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Structural Investigation of Molten Alkali Silicates by Raman Spectroscopy[†]

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Abstract

Raman spectra of alkali silicates $Na_2O \cdot 2SiO_2$, $Na_2O \cdot SiO_2$ and $M_2O \cdot 4SiO_2$ ($M = K$, Rb) from glasses to melts were measured by using high temperature Raman spectroscopic technique. The band broadening, the frequency shifts and the change of the intensity ratio of the bands attributed to Si-O vibration modes with increasing temperature were interpreted in terms of the depolymerization process of the anionic structural units. It is concluded that the melt structures of these silicates are not necessarily similar to the corresponding glass structures.

KEY WORDS: (Alkali silicate) (Glass) (Melt) (Raman spectroscopy)

1. Introduction

In metallugical or welding process, silicate mixtures applied to slag or flux are always used in the molten states. Therefore, it has become important to understand the molten structures which gorven various physical properties, such as viscosity, density, electrical conductance and self-diffusion etc., of molten silicates. Silicates with SiO_4 tetrahedral three-dimensional network structure easily form the glasses by solidification from the melts with high melting points. Therefore, these molten structures have been estimated from the corresponding glass structures because of the experimental difficulties. However, it is not made clear that the glass structure is similar to the corresponding melt structure. Recently X-ray structural analysis of both silicate melts and glasses was reported by Waseda et al.[1]-[3]. The results only indicated that the structural units of both silicate melts and glasses are SiO_4 tetrahedron, and did not discuss the coexisting anionic structures of a broad range of both silicate melts and glasses.

It is generally accepted that the introduction of alkali oxides to SiO_2 breaks the Si-O-Si bridging bonds of SiO_4 tetrahedral three-dimensional structure, creating various polymeric anionic units with non-bridging oxygens (NBO). The number of NBO increases with increasing alkali oxide content, and also with increaging temperature.

Raman spectroscopy is a very useful method for the identification of distinct anionic units in silicate melts and glasses. The stretching vibrational bands of the Si-O bond in silicates can be easily observed in the frequency range from 800 to 1200 cm^{-1}. Many previous works[4]-[14] on silicate glasses by Raman spectroscopy were reported. Brawer et al.[5] indicated that the characteristic alkali silicate glass vibrations were connected in random fashion to form the glass structures increasing in disorder in the direction K→Na→Li. Mysen et al.[6],[7] pointed out the coexistence of anionic species such as SiO_4^{4-} monomer, $Si_2O_7^{6-}$ dimer, SiO_3^{2-} chain or ring, $Si_2O_5^{2-}$ sheet, and SiO_2 three-dimensional structural unit with four, three, two, one and zero NBO, respectively, in alkali and alkaline earth silicate glasses from Raman spectroscopic measurement. Tsunawaki et al.[8],[9] reported the fractions of bridging, non-bridging and free oxygens in PbO-SiO_2, CaO-SiO_2 and CaO-SiO_2-CaF_2 glasses from the intensities of the Si-O stretching Raman bands. Recently Furukawa et al.[10] remeasured Na_2O-SiO_2 glasses using a new Raman spectroscopic data.

In this study, Raman spectra of the molten alkali silicates $Na_2O \cdot 2SiO_2$, $Na_2O \cdot SiO_2$ and $M_2O \cdot 4SiO_2$ ($M = K$, Rb) were measured in order to make clear thier molten structures. Furthermore, the temperature dependence of these structures from glasses to melts is also discussed by Raman spectroscopy.

2. Experimental

All starting binary alkali silicate glasses were prepared from analytical reagant grade SiO_2, Li_2CO_3, Na_2CO_3, K_2CO_3 and Rb_2CO_3. About 5 g batches were well mixed and melted at the temperature of about 100 °C above their melting points in a Pt crucible inside electrical furnace for about 2 hours. After

melting, the melts were allowed to cool in air.

Raman spectra were measured on a JASCO Model R-800 double-grating spectrometer at a scattering angle of 90°. The excitation source was 514.5 nm (19435.6 cm^{-1}) or 488.0 nm (20492.0 cm^{-1}) line of NEC GLG 3300 Ar ion laser at a power level from 300 to 800 mW.

A furnace for high temperature Raman spectroscopic measurements was fabricated as shown in **Fig. 1**. The
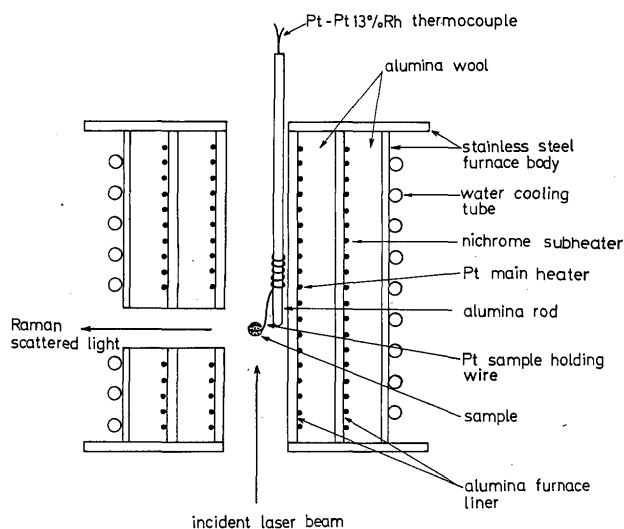

Fig. 1 Schematic diagram of a furnace for high temperature Raman spectroscopy.

heating elements consist of the Pt main heater and the nichrome subheater in order to maintain high temperature easily. A small window was cut in the furnace body to allow exit of Raman scattered light. As shown in Fig. 1, the molten sample was placed on the Pt ring wire by its surface tension. The furnace can produce a maximum sample temperature of 1500°C, but high temperature Raman spectroscopic measurement was limited to 1200°C due to the thermal radiation from the sample and the furnace. The sample temperature was controlled within a maximum error of 5°C throughout the measurement. The uncertainty in the sample temperature due to local heating by laser is usually ignored.

3. Results and Discussion

The Raman spectra of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot SiO_2$ from glasses to melts are shown in **Fig. 2** and **3**, respectively. These spectra change in a systematic manner with temperature. As shown in Fig. 2, the band near 550 cm^{-1} due to Si-O-Si bending vibration becomes broader with increasing temperature. The band widths of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot SiO_2$ are plotted as a function of temperature in **Fig. 4**. These band

widths increase with increasing temperature. Furukawa et al. suggested on the basis of the normal mode calculation for $Si_2O_6^{4-}$ chain and $Si_2O_5^{2-}$ sheet units that the band positions due to Si-O-Si vibration change with changing Si-O-Si bond angle. Since the Raman spectrum of any disordered solid is a superposition of the spectra of the individual disordered units, the obtained results indicate that the anionic structural units in the melts have more various Si-O-Si bond angles than those in the corresponding glasses. Soules[15] recently reported that there was a broad distribution of Si-O-Si bond angles for Na_2O-SiO_2 glasses deduced from his molecular dynamic calculation, and that it changed with increasing temperature. Several bands due to the stretching vibration of the Si-O bond were observed in the frequency range from 800 to 1200 cm^{-1}. In the Raman spectra of $Na_2O \cdot 2SiO_2$, the band near 950 cm^{-1} tends to increase in relative intensity with increasing temperature, while the band near 1100 cm^{-1} seems to decrease. Further, these two bands shift to lower frequencies, and become broader with increasing temperature. In the Raman spectra of $Na_2O \cdot SiO_2$, the bands near 880 and 970 cm^{-1} shift to lower frequencies, and become broader with increasing temperature. The systematic change of the

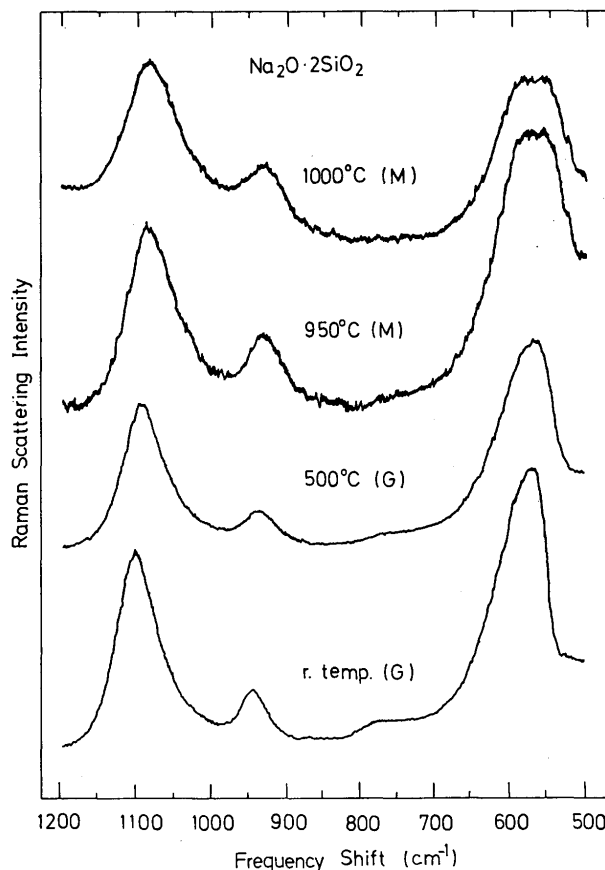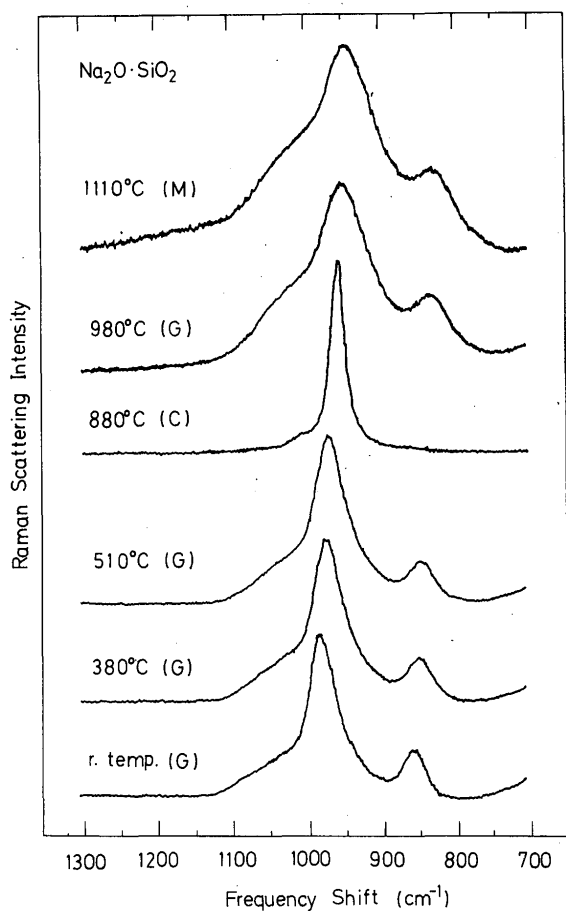**Fig. 2** Raman spectra of $Na_2O \cdot 2SiO_2$ from glass (G) to melt (M).

Na₂O·SiO₂

1110°C (M)

980°C (G)

880°C (C)

510°C (G)

380°C (G)

r. temp. (G)

Raman Scattering Intensity

1300 1200 1100 1000 900 800 700

Frequency Shift (cm⁻¹)

Fig. 3 Raman spectra of Na₂O·SiO₂ from glass (G) to melt
(M). Spectrum (C) was obtained as the material
crystallized at 880°C.

80

Na₂O·SiO₂
o Glass
● Melt

60

1088°C M.P.

40

Peak Width (cm⁻¹)

Na₂O·2SiO₂

874°C M.P.

100

80

0 200 400 600 800 1000 1200
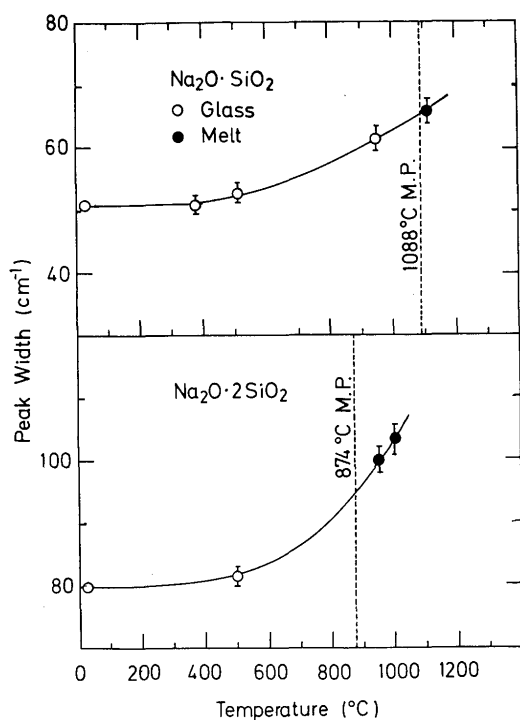
Temperature (°C)

Fig. 4 Half widths against temperature for the near 550 cm⁻¹
bands of Na₂O·2SiO₂ and Na₂O·SiO₂.

K₂O·4SiO₂

1000 °C (M)

870 °C (M)

720 °C (G)

520°C (G)

470°C (G)

r. temp. (G)

Raman Scattering Intensity

1300 1200 1100 1000 900 800

Frequency Shift (cm⁻¹)
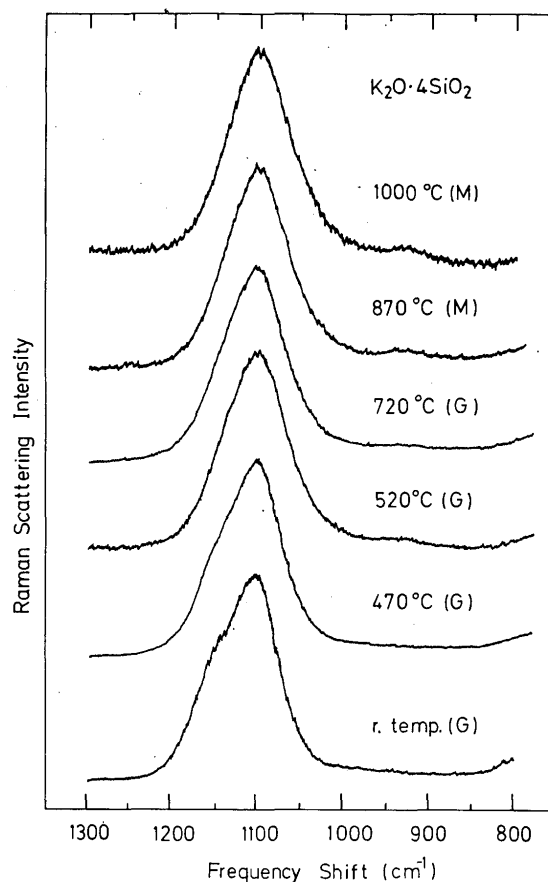
Fig. 5 Raman spectra of K₂O·4SiO₂ from glass (G) to melt
(M).

Rb₂O·4SiO₂

1030°C (M)

870 °C (G)

750 °C (G)

510°C (G)

r. temp. (G)

Raman Scattering Intensity

1300 1200 1100 1000 900 800

Frequency Shift (cm⁻¹)

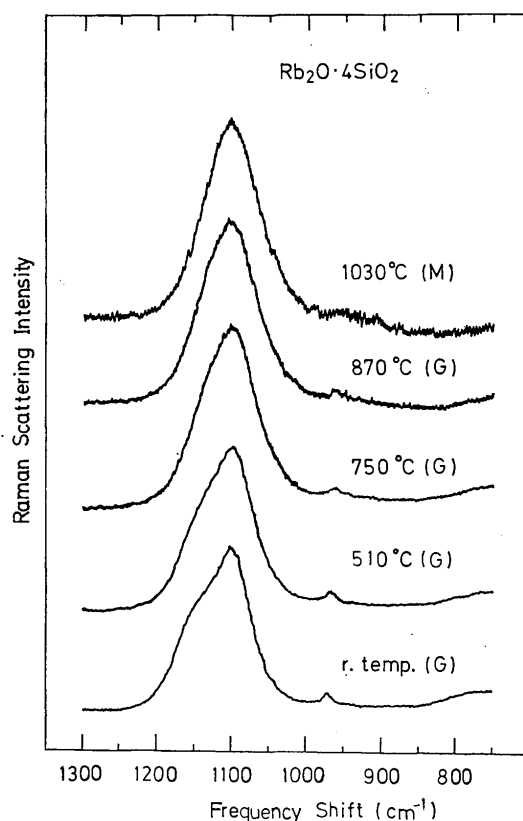**Fig. 6** Raman spectra of Rb₂O·4SiO₂ from glass (G) to melt
(M).

Si-O stretching band with increasing temperature reflects the rupture of the Si-O-Si bonds between SiO_4 tetrahedra, that is, the creation of various anionic structural units with more NBO.

Figures 5 and **6** show the Raman spectra of $M_2O \cdot 4SiO_2$ (M=K, Rb). The strong band was observed near 1100 cm^{-1}. The weak band was observed as a shoulder near 1160 cm^{-1} at room temperature, and this shoulder decreased as the temperature increases.

Konijnendijk et al.[11]-[13] suggested on the basis of the Raman spectra of alkali silicate glasses and crystals and alkali-aluminosilicate glasses that the bands at 960 and 1080 cm^{-1} were due to the SiO_4 tetrahedra with two and one NBO, respectively. From the new Raman spectral data of Na_2O-SiO_2 glasses, Furukawa et al.[10] [14] considered that the bands at 950 and 1100 cm^{-1} are attributed to the Si-O stretching vibration containing two and one NBO, respectively. Mysen et al.[6],[7] showed that the Si-O stretching bands observed in the frequency range from 800 to 1200 cm^{-1} were assigned to the following anionic structural units: SiO_4^{4-} monomer (850 to 880 cm^{-1}), $Si_2O_7^{6-}$ dimer (900 to 920 cm^{-1}), SiO_3^{2-} chain (950 to 980 cm^{-1}),

$Si_2O_5^{2-}$ sheet (1050 to 1100 cm^{-1}) and SiO_2^0 3D-framework (1060, 1090 cm^{-1}). Moreover, Tsunawaki et al.[9],[10] reported the similar results concerning PbO-SiO_2, CaO-SiO_2 and CaO-SiO_2-CaF_2 glasses. These above-mentioned results are summarized in **Table 1**. With these discussions in mind, the Raman spectra of $M_2O \cdot 4SiO_2$ (M=K, Rb) were deconvoluted in the frequency range from 900 to 1300 cm^{-1} into individual bands with Gaussian peak by following technique. First, the tail of low frequency continuum was eliminated, assuming it to be straight in the fequency range. Second, all bands were considered symmetric. Third, each Raman spectrum from 900 to 1200 cm^{-1} consists four bands near 960, 1050, 1100 and 1150 cm^{-1}. These bands near 960, 1100 and 1150 cm^{-1} were attributed to the vibration of the SiO_4 tetrahedra with two, one and zero NBO, respectively. **Figure 7** is an example of $Rb_2O \cdot 4SiO_2$ glass (at room temperature) and melt (at 1030°C). **Figure 8** shows the fractions of SiO_4 tetrahedra with two, one and zero NBO calculated from the Gaussian area as a function of temperature. These fractions of SiO_4 tetrahedra indicated by number 0 decrease from 0.6 to 0.2 in the

Table 1   Raman frequencies due to Si-O stretching vibrations of structural units in silicate glasses.

| Glass	Frequency (cm^{-1})	NBO number	Structural units	Reference
Alkali silicates	960	2		11)–13)
Alkali-alumino-silicates	1080	1		
PbO-SiO_2	890	4	SiO_4^{4-}	8)
	920	3	$Si_2O_7^{6-}$	
	960	2	$Si_4O_{12}^{8-}$ ring or $(SiO_3^{2-})_n$ chain	
	1030	1		
	1150	0		
CaO-SiO_2	880	4		9)
CaO-SiO_2-CaF_2	920	3		
	975	2		
	1050	1		
Na_2O-SiO_2	950	2		10)
	1100	1		
Alkali silicates	850~870	4	SiO_4^{4-} monomer	6)
Alkaline earth silicates	905~920	3	$Si_2O_7^{6-}$ dimer	
	950~970	2	SiO_3^{2-} chain	
	1050~1100	1	$Si_2O_5^{2-}$ sheet	
Alkali silicates	850~880	4	SiO_4^{4-} monomer	7)
Alkaline earth silicates	900~920	3	$Si_2O_7^{6-}$ dimer	
	950~970	2	SiO_3^{2-} chain	
	1050~1100	1	$Si_2O_5^{2-}$ sheet	
	1060~1190	0	SiO_2	

NBO: non-bridging oxygen
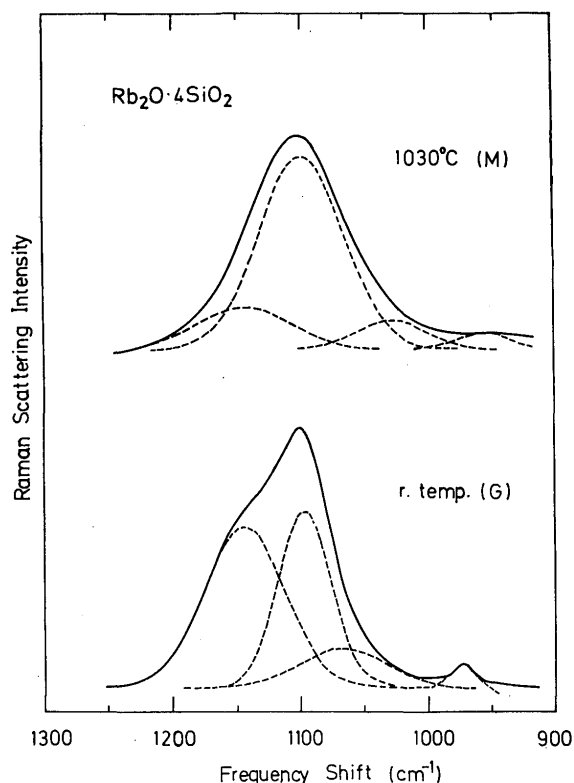
Fig. 7 Raman spectra of $Rb_2O \cdot 4SiO_2$ glass (G) and melt (M) separated into four Gaussian bands.

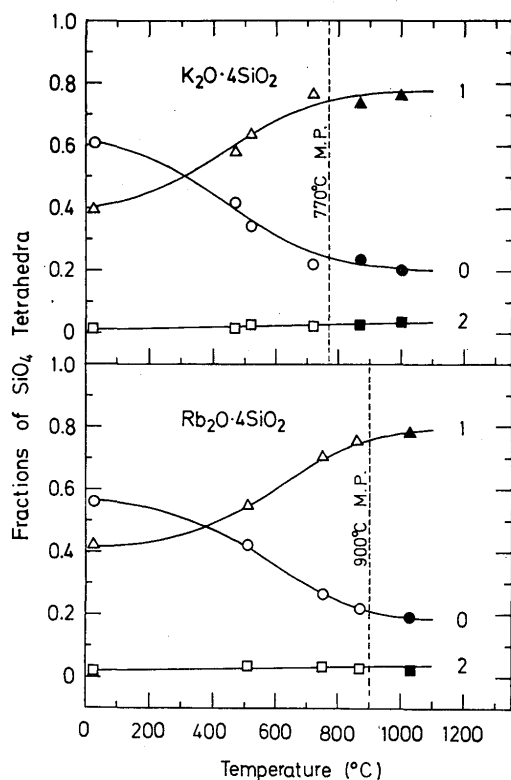**Fig. 8** Temperature dependence of the fractions of SiO_4 tetrahedra with zero, one and two non-bridging oxygens (NBO) in $M_2O \cdot 4SiO_2$ (M = K, Rb).

case of both $K_2O \cdot 4SiO_2$ and $Rb_2O \cdot 4SiO_2$ with increasing temperature, while the fractions of SiO_4 tetrahedra indicated by number 1 increase from 0.2 to 0.6. On the other hand, the slight fractions of SiO_4 tetrahedra indicated by number 2 change little. The obtained results were interpreted as follows. The Si-O bonds of three-dimensional SiO_4 tetrahedral network are broken with increasing temperature so that the average size of the anionic structural units decreases. Furthermore, the band broadening and shifting to lower frequency due to an increasing temperature result from increasing nature of the SiO_4 tetrahedra as well as weakening Si-O bond force. From these results, it is concluded that the melt structures in alkali silicates are not necessarily similar to the corresponding glass structures.

4. Conclusions

We can summarize the obtained results concerning the Raman spectra of $Na_2O \cdot 2SiO_2$, $Na_2O \cdot SiO_2$ and $M_2O \cdot 4SiO_2$ (M = K, Rb) from glasses to melts as follows. The systematic changes of their Raman bands attributed to Si-O vibration modes with increasing temperature, that is, the band broadening, the frequency shifts and the change of the intensity ratio of these bands, result from the depolymerization process of the coexisting structural units. It is concluded that these melt structures are not necessarily similar to the corresponding glass structures.

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