

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  $\sim 800$ - and  $\sim 1100$ - $cm^{-1}$  absorptions are positive, as was found for the sodium silicate glasses.<sup>4</sup>

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  $\gamma_i$ , 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  $\chi$  is the isothermal compressibility of material. In all cases where comparisons are possible, the  $\gamma_i$  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 glasses<sup>4</sup> 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 $\nu_i$

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  $\sim 460$   $cm^{-1}$ , which does not show any appreciable change. Krüger,<sup>3</sup> 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  $\sim 800$ - $cm^{-1}$  band, and the appearance of an absorption at  $\sim 960$   $cm^{-1}$ , which is due to the nonbridging Si-O<sup>-</sup> 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  $\sim 960$ - $cm^{-1}$  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 ( $\sim 460$   $cm^{-1}$ ) 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<sup>-</sup> vibration remains invariant. The pressure effects may be considered to cause some ordering of structure, as was previously reported for quartz and fused silica.<sup>13</sup>

### D. Thermal expansion and the Grüneisen parameters

The observed negative thermal expansion coefficients,  $\alpha_v$ , 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.<sup>20,21</sup> The coefficient  $\alpha_v$  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,  $\rho$  is density, and  $C_p$  and  $C_v$  are specific heats at constant pressure and volume, respectively.  $\bar{\gamma}_{th}$  is also related to  $\gamma_i$  and  $C_v$  by the relationship

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

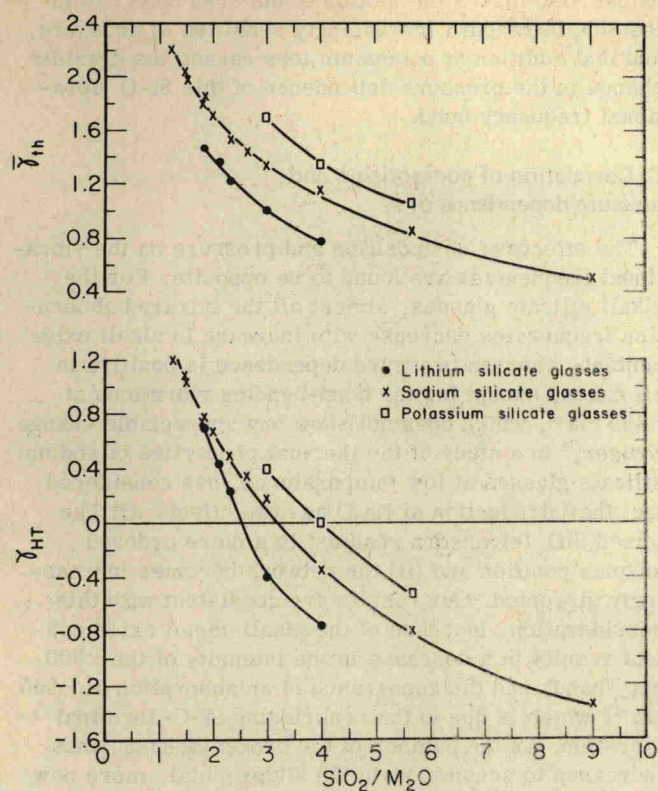


FIG. 7. Plots of  $\bar{\gamma}_{th}$  and  $\gamma_{HT}$  vs  $SiO_2/M_2O$  ratio for the  $Li_2O-$ ,  $Na_2O-$ , and  $K_2O-SiO_2$  glasses (from Ref. 2).

where  $\gamma_i$  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  $\gamma_{HT}$ .  $\gamma_{HT}$  calculated from the pressure derivatives of the elastic parameters,<sup>22,23</sup> assuming that only the acoustic modes contribute to  $\gamma$ , are listed in Tables V and VI.

For the sodium silicate glasses, it was found that  $\bar{\gamma}_{th}$  and  $\gamma_{HT}$  increase as more  $Na_2O$  enters the silica network. For the  $SiO_2/Na_2O$  ratio of 4 and larger,  $\gamma_{HT}$  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  $\gamma_i$ ,  $\gamma_{HT}$ , and  $\bar{\gamma}_{th}$  for the  $Li_2O$  and  $K_2O-SiO_2$  glasses. Figure 7 shows plots of  $\bar{\gamma}_{th}$  and  $\gamma_{HT}$  versus the  $SiO_2/M_2O$  ratio<sup>2</sup> for these and  $Na_2O-SiO_2$  glasses. In both plots the  $\bar{\gamma}_{th}$  and  $\gamma_{HT}$  values increase in the following order:  $K > Na > Li$  silicate glasses. At lower  $SiO_2/M_2O$  ratios, the  $\gamma_{HT}$  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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