

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 $\approx 40 \text{ kbar}$, of all the main infrared absorption frequencies, which are pressure sensitive, are found to be positive. The values of $d\nu_i/dP$ 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.

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I. INTRODUCTION

It has been demonstrated that the addition of an alkali-metal oxide, such as Na_2O , to the SiO_4 tetrahedral network in silicate glasses, in addition to effecting a minor role of network filling at low concentration, causes re-adjustment 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

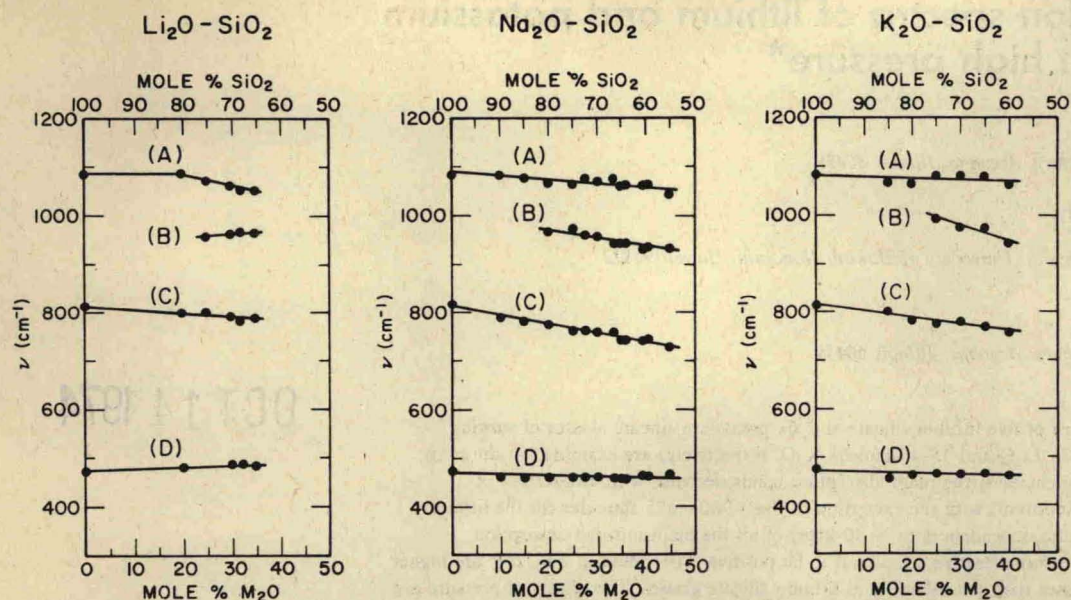


FIG. 1. Plots of vibrational mode frequency vs composition in mole% M_2O , where M is Li, Na, or K. Zero mole% M_2O is for fused silica. (A) Tetrahedral Si-O stretching vibration. (B) Terminal Si-O stretching vibration. (C) Si-O-Si bridged stretching vibration between tetrahedra. (D) Bending vibration 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 $< 650 \text{ cm}^{-1}$ with water vapor and

Hg emission lines, and with the low-frequency absorptions of solid yellow HgO. For the high-pressure infrared absorption measurements $< 650 \text{ cm}^{-1}$, the opposed diamond cell and the Perkin-Elmer 301 spectrophotometer equipped with a $6\times$ beam condenser were used. Mid-infrared measurements at high pressures were made with a Beckman IR-12 spectrophotometer also equipped with a $6\times$ beam condenser.¹⁶ 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}

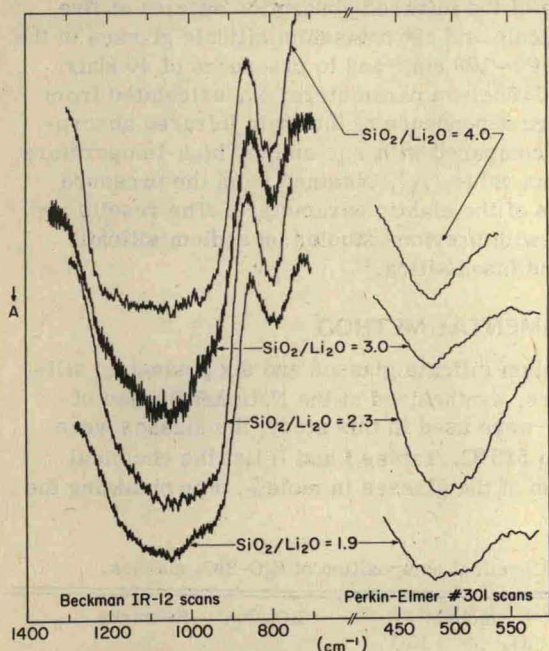


FIG. 2. Spectra ($1200\text{--}700 \text{ cm}^{-1}$) of lithium silicate glasses with varying ratios of $\text{SiO}_2/\text{Li}_2\text{O}$ at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300 cm^{-1}) of the same glasses, observed by using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

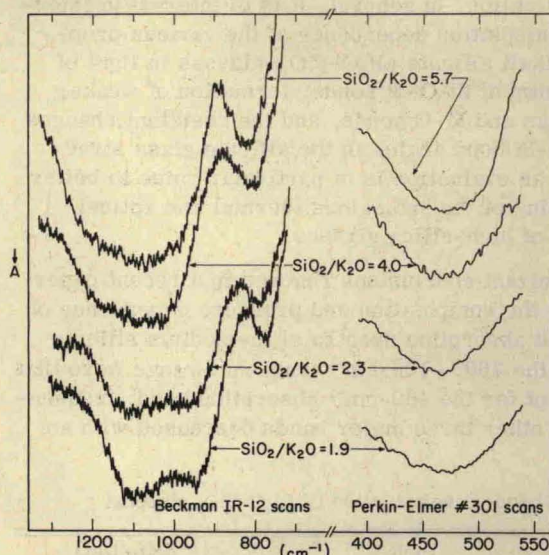


FIG. 3. Spectra ($1200\text{--}700 \text{ cm}^{-1}$) of potassium silicate glasses with varying ratios of $\text{SiO}_2/\text{K}_2\text{O}$ at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300 cm^{-1}) of the same glasses, observed by using 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 $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ 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 $\sim 0.11 \text{ cm}^{-1}/\text{mole}\%$ $M_2\text{O}$, 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 $\text{Li}_2\text{O}-\text{SiO}_2$ glasses but is weakened in $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ 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 $\text{K}_2\text{O}-\text{SiO}_2$ glasses but increases in $\text{Li}_2\text{O}-\text{SiO}_2$ 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}

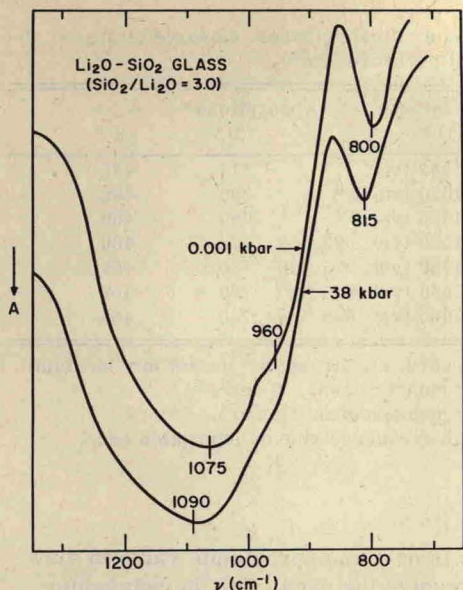


FIG. 4. Spectra of lithium silicate glass (25 mole% Li_2O) in the frequency range 1200–700 cm^{-1} at varying pressures.

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 $\sim 800\text{-cm}^{-1}$ 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 $\sim 480\text{ cm}^{-1}$ 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.

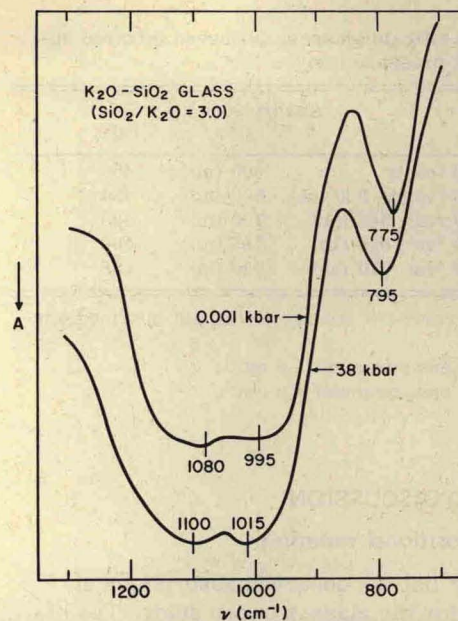


FIG. 5. Spectra of potassium silicate glass (25 mole% K_2O) in the frequency range 1200–700 cm^{-1} at varying pressures.

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 $\equiv\text{Si-O}^-\text{M}^+\equiv\text{Si-O-Si}\equiv$ 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 $\sim 460\text{-cm}^{-1}$ 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 $\sim 470\text{ cm}^{-1}$ 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.

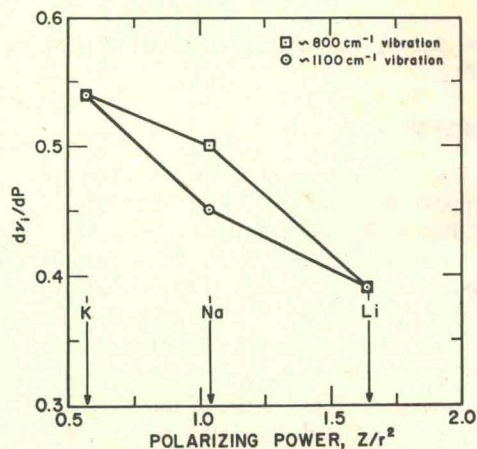


FIG. 6. Plot of dv_i/dP vs polarizing power (Z/r^2) for M_2O-SiO_2 glasses, where $M=Li, Na,$ or K . (Z = electronic charge, and r = radius (Ref. 19) of the alkali ion.)

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 ~ 460 cm^{-1} , which does not show any appreciable change. Krüger,³ 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 ~ 960 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 (~ 460 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 $T < 200$ 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 by the relationship

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

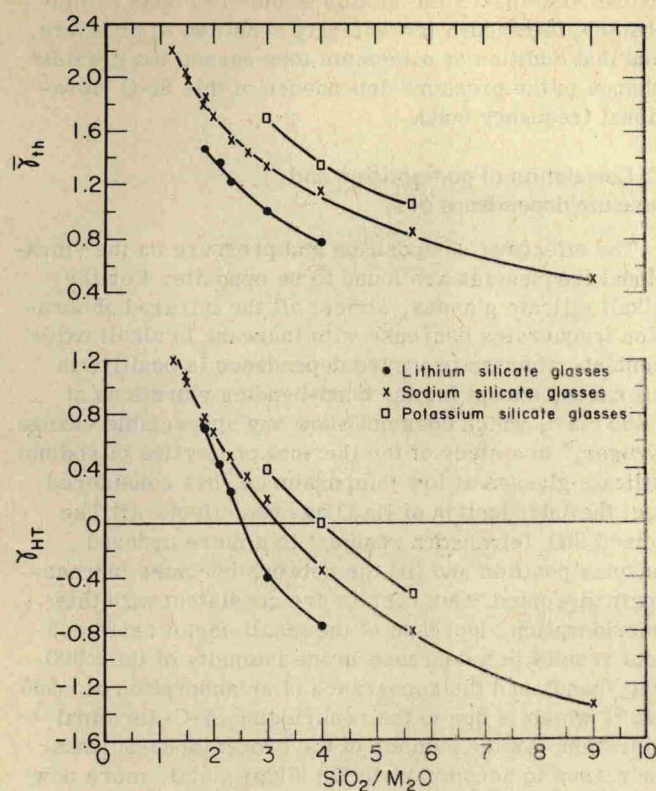


FIG. 7. Plots of $\bar{\gamma}_{th}$ and γ_{HT} vs SiO_2/M_2O ratio for the Li_2O -, Na_2O -, and K_2O - SiO_2 glasses (from Ref. 2).

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 $\bar{\gamma}_{th}$ 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 $\bar{\gamma}_{th}$ 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 $\bar{\gamma}_{th}$ for the Li_2O and K_2O - SiO_2 glasses. Figure 7 shows plots of $\bar{\gamma}_{th}$ and γ_{HT} versus the SiO_2/M_2O ratio² for these and Na_2O - SiO_2 glasses. In both plots the $\bar{\gamma}_{th}$ 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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