

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

John R. Ferraro

Argonne National Laboratory, Argonne, Illinois 60439

Murli H. Manghnani

Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822

Louis J. Basile

Argonne National Laboratory, Argonne, Illinois 60439

(Received 16 July 1973)

Infrared absorption spectra of five lithium silicate and six potassium silicate glasses of varying composition (20–35 mole%  $\text{Li}_2\text{O}$  and 15–40 mole%  $\text{K}_2\text{O}$ , respectively) are examined in the range 1500–100  $\text{cm}^{-1}$ . 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  $-960 \text{ cm}^{-1}$  shoulder for the lithium silicate glasses. The pressure dependences to  $\sim 40$  kbar, of all the main infrared absorption frequencies, which are pressure sensitive, are found to be positive. The values of  $dv_i/dP$  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  $\gamma$ 's,  $\gamma_i$ , 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  $\gamma_i$ ,  $\gamma_{\text{th}}$ , and  $\gamma_{\text{HT}}$  generally increase with  $M_2\text{O}$  content in alkali silicate glasses.

OCT 14 1974

## I. INTRODUCTION

It has been demonstrated that the addition of an alkali-metal oxide, such as  $\text{Na}_2\text{O}$ , to the  $\text{SiO}_4$  tetrahedral network in silicate glasses, in addition to effecting a minor role of network filling at low concentration, causes re-adjustment of the  $\text{SiO}_4$  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,<sup>1</sup> elastic,<sup>2</sup> and thermal properties,<sup>3</sup> and infrared absorption spectra of sodium silicate glasses,<sup>4–14</sup> 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- $\text{cm}^{-1}$  frequency range were that first, except for the 460- $\text{cm}^{-1}$  absorption band, frequencies of the other three major bands decreased with an

increase in  $\text{Na}_2\text{O}$  content; second, the pressure dependence of the three major infrared vibrational modes  $\nu_i$  was positive; and third, the values of mode Grüneisen gamma,  $\gamma_i$ , calculated from  $dv_i/dP$ , were larger than those found for fused silica and that  $\gamma_i$  for the  $\sim 800\text{-cm}^{-1}$  band appears to increase (outside experimental errors) with  $\text{Na}_2\text{O}$  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  $\text{cm}^{-1}$  and to pressures of 40 kbar. The mode Grüneisen parameters,  $\gamma_i$ , calculated from the pressure dependence of the main infrared absorptions, are compared with  $\bar{\gamma}_{\text{th}}$ , and the high-temperature limit gamma value,  $\gamma_{\text{HT}}$ , obtained from the pressure coefficients of the elastic parameters. The results are correlated with previous studies on sodium silicate glasses<sup>4</sup> and fused silica.<sup>14</sup>

## 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%		$\text{SiO}_2/\text{Li}_2\text{O}$
	$\text{SiO}_2$	$\text{Li}_2\text{O}$	
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
	$\text{SiO}_2$	$\text{K}_2\text{O}$		
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

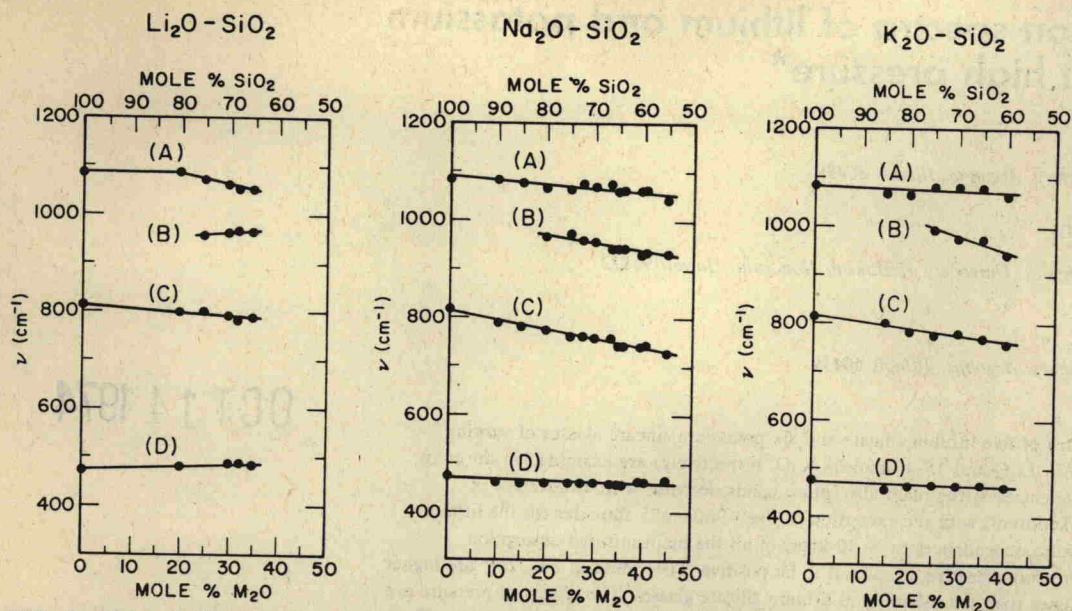


FIG. 1. Plots of vibrational mode frequency vs composition in mole%  $M_2O$ , where  $M$  is Li, Na, or K. Zero mole%  $M_2O$  is for fused silica. (A) Tetrahedral Si-O stretching vibration. (B) Terminal Si-O stretching vibration. (C) Si-O-Si bridged stretching vibration between tetrahedra. (D) Bending 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  $\text{cm}^{-1}$  were obtained by using a diamond anvil cell and Beckman IR-12 spectrophotometer. The spectra in the range < 650 to 300  $\text{cm}^{-1}$  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.<sup>16</sup> 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.<sup>15,16</sup>

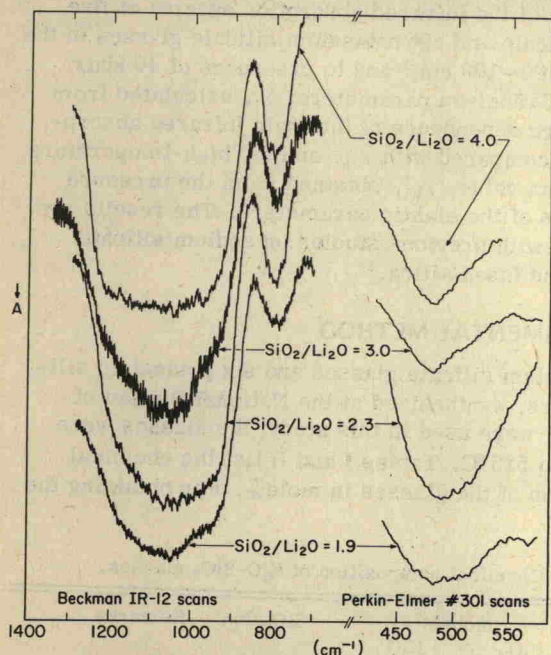


FIG. 2. Spectra (1200–700  $\text{cm}^{-1}$ ) of lithium silicate glasses with varying ratios of  $\text{SiO}_2/\text{Li}_2\text{O}$  at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300  $\text{cm}^{-1}$ ) of the same glasses, observed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

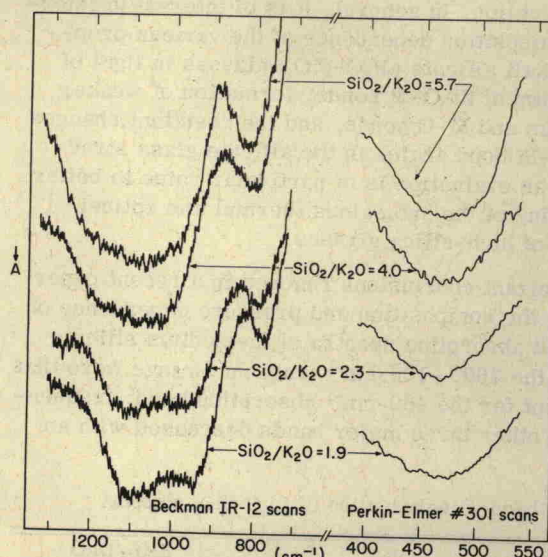


FIG. 3. Spectra (1200–700  $\text{cm}^{-1}$ ) of potassium silicate glasses with varying ratios of  $\text{SiO}_2/\text{K}_2\text{O}$  at ambient pressure, observed by using a diamond cell with a Beckman IR-12 spectrophotometer. The spectra (600 to 300  $\text{cm}^{-1}$ ) of the same glasses, observed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