

|              |   |
|--------------|---|
| Title        | Structural Investigation of Molten Alkali Silicates by Raman Spectroscopy(MATERIALS METALLURGY AND WELDABILITY) |
| Author(s)    | Iwamoto, Nobuya; Umesaki, Norimasa; Dohi, Kenji   |
| Citation     | Transactions of JWRI. 1982, 11(1), p. 55-59   |
| Version Type | VoR   |
| URL          | <a href="https://doi.org/10.18910/4253">https://doi.org/10.18910/4253</a>                                       |
| rights       |   |
| Note         |   |

*Osaka University Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

Osaka University

# Structural Investigation of Molten Alkali Silicates by Raman Spectroscopy†

Nobuya IWAMOTO\*, Norimasa UMESAKI\*\* and Kenji DOHI\*\*\*

## Abstract

*Raman spectra of alkali silicates  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot \text{SiO}_2$  and  $\text{M}_2\text{O}\cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ) 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 metallurgical 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 govern various physical properties, such as viscosity, density, electrical conductance and self-diffusion etc., of molten silicates. Silicates with  $\text{SiO}_4$  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.<sup>1)-3)</sup>. The results only indicated that the structural units of both silicate melts and glasses are  $\text{SiO}_4$  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  $\text{SiO}_2$  breaks the Si-O-Si bridging bonds of  $\text{SiO}_4$  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 increasing 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  $\text{cm}^{-1}$ . Many

previous works<sup>4)-14)</sup> on silicate glasses by Raman spectroscopy were reported. Brawer et al.<sup>5)</sup> indicated that the characteristic alkali silicate glass vibrations were connected in random fashion to form the glass structures increasing in disorder in the direction  $\text{K}\rightarrow\text{Na}\rightarrow\text{Li}$ . Mysen et al.<sup>6),7)</sup> pointed out the coexistence of anionic species such as  $\text{SiO}_4^{4-}$  monomer,  $\text{Si}_2\text{O}_7^{6-}$  dimer,  $\text{SiO}_3^{2-}$  chain or ring,  $\text{Si}_2\text{O}_5^{2-}$  sheet, and  $\text{SiO}_2$  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.<sup>8),9)</sup> reported the fractions of bridging, non-bridging and free oxygens in  $\text{PbO}\text{-SiO}_2$ ,  $\text{CaO}\text{-SiO}_2$  and  $\text{CaO}\text{-SiO}_2\text{-CaF}_2$  glasses from the intensities of the Si-O stretching Raman bands. Recently Furukawa et al.<sup>10)</sup> re-measured  $\text{Na}_2\text{O}\text{-SiO}_2$  glasses using a new Raman spectroscopic data.

In this study, Raman spectra of the molten alkali silicates  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot \text{SiO}_2$  and  $\text{M}_2\text{O}\cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ) were measured in order to make clear their 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 reagent grade  $\text{SiO}_2$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Rb}_2\text{CO}_3$ . 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

† Received on March 31, 1982

\* Professor

\*\* Research Instructor

\*\*\* Graduate Student

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka, Japan

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  $90^\circ$ . The excitation source was 514.5 nm ( $19435.6\text{ cm}^{-1}$ ) or 488.0 nm ( $20492.0\text{ cm}^{-1}$ ) 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

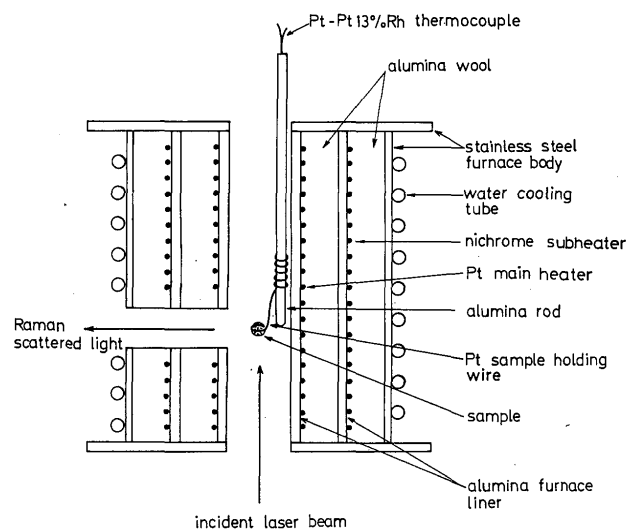


Fig. 1 Schematic diagram of a furnace for high temperature Raman spectroscopy.

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  $1500^\circ\text{C}$ , but high temperature Raman spectroscopic measurement was limited to  $1200^\circ\text{C}$  due to the thermal radiation from the sample and the furnace. The sample temperature was controlled within a maximum error of  $5^\circ\text{C}$  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  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O}\cdot\text{SiO}_2$  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  $550\text{ cm}^{-1}$  due to Si-O-Si bending vibration becomes broader with increasing temperature. The band widths of  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O}\cdot\text{SiO}_2$  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  $\text{Si}_2\text{O}_6^{4-}$  chain and  $\text{Si}_2\text{O}_5^{2-}$  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<sup>15)</sup> recently reported that there was a broad distribution of Si-O-Si bond angles for  $\text{Na}_2\text{O}\cdot\text{SiO}_2$  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  $1200\text{ cm}^{-1}$ . In the Raman spectra of  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ , the band near  $950\text{ cm}^{-1}$  tends to increase in relative intensity with increasing temperature, while the band near  $1100\text{ cm}^{-1}$  seems to decrease. Further, these two bands shift to lower frequencies, and become broader with increasing temperature. In the Raman spectra of  $\text{Na}_2\text{O}\cdot\text{SiO}_2$ , the bands near  $880$  and  $970\text{ cm}^{-1}$  shift to lower frequencies, and become broader with increasing temperature. The systematic change of the

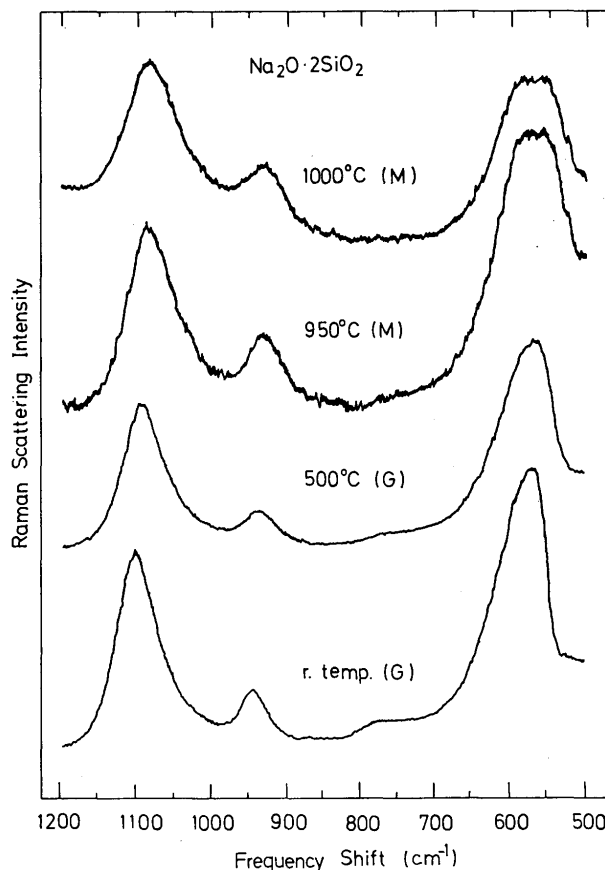


Fig. 2 Raman spectra of  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$  from glass (G) to melt (M).

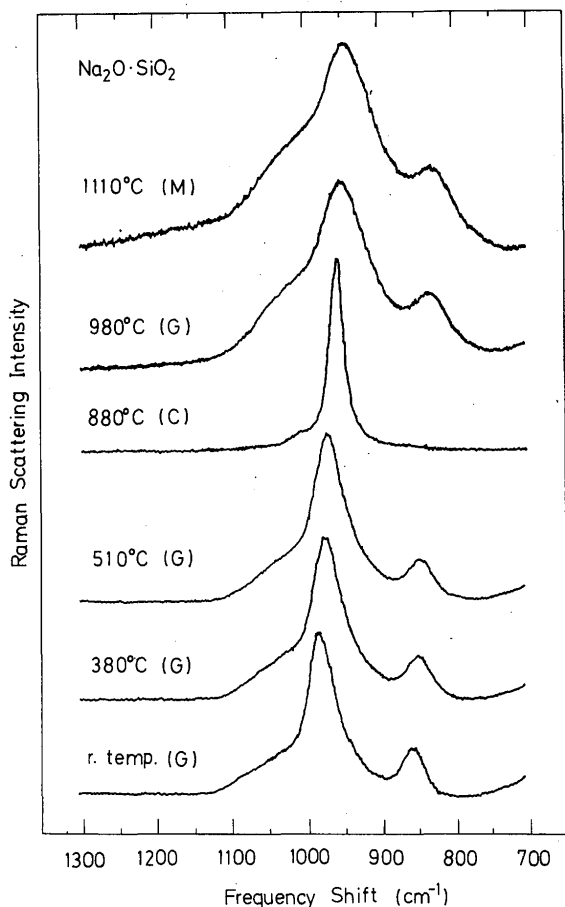


Fig. 3 Raman spectra of  $\text{Na}_2\text{O}\cdot\text{SiO}_2$  from glass (G) to melt (M). Spectrum (C) was obtained as the material crystallized at  $880^\circ\text{C}$ .

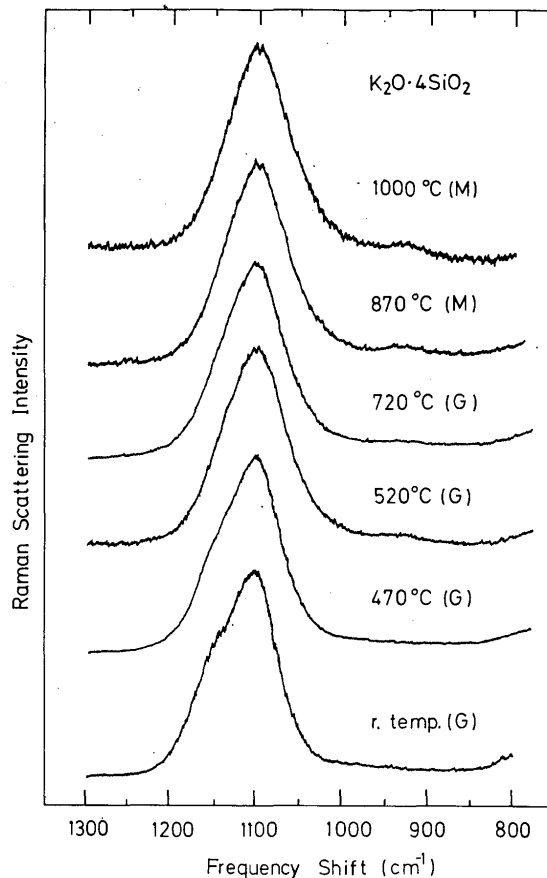


Fig. 5 Raman spectra of  $\text{K}_2\text{O}\cdot 4\text{SiO}_2$  from glass (G) to melt (M).

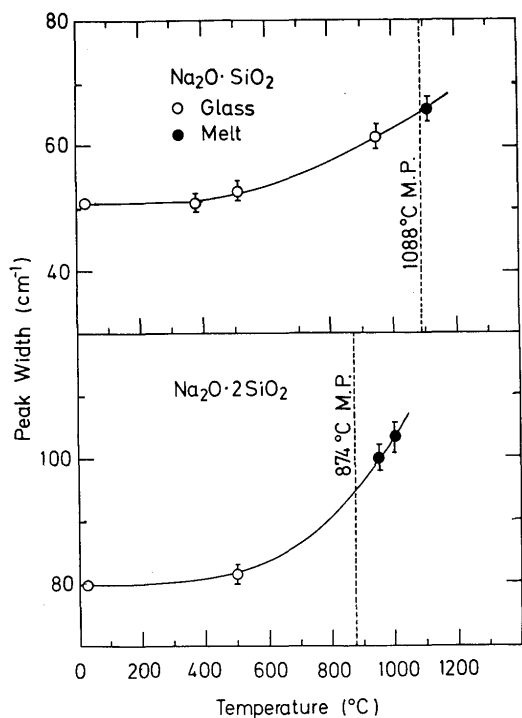


Fig. 4 Half widths against temperature for the near  $550\text{ cm}^{-1}$  bands of  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O}\cdot\text{SiO}_2$ .

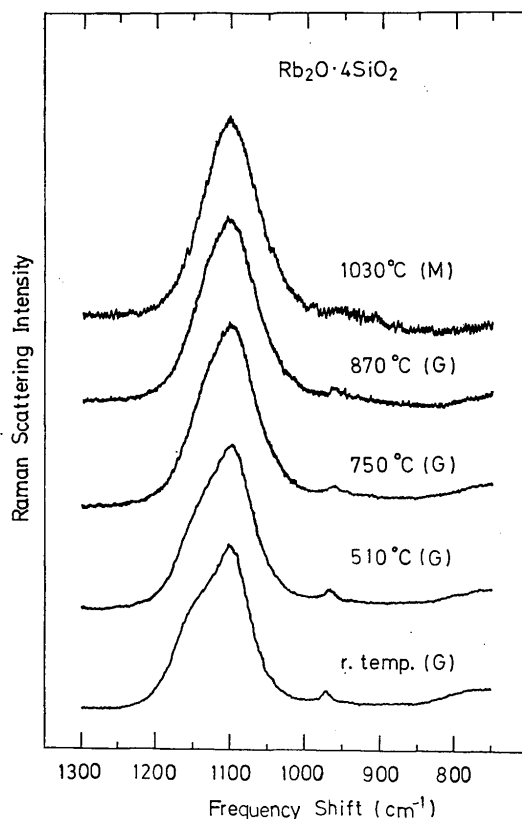


Fig. 6 Raman spectra of  $\text{Rb}_2\text{O}\cdot 4\text{SiO}_2$  from glass (G) to melt (M).

Si-O stretching band with increasing temperature reflects the rupture of the Si-O-Si bonds between  $\text{SiO}_4$  tetrahedra, that is, the creation of various anionic structural units with more NBO.

Figures 5 and 6 show the Raman spectra of  $\text{M}_2\text{O} \cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ). The strong band was observed near  $1100 \text{ cm}^{-1}$ . The weak band was observed as a shoulder near  $1160 \text{ cm}^{-1}$  at room temperature, and this shoulder decreased as the temperature increases.

Konijnendijk et al.<sup>11)-13)</sup> suggested on the basis of the Raman spectra of alkali silicate glasses and crystals and alkali-aluminosilicate glasses that the bands at  $960$  and  $1080 \text{ cm}^{-1}$  were due to the  $\text{SiO}_4$  tetrahedra with two and one NBO, respectively. From the new Raman spectral data of  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses, Furukawa et al.<sup>10) 14)</sup> considered that the bands at  $950$  and  $1100 \text{ cm}^{-1}$  are attributed to the Si-O stretching vibration containing two and one NBO, respectively. Mysen et al.<sup>6), 7)</sup> showed that the Si-O stretching bands observed in the frequency range from  $800$  to  $1200 \text{ cm}^{-1}$  were assigned to the following anionic structural units:  $\text{SiO}_4^{4-}$  monomer ( $850$  to  $880 \text{ cm}^{-1}$ ),  $\text{Si}_2\text{O}_7^{6-}$  dimer ( $900$  to  $920 \text{ cm}^{-1}$ ),  $\text{SiO}_3^{2-}$  chain ( $950$  to  $980 \text{ cm}^{-1}$ ),

$\text{Si}_2\text{O}_5^{2-}$  sheet ( $1050$  to  $1100 \text{ cm}^{-1}$ ) and  $\text{SiO}_2$  3D-framework ( $1060, 1090 \text{ cm}^{-1}$ ). Moreover, Tsunawaki et al.<sup>9), 10)</sup> reported the similar results concerning  $\text{PbO}-\text{SiO}_2$ ,  $\text{CaO}-\text{SiO}_2$  and  $\text{CaO}-\text{SiO}_2-\text{CaF}_2$  glasses. These above-mentioned results are summarized in Table 1. With these discussions in mind, the Raman spectra of  $\text{M}_2\text{O} \cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ) were deconvoluted in the frequency range from  $900$  to  $1300 \text{ cm}^{-1}$  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 frequency range. Second, all bands were considered symmetric. Third, each Raman spectrum from  $900$  to  $1200 \text{ cm}^{-1}$  consists four bands near  $960, 1050, 1100$  and  $1150 \text{ cm}^{-1}$ . These bands near  $960, 1100$  and  $1150 \text{ cm}^{-1}$  were attributed to the vibration of the  $\text{SiO}_4$  tetrahedra with two, one and zero NBO, respectively. Figure 7 is an example of  $\text{Rb}_2\text{O} \cdot 4\text{SiO}_2$  glass (at room temperature) and melt (at  $1030^\circ\text{C}$ ). Figure 8 shows the fractions of  $\text{SiO}_4$  tetrahedra with two, one and zero NBO calculated from the Gaussian area as a function of temperature. These fractions of  $\text{SiO}_4$  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 ( $\text{cm}^{-1}$ ) | NBO number | Structural units  | Reference |
|---|--------------------------------|------------|---|-----------|
| Alkali silicates  | 960                            | 2          |   | 11)-13)   |
| Alkali-alumino-silicates  | 1080                           | 1          |   |           |
| $\text{PbO}-\text{SiO}_2$   | 890                            | 4          | $\text{SiO}_4^{4-}$   | 8)        |
|   | 920                            | 3          | $\text{Si}_2\text{O}_7^{6-}$  |           |
|   | 960                            | 2          | $\text{Si}_4\text{O}_{12}^{8-}$ ring or $(\text{SiO}_3^{2-})_n$ chain |           |
|   | 1030                           | 1          |   |           |
|   | 1150                           | 0          |   |           |
| $\text{CaO}-\text{SiO}_2$<br>$\text{CaO}-\text{SiO}_2-\text{CaF}_2$ | 880                            | 4          |   | 9)        |
|   | 920                            | 3          |   |           |
|   | 975                            | 2          |   |           |
| $\text{Na}_2\text{O}-\text{SiO}_2$                                  | 1050                           | 1          |   | 10)       |
|   | 950                            | 2          |   |           |
|   | 1100                           | 1          |   |           |
| Alkali silicates  | 850~870                        | 4          | $\text{SiO}_4^{4-}$ monomer   | 6)        |
| Alkaline earth silicates  | 905~920                        | 3          | $\text{Si}_2\text{O}_7^{6-}$ dimer                                    |           |
|   | 950~970                        | 2          | $\text{SiO}_3^{2-}$ chain   |           |
|   | 1050~1100                      | 1          | $\text{Si}_2\text{O}_5^{2-}$ sheet                                    |           |
| Alkali silicates<br>Alkaline earth silicates                        | 850~880                        | 4          | $\text{SiO}_4^{4-}$ monomer   | 7)        |
|   | 900~920                        | 3          | $\text{Si}_2\text{O}_7^{6-}$ dimer                                    |           |
|   | 950~970                        | 2          | $\text{SiO}_3^{2-}$ chain   |           |
|   | 1050~1100                      | 1          | $\text{Si}_2\text{O}_5^{2-}$ sheet                                    |           |
|   | 1060~1190                      | 0          | $\text{SiO}_2$  |           |

NBO: non-bridging oxygen

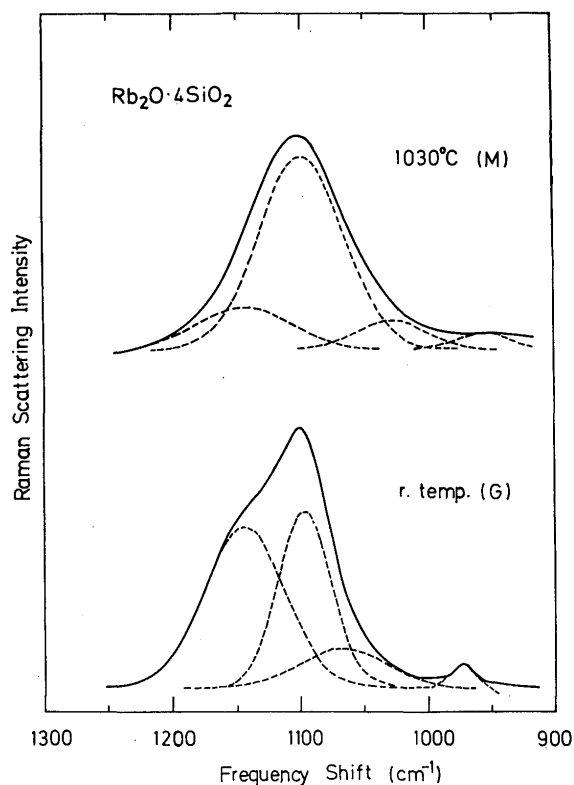


Fig. 7 Raman spectra of  $\text{Rb}_2\text{O}\cdot 4\text{SiO}_2$  glass (G) and melt (M) separated into four Gaussian bands.

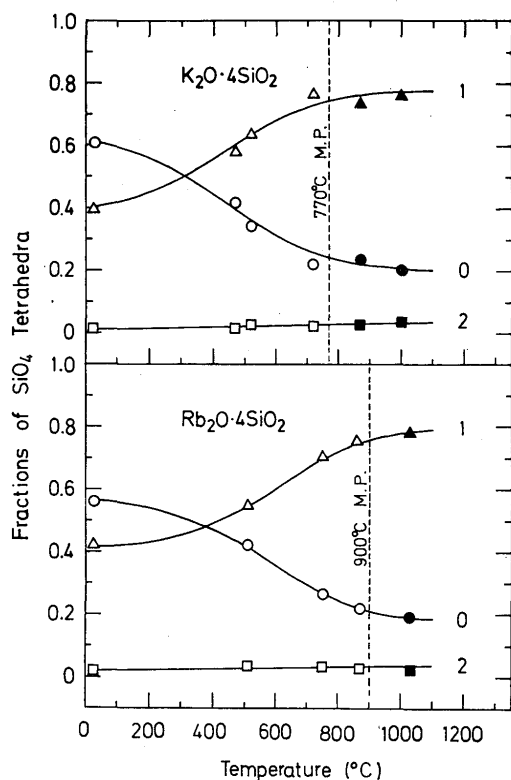


Fig. 8 Temperature dependence of the fractions of  $\text{SiO}_4$  tetrahedra with zero, one and two non-bridging oxygens (NBO) in  $\text{M}_2\text{O}\cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ).

case of both  $\text{K}_2\text{O}\cdot 4\text{SiO}_2$  and  $\text{Rb}_2\text{O}\cdot 4\text{SiO}_2$  with increasing temperature, while the fractions of  $\text{SiO}_4$  tetrahedra indicated by number 1 increase from 0.2 to 0.6. On the other hand, the slight fractions of  $\text{SiO}_4$  tetrahedra indicated by number 2 change little. The obtained results were interpreted as follows. The Si-O bonds of three-dimensional  $\text{SiO}_4$  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  $\text{SiO}_4$  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  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot \text{SiO}_2$  and  $\text{M}_2\text{O}\cdot 4\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Rb}$ ) 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.

#### References

- 1) Y. Waseda and H. Suito: *Tetsu to Hagane*, 62 (1976), p. 1493, (in Japanese).
- 2) Y. Waseda, H. Suito and Y. Shiraishi: *J. Japan Inst. Metals*, 41 (1977), p. 1068, (in Japanese).
- 3) Y. Waseda and J.M. Toguri: *Met. Trans.*, 8B (1977), p. 563.
- 4) M. Hass: *J. Phys. Chem. Solids*, 31 (1970), p. 415.
- 5) S.A. Brawer and W.B. White: *J. Chem. Phys.*, 63 (1975), p. 2421.
- 6) B.O. Mysen, D. Virgo and C.M. Scarfe: *Am. Mineral.*, 65 (1980), p. 690.
- 7) D. Virgo, B.O. Mysen and I. Kushiro: *Science*, 208 (1980), p. 1371.
- 8) N. Iwamoto, Y. Tsunawaki and M. Miyago: *J. Japan Inst. Metals*, 43 (1979), p. 1138, (in Japan).
- 9) Y. Tsunawaki, N. Iwamoto, T. Hatori and A. Mitsuishi: *J. Non-Crystalline Solids*, 44 (1981), p. 369.
- 10) T. Furukawa, K.E. Fox and W.B. White: *J. Chem. Phys.*, 75 (1981), p. 3226.
- 11) W.L. Konijnendijk: *Philips Res. Rep. Suppl.*, (1975), p. 216.
- 12) W.L. Konijnendijk and J.M. Stevels: *J. Non-Crystalline Solids*, 20 (1976), p. 447.
- 13) W.L. Konijnendijk: *Glastechn. Ber.*, 48 (1975), p. 216.
- 14) T. Furukawa and W.B. White: *J. Non-Crystalline Solids*, 38 & 39 (1980), p. 87.
- 15) T.F. Soules: *J. Chem. Phys.*, 71 (1979), p. 4573.