TABLE III. Lithium silicate glasses. Observed infrared absorptions at ambient pressure (cm⁻¹).

Glass (mole% Li_2O)	Absorptions [a]		
	(1) [b]	(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

[a] Abbreviations: v = very; s = strong; b = broad; m = medium; sh = shoulder.
[b] Limit of frequency measurement ± 5 cm⁻¹.
[c] Limit of frequency measurement ± 3 cm⁻¹.

TABLE IV. Potassium silicate glasses. Observed infrared absorptions at ambient pressure (cm⁻¹).

Glass (mole% K_2O)	Absorptions [a]		
	(1) [b]	(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

[a] Abbreviations: v = very; s = strong; b = broad; m = medium.
[b] Limit of frequency measurement ± 5 cm⁻¹.
[c] Limit of frequency measurement ± 3 cm⁻¹.
[d] Asymmetric on high-frequency side of absorption band.

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 ~1100-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 $d\nu_i/dC$, where C is the mole% M_2O present in the glass, we have, from the least-squares analysis of the data, the values of $d\nu_i/dC$ for the ~1100-cm⁻¹ band in the lithium, sodium, and potassium glasses as -2.87, -1.04, and ~ 0.11 cm⁻¹/mole% M_2O, 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_2O content; for the potassium glasses, there is no appreciable change.

The ~960-cm⁻¹ absorption represents the nonbridging Si-O terminal stretching. Simon[14] 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 (~995 cm⁻¹) for a potassium glass (Fig. 3) and lowest (~960 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 ~1100-cm⁻¹ band with increasing Na_2O content, appears as a small shoulder near ~960 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 $d\nu_i/dC$ estimated for this band in the lithium glasses is 1.08

cm⁻¹/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 $d\nu_i/dC$ is ~ -2.00 cm⁻¹/mole% which is the same as the value obtained for the sodium system. (For a comparison of the behavior of $d\nu_i/dC$ 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 glasses[2]: 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 ~800-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_2O 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 ~460-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 ~1100-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 ~800-cm⁻¹ band. Similar effects are observed in the potassium glasses (Fig. 3). However, the intensity of the ~800-cm⁻¹ band decreases more appreciably with increasing K_2O content, and the intensity of the Si-O terminal nonbridging stretching absorption at ~960 cm⁻¹ increases and becomes as strong as that of the ~1100-cm⁻¹ band at a SiO_2/K_2O molar ratio of 3.0. Also seen in Fig. 3 is a decrease both in intensity and in frequency of the ~800-cm⁻¹ band in the potassium glasses as the K_2O content increases. Similar effects of the absorption bands ~1100 and 800 cm⁻¹
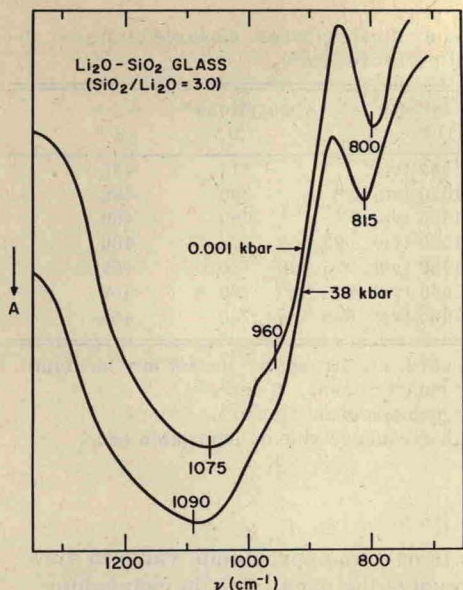
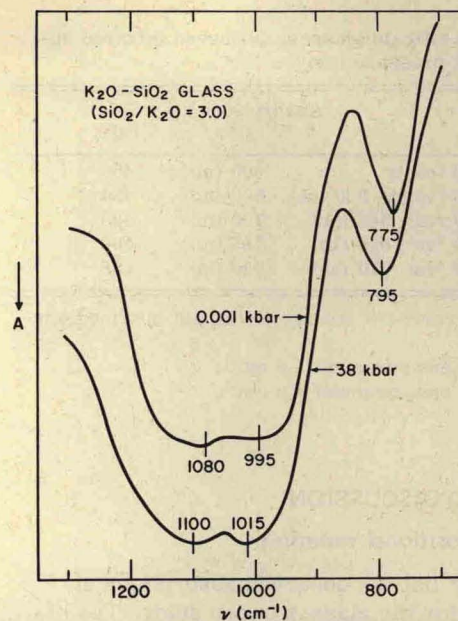FIG. 4. Spectra of lithium silicate glass (25 mole% Li_2O) in the frequency range 1200—700 cm^{-1} at varying pressures.

FIG. 5. Spectra of potassium silicate glass (25 mole% K_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 K > Na > Li silicate glasses.[17] Revesz[18] 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

this author, the lower the electronegativity of the alkali metal (the order of electronegativity being Li > Na > K), the larger is the π contribution to the $\equiv Si-O^-M^+ \equiv Si-O-Si \equiv$ 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 ~460-cm^{-1} band, which does

TABLE V. Comparison of the mode Grüneisen parameters γ_i with γ_{HT} and $\bar{\gamma}_{th}$ 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})	$d\nu_i/dP$ (cm^{-1}/kbar)	χ^a ($Mbar^{-1}$)	γ_i	$\gamma_{HT}{}^a$	$\bar{\gamma}_{th}{}^a$
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		

[a] Data from Ref. 2.
[b] Shoulder to this peak too weak to follow with pressure.

TABLE VI. Comparison of the mode Grüneisen parameters γ_i with γ_{HT} and $\bar{\gamma}_{th}$ 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})	$d\nu_i/dP$ (cm^{-1}/kbar)	χ^a ($Mbar^{-1}$)	γ_i	$\gamma_{HT}{}^a$	$\bar{\gamma}_{th}{}^a$
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	...	...		

[a] Data from Ref. 2.