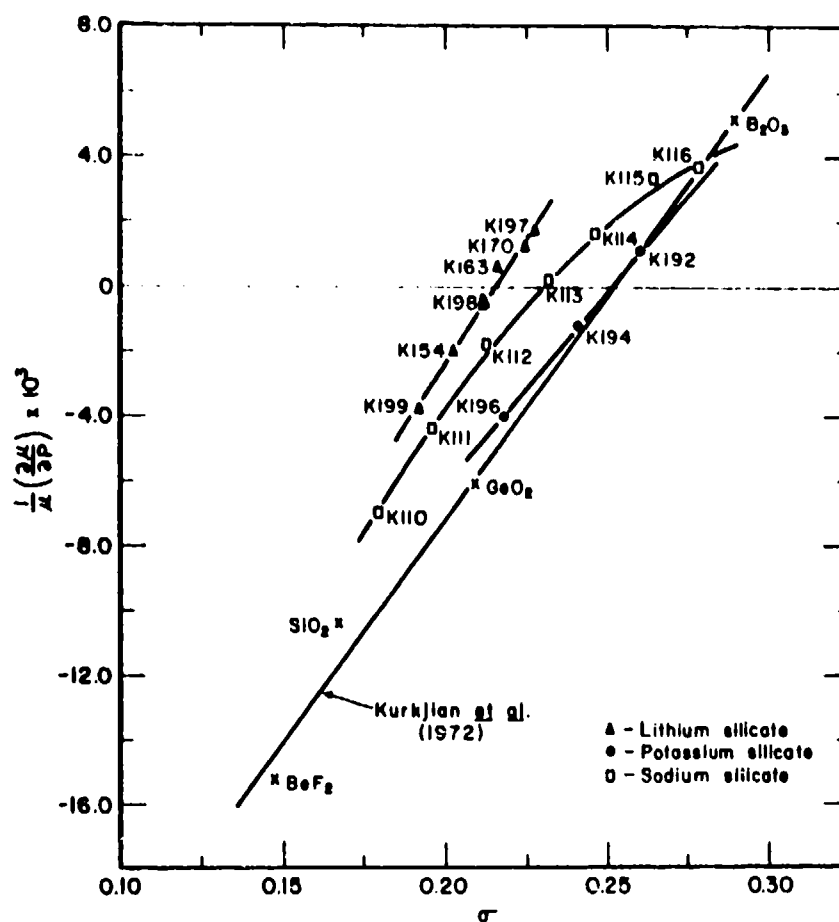


Fig. 6. $\frac{1}{\mu} \left(\frac{\partial \mu}{\partial P} \right)$ versus Poisson's ratio in several M_2O-SiO_2 glasses. The linear relationship for BeF_2 , SiO_2 , GeO_2 , and B_2O_3 , taken from Kurkjian et al. (1972), is shown here for comparison.

Reference

- [1] C.R. Kurkjian, J.T. Krause, H.J. McSkimin, P. Andreatch,
and T.B. Bateman, in Amorphous Materials, edited by
R.W. Douglas and B. Ellis, John Wiley and Sons, 463 (1972).

SECTION III
THERMAL EXPANSIVITY OF ALKALI SILICATE
GLASSES BETWEEN 25 AND 300°C

Introduction

A solid expands on heating because the atomic configuration corresponding to minimum free energy changes with temperature. Contributions to the free energy and hence to the thermal expansion of silicate glasses arise mostly from the kinetic energy of lattice vibrations and to a significantly lesser degree from potential energy of the atoms in the lattice.

It has been shown [1-3] that those vibrations in a network for which volume dependence of vibrational frequency (dw/dV) is negative make a negative contribution to thermal expansion. In silica structures such a negative contribution arises from the low frequency transverse of oxygen atoms between pairs of tetrahedrally coordinated atoms [4,5]; such vibrations are relatively more easily excited at low temperatures [6].

Smyth [5] has pointed out that ideally transverse vibration of oxygen atoms would be freest if the Si-O-Si angle were 180°. In fused silica this angle is around 148° but the transverse oxygen vibrations still contribute to the negative thermal expansion at low temperatures. At room temperature and above, fused silica has a small positive coefficient of thermal expansion, which indicates that these transverse modes are operative at room temperature and are, to some extent,

contributing negatively to the thermal expansion. Investigation of the thermal expansivity of alkali silicate glasses should provide a better understanding of the role of the transverse vibrational modes in the glass properties.

Additions of alkali oxide (M_2O) to silica results in network-filling, breaking of the Si-O-Si bonds and formation of weaker Si-O-M bonds, and modification of the Si-O-Si angles. The strength of the binding forces between M^+ and O^{2-} ions, and the polarizability of O^{2-} ions will also vary with M_2O content. Previous studies of the thermal expansion properties of alkali silicate glasses [7-10] show that the expansivity depends on the type and amount of M_2O present.

The purpose of this research is to systematically investigate the effects of composition as well as temperature on the thermal expansion properties of binary M_2O-SiO_2 glasses, where M is Li, Na, and K, and to interpret the results in terms of structural changes and the variations in restoring forces between metal and oxygen ions, and the polarizability of O^{2-} ions.

Experimental Methods

The Fizeau interferometer method [11,12] was used to measure linear thermal expansivity of 22 alkali silicate glasses (which included eight Li_2O-SiO_2 , eight Na_2O-SiO_2 , and six K_2O-SiO_2 glasses; see Table 1) as a function of temperature in the range of 25 to 300°C. The furnace assembly,

Table 1. Chemical composition, the temperature dependence of linear thermal expansion of alkali silicate glasses, expressed as $\alpha_L(T) = A_0 + A_1 T + A_2 T^2$, and the calculated α_L values at 25°C. Units: α_L in $10^{-6}/^\circ\text{C}$; A_0 in $10^{-4}/^\circ\text{C}$; A_1 in $10^{-6}/(^\circ\text{C})^2$; A_2 in $10^{-8}/(^\circ\text{C})^3$

Glass No.	Composition, Mole%		A_0	A_1	A_2	α_L (25°C)
	SiO ₂	H ₂ O				
<u>Li₂O-SiO₂ Glasses</u>						
K-199	80	20	-1.3293	5.202	0.46062	5.43
K-154	75	25	-1.6713	6.569	0.46248	6.80
K-171	72	28	-1.9034	7.458	0.62239	7.77
K-198	72	28	-1.8254	7.133	0.67322	7.47
K-163	70	30	-1.9721	7.720	0.67216	8.06
K-170	68	32	-2.1431	8.396	0.70609	8.75
K-162	65	35	-2.1546	8.432	0.74706	8.81
K-197	65	35	-2.2377	8.737	0.85621	9.17
<u>Na₂O-SiO₂ Glasses</u>						
K-110	90	10	-1.0586	4.193	0.16548	4.12
K-111	85	15	-1.7975	7.149	0.16474	7.23
K-112	80	20	-2.3707	9.421	0.24623	9.67
K-113	75	25	-2.667	10.509	0.63500	10.83
K-114	70	30	-2.9657	11.666	0.78764	12.06
K-115	65	35	-3.4432	13.576	0.78685	13.97
K-116	60	40	-3.5612	14.193	0.89775	14.64
K-117	55	45	-3.9575	15.522	0.98450	16.01
<u>K₂O-SiO₂ Glasses</u>						
K-196	85	15	-2.1892	8.727	0.12064	8.79
K-194	80	20	-2.7581	10.928	0.41740	11.14
K-192	75	25	-3.3162	13.150	0.48740	13.39
K-191	70	30	-3.9197	15.557	0.48657	15.80
K-189	65	35	-4.2321	16.766	0.64989	17.09
K-187-1	60	40	-4.6186	18.270	0.81867	18.68

interferometer, the photoelectric fringe detector, and viewing apparatus, manufactured by the Gaertner Scientific Company, were used in the experiments.

Test Specimens. The same alkali silicate glasses employed in the attenuation study (Section I of this report) were used. The test specimens were prepared by coring out three 6-mm-diameter, 10-mm-long cylinders from each glass; these were flat-ended at one end and coned at the other (at 45°). Both ends were then polished with 1-micron diamond compound optically flat to $(1/4)\lambda$ of green mercury light. The difference in length of the three specimens was between 0.01 and 0.02 mm, which resulted in formation of 7 to 10 fringes.

Temperature Cycles. Temperature of test specimens during the heating cycle was continuously increased every 8 to 10 minutes at an approximate rate of $50^\circ/\text{hour}$. The fringe count and temperature were continuously monitored with a strip-chart recorder and a precision potentiometer. The initial temperature (T_0) was taken as 25°C .

During the cooling cycle, the temperature of the specimens decreased at a slower rate-- $30^\circ\text{C}/\text{hour}$. The initial temperature (T_0) in the cooling cycle was chosen as 300°C .

Theory of Interferometer Method. The method involves observing passage of Fizeau fringes, formed by interference of light beams reflected from two almost parallel glass surfaces separated by a distance. The condition for destructive

interference is $N\lambda_v = 2nd$, where N is an integer, λ_v is the wavelength of light in vacuum, n is the optical index of medium, and d is the optical distance between the two surfaces. For constructive interference the condition is $(N + 1)\lambda = 2nd$. The number of fringes crossing the field of view will depend upon optical path, that is, on the initial length and the expansivity of material under investigation. If the initial length of the test specimen and the optical index of the air at temperature T_0 are L_0 and n_0 , respectively, we have

$$N_0 = \frac{2n_0 L_0}{\lambda_v} \quad (1)$$

In the present case we used the green mercury light, for which $\lambda_v = 5.461 \times 10^{-5}$ cm. Similarly, at a higher given temperature T_1 , we have

$$N_1 = \frac{2}{\lambda_v} (n_0 + \Delta n) (L_0 + \Delta L) \quad (2)$$

where Δn and ΔL are the changes in n and L , respectively. In the Fizeau interferometer method used here, the fringe count $m = (N_1 - N_0)$ and is related to ΔL as:

$$m \approx \frac{2n_0 \Delta L + 2L_0 \Delta n}{\lambda_v} \quad (3)$$

Therefore, the coefficient of linear thermal expansion (α_l) is:

$$\alpha_L = \frac{\Delta L}{L_0 \Delta T} = \frac{m \lambda_v}{2 L_0 n_0 \Delta T} - \frac{\Delta n}{n_0 \Delta T} \quad (4)$$

where $\Delta T = T_1 - T_0$.

Calculation of α_L

The number of fringes varies as a function of temperature and can be expressed at reference temperature T_1 and initial temperature T_0 as follows:

$$N_1 = a + a_1 T_1 + a_2 T_1^2 \quad (5A)$$

$$\text{and } N_0 = a + a_1 T_0 + a_2 T_0^2 \quad (5B)$$

where N_1 and N_0 are number of fringes at T_1 and T_0 , respectively; a , a_1 and a_2 are the coefficients. If $T_1 > T_0$ the number of fringes increases from T_0 to T_1 ; the thermal expansion ($\Delta L/L_0$) can then be derived from eqs. (4) and (5):

$$\begin{aligned} \left(\frac{\Delta L}{L_0} \right)_P &= m \lambda_v / 2 L_0 n_0 - \Delta n / n_0 = m K_0 - K_1 \\ &= K_0 [a_1 (T_1 - T_0) + a_2 (T_1^2 - T_0^2)] - K_1 \end{aligned} \quad (6)$$

where $K_0 = \lambda_v / 2 L_0 n_0$, $K_1 = \Delta n_0 / n_0$, and P signifies a case of increasing temperature ($T_1 > T_0$). In the case of decreasing temperatures ($T_2 < T_0$), the number of fringes decreases with decreasing temperature (case Q). Assume in this case N_2 and

N'_0 to be the number of fringes at T_2 and T_0 , respectively.

The corresponding equations are:

$$N_2 = b + b_1 T_1 + b_2 T_1^2 \quad (7A)$$

$$N'_0 = b + b_1 T_0 + b_2 T_0^2. \quad (7B)$$

In this case, the thermal expansion is negative and the corresponding relationship to eq. (6) is given by

$$\left(\frac{\Delta L}{L_0} \right)_Q = -mK_0 + K_1 = -K_0 [b_1(T_2 - T_0) + b_2(T_1^2 - T_0^2)] K_1 \quad (8)$$

From eqs. (6) and (8), the mean value of thermal expansion is given by:

$$\begin{aligned} \left(\frac{\Delta L}{L_0} \right)_{\text{mean}} &= \frac{\left(\frac{\Delta L}{L_0} \right)_P + \left(\frac{\Delta L}{L_0} \right)_Q}{2} = \frac{K_0}{2} \left[-T_0(a_1 - b_1) - \right. \\ &\quad \left. T_0(a_2 - b_2) + T_1(a_1 - b_1) + T_1(a_2 - b_2) \right] \\ &= K[A + BT_1 + CT_1^2] \end{aligned} \quad (9)$$

where,

$$K = K_0/2 = \lambda_v/4L_0 n_0,$$

$$A = -T_0(a_1 - b_1) - T_0(a_2 - b_2),$$

$$B = (a_1 - b_1) , \text{ and}$$

$$C = (a_2 - b_2) .$$

Therefore, the mean coefficient of linear thermal expansion (α_L) is determined from eq. (10):

$$\begin{aligned} (\alpha_L)_{\text{mean}} &= \frac{1}{\Delta T} \left(\frac{\Delta L}{L_0} \right)_{\text{mean}} \\ &= \frac{K}{T} (A + BT_1 + CT_1^2) . \end{aligned} \quad (10)$$

The general form of eq. (10) is:

$$\alpha_L(T) = \frac{K}{\Delta T} (A + BT + CT^2) . \quad (11)$$

The experimental procedure in the determination of function $\alpha_L(T)$ involves first, counting fringes as a function of temperature and evaluation of the coefficients A, B, and C by the least-squares method and second, calculation of thermal expansivity $(\Delta L/L_0)$ as a function of temperature using eqs. (9) and (11).

Results and Discussion

Results of the measurements of the fractional length change ($\Delta L/L_0$), normalized to zero at 25°C, for the three types of alkali silicate glasses to 300°C are shown in Figures 1-3. The least-squares analysis of both increasing and decreasing temperature data was made to obtain the best-fit expansion versus temperature curves (Figs. 1-3). The ($\Delta L/L_0$) versus temperature data were analyzed to obtain best-fit equation expressing the temperature dependence of α_l for each of the glasses: $\alpha_l(T) = A_0 + A_1T + A_2T^2$, where A_0 , A_1 and A_2 are the constant coefficients for a given glass (Table 1). These relations were then used to calculate α_l at the various temperatures. Figures 4 and 5 show the composition dependence of α_l for the three types of alkali silicate glasses calculated at 25°C and at the three higher temperatures (100 to 300°C), respectively. As can be seen from Figures 1-5, the expansivity of the three types of alkali silicate glasses varies systematically with composition and temperature.

Thermal Hysteresis. In the case of Li_2O-SiO_2 and K_2O-SiO_2 glasses the thermal expansion was investigated as a function of both increasing and decreasing temperatures (Figs. 1 and 3). The results show that the expansion values are lower for the cooling cycle than for the heating cycle. The thermal hysteresis effect, caused mostly by the difference in the heating and cooling rates, is relatively more conspicuous in the K_2O-SiO_2

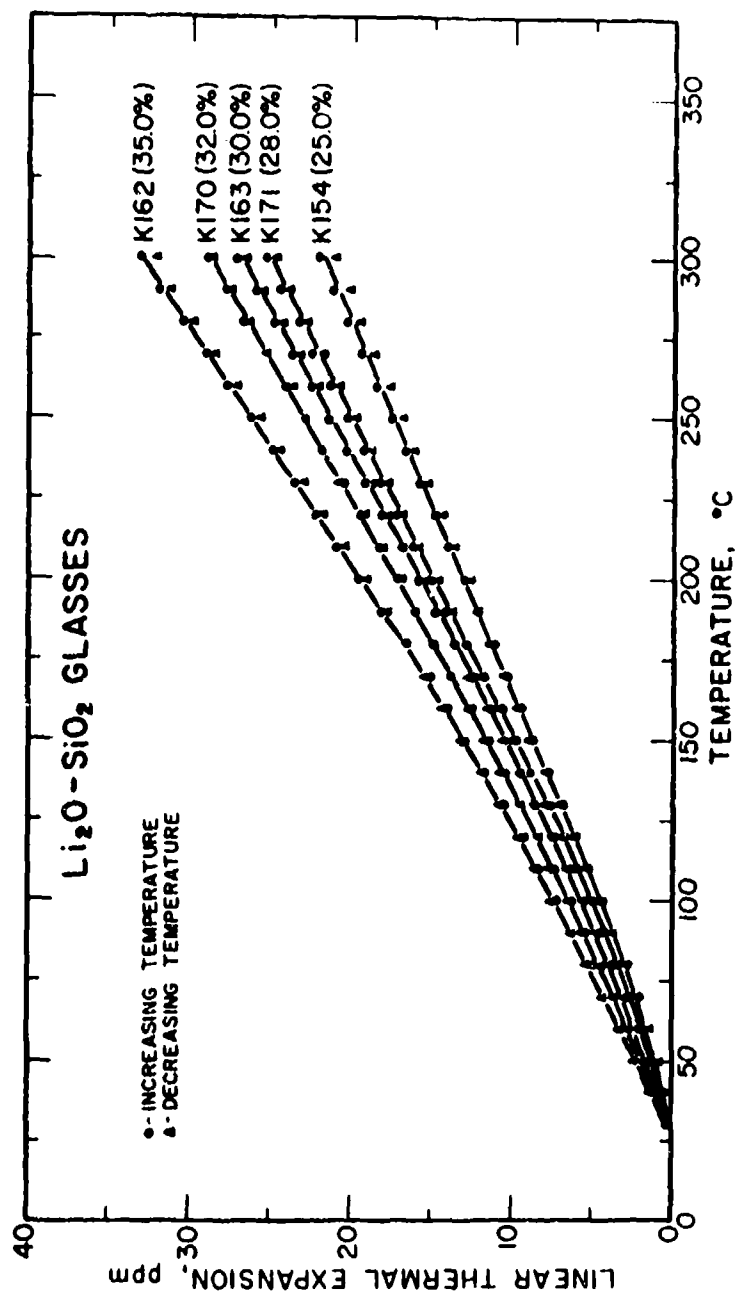


Fig. 1. Temperature dependence of the linear thermal expansion ($\Delta L/L_0$) of binary lithium silicate glasses.

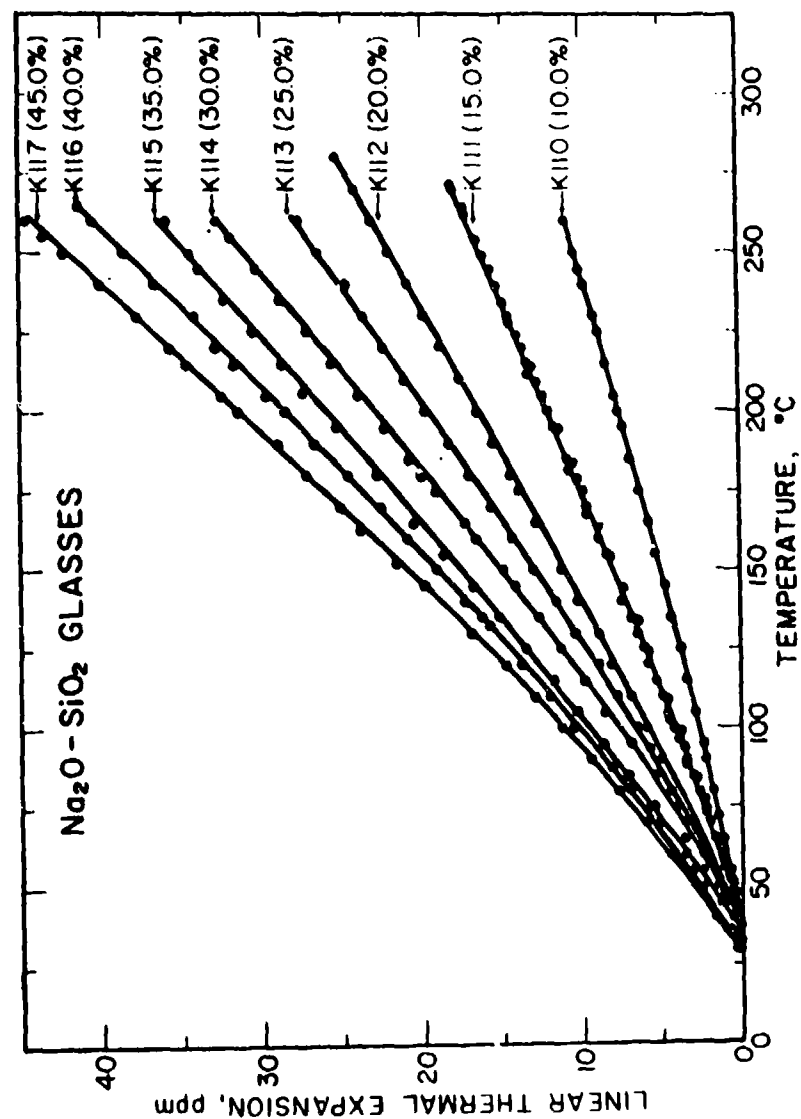


Fig. 2. Temperature dependence of the linear thermal expansion ($\Delta L/L_0$) of binary sodium silicate glasses.

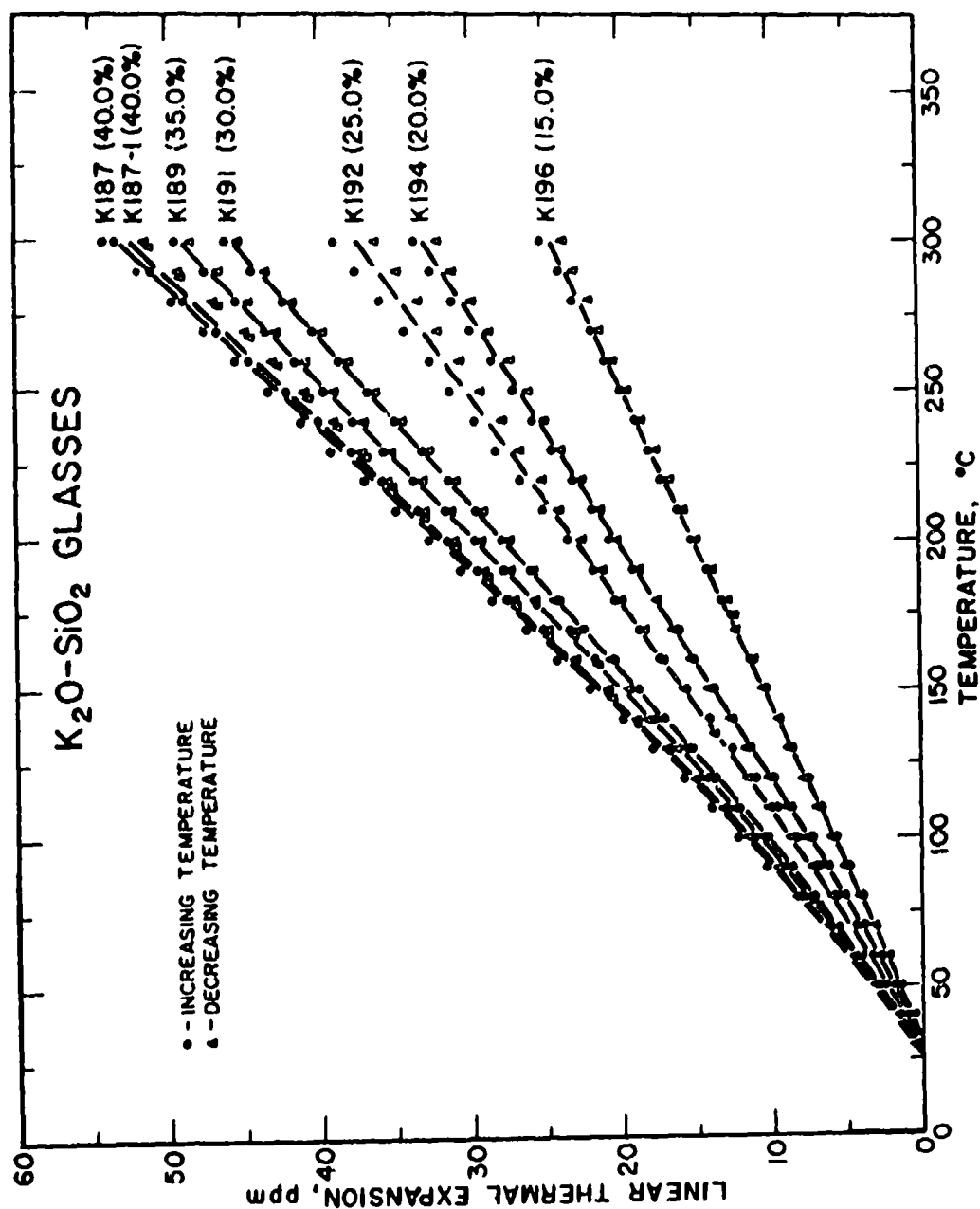


Fig. 3. Temperature dependence of the linear thermal expansion ($\Delta L/L_0$) of binary potassium silicate glasses.

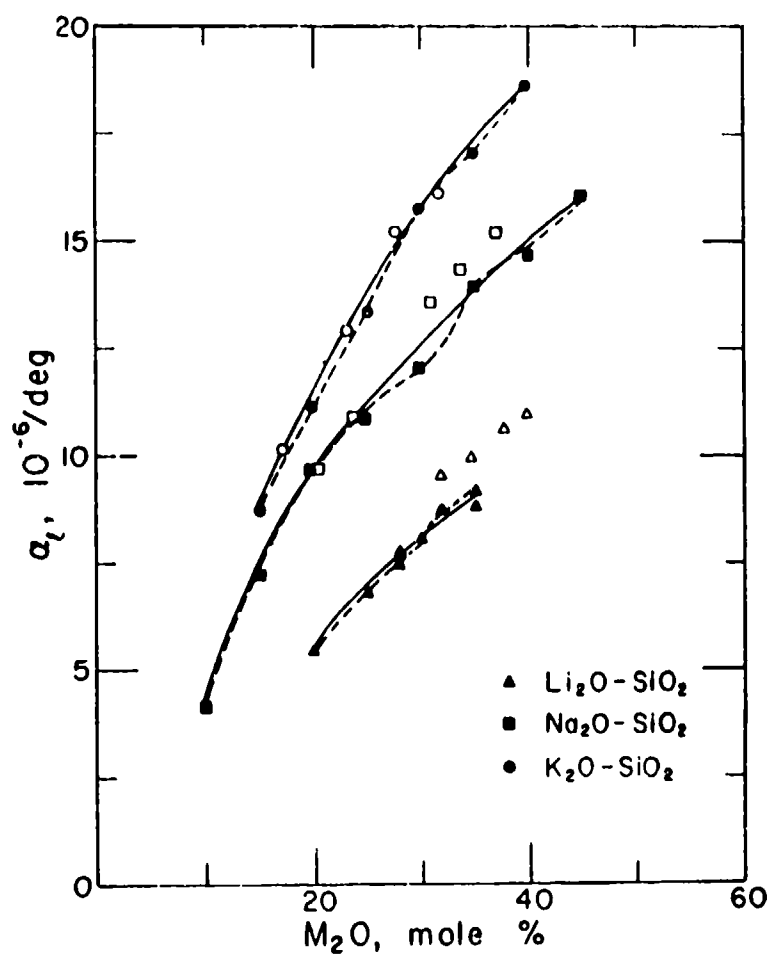


Fig. 4. Composition dependence of the linear thermal expansion coefficient (α_L) for binary alkali silicate glasses at 25°C. The dashed lines indicate the breaks in the composition dependence of α_L and the solid lines represent the mean curves based on the present study. The open symbols correspond to Shermer's data [10].

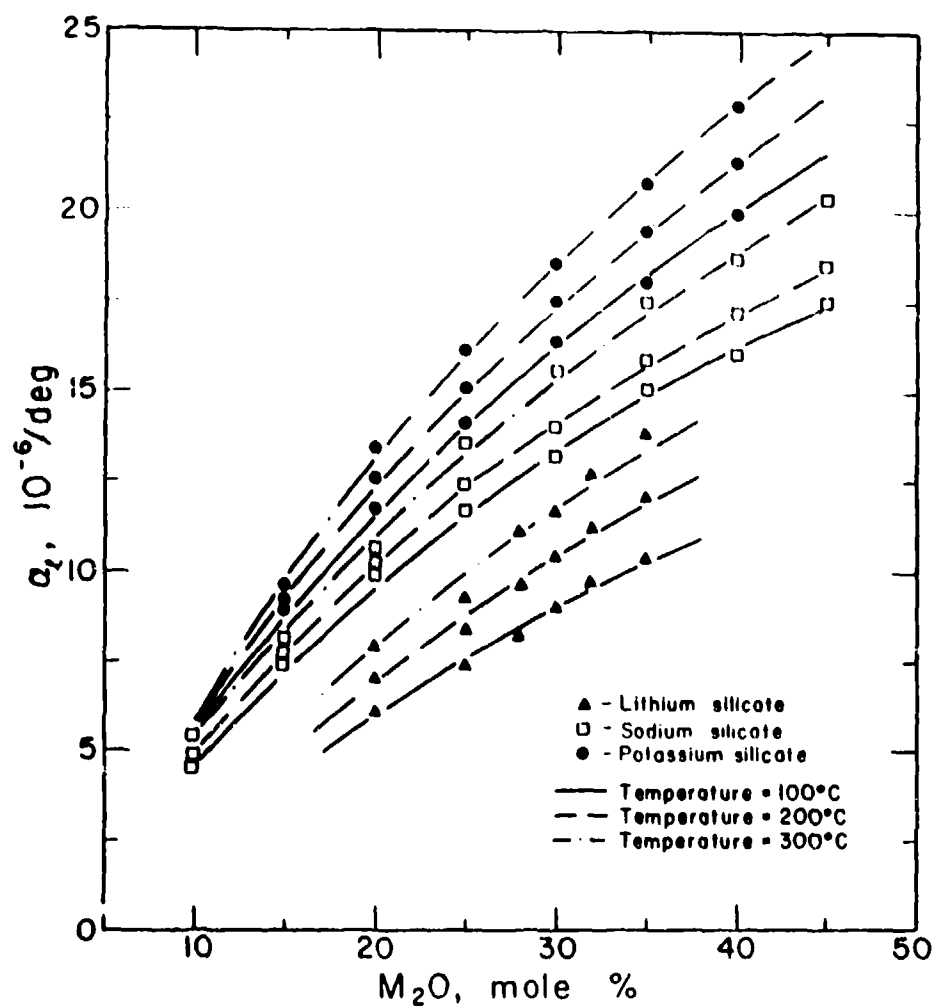


Fig. 5. Composition dependence of the mean linear thermal expansion coefficient (α_L) for binary alkali silicate glasses at the various temperatures.

glasses than in the $\text{Li}_2\text{O-SiO}_2$ glasses, and may be explained by the larger thermal stresses present in the $\text{K}_2\text{O-SiO}_2$ glasses due to the larger size of the K^+ ions as compared to the Li^+ ions.

Temperature Dependence of Thermal Expansion. The thermal expansion of the alkali silicate glasses increases rapidly with increase in temperature (α_ℓ varies as quadratic in temperature). The temperature dependence of α_ℓ is quite similar for the three types of alkali silicate glasses (Figs. 1-3 and 5). The minor breaks in the α_ℓ -composition trends at room temperature (Fig. 4) can also be found to some extent at high temperatures (Fig. 5). For given M_2O content, the relative change in α_ℓ with increasing temperature has the trend: $\text{Li}_2\text{O-SiO}_2 > \text{Na}_2\text{O-SiO}_2 > \text{K}_2\text{O-SiO}_2$.

Composition Dependence of Thermal Expansion. The present room-temperature α_ℓ values for the alkali silicate glasses are in fairly good agreement with the previous data [10], except for slightly ($\sim 10\%$) lower values for the $\text{Li}_2\text{O-SiO}_2$ glasses determined in this study (Fig. 4). However, the present study confirms the earlier finding that, in general, the expansivity of the alkali silicate glasses increases with increasing M_2O content, the rate of increase being relatively higher for the low- M_2O glasses (Fig. 4); similar relation between α_ℓ and composition also holds true at higher temperatures (Fig. 5).

To interpret the composition dependence of thermal expansion we should understand the role of M_2O added to SiO_2 structure. Besides filling the interstitial space in the silica network

structure which results in the decrease of the openness of the silica structure, the addition of M_2O also causes destruction of the continuity of the silica structure (Si-O-Si bonds) and formation of the nonbridging oxygens and weaker Si-O-M bonds which result in the higher expansivity of glass [7,9,13]. The results plotted in Figs. 4 and 5 show increasing α_l with increasing M_2O content. (By corollary, the elastic moduli decrease with increase in M_2O content, as mentioned in Section II of this report.)

The room temperature α_l values of the Na_2O-SiO_2 and K_2O-SiO_2 glasses containing 15 mole % M_2O are, respectively, about 13 and 16 times that of silica for which $\alpha_l \approx 5.5 \times 10^{-7}/deg$ [Table 1]. Such a rapid increase in the α_l upon addition of small amounts of M_2O may be explained by appreciable changes in the asymmetry caused by the introduction of the nonbridging O^{2-} ions into the "flawless" Bernal liquid structure of silica [14]. (Si-O bond for a nonbridging O^{2-} ion is stronger than for a bridging O^{2-} ion). Subsequent additions of M_2O bring about relatively less drastic disproportionation of the stronger and weaker binding forces.

In a finer analysis of Figures 4 and 5, we can also see that α_l does not vary smoothly with M_2O content, especially in the case of Na_2O-SiO_2 glasses; rather, there are breaks in the α_l -composition trends (indicated by dashed lines in Fig. 4). The breaks occur approximately at 30, 28, and 26 M_2O mole %

composition of the $\text{Li}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$ glasses, respectively. In all three cases, the α_g increases above these compositions. At higher M_2O contents, (~ 32 mole % K_2O and ~ 36 mole % Na_2O) the respective α_g seem to decrease slightly from the normal trend. Such changes in α_g are not unexpected in view of the fact that alkali silicate glasses do not have randomness of the silica-alkali structures [14-16] which would have otherwise produced smooth functions of α_g versus M_2O composition. Most probably the formation of superlattice structure consisting of submicroscopic crystallites causes the α_g to increase.

In the study of thermal expansivity of sodium silicate glasses, Blau [18] found breaks in the expansivity-composition curves at certain ratios of bridging and nonbridging oxygens, and he interpreted this as being some sort of a regularity in the distribution of the bridging and nonbridging O^{2-} ions. Parallel to this, we relate the breaks in the expansivity-composition trends to the varying degree of submicroscopic heterogeneity in the glasses [14].

The difference in the thermal expansion behavior of alkali silicate glasses having similar M_2O content is related to the different polarizability of nonbridging O^{2-} ions, which is mainly governed by the field strength and the size of M^+ ions [14]. The field strength of M^+ ions decreases in the order $\text{Li}^+(0.23) > \text{Na}^+(0.19) > \text{K}^+(0.13)$; their ionic size varies in

the opposite trend: $K^+(1.33) > Na^+(0.95) > Li^+(0.60)$. Large size and low field strength of K^+ ions introduce relatively high polarizability of nonbridging O^{2-} ions and weak Si-O-Si bonds, resulting in the high thermal expansion coefficients of K_2O-SiO_2 glasses as compared to the Na_2O-SiO_2 and Li_2O-SiO_2 glasses.

Contributions of the Various Oxides. The thermal expansion contributions of the oxides composing the glasses can be evaluated from the experimental values of the expansion coefficients of silicate glasses, assuming the additive property of these contributions [17,18]:

$$\alpha_L = \sum_i \alpha_i x_i \quad (12)$$

where α_L is the linear expansion coefficient of the glass, α_i are the empirical linear expansion coefficients of the oxides present, and x_i are the mole % of the oxides. The α_i thus calculated for Li_2O , Na_2O and K_2O in the alkali silicate glasses (Table 2) are found to be slightly lower than those determined from the other silicate and alumino-silicate glasses [18]. Using these α_i 's, the α_L values can be calculated and compared with the experimental α_L values for the glasses (Table 3). Since the agreement between the experimental and calculated values is good (Table 3), the eq. (4) seems to hold well for the alkali silicate glasses. In other words, although the α_L -composition relations for the alkali silicate glasses are

Table 2. Empirical coefficients of the thermal expansion contributions (α_1) of alkali oxides to the linear thermal expansion of alkali silicate glasses at 25°C

Glass type	Oxide	$\alpha_1, 10^{-8}/\text{deg mole } \%$	
		This study	Reference [17]
Li ₂ O-SiO ₂	Li ₂ O	24.670	27.0
	SiO ₂	0.843	0.63-3.8
Na ₂ O-SiO ₂	Na ₂ O	34.268	39.50
	SiO ₂	2.266	0.63-3.8
K ₂ O-SiO ₂	K ₂ O	43.028	46.50
	SiO ₂	3.194	0.63-3.8

Table 3. Comparison of experimental and predicted thermal expansion coefficients (α_p in $10^{-6}/\text{deg}$) for the alkali silicate glasses at 25°C. The SiO_2 content (in mole%) of the glass is given in parentheses

Glass No.	Experimental	Predicted
<u>$\text{Li}_2\text{O-SiO}_2$ Glasses</u>		
K-119 (80)	5.43	5.61
K-154 (75)	6.80	6.80
K-157 (72)	7.77	7.51
K-198 (72)	7.47	7.51
K-163 (70)	8.06	7.99
K-170 (68)	8.75	8.47
K-162 (65)	8.81	9.18
K-197 (65)	9.17	9.18
<u>$\text{Na}_2\text{O-SiO}_2$ Glasses</u>		
K-110 (90)	4.12	5.47
K-111 (85)	7.23	7.07
K-112 (80)	9.67	8.66
K-113 (75)	10.83	10.27
K-114 (70)	12.06	11.87
K-115 (65)	13.97	13.47
K-116 (60)	14.64	15.07
K-117 (55)	16.01	16.67
<u>$\text{K}_2\text{O-SiO}_2$ Glasses</u>		
K-196 (85)	8.79	9.16
K-194 (80)	11.14	11.16
K-192 (75)	13.39	13.15
K-191 (70)	15.80	15.14
K-189 (65)	17.09	17.13
K-187-1 (60)	18.68	19.12

not strictly monotonic, the mean relations (indicated by solid curves in Fig. 4) are useful in predicting α_l from the composition of an alkali silicate glass.

One of the most interesting results from this study is that the α_1 for SiO_2 is not uniform in the three types of alkali silicate glasses; it varies from 0.843/deg mole % in the $\text{Li}_2\text{O-SiO}_2$ glasses to 3.194/deg mole % in the $\text{K}_2\text{O-SiO}_2$ glasses--a variation of the order of 4 (Table 2), which is comparable to that found in the other glasses ($0.5\text{--}3.8 \times 10^{-8}$ /deg mole %) [17]. The large variation in the SiO_2 contribution may be explained by the large difference in the force constants of the Si-O bonds involving the nonbridging O^{2-} ions in the three types of alkali silicate glasses.

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SECTION IV
EFFECTS OF PHASE SEPARATION ON ELASTIC
PROPERTIES AND THERMAL EXPANSIVITY

The phase studies were conducted by Mr. John Kay, R.P.I.
The following method was used by him:

Fracture surfaces of the glasses were obtained, and etched
as follows:

K_2O-SiO_2 glasses	-	10 seconds 2% HCl
some Li_2O-SiO_2 glasses	-	10 seconds 2% HCl
other Li_2O-SiO_2 glasses	-	10 seconds 2% HF
Na_2O-SiO_2 glasses	-	10 seconds 2% HF

Replica samples were made by shadowing a collodion replica
of the sample surface with chromium and then coating it with
carbon. Replicated surfaces were then viewed in a Hitachi HU-
LLB electron microscope operated at 100 KV.

Results and Discussion

Phase separation is everywhere present in alkali silicate
glasses. The volumetric percentage of relatively silica-rich
phase varies from 11 to 15% in high- M_2O glasses to as high as
65 to 70% in glasses with 25 to 30% M_2O , and the particle size
varies from 200 Å or less to 1/2 micron (Table 1).

In spite of large variations in phase separation (amount
and size), the trends of elastic property-composition are
quite systematic (see figures in section II).

We chose three $\text{Li}_2\text{O-SiO}_2$ glass samples (198, 171B, and K171A) with the same composition (28 mole % Li_2O) and varying degrees of phase separation to study the effects of phase separation. K198 has an evenly dispersed phase separation with particle size averaging about $1000 \text{ \AA}$ in diameter (Plate I). 171B has an unevenly dispersed phase separation, the particle size being 500 to $100 \text{ \AA}$ (Plate II). This glass showed square-shaped crystals of about 0.75μ edge-length. Glass 171A has an evenly dispersed phase separation, the average particle size being $\sim 1000 \text{ \AA}$.

Thus, in terms of particle size and composition, these specimens are quite similar. Inspection of Table 2 shows that there is no systematic variation in properties with the variation in the degree of phase separation, except in the pressure and temperature derivatives of the moduli and thermal expansion. The α_ρ and dM/dT values seem to increase when phase separation increases.



above: Plate I. Electron micrograph of K-135 glass (X360,000).
 upper right: Plate II. Electron micrograph of K171B glass
 (X360,000).
 lower right: Plate III. Electron micrograph of K171A glass
 (X360,000).

Table 1. Volumetric percentage and particle size of phase separation in alkali silicate glasses

Glass No.	Composition (mole %)		Volume %	Average Particle Size
	M ₂ O	SiO ₂		
<u>Li₂O-SiO₂ Glasses</u>				
K199	20.0	80.0	64	1/2 μ
K154	25.0	75.0	25	300-1500 Å
K171A	28.0	72.0	37	1000 Å
K171B	28.0	72.0	22	500-1000 Å
K198	28.0	72.0	17	1000 Å
K163	30.0	70.0	65-70	0.25-1 μ
K170	32.0	68.0	62	3200 Å
K162	35.0	65.0	70,11	1/2 μ
K197	35.0	65.0	11	3500 Å
<u>Na₂O-SiO₂ Glasses</u>				
K110	10.0	90.0	60	500 Å
K112	20.0	80.0	45	500 Å
K114	30.0	70.0	26	1200 Å
K115	35.0	65.0	47	650 Å
K116	40.0	60.0	15	1000 Å
<u>K₂O-SiO₂ Glasses</u>				
K196	15.0	85.0	15	400 Å
K194	20.0	80.0	75	700 Å
K192	25.0	75.0	50	200 Å

Table 2. Properties of three $\text{Li}_2\text{O-SiO}_2$ glasses (containing 28 mole % Li_2O) with varying degrees of phase separation of silica-rich phase

	K 198	K 171B	K 171A
SiO_2 -rich phase, volume %	17	22	37
ρ , g/cm^3	2.322	2.322	2.322
V_p , km/sec	6.153	6.149	6.149
V_s , km/sec	3.720	3.720	3.722
K , kbar	450.4	449.6	449.2
μ , kbar	321.4	321.3	321.6
σ	.212	.211	.211
(dK/dP)	3.42	3.59	2.94
$(d\mu/dP)$	-.17	-.14	-.19
(dK/dT) , kbar/deg	-.043	-.052	-.014
$(d\mu/dT)$, kbar/deg	-.083	-.079	-.132
α_2 , $10^{-6}/\text{deg}$	7.47		7.7

SECTION V
EFFECTS OF COMPOSITION, PRESSURE, AND TEMPERATURE
ON THE ELASTIC PROPERTIES OF SiO_2 - TiO_2 GLASSES

Introduction

SiO_2 - TiO_2 glasses containing low concentrations of TiO_2 (up to 11 wt %) form in homogeneous phase [1-3]; TiO_2 plays the role of network former just as SiO_2 does. Interest in the SiO_2 - TiO_2 glass system has recently developed because of its low thermal expansion properties. The SiO_2 - TiO_2 glass (Corning Code 7971) containing 7.4 wt % TiO_2 has nearly zero thermal expansion [4, 5] in the temperature range of 0 to 300°C. In a recent systematic study [6], it has been shown that small amounts of TiO_2 (up to 10 wt %) added to fused silica cause a linear decrease in the coefficients of thermal expansion of silica glass. More recently, Schultz [7, 8] has discovered unique annealing methods for developing the low-expansion SiO_2 - TiO_2 glass containing 12-20 wt % TiO_2 .

Variations in the thermal expansion and other vibrational properties of the SiO_2 - TiO_2 glasses, caused by the compositional variations, are directly related to the variations in the structure and lattice vibrations of the glass network. A number of workers have studied the effect of TiO_2 content on the various properties of the SiO_2 - TiO_2 and related silicate glasses [6-19] and have interpreted the results in terms of

the changes in structure and coordination of the silicon and titanium ions. However, the elastic properties of the SiO_2 - TiO_2 glasses have so far not been systematically investigated.

The purpose of this section is to report on the elastic properties of the SiO_2 - TiO_2 glasses as a function of composition, pressure, and temperature, and to correlate the results with the variations in thermal expansion and other related anharmonic parameters.

Experimental Methods

Glass Specimens. The seven SiO_2 - TiO_2 glasses used in this study were kindly supplied to us by Dr. P.C. Schultz of the Corning Glass Works. These were prepared by flame hydrolysis [6]. The TiO_2 content of the glasses ranges from 1.3 to 9.4 wt % (Table 1). Also included in this study is fused silica (Corning Code 7940), purchased from the Corning Glass Works.

Elastic measurements were made on the glasses in as-produced, unannealed state as well as after annealing. The annealing process involved heating the glasses to 1020°C for about 1-1/2 hours, and then cooling them slowly from 1020 to 700°C at a rate of $5^\circ\text{C}/\text{hour}$, and then allowing them to cool inside the furnace from 700°C to room temperature.

Density of the glass specimen was measured by the Archimedes method. The pulse superposition method [20] of measuring ultrasonic velocities was used. The details of the electronics

Table 1. Chemical composition, and the elastic parameters of $\text{SiO}_2\text{-TiO}_2$ glasses at 1 bar and 25°C. All the glass specimens were annealed before the measurements

Glass No.	Composition, wt %		$\rho, 3$ g/cm ³	$V_p,$ km/sec	$V_s,$ km/sec	K, kbar	$\mu,$ kbar	E, kbar	σ
	SiO_2	TiO_2							
7940A (fused silica)	100	0	2.2007	5.947	3.769	361.6	312.6	728.0	.1645
T4A	98.7	1.3	2.2005	5.911	3.746	357.1	308.8	719.1	.1643
T1A	97.2	2.8	2.2001	5.872	3.717	353.2	304.0	708.8	.1656
T5A	95.4	4.6	2.1995	5.833	3.692	348.7	299.8	697.0	.1659
T6A	94.0	6.0	2.1992	5.803	3.672	345.3	296.5	691.6	.1662
T2A	92.7	7.3	2.1986	5.758	3.635	341.5	290.51	679.0	.1686
ULE 7971A	92.5	7.5	2.1993	5.783	3.653	344.2	293.5	625.6	.1680
T3A	90.6	9.4	2.1985	5.719	3.607	337.7	286.0	669.1	.1698

and high pressure and temperature equipment used, and the procedure to reduce the basic data are described elsewhere [19].

Results and Discussion

Effect of Annealing. The relations between composition and the elastic parameters, especially K and σ , are not so well defined for the unannealed glasses (Figs. 1-3). Following annealing, the relationships become systematic and more or less linear. It is interesting to note that annealing brings about an increase in V_g and ρ , but decrease in V_p . Similarly, μ and E increase and K decreases (that is, compressibility increases) after annealing. Annealing causes the removal of strains and rearrangement of the glass network such that the structure becomes more compact. We have also found compaction effect of annealing in a SiO_2 - TiO_2 glass containing 14.7 wt % TiO_2 . According to Schultz [personal communication, 1974], this compaction is related to a coordination change of titanium in the glass from 4 to 6. Based on Schultz's work [7-8], the effect of coordination change seems to occur in only high- TiO_2 (> 10 wt %) glasses.

Elastic Parameters at 1 bar and 25°C. The results of the elastic parameters as a function of composition are shown in Table 1 and Figures 1-3. McSkimin's (unpublished) data on V_p , V_g , E , and μ for fused silica and the Corning Code 7971 glass are in agreement with the present results. The elastic parameters (longitudinal velocity; V_p , shear velocity, V_g ; bulk

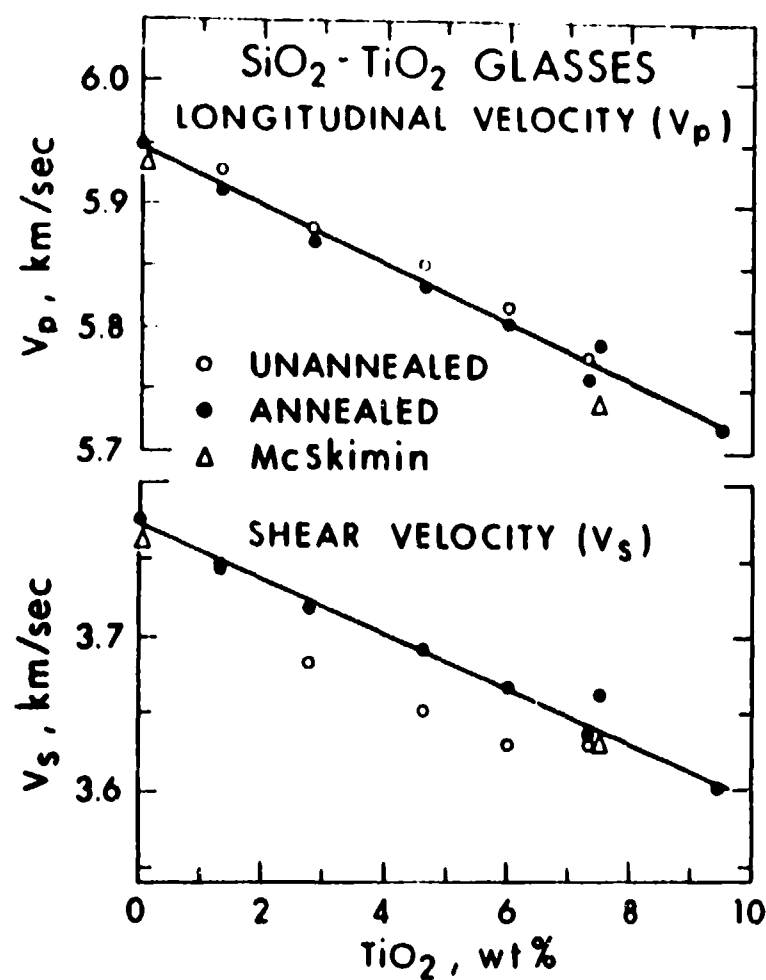


Fig. 1. Longitudinal (V_p) and shear wave (V_s) velocities versus TiO₂ content. Annealing causes a decrease in V_p and an increase in V_s . Triangles are McSkimin's (unpublished) 1972 data.

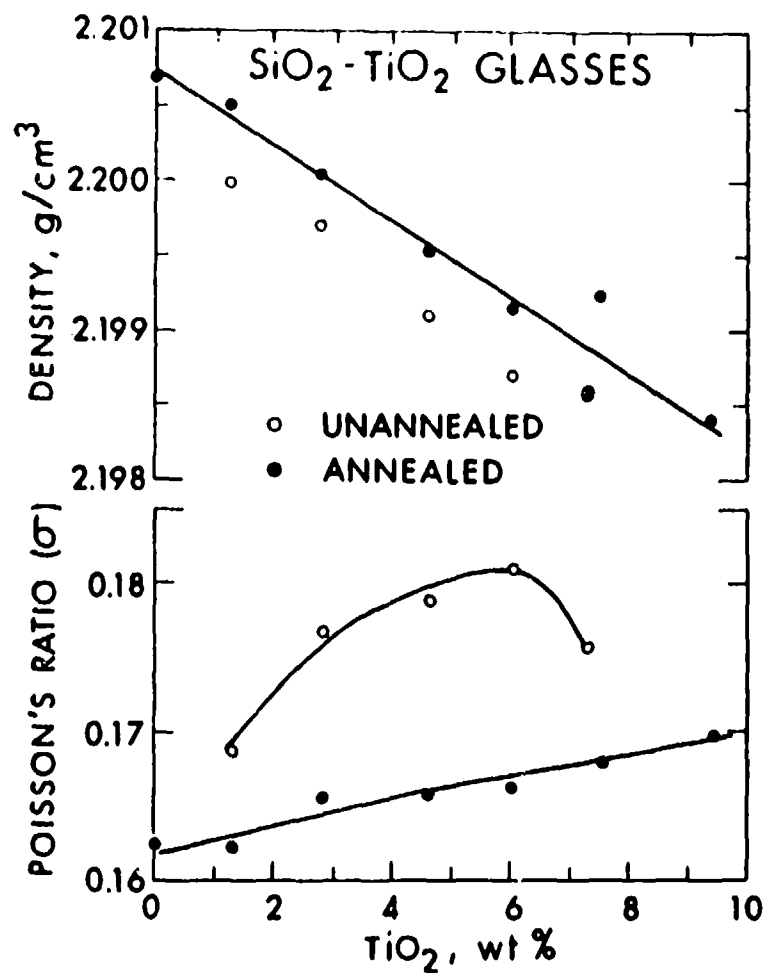


Fig. 2. Density (ρ) and Poisson's ratio (σ) versus TiO₂ content. Annealing causes an increase in ρ and a decrease in σ .

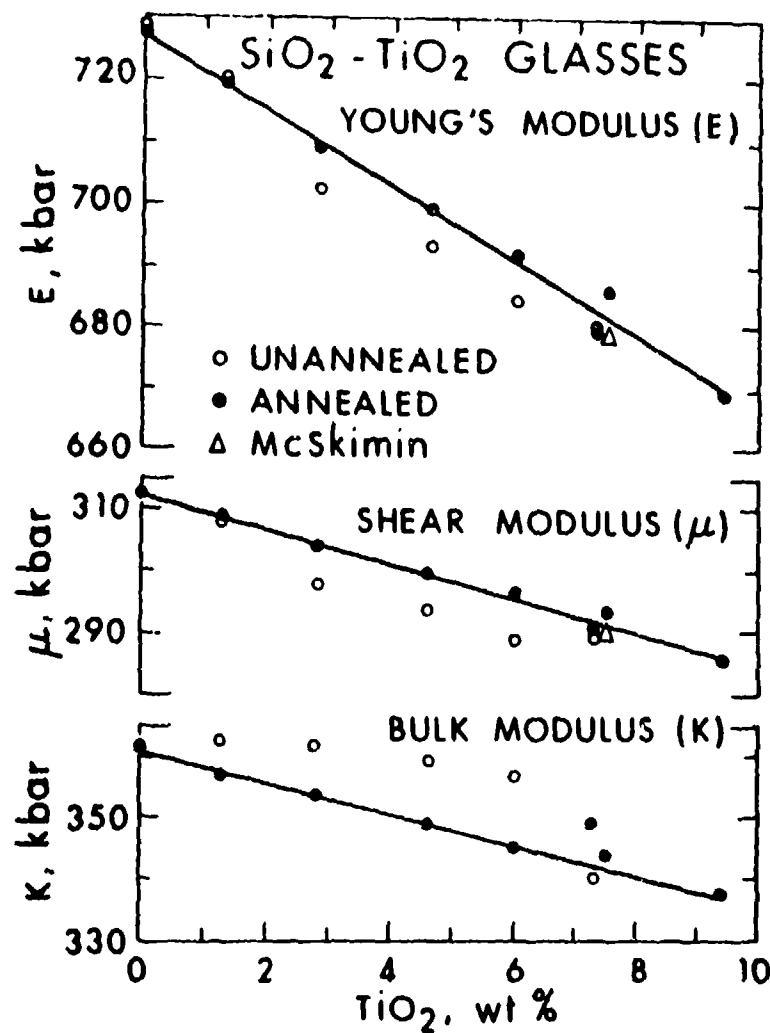


Fig. 3. Bulk (K), shear (μ) and Young's (E) moduli versus TiO₂ content. Annealing causes a decrease in K, and an increase in μ and E. Triangles are McSkimin's (unpublished) 1972 data.

modulus, K ; shear modulus, μ ; Young's modulus, E) and density (ρ) of the annealed SiO_2 - TiO_2 glasses decrease more or less linearly with increase in the TiO_2 content. However, Poisson's ratio for these glasses increases linearly with TiO_2 content.

The decreases in the moduli are interpreted to be caused by weakening of the silica network. The Ti^{4+} ions have lower field strength than the Si^{4+} ions, and the average length of Ti-O bond is considered to be larger than that of the Si-O bond; hence the Ti-O and Si-O-Ti bonds in SiO_2 - TiO_2 glasses are weaker than the corresponding Si-O and Si-O-Si bonds in silica glass. This view has been well supported by infrared absorption studies [9].

At low TiO_2 concentrations, Si-equivalent fourfold Ti ions exist in the coordination [1-3]. Hence a decrease in ρ with increasing TiO_2 content (Fig. 2) seems, at first, surprising in view of the fact that substituted Ti^{4+} ions are heavier than the Si^{4+} ions. Evans [1] has clearly demonstrated that the additions of small amounts of TiO_2 to the SiO_2 - TiO_2 solid solution (cristobalite phase) cause the tetragonal a_0 and c_0 d-spacings of this phase to increase. Such an effect would explain the variations in density of the SiO_2 - TiO_2 glasses. A decrease in density can thus be interpreted as being due to the increasing openness of the structure as TiO_2 is added. It appears that Si-O-Si and Si-O-Ti angles change such that the openness of the structure increases. That is, the Ti^{4+} ions would repel the O^{2-} ions farther than the Si^{4+} ions do.

Pressure Dependence of the Elastic Moduli

The pressure derivatives of the compressional and shear velocities, (dV_p/dP) and dV_s/dP , decrease with increase in TiO_2 content (Table 2; Fig. 4); the variation of (dV_s/dP) with composition is more systematic. There is a good agreement between McSkimin's and the present values of $(d\mu/dP)$ and (dE/dP) for fused silica and the Corning Code 7971 glass (Fig. 5). As in fused silica, the values of (dK/dP) , $(d\mu/dP)$, and (dE/dP) in SiO_2 - TiO_2 glasses are negative (anomalous) and become increasingly negative (more anomalous than fused silica) with increasing TiO_2 content (Table 2; Fig 5). Values of $d\mu/dP$ for all the glasses are negative (anomalous). This parameter becomes more negative with increase in TiO_2 content up to ~5 wt % TiO_2 , above which it becomes less negative (Fig. 6). The anomalous elastic behavior under pressure in fused silica has been explained in terms of its low (near-zero) thermal expansion. The presence of the low-frequency vibrational modes for which $d\omega/dV$ (where ω is frequency) is positive [6]. The presence of such modes also leads to an explanation for the negative thermal expansion of the SiO_2 - TiO_2 glasses [6]. The negative thermal expansion in SiO_2 - TiO_2 glasses has been attributed to the presence of the vibrational modes for which $d\omega/dV$ is positive [6], and this condition, characteristic of open structures, leads to negative values of (dM/dP) , where M is any modulus [21]. It then appears that the addition of TiO_2 causes changes in the vibrational

Table 2. Pressure and temperature derivatives of the elastic parameters of SiO_2 - TiO_2 glasses at 25°C and 1 bar, respectively. All the glass specimens were annealed before the measurements.

Glass No.	Composition, wt %		dK/dP	$d\rho/dP$, g/cm^3	$d\mu/dP$	dE/dP	$d\sigma/dP$, Mbar	dK/dT , kbar/deg	$d\mu/dT$, kbar/deg	dE/dT , kbar/deg	$d\sigma/dT$, $\text{deg}^{-1} \times 10^4$
	SiO_2	TiO_2									
7970A (fused silica)	100	0	-5.37	6.68	-3.53	-8.82	-1.01	.124	.051	.148	.45
T4A	98.7	1.3	-5.68	6.78	-3.56	-9.00	-1.24	.121	.052	.149	.43
T1A	97.2	2.8	-5.42	6.80	-3.56	-8.87	-1.00	.121	.050	.145	.43
T5A	95.4	4.6	-5.97	7.01	-3.55	-9.13	-1.52	.119	.050	.143	.44
T6A	94.0	6.0	-5.85	7.06	-3.54	-9.05	-1.42	.119	.048	.141	.44
T2A	92.7	7.3	-5.96	7.20	-3.60	-9.20	-1.47	.120	.048	.140	.45
ULE 7971A	92.5	7.5	-5.88	7.10	-3.60	-9.16	-1.36	.119	.047	.138	.46
T3A	90.6	9.4	-5.77	7.26	-3.59	-9.09	-1.30	.117	.047	.137	.46

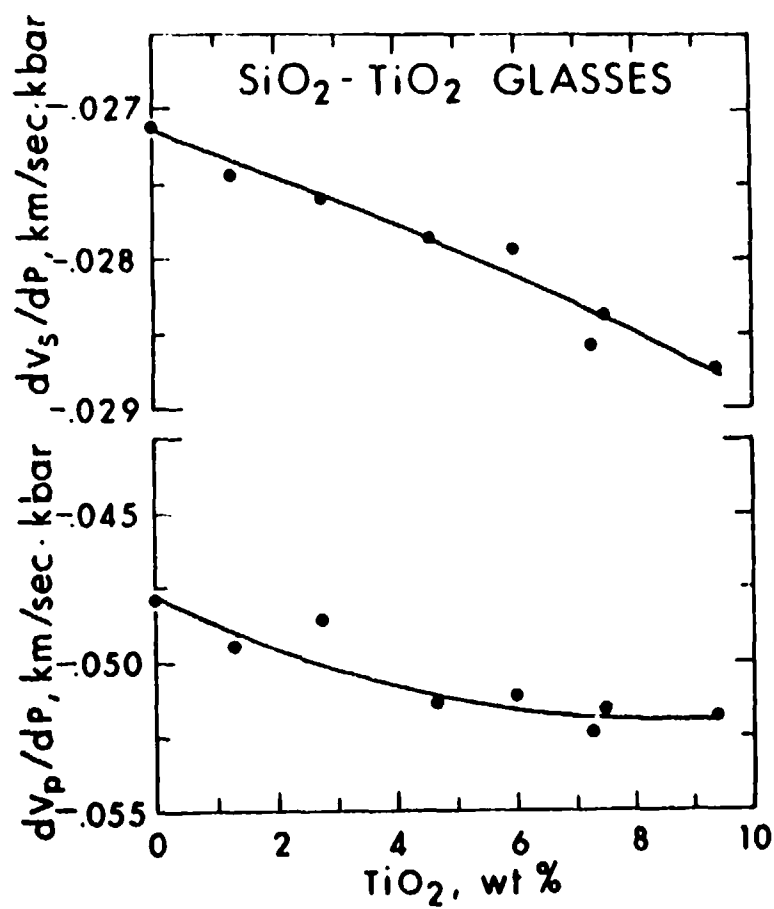


Fig. 4. Composition dependence of (dV_p/dP) and (dV_s/dP) glasses in SiO_2-TiO_2 .

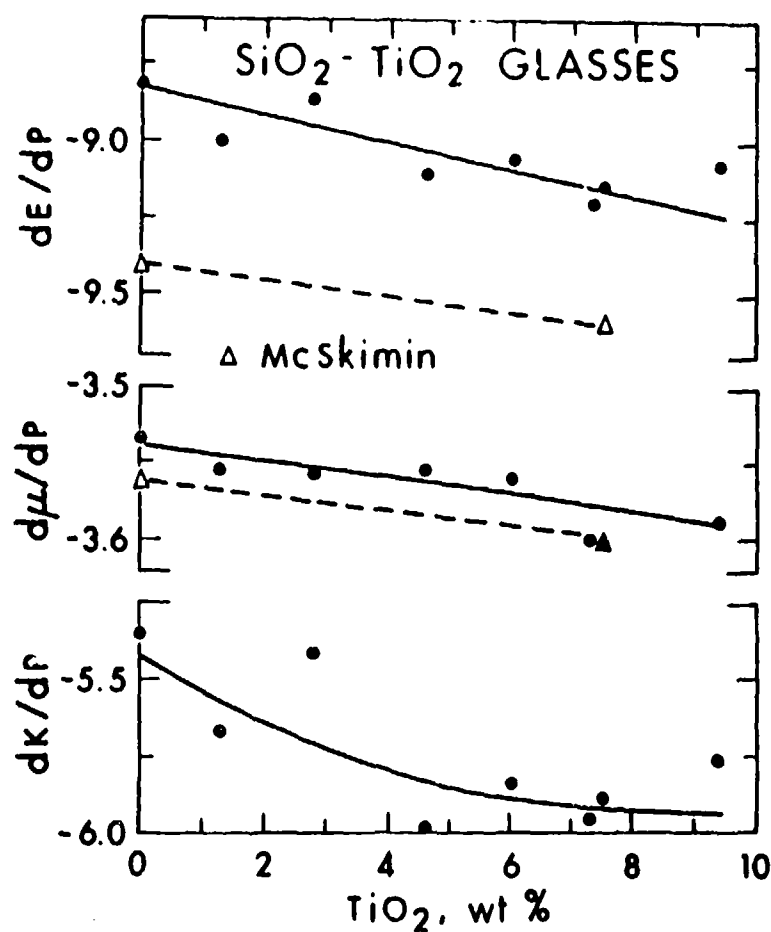


Fig. 5. Composition dependence of dE/dP , $d\mu/dP$, and dK/dP in SiO_2 - TiO_2 glasses. Open triangles are McSkimin's (unpublished) 1972 data; solid triangle is superimposition of the present and McSkimin's data for $d\mu/dP$.

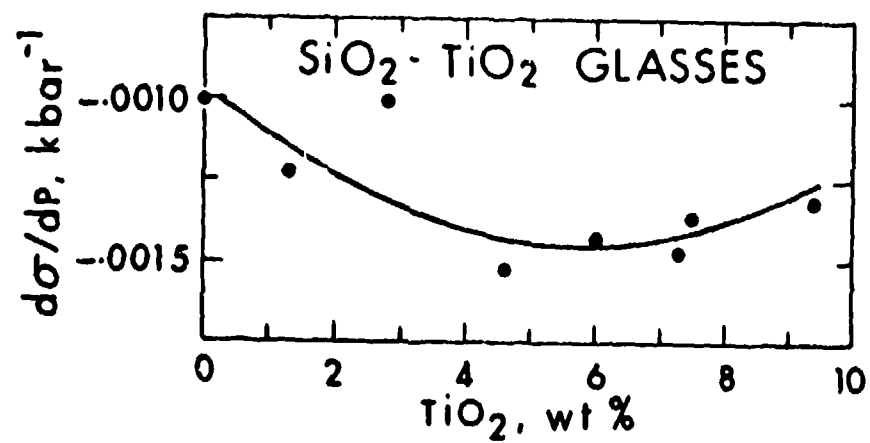


Fig. 6. $d\sigma/dP$ versus TiO₂ content.

properties of such modes so that $d\omega/dV$ becomes more positive, leading to more negative thermal expansion and more anomalous elastic behavior under pressure. Thus, the more negative values of dM/dP with increasing TiO_2 content are compatible with the thermal expansion data.

Densification

The pressure-density data for a solid can be used for calculating its bulk modulus, K_0 , and initial pressure derivative $K'_0 = (\partial K/\partial P)_{P=0}$ through the Birch-Murnaghan equation of state [24]:

$$P = (3/2 K_0 \{(\rho_0/\rho)^{7/3} - (\rho_0/\rho)^{5/3}\} \{1 - \xi [(\rho_0/\rho)^{2/3} - 1]\}) \quad (1)$$

where $\xi = 3(4 - K'_0)/4$. Inversely, if K_0 and K'_0 are known, (ρ/ρ_0) can be evaluated as a function of pressure.

Using eq. (1) and the data for fused silica and the SiO_2 - TiO_2 glasses containing 7.3 wt % TiO_2 (Table 2), (ρ/ρ_0) was calculated to 60 kbar (Fig. 7). As seen, the glass containing TiO_2 shows higher densification (ρ/ρ_0) . At 20 kbar the difference between (ρ/ρ_0) ratios would be ~7%.

Mode Grüneisen Parameters

The mode Grüneisen parameters γ_i are evaluated from the pressure dependence of acoustic mode velocity V_i :

$$\gamma_i = \frac{1}{V_i \beta} \left(\frac{dV_i}{dP} \right),$$

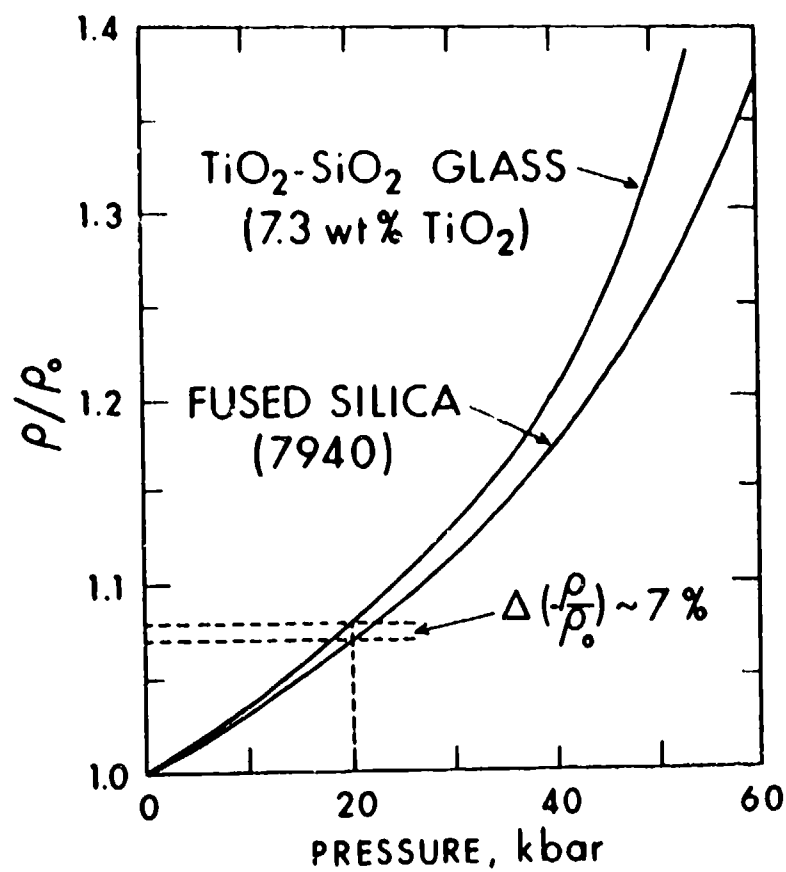


Fig. 7. Densification of fused silica and SiO₂-TiO₂ glass containing 7.3 wt % TiO₂.

where β is the isothermal compressibility. Assuming only the contributions from acoustic mode, the high- and low-temperature limiting values of the Gruneisen parameter, γ_{HT} and γ_{LT} , can be evaluated from (dV_g/dP) and (dV_p/dP) using the known relations [22,23]. As in fused silica, the γ_{HT} values for all the SiO_2 - TiO_2 glasses are negative (Fig. 8). As seen, γ_{HT} becomes more negative with TiO_2 content.

Temperature Dependence of Elastic Moduli

The temperature and composition dependence of K , μ and E measured to $300^\circ C$ are shown in Figure 9. The temperature derivatives of the moduli (dM/dT) are positive (anomalous) and remain the same in the temperature range of the investigation. The values of (dM/dT) decrease with increase in TiO_2 content (Fig. 10). That is, the glasses become less anomalous in the thermal behavior, in contrast to the more anomalous behavior under pressure.

The contributions to total change in modulus M due to temperature effect can be considered as intrinsic and extrinsic parts:

$$dM = \left(\frac{\partial M}{\partial T} \right)_V dT + \left(\frac{\partial M}{\partial V} \right)_T dV \quad (2)$$

(total) (intrinsic) (extrinsic)

It can be shown that the measured total (dM/dT) is related to the measures $(\partial M/\partial P)_T$:

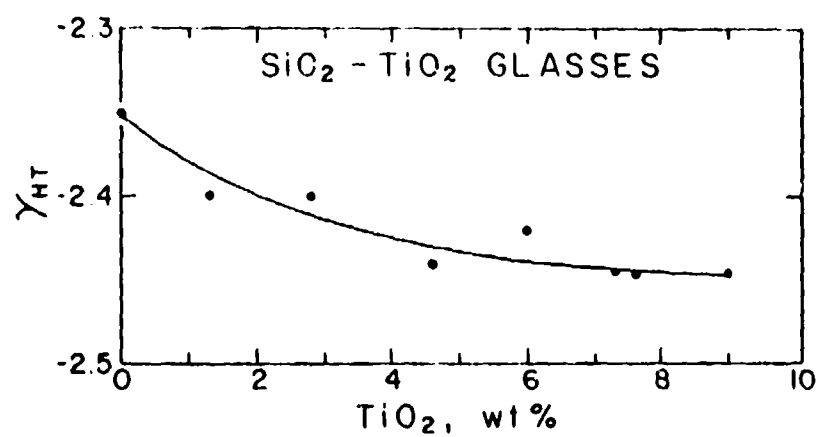


Fig. 8. Variation of Grüneisen parameter γ_{HT} in SiO₂-TiO₂ glasses.

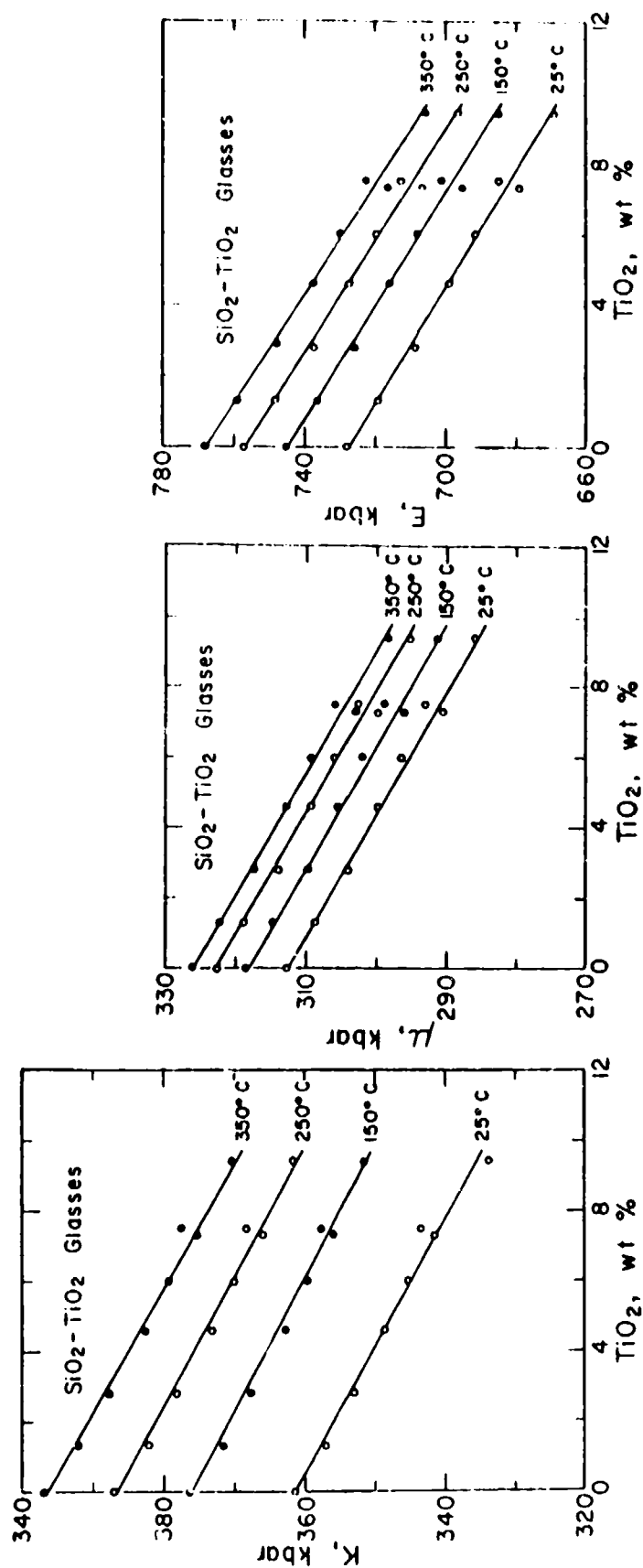


Fig. 9. Bulk (K), shear (μ), and Young's (E) moduli versus TiO_2 content for SiO_2 - TiO_2 glasses at different temperatures.

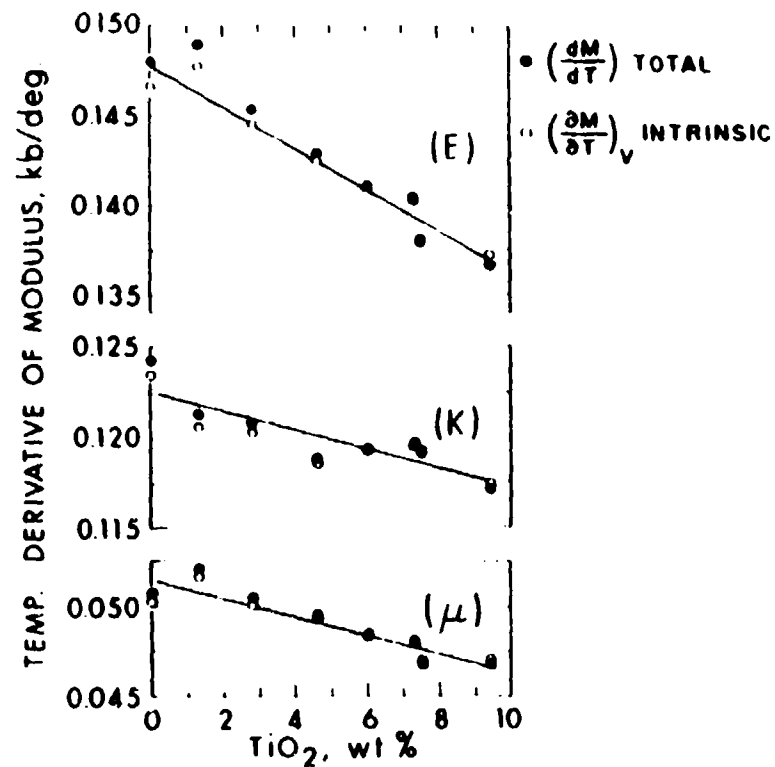


Fig. 10. Composition dependence of the total and intrinsic temperature derivatives of bulk (K), shear (μ), and Young's (E) moduli of SiO_2 - TiO_2 glasses.

$$\left(\frac{dM}{dT}\right)_P = \left(\frac{\partial M}{\partial T}\right)_V - \alpha K \left(\frac{\partial M}{\partial P}\right)_T$$

(total) (intrinsic) (extrinsic)

Using the data of Tables 1 and 2, and the thermal expansion coefficients [6], the two contributions were calculated (Table 3). As seen, the main contributions to total (dM/dT) are from the intrinsic effect (see also Fig. 10).

Summary and Conclusions

The density and elastic parameters of the SiO_2 - TiO_2 glasses studied show more or less systematic variation with composition.

V_p , V_s , ρ , E , K , and μ decrease more or less linearly with increase in TiO_2 content. Poisson's ratio for the unannealed glasses first increases and then decreases with increase in TiO_2 content, whereas the annealed glasses show increasing values of σ in a systematic manner. The systematic variations of elastic properties indicate that the coordination number of Ti^{4+} ions remains the same [4] in this range of composition; this is in agreement with earlier studies.

Annealing causes density and V_s to increase, and V_p to decrease. The temperature-dependence of moduli is mainly due to intrinsic effect for these glasses. The temperature derivatives of moduli are positive and anomalous, and become less anomalous with increase in TiO_2 content.

Table 3. Intrinsic and extrinsic contributions to the total temperature derivatives of bulk (k) and shear (μ) moduli in SiO_2 - TiO_2 glasses

Glass	TiO_2 wt. %	$\frac{dk}{dT}$ (total)	$-\left(\frac{\partial k}{\partial T}\right)_V$ (intrinsic)	$-\alpha k \left(\frac{\partial k}{\partial P}\right)_T$ (extrinsic)	$\frac{d\mu}{dT}$ (total)	$-\left(\frac{\partial \mu}{\partial T}\right)_V$ (intrinsic)	$-\alpha k \left(\frac{\partial \mu}{\partial P}\right)_T$ (extrinsic)
Fused silica							
Corning Code							
7940	0	.1243	.1235	$+7.89 \times 10^{-4}$	5.08×10^{-2}	5.02×10^{-2}	$+1.67 \times 10^{-6}$
T4A	1.3	.1213	.1206	+7.36	5.21	5.02	+1.50
T1A	2.8	.1208	.1203	+4.99	5.05	5.02	+1.08
T5A	4.6	.1188	.1185	+2.90	4.95	4.93	+0.58
T6A	6.0	.1193	.1193	+0.81	4.84	4.84	+0.16
T2A	7.3	.1196	.1200	-1.01	4.80	4.81	-0.21
ULE7971A	7.5	.1191	.1192	-1.30	4.68	4.69	-0.27
T3A	9.4	.1171	.1174	-3.77	4.68	4.70	-0.82

Adding of TiO_2 to SiO_2 structure causes pressure derivatives of the velocities and moduli to become more negative (i.e., more anomalous). That is, the anomalous behavior of fused silica is enhanced by addition of TiO_2 . In contrast, the temperature dependence of moduli is less anomalous as TiO_2 is added.

The acoustic mode gammas, γ_{HT} , become negative when TiO_2 content of glass increases. This is in agreement with the thermal expansion studies. Decrease in thermal expansion with addition of TiO_2 is related to the influence of TiO_2 on acoustic lattice vibration frequencies.

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PUBLISHED PAPERS

PRESSURE AND TEMPERATURE DEPENDENCE OF THE ELASTIC MODULI
OF $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ GLASSES

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I. Introduction

II. Experimental Methods

The diagram illustrates the experimental setup for measuring the heat of explosion. It features a high-pressure gas supply system starting with a Nitrogen Gas Supply (2000 PSI) connected to Intensifier 1, which in turn connects to Intensifier 2. The output of Intensifier 2 feeds into a Pressure Vessel. Inside the Pressure Vessel, a Sample is placed within an Explosion Shield, which is surrounded by a Copper Coil. Pt & Thermocouple Leads are connected to the vessel for temperature monitoring. The Pressure Vessel is linked to a Gas/GN Separator, which then connects to a DWT 300 Dead Weight Tester for precise pressure measurement.

200,000 PSI PRESSURE SYSTEM

Fig. 1. Pressure-generating system.

X- and Y-cut quartz transducers of 30 MHz natural resonant frequency were used to generate the compressional and shear waves in the specimen. A two-stage pressure-generating system¹ (Fig. 1) was used in which the initial gas pressure of ≈ 2000 psi was intensified to 40,000 psi in the first stage and 200,000 psi in the second stage. Nitrogen was the pressure medium. Measurements were made following increasing and decreasing pressure cycles to 100,000 psi (≈ 6.9 kbars). An interval of 15 to 20 min was usually allowed between the pressure change and a pulse repetition frequency (prf) measurement. The pressure on the specimen was monitored using

¹Resin 278-V9, Dow Chemical Co., Midland, Mich.
²Harwood Engineering Co., Inc., Walpole, Mass.

Table I. Chemical Compositions of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses

Glass No.	Code No. (Ref. 1)	Constituents (mol%)		
		Na_2O	TiO_2	SiO_2
1	E1986	30.0	20.0	50.0
2	E1909	25.0	20.0	55.0
3	E1990	17.5	20.0	62.5
4	E2011	27.5	25.0	47.5
5	E2010	22.5	25.0	52.5
6	E1991	17.5	25.0	57.5

a 120- Ω Manganin coil placed inside the vessel and a resistance bridge*; the coil was calibrated for pressure with a dead-weight tester† to 60,000 psi. Uncertainties in the absolute pressures measured with the dead-weight tester are estimated to be $<0.1\%$ at 60,000 psi. Thus the reported pressure derivatives of the elastic moduli are $<\pm 1\%$ in error. During a prf measurement, the test specimen in the pressure vessel was maintained at $25 \pm 0.1^\circ\text{C}$ by constant-temperature water circulating in coils wound around the vessel.

The temperature dependence of the elastic moduli of these glasses was investigated to 300°C by using a thermally insulated furnace powered by a solid-state temperature-control device. A special high-temperature rubber seal was used to bond the transducer to the specimen, which was heated at a rate of $\approx 2^\circ\text{C}/\text{min}$. Specimen temperature was increased in intervals of $\approx 10^\circ\text{C}$ and maintained to $\pm 0.1^\circ\text{C}$ during prf measurements.

III. Specimens

The physical properties of glass specimens from the same batch as those used in the present study‡ were reported by Hanulton and Cleek‡; their compositions are given in Table I. All the specimens were heated for 4 to 6 h at a temperature $\approx 40^\circ\text{C}$ below the sag point and cooled at $2.5^\circ\text{C}/\text{h}$ to 350°C (see Ref. 1).

Investigation§ of the crystallization behavior of glasses in the system $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ has shown that those with compositions similar to those in Table I form in homogeneous phases. Phase separation occurs only when the TiO_2 content is higher ($>30 \text{ mol}\%$) and/or the SiO_2 content lower ($<10 \text{ mol}\%$). Variations in the elastic moduli, measured under atmospheric conditions in three mutually perpendicular directions in each of the six specimens, were within experimental error, thus characterizing the isotropic behavior of the specimens.

IV. Discussion of Results

(1) Measurements at 1 Bar and 25°C

The elastic properties of the glasses measured at 1 bar and 25°C are given in Table II. The relations between these

*Carey-Foster bridge, Harwood Engineering Co., Inc.

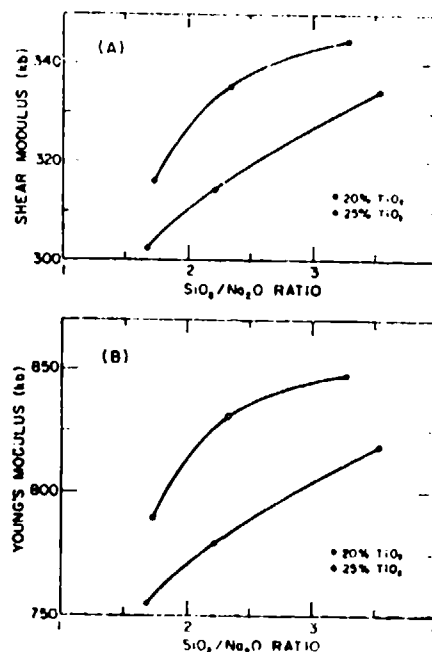
†DWT 300, Harwood Engineering Co., Inc.

‡Obtained through the courtesy of G. W. Cleek, National Bureau of Standards, Washington, D. C.

Table II. Elastic Properties of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses at 1 Bar and 25°C

Glass No.	$\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio	Y	ρ (g/cm^3)	v_p (km/s)	v_s (km/s)	K (kbars)	μ (kbars)	E (kbars)	σ
1	1.67	2.00	2.749	5.731	3.315	500.0	302.1	754.4	0.249
2	2.22	2.36	2.740	5.794	3.386	501.1	314.1	779.5	.241
3	3.54	2.80	2.703	5.895	3.516	493.9	334.2	818.0	.224
4	1.73	1.79	2.811	5.806	3.353	526.4	315.9	789.8	.250
5	2.33	2.19	2.800	5.906	3.461	529.5	334.5	830.7	.239
6	3.28	2.52	2.771	5.955	3.526	523.4	344.5	847.5	.230

NOTE: Y=structural parameter, ρ =density, v_p =compressional wave velocity, v_s =shear wave velocity, K=bulk modulus, μ =shear modulus, E=Young's modulus, and σ =Poisson's ratio.

Fig. 2. Plots of (A) shear modulus and (B) Young's modulus vs $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses.

properties and chemical composition can be interpreted in terms of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio or in terms of the structural parameter Y, as introduced by Trap and Stevels¹⁰ in discussing SiO_2 -based glasses. The parameter Y, which represents the number of bridging oxygen ions/ SiO_4 tetrahedron, is computed as $Y = 6 - 200/p$, where p is the SiO_2 content (in mol%). Thus, for pure SiO_2 glass $Y=4$; it decreases as network-modifying oxides are introduced. In the present case, the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio and Y parameter (Table II) have the same significance in that both represent a measure of the number of Si-O-Si bridges and the openness of the structure. For glasses with similar TiO_2 contents, the compressional and shear wave velocities (v_p and v_s) and the shear and Young's moduli (μ and E) increase and the density (ρ) and Poisson's ratio (σ) decrease with increasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio (and Y). These increases in μ and E are not linear (Fig. 2); the rate of increase is greater for the lower $\text{SiO}_2/\text{Na}_2\text{O}$ ratios. Figure 2 also shows that increasing the TiO_2 content increases the moduli; further, for the glasses with the higher TiO_2 content the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in increasing the moduli is less. The relations shown in Fig. 2 can be used to estimate the moduli of glasses of intermediate composition.

The bulk modulus, K, varies neither as appreciably nor as uniformly as the other moduli with the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. Comparison of the data for glasses 1 and 3 and for glasses 4 and 6 shows that the lower the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, the higher the bulk modulus (and the lower the compressibility). Similar findings

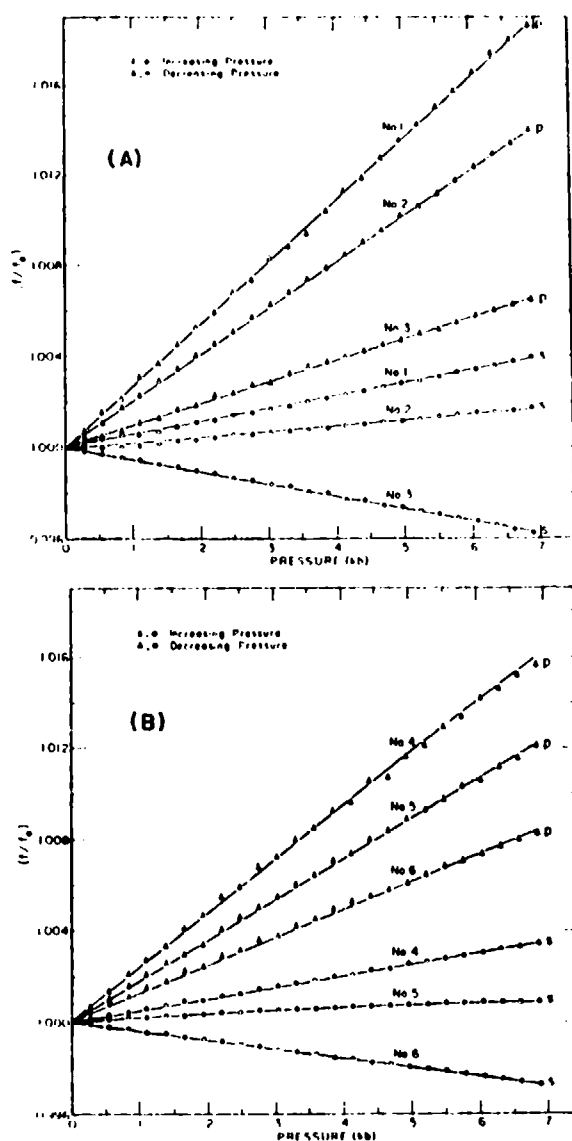


Fig. 3. Plots of frequency ratio, f/f_0 , vs pressure for (A) glasses containing 20% TiO_2 , and (B) glasses containing 25% TiO_2 (p indicates longitudinal wave; s, shear wave).

were reported by Weir and Shartsis¹² in their study of alkali silicate glasses. The explanation for the decrease in compressibility with decreasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio is that the degree of atomistic void-space in the glass structure diminishes with the introduction of Na_2O .

(2) Measurements Under Pressure

Plots of the prf ratio, f/f_0 , where f and f_0 are the frequencies at a given pressure and at 1 bar, respectively, vs pressure for

the longitudinal and shear modes of wave propagation are shown in Fig. 3. These relations exhibit no hysteresis, indicating that the glasses are completely elastic in this pressure range and do not undergo the permanent densification that may occur at much higher pressures.

(A) **Densification** Densification of silica and silicate glasses under pressure has been the subject of several studies.¹³⁻¹⁶ Bridgman and Simon¹³ reported that vitreous SiO_2 undergoes a permanent densification of 7% at 200 kbars and that no observable densification occurs below 100 kbars, whereas Cohen and Roy¹⁴ achieved a 7% densification of SiO_2 glass at only 55 kbars. The threshold pressure and the rate of increase of density are functions of glass composition and temperature and the degree of the nonhydrostatic nature of the applied pressure. It has also been pointed out¹⁵ that the shearing effect under nonhydrostatic conditions is important in densification. The densification of a silicate glass is regarded as the "folding up" of its disordered vitreous structure, such that the Si-O bond angles are altered without apparent changes in the tetrahedral Si-O distances. Most studies of the densification of glasses have been conducted at very high pressures.^{13,16}

In situ densification at pressures much lower than the threshold pressures, in the pressure range in which the behavior of the glasses is completely elastic, can be studied precisely using ultrasonic measurements. The specimen length and density ratios (l/l_0 and ρ/ρ_0) at pressure P are given by¹⁷:

$$(l/l_0) = (\rho/\rho_0)^{1/\alpha} = \left[1 + \frac{1 + \alpha\gamma T}{\rho_0} \int_0^P \frac{dP}{3A - 4B} \right]^{1/\alpha} \quad (1)$$

where α is the coefficient of volumetric thermal expansion, γ is the Gruenisen parameter, T is the temperature ($^{\circ}\text{K}$), $A = v_p(f/f_0)^2$, and $B = v_s(f/f_0)^2$; the zero subscripts indicate values under ambient conditions (1 bar and 25°C). Using Eq. (1), ρ/ρ_0 at pressures to ≈ 7 kbars was calculated for all the glasses; in all cases, the relation between ρ/ρ_0 and P was linear. The ρ/ρ_0 values at 6.9 kbars are listed in Table III. The glasses with the higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratios show the greater compression (i.e. have higher ρ/ρ_0 values), and those with the lower TiO_2 content (glasses 1-3) exhibit a more pronounced effect of increasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratios in increasing compression.

(B) **Pressure Derivatives of Elastic Properties:** The velocities (v_p and v_s) and the elastic moduli at a given pressure were calculated from the measured prf's for the compressional and shear modes (f_p and f_s):

$$\begin{aligned} \text{Compressional velocity, } v_p &= 2lf_p \\ \text{Shear velocity, } v_s &= 2lf_s \\ \text{Bulk modulus, } K &= \rho(v_p^2 - v_s^2/3) \\ \text{Shear modulus, } \mu &= \rho v_s^2 \\ \text{Young's modulus, } E &= (9K\mu)/(3K + \mu) \\ \text{Poisson's ratio, } \sigma &= 1 - (E/2\mu) \end{aligned}$$

The pressure derivatives thus determined (Table III) are systematically related to composition, i.e. to the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. The relation between the elastic-wave velocities (v_p and v_s) and pressure is shown in Fig. 4; v_p increases with pressure in all cases. The value of (dv_p/dP) is positive and decreases with increasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, whereas (dv_s/dP)

Table III. Pressure Derivatives of the Elastic Properties of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses

Glass No.	dv_p/dP (km/s-Mbars)	dv_s/dP (km/s-Mbars)	dK/dP	$d\mu/dP$	dE/dP	$d\sigma/dP$ (Mbars ⁻¹)	ρ/ρ_0 (at 6.9 kbars)
1	12.0	-0.20	4.85	0.53	2.29	1.57	1.0130
2	8.03	-1.24	3.62	0.37	1.76	1.34	1.0132
3	1.69	-4.19	2.89	-0.15	0.47	1.24	1.0136
4	9.69	-0.35	4.00	0.51	2.03	1.19	1.0125
5	6.70	-1.64	3.64	0.29	1.56	1.25	1.0128
6	3.43	-3.55	3.05	-0.06	0.73	1.29	1.0128

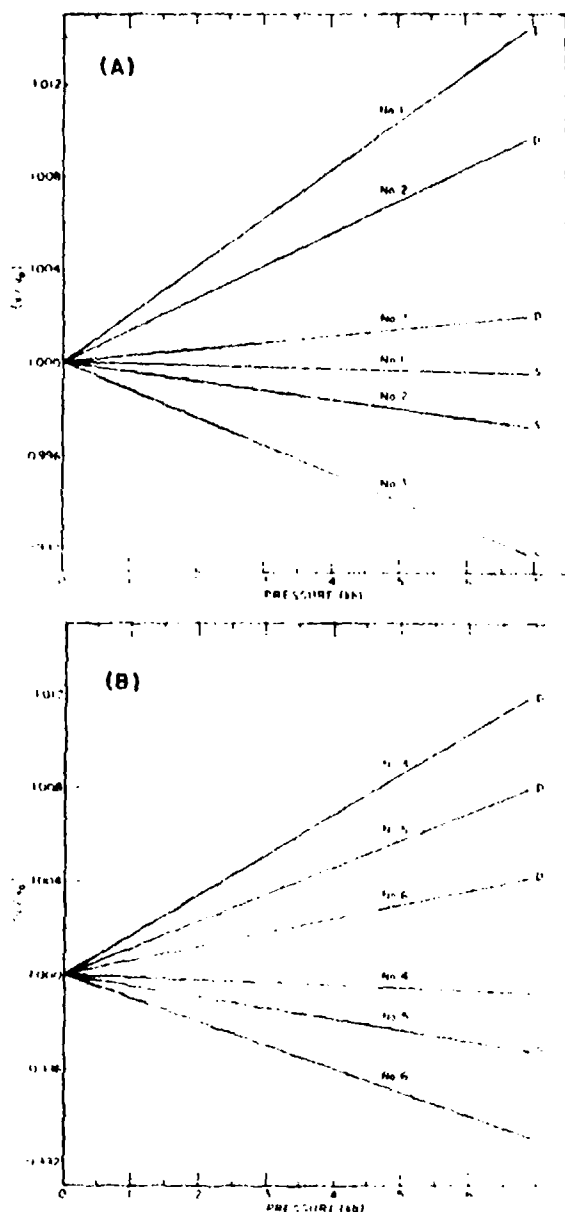


Fig. 4. Plots of velocity ratio, v/c , vs pressure for (A) glasses Nos. 1-3 and (B) glasses Nos. 4-6 (p indicates longitudinal wave; s , shear wave; v , velocity at 1 bar).

is negative and becomes increasingly negative with increasing SiO₂/Na₂O ratio.

For all the glasses, the bulk modulus increases with pressure (Fig. 5(A)); this behavior is normal. For most crystalline oxide solids, dK/dP varies from 4 to 6 at pressures near zero; for the glasses investigated, dK/dP varied from 2.59 to 4.85. In general, dK/dP decreases linearly with increasing SiO₂/Na₂O ratio (Fig. 6(A)). However, the relations clearly differ with TiO₂ content. It is predicted that dK/dP will be zero for the glass with 20 mol% TiO₂ and an SiO₂/Na₂O ratio of 22.9. The shear modulus decreases with pressure for glasses 3 and 6 (which have the maximum SiO₂/Na₂O ratio) and increases with pressure for the other glasses (Fig. 5(B)). Further, in contrast to the relation between dK/dP and the SiO₂/Na₂O ratio, which is linear, that between $d\mu/dP$ and the SiO₂/Na₂O ratio is not (Fig. 6(B)).

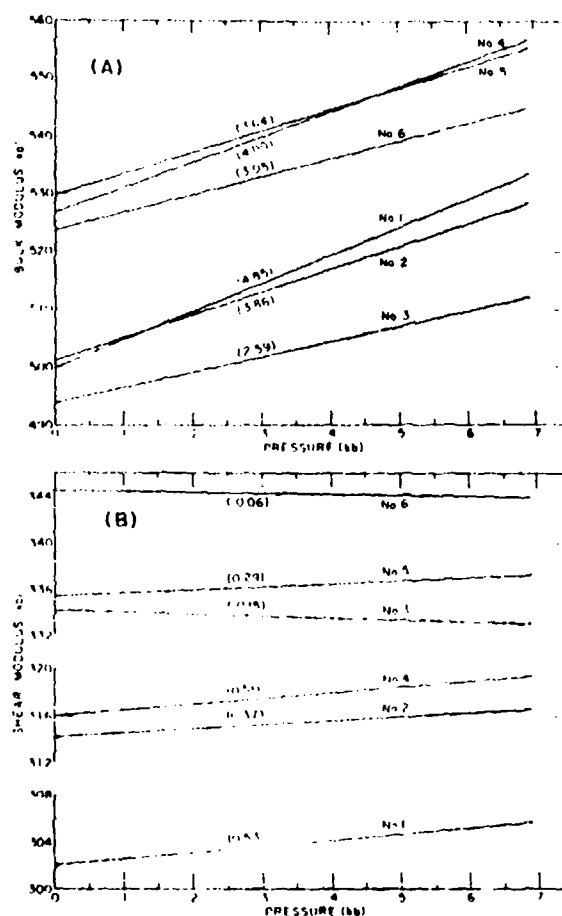


Fig. 5. Pressure dependence of (A) bulk modulus and (B) shear modulus for the glasses; pressure derivatives are given in parentheses.

For all the glasses studied, dE/dP ranges from 2.29 to 0.47 and decreases with increasing SiO₂/Na₂O ratio. The values of $d\sigma/dP$ are positive and range from 1.19 to 1.57/Mbar (Fig. 7).

(3) Measurements to 300°C. at 1 Bar

The temperature dependence of elastic moduli is a measure of changes in the intrinsic structure of a material and involves both the odd- and even-powered terms of the anharmonic expansion. The effects of temperature on the elastic properties were investigated to 300°C. The variation with temperature, T , of any modulus, M , is given by:

$$\frac{M_T}{M_0} = \frac{\rho_T}{\rho_0} \left(\frac{f_T}{f_0} \right)^2 \left(\frac{L_T}{L_0} \right)^2 = \left(\frac{f_T}{f_0} \right)^2 \frac{L_T}{L_0} \quad (2)$$

The length ratio (L_T/L_0) was estimated from thermal expansion data¹⁰ and used to compute the elastic moduli. Figure 8 and Table IV show the temperature dependencies of the bulk and shear moduli. The dK/dT and $d\mu/dT$ values become increasingly negative with increasing temperature and, for a given temperature, become systematically less negative with increasing SiO₂/Na₂O ratio. This result is obviously related to the anomalous temperature behavior of vitreous SiO₂, which is known to exhibit positive dM/dT values^{11,12} ($dK/dT=0.111$ kbars/°C; $d\mu/dT=0.045$ kbars/°C). Thus, as the amount of SiO₂ in the composition of Na₂O-TiO₂-SiO₂ glasses increases, dM/dT becomes less negative (more positive). The relations between dK/dT and $d\mu/dT$ and the SiO₂/Na₂O ratio, although

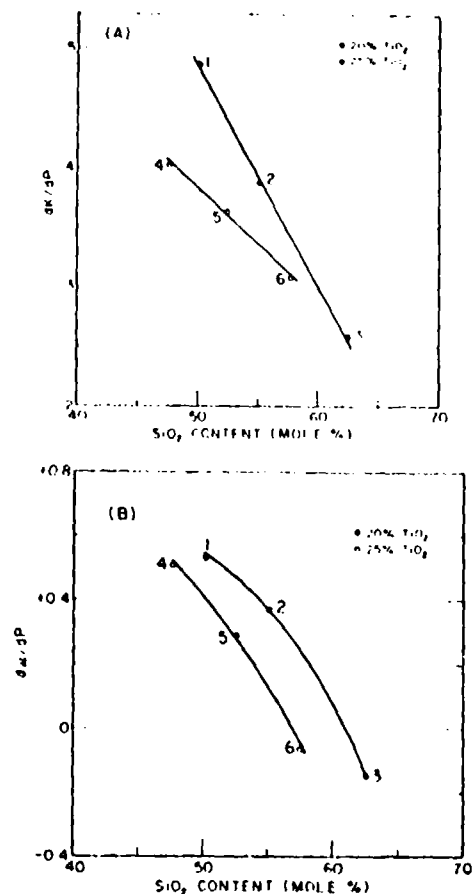


Fig. 6. Relation between (A) dK/dP and (B) $d\mu/dP$ and SiO_2 content for $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses.

nonlinear, can be used to predict the elastic behavior of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses under various temperature conditions.

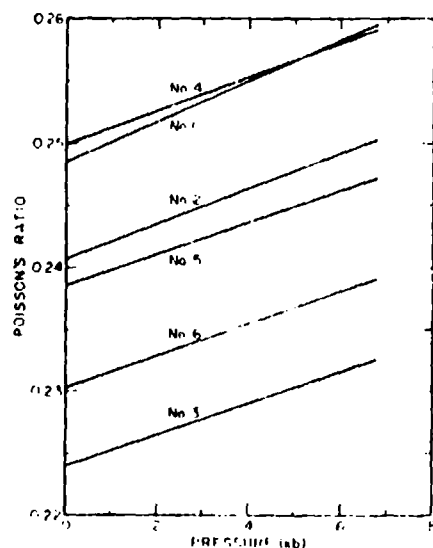


Fig. 7. Poisson's ratio as a function of pressure for the glasses.

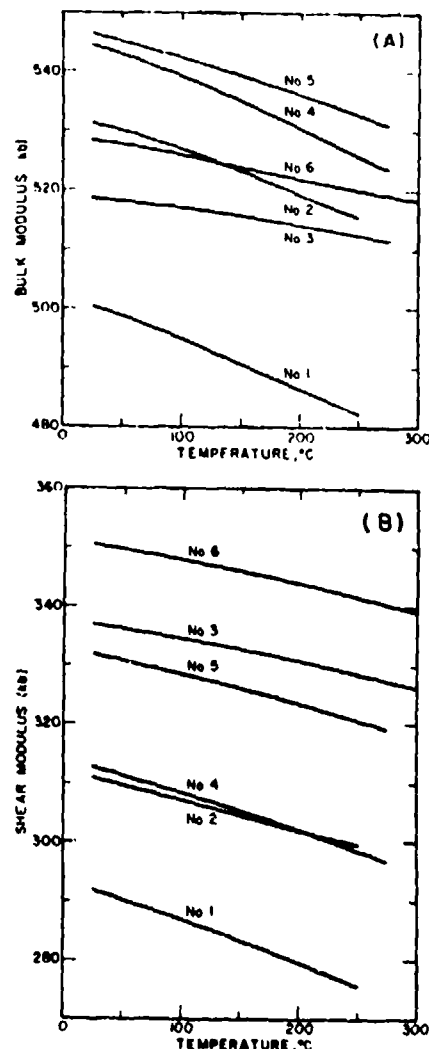


Fig. 8. Temperature dependence of (A) bulk modulus and (B) shear modulus of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses.

The total temperature derivative of an elastic modulus, M , given by $(dM/dT)_P$, is related to the intrinsic (temperature) and extrinsic (volume) effects by

$$\left(\frac{dM}{dT}\right)_P = \left(\frac{\partial M}{\partial T}\right)_P - \alpha K \left(\frac{\partial M}{\partial P}\right)_P \quad (3)$$

where α is the coefficient of volumetric thermal expansion. Using the data given in Tables II through IV, the intrinsic and extrinsic coefficients in Eq. (3) were calculated (Table V). In all cases, $(dK/dT)_P$ is negative and $(\partial K/\partial T)_P$ is positive, implying that the sign of $(dK/dT)_P$ is governed by the sign of $(\partial K/\partial P)_P$, i.e. that the observed temperature dependence of K results primarily from volume change (thermal expansion). The contribution to $(dK/dT)_P$ of the intrinsic (temperature) effect, with opposite sign, varies from 1 to $\approx 44\%$ of the observed $(dK/dT)_P$. In the case of the temperature dependence of μ , the main contribution to $(d\mu/dT)_P$ is the intrinsic (temperature) effect; very small contributions result from volume change. In the case of glasses 3 and 6, which have higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratios than the other two specimens in a series of glasses with similar TiO_2 contents, the sign of the contribution from the extrinsic effect (volume change) is opposite to that

Table IV. Temperature Dependence of the Elastic Properties of Na₂O-TiO₂-SiO₂ Glasses

Glass No.	Linear thermal expansion coeff. ($\times 10^6$)	SiO ₂ /Na ₂ O molar ratio	K (kbars)	μ (kbars)	ν	dK/dT (kbars/°C)	$d\mu/dT$ (kbars/°C)	$d\nu/dT$ (°C ⁻¹ $\times 10^6$)
1	134	1.67	500.3	291.8	0.256	-0.081	-0.071	1.7
2	116	2.22	531.1	310.9	.255	-0.070	-0.051	0.7
3	89	3.54	518.6	336.9	.233	-0.025	-0.036	1.3
4	124	1.73	544.2	312.6	.259	-0.080	-0.063	1.0
5	107	2.33	546.4	331.9	.247	-0.057	-0.048	0.9
6	89	3.28	528.3	350.3	.228	-0.035	-0.038	1.0

Table V. Intrinsic and Extrinsic Coefficients for Eq. (3)*

Glass No.	Measured $\left(\frac{dM}{dT}\right)_P$ (kbars/°C)	Calculated $\left(\frac{dM}{dT}\right)_P$ (kbars/°C)	Measured $\nu K \left(\frac{dM}{dP}\right)_T$ (kbars/°C)
		M = bulk modulus, K	
1	-0.081	+0.0165 (20.4) [†]	-0.0975 (120.4)
2	-0.070	+0.0013 (1.9) [†]	-0.0713 (101.9)
3	-0.025	+0.0109 (43.6) [†]	-0.0359 (143.6)
4	-0.080	+0.0010 (1.3) [†]	-0.0810 (101.3)
5	-0.057	+0.0068 (11.9) [†]	-0.0638 (111.9)
6	-0.035	+0.0080 (22.9) [†]	-0.0430 (122.9)
		μ = shear modulus, μ	
1	-0.071	-0.0663 (84.9)	-0.0107 (15.1)
2	-0.051	-0.0442 (86.7)	-0.0068 (13.3)
3	-0.036	-0.0381 (105.8)	+0.0021 (5.8) [†]
4	-0.063	-0.0527 (83.7)	-0.0103 (16.3)
5	-0.048	-0.0429 (89.4)	-0.0051 (10.6)
6	-0.038	-0.0388 (102.1)	+0.0008 (2.1) [†]

*Contributions to total effect (in %) are shown in parentheses.

[†]Sign is opposite that of dM/dT .

of $(d\mu/dT)_P$ because $(d\mu/dP)_T$ in these cases is negative. When the temperature variations of both K and μ are considered (Table V), a tendency of the extrinsic effect (volume change) to decrease with decreasing SiO₂/Na₂O ratio is noted.

V. Summary

(1) The elastic moduli of the Na₂O-TiO₂-SiO₂ glasses vary systematically with composition; the SiO₂/Na₂O ratio is the most important factor. A network-modifying oxide such as TiO₂ increases the moduli and their pressure derivatives.

(2) The Na₂O-TiO₂-SiO₂ glasses studied behave as normal crystalline solids under pressure and temperature except for Nos. 3 and 6, which exhibit negative $d\mu/dP$ values. This anomaly is related to the vitreous SiO₂ content. The pressure and temperature derivatives of the moduli vary systematically but not always linearly with the SiO₂/Na₂O ratio. These relations can be used to predict the elastic behavior of glass at moderately high pressures and temperatures.

(3) The observed effect of temperature on the bulk moduli of the glasses investigated results primarily from volume changes associated with thermal expansion. The temperature dependence of shear moduli of these glasses, however, is related principally to the intrinsic (temperature) effect.

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INFRARED SPECTRA OF SEVERAL GLASSES
AT HIGH PRESSURES

By

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(HIG Contribution No. 414)

Infrared spectra of several glasses at high pressures*

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The infrared absorption spectra of crystalline α -quartz, fused silica, and Pyrex and Vycor (Corning Glass Works) glasses were studied at pressures up to 58.8 kb. The spectra of the fused silica and glasses are more simple than those of α -quartz, and their three main absorption bands appear at higher frequencies than in the case of α -quartz. The intertetrahedral Si stretching mode at $\sim 800\text{ cm}^{-1}$ is found to be comparatively more sensitive to pressure, whereas the intratetrahedral Si-O stretching mode at $\sim 1100\text{ cm}^{-1}$ is less affected by pressure. The Grüneisen gammas γ_i , calculated from the pressure dependence of the infrared vibration mode frequencies, are compared with the γ_{ijk} values and those deduced from the pressure dependences of the elastic parameters. The negative γ values are discussed in terms of the anomalous thermal expansion and elastic behaviour of glasses.

Glass is a possible material for the hulls of undersea vehicles and, therefore, there has been considerable interest in the study of its structure and the behaviour under pressure. Various physical tools have been used to characterise the glassy state and to elucidate the structure; one of these is vibrational spectroscopy. Much effort has already been devoted to the infrared study of glasses at ambient temperatures and pressures. Infrared absorption studies have been made on the crystalline polymorphs and the vitreous forms of SiO_2 (1-13) and several Raman studies (14-17) have also been conducted on quartz at high temperatures. More recently the Raman spectrum of α -quartz was studied under pressure.⁽¹⁸⁾ However, the infrared absorption spectra of glasses at high pressures have not been investigated to any great extent.⁽¹⁹⁾

The basic structure of various polymorphs of silica and silicate glasses consists of SiO_4 groups in which silicon atoms are tetrahedrally bound to four oxygen atoms, each being common to two tetrahedra. Thus, each oxygen atom is coordinated to two silicon atoms and six oxygen atoms. In silica based glasses the

arrangement of the individual SiO_4 tetrahedra is repeated in a random fashion. The infrared spectra of the silicate glasses correspond to the vibrations of the SiO_4 groups and are characterised by at least three main absorption bands at ~ 1100 , ~ 800 , and $\sim 460\text{ cm}^{-1}$. Lippincott *et al.*⁽⁷⁾ assigned the various absorptions based on a T_d symmetry: the high-frequency absorption, $\sim 1100\text{ cm}^{-1}$, to the Si-O stretching mode corresponding to the motion of silicon and oxygen atoms in opposite directions within tetrahedra, $\leftarrow\text{SiO}\rightarrow\leftarrow\text{Si}$; the intermediate frequency absorption, $\sim 800\text{ cm}^{-1}$, to the Si stretching mode in which the Si stretches between tetrahedra, $\leftarrow\text{SiOSi}\rightarrow$; and the low frequency absorption, $\sim 460\text{ cm}^{-1}$, to the bending modes which involve a combination of the O-Si-O bending mode within the tetrahedra, and the Si-O-Si bending mode between the tetrahedra. Normally, this latter absorption appears as a broad band in the infrared; its position has been evaluated in terms of the changes which occur in the Si-O-Si angle between tetrahedral units in the glass structure.^(20, 21) Anderson & Dienes⁽²²⁾ have pointed out that the low frequency Si-O-Si bending vibration is responsible for the anomalous behaviour of vitreous silica under pressure (that is the increase in compressibility with pressure). One of the aims of this study was to investigate the pressure dependences of the infrared vibrational frequencies for α -quartz and the silicate glasses, and to correlate the results in terms of their anomalous thermal expansion and elastic behaviour.

Experimental

Corning Glass Works glasses of commercial grade were employed in this study. The specimens were crushed in a ball mill, and finally powdered by extensive grinding in an agate mortar.

The infrared absorption spectra at ambient conditions were obtained by use of a Beckman IR-12 spectrophotometer and the KBr pellet method was used.

An opposed diamond anvil cell linked with a Perkin-Elmer No. 301 spectrophotometer equipped with a $6\times$ beam condenser was used to obtain the low frequency infrared absorption spectra ($<650\text{ cm}^{-1}$) at high pressure. Studies $>650\text{ cm}^{-1}$ at high pressures were made with a Beckman IR-12 equipped with a $6\times$ beam condenser. The powdered sample was loaded in the cell, and the pressure alternately increased and

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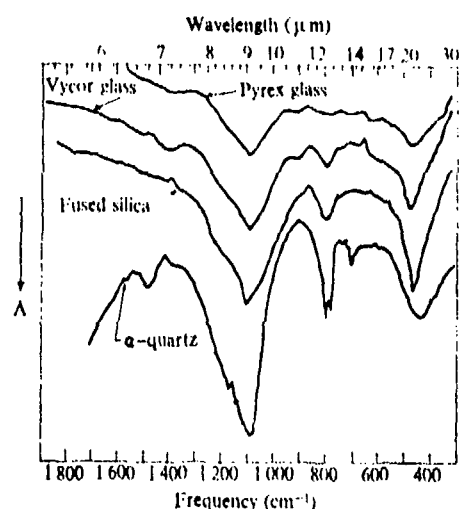


Figure 1. Infrared spectra of α -quartz and several glasses

decreased to distribute the material evenly between the anvils. During the pressure cycling the sample was observed under a microscope. A description of the pressure cell and the method used in pressure calibration has been previously reported.^(23, 24)

Results

Infrared spectra of α -quartz and silicate glasses

The material α -quartz, belongs to the trigonal system and has a D_3 symmetry with 3 SiO_2 units per primitive unit cell.⁽²⁵⁾ Thus a total of 24 optical modes of A_1 , A_2 , and E species are predicted

$$I' = 4A_1(R) + 4A_2(IR) + 8E(IR, R)$$

where R and IR represent the Raman and infrared activity, respectively. The infrared spectrum is observed to be simpler than that predicted by the selection rules using the D_3 symmetry; however, some question has arisen concerning the suitability of assigning the spectrum of α -quartz in terms of a D_3 symmetry as five A_1 polarised Raman active bands are observed instead of the four predicted by the selection rules.

Figure 1 compares the infrared spectra of the three glasses with that of α -quartz. As can be seen, the spectra of the glasses are simpler and have only three main absorption bands, whereas α -quartz shows

Table 1. Assignments of the principal vibrational frequencies of α -quartz, fused silica, and Vycor and Pyrex glasses

Vibrational mode	Frequency (cm^{-1}) in α -quartz	Fused silica	Vycor	Pyrex
$\delta_{\text{SiOSi}} + \delta_{\text{OSiO}}$	459	475	469	471
$\nu_{\text{Si-O-Si}} \rightarrow$	783 and 800 (doublet)	815	814	812
$\nu_{\text{Si-O}} \rightarrow \leftarrow \text{Si}$	1082	1087	1100	1095
$\nu_{\text{Si-O}} \leftarrow \text{Si}$	1168	—	—	—
ν_{HO}	—	—	1384	1390

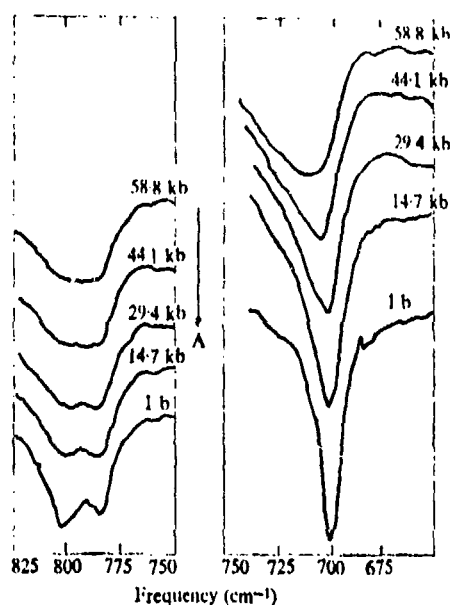


Figure 2. Pressure dependences of the Si stretching vibrations in α -quartz

additional absorptions at ~ 700 (w) and ~ 1480 cm^{-1} (m to w), and a doublet is observed near 800 cm^{-1} . The observed frequencies of the major bands at atmospheric pressure are given in Table 1. The three main characteristic absorptions of fused silica and of Vycor and Pyrex glasses are at higher frequencies than those of α -quartz, indicating larger force constants for these vibrations.

Pressure dependences of the infrared vibrations

α -quartz. Table 2 and Figure 2 present the pressure dependences of the vibrational frequencies of α -quartz. As shown, the frequency of the broad Si-O stretching band at ~ 1080 cm^{-1} decreases slightly and the shoulder at 1168 cm^{-1} shows negligible change with

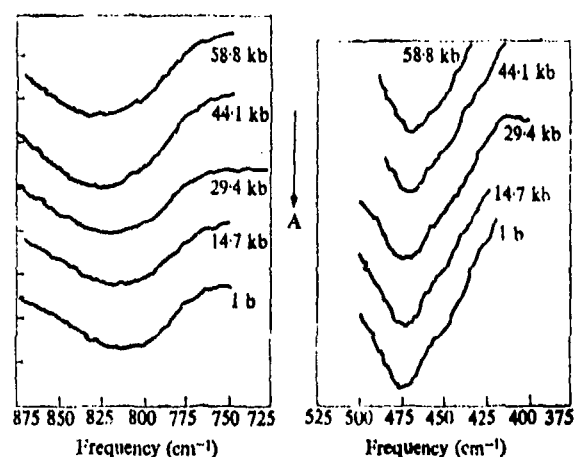


Figure 3. Pressure dependence in fused silica
(a) The Si stretching vibration
(b) The SiOSi and OSiO bending vibrations

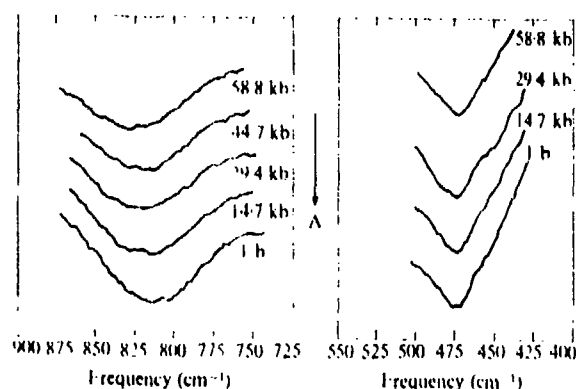


Figure 4. Pressure dependence in Vycor glass

(a) The Si stretching vibration
(b) The SiOSi and OSiO bending vibrations

increasing pressure. The Si stretching frequencies at ~ 700 – 800 cm^{-1} and the mixed bending mode at ~ 460 cm^{-1} are relatively more sensitive to pressure and have positive dependence. The frequency of the doublet at 783 and 798 cm^{-1} increases up to ~ 30 kb, at which pressure it disappears, and a single broad band appears. The latter shows little pressure dependence at higher pressures.

Fused silica. Figure 3 and Table 2 show the effects of pressure on the infrared vibrations of fused silica. The frequency of the mixed bending mode in fused silica near 475 cm^{-1} decreases with increasing pressure, but that of the Si stretching near 815 cm^{-1} increases and that of the Si–O stretching mode near 1090 cm^{-1}

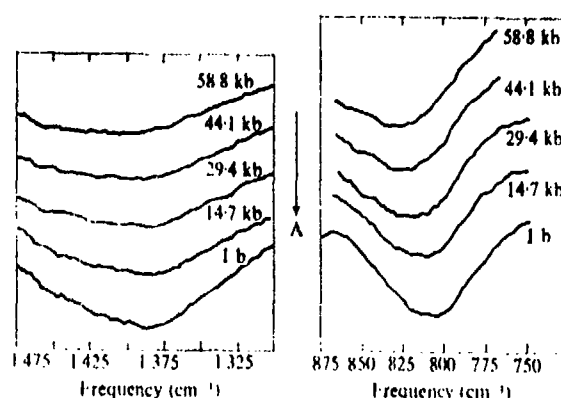


Figure 5. Pressure dependence in Pyrex glass

(a) The B–O stretching vibration
(b) The Si stretching vibration

shows no change, within experimental error, with increasing pressure.

Vycor and Pyrex glasses. Figures 4 and 5 and Table 2 show the effects of pressure on the vibrational frequencies of Vycor and Pyrex glasses. The frequency of the mixed bending mode for both of these glasses near 469 cm^{-1} is observed to be independent of pressure. For both glasses, which contain B_2O_3 (3% in Vycor and 13% in Pyrex) the B–O stretching mode at ~ 1385 cm^{-1} shifts towards higher frequency. The mode at ~ 1100 cm^{-1} decreases in frequency with pressure for Vycor, and is independent of pressure for Pyrex. For both glasses the Si stretching vibration increases in frequency with pressure.

Table 2. Effect of pressure on the principal vibrational frequencies of crystalline α -quartz, fused silica, and Vycor and Pyrex glasses*

Pressure (kb)	Frequency (cm^{-1}) Si–O–Si O–Si–O bending	Si stretching	Si stretching	Si–O stretching	B–O stretching
α-quartz					
0.001	459 $\pm$ 2	698 $\pm$ 2	783 $\pm$ 2	1082 $\pm$ 3	
14.7	460 $\pm$ 2	700 $\pm$ 2	785 $\pm$ 2	1081 $\pm$ 3	
29.4	461 $\pm$ 2	702 $\pm$ 2	787 $\pm$ 2	1081 $\pm$ 3	
44.1	463 $\pm$ 2	704 $\pm$ 2	790 $\pm$ 3	1080 $\pm$ 3	
58.8	464 $\pm$ 2	707 $\pm$ 2	792 $\pm$ 3	1078 $\pm$ 3	
Fused silica					
0.001	475 $\pm$ 2		815 $\pm$ 3		
14.7	472 $\pm$ 2		818 $\pm$ 3		
29.4	472 $\pm$ 2		820 $\pm$ 3		
44.1	471 $\pm$ 2		822 $\pm$ 3		
58.8	(split at 461.5) 471 $\pm$ 2		825 $\pm$ 3		
Vycor					
0.001			814 $\pm$ 3	1100 $\pm$ 3	1384 $\pm$ 3
14.7			817 $\pm$ 3	1098 $\pm$ 3	1386 $\pm$ 3
29.4			820 $\pm$ 3	1096 $\pm$ 3	1387 $\pm$ 3
44.1			823 $\pm$ 3	1095 $\pm$ 3	1390 $\pm$ 3
58.8			827 $\pm$ 3	1093 $\pm$ 3	1392 $\pm$ 3
Pyrex					
0.001			812 $\pm$ 5		1390 $\pm$ 5
14.7			815 $\pm$ 5		1392 $\pm$ 5
29.4			818 $\pm$ 5		1395 $\pm$ 5
44.1			822 $\pm$ 5		1400 $\pm$ 5
58.8			828 $\pm$ 5		1405 $\pm$ 5

* Only vibrations showing pressure dependence are included.

Discussion

Pressure dependence of the infrared vibrations

The infrared active vibrations studied under pressure may be considered to be of two types, a stretching and a bending type. Among the stretching types, one main absorption band near 1100 cm^{-1} is related to the Si-O stretching vibration within the tetrahedron (intratetrahedral), and the other band near 800 cm^{-1} is related to the Si stretching, $\leftarrow\text{SiOSi}\rightarrow$, between the tetrahedra (intertetrahedral). Among the bending types, one mode is related to the Si-O-Si bending and the other to O-Si-O bending. The force constant, f_r , related to the intratetrahedral Si-O stretching type vibration is larger than that of either of the two bending types, f_α and f_β . One would, therefore, expect the Si-O bond within the tetrahedron to be comparatively less sensitive to pressure. Similar behaviour of this stretching vibration towards pressure has been found for other compounds involving tetrahedral structure, for example, sulphates and permanganates.⁽²⁶⁾ In the case of the bending vibration, both an intermolecular vibration, δ_{SiOSi} and an intramolecular vibration, δ_{OSiO} , are involved. The intermolecular mode involves a motion of the atoms during the vibration which is pseudolattice-like and should be sensitive to pressure, and the intramolecular mode should be insensitive to pressure. In a silicate glass the pressure dependences of the intermolecular vibrations are therefore closely related to the compressibility of the glass structure. The increase in frequency indicates a decrease in volume (increase in density) of the glass network, and a concurrent increase in the force constant. The intratetrahedral SiO vibrations are insensitive to pressure, and it is suggested that the individual SiO_4 tetrahedra are not significantly affected by pressure up to the pressures used, and thus the compression occurs along the network whereby the tetrahedra move in closer to one another. This is verified by the results which show that the intermolecular mode, ν_{SiOSi} , is sensitive to pressure. The small sensitivity to pressure of the absorption at 460 cm^{-1} may be due to the fact that both a mode sensitive to pressure (δ_{SiOSi}) and one which is not sensitive (δ_{OSiO}) are found beneath the broad envelope. The net result is to diminish the effect of pressure.

It is of interest to note that the frequency of the Si-O stretching vibration α -quartz decreases with pressure ($d\nu/dP = -0.07\text{ cm}^{-1}/\text{kb}$) as given in Table 3. However, frequency changes with pressure could not be ascertained, within the experimental error, for fused silica and the Vycor and Pyrex glasses.

The Si stretching vibrations in α -quartz are represented by absorption bands at 698, 783, and 800 cm^{-1} , the latter two forming a doublet which disappears at pressures above 30 kb as shown in Figure 2. Corresponding Si stretching vibrational frequencies in fused silica and Vycor and Pyrex glasses at zero pressure are 815, 814, and 812 cm^{-1} , respectively. In all cases, there is a systematic increase in the Si stretching frequencies with pressure, the largest increase being in the case of Pyrex glass ($d\nu/dP = 0.27\text{ cm}^{-1}/\text{kb}$). The results indi-

cate that the compression of glass takes place along network chains, thus causing the tetrahedra to move closer to one another. This effect appears to follow the order Pyrex > Vycor > fused silica $\sim \alpha$ -quartz, and may be indicative of an ordering process occurring in these glasses under pressure. It is known that when one adds a modifier such as Na_2O to quartz, the frequency of the ν_{SiOSi} vibration at $\sim 800\text{ cm}^{-1}$ is decreased.⁽⁴⁾ To accommodate the sodium ions the tetrahedra must move further apart, weakening the force constants and causing a shift to lower frequency. The effects of pressure appear, as one would expect, to give opposite results.

The bending region, manifested by the broad infrared absorption near 460 cm^{-1} , involves motion within as well as between the tetrahedral groups, i.e. O-Si-O within the tetrahedra and Si-O-Si linking the tetrahedra. As the effect of pressure on the former mode is not expected to be very large, any pressure dependence noted for this frequency primarily reflects the change in the vibration of the Si-O-Si bending bond linking the tetrahedra. Borelli & Su⁽¹⁾ as well as other workers have noted that the corresponding Si-O-Si bending force constant, f_β , would be most affected by the degree of disorder in glass structure. One would, therefore, expect to find some interrelation among the three following parameters of glass structure: the degree of disorder, the bond angle, β , and the molar volume. However, because of the overlap of two modes occurring at $\sim 460\text{ cm}^{-1}$, no definite conclusions can be drawn at this time.

As pressure would cause Si-O-Si bond angles in the glass structure to vary, the pressure dependency of the vibrational frequency of the Si-O-Si bending mode must principally reflect a change in the bond angle, β . In the present study the authors found that the 460 cm^{-1} mode shifted towards higher frequency for α -quartz ($d\nu/dP = 0.09\text{ cm}^{-1}/\text{kb}$), towards lower frequency for fused silica ($d\nu/dP = -0.07\text{ cm}^{-1}/\text{kb}$), and remained unchanged for Vycor and Pyrex glasses as shown in Table 3. These differences between the findings for fused silica and those for Vycor and Pyrex glasses were unexpected, and may be due to the presence of boron in the Vycor and Pyrex glasses.

Thermal expansion and the Grüneisen parameters

Fused silica and Pyrex have negative thermal expansion coefficients, α_V , below 200K but these are reduced by network filling agents such as B_2O_3 , Al_2O_3 , or Na_2O .⁽²⁷⁾ In order to explain negative coefficients of thermal expansion it has been suggested that the low frequency transverse vibration of the oxygen atom in the Si-O-Si network, which would be most easily excited at low temperatures, causes the lattice to contract.^(28, 29)

The volume coefficient of thermal expansion, α_V , is related through lattice dynamics to specific heat at constant pressure, C_p , the adiabatic bulk modulus, K_s , and the density ρ

$$\alpha_V = \frac{\gamma_{\text{th}} C_p \rho}{K_s} \quad (1)$$

Table 3. Grüneisen parameters calculated for the various glasses

Mode	ν_i (cm ⁻¹)	$d\nu_i/dP$ (cm ⁻¹ /kbar)	χ (kbar ⁻¹)	Calculated γ_i
<i>α-quartz</i>				
$\delta_{\text{SiO}_2} + \delta_{\text{SiO}_2}$	459	0.09	0.0026738	0.07
$\nu_{\text{SiO}_2} \rightarrow$	698	0.15		0.08
$\nu_{\text{SiO}_2} \rightarrow$	783	0.14		0.07
	800	no shift		—
$\nu_{\text{SiO}_2} \rightarrow \leftarrow \text{Si}$	1082	-0.07		-0.02
$\nu_{\text{SiO}_2} \leftarrow \text{Si}$	1168	no shift		—
<i>Fused silica</i>				
$\delta_{\text{SiO}_2} + \delta_{\text{SiO}_2}$	475	-0.07	0.0030211	-0.05
$\nu_{\text{SiO}_2} \rightarrow$	815	0.17		0.07
$\nu_{\text{SiO}_2} \leftarrow \text{Si}$	1095	no shift		—
<i>Vycor</i>				
$\delta_{\text{SiO}_2} + \delta_{\text{SiO}_2}$	469	no shift	0.0038183	—
$\nu_{\text{SiO}_2} \rightarrow$	814	0.22		0.07
$\nu_{\text{SiO}_2} \leftarrow \text{Si}$	1095	no shift		—
ν_{SiO_2}	1384	0.14		0.03
<i>Pyrex</i>				
$\delta_{\text{SiO}_2} + \delta_{\text{SiO}_2}$	471	no shift(?)	0.002887	—
$\nu_{\text{SiO}_2} \rightarrow$	812	0.27		0.12
$\nu_{\text{SiO}_2} \leftarrow \text{Si}$	1095	no shift		—
ν_{SiO_2}	1390	0.26		0.06

The $\bar{\gamma}_{\text{th}}$ term derived from αV measurements is, in turn, related to the average of the volume dependences of the acoustic and optical mode frequencies, ν_i , weighted by the contribution, C_{pi} , that each vibrational mode makes to the total specific heat, C_p .

$$\bar{\gamma}_{\text{th}} = \frac{\sum_{i=1}^{3N} \gamma_i C_{pi}}{\sum_{i=1}^{3N} C_{pi}} \quad (2)$$

where the Grüneisen parameter, γ_i , is determined by

$$\gamma_i = - \frac{d \ln \nu_i}{d \ln V} = \frac{K_T}{\nu_i} \left(\frac{d \nu_i}{d P} \right)_T \quad (3)$$

where, K_T , is the isothermal bulk modulus.

The two limiting values of $\bar{\gamma}_{\text{th}}$ (high temperature gamma, γ_{HT} , and low temperature gamma, γ_{LT}) can also be calculated from the pressure derivatives of the elastic parameters,⁽³⁰⁾ assuming that only the acoustical modes contribute to γ

$$\gamma_{\text{HT}} = (\gamma_p + 2\gamma_s)/3 \quad (4)$$

$$\gamma_{\text{LT}} = \frac{(v_s/v_p)^3 \gamma_p + 2\gamma_s}{2 + (v_s/v_p)^3} \quad (5)$$

where

$$\gamma_s = 1/3 + K_T(\partial \ln v_s / \partial P)_T \quad (6)$$

and

$$\gamma_p = 1/3 + K_T(\partial \ln v_p / \partial P)_T. \quad (7)$$

Table 4. Values of the Grüneisen parameters for α -quartz, fused quartz, and Vycor and Pyrex glasses

	$\bar{\gamma}_{\text{th}}$	γ_{HT}	γ_{LT}
α -quartz	0.69*		
Fused quartz	0.04	2.40	2.32
Vycor	0.04	1.80	1.80
Pyrex	0.22	1.81	1.80

* From Reference 31.

Here γ_p and γ_s are the gamma contributions due to compressional and shear wave propagation and v_p and v_s represent compressional and shear velocities.

One of the unique aspects of glasses, fused silica in particular, is that the low temperature C_p is significantly greater than that calculated from the Debye theory and elastic modulus data. This is presumed to arise from the optical modes which are of lower frequency than the acoustic modes but which, nevertheless, produce a large contribution to low temperature C_p . There is, however, no direct evidence that optical frequencies are excited at such low temperatures.

Another unique characteristic of silica glasses is that their acoustical frequencies, as represented by the velocities of ultrasonic waves, decrease with hydrostatic pressure in both the transverse and the longitudinal modes. If one attempts to calculate the average $\bar{\gamma}$ from the acoustical γ_s and γ_p based on the volume dependence of the room temperature acoustic velocities as shown in Equations 4-7, it is found that the calculated high temperature limiting value, γ_{HT} , is considerably smaller than the $\bar{\gamma}_{\text{th}}$ obtained from the αV measurements at 298K for all glasses considered in the present paper. A comparison of the $\bar{\gamma}_{\text{th}}$ and γ_{HT} values for all three glasses is shown in Table 4. The γ_{HT} values are all in the range of -2 whereas the $\bar{\gamma}_{\text{th}}$ for fused silica and Vycor at 298K are slightly positive and the Pyrex $\bar{\gamma}_{\text{th}}$ is about +0.2. The conclusion from these calculations is that the optical γ_i must contribute a major part to $\bar{\gamma}_{\text{th}}$ at room temperatures and that the average optical mode, γ_i , is slightly positive for fused silica and Vycor glass and clearly positive for Pyrex glass. These conclusions are in good agreement with the values of the optical, γ_i , obtained from the present work and listed in Table 3.

As the present work and the measurement of the pressure derivatives of the ultrasonic velocities⁽³²⁾ were both carried out at room temperatures, the authors cannot make a direct contribution towards explaining

the negative γ_{th} in the silica glasses at lower temperatures. One conceivable model is that the freezing out of the optic modes with decreasing temperature increases the influence of the acoustic mode, γ_t 's, and thus reduces, γ_{th} , to negative values. This explanation presumes, then, that optical modes become less important below 200K and that they are then probably not responsible for the excess C_p . Measurements of the acoustic and optical mode, γ_t 's, at low temperatures would be of great value in understanding the unique thermal properties of silica glasses.

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INFRARED ABSORPTION SPECTRA OF SODIUM SILICATE
GLASSES AT HIGH PRESSURES

By

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(HIG Contribution No. 465)

Infrared absorption spectra of sodium silicate glasses at high pressures*

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Infrared absorption spectra of 12 sodium silicate glasses of varying composition (10 to 45 mole% Na_2O) are examined at varying pressures to 58.8 kbar. The pressure dependences of all the infrared absorption frequencies studied are found to be positive. Grüneisen γ 's are evaluated from the pressure dependence of the infrared vibrations and elastic parameters. The results are compared with those obtained from previous high-pressure studies of α -quartz and several other silicate glasses.

INTRODUCTION

Physical properties such as elastic moduli and mechanical strength of silicate glasses are related to the density of the Si-O-Si bridges in the random-network structure of glasses.¹ The addition of Na_2O as a network modifier causes a breakdown of some of the Si-O-Si bridges and the formation of weaker Si-O-Na bridges and some terminal Si-O bonds—in proportion to the amount of Na_2O added. Further, some of the Si-O-Si bridges between the SiO_4 tetrahedra may be stretched to accommodate the sodium ion in the network. As a result, the elastic moduli and strength of Na_2O - SiO_2 glasses decrease with an increase in the Na_2O content.^{1,2}

Several infrared investigations have been conducted on sodium silicate glasses.³⁻⁹ Hanna and co-workers^{3,4} have examined the infrared absorption spectra from 2500 to 50 cm^{-1} at ambient pressure, and others⁵⁻⁹ have investigated the infrared reflectance spectra of the glasses. However, the pressure dependence of the infrared spectra of such glasses has not been investigated. This paper reports on a high-pressure study of the infrared spectra of 12 sodium silicate glasses from 1600 to 80 cm^{-1} . The mode Grüneisen parameters, γ_i , are calculated from the pressure dependence of all of the infrared vibration mode frequencies examined, and the values compared with the high-temperature limit of $\bar{\gamma}_H$, γ_{HT} arrived at from the pressure coefficients of the elastic parameters. The results are correlated with previous pressure studies on α -quartz and several other silicate glasses.¹⁰

EXPERIMENTAL METHODS

Eight sodium silicate glasses (K nomenclature) from the National Bureau of Standards and four (JRS nomenclature) from Sweet and White⁸ at Pennsylvania State University were used in this study. Table I lists the chemical composition of the glasses in mole%.

The specimens were crushed in a ball mill finely powdered by extensive grinding in an agate mortar. The midinfrared absorption spectra at ambient conditions were obtained using KBr pellets and employing a Beckman IR-12 spectrophotometer. The spectra from 650 to 80 cm^{-1} were obtained with polyethylene pellets using a Perkin-Elmer Model No. 301 spectrophotometer. The region from 166 to 80 cm^{-1} was also checked with heavy concentrations of the glasses in Nujol. The instruments were calibrated in the midinfrared region with polystyrene film; and at frequencies $< 650 \text{ cm}^{-1}$ with water vapor, the Hg emission lines and with low-frequency absorptions of solid HgO .

For the high-pressure measurements in regions of 333 to 80 cm^{-1} we used an opposed diamond cell linked with the Perkin-Elmer No. 301 spectrophotometer equipped with a 6 $\times$ beam condenser.¹¹ Midinfrared studies at high pressures were made with a Beckman IR-12 spectrophotometer equipped with a 6 $\times$ beam condenser.¹² The powdered sample was loaded in the cell, and the pressure alternately increased and decreased to distribute the material evenly between the anvils. During the pressure cycling, the sample was observed with a microscope. A description of the pressure cell and the method used in pressure calibration has been previously reported.¹¹⁻¹³

TABLE I. Composition of $\text{Na}_2\text{O}-\text{SiO}_2$ glasses.

Sample No.	mole %		Ratio $\text{SiO}_2/\text{Na}_2\text{O}$
	SiO_2	Na_2O	
K-110	90	10	9.0
K-111	85	15	5.7
K-112	80	20	4.0
K-113	75	25	3.0
K-114	70	30	2.3
K-115	65	35	1.9
K-116	60	40	1.5
K-117	55	45	1.2
JRS-2	66.9	33.1	2.0
JRS-3	64.5	35.5	1.8
JRS-4	60.4	39.6	1.5
JRS-5	72.5	27.5	2.6

RESULTS AND DISCUSSION

A. Infrared absorption spectra at varying pressures

Table II lists the infrared absorption bands at ambient pressure for the sodium silicate glasses under study, and Fig. 1 displays several typical spectra. Figure 2 illustrates the effects of adding Na_2O to silica on the various absorptions between $1400-350\text{ cm}^{-1}$. The increasing content of Na_2O causes a decrease in frequency of the three absorptions at ~ 1100 , ~ 960 , and $\sim 790\text{ cm}^{-1}$, and an increase for the $\sim 460\text{-cm}^{-1}$ absorption. It is of interest to note that as the Na_2O content increases, the $\sim 790\text{-cm}^{-1}$ band shifts toward a lower frequency than that found in α -quartz, and the intensity is considerably reduced. Since the number of Si-O-Si bridging units in the network decreases with an increase in the Na_2O content, it is expected that a decrease in intensity of this absorption would also occur. The low-frequency shift of the remaining Si-O-Si bridging units is consistent with a stretching of the Si-O bond as Na_2O enters the network. The ambient-pressure results are substantially in agreement with the reflectance work of Sweet and White⁸ and the absorption studies of Hanna and Su.^{3,4}

Although it is recognized that it may be incorrect to characterize an absorption band by a particular type of vibration in an amorphous material such as glass,¹³ we find it convenient for purposes of the discussion in this paper to indicate that the four modes of vibration on interest may involve the following motions:

- (a) $\sim 1100\text{ cm}^{-1}$, Si-O stretching within the tetrahedra;^{6,14}
- (b) $\sim 960\text{ cm}^{-1}$, Si-O terminal, nonbridged stretching;⁸
- (c) $\sim 790\text{ cm}^{-1}$, Si-O-Si bridged stretching between tetrahedra; (d) $\sim 460\text{-cm}^{-1}$, bending modes involving Si-O-Si and O-Si-O. It should be emphasized that more definitive assignments for fused and crystalline silica have not been made.^{13,15-18}

Under conditions of our experiments no significant absorptions were found lower than the broad band at $\sim 460\text{ cm}^{-1}$. Our measurements were carried out to 80 cm^{-1} . The pressure experiment is essentially a thin-film measurement, and under these conditions the glasses appeared to be transparent. When the glasses were measured in the far-infrared region as thick glasses, some weak absorptions were noted.

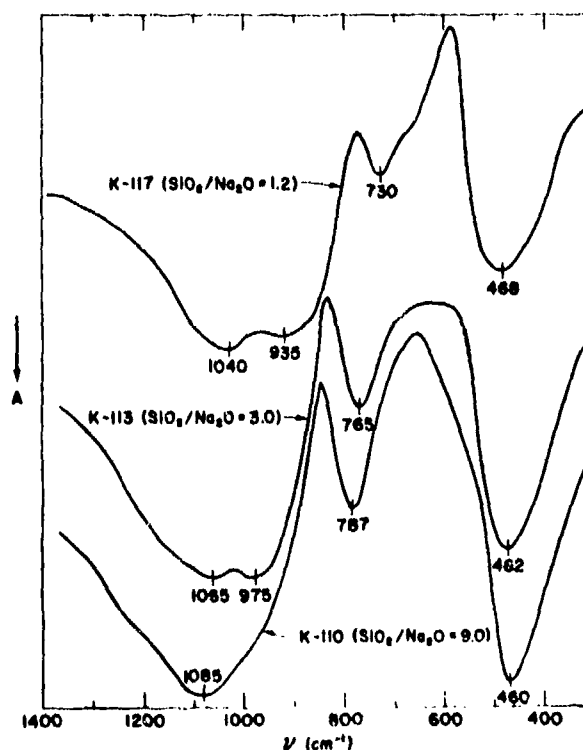
TABLE II. Sodium silicate glasses. Observed infrared absorptions at ambient pressure (cm^{-1}). Abbreviations: s = strong; m = medium; v = very; b = broad; w = weak

Glass (mole % Na_2O)	ν		
α quartz(0)	1082(va) ^a	783(m)	459(s)
		800(m)	
Fused silica(0)	1087(va)	815(m)	475(s)
(10)	1085 ^a (va, b)	787(m)	460(s)
(15)	1075 ^b (va, b)	785(m)	461(s)
(20)	1065(va, b)	965(sh)	775(m)
(25)	1065(va)	975(va)	765(m)
(27.5)	1075(va)	960(va)	765(m)
(30)	1070(va)	960(va)	760(m)
(33.1)	1075(va)	940(va)	760(m)
(35)	1070(va)	940(va)	755(m)
(35.5)	1075(va)	940(va)	760(w)
(39.6)	1060(va)	930(va)	745(w)
(40)	1060(va)	935(va)	750(w)
(45)	1040(va)	935(va)	730(w)

^a Asymmetric on high- and low-frequency sides of band.

^b Very weak shoulder 980 cm^{-1} , 1220 cm^{-1} .

Table III presents the pressure dependence for the four main vibration modes, in terms of $d\nu_i/dP$, for the sodium silicate glasses. It is observed that $d\nu_i/dP$ values for all the absorption bands are higher than those for α -quartz and other silicate glasses.¹⁰ Figure 3 presents typical infrared spectra (sample K-116) under high pressures. With an increase in pressure, frequencies of the three bands shift toward higher frequencies.

FIG. 1. Spectra ($1400-350\text{ cm}^{-1}$) of several sodium glasses at varying concentrations of $\text{SiO}_2/\text{Na}_2\text{O}$ at ambient pressure.

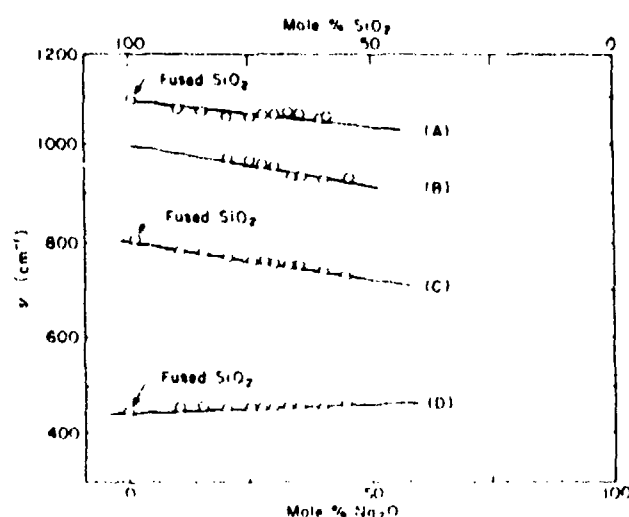


FIG. 2. (A) Plot of tetrahedra SiO stretching vibration vs mole% of Na_2O . (B) Plot of terminal SiO stretching vibration vs mole% of Na_2O . (C) Plot of SiOSi stretching vibration vs mole% of Na_2O . (D) Plot of bending vibrations vs mole% of Na_2O .

In pressure studies made on α -quartz, fused silica, Vycor, and Pyrex glasses, the pseudolatticelike Si stretching mode at $\sim 800 \text{ cm}^{-1}$ was found to be most pressure dependent.¹⁰ For the sodium silicate glasses, all of the vibration modes studied are pressure sensitive, especially the tetrahedral Si-O stretching ($\sim 1100 \text{ cm}^{-1}$) and the bridging Si-O-Si stretching ($\sim 790 \text{ cm}^{-1}$) modes, and the terminal Si-O stretching ($\sim 960 \text{ cm}^{-1}$) mode. The effect of Na_2O on $d\nu_i/dP$ appears to be greater than the effect of B_2O_3 on $d\nu_i/dP$ in Vycor and Pyrex glasses. Differences between the effects of B_2O_3 and Na_2O on $d\nu_i/dP$ in silicate glasses are not unexpected since B_2O_3 is a glass former and strengthens the glass (e.g., elastic moduli increase as B_2O_3 increases),^{1,2} whereas Na_2O is a glass modifier and weakens the glass.

The mode Grüneisen γ , γ_i , in Table III are evaluated from the relation

$$\gamma_i = \frac{K_T}{\nu_i} \left(\frac{d\nu_i}{dP} \right), \quad (1)$$

where K_T is the isothermal bulk modulus.

Whenever comparisons are possible, the sodium silicate glasses demonstrate γ_i values which are higher than those calculated for α -quartz and other silicate glasses,¹⁰ and in every case are positive. The α -quartz and fused silica glass demonstrate negative γ_i values for some modes and also show anomalous thermal expansion and elastic behavior.^{10,19} The positive γ_i values for the sodium silicate glasses are consistent with the effects of network filling agents such as Na_2O in diminishing these anomalies.²⁰ The higher ionic character of the sodium silicate glasses is also contributory to the higher sensitivity to pressure as opposed to the pure silicate glasses or those incorporating the more covalent boron atoms into the glass framework.^{1,21,22}

Contrary to what was found for α -quartz and other silicate glasses,¹⁰ even the modes involving the motions of the atoms within the SiO_4 tetrahedra in the sodium silicate glasses are significantly pressure sensitive. Thus, with an increase in pressure, the sodium silicate glasses demonstrate compression along the intertetrahedral linkages, but in addition some distortions of the individual tetrahedra²⁰ must occur. This difference from α -quartz and related nonmodified silicate glasses must relate to the insertion of the modifying sodium ions in the interstices of the glasses.

B. Thermal expansion and the Grüneisen parameters

The observed negative thermal expansion coefficients, α_v , at $T < 200^\circ \text{K}$ for fused silica and Pyrex and the effects of diminishing this anomaly by the addition of a network filling agent such as Na_2O is of considerable interest.^{23,24} The coefficient, α_v , is related to $\bar{\gamma}_{th}$ through the relation

$$K_T \bar{\gamma}_{th} = \alpha_v K_T / \rho C_v, \quad (2)$$

where K_T is the isothermal bulk modulus, ρ and C_v are density and specific heat at constant volume. $\bar{\gamma}_{th}$ is also related to γ_i and $C_{v,i}$ by the relationship

$$\bar{\gamma}_{th} = \sum_{i=1}^3 \gamma_i C_{v,i} / \sum_{i=1}^3 C_{v,i}. \quad (3)$$

TABLE III. Mode Grüneisen parameters calculated for various sodium silicate glasses.

Glass (mole % Na_2O)	ν_i (cm^{-1})	$d\nu_i/dP$ ($\text{cm}^{-1}/\text{kbar}$)	χ (kbar^{-1})	Calculated γ_i
α -quartz(0)	783 800	0.14	0.002 87	0.07
Fused silica(0)	815	0.17	0.003 02	0.07
Vycor(0)	814	0.22	0.003 82	0.07
Pyrex(4)	812	0.27	0.002 89	0.12
(10)	787	0.64	0.002 95	0.28
(25)	765	0.50	0.002 70	0.24
(35)	755	0.48	0.002 52	0.25
(35, 5)	760	0.50	0.002 53	0.26
(40)	750	0.50	0.002 51	0.27
(45)	730	0.56	0.002 32	0.33
α -quartz(0)	1082	-0.07	0.002 67	-0.02
(10)	1085	0.46	0.002 95	0.14
(25)	1065	0.45	0.002 70	0.16
(35)	1070	0.48	0.002 52	0.18
(35, 5)	1075	0.50	0.002 53	0.18
(40)	1060	0.42	0.002 51	0.16
(45)	1040	0.42	0.002 32	0.17
(25)	975	0.45	0.002 87	0.17
(35)	940	0.35	0.002 52	0.15
(35, 5)	940	0.50	0.002 53	0.21
(40)	935	0.40	0.002 51	0.17
(45)	935	0.45	0.002 32	0.21
α -quartz(0)	459	0.09	0.002 67	0.07
Fused silica(0)	475	-0.07	0.003 02	-0.05
(10)	460	0.19	0.002 95	0.14
(25)	462	0.13	0.002 70	0.10
(35)	458	0.16	0.002 52	0.14
(35, 5)	458	0.21	0.002 53	0.18
(40)	460	0.13	0.002 51	0.11
(45)	468	0.18	0.002 32	0.18

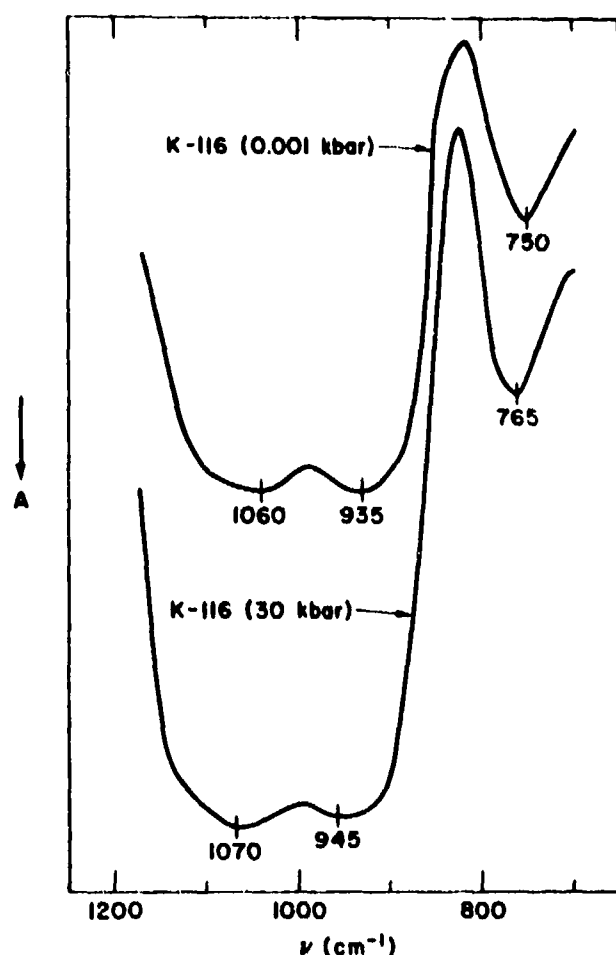


FIG. 3. Spectra of the K-116 glass at varying pressures from 1200–700 cm^{-1} .

where γ_i is defined by Eq. (1) and C_p is the specific-heat contribution for each vibrational mode to the total Einstein specific heat.

Since the thermal expansion data were obtained at room temperature and above, we will consider only the high-temperature limit of $\bar{\gamma}_{ih}$ designated as γ_{NT} . γ_{NT} may be calculated from the pressure derivatives of the elastic parameters, assuming only the acoustic modes contributing to γ :

$$\gamma_{NT} = \frac{1}{3}(\gamma_p + 2\gamma_s), \quad (4)$$

where

$$\gamma_p = \frac{1}{3} + K_T \left(\frac{\partial \ln \nu_p}{\partial \ln P} \right)_T \quad (5)$$

and

$$\gamma_s = \frac{1}{3} + K_T \left(\frac{\partial \ln \nu_s}{\partial \ln P} \right)_T. \quad (6)$$

Here γ_p and γ_s are the γ contributions to the compressional and shear-wave propagation, and ν_p and ν_s represent, respectively, compressional and shear acoustic wave velocities.^{25,26}

Table IV shows a comparison of $\bar{\gamma}_{ih}$ and γ_{NT} for the sodium silicate glasses at 298°K. The values for α -quartz, fused silica, Vycor, and Pyrex are also included. We have no ready explanation for the observed differences in the $\bar{\gamma}_{ih}$ and γ_{NT} values.

It is significant to note that as the Na_2O content increases, the optical γ_i values are observed to increase (Table III). The $\bar{\gamma}_{ih}$ parameter increases slightly, but the γ_{NT} values increase significantly, and are much more sensitive to compositional changes occurring in the glasses. It may also be observed that the negative γ_{NT} values are related to the anomalous behavior in α -quartz and fused silica, for as Na_2O enters the glass, γ_{NT} becomes increasingly more positive and the anomaly decreases. Since Raman-active modes have not been examined under pressure, definite conclusions were not possible. However, the positive pressure dependences of the infrared-active modes examined, correlated with the absence of any negative thermal expansion observed for sodium silicate glasses.

SUMMARY

Infrared absorption spectra of sodium silicate glasses vary systematically with composition and pressure. The following findings are noteworthy:

- (i) The strong broad band at $\sim 1100 \text{ cm}^{-1}$ due to Si-O stretching within the tetrahedron splits; the frequencies of both of the resultant bands decrease with substitution of Na_2O in the structure. With an increase in pressure these bands show a shift toward higher frequency.
- (ii) The frequency and intensity of the bridging Si-O-Si stretching mode at $\sim 790 \text{ cm}^{-1}$ decreases with an increase in Na_2O content. The frequency was found to increase with pressure.
- (iii) The low-frequency band, due to Si-O-Si and O-Si-O bending modes, slightly increases in frequency with Na_2O content, and with increasing pressure.
- (iv) All values of $d\nu_i/dP$ for the four optical vibrational modes examined are positive.

TABLE IV. Thermal and elastic data and the Grüneisen parameter values for the $\text{Na}_2\text{O-SiO}_2$ glasses.

(mole % Na_2O)	$\bar{\gamma}_{ih}$	γ_{NT}
(10)	0.003	-1.35
(15)	0.004	-0.84
(20)	0.006	-0.31
(25)	0.007	-0.17
(27.5)	0.008	0.32
(30)	0.008	0.49
(33.1)	0.009	0.68
(35)	0.011	0.71
(35.5)	0.010	0.74
(39.6)	0.011	0.93
(40)	0.012	1.03
(45)	0.013	1.08
α -quartz(0)	0.63 ^a	...
Fused silica(0)	0.04	-2.32
Vycor(0)	0.04	-1.80
Pyrex(4)	0.22	-1.80

^a N. Soga, J. Geophys. Res. 72, 4227 (1967).

(v) The γ_i 's calculated from $d\nu_i/dP$ are higher than those for α -quartz and high-silica glasses, reflecting the increase in ionic character of the glasses as the Na_2O content increases.

(vi) As the Na_2O content is increased in the sodium glasses, the value of γ_{NT} increases significantly, correlating with an absence of negative thermal expansion in these glasses.

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Erratum: Infrared absorption spectra of sodium silicate glasses at high pressures **[J. Appl. Phys. 43, 4595 (1972)]**

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In the manuscript on the high-pressure effects on the infrared absorption spectra of sodium silicate glasses, two errors appeared inadvertently. These are

1. Equation (5) on p. 4598 should read as follows:

$$\gamma_s = \frac{1}{3} + K_T \left(\frac{\partial \ln \nu_s}{\partial P} \right) \quad (5)$$

2. Table IV should read as follows:

TABLE IV. Thermal and elastic data and the Grüneisen parameter values for the Na₂O-SiO₂ glasses.

(mole% Na ₂ O)	$\bar{\gamma}_{th}$ *	$\bar{\gamma}_{HT}$
(10)	0.498	-1.35
(15)	0.854	-0.81
(20)	1.147	-0.35
(25)	1.334	-0.17
(27.5)	1.432	0.34
(30)	1.532	0.49
(33.1)	1.700	0.67
(35)	1.847	0.76
(35.5)	1.792	0.74
(38.6)	1.975	1.02
(40)	2.027	1.07
(45)	2.20	1.18
α -quartz (0)	0.694 ^a	0.48
Fused silica (0)	0.04	-2.32
Vycor (0)	0.04	-1.80
Pyrex (4)	0.22	-1.80

^aN. Soga, J. Geophys. Res. 73, 4227 (1968).

* The listed $\bar{\gamma}_{th}$ values should be divided by 3.

INFRARED ABSORPTION SPECTRA OF LITHIUM AND POTASSIUM
SILICATE GLASSES AT HIGH PRESSURE

By

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(HIG Contribution No. 544)

Infrared absorption spectra of lithium and potassium silicate glasses at high pressure*

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Infrared absorption spectra of five lithium silicate and six potassium silicate glasses of varying composition (20–35 mole% Li_2O and 15–40 mole% K_2O , respectively) are examined in the range 1500–100 cm^{-1} . The frequencies of the main absorption bands decrease with an increase of alkali-metal oxide ($M_2\text{O}$) content, with the exception of the 960 cm^{-1} shoulder for the lithium silicate glasses. The pressure dependences to ~ 40 kbar, of all the main infrared absorption frequencies, which are pressure sensitive, are found to be positive. The values of $d\nu/dP$ are higher for potassium silicate glasses than for sodium and lithium silicate glasses. The effects of pressure are found to be opposite to the compositional effects. The Grüneisen mode γ 's, γ_i , evaluated from the pressure dependence of the infrared absorption frequencies, are apparently related to the polarizing power of the alkali-metal ion. The results discussed in light of previous high-pressure infrared absorption studies of fused silica and sodium silicate glasses clearly indicate that γ_i , γ_{th} , and γ_{HT} generally increase with $M_2\text{O}$ content in alkali silicate glasses.

I. INTRODUCTION

It has been demonstrated that the addition of an alkali-metal oxide, such as Na_2O , to the SiO_2 tetrahedral network in silicate glasses, in addition to effecting a minor role of network filling at low concentration, causes readjustment of the SiO_4 tetrahedra and, as a consequence, produces some structural distortion. These effects are accompanied by breakdown of the Si-O-Si bonds, and the formation of weaker, more ionic bonds with increasing alkali oxide content. The variations in the mechanical,¹ elastic,² and thermal properties,³ and infrared absorption spectra of sodium silicate glasses,^{4–14} having different composition, reflect such structural modification. In general, it is of interest to interpret the composition dependence of the various properties of alkali silicate ($M_2\text{O-SiO}_2$) glasses in light of the breakdown of Si-O-Si bonds, formation of weaker Si-O-M links and Si-O bonds, and the resultant changes in the Si-O-Si bond angles in the silicate glass structure. Such an evaluation is of particular value to better understanding of the anomalous thermal and optical properties of high-silica glasses.

The important conclusions reached in a recent paper concerning the composition and pressure dependence of the infrared absorption spectra of the sodium silicate glasses in the 1600–100- cm^{-1} frequency range were that first, except for the 460- cm^{-1} absorption band, frequencies of the other three major bands decreased with an

increase in Na_2O content; second, the pressure dependence of the three major infrared vibrational modes ν_i was positive; and third, the values of mode Grüneisen gamma, γ_i , calculated from $d\nu_i/dP$, were larger than those found for fused silica and that γ_i for the $\sim 800\text{-cm}^{-1}$ band appears to increase (outside experimental errors) with Na_2O content and ionic character of the glass.

This paper is an extension of an earlier study; its purpose is to report on the composition and pressure dependence of the infrared absorption spectra of five lithium silicate and six potassium silicate glasses in the range of 1500–100 cm^{-1} and to pressures of 40 kbar. The mode Grüneisen parameters, γ_i , calculated from the pressure dependence of the main infrared absorptions, are compared with $\bar{\gamma}_{\text{th}}$, and the high-temperature limit gamma value, γ_{HT} , obtained from the pressure coefficients of the elastic parameters. The results are correlated with previous studies on sodium silicate glasses⁴ and fused silica.¹⁴

II. EXPERIMENTAL METHOD

Five lithium silicate glasses and six potassium silicate glasses, synthesized at the National Bureau of Standards, were used in this study; the glasses were annealed to 525 °C. Tables I and II list the chemical composition of the glasses in mole%. For obtaining the

TABLE I. Chemical composition of $\text{Li}_2\text{O-SiO}_2$ glasses.

Sample No.	mole%		$\text{SiO}_2/\text{Li}_2\text{O}$
	SiO_2	Li_2O	
1	80	20	4.00
2	75	25	3.00
3	70	30	2.33
4	68	32	2.13
5	65	35	1.86

TABLE II. Chemical composition of $\text{K}_2\text{O-SiO}_2$ glasses.

Sample No.	mole%		$\text{SiO}_2/\text{K}_2\text{O}$	Remarks
	SiO_2	K_2O		
1	85	15	5.7	
2	80	20	4.0	
3	75	25	3.0	
4	70	30	2.33	Phase separation
5	65	35	1.86	Phase separation
6	60	40	1.50	Phase separation

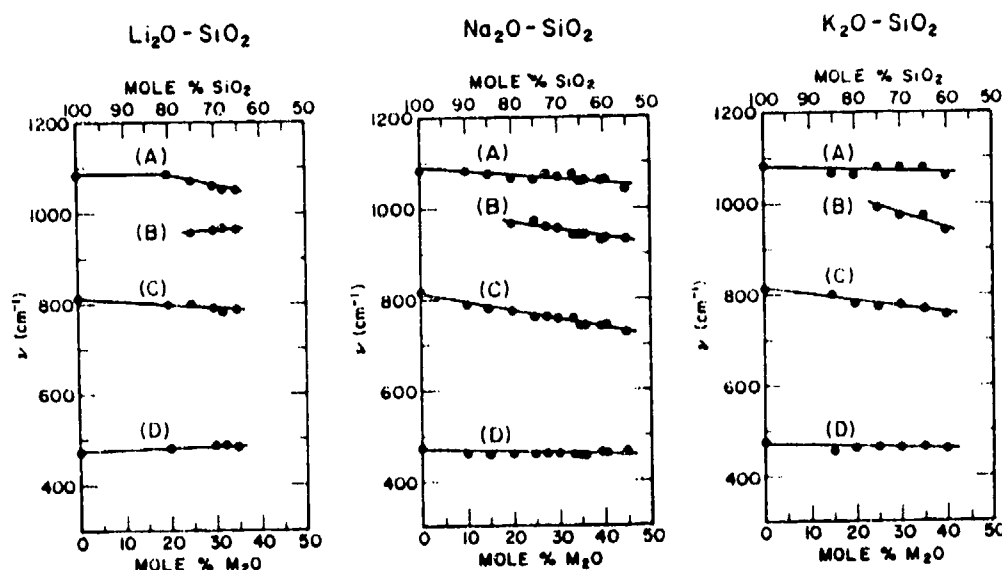


FIG. 1. Plots of vibrational mode frequency vs composition in mole% M_2O , where M is Li, Na, or K. Zero mole% M_2O is for fused silica. (A) Tetrahedral Si-O stretching vibration. (B) Terminal Si-O stretching vibration. (C) Si-O-Si bridged stretching vibration between tetrahedra. (D) Bending vibration involving Si-O-Si and O-Si-O.

infrared absorption spectra, small portions of the glasses were crushed and finely powdered by extensive grinding in an agate mortar. The procedures of sample grinding and preparation were conducted in a dry box flushed with dry nitrogen. The mid-infrared spectra from 1500 to 650 cm^{-1} were obtained by using a diamond anvil cell and Beckman IR-12 spectrophotometer. The spectra in the range <650 to 300 cm^{-1} were obtained by using a diamond anvil cell and a Perkin-Elmer model No. 301 spectrophotometer. The instruments were calibrated in the mid-infrared region with polystyrene film, and at frequencies <650 cm^{-1} with water vapor and

Hg emission lines, and with the low-frequency absorptions of solid yellow HgO. For the high-pressure infrared absorption measurements <650 cm^{-1} , the opposed diamond cell and the Perkin-Elmer 301 spectrophotometer equipped with a 6× beam condenser were used. Mid-infrared measurements at high pressures were made with a Beckman IR-12 spectrophotometer also equipped with a 6× beam condenser.¹⁴ The powdered sample was loaded in the cell in a dry box, and the pressure applied in incremental steps. During the pressure cycling, the sample in the cell was observed with a microscope. A description of the pressure cell and the method used in pressure calibration have been previously reported.^{15,16}

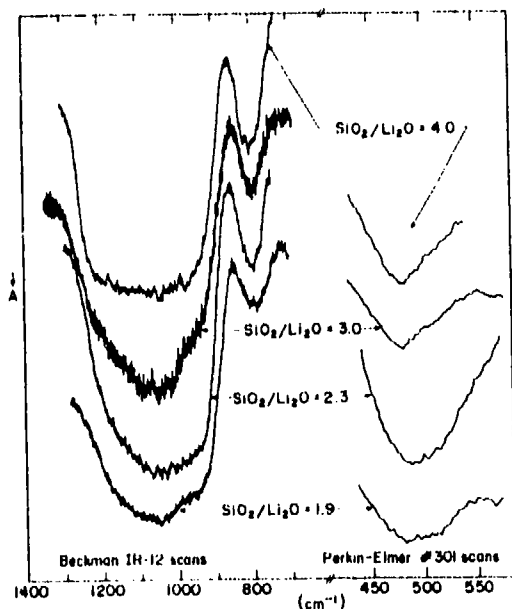


FIG. 2. Spectra (1200–700 cm^{-1}) of lithium silicate glasses with varying ratios of $\text{SiO}_2/\text{Li}_2\text{O}$ at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300 cm^{-1}) of the same glasses, observed by using a diamond cell with a Perkin-Elmer No. 301 spectrophotometer, are also shown here.

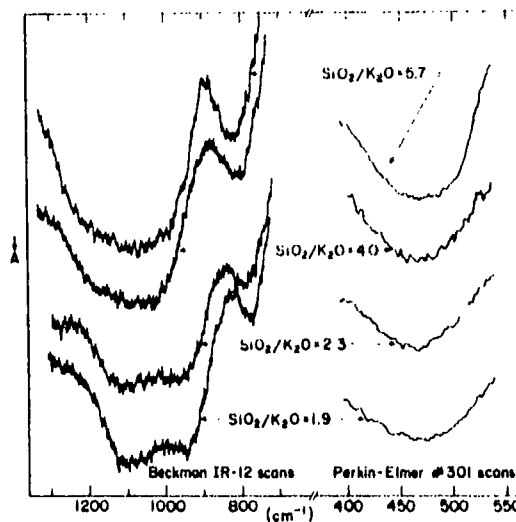


FIG. 3. Spectra (1200–700 cm^{-1}) of potassium silicate glasses with varying ratios of $\text{SiO}_2/\text{K}_2\text{O}$ at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300 cm^{-1}) of the same glasses, observed by using a diamond cell with a Perkin-Elmer No. 301 spectrophotometer, are also shown here.

TABLE III. Lithium silicate glasses. Observed infrared absorptions at ambient pressure (cm^{-1}).

Glass (mole% Li_2O)	(1) ^b	Absorptions ^a (2) ^c	(3) ^c
20	1090 (vs, b)	800 (m)	480
25	1075 (vs, b); 960 (sh)	800 (m)	484
30	1060 (vs); 965 (sh)	790 (m)	488
32	1050 (vs); 970 (sh)	785 (m)	486
35	1050 (vs); 970 (sh)	790 (m)	488

^aAbbreviations: v = very; s = strong; b = broad; m = medium; sh = shoulder.

^bLimit of frequency measurement $\pm 5 \text{ cm}^{-1}$.

^cLimit of frequency measurement $\pm 3 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

A. Effects of compositional variation

Tables III and IV list the observed absorptions at ambient pressure for the glasses under study. The effects of increasing Li_2O or K_2O content in the glass composition are illustrated in Fig. 1, which also includes for comparison, the previously reported results of some sodium silicate glasses.⁴ Typical spectra for the Li_2O - SiO_2 and K_2O - SiO_2 glasses studied here are displayed in Figs. 2 and 3, respectively. The frequency of the $\sim 1100\text{-cm}^{-1}$ band, related to the Si-O stretching within the tetrahedral, decreases with an increase of alkali content in both glass types (see also Fig. 1), the effect being more marked in the lithium glasses. The relationship in the potassium glasses is not as well defined—the frequency increases slightly or remains invariant with the K_2O content. If we represent the composition dependence of frequency by dv_i/dC , where C is the mole% $M_2\text{O}$ present in the glass, we have, from the least-squares analysis of the data, the values of dv_i/dC for the $\sim 1100\text{-cm}^{-1}$ band in the lithium, sodium, and potassium glasses as -2.87 , -1.04 , and $-0.11 \text{ cm}^{-1}/\text{mole}\%$ $M_2\text{O}$, respectively. This clearly indicates that the Si-O vibrational bond force constants may be weakened to a much greater extent in the lithium glasses than in the sodium glasses as a result of increased $M_2\text{O}$ content; for the potassium glasses, there is no appreciable change.

The $\sim 960\text{-cm}^{-1}$ absorption represents the nonbridging Si-O terminal stretching. Simon¹⁴ has commented that this band appears in alkali silicate glasses at nearly the same frequency whenever the alkali metal oxide content reaches a value of 25 mole%. Our results are in agreement with the latter conclusion, but it is found that the frequency at which this band appears in the three types of alkali silicate glasses studied varies with the type of alkali metal present, being highest ($\sim 995 \text{ cm}^{-1}$) for a potassium glass (Fig. 3) and lowest ($\sim 960 \text{ cm}^{-1}$) for a lithium silicate glass (Fig. 2). This absorption band, which appeared as a shoulder in the sodium glasses containing 25 mole% Na_2O or more and which showed a definite separation from the $\sim 1100\text{-cm}^{-1}$ band with increasing Na_2O content, appears as a small shoulder near $\sim 960 \text{ cm}^{-1}$ in the lithium glass containing 25 mole% Li_2O . It remains as a shoulder even at a higher concentration, 35 mole% Li_2O (Fig. 2). The value of dv_i/dC estimated for this band in the lithium glasses is 1.08

TABLE IV. Potassium silicate glasses. Observed infrared absorptions at ambient pressure (cm^{-1}).

Glass (mole% K_2O)	(1) ^b	Absorptions ^a (2) ^c	(3) ^c
Fused silica (0)	1087 (vs)	815	475
15	1070 (vs, b) ^d	800	466
20	1065 (vs, b) ^d	780	469
25	1080 (vs); 995 (vs)	775	466
30	1080 (vs); 975 (vs)	780	469
35	1080 (vs); 975 (vs)	770	469
40	1065 (vs); 945 (vs)	755	464

^aAbbreviations: v = very; s = strong; b = broad; m = medium.

^bLimit of frequency measurement $\pm 5 \text{ cm}^{-1}$.

^cLimit of frequency measurement $\pm 3 \text{ cm}^{-1}$.

^dAsymmetric on high-frequency side of absorption band.

$\text{cm}^{-1}/\text{mole}\%$; this is only an approximate value in view of the failure to resolve the band. For the potassium glasses, this absorption is a very strong resolved band appearing at 995 cm^{-1} in the glass containing 25 mole% K_2O (Fig. 3). In contrast to the lithium glasses, the frequency of this band decreases with increase of potassium content, similar to that observed previously for the sodium system.⁴ The value of dv_i/dC is $\sim -2.00 \text{ cm}^{-1}/\text{mole}\%$ which is the same as the value obtained for the sodium system. (For a comparison of the behavior of dv_i/dC for the band, see Fig. 1 curves labeled B.) This clearly suggests that, as a result of increasing amounts of alkali-metal oxide, the Si-O bond is strengthened in Li_2O - SiO_2 glasses but is weakened in Na_2O - SiO_2 and K_2O - SiO_2 glasses. A similar effect is also found in a study of Young's moduli of these glasses²; the Young's modulus decreases in the Na_2O and K_2O - SiO_2 glasses but increases in Li_2O - SiO_2 glasses as the amount of alkali oxide increases.

The frequency of the $\sim 800\text{-cm}^{-1}$ band which is related to the Si-O-Si bridged stretching between the tetrahedra, is observed to decrease with an increase in the $M_2\text{O}$ content in all three glass types (plots C, Fig. 1), the decrease in the sodium and potassium glasses being larger than that in the lithium glasses.

The frequency of the $\sim 460\text{-cm}^{-1}$ band, which represents the bending modes involving Si-O-Si and O-Si-O, does not appreciably vary with composition in all three cases (plots D, Fig. 1).

An examination of Fig. 2 shows that as the alkali oxide content of the lithium glasses increases, the intensity of the $\sim 1100\text{-cm}^{-1}$ band decreases, a consequence of the decrease in the number of the Si-O-Si bridges that is also reflected by a very slight decrease in the intensity of the $\sim 800\text{-cm}^{-1}$ band. Similar effects are observed in the potassium glasses (Fig. 3). However, the intensity of the $\sim 800\text{-cm}^{-1}$ band decreases more appreciably with increasing K_2O content, and the intensity of the Si-O terminal nonbridging stretching absorption at $\sim 960 \text{ cm}^{-1}$ increases and becomes as strong as that of the $\sim 1100\text{-cm}^{-1}$ band at a $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio of 3.0. Also seen in Fig. 3 is a decrease both in intensity and in frequency of the $\sim 800\text{-cm}^{-1}$ band in the potassium glasses as the K_2O content increases. Similar effects of the absorption bands ~ 1100 and 800 cm^{-1}

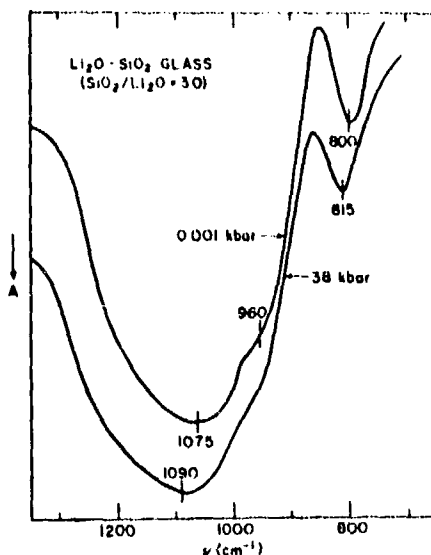


FIG. 4. Spectra of lithium silicate glass (25 mole% Li_2O) in the frequency range 1200–700 cm^{-1} at varying pressures.

were also observed when the Na_2O content increased in sodium glasses.⁴

When all the results for the three types of glasses are compared, the compositional effect on the ~1100- and 960- cm^{-1} bands in the lithium glasses is more obvious than found in the other two glass types. On the other hand, the compositional effects on the ~800- cm^{-1} band are the least apparent in lithium glasses, probably due to the small size and large electronegativity of Li^+ , which results in a less ionic Li-O bond. One might correlate the above-mentioned effects with the behavior of silicate glass under compression. To do so, let us consider the compressibility of vitreous silica, which is higher than in any other alkali silicate glass, and which decreases as alkali-metal oxide is added. The decrease in compressibility is in the order $\text{K} > \text{Na} > \text{Li}$ silicate glasses.¹⁷ Revesz¹⁸ has commented upon the effect of electronegativity of the alkali metal of the oxide, added on the π bonding between Si and O, and its effect on the compressibility of silicate glass. According to

TABLE V. Comparison of the mode Grüneisen parameters γ_i with γ_{HT} and $\bar{\gamma}_{\text{th}}$ for various lithium silicate glasses. Note that the band at ~480 cm^{-1} shows no shift with pressure within experimental error.

Glass (mole% Li_2O)	ν_i (cm^{-1})	$d\nu_i/dP$ ($\text{cm}^{-1}/\text{kbar}$)	χ^a (Mbar $^{-1}$)	γ_i	γ_{HT}^a	$\bar{\gamma}_{\text{th}}^a$ *
20	800	0.26	2.446	0.13	-0.76	0.77
25	800	0.39	2.314	0.21	-0.40	0.99
30	790	0.39	2.174	0.23	0.23	1.22
32	785	0.39	2.092	0.24	0.43	1.36
35	790	0.39	2.027	0.24	0.71	1.46
20	1090 ^b	0.26	2.446	0.10		
25	1075 ^b	0.39	2.314	0.16		
30	1060 ^b	0.26	2.174	0.11		
32	1050 ^b	0.26	2.092	0.12		
35	1050 ^b	0.26	2.027	0.12		

^aData from Ref. 2.

^bShoulder to this peak too weak to follow with pressure.

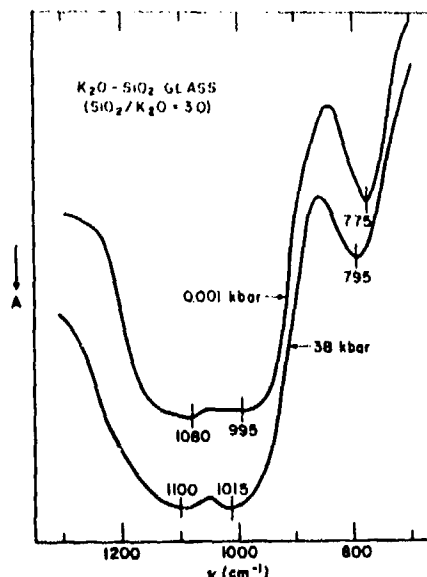


FIG. 5. Spectra of potassium silicate glass (25 mole% K_2O) in the frequency range 1200–700 cm^{-1} at varying pressures.

this author, the lower the electronegativity of the alkali metal (the order of electronegativity being $\text{Li} > \text{Na} > \text{K}$), the larger is the π contribution to the $\pi\text{-Si-O-M}^+-\text{Si-O-Si}$ bond. Thus, the higher electronegativity will result in the lower compressibility of an alkali silicate glass; the available experimental data on the compressibility of alkali silicate glasses support this conclusion.²

B. Pressure effects

Tables V and VI present the pressure dependence of the pressure-sensitive infrared absorption frequencies for the lithium and potassium glasses. Figures 4 and 5 depict typical spectra of some of these glasses under pressure. Except for the ~460- cm^{-1} band, which does

TABLE VI. Comparison of the mode Grüneisen parameters γ_i with γ_{HT} and $\bar{\gamma}_{\text{th}}$ for various potassium silicate glasses. Note that the band at ~470 cm^{-1} shows no shift with pressure within experimental error.

Glass (mole% K_2O)	ν_i (cm^{-1})	$d\nu_i/dP$ ($\text{cm}^{-1}/\text{kbar}$)	χ^a (Mbar $^{-1}$)	γ_i	γ_{HT}^a	$\bar{\gamma}_{\text{th}}^a$ *
15	800	0.26	3.212	0.10	-0.52	1.06
20	780	0.66	3.163	0.27	~0	1.34
25	775	0.52	3.095	0.22	0.39	1.69
30	780	0.52	...	...	...	...
35	770	0.52	...	...	...	...
40	755	0.52	...	...	...	...
15	1070	0.52	3.212	0.15		
20	1065	0.40	3.163	0.12		
25	1080	0.52	3.095	0.16		
30	1080	0.66	...	...		
35	1080	0.66	...	...		
40	1065	0.26	...	...		
25	995	0.52	3.095	0.17		
30	975	0.66	...	...		
35	975	0.52	...	...		
40	945	0.52	...	...		

^aData from Ref. 2.

* The listed $\bar{\gamma}_{\text{th}}$ values should be divided by 3.

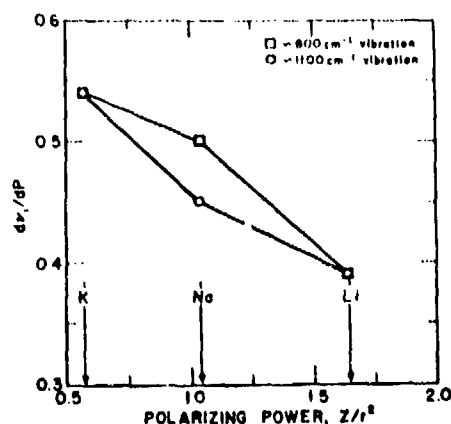


FIG. 6. Plot of dv_i/dP vs polarizing power (Z/r^2) for M_2O - SiO_2 glasses, where $M = Li, Na, \text{ or } K$. (Z = electronic charge, and r = radius (Ref. 19) of the alkali ion.)

not appreciably vary with pressure, the dv_i/dP values for the ~ 800 - and ~ 1100 - cm^{-1} absorptions are positive, as was found for the sodium silicate glasses.⁴

For a given molar content of alkali oxide, the dv_i/dP values for the potassium silicate glasses are similar to those for sodium glasses and higher than those for lithium silicate glasses. The dv_i/dP values for all the absorption bands considered appear to be more or less related to the type of alkali metal present rather than to the amount of alkali oxide in the glass. One explanation possibly lies in the difference in the polarizing power Z/r^2 (where Z is the electronic charge and r the ionic radius) of the three alkali metals involved in the composition of the glasses. Figure 6 shows a plot of dv_i/dP versus the polarizing power (Z/r^2) of the three alkali-metal ions. It can be seen that as the Z/r^2 value of the alkali ion decreases, the dv_i/dP value, for a given mode of vibration increases, the pressure dependencies being in the order of $K > Na > Li$ silicate glasses.

The mode Grüneisen parameters γ_i , tabulated in Tables V and VI, are evaluated from the relation

$$\gamma_i = \frac{1}{\nu_i \chi} \left(\frac{d\nu_i}{dP} \right), \quad (1)$$

where χ is the isothermal compressibility of material. In all cases where comparisons are possible, the γ_i values for the alkali silicate glasses are higher than those for fused silica and reflect the more ionic character of the former. The results are consistent with the fact that the effects of adding alkali-metal oxide to silica will diminish both the anomalous thermal expansion and the elastic behavior of fused silica and high-silica glasses. In general, the higher sensitivity to pressure of the vibrational frequencies for the alkali silicate glasses, as compared to that for fused silica, and particularly the increasing dv_i/dP values from lithium to potassium silicate glasses, is a consequence of the increasing ionic character of the glasses as one proceeds from fused silica to $Li \rightarrow Na \rightarrow K$ silicate glasses. The previous study of sodium silicate glasses⁴ and the present results indicate that the insertion of these

oxides also makes the motion of the Si-O bond within the SiO_4 tetrahedra increasingly sensitive to pressure, and that addition of potassium ions causes the greatest change in the pressure dependence of this Si-O vibrational frequency bond.

C. Correlation of composition and pressure dependence of ν_i

The effects of composition and pressure on the vibrational frequencies are found to be opposite. For the alkali silicate glasses, almost all the infrared absorption frequencies decrease with increase in alkali oxide content, whereas pressure dependence is positive in all cases, except for the bond-bending vibrations at $\sim 460 \text{ cm}^{-1}$, which does not show any appreciable change. Krüger,⁵ in a study of the thermal properties of sodium silicate glasses at low temperatures, has considered that the introduction of Na_2O has two effects: (i) The joined SiO_4 tetrahedra readjust to a more ordered angular position and (ii) the network becomes increasingly disrupted. Our results are consistent with this consideration. Increase of the alkali-metal oxide content results in a decrease in the intensity of the ~ 800 - cm^{-1} band, and the appearance of an absorption at $\sim 960 \text{ cm}^{-1}$, which is due to the nonbridging Si-O⁻ terminal vibration. As the number of the broken Si-O-Si links increases to accommodate the alkali metal, more new terminal bonds are created, thus causing the intensity of the ~ 960 - cm^{-1} band to increase. The Si-O stretching bonds within the tetrahedra also change, and probably weaken slightly. In all cases the frequency decreases with an increase of alkali-metal oxide, except in the case of the bending vibration frequency ($\sim 460 \text{ cm}^{-1}$) which reflects little change. One would expect that the Si-O-Si and O-Si-O bond angles also change with the addition of alkali-metal oxide. However, no conclusions on the bond angles can be made from the present study of the infrared absorption frequency.

The pressure effects are opposite to the effects of composition. All frequencies shift back toward the position of the frequencies for fused silica, with the exception that the terminal Si-O⁻ vibration remains invariant. The pressure effects may be considered to cause some ordering of structure, as was previously reported for quartz and fused silica.¹³

D. Thermal expansion and the Grüneisen parameters

The observed negative thermal expansion coefficients, α_v , at $T < 200 \text{ K}$ for fused silica and a borosilicate glass, and the effects of diminishing this anomaly by the addition of a network-filling agent such as M_2O is of considerable interest.^{20,21} The coefficient α_v is related to $\bar{\gamma}_{th}$ through the relation

$$\bar{\gamma}_{th} = \alpha_v K_S / \rho C_p = \alpha_v K_T / \rho C_v = \alpha_v / \rho C_v \chi \quad (2)$$

where K_S and K_T are the adiabatic and isothermal bulk moduli, ρ is density, and C_p and C_v are specific heats at constant pressure and volume, respectively. $\bar{\gamma}_{th}$ is also related to γ_i and $C_{v,i}$ by the relationship

$$\bar{\gamma}_{th} = \frac{\sum_{i=1}^{3n} \gamma_i C_{v,i}}{\sum_{i=1}^{3n} C_{v,i}} \quad (3)$$

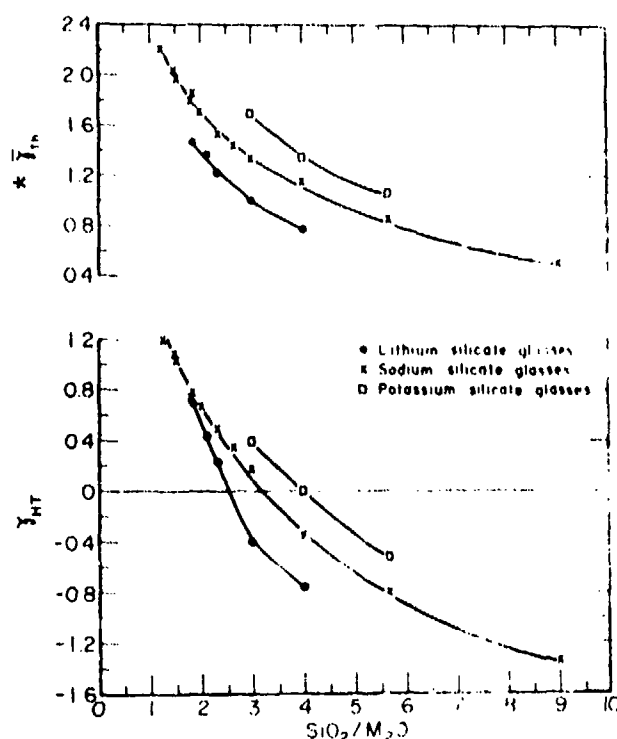


FIG. 7. Plots of $\bar{\alpha}_{th}$ and γ_{HT} vs SiO_2/M_2O ratio for the Li_2O -, Na_2O -, and K_2O - SiO_2 glasses (from Ref. 2).

where γ_i is defined by Eq. (1) and C_{vi} is the specific heat contribution for each vibrational mode to the total Einstein specific heat

Since the thermal expansion data were obtained at room temperature and above, we will consider only the high-temperature limit of $\bar{\alpha}_{th}$ designated as γ_{HT} . γ_{HT} calculated from the pressure derivatives of the elastic parameters,^{22,23} assuming that only the acoustic modes contribute to γ , are listed in Tables V and VI.

For the sodium silicate glasses, it was found that $\bar{\alpha}_{th}$ and γ_{HT} increase as more Na_2O enters the silica network. For the SiO_2/Na_2O ratio of 4 and larger, γ_{HT} was negative and this was correlated with the anomalous behavior found in fused silica and high-silica glasses. Tables V and VI show comparison of γ_i , γ_{HT} , and $\bar{\alpha}_{th}$ for the Li_2O and K_2O - SiO_2 glasses. Figure 7 shows plots of $\bar{\alpha}_{th}$ and γ_{HT} versus the SiO_2/M_2O ratio² for these and Na_2O - SiO_2 glasses. In both plots the $\bar{\alpha}_{th}$ and γ_{HT} values increase in the following order: $K > Na > Li$ silicate glasses. At lower SiO_2/M_2O ratios, the γ_{HT} values appear to converge to 1.0. This trend then correlates with the decrease in the degree of anomalous (negative)

thermal expansion due to the addition of alkali-metal oxide to fused SiO_2 .

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* Consistent with the corrections made in Tables V and VI, the ordinate axis in the upper plot of Fig. 7 is now $3\bar{\alpha}_{th}$.

A STUDY OF $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ GLASSES
BY INFRARED SPECTROSCOPY

By

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(HIG Contribution No. 554)

A Study of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses by Infrared Spectroscopy*

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The infrared absorption spectra of six $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses in the frequency range of 1600 to 200 cm^{-1} are reported. These glasses, having a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 1.67 to 3.54, and containing 20 or 25 mole % TiO_2 , demonstrate two main absorptions at $\sim 950 \text{ cm}^{-1}$ and at $\sim 450 \text{ cm}^{-1}$. A weak absorption at $\sim 700 \text{ cm}^{-1}$ becomes progressively weaker in intensity, and a weak shoulder at 1050 cm^{-1} appears with increasing Na_2O content. The frequency of the absorption band at $\sim 950 \text{ cm}^{-1}$ is found to decrease markedly and systematically with a decrease in the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, whereas the frequency of the band at $\sim 450 \text{ cm}^{-1}$ shows a slight increase. The infrared results may be interpreted in terms of a lowering of symmetry occurring for the SiO_4 units. The effect of TiO_2 content on the relationship between vibrational frequency is discussed. The frequency composition curves for glasses containing 20 and 25 mole % of TiO_2 intersect at $\text{SiO}_2/\text{Na}_2\text{O}$ ratio ~ 2 . A reversal in the frequency vs $\text{SiO}_2/\text{Na}_2\text{O}$ ratio relation was also found at $\text{SiO}_2/\text{Na}_2\text{O} \sim 2$ for the sodium silicate glasses.

INDEX HEADINGS: Infrared spectroscopy; $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses; Compositional effects.

INTRODUCTION

The glasses in the ternary $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ system have been employed by several workers to demonstrate the effect of modifying ions, such as Ti^{4+} and Na^+ , on the optical, thermal, electrical, and other physical properties¹⁻⁶ of silicate glasses. In most of these studies, the role of Ti^{4+} has been particularly emphasized.

Recently a study of the pressure and temperature dependence of the elastic properties of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses has been reported.⁶ The purposes of this paper are to report the infrared absorption characteristics of the same $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses and to interpret the effects of composition on the structural state as revealed by the infrared absorption spectra.

In simple binary glasses, such as those in the system $\text{Na}_2\text{O-SiO}_2$, the various physical properties such as mechanical strength and elastic moduli are related to a number of the Si-O-Si links in the random network of silica tetrahedra.⁷ The addition of Na_2O as a modifier causes the breakdown of these links and the formation of weaker Si-O-Na terminal links as reflected by the decrease in the Young's moduli of glasses in the binary $\text{Na}_2\text{O-SiO}_2$ glasses as the Na_2O content is increased.⁷⁻⁹ It is of interest to understand how such a modification of the structure is affected in the presence of Ti^{4+} ions which occupy intratetrahedral positions at low concentration and the intertetrahedral positions at a high concentration of TiO_2 .⁸ We have carried out this study to

shed some new light on the changing role of a modifying oxide (Na_2O) added to SiO_2 structure containing another network-forming oxide (TiO_2) in which the cation Ti^{4+} has different field strength,⁸ Z/A^2 , than that of Si^{4+} .

I. EXPERIMENTAL PROCEDURE

The six glasses employed in this study were obtained through the courtesy of G. W. Cleek, National Bureau of Standards, who has previously reported their physical and optical properties.¹ The pressure and temperature dependence of the elastic moduli of the same glasses has been recently reported.⁶ Their chemical composition is given in Table I.

The mid-infrared absorption spectra of these glasses in the range of 1600 to 200 cm^{-1} were obtained with a Beckman IR-12 spectrophotometer, using the KBr pellet technique. The instrument was calibrated in the mid-infrared region with polystyrene film and CO gas, and in the low frequency region with H_2O vapor and solid yellow HgO.

II. RESULTS AND DISCUSSION

Figs. 1 and 2 show the infrared absorption spectra of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses containing 20 and 25 mole % TiO_2 , respectively. Table I lists their composition and the vibrational frequency assignments for the two main absorption bands at ~ 950 and $\sim 450 \text{ cm}^{-1}$.

A. Symmetry of SiO_4 Units in $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses

As Na_2O and TiO_2 are added to the base silicate glass, the symmetry of the SiO_4 tetrahedra should decrease, and this will affect the vibrational spectra of the glass. Table II illustrates the correlation table for the symmetry T_d and the lower symmetries D_{3d} , C_{3v} , and C_{2v} . It may be observed that two F_2 infrared-active modes (stretching and bending) in T_d symmetry will

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TABLE I. Chemical composition and the infrared absorption frequency assignments for the ~ 950 and ~ 450 cm^{-1} vibration modes in $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ glasses.

Glass serial No.	Na ₂ O	TiO ₂	SiO ₂	SiO ₂ :Na ₂ O ratio	SiO ₂ :SiO ₂ bending modes frequency (cm^{-1})	Si-O terminal stretching mode frequency (cm^{-1})
1	17.5	20.0	62.0	3.54	452 ± 3	900 ± 3
2	25.0	20.0	55.0	2.20	460 ± 5	905 ± 5
3	30.0	20.0	50.0	1.67	465 ± 5	920 ± 5
4	17.5	25.0	57.5	3.20	447 ± 5	905 ± 5
5	22.5	25.0	52.5	2.33	455 ± 5	902 ± 5
6	27.5	25.0	47.5	1.73	470 ± 5	915 ± 5

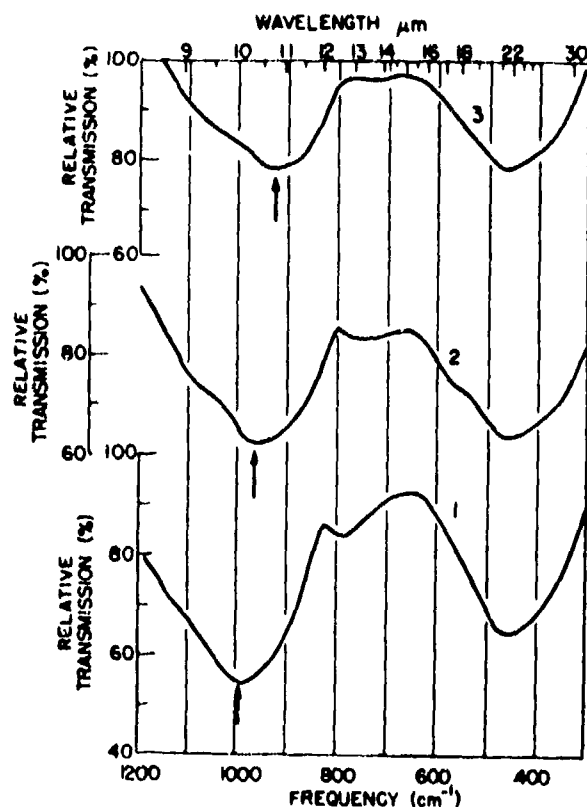


FIG. 1. Infrared absorption spectra of $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ glasses containing 20 mole % TiO_2 . Glass 1 contains 17.5 mole % Na_2O and 62.0 mole % SiO_2 ; glass 2 contains 25.0 mole % Na_2O and 55.0 mole % SiO_2 ; glass 3 contains 30.0 mole % Na_2O and 50.0 mole % SiO_2 .

correlate to four infrared-active modes ($2B_2 + 2E$) in the D_{2d} symmetry. For C_{2v} symmetry the two E_2 modes correlate to six modes, active in the infrared and Raman. Three of these modes will be A_1 type and three will be E type. For C_{2v} symmetry eight modes will become active in the infrared and nine modes in the Raman. Thus, the infrared-active modes for the vibrations involving SiO_4 units, based on each symmetry, are as follows:

$$\begin{aligned} T_d \text{ symmetry} - \Gamma_{\text{IR}} &= 2F_2 \\ D_{2d} \text{ symmetry} - \Gamma_{\text{IR}} &= 2B_2 + 2E \\ C_{2v} \text{ symmetry} - \Gamma_{\text{IR}} &= 3A_1 + 3E \\ C_{2v} \text{ symmetry} - \Gamma_{\text{IR}} &= 4A_1 + 2B_1 + 2B_2 \end{aligned}$$

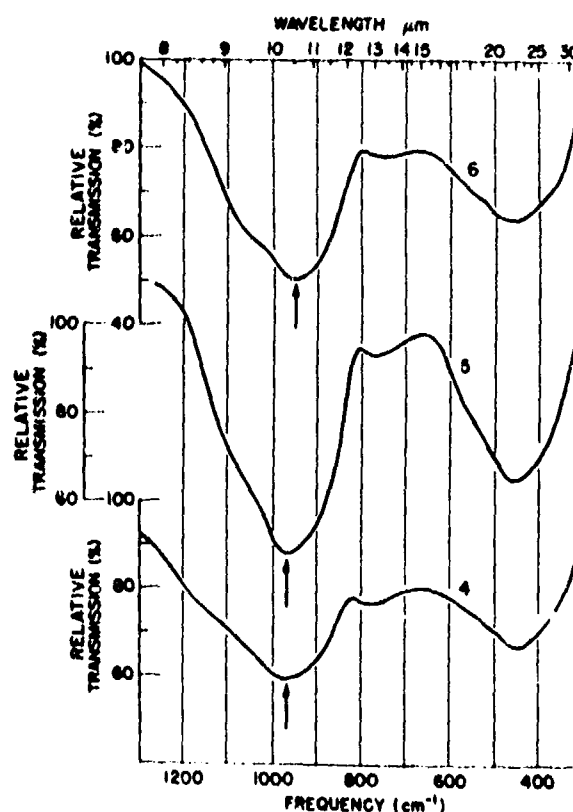


FIG. 2. Infrared absorption spectra of $\text{Na}_2\text{O}-\text{TiO}_2$ glasses containing 25 mole % TiO_2 . Glass 4 contains 17.5 mole % Na_2O and 57.5 mole % SiO_2 ; glass 5 contains 22.5 mole % Na_2O and 52.5 mole % SiO_2 ; glass 6 contains 27.5 mole % Na_2O and 47.5 mole % SiO_2 .

TABLE II. Correlation chart for T_d , D_{2d} , C_{2v} and C_{2v} symmetries.

C_{2v}	C_{2v}	T_d	D_{2d}
4A ₁ (IR, R)	3A ₁ (IR, R)	1A ₁ (R)	2A ₁ (R)
1A ₂ (R)	1E ₂ (R)	1E ₂ (R)	1B ₂ (R)
2B ₁ (IR, R)	3E ₂ (IR, R)	1F ₂ (IR, R)	2B ₁ (IR, R)
2B ₂ (IR, R)	1F ₂ (IR, R)	1F ₂ (IR, R)	2B ₂ (IR, R)

The infrared spectra of the $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ glasses remain rather simple. Our experimental results provide evidence for a D_{2d} symmetry for the SiO_4 units, although the C_{2v} symmetry cannot be eliminated. No evidence for a C_{2v} symmetry is observed.

At least two stretching modes appear in the infrared spectrum: a shoulder at ~ 1050 cm^{-1} and a main absorption at 900 cm^{-1} (in the 20% TiO_2 glass, No. 1). The region is very broad. In the bending region, only a broad absorption appears at 452 cm^{-1} (in the 20% TiO_2 glass, No. 1). The broadness of the band is indicative of the overlapping of several modes, each having equivalent energy. This band was not resolvable at room temperature.

Table III summarizes the frequency assignments for the SiO_4 vibrations existing in a D_{2d} symmetry. No evidence was obtained for Ti-O vibrations in these glasses, scanning the infrared region to 200 cm^{-1} . Rutile¹⁰ has strong bands at 695 and 608 cm^{-1} and weak

TABLE III. Infrared assignments for the SiO_4 tetrahedron vibrations in D_{2d} symmetry.

D_{2d}	Assignment	Approximate frequency position (cm^{-1})
B_1	SiO terminal stretch	~ 950
B_1	SiO_2 bending	~ 450
E	SiO stretch	~ 1050 (sh)
E	SiO_2 bending	~ 450

bands at 423 and 352 cm^{-1} , while the Ba_2TiO_4 ¹¹ shows infrared absorptions at 770 and 371 cm^{-1} . The region of 600 to 700 cm^{-1} in $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ glasses is free of absorption. The lower frequency region at ~ 450 cm^{-1} is obscured because of the broad absorption occurring in the region.

B. Assignments for the Intermolecular Vibrations

The weak vibration at ~ 700 cm^{-1} has been assigned to the $\leftarrow \text{SiOSi} \rightarrow$ stretching mode between the SiO_4 tetrahedra.^{12,14} The bending mode Si-O-Si has been assigned in the energy region of the broad envelope occurring at ~ 450 cm^{-1} .^{12,15}

C. Relation of Vibrational Frequencies with Composition in $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ Glasses

Referring to Figs. 1 and 2 and Table III, the absorption at ~ 950 cm^{-1} is attributed to the Si-O terminal nonbridged vibration, and the ~ 450 cm^{-1} absorption is attributed to the vibrations involving Si-O-Si and O-Si-O bending modes, referred to and discussed in an earlier paper.^{12,15} The shoulder at ~ 1050 cm^{-1} , appearing as the Na_2O content increases, is assigned to the Si-O stretch within the SiO_4 unit. Absorption at ~ 700 cm^{-1} , due to Si-O-Si bridged stretching between tetrahedra, which is strong in glasses (3 and 6) containing low Na_2O content, becomes weaker as the Na_2O content is increased (compare the spectra of glasses 1 $\rightarrow$ 3 and of 4 $\rightarrow$ 6 in Figs. 1 and 2, respectively).

Fig. 3 illustrates the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the two main absorption frequencies (~ 950 and ~ 450 cm^{-1}), respectively, for the $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ glasses. The previous results for the sodium silicate glasses¹⁴ are also included for comparison. As seen, the frequency of the ~ 950 cm^{-1} absorption band decreases systematically and nonlinearly as the Na_2O content is increased (i.e., as the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio decreases). The frequency-composition curves for the two types of $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ glasses, one containing 20 and the other 25 mole % TiO_2 , intersect at $\text{SiO}_2/\text{Na}_2\text{O}$ ratio ~ 2 , corresponding to ~ 28 molar % of Na_2O . The effect of increasing Na_2O content on the ~ 450 cm^{-1} absorption is opposite and less marked—the frequency increases slightly with a decrease in $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. Here again, the two curves for the 20 and 25 mole % TiO_2 composition intersect at $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of ~ 2 . It is of interest to note from Fig. 3 that the relation of frequency vs $\text{SiO}_2/\text{Na}_2\text{O}$ for sodium silicate glasses inverts at $\text{SiO}_2/\text{Na}_2\text{O}$ ratio value slightly less than 2 (~ 18 mole % Na_2O). The inversion effect for the sodium silicate

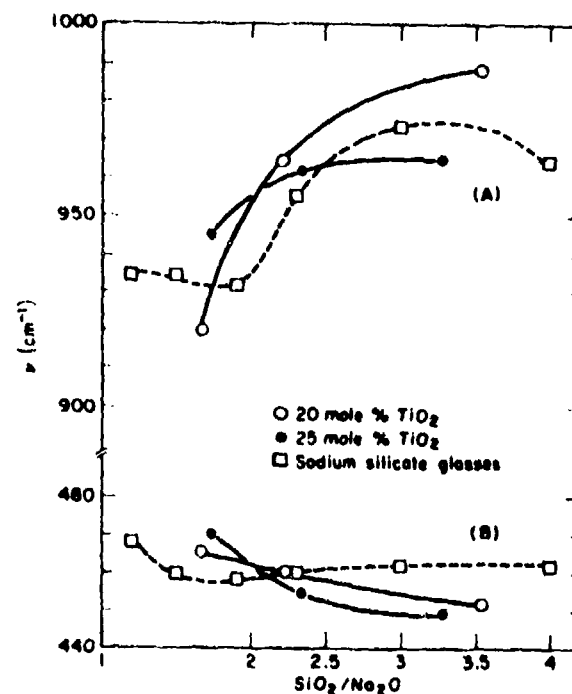


FIG. 3. Frequency vs $\text{SiO}_2/\text{Na}_2\text{O}$ ratio for Si-O stretching (~ 950 cm^{-1}) and for the SiO_2 bending modes (~ 450 cm^{-1}).

glasses corresponds to Na_2O content of 35 mole %, the structure parameter $y = (6 - 200/p)$, where p is mole % SiO_2 ,¹⁶ being equal to ~ 3 . Whether the causes of the two observations at $\text{SiO}_2/\text{Na}_2\text{O} \sim 2$ for the $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glasses are related is not established. On comparing the results of parts A and B in Fig. 3, it is found that the role of TiO_2 content in enhancing and diminishing the composition dependence of the vibration frequencies of the ~ 950 and ~ 450 cm^{-1} absorption bands, respectively, is not similar. Increase of TiO_2 content diminishes the effect on the ~ 950 cm^{-1} absorption frequency and enhances it for the ~ 450 cm^{-1} frequency.

III. SUMMARY

1. Data are presented to indicate that the symmetry of the SiO_4 units in $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ glasses has lowered from T_d to D_{2d} (or C_{4v} symmetry).

2. The two main absorptions at ~ 950 cm^{-1} and ~ 450 cm^{-1} occur at lower frequency than in the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glasses and fused silica. Significant shifts toward lower frequency occur as the Na_2O content is increased.

3. Frequency of the terminal Si-O stretching mode (~ 950 cm^{-1}) is more sensitive to added Na_2O than the SiO_2 bending modes are.

4. The effect of adding Na_2O on the Si-O terminal stretching mode (~ 950 cm^{-1}) is opposite to that found for the SiOSi and O-Si-O bending modes—decreasing frequency occurring for the stretching mode as the Na_2O content increases, and increasing frequency for the bending modes with an increase in Na_2O content.

5. For each absorption (20 and 25% TiO_2), the frequency vs $\text{SiO}_2/\text{Na}_2\text{O}$ ratio curves intersect at ~ 2 .

6. No evidence for TiO vibrations was obtained in this work.¹⁷

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17. One of the referees of this paper commented on the recent Raman study [see M. C. Tobin and T. Baak, *J. Opt. Soc. Am.* **58**, 1459 (1968)], in which a related glass containing 10% titanium exhibited vibrations assigned to TiO motions. The reasons for the differences are not immediately apparent, but our glasses contain more Na_2O , and vibrations due to the latter effects could obscure any TiO vibrations.

EFFECTS OF COMPOSITION, PRESSURE, AND
TEMPERATURE ON THE ELASTIC, THERMAL, AND ULTRASONIC
ATTENUATION PROPERTIES OF SODIUM SILICATE GLASSES

By

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(HIG Contribution No. 598)

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EFFECTS OF COMPOSITION, PRESSURE, AND TEMPERATURE ON
THE ELASTIC, THERMAL, AND ULTRASONIC ATTENUATION
PROPERTIES OF SODIUM SILICATE GLASSES

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INTRODUCTION

In the course of reviewing various thermal and elastic properties of glasses, it has been clearly shown (refs. 1-2) that two types of anomalous behavior exist in the vibrational properties of inorganic glasses. The first is related to abnormally low-frequency vibrational modes for which volume dependence of frequency (i.e., $d\omega/dV$) is positive, and includes anomalous properties such as negative thermal expansion coefficient, positive temperature derivative of elastic moduli and negative pressure derivative of elastic moduli, all of which are characteristic of the tetrahedral glasses like fused silica. The second type depends solely upon the low-frequency vibrational modes and includes properties such as large acoustic loss, excess specific heat, and low-frequency Raman scattering, all of which are characteristic of glassy state, in general. This paper reports on the elastic moduli, thermal expansion and acoustic loss in fused silica, and in seven sodium silicate glasses, as the function of composition, pressure, and temperature. Although several investigations on the elastic and thermal properties of alkali silicate glasses have been carried out (e.g., refs. 1, 3-6), virtually no data exist on ultrasonic attenuation in such glasses, except for some lower frequency, high-temperature data (ref. 22).

The elastic properties of simple silicate glasses in general depend on the density of the Si-O-Si bonds in the random network of silica. The addition of a network-modifier such as Na_2O results in a breakdown of some of those bonds and the formation of relatively weaker Si-O-Na bonds in proportion to the Na_2O added. In this manner, Charles (ref. 7) has shown that Young's modulus in the Na_2O - SiO_2 glass system decreases systematically with increase in Na_2O content.

It is of interest to study the changes in the anomalous behavior of tetrahedral silica-like glasses as they are progressively modified by the addition of Na_2O . The purpose of this study is to investigate the elastic, thermal, and ultrasonic attenuation properties of the glasses in the Na_2O - SiO_2 glass system in an effort to elucidate the structural changes in the random silica-based network, and the mechanism involved.

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Strength (II) and Hardness. Viscoelasticity and Elasticity.)

EXPERIMENTAL TECHNIQUES

Fused silica (CGW code 7940), obtained from the Corning Glass Works, Corning, New York, and seven sodium silicate glasses, synthesized at the National Bureau of Standards, Washington, D.C., were used in this study. The chemical composition and annealing temperatures of the sodium silicate glasses are given in Table 1. Right circular cylinders, 1.25 cm long, were prepared from the glass samples for the velocity measurements as function of pressure (to 5 kbar at 298° K) and temperature (298-498° K at 1 bar); cylinders of approximately the same length but larger diameter (~2 cm) were used for the low-temperature (80-298° K) attenuation and velocity measurements, in order to minimize the errors of the side-wall effects in attenuation work. The end-faces of cylindrical specimens were paralleled to within 1 part in 10^4 parts, and polished flat to $\pm 1/2$ wavelength of sodium light.

The pulse superposition technique (ref. 8) was employed for studying the pressure and temperature dependence of ultrasonic velocities and, hence, of the moduli. X- and Y-cut quartz transducers, 0.65 cm diameter, having 20 MHz natural resonant frequency were used to generate compressional and shear waves in the specimen; 30 MHz transducers were used for attenuation measurement. The bonding materials between the specimen and transducer were: Dow-Corning 276-V9 resin for the pressure measurements at high pressure; HT-424 epoxy (manufactured by American Cyanamid Co.) at high temperatures (298-498° K); and 'Nonaq' stopcock grease (Fisher Scientific Co.) for the low-temperature velocity and attenuation measurements. The details of the ultrasonic equipment, the high-pressure and high-temperature apparatus, and the procedure for evaluating the pressure and temperature velocity data have been described previously (ref. 9). The basic experimental measurement was the pulse repetition frequency (PRF) of the carrier rf wave applied to the transducer attached to one plane-paralleled faces of the specimen. At the 'resonant' condition, ignoring the effects of the bond, the velocity is given by $v = 2fl$ where f is PRF rate (i.e., reciprocal of a round-trip delay time) and l is length of the specimen. For evaluating velocities and moduli at high and low temperatures (above and below 298° K, respectively), corrections were applied for path-length changes, using the measured expansivity data (in the 298-498° range). The results, to be discussed later, are shown in Fig. 4.

The "modified" pulse-echo-overlap (ref. 10) was employed for making the low-temperature measurements of ultrasonic velocities and attenuation simultaneously, and liquid-N₂ dewar and the electronic equipment similar

to that given in ref. 10. The method allowed a continuous recording of attenuation with temperature, the resolution of measured attenuation values being 0.04 dB or better. The accuracy of the measured velocity is estimated to be .03% or better.

DISCUSSION OF RESULTS

1. Elastic Moduli at Ambient Conditions. The elastic parameter measurements for fused silica and the $\text{Na}_2\text{O-SiO}_2$ glasses at 20 MHz are listed in Table 1. The density of the $\text{Na}_2\text{O-SiO}_2$ glasses continuously increases

Table 1
Composition, and elastic and thermal properties of fused silica and $\text{Na}_2\text{O-SiO}_2$ glasses at ambient conditions

Glass No.	Composition, mole %		Annealing temp., °C	$\bar{M}$, g	ρ , g/cm ³	V_s , km/sec	V_p , km/sec	ν_D , K	C_p , cal/g-deg	$\alpha \times 10^5$, deg ⁻¹	E , kbar	ν_{th}	ν_{NT}
	SiO_2	Na_2O											
Fused silica (7980)	100	0	1,020	20.02	2.202	5.941	3.764	498.7	0.2597	0.123	361.2	0.019	-2.37
K110	90	10	575	20.08	2.288	5.565	3.478	467.0	0.2634	1.236	338.8	0.166	-1.35
K111	85	15	540	20.11	2.336	5.457	3.355	453.9	0.2643	2.139	344.6	0.285	-0.81
K112	80	20	520	20.14	2.383	5.382	3.251	443.2	0.2654	2.863	354.5	0.382	-0.35
K113	75	25	510	20.18	2.431	5.347	3.159	434.3	0.2660	3.248	370.5	0.445	0.17
K114	70	30	495	20.21	2.474	5.348	3.101	429.4	0.2664	3.628	389.6	0.511	0.49
K115	65	35	474	20.24	2.495	5.361	3.038	422.4	0.2665	4.191	410.0	0.616	0.77
K116	60	40	450	20.27	2.520	5.401	2.993	418.1	0.2666	4.393	430.6	0.676	1.07

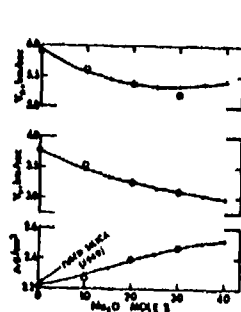


Fig. 1 Density, V_s and V_p as function of Na_2O content. Open circles represent unpublished data of Kurkjian and Krause.

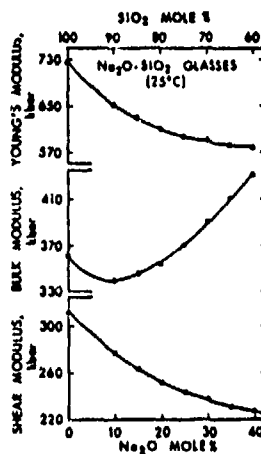


Fig. 2
Composition dependence of the elastic moduli.

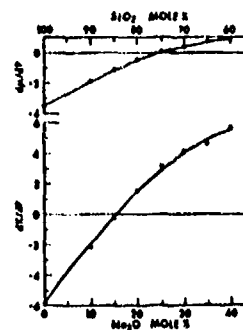


Fig. 3
 dK/dP and du/dP versus Na_2O content.

with increasing Na_2O content, however, the velocities of both the compressional (V_p) and shear (V_s) waves decrease. Good agreement is found with the unpublished velocity data of Krause and Kurkjian (personal communication, 1974), as seen in Fig. 1. The present data indicate a minimum in V_p near 25 mole % Na_2O composition; thereafter V_p seems to increase with increasing Na_2O content. Fig. 2 shows the composition dependence of shear (μ), bulk (K), and Young's (E) moduli. Both μ and E decrease non-linearly but systematically with increasing Na_2O content; K modulus in fused silica appears at first to decrease when Na_2O is added but, above 10-12 mole % Na_2O , it continuously increases. These results show that the role of added Na^+ is twofold: (1) the ions fill-in the void space in silica structure; and (2) they modify the Si-O-Si bonds, forming weaker Si-O-Na bonds in proportion to the amount of Na_2O added and causing moduli to decrease (ref. 7).

2. Pressure and Temperature Dependence of Elastic Moduli. The pressure dependence of the elastic moduli of $\text{Na}_2\text{O-SiO}_2$ glasses is found to be linear, within experimental error, in the pressure range of this study (5 kbar). Lower soda-content glasses appear more anomalous (i.e., dK/dP and $d\mu/dP$ are both more negative); the anomalous behavior systematically decreases (i.e., becomes less negative) with increase in Na_2O content (fig. 3). At lower Na_2O content (≤ 20 mole %), the values of dK/dP and $d\mu/dP$ change more rapidly with composition than at higher content (> 20 mole %). From Fig. 3, dK/dP and $d\mu/dP$ are zero for glasses containing approximately 16 and 25 mole % Na_2O , respectively.

The results of the temperature dependence of fractional velocities, $(V_p)_T/(V_p)_{298}$ and $(V_s)_T/(V_s)_{298}$, and of shear modulus are shown in Figs. 4 and 5, respectively. Except for glasses K110 and K111 (containing

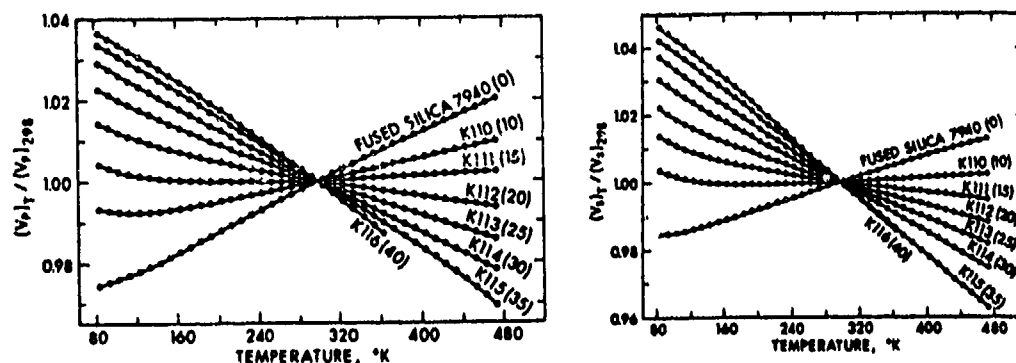


Fig. 4 Longitudinal- (left) and shear-wave (right) velocity ratio versus temperature. The values in parentheses represent Na_2O mole %.

10 and 15 mole % Na_2O , respectively), the temperature dependence of V_p (above 298°K) in all of the others is normal (i.e., negative temperature derivatives); for V_s , only K110 shows anomalous behavior (i.e., positive temperature derivative). The values of dK/dT and $d\nu/dT$ from both the high- and low-temperature measurements at 298°K are in good agreement (Fig. 6).

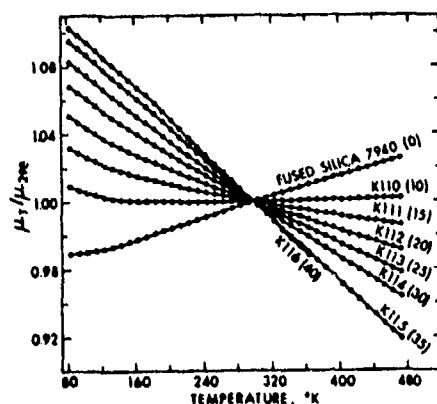


Fig. 5 Shear modulus ratio versus temperature.

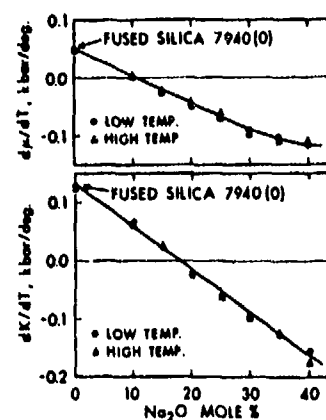


Fig. 6 dK/dT and $d\nu/dT$ versus Na_2O content.

Here it is again noted that the degree of anomalous behavior (positive dK/dT and $d\nu/dT$) decreases with addition of Na_2O . The composition dependence of dK/dT is linear; but that of $d\nu/dT$ is somewhat nonlinear, at least for higher Na_2O content.

In the course of a study of the acoustic spectra of $\text{Na}_2\text{O-GeO}_2$ glasses (ref. 11), it was pointed out that a 30% $\text{Na}_2\text{O-70% GeO}_2$ glass shows low-temperature thermal relaxation at $\sim 125^\circ \text{K}$. The low-temperature results in Figs. 4 and 5, showing reversals in the anomalous behavior of fused silica and the K111 and K112 glasses, also indicate such thermal relaxation. The minima in the velocity and modulus (around $\sim 120^\circ \text{K}$), caused by the thermal relaxation, is seen to shift to higher temperatures with increase in the Na_2O content; also, the magnitude of thermal relaxation decreases, as indicated by increasing linearity of the curves, with increasing Na_2O content.

3. Grüneisen Parameters. The thermal Grüneisen parameters, $\gamma_{th} = \alpha_V K_S / \rho C_p = \alpha_V K_T / \rho C_v$, were evaluated using measured α_V , K_S and ρ values, and calculated C_v values; the latter were obtained from the Debye theory (ref. 12). Values of Debye temperature (θ_D), C_v , and γ_{th} are given in Table 1. The γ_{th} values systematically increase with increase in Na_2O

content (fig. 7) which systematic increase is also reflected in the

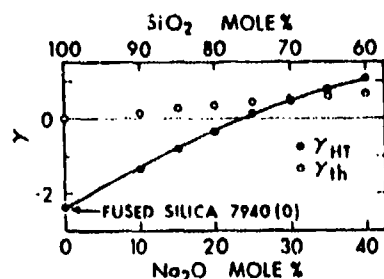


Fig. 7 γ_{th} and γ_{HT} as functions of Na_2O content.

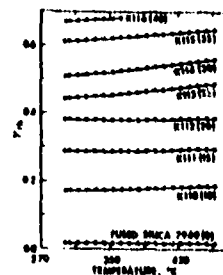


Fig. 8 γ_{th} as function of temperature.

pressure and temperature derivative values. The high-temperature limiting values of mode Grüneisen parameter, γ_{HT} , can be evaluated from pressure dependence of velocities (ref. 13). The values of γ_{HT} increase more rapidly than γ_{th} does with increasing Na_2O content (fig. 7). Although the γ_{HT} values are negative and larger than the γ_{th} values, both Grüneisen parameters increase when Na_2O is added to the silica structure.

Temperature dependence of γ_{th} in the range of 298-498° K is shown in Fig. 8. In fused silica and the lower soda-content glasses, the γ_{th} value is more or less temperature-invariant. For higher soda-content glasses, γ_{th} increases more rapidly with temperature.

4. Ultrasonic Attenuation. Large ultrasonic attenuation occurs in simple inorganic oxide glasses such as SiO_2 , GeO_2 , B_2O_3 , and As_2O_3 at various temperatures in the range from $\sim 50^\circ$ to $\sim 250^\circ$ K (refs. 14-21). Anderson and Bömmel (ref. 14) proposed a structural relaxation mechanism to explain the attenuation spectrum for fused silica at low temperatures. According to them, thermally activated lateral shifting of an oxygen atom between two equivalent equilibrium positions, perpendicular to the Si-O-Si bond, is a source of structural relaxation which also explains the negative thermal expansion and excess specific heat anomalies at low temperatures in fused silica. An alternate mechanism, which involves the movement of the oxygen atom in the direction of the Si-O-Si bond rather than perpendicular to it, has been proposed in a two-bond-length model (refs. 15-16).

Compared to the amount of work on fused silica, very little work has been done on the study of relaxational processes in sodium silicate glasses except at low frequencies (.01 and 10 Hz) where the attenuation occurs due to ionic migration of Na^+ (refs. 17, 22) and possibly oxygen ions (refs. 22-24). The Na^+ -migration relaxation is a stress-induced phenomenon, resolvable at frequencies of the order of KHz.

Figures 9 and 10 show the composition dependence of longitudinal and

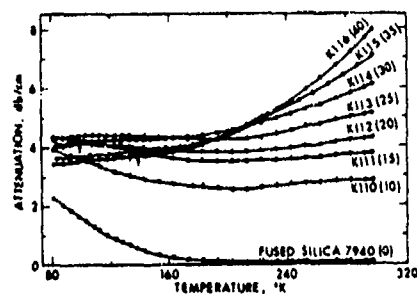


Fig. 9
Temperature dependence of
attenuation (longitudinal mode).

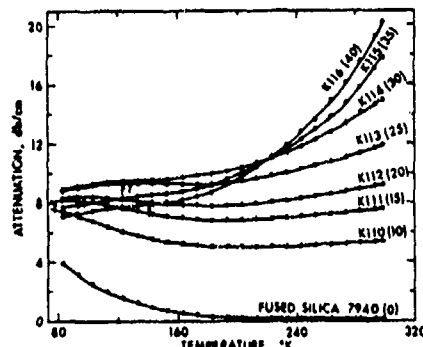


Fig. 10
Temperature dependence of
attenuation (shear mode).

shear attenuation at 30 MHz, respectively, for the $\text{Na}_2\text{O-SiO}_2$ glasses at ambient conditions. As seen, the attenuation due to shear-wave propagation is approximately twice that due to longitudinal-wave propagation, which supports the previous conclusion (ref. 19) that the loss is in large part sensitive to shear distortion. The temperature dependence of longitudinal and shear ultrasonic attenuation are plotted in Fig. 11. The

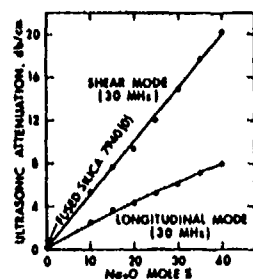


Fig. 11 Ultrasonic attenuation as
function of Na_2O content.

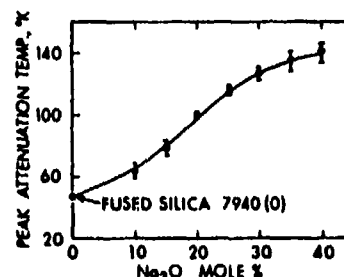


Fig. 12 Peak attenuation tempera-
ture versus Na_2O content.

present 30 MHz attenuation data for fused silica are in good qualitative agreement with previous 20 MHz data (ref. 14, 16, 21) with respect to the shape of the attenuation-temperature curve, although our attenuation values at 30 MHz are larger. Figures 9 and 10 show increasing broadening of the attenuation peaks with increasing concentration of Na_2O . This is probably due either to thermal broadening (ref. 14) or to a wider distribution of activation energy; the width of the loss peak (e.g., in fused silica; refs. 14, 16) has been interpreted in light of the distribution of activation energy. Alternately, the broadening could also be due to the superposition of the high temperature Na^+ -migration relaxation on the structural relaxation, at least, for the low-silica glasses.

One of the most interesting findings of this study is the shifting of the peak attenuation temperature (in the low-temperature range) with increasing Na_2O content; the peak attenuation temperature for each glass is indicated by an arrow (figs. 9 and 10). Because of the broadness of the attenuation curves, there is significant uncertainty in determining the peak temperatures. Also, since the peak attenuation temperatures for glasses K110 and K111 would fall below 80°K --outside the temperature range of this study--the peak attenuation temperatures for these glasses were estimated by extrapolating the attenuation versus temperature curves (Figs. 9 and 10); hence the relationship shown in Fig. 12 is subject to further uncertainty.

However, compared to the peak attenuation temperature of 47°K for fused silica (refs. 14, 16), the peaks for the $\text{Na}_2\text{O-SiO}_2$ glasses certainly appear to be composition-dependent. Since the peak attenuation temperature increases with increase in the Na_2O content, the effect of adding Na_2O to SiO_2 is opposite that of adding Na_2O to GeO_2 (ref. 11), although there are structural similarities between fused SiO_2 and GeO_2 (both glasses have tetrahedral structures).

For the low-temperature structural relaxation mechanism, such as that present in fused silica (ref. 14) and presumably also in the $\text{Na}_2\text{O-SiO}_2$ glasses, it would be of interest to compute from the frequency-dependence of the peak attenuation temperatures the most probable activation energies for different concentrations of Na_2O . However, as attenuation data at different frequencies are not yet available for these glasses, no attempt can be made to calculate the activation energies for these glasses (for fused silica, activation energy is ~ 1030 cal/mole; ref. 14). However, from the shift of the peaks to higher temperatures (Fig. 12), it is suggested that in some systematic fashion the activation energy increases with Na_2O , contrary to that found for the $\text{Na}_2\text{O-GeO}_2$ system (ref. 11). Although the high-temperature Na^+ relaxation ($>250^\circ \text{K}$) seems to obscure the low-temperature side of the attenuation curve, at least, for higher Na_2O content glasses, it is clearly inferred from the magnitudes of attenuation curves of the $\text{Na}_2\text{O-SiO}_2$ glasses (figs. 9 and 10) that the magnitude of attenuation, and thereby relaxation strength, decreases with increasing Na_2O . As a phenomenon, this behavior can be interpreted on the basis of a structural model in which the Na_2O molecule modifies the existing Si-O-Si bonding sites. This modification may result in the formation of a weaker Si-O-Na bond or an unbridged Si-O- bond. The former would impede the movement of the oxygen atoms, and since movement of the oxygen atom is the cause of attenuation this would result in decrease in the attenuation, accompanied by the increase in the activation energy as revealed by the

shifting of the attenuation peak to higher temperatures. The latter modification would, however, make no contribution to attenuation. In other words, a loosening of structure occurs with the addition of soda, which is in agreement with the low frequency internal friction work (ref. 22).

In high-soda glasses, at 30 MHz, one would expect to find Na^+ relaxation at temperatures above room temperature. Near room temperature (Figs. 10 and 11), the temperature-dependence of both longitudinal and shear attenuation increases with increasing Na_2O . The effect of composition on the internal friction at much lower frequencies (.01-Hz) for $\text{Na}_2\text{O-SiO}_2$ glasses studied by Forry (ref. 22) shows a decrease both in intensity and peak temperature as Na_2O content increases. In light of this and our results, it may be concluded that the expected high-temperature attenuation peak is shifting toward lower temperatures with increasing Na_2O . A similar shift in Na^+ relaxation temperatures has also been observed in the $\text{Na}_2\text{O-GeO}_2$ glasses (ref. 11). This type of high-temperature relaxation requires large activation energy compared to low-temperature structural relaxation. It is desirable to investigate further the composition dependence of Na^+ relaxation at high temperatures and low frequencies in other types of glasses.

5. Summary

- a. Elastic moduli of $\text{Na}_2\text{O-SiO}_2$ glasses and their pressure and temperature derivatives vary systematically with composition. Increasing Na_2O content results in decrease of μ and E moduli. K modulus first decreases ($\sim 10\%$ Na_2O) and then increases with increase in Na_2O . Low-soda glasses exhibit anomalous behavior under pressure and temperature. The degree of anomalous behavior decreases with increasing Na_2O , i.e., the pressure derivatives of moduli increase and the temperature derivatives decrease with increase in Na_2O .
- b. The Grüneisen parameters γ_{th} and γ_{HT} increase with Na_2O . The disparity between the γ_{th} and γ_{HT} values decreases as Na_2O increases; at 70 mole % Na_2O glass composition, the two values are the same. γ_{th} increases with temperature; the temperature dependence of γ_{th} increases with increase in Na_2O .
- c. At room temperature, shear-wave attenuation at 30 MHz is larger (~ 2 times) than the longitudinal-wave attenuation; both types of losses, however, increase with Na_2O .
- d. The low-temperature attenuation peak (due to structural relaxation) observed in fused silica at $\sim 47^\circ \text{K}$ is also found in $\text{Na}_2\text{O-SiO}_2$ glasses. The peak attenuation temperature is found to increase with increase in Na_2O ,

indicating that the activation energy is increasing with Na_2O , contrary to what has been previously reported for $\text{Na}_2\text{O-GeO}_2$ glasses (ref. 11). The attenuation-temperature curves at these low temperatures show a reversed relationship compared to that found at room temperature, i.e., the attenuation peak height decreases with increasing Na_2O . Explanation is offered in terms of the formation of Si-O-Na bonds, which are weaker than Si-O-Si bonds.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report concerns the M_2O-SiO_2 and SiO_2-TiO_2 glass systems. Elastic, thermal and infrared absorption characteristics of nineteen simple binary M_2O-SiO_2 glasses, where M is Li, Na or K, have been studied at ambient conditions as well as function of pressure and temperature. M_2O content of these glasses ranges from 10 to 45 mole %. Elastic moduli were investigated to 5 kbar and to 300°C, thermal expansivity to 300°C, and infrared absorption to 58.8 kbar. (cont'd.)		

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20. ABSTRACT (cont'd.) 1473A)

→ The elastic properties of the M_2O-SiO_2 glasses vary systematically with composition. Addition of M_2O to SiO_2 structure causes increase in bulk modulus (K) of all the glasses, decrease in shear (μ) and Young's moduli (E) of all but the Li_2O-SiO_2 glasses, and increase in Poisson's ratio. Low M_2O glasses show anomalous elastic behavior under pressure, that is, dM/dP , where M is any modulus, is negative. The values of dM/dP increase linearly with M_2O content. Likewise dM/dT for the M_2O-SiO_2 glasses decreases with M_2O content.

→ Effect of phase separation on the elastic properties is not significant; however, their temperature dependence is sensitive to phase separation.

→ Ultrasonic longitudinal (α_p) and shear (α_s) wave attenuation are found to be linearly proportional to frequency. Both α_p and α_s increase with M_2O content; α_p/α_s ratio varies from 2 to 2.6. (approximately)

→ The low-temperature attenuation peak found in fused silica at $\sim 47^\circ K$ broadens and shifts to higher temperature with increase in M_2O content. Implication of this is discussed in terms of transverse oxygen vibrations.

Coefficient of the thermal expansion (α_l) of M_2O-SiO_2 glasses increases in the order: $K_2O-SiO_2 > Na_2O-SiO_2 > Li_2O-SiO_2$ glasses, and increases with increase in M_2O content. The α_l is found to vary quadratically with temperature.

Elastic properties of SiO_2-TiO_2 glasses containing up to $\sim 10\% TiO_2$, investigated to 5 kbar and $300^\circ C$, show that annealing causes density and V_s to increase, and V_p to decrease. The elastic properties of the annealed glasses vary systematically and more or less linearly with composition. Due to the weakening of structure, all the moduli decrease. Addition of TiO_2 also causes the glasses to become more anomalous under pressure and temperature (dM/dP and dM/dT become more negative and more positive, respectively). This behavior, consistent with the thermal expansion data, appears to be caused by increasing openness of the structure.

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