

## A Raman spectroscopic study of glasses in the system CaO–MgO–SiO<sub>2</sub>

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### Abstract

The Raman spectra of a number of glasses in the system CaO–MgO–SiO<sub>2</sub> have been prepared using solar furnace techniques. The spectra of glasses along the SiO<sub>2</sub>–CaO, SiO<sub>2</sub>–MgO and SiO<sub>2</sub>–Ca<sub>0.5</sub>Mg<sub>0.5</sub>O joins are similar to those obtained in other studies, and are interpreted in terms of vibrations of tetrahedral silicate units with zero, one, two, three and four non-bridging oxygens, consistent with previous discussions. Some glasses were prepared with bulk compositions within the CaO–MgO–SiO<sub>2</sub> two-liquid field, using both a “normal” and a fast quench rate. The normal-quenched glasses were opaque and unmixed, the fast-quenched samples transparent and homogeneous. Both sets of samples had identical spectra, and the implications of this are discussed. Finally, a number of samples with varying Ca/Mg ratio at constant high silica content were studied. Their Raman spectra are discussed along with results of previous studies on alkali and alkaline earth silicate glass systems to develop a molecular site model which describes the effect of changing metal cation on the distribution of silicate species.

### Introduction

A considerable number of studies have used Raman spectroscopy to investigate the structures of silicate glasses and melts, many of which have been applied to understanding properties important in geological processes. In the present study, a number of glasses were prepared in the system CaO–MgO–SiO<sub>2</sub> using solar furnace melting and fast quench techniques. There have been several previous studies on glasses and melts in this system (e.g., Etchepare, 1970a, 1972; Konijendijk, 1975; Brawer and White, 1977; Sharma et al., 1979; Sharma and Yoder, 1979; Virgo et al., 1980; Kashio et al., 1980; Mysen et al., 1980a,b, 1982a,b; Mysen and Virgo, 1980; Tsunawaki et al., 1981; McMillan et al., 1981; McMillan and Piriou, 1983; Piriou and McMillan, 1983a,b) whose results are compared with the present observations. Finally, a number of samples with bulk compositions within the two-liquid field of the liquidus CaO–MgO–SiO<sub>2</sub> phase diagram were prepared by quenching from the liquid at different quench rates. The Raman spectra of these glasses give some insight into the nature of unmixing in this system, and lead to a discussion of the rôle of metal cations in determining the structures of these and other silicate glasses and melts.

### Experimental procedure

#### Sample preparation and characterization

Glass samples for this study were prepared from reagent-grade oxide mixes or gels by solar melting at the French solar furnace facility (CNRS Odeillo). Temperatures at the sample could not

be controlled or accurately measured, but were estimated at 2000–2500°C. Normal quenching (NQ) was achieved by simply removing the sample from the beam and allowing to cool in air, to give a quench rate of around 10<sup>3</sup>°C/s. Super-quenched (SQ) samples were obtained by splat quenching on the water-cooled sample stage. The quench rate by this method is of the order of 10<sup>5</sup>–10<sup>6</sup>°C/s. Melting was ascertained by visual observation of the samples during heating, and by optical, Raman and X-ray study of the quenched products. Further details of this preparation method are discussed in Coutures et al., (1978), McMillan (1981), and McMillan et al. (1982).

Samples were analyzed using a Cameca MS-46 electron microprobe with a 15 kV accelerating voltage and near 25 nA beam current for a 2 μm spot size. Data were reduced using the program FRAME (Heinrich, 1972). Twenty to thirty point counts were obtained for each sample, and a relative homogeneity index H was calculated following similar reasoning to Boyd and Finger (1975) (see McMillan et al., 1982). Values of H near unity indicate that the sample is homogeneous in that oxide component. Most glass samples in this study were found to be homogeneous, and Raman spectra obtained from different parts of a given sample were identical. Some samples with compositions within the CaO–MgO–SiO<sub>2</sub> miscibility gap (Levin et al., 1964, p. 211; Fig. 1) were found to be inhomogeneous, and were analyzed by X-ray fluorescence using a Philips PW 1410 vacuum spectrometer and the low-dilution disc method of Thomas and Haukka (1978). Some such samples showed differences in Raman spectra between parts of the same sample, as discussed in the text. Analytical results are reported in Table 1, and sample compositions studied are shown in Figure 1.

#### Raman spectroscopy

All transparent NQ samples were polished for polarized 90° Raman scattering, while opaque glasses were run by glancing

Table 1. Glass compositions studied in the CaO-MgO-SiO<sub>2</sub> system.

(a) The SiO <sub>2</sub> -CaMgSiO <sub>4</sub> join (Figures 3, 4).									
Sample	mole % oxide			method(a)		homogeneity(b)			
	CaO	MgO	SiO <sub>2</sub>	ε(c)	#(d)	CaO	MgO	SiO <sub>2</sub>	
1 SQ(e)	33.2	32.4	34.3	100.0	XRF	-	-	-	-
2 SQ	34.5	31.8	33.7	100.0	SEM	-	-	-	-
2 SQ	35.9	27.8	36.2	101.4	EMP	27	1	1	1
2 SQ	0.6(f)	0.7	0.6	1.8	-	-	-	-	-
2 SQ	37.4	27.4	35.2(g)	100.0	AA	-	-	-	-
3 NQ	33.5	25.4	41.1	99.4	EMP	21	1	1	1
3 NQ	0.9	0.7	0.9	0.9	-	-	-	-	-
3 NQ	34.6	24.7	40.8	100.0	AA	-	-	-	-
4 NQ	32.0	23.3	44.7	100.0	EMP	18	1	1	1
4 NQ	0.7	0.7	0.7	2.4	-	-	-	-	-
4 NQ	33.1	24.2	42.7	100.0	AA	-	-	-	-
5 NQ	31.3	22.7	45.9	99.5	EMP	21	1	1	1
5 NQ	0.8	0.8	0.8	1.3	-	-	-	-	-
5 NQ	30.7	23.2	46.2	100.0	AA	-	-	-	-
6 NQ	29.5	22.4	48.1	100.8	EMP	17	1	1	1
6 NQ	0.5	0.7	0.7	1.1	-	-	-	-	-
6 NQ	31.1	22.4	46.5	100.0	AA	-	-	-	-
7 NQ	27.9	21.2	51.0	101.1	EMP	24	2	2	2
7 NQ	1.4	1.1	1.5	3.8	-	-	-	-	-
7 NQ	28.8	21.3	49.9	100.0	AA	-	-	-	-
8 NQ	27.8	20.2	52.0	98.9	EMP	20	1	1	1
8 NQ	0.4	0.5	0.4	1.3	-	-	-	-	-
8 NQ	28.2	20.4	51.4	100.0	AA	-	-	-	-
9 NQ	26.0	18.0	56.0	99.6	EMP	21	1	2	2
9 NQ	0.8	1.3	1.8	2.0	-	-	-	-	-
9 NQ	25.3	19.3	55.4	100.0	AA	-	-	-	-
10 SQ	21.8	20.5	57.6	99.4	EMP	21	1	1	1
10 SQ	0.6	0.4	0.5	1.8	-	-	-	-	-
10 NQ	22.1	21.8	56.1	100.0	AA	-	-	-	-
SiO <sub>2</sub>	-	-	100.0	100.0	(h)	-	-	-	-
NQ	-	-	-	-	-	-	-	-	-

angle reflection. The SQ glasses were generally too small and friable for mounting and polishing, and unpolarized or partially-polarized spectra were obtained from unpolished samples. Most spectra were obtained at CNRS Bellevue (France) using a Spectra-Physics 165 Ar<sup>+</sup> laser and Coderg PHO double monochromator. A number of spectra for samples of poor optical quality were run at ENSTA, Palaiseau with a Coherent Ar<sup>+</sup> laser and Coderg T800 triplet monochromator. Glass spectra were obtained using the 4800 or 5145 Å lines of the argon lasers, with 500–1000 mW power at the sample, and resolving slits of near 4 cm<sup>-1</sup>. The room-temperature spectra reported here were not reduced to remove effects of thermal population (e.g., Leadbetter and Stringfellow, 1974; Piriou and Alain, 1979). This procedure removes the pseudo-band near 50–100 cm<sup>-1</sup> and reduces the relative intensity below around 600 cm<sup>-1</sup> (Hass, 1969; Shuker and Gammon, 1970), but does not substantially change the band contours discussed here.

Unresolved bands were decomposed using a curve-fitting technique with a DuPont 310 curve-resolver as described previously (McMillan et al., 1982). Results of curve-fitting experiments for glasses along the SiO<sub>2</sub>-CaMgSiO<sub>4</sub> join are shown in Figure 4 and Table 2, and are discussed below. The method followed is illustrated in Figure 2 for sample 9 with 52 mole % SiO<sub>2</sub>. The component bands fitted at 1058, 972 and 868 cm<sup>-1</sup> correspond to the obvious features in the experimental spectrum indicated by arrows. The intensities of these bands were optimized to reproduce the high- and low-frequency sides of the observed band contour, while the 914 and 1154 cm<sup>-1</sup> components were introduced to complete the fit. In the present

Table 1. (cont.)

Sample	mole % oxide			method		homogeneity			
	CaO	MgO	SiO <sub>2</sub>	ε	#	CaO	MgO	SiO <sub>2</sub>	
(b) The CaMgSiO <sub>4</sub> -SiO <sub>2</sub> miscibility gap (Figure 7).									
SiO <sub>2</sub> SQ	-	-	99.8	98.7	EMP	22	-	-	1
11 NQ	20.7	14.6	64.6	0.7	1.7	96.2(j)	EMP	22	2
4	1.5	1.6	2.9	1.0	-	-	-	-	-
11 NQ	20.8	15.2	64.0	104.0(k)	XRF	-	-	-	-
12(1) NQ	22.3	14.4	63.3	95.3	EMP	12	5	5	6
(m)	3.4	2.4	4.5	8.2	-	-	-	-	-
12(2) NQ	4.7	2.0	92.5	93.8	EMP	11	17	29	10
12 NQ	5.5	5.5	9.3	8.9	-	-	-	-	-
12 NQ	14.5	11.3	74.2	107.5	XRF	-	-	-	-
13 NQ	7.0	4.4	88.5	93.4	EMP	23	13	11	9
13 NQ	4.9	3.2	8.1	2.1	-	-	-	-	-
13 NQ	8.9	7.5	83.5	108.2	XRF	-	-	-	-
11 SQ	17.9	13.8	68.2	99.6	EMP	27	2	3	4
12 SQ	1.5	1.6	2.9	1.7	-	-	-	-	-
12 SQ	15.9	12.1	71.9	100.4	EMP	26	6	6	7
13 SQ	3.2	2.9	6.0	1.0	-	-	-	-	-
13 SQ	7.6	6.1	86.3	99.8	EMP	22	2	2	2
	0.8	0.7	1.2	1.2	-	-	-	-	-
(c) The SiO <sub>2</sub> -CaO join (Figure 8)									
14 SQ	59.2	-	40.8	100.7	EMP	24	1	-	1
15 SQ	0.8	-	0.8	1.4	-	-	-	-	-
15 SQ	49.1	-	50.9	100.9	EMP	21	1	-	1
16 NQ	0.5	-	0.5	1.0	-	-	-	-	-
16 NQ	42.2	-	57.8	100.5	EMP	21	1	-	1
17 NQ	0.7	-	0.7	1.3	-	-	-	-	-
17 NQ	37.8	-	62.2	98.7	EMP	17	2	-	2
18 NQ	0.7	-	0.7	1.4	-	-	-	-	-
18 NQ	34.6	-	65.3	99.9	EMP	19	2	-	2
19 NQ	1.8	-	1.8	1.1	-	-	-	-	-
19 NQ	28.2	-	71.8	98.4	EMP	18	4	-	4
20 NQ	3.5	-	3.5	1.8	-	-	-	-	-
20 NQ	15.2	-	84.8	97.0	EMP	23	14	-	8
20 NQ	7.7	-	7.7	3.9	-	-	-	-	-
20 NQ	11.2	-	88.8	102.6	XRF	-	-	-	-

Table 1. (cont.)

Sample	mole % oxide			method		homogeneity			
	CaO	MgO	SiO <sub>2</sub>	ε	#	CaO	MgO	SiO <sub>2</sub>	
(d) The SiO <sub>2</sub> -MgO join (Figure 8)									
21 SQ	-	53.0	47.0	100.0	EMP	29	-	1	2
22 SQ	-	1.2	1.2	126	-	-	-	-	-
22 SQ	-	51.0	49.0	101.1	EMP	19	-	1	2
23 SQ	-	1.5	1.5	1.8	-	-	-	-	-
23 SQ	-	29.8	70.1	100.0	EMP	23	-	1	1
23 NQ	-	0.6	0.6	1.5	-	-	-	-	-
23 NQ	-	30.3	69.6	93.6	EMP	19	-	5	4
23 NQ	-	2.7	2.7	1.0	-	-	-	-	-
23 NQ	-	30.9	69.1	99.6	XRF	-	-	-	-
(e) High-silica samples (Figure 9).									
19 NQ	28.2	-	71.8	98.4	EMP	18	4	-	4
11 SQ	3.5	-	3.5	1.8	-	-	-	-	-
11 SQ	17.9	13.8	68.2	99.6	EMP	27	2	3	4
12 SQ	1.5	1.6	2.9	1.7	-	-	-	-	-
12 SQ	15.9	12.1	71.9	100.4	EMP	26	6	6	7
23 SQ	3.2	2.9	6.0	1.0	-	-	-	-	-
23 SQ	-	29.8	70.1	100.0	EMP	23	-	1	1
	-	0.6	0.6	1.5	-	-	-	-	-

- Notes: (a) Analysis method: XRF - X-ray fluorescence, EMP-electron microprobe, AA - atomic absorption analysis in the Université de Paris VI, SEM-energy-dispersive scanning electron microscopy. (b) Homogeneity index (see section on Experimental Techniques). (c) Sum of weight per cent oxides for EMP and XRF. (d) Number of points in EMP traverse. (e) SQ -super quench; NQ - normal quench (see text). (f) Two standard deviations (2σ) for EMP analyses. (g) SiO<sub>2</sub> by difference. (h) High-purity silica samples from Electro-Quartz Co., France. (Tetrasil SE: < 10 ppm H<sub>2</sub>O, < 1 ppm impurities). (j) Poor EMP totals due to differential polish on surface of unmixed samples. (k) Poor XRF totals due to standard curve used (Problems in making discs with high CaO, MgO contents). (m) Sample 12-NQ analyzed as two composition populations (1) and (2).

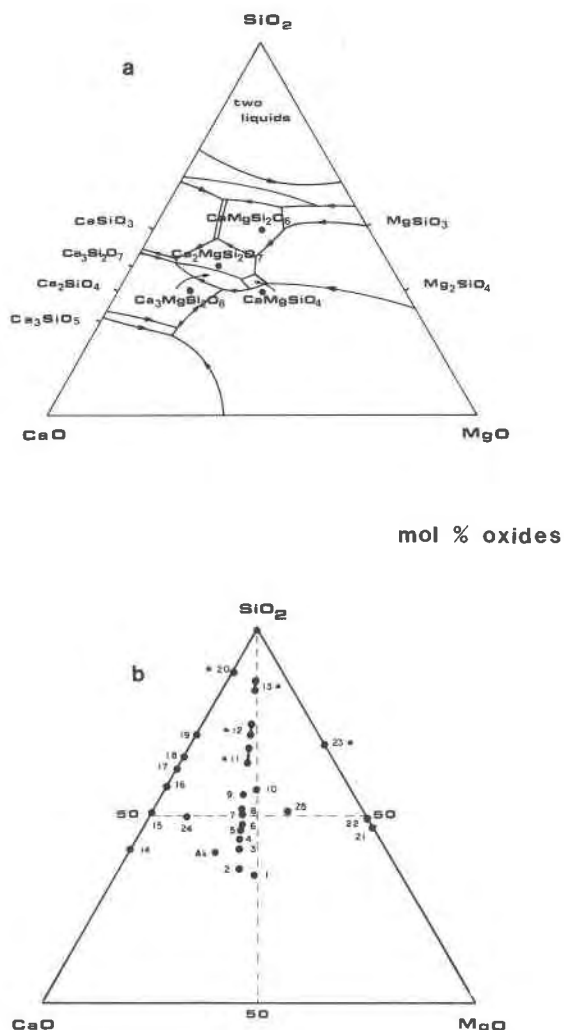


Fig. 1. (a) Schematic liquidus phase diagram for the system CaO-MgO-SiO<sub>2</sub>, redrawn from Levin et al. (1964). (b) Compositions of glasses examined in this study. Numbers correspond to sample numbers in Table 1. Those marked with an asterisk (11, 12, 13, 20, 23) are average bulk compositions of inhomogeneous samples. The two points shown connected by a tie-line for samples 11, 12 and 13 refer to NQ (higher silica) and SQ (lower silica) samples (see Table 1).

study, it was assumed that these Gaussian components did not change in position or width with silica content, in order to provide some constraints for the fitting procedure. Although the fitting method is obviously rather crude, and the above assumption not obviously valid, the major fitted bands agree generally with those found by other workers for similar systems (Mysen et al., 1980a,b,c,d, 1981a,b, 1982a,b; Mysen and Virgo, 1980a). The validity of such fits has been discussed by Mysen et al. (1982b), McMillan and Piriou (1983), and McMillan (1984). The polarization characteristics of the component bands were measured from their intensities in the parallel (VV) and perpendicular (VH) polarized spectra. The depolarization ratios,  $\rho = (I_{VH}/I_{VV})$ , are quoted in Table 2. Only totally symmetric

vibrations of a cubic point group are completely polarized, with  $\rho = 0$ . Asymmetric modes of all point groups are depolarized, with  $\rho = 3/4$  for plane-polarized incident light, while other symmetric vibrations are polarized with  $0 < \rho < 3/4$  (Herzberg, 1945, p. 246-249). In the present discussion, the degree of polarization is used to compare polarized bands with different values of  $\rho$  between 0 and 0.75.

## Results and discussion

### The SiO<sub>2</sub>-CaMgSiO<sub>4</sub> glass series

The polarized Raman spectra of these glasses are shown in Figure 3. Due to selective evaporation of component oxides during the solar furnace preparations, samples 2 to 9 lie slightly off the join, but this is not believed to have a major effect on the spectral variations with silica content. The spectra obtained are comparable with the results of previous studies on the SiO<sub>2</sub>-CaMgSiO<sub>4</sub> system (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a). Sample 10 was prepared in a conventional Deltech furnace, and has a composition on the low-silica limit of the liquidus SiO<sub>2</sub>-CaMgSiO<sub>4</sub> miscibility gap. Those samples with compositions within the two-liquid field are discussed in a later section. Samples 1 and 2 could only be obtained using the super-quench technique, and no polarization information was obtained for sample 2, while the spectrum of sample 1 is only partially polarized (McMillan et al., 1981). The spectra are most easily discussed in three sections: the high-frequency region above 800 cm<sup>-1</sup>; a low-frequency region between 400 and 700 cm<sup>-1</sup>; and the mid-range region from 700 to 800 cm<sup>-1</sup>.

*The high-frequency region.* Sample 1 at the orthosili-

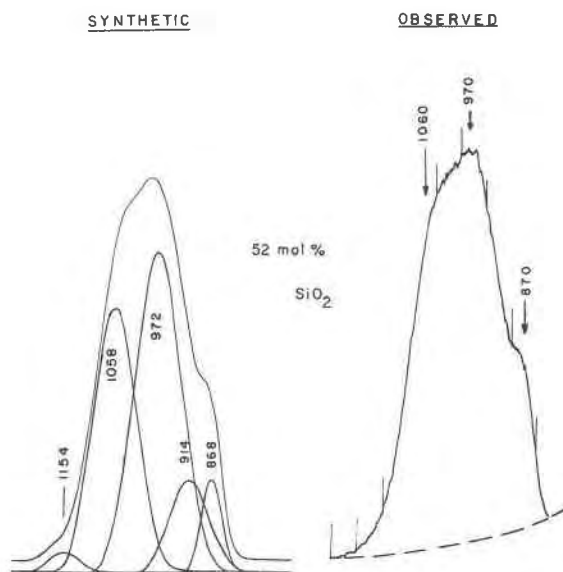


Fig. 2. Results of a curve-fitting experiment on the high-frequency region of sample number 9 (52 mol % silica) along the SiO<sub>2</sub>-CaMgSiO<sub>4</sub> glass join.

Table 2. Results of curve-fitting experiments on high-frequency (1200-800 cm<sup>-1</sup>) bands for spectra of the SiO<sub>2</sub>-CaMgSiO<sub>4</sub> glass series (Fig. 3)

Sample	I. Band positions and relative intensities from Figure 4.							
	10(a)	9	8	7	6	5	4	3
VV								
1156(b)	(c) 1148 (8)	1152 (4)	1154 (3)	1142 (3)	1154 (3)	1154 (2)	1080 (10)	
	1080(d) (5)	1075 (9)	1076 (6)	1075 (6)	1076 (6)	1075 (6)	1075 (6)	
1065 (42)	1056 (50)	1052 (41)	1058 (32)	1045 (44)	1061 (28)	1055 (30)	1055 (30)	
975 (39)	968 (32)	977 (45)	970 (32)	964 (36)	982 (49)	975 (44)	975 (44)	
910 (9)	900 (5)	916 (11)	908 (10)	914 (12)	916 (13)	909 (10)	909 (10)	
864 (5)	(e)	871 (6)	864 (5)	868 (7)	861 (3)	871 (8)	870 (5)	
Sample	6	5	4	3	2	1	0	
VV								
1162 (1)		1160 (1)	1154 (<1)	1069 (13)	1055 (7)	1048 (7)	1064 (23)	
	1070 (11)	1071 (15)	1058 (14)	1048 (13)	1055 (7)	1048 (7)	1048 (7)	
1060 (20)	1046 (26)	1059 (16)	1058 (14)	1048 (13)	1055 (7)	1048 (7)	1048 (7)	
983 (50)	966 (46)	975 (54)	976 (46)	970 (42)	973 (33)	966 (40)	966 (40)	
909 (20)	894 (12)	907 (19)	911 (15)	900 (19)	906 (41)	898 (23)	898 (23)	
874 (8)	862 (5)	866 (11)	864 (7)	858 (8)	854 (19)	856 (6)	856 (6)	
Sample	2 (1)(f)	1 (1)(f)	1 (1)(f)	1 (1)(f)	1 (1)(f)	1 (1)(f)	1 (1)(f)	
VV+VH		VV	VH	VH	VH	VH	VH	
1054 (7)		1048 (4)	1044 (5)	1044 (5)	1044 (5)	1044 (5)	1044 (5)	
976 (13)		962 (16)	961 (26)	961 (26)	961 (26)	961 (26)	961 (26)	
911 (39)		909 (23)	905 (29)	905 (29)	905 (29)	905 (29)	905 (29)	
859 (41)		854 (56)	855 (6) (40)	855 (6) (40)	855 (6) (40)	855 (6) (40)	855 (6) (40)	
2 (11)(f)		1 (11)(f)	1 (11)(f)	1 (11)(f)	1 (11)(f)	1 (11)(f)	1 (11)(f)	
VV+VH		VV	VH	VH	VH	VH	VH	
934 (32)		933 (26)	931 (48)	931 (48)	931 (48)	931 (48)	931 (48)	
907 (27)		899 (18)	900 (17)	900 (17)	900 (17)	900 (17)	900 (17)	
856 (41)		855 (56)	854 (6) (35)	854 (6) (35)	854 (6) (35)	854 (6) (35)	854 (6) (35)	

## II. Mean band positions, widths and depolarization ratios.

Major bands:	Position (g)	width (h)	$\frac{p}{h}$
	1056 ± 6 cm <sup>-1</sup>	~ 100 cm <sup>-1</sup>	~ 0.2 (j)
	972 ± 6 cm <sup>-1</sup>	~ 100	~ 0.1
	906 ± 6 cm <sup>-1</sup>	~ 80	~ 0.1 (e)
	862 ± 6 cm <sup>-1</sup>	~ 80	< 0.1 (e)
Other bands:	1156 ± 4 cm <sup>-1</sup>	~ 100	0.5 - 0.8
	933 ± 1 cm <sup>-1</sup>	~ 180	~ 0.6

## III. Notes.

- a. Sample number - see Table 1 and Figure 1.  
 b. Measured band position from Figure 4 in cm<sup>-1</sup>. Although major band positions were initially constrained to be constant, some adjustments were necessary. These and error in measurements account for the scatter in these data.  
 c. Per cent relative band intensities, used to construct Figure 6.  
 d. This component is probably not a true single band, due to its large and variable half-width (150-200 cm<sup>-1</sup>) and its non-systematic changes in intensity and position with composition. This probably reflects two or more unresolved components contributing to the Raman band in this region. This band is probably almost completely polarized, and its intensity in VH spectra 10-3 is probably due to small orientation errors in the polished samples. Sample 1 was unpolarized and not oriented, hence its spectra are only partially polarized, and the high apparent VH intensity of the 862 band is not real (McMillan et al., 1981; Pirou and McMillan, 1983a). These are two alternative fits for spectra 1 (VV, VH) and 2 (VV + VH). Sample 1 is near CaMgSiO<sub>4</sub> in composition, and its dominant 862 band probably corresponds to the ν<sub>1</sub> vibration of tetrahedral SiO<sub>4</sub> units (McMillan et al., 1981; Pirou and McMillan, 1983a). The weak band near 700 cm<sup>-1</sup> indicates the presence of some higher-polymerized silicate species, probably mainly Si<sub>2</sub>O<sub>7</sub> groups, hence the inclusion of the 900 band in both fits. Higher polymers would give rise to the 1056 and 972 bands included in fits 1(i) and 2(i). However, it has been suggested that ν<sub>3</sub> vibrations of isolated SiO<sub>4</sub> tetrahedra should give a broad depolarized band near 900-950 cm<sup>-1</sup> (McMillan et al., 1981; Pirou and McMillan, 1983a). Inclusion of this band at 933 cm<sup>-1</sup> gives fits 1(i) and 2(i). It was not possible to fit spectrum 3 with only this 933 band. Spectra 1 and 2 probably contain components of the 1056, 972 and 933 bands.  
 g. Given as mean ± 1 σ of measured values.  
 h. Mean band width at half height.  
 i. Due to interference from 1080 "band", mean position calculated from spectra VV [10-4, 1(i)], VH [10-8, 1(i)] and 2(i), and depolarization ratio from spectra 10-8 only.  
 j. The major bands at 1056, 972, 906 and 862 cm<sup>-1</sup> in both VV and VH spectra seem reasonable, and agree with those found by other workers (e.g., Mysen et al., 1980a, 1982a,b). Weaker bands, especially in the VH spectra, do not give such a satisfactory fit. The depolarized 1156 band seems to be real. The VH band at 1080 (see note d) probably contains contributions from at least two independent bands. The maximum of this "band" shifts to lower frequency with decreasing silica content, suggesting that the lower frequency contribution is more important than weak contributions from these components should be present in the VV spectra, but have not been considered here. Finally, the depolarized 933 band appears real from samples 1 and 2, and should also be present in VV and VH spectra for higher silica compositions. This band has likewise been ignored here.

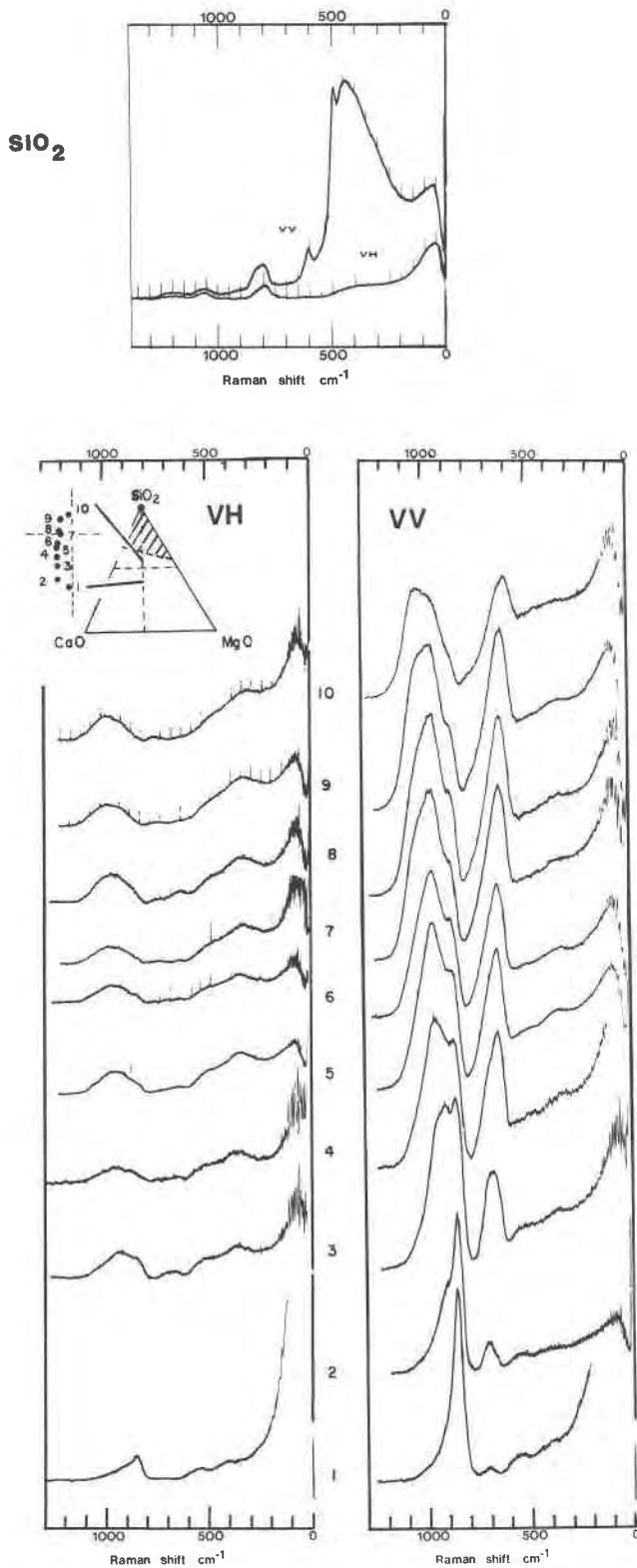


Fig. 3. Polarized (VV and VH) Raman spectra of glasses 1–10 near the  $\text{SiO}_2\text{-CaMgSiO}_4$  join.

cate composition shows a strong band near  $850\text{ cm}^{-1}$  with an asymmetric tail to higher frequency. The  $850\text{ cm}^{-1}$  band may be completely polarized within experimental uncertainty (McMillan et al., 1981; Piriou and McMillan, 1983a), while the high-frequency component has a high depolarization ratio. With increasing silica content, the  $850\text{ cm}^{-1}$  band decreases in relative intensity, while new bands grow at higher frequency. At sample 3, the major high frequency peak is at  $910\text{ cm}^{-1}$ , with a pronounced shoulder near  $1000\text{ cm}^{-1}$ . Between samples 4 and 9, this shoulder develops into the major band in the spectrum, while a further shoulder near  $1050\text{ cm}^{-1}$  becomes apparent for sample 7. This  $1050\text{ cm}^{-1}$  shoulder increases in relative intensity between samples 7 and 10, to become the dominant high-frequency band of sample 10. The VH spectra show all these bands to be highly, but not completely polarized. The VH polarized spectra also show different asymmetric band contours to the corresponding VV spectra, suggesting that the various components bands have different depolarization ratios. The spectrum of vitreous silica at the top of Figure 3 shows two weak bands near  $1200$  and  $1060\text{ cm}^{-1}$  which Furukawa et al. (1981) found to be depolarized ( $\rho \sim 0.75$ ). Seifert et al. (1982) and Mysen et al. (1982a) have suggested that the broad  $1200\text{ cm}^{-1}$  band may have two components, at  $1209$  and  $1160\text{ cm}^{-1}$ .

For a clearer view of spectral changes as a function of silica content, these high-frequency bands were deconvoluted into Gaussian components, as described above. The results of this curve-fitting are shown in Figure 4 and Table 2. Four major component bands were found for samples 1–10; at  $862$ ,  $906$ ,  $972$  and  $1056\text{ cm}^{-1}$ , in reasonable agreement with Mysen et al., (1980a, 1982a,b) and Mysen and Virgo (1980). These were all highly polarized, with  $\rho$  ranging from  $< 0.1$  (for the  $862\text{ cm}^{-1}$  band) to around  $0.2$ . The variation in relative intensity of these major bands with silica content is shown in Figure 5. The  $862\text{ cm}^{-1}$  band is dominant at the orthosilicate composition, the  $906\text{ cm}^{-1}$  band near the pyrosilicate with 40 mole % silica, and the  $972\text{ cm}^{-1}$  band at the metasilicate composition (50 mole % silica). The  $1056\text{ cm}^{-1}$  band has not yet reached a maximum in relative intensity at 58 mole % silica. These variations are similar to those observed by Furukawa et al. (1981) for the  $950\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  bands in the  $\text{SiO}_2\text{-Na}_2\text{O}$  glass series, and who found the  $1100\text{ cm}^{-1}$  band to be maximized at the disilicate composition with 67 mole % silica. On the basis of the positions, intensities and polarization characteristics of these bands, the silica content at which they have maximum intensity, and comparison of corresponding glass and crystal spectra, previous workers have concluded that the  $862$ ,  $906$ ,  $972$  and  $1056\text{ cm}^{-1}$  bands correspond to symmetric silicon–oxygen stretching vibrations of silicate tetrahedral units with respectively four, three, two and one non-bridging oxygen (e.g., Brawer and White, 1975; Verweij and Konijnendijk, 1976; Virgo et al., 1980; Mysen et al., 1980a, 1982a; Furukawa et al., 1981 and

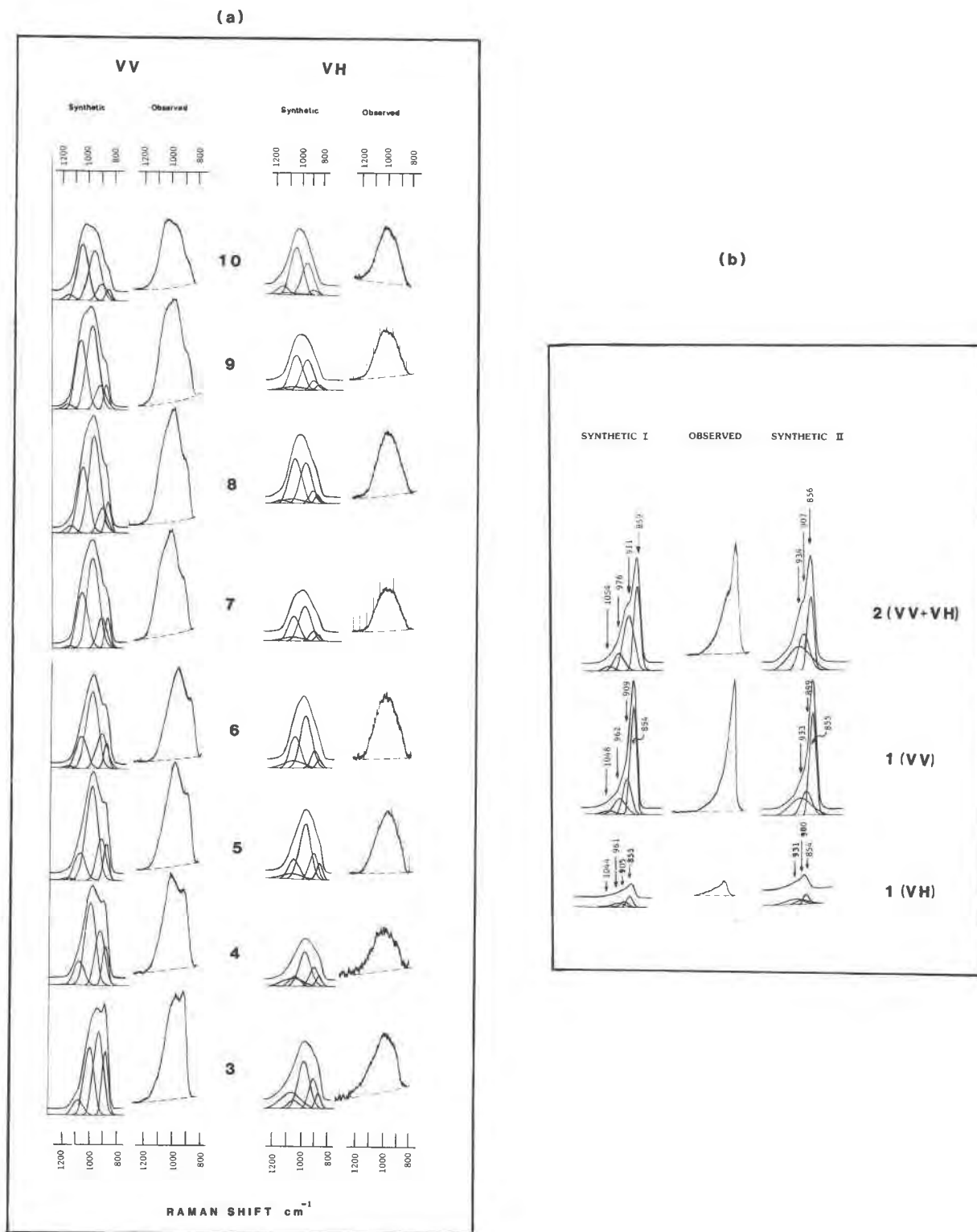


Fig. 4. Curve-fitting experiments on the high-frequency bands of the  $SiO_2-CaMgSiO_4$  glass series in Fig. 3. In each case, the observed unresolved band contour is shown at right for comparison with the synthetic sum of components. The dashed line shows the assumed baseline, which could not be reproduced for the synthetic reconstruction. Measured component band positions are given in Table 2, along with relative band intensities, half-widths and depolarization ratios, and a general discussion of these data.

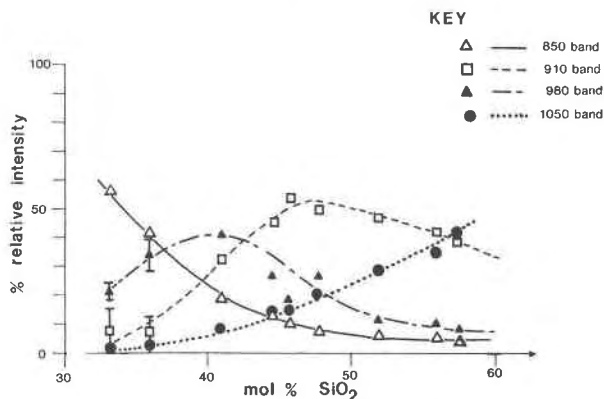


Fig. 5. Relative high-frequency component band intensities from VV polarized spectra in the SiO<sub>2</sub>-CaMgSiO<sub>4</sub> glass series (from Fig. 4 and Table 2). The error bars shown for the component bands for samples 1 and 2 represent the relative intensities obtained from alternative deconvolutions I and II, which are thought to be extreme cases (see Table 2 and Fig. 4).

many others: summarized in McMillan, 1984). These units are shown schematically in Figure 6, and are referred to here as SiO<sub>4</sub>, -SiO<sub>3</sub>, =SiO<sub>2</sub>, and ≡SiO groups. These are equivalent to the Q<sup>0</sup>, Q<sup>1</sup>, Q<sup>2</sup>, and Q<sup>3</sup> species referred to by other workers (e.g., Matson et al., 1983) in notation borrowed from NMR spectroscopic studies (Englehardt et al., 1975). The present notation is used here for its pictorial value, and its simple extension to aluminosilicate systems (McMillan et al., 1982). There are a number of other weak components present in the high-frequency spectra associated with the above major bands, which may be due to asymmetric stretching vibrations of these units within the glass (see e.g., Furukawa and White, 1980; Mysen et al., 1980a; Furukawa et al., 1981; Matson et al., 1983; McMillan, 1984; also footnote to Table 2).

There have been a number of interpretations of the 1200 and 1060 cm<sup>-1</sup> bands observed for vitreous silica (see McMillan, 1984). For the purposes of the present discussion, these are assigned to asymmetric silicon-oxygen stretching motions within the fully-polymerized silica glass framework (McMillan et al., 1982). In the present notation, this framework is represented as =Si=.

**The low-frequency region.** The spectrum of sample 1 shows a weak, polarized band at 704 cm<sup>-1</sup>. The Raman spectra of crystalline calcium magnesium orthosilicates do not show any band in this region (Piriou and McMillan, 1983a), while the band increases in intensity with increasing silica content (Virgo et al., 1980; Mysen et al., 1980a, 1982a; this work, Fig. 3). All of the above authors concluded that this 704 cm<sup>-1</sup> band was due to a symmetric stretching motion of or about the bridging oxygen in dimer units, Si<sub>2</sub>O<sub>7</sub>, within the glass structure. The presence of such units within a glass at the orthosilicate composition (sample 1; Table 1) suggests that some

oxygen within the glass is NOT bound to silicon, but only to magnesium and/or calcium.

With increasing silica content (samples 3 to 10), this band increases in intensity, becomes asymmetric, and shifts its maximum to lower frequency, to near 620 cm<sup>-1</sup> for sample 10 (Fig. 3). From studies of alkali silicate glass

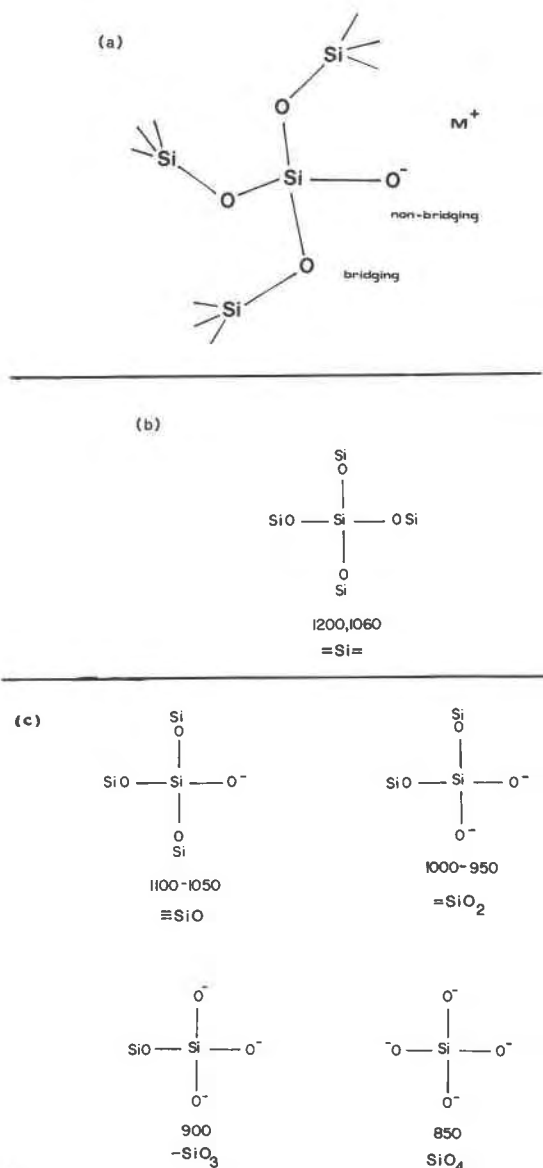


Fig. 6. Silicate structural units. (a) Schematic indicating the nature of bridging and non-bridging oxygen in the present context. M<sup>+</sup> may also refer to 0.5 M<sup>2+</sup>, as in the alkaline earth series. (b) The weak, depolarized bands at 1200 and 1060 cm<sup>-1</sup> are assigned to asymmetric silicon-oxygen stretching vibrations within a fully-polymerized tetrahedral network =Si=. (c) The four major polarized high-frequency bands are generally assigned to symmetric stretching vibrations of tetrahedral silicate units with one, two, three and four non-bridging oxygens.

series (e.g., Brawer and White, 1975; Konijnendijk and Stevels, 1976; Verweij and Konijnendijk, 1976; Furukawa et al., 1981) it is likely that the dominant  $430\text{ cm}^{-1}$  band of vitreous silica represents the continuation of this band to high silica content. The band is always highly polarized (Verweij, 1979a,b; this work, Fig. 3). The asymmetry of this band in these room-temperature spectra is partly due to thermal population effects, and may partly be due to the presence of discrete component bands as for the high-frequency band group. Attempts at curve-fitting using up to six Gaussian components were unsuccessful, and the problem was deemed too unconstrained for meaningful deconvolution at the present level.

All of the previous studies on this and similar systems (see McMillan, 1984) have associated the  $400\text{--}700\text{ cm}^{-1}$  band with the presence of bridging oxygens corner-shared between adjacent  $\text{SiO}_4$  tetrahedra (see Fig. 6), indicating silicate units more polymerized than the isolated orthosilicate tetrahedron. The detailed motions giving rise to this low-frequency band are as yet unclear, and may change as a function of the particular silicate group involved. Isotopic studies on  $\text{Si}_2\text{O}_7$  dimers in crystalline pyrosilicates suggest considerable silicon motion associated with the  $700\text{ cm}^{-1}$  vibration (Tarte et al., 1973), consistent with its assignment to a symmetric stretch of the  $-\text{SiO}_3$  groups about their bridging oxygen (e.g., Lazarev, 1972, p. 63–72). However, the  $430\text{ cm}^{-1}$  band of vitreous silica shows a large  $^{18}\text{O}/^{16}\text{O}$  isotopic shift consistent with mainly oxygen motion, suggested to be in the plane bisecting the Si–O–Si bridge (e.g., Galeener and Mikkelsen, 1981).

*The mid-range region.* Vitreous silica shows an asymmetric band near  $800\text{ cm}^{-1}$ , with probable components at  $790$  and  $830\text{ cm}^{-1}$  (e.g., Seifert et al., 1982). Comparison of VV and VH spectra shows that the lower frequency component has a higher depolarization ratio (Fig. 3). Vibrational calculations have associated modes in this region with mainly motion of silicon (e.g., Laughlin and Joannopoulos, 1977; Furukawa et al., 1981), consistent with the results of the isotopic exchange studies of Galeener and Mikkelsen (1981) and Galeener and Geissberger (1983). Laughlin and Joannopoulos (1977) and Piriou and McMillan (1983b) suggested that the silicon motion was symmetric about the bridging oxygens, consistent with the observed infrared and Raman intensities (see McMillan et al., 1982). In alkali silicate glass systems, this band broadens and shifts to slightly lower frequency with decreasing silica content, to around  $750\text{ cm}^{-1}$  at 55 mole % silica (e.g., Brawer and White, 1975; Verweij and Konijnendijk, 1976; Furukawa et al., 1981; Mysen et al., 1982a). The band is observed in the present  $\text{SiO}_2\text{--CaMgSiO}_4$  glasses as a weak shoulder in the VV spectra, and as an asymmetric band near  $780\text{ cm}^{-1}$  in the VH spectra (Fig. 3; also Virgo et al., 1980; Mysen et al., 1980a, 1982a). This band may not be clearly distinguished for samples with less than 50 mole % silica.

It is possible that the mid-range bands in these silicate glass series are similar to the  $800\text{ cm}^{-1}$  band of vitreous

silica, and due predominantly to motion of silicon against its oxygen "cage". It is of interest that bands are observed in this region in the infrared and Raman spectra of crystalline sheet silicates (e.g., Brawer and White, 1975; Pavinich et al., 1976; Verweij and Konijnendijk, 1976; Verweij, 1979b), but not in the spectra of calcium magnesium chain silicates (e.g., Etchepare, 1970a, 1972; Omori, 1971; White, 1975; Zulumyan et al., 1976; Conjeaud and Boyer, 1980). McMillan (1981) suggested that such "silicon cage motions" might only be resolved in silicate structures with a high degree of polymerization where associated oxygen motion would be hindered, and that these vibrations might couple with vibrations of the bridging oxygens (giving rise to the  $700\text{--}400\text{ cm}^{-1}$  band set) for lower silicate polymerizations.

#### *The $\text{SiO}_2\text{--CaMgSiO}_4$ miscibility gap*

Three samples were prepared with bulk compositions within the  $\text{SiO}_2\text{--CaMgSiO}_4$  two-liquid field (Fig. 1). One set of glasses was prepared by normal quenching, and gave opaque samples which were macroscopically inhomogeneous and presumably unmixed (Table 1 and inset to Fig. 7). A second set were re-melted then super-quenched, to give optically transparent glasses which were much more homogeneous to electron microprobe analysis (Table 1). Sample 12 had a bluish tinge, but samples 11 and 13 were colorless, implying inhomogeneities smaller than several hundred Angstroms (Voishvillo, 1962; Andreev, 1978). The spectra of these two sets of glass samples are compared in Figure 7. Also shown are the spectra of vitreous silica and of sample 10, with compositions near the poles of the liquidus miscibility gap in the  $\text{SiO}_2\text{--CaMgSiO}_4$  system (see Fig. 1).

The spectra of the normal-quenched opaque unmixed samples 11 to 13 are simple superpositions of the spectra of  $\text{SiO}_2$  and sample 10, varying inversely in relative intensity as the two-liquid field is traversed. This is the expected behavior for a two-phase sample with varying relative proportions of each phase. It is of interest that the spectra of the super-quenched and optically transparent glasses show exactly the same behavior, which has several implications. First, the same vibrating units are present in both the opaque and the transparent samples, suggesting no difference in molecular structure between the two sets of samples as sampled by the Raman experiment. The major difference between the opaque and transparent samples then probably lies in the size of the individual structural units responsible for macroscopic inhomogeneity. Glass and liquid immiscibility is commonly detected and measured by the onset of visible opalescence in the sample (e.g., Haller et al., 1974) which occurs when density fluctuations are of the order of several hundred Angstrom units across (Voishvillo, 1962; Andreev, 1978). The present study shows that Raman spectroscopy is insensitive to size changes in the structural unit on a hundred Angstrom level, which would be consistent with Raman band localization arguments (see McMillan,



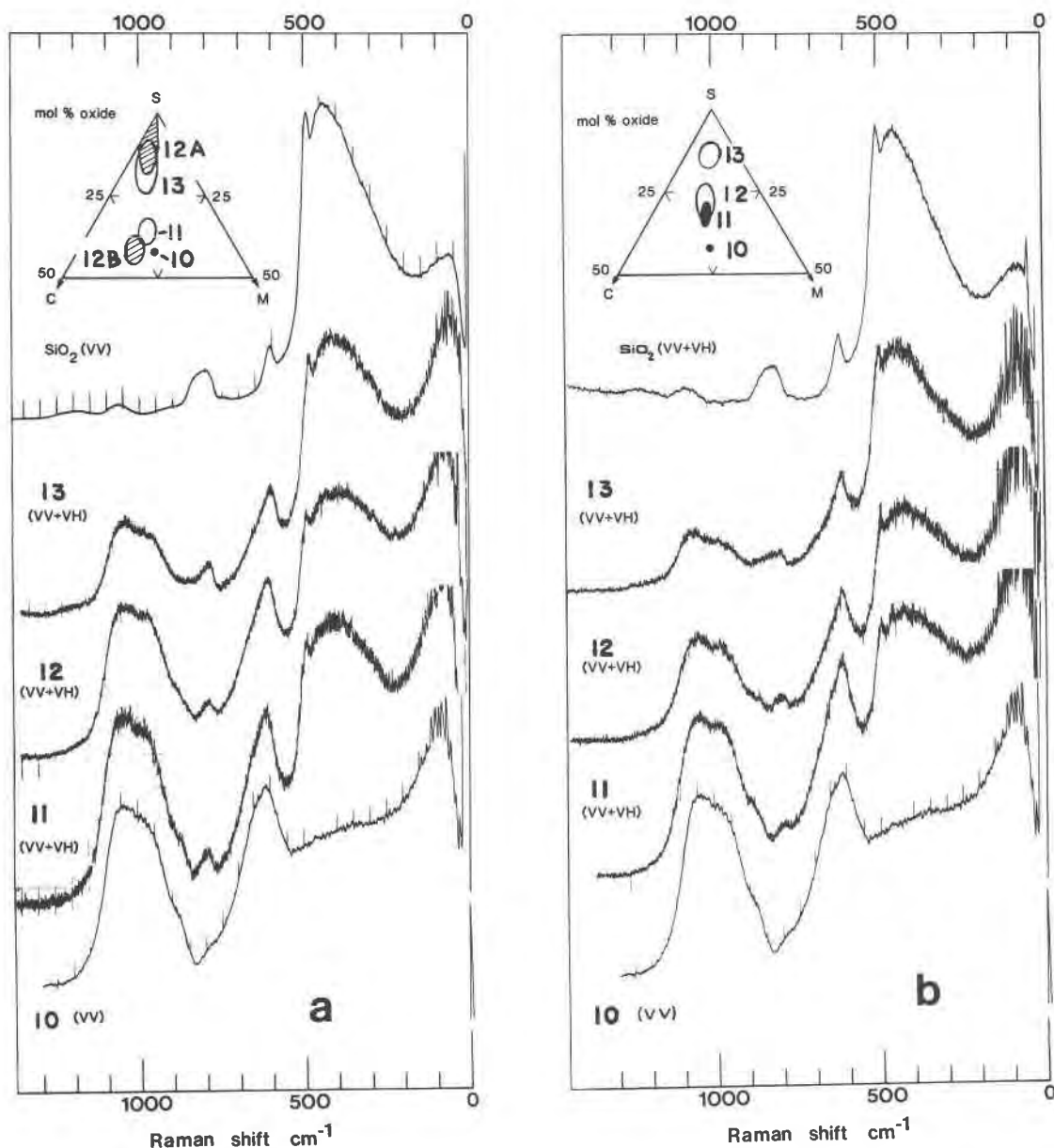


Fig. 7. Crossing the  $\text{SiO}_2\text{-CaMgSiO}_4$  miscibility gap (samples 11, 12 and 13). Spectra (a) correspond to normal-quenched, opaque glasses, while (b) shows the spectra of super-quenched, transparent glasses of similar bulk compositions to those in (a). The samples in (b) were re-melted for super-quench, hence had slightly lower silica content due to volatilization (see text, and Table 1), which explains the band intensity differences between spectra (a) and (b).

1984). It also suggests that the molecular groups precursor to phase separation are present in the transparent glass series, which would classically be termed "homogeneous". This places limits on the structural significance of miscibility gaps determined by opalescence and clearing temperatures. Finally, there is no evidence in the  $\text{SiO}_2\text{-CaMgSiO}_4$  glass series for intermediate structures between those at the poles of the classical miscibility gap, in contrast to the  $\text{SiO}_2\text{-Na}_2\text{O}$  and  $\text{SiO}_2\text{-K}_2\text{O}$  glass series

where a continuous set of changes is found (e.g., Etchepare, 1970b; Brawer and White, 1975; Konijnendijk and Stevels, 1976; Verweij and Konijnendijk, 1976; Furukawa et al., 1981; Mysen et al., 1982; Matson et al., 1983).

#### *The $\text{SiO}_2\text{-CaO}$ and $\text{SiO}_2\text{-MgO}$ glass series*

The unpolarized Raman spectra of glasses along the  $\text{SiO}_2\text{-CaO}$  and  $\text{SiO}_2\text{-MgO}$  joins are shown in Figure 8. The spectra are similar to those obtained in previous

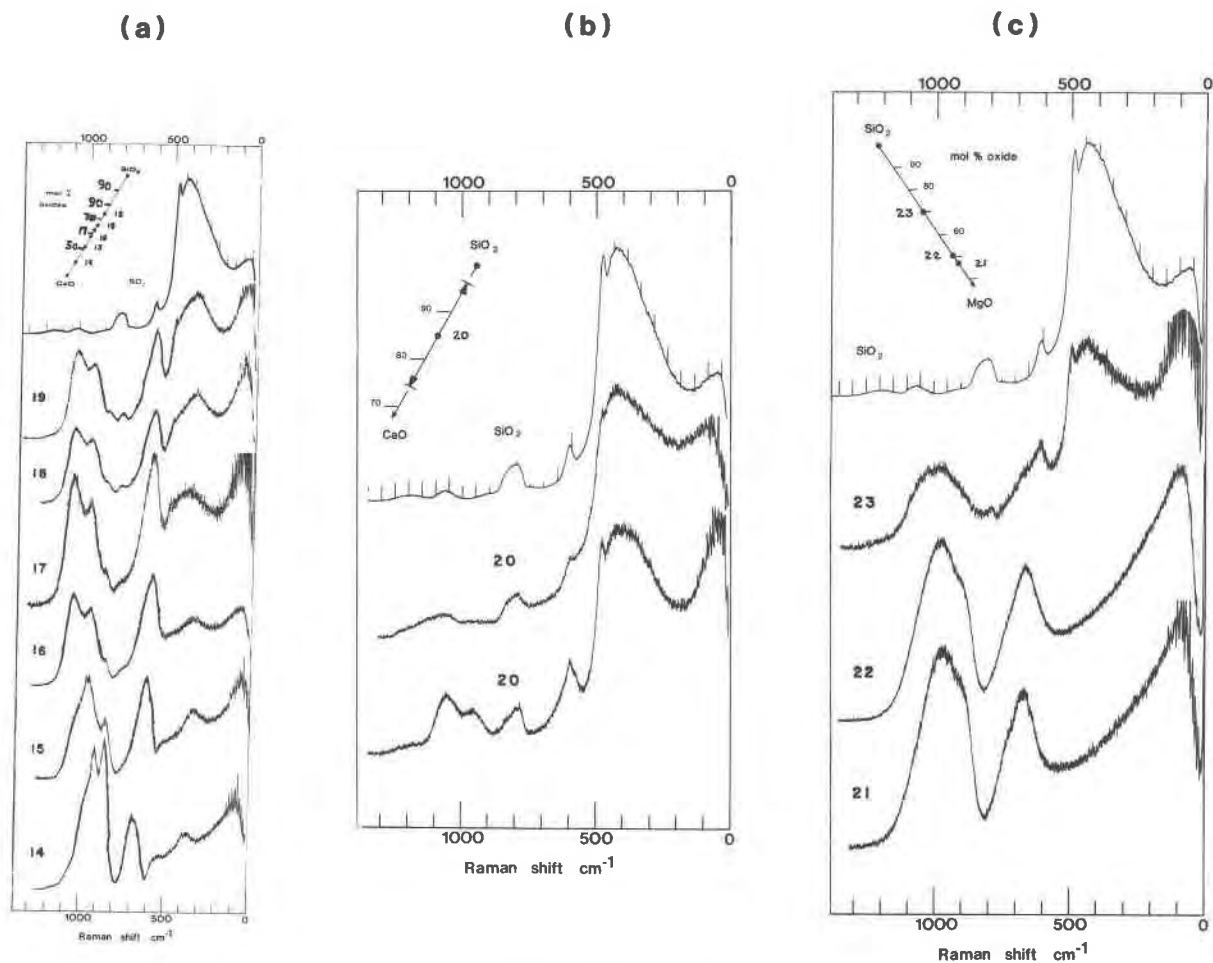


Fig. 8. Unpolarized (VV + VH) Raman spectra of glasses (a) 14–19 and (c) 21–23 and  $\text{SiO}_2$ , respectively along the  $\text{SiO}_2$ –CaO and  $\text{SiO}_2$ –MgO joins. CaO– $\text{SiO}_2$  sample 20 (b) was opaque and inhomogeneous, with approximate compositional limits as shown in the inset. The two spectra were taken from different parts of the sample. From their form, these correspond to higher-silica and lower-silica regions.

studies (e.g., Kashio et al., 1980; Mysen and Virgo, 1980; Mysen et al., 1980a,b, 1982a,b; Tsunawaki et al., 1981) and show similar changes with silica content to the  $\text{SiO}_2$ –CaMgSiO<sub>4</sub> glass series. The individual bands in the  $\text{SiO}_2$ –CaO series are better-resolved than those for the  $\text{SiO}_2$ –MgO glasses. Brawer and White (1977) studied series of sodium silicate glasses containing calcium or magnesium, and found the bands for the calcic glasses better-resolved than for the magnesian compositions. Some of the  $\text{SiO}_2$ –CaO and  $\text{SiO}_2$ –MgO samples had compositions within the CaO–MgO– $\text{SiO}_2$  two-liquid field, and both opaque unmixed and transparent “homogeneous” glasses were prepared by normal- and fast-quench techniques. As for the  $\text{SiO}_2$ –CaMgSiO<sub>4</sub> series, both sets of samples had identical Raman spectra.

The binary calcium silicate sample 20 prepared by normal quenching was found to be very inhomogeneous, with a bulk composition near 85 mole % silica but

variations of  $\pm 10$  mole % in silica content within the sample (Table 1). A number of spectra were obtained from different parts of the sample, and none were exactly alike. The two most extreme spectra observed are shown in Figure 8b. The spectrum with higher intensity in the high-frequency region corresponds to the area with lower silica content. This low-silica spectrum is similar in form to the spectrum of samples 18 and 19, within the  $\text{SiO}_2$ –CaO miscibility gap, but with different relative intensity of the high-frequency and low-frequency parts. These are generally indicative of the relative proportions of respectively low-silica and high-silica unmixed regions, as discussed above for the  $\text{SiO}_2$ –CaMgSiO<sub>4</sub> series.

The spectrum for the higher silica part of sample 20 shows a different type of spectrum (Fig. 8b). The 430  $\text{cm}^{-1}$  band of vitreous silica still dominates the spectrum, but its “defect” bands at 500 and 600  $\text{cm}^{-1}$  seem suppressed relative to both  $\text{SiO}_2$  glass and the lower-silica

part of sample 20. The high-frequency region shows only a weak, broad, asymmetric band, in contrast to the constant band pattern indicative of the depolymerized silicate units of the unmixed spectra. Polarization studies (not shown) indicate that this weak band is a combination of three bands. The depolarized bands of vitreous silica may be identified at 1060 and 1200 cm<sup>-1</sup>, with a new polarized band appearing near 1100 cm<sup>-1</sup>. This is similar to the spectra observed for silica glass with small additions of alkali oxides, M<sub>2</sub>O (Stolen and Walrafen, 1976; Mysen et al., 1982; Matson et al., 1983), KAlO<sub>2</sub> (McMillan et al., 1982) and Al<sub>2</sub>O<sub>3</sub> (McMillan and Piriou, 1982). It is suggested that the polarized 1100 cm<sup>-1</sup> band corresponds to the symmetric stretching vibration of a small proportion of ≡SiO units, within a silica glass framework only slightly perturbed by the presence of CaO component (see also McMillan and Piriou, 1982).

### Interpretations and structural models

Consistent with the results of previous studies, the observed high-frequency bands have been assigned to silicon-oxygen stretching motions of =Si=, ≡SiO, =SiO<sub>2</sub>, -SiO<sub>3</sub> and SiO<sub>4</sub> groups within the glass structure (see Fig. 6). Their observed relative intensity variation as a function of silica content is consistent with a decrease in the average polymerization of the silicate units as the silica content is decreased, and that some distribution of polymerized species is present at a given silica content (Figs. 3-5, 8; also e.g., Furukawa et al., 1981; Mysen et al., 1982a). Most previous studies have not considered the detailed arrangement of these molecular groups, only their relative distribution as a function of silica content (see McMillan, 1984). Brawer and White (1975) proposed that individual silicate tetrahedral units might show bond length and angle disorder, and that adjacent units could have different polymerization. This model allows for continuous depolymerization of the silica glass network on addition of metal oxide component, by creation of silicate tetrahedra with non-bridging oxygens at random throughout the structure. More recently Mysen, Virgo and co-workers (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a) have proposed a model based on discrete anionic silicate structural units. At any given silica content, the melt or glass structure will contain a distribution of orthosilicate and pyrosilicate dimer groups, infinite chain and sheet structures, and three-dimensional network units. This latter model implies that the Raman bands used to characterize these long-range structures are in fact specific to such structures and exclude other possibilities, such as the random arrangement of silicate units proposed by Brawer and White (1975). A number of authors have discussed the localization of the dominant Raman bands in silicate glasses (e.g., Bell and Dean, 1970; Bell et al., 1970; Brawer, 1975; Furukawa et al., 1981; McMillan and Piriou, 1983; McMillan, 1984). It seems likely that the major high-frequency bands are highly localized within a given silicate tetrahedral unit,

and are relatively insensitive to the nature of adjacent tetrahedral units. This excludes the use of the high-frequency Raman bands of silicate glasses to characterize long-range structures such as infinite sheets and chains. This implies that although the Raman spectra are consistent with the model of Virgo et al. (1980) and Mysen et al. (1980a, 1982a), they are equally consistent with that of Brawer and White (1975). In the present article, the molecular groups ≡SiO, =SiO<sub>2</sub>, and -SiO<sub>3</sub> are not assigned to any particular long-range structure. By definition, the groups SiO<sub>4</sub> and =Si= denote respectively a silicate tetrahedral unit with four non-bridging oxygens, and a silicate unit corner-sharing all four oxygens as part of a fully-polymerized network.

To investigate the effect of different metals on the distribution of silicate species, it is of interest to compare the spectra of glasses with the same silica content. This was done in the present study for CaO-MgO-SiO<sub>2</sub> glasses with near 70 mole % silica. The spectra of these glasses are shown in Figure 9. The high-frequency bands of the

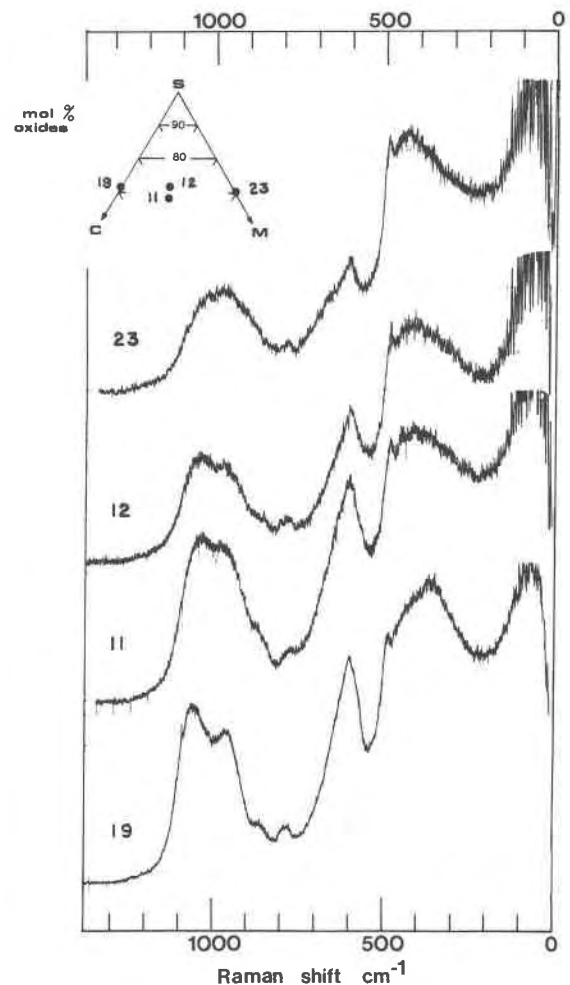


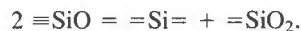
Fig. 9. The effect of calcium/magnesium substitution on the spectra of glasses with near 70 mole % silica.

$\text{CaO-SiO}_2$  glass (19) are well-resolved at 1060 and 970  $\text{cm}^{-1}$ . The dominant 1060  $\text{cm}^{-1}$  band indicates a high proportion of  $\equiv\text{SiO}$  units, while the 970  $\text{cm}^{-1}$  is due to  $=\text{SiO}_2$  groups. The weak band at 860  $\text{cm}^{-1}$  indicates the presence of isolated  $\text{SiO}_4$  tetrahedra. The 900  $\text{cm}^{-1}$  band expected for  $-\text{SiO}_3$  groups is probably unresolved from the higher frequency group (see Figs. 3 and 4; also Mysen et al., 1982b). The  $\text{SiO}_2\text{-CaMgSiO}_4$  samples 11 and 12 have silica contents of respectively 68 and 72 mole % silica. The high-frequency bands are less well-resolved than those of the calcic glass. The 1060  $\text{cm}^{-1}$  band remains more intense than the shoulder at 980  $\text{cm}^{-1}$ ; but less so than for sample 19. Finally, the  $\text{SiO}_2\text{-MgO}$  glass (23) shows no bands resolved at high frequency, but only a broad asymmetric maximum between 960 and 1080  $\text{cm}^{-1}$ , where the lower-frequency part seems to predominate. These observations suggest that, if Mg/Ca substitution affects the absolute intensities of the 1060 and 970  $\text{cm}^{-1}$  bands in the same way, the relative proportion of  $=\text{SiO}_2$  to  $\equiv\text{SiO}$  groups increases as magnesium is substituted for calcium in the glass structure.

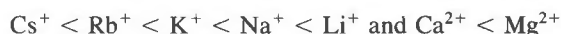
Related observations have been noted in studies of other silicate glass systems. The spectra of alkali silicate glasses with above 60 mole % silica are dominated by a band near 1100  $\text{cm}^{-1}$  due to  $\equiv\text{SiO}$  units with a weaker band near 950  $\text{cm}^{-1}$  associated with  $=\text{SiO}_2$  groups (e.g., Brawer and White, 1975; Verweij and Konijnendijk, 1976; Konijnendijk and Stevels, 1976). Brawer and White (1975) noted that the 950  $\text{cm}^{-1}$  band was relatively more prominent in the order  $\text{K} < \text{Na} < \text{Li}$ , at a given silica content. Matson et al. (1983) have obtained Raman spectra for a wider range of alkali silicate glasses, and find that the relative intensity of the 950  $\text{cm}^{-1}$  band increases in the sequence  $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$  at fixed silica content. This band was also observed to appear at higher silica content in these glass series in the same order. At the same time, there is an increased intensity near 450  $\text{cm}^{-1}$  in the same order, attributed to an increased proportion of silica-like network ( $=\text{Si}=\text{Si}$  units) in the glass structure. Brawer and White (1977) studied series of high-silica  $\text{CaO-Na}_2\text{O-SiO}_2$  and  $\text{MgO-Na}_2\text{O-SiO}_2$  glasses. They observed increased proportions of  $=\text{SiO}_2$  and  $=\text{Si}=\text{Si}$  units relative to  $\equiv\text{SiO}$  groups as the alkaline earth cation was substituted for sodium, with magnesium having more effect than calcium. Finally, the results of Mysen et al. (1982a) for  $\text{SiO}_2\text{-Na}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{CaO}$  and  $(\text{Ca,Mg})\text{O}$  glass series show that, at given high silica content, the 1000–950  $\text{cm}^{-1}$  band indicative of  $=\text{SiO}_2$  units is relatively more important in the order  $\text{Na} < \text{Ba} < \text{Ca}$  ( $\text{Ca,Mg}$ ), compared with the 1100–1050  $\text{cm}^{-1}$  band associated with  $\equiv\text{SiO}$  units. These observations may be rationalized by the following model, termed the "molecular site model" (McMillan, 1981; McMillan and Piriou, 1983).

If it assumed that all oxygen is coordinated to silicon, and that local electrostatic charge balance must be satisfied, then a given metal cation will have an appropriate combination of bridging and non-bridging oxygens in its

coordination sphere. The non-bridging oxygens may be described by the silicate molecular units  $\text{SiO}_4$ ,  $-\text{SiO}_3$ ,  $=\text{SiO}_2$  and  $\equiv\text{SiO}$ , and may be used to define types of cation site. The model is most simply discussed for high silica content, where  $=\text{SiO}_2$ ,  $\equiv\text{SiO}$  and uncharged  $=\text{Si}=\text{Si}$  units predominate, and for singly- and doubly-charged cations  $\text{M}^+$  and  $\text{M}^{2+}$ . A single site  $\equiv\text{SiO}$  defines a site for one  $\text{M}^+$  cation, while the doubly-charged site  $=\text{SiO}_2$  may accommodate one  $\text{M}^{2+}$ , or two  $\text{M}^+$  cations. Finally, a coupled site [ $\equiv\text{SiO}$ ] $_2$ , with two discrete  $\equiv\text{SiO}$  units within the coordination sphere, may be formulated to house a single  $\text{M}^{2+}$  or two  $\text{M}^+$  cations. The uncharged unit  $=\text{Si}=\text{Si}$  has no associated cation. At a given silica content, the relative proportion of these sites will be a function of the metal cation. Large cations  $\text{M}^+$  should prefer the single site  $\equiv\text{SiO}$ , since occupation of  $=\text{SiO}_2$  sites would lead to steric crowding, while smaller  $\text{M}^+$  cations should allow a higher proportion of  $=\text{SiO}_2$  sites. Doubly-charged cations  $\text{M}^{2+}$  of large ionic radius should preferentially occupy the more open, coupled site [ $\equiv\text{SiO}$ ] $_2$ , while smaller  $\text{M}^{2+}$  cations will favor the higher charge concentration offered by the  $=\text{SiO}_2$  sites. At constant silica content, the overall distribution of silicate molecular units is fixed by the "reaction"



The above reasoning suggests that this reaction will be driven to the right for small, doubly-charged cations, and to the left for large, singly-charged cations. This is consistent with the experimental observations discussed above, where bands for  $=\text{SiO}_2$  and  $=\text{Si}=\text{Si}$  units become more prominent at the expense of  $\equiv\text{SiO}$  groups, at similar silica content in the order



The formation of  $=\text{Si}=\text{Si}$  and  $=\text{SiO}_2$  units from  $\equiv\text{SiO}$  groups is a charge concentration effect, since the  $=\text{Si}=\text{Si}$  unit has no associated cation. The clustering induced by this charge concentration may be regarded as incipient immiscibility, and suggests that the tendency for unmixing should increase in the order  $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$  for the alkalis, and  $\text{Ca} < \text{Mg}$  for the alkaline earth silicates. The model also suggests that the low-silica limit of the two-phase region should move toward more basic compositions, in the same order.

It has long been known that liquids in the systems  $\text{SiO}_2\text{-MgO}$ ,  $\text{CaO}$  and  $\text{SrO}$  show large miscibility gaps at high silica content (e.g., Greig, 1927), while  $\text{SiO}_2\text{-BaO}$  and  $\text{SiO}_2\text{-Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and perhaps  $\text{K}_2\text{O}$  show metastable immiscibility in high silica glasses (e.g., Charles, 1966, 1967, 1969; Galakhov and Varshal, 1973; Haller et al., 1974; Hess, 1977). In all cases, the silica-rich liquid is near pure silica (90–100 mole %  $\text{SiO}_2$ ), while the composition of the metal oxide-rich liquid or glass becomes progressively richer in metal oxide in the order  $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$  for alkaline earth oxides, and for the alkalis,  $\text{K} < \text{Na} < \text{Li}$ , with Li between Mg and Ca, Na between Sr

and Ba, and K lower than Ba (e.g., Kracek, 1939; Charles, 1967; Galakhov and Varshal, 1973; Hess, 1977). The above model based on the Raman spectroscopic results is certainly consistent with the observed immiscibility behavior of alkali and alkaline earth silicate melts and glasses. Matson et al. (1983) have recently developed a similar but independent model from their Raman studies of alkali silicate glasses. The model has also been extended to simple aluminosilicate compositions by McMillan et al. (1982) and Navrotsky et al. (1982), where it successfully rationalized heats of mixing along the SiO<sub>2</sub>–NaAlO<sub>2</sub> and SiO<sub>2</sub>–Ca<sub>0.5</sub>AlO<sub>2</sub> glass joins, and predicted some tendency for unmixing in the system SiO<sub>2</sub>–Mg<sub>0.5</sub>AlO<sub>2</sub>.

In all of the alkali and alkaline earth silicate miscibility gaps described above, the high silica limit of the two-phase region lies near 90–95 mole % silica, suggesting that a few per cent metal oxide component may dissolve in the silica glass network before leading to macroscopic phase separation. The spectrum of the high-silica SiO<sub>2</sub>–CaO glass 20 (Figure 8b) shows a weak band assigned to ≡SiO units near 1100 cm<sup>-1</sup> between the two silica bands at 1060 and 1200 cm<sup>-1</sup>. The major features of the silica glass spectrum are not changed, except that the two defect peaks at 500 and 600 cm<sup>-1</sup> are less prominent than in vitreous silica. It is suggested that these few per cent of metal oxide component may be accepted into the silica glass structure with formation of some ≡SiO units, without disrupting the overall glass network, and that this mechanism may suppress the structural "defect" responsible for the 500 and 600 cm<sup>-1</sup> bands. A similar effect was noted for small additions of Al<sub>2</sub>O<sub>3</sub> to silica glass (McMillan and Piriou, 1982), and also for additions of KAlO<sub>2</sub> and alkali oxides where no stable immiscibility is known (e.g., Stolen and Walrafen, 1976; McMillan et al., 1982; Mysen et al., 1982a; Matson et al., 1983).

The above site model appears to give a useful molecular description of structural factors possibly responsible for the unmixing behavior observed in simple silicate systems. The model becomes of less value as the silica content is decreased, with formation of –SiO<sub>3</sub> and SiO<sub>4</sub> groups. Associated with these would be various combinations of M<sup>+</sup> and M<sup>2+</sup> cations, each controlled by a variety of factors, such as cation–oxygen bonding, and cation–cation repulsion effects. The sites –SiO<sub>3</sub> and SiO<sub>4</sub> may also be considered coupled to =SiO<sub>2</sub> and ≡SiO, further complicating the problem. Similarly, the model may not yet be simply formulated for higher valence cations. Finally, it is noted that the model will work best when electrostatic charge balance is most rigorous, or when the cation–oxygen association is maximized. However, as this association is increased, it may perturb the silicate bonding interaction. It is of interest that the major silicate bands are observed to broaden in the order Cs < Rb < K < Na < Li < Ca < Mg in alkali and alkaline earth silicate glass systems, which may partly reflect an increased perturbation of the silicate units as the cation strength increases.

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