

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% Na₂O) 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 Na₂O 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 Na₂O added. Further, some of the Si-O-Si bridges between the SiO₄ tetrahedra may be stretched to accommodate the sodium ion in the network. As a result, the elastic moduli and strength of Na₂O-SiO₂ glasses decrease with an increase in the Na₂O 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 $\bar{\gamma}_{th}$, 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 White⁶ 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 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× beam condenser.¹¹ Midinfrared studies at high pressures were made with a Beckman IR-12 spectrophotometer equipped with a 6× 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.¹¹⁻¹²

TABLE I. Composition of Na₂O-SiO₂ glasses.

| Sample No. | mole % | | Ratio |
|------------|------------------|-------------------|-------------------------------------|
| | SiO ₂ | Na ₂ O | SiO ₂ /Na ₂ O |
| 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 Na₂O to silica on the various absorptions between 1400–350 cm⁻¹. The increasing content of Na₂O causes a decrease in frequency of the three absorptions at ~1100, ~960, and ~790 cm⁻¹, and an increase for the ~460-cm⁻¹ absorption. It is of interest to note that as the Na₂O content increases, the ~790-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 Na₂O 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 Na₂O enters the network. The ambient-pressure results are substantially in agreement with the reflectance work of Sweet and White⁶ 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:

- ~1100 cm⁻¹, Si-O stretching within the tetrahedra;^{6,14}
- ~960 cm⁻¹, Si-O terminal, nonbridged stretching;⁶
- ~790 cm⁻¹, Si-O-Si bridged stretching between tetrahedra; (d) ~460-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 now been made.^{13,15-19}

Under conditions of our experiments no significant absorptions were found lower than the broad band at ~460 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.

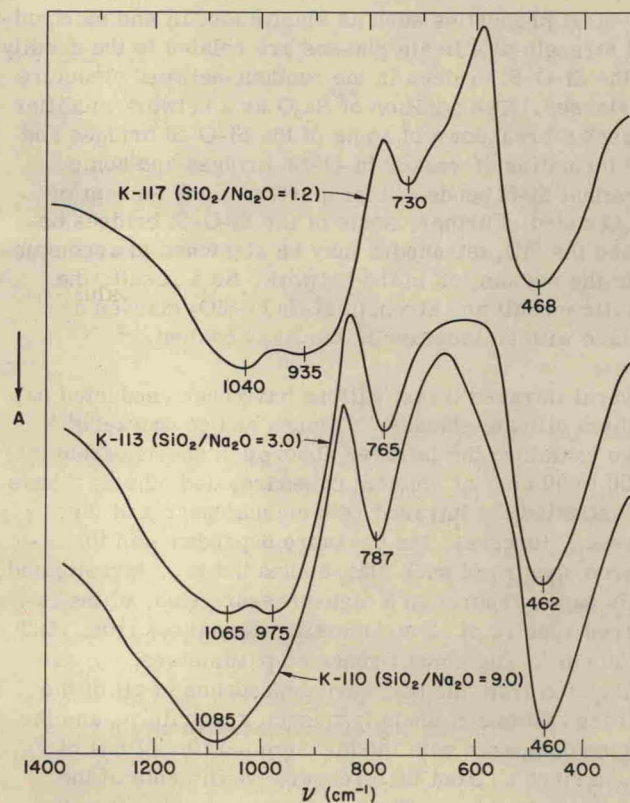
TABLE II. Sodium silicate glasses. Observed infrared absorptions at ambient pressure (cm⁻¹). Abbreviations: s = strong; m = medium; v = very; b = broad; w = weak.

| Glass (mole % Na ₂ O) | ν | | |
|----------------------------------|---------------------------|---------|--------|
| α quartz(0) | 1082(vs) ^a | 783(m) | 459(s) |
| | | 800(m) | |
| Fused silica(0) | 1087(vs) | 815(m) | 475(s) |
| (10) | 1085 ^a (vs, b) | 787(m) | 460(s) |
| (15) | 1075 ^b (vs, b) | 785(m) | 461(s) |
| (20) | 1065(vs, b) | 965(sh) | 775(m) |
| (25) | 1065(vs) | 975(vs) | 765(m) |
| (27.5) | 1075(vs) | 960(vs) | 765(m) |
| (30) | 1070(vs) | 960(vs) | 760(m) |
| (33.1) | 1075(vs) | 940(vs) | 760(m) |
| (35) | 1070(vs) | 940(vs) | 755(m) |
| (35.5) | 1075(vs) | 940(vs) | 760(w) |
| (39.6) | 1060(vs) | 930(vs) | 745(w) |
| (40) | 1060(vs) | 935(vs) | 750(w) |
| (45) | 1040(vs) | 935(vs) | 730(w) |

^aAsymmetric on high- and low-frequency sides of band.

^bVery weak shoulder 980 cm⁻¹, 1220 cm⁻¹.

Table III presents the pressure dependence for the four main vibration modes, in terms of dv_i/dP , for the sodium silicate glasses. It is observed that dv_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 cm⁻¹) of several sodium glasses at varying concentrations of SiO₂/Na₂O at ambient pressure.