

# Structural analysis of molten Na<sub>2</sub>O-NaF-SiO<sub>2</sub> system by Raman spectroscopy and molecular dynamics simulation

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To determine the effect of F ions in the molten alkali silicate systems on their structures, quenched Na<sub>2</sub>O-SiO<sub>2</sub>-NaF systems were investigated by Raman spectroscopy and molecular dynamics simulation. The systematic increase of 1100 cm<sup>-1</sup> band intensity in the Raman spectra of the silicate melts accompanying the replacement of F for O provides the evidence for concomitant polymerization of melts. From the molecular dynamics simulation, it was confirmed that most of substituted F was mainly coordinated to Na<sup>+</sup> ions but not Si<sup>4+</sup> ions. These results were consistent with the mechanism in which F associated with otherwise network-modifying Na rather than with network-forming Si. Since F was associated to Na<sup>+</sup> ions, the replace of O ion by two F ions promote the polymerization of silicate melts.

Keywords: fluorine; molten flux; slag structure; molecular dynamics simulation; Raman spectroscopy.

## Introduction

The partial substitution of fluorine anions for oxygen in molten silicates and aluminosilicates shows drastic effects on physical properties, such as fluidity and the melting point of systems<sup>1</sup>. Therefore, fluxes and slags containing fluoride were widely used in the hot metal treatment of the steel making process. Steel industries, however, are now forced to decrease the usage of fluoride to meet the recent environmental requirement. To develop a new process without fluoride usage, we must know the role of the fluoride in molten silicates and aluminosilicates quantitatively to design new fluxes and slags. Although many investigations into the physical and chemical properties of fluoride-contained melts have been conducted<sup>2-4</sup>, the roles of F on the properties of molten silicates and aluminosilicates are still obscure.

The Na<sub>2</sub>O-NaF-SiO<sub>2</sub> system was chosen as a first step of the investigation of the role of F in silicate melts, since it had a much wider liquid phase area compared with that of the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system at the same temperature. Consequently, it made it possible to vary the composition for the measurements so that the role of F could be more clearly identified. Generally speaking, industrial mould fluxes contained not only the alkaline-earth metal cation of Ca<sup>2+</sup>, but also the alkali metal cations such as Na<sup>+</sup>. So far, most of investigations of the role of F were mainly focused on the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system. But a few works were conducted for the Na<sub>2</sub>O-NaF-SiO<sub>2</sub> system. Therefore, it can be useful to investigate the behaviour of F in the Na<sub>2</sub>O-NaF-SiO<sub>2</sub> system for understanding the structure of the practical mould fluxes.

Raman spectroscopy is well suited to evaluating these long-range order structures of silicate melts. Therefore, in this investigation, Raman spectroscopic measurement was applied to investigate the effect of F. It is also well known that molecular dynamics calculation gives much information on the structural details such as bond angle

distributions or pair functions that are difficult to obtain by Raman measurements<sup>2</sup>. Therefore, in this investigation, molecular dynamics simulations were also employed to investigate the structural role of F<sup>-</sup> ions in molten alkali-silicate melts and simulated results were compared and discussed with the measured Raman spectra.

## Raman spectroscopy measurements

The detail of Raman spectroscopic measurements was described previously<sup>3</sup>. Appropriate portions of reagent grade Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub> and NaF powders were mixed together in an agate mortar in air and placed in a Pt crucible. The mixture was heated at 1073 K for 10.8 ks to decarbonate and then fired in a muffle furnace at 1673 K for 7.2 ks. The melted mixture was quenched into a water-cooled copper flat mould and then ground to form a powder. The prepared powder was melted again as a bead (only about 5 mg) at 1673 K on a Pt-Pt alloy thermocouple wire loop in air and quenched. Quenching was achieved by switching off the power to the hot thermocouple. The prepared sample was broken into several pieces of about 3×3 mm and used for measurement.

The initial compositions of the samples are presented in Table I. In the Table, Na<sub>2</sub>F<sub>2</sub> is used instead of NaF, since it is convenient to consider the substitution of 2F<sup>-</sup> to O<sup>2-</sup> (2F<sup>-</sup> → O<sup>2-</sup>). After the samples were prepared, their contents were analysed by the Energy Dispersion X-ray method (EDX). Their compositions were found to be almost the same as the nominal compositions within the resolution of EDX (about 1%).

Raman spectra of samples were obtained with an automatic micro-Raman system (JASCO NRS-2000). Silicate samples were excited by the 514.5 nm line of a coherent Ar<sup>+</sup> laser (NEC GLG-2162) operating at 300 mW. The CCD detector was maintained at a constant temperature of liquid nitrogen and all the Raman spectra measurements of samples were made at room temperature. Unpolarized

**Table I**  
Compositions (mol%) of samples studied in the system  
Na<sub>2</sub>O-Na<sub>2</sub>F<sub>2</sub>-SiO<sub>2</sub>

	SiO <sub>2</sub>	Na <sub>2</sub> O	Na <sub>2</sub> F <sub>2</sub>
Na <sub>2</sub> O·SiO <sub>2</sub>	50.00	50.00	0.00
10SiO <sub>2</sub> -9Na <sub>2</sub> O-Na <sub>2</sub> F <sub>2</sub>	50.00	45.00	5.00
10SiO <sub>2</sub> -8Na <sub>2</sub> O-2Na <sub>2</sub> F <sub>2</sub>	50.00	40.00	10.00
10SiO <sub>2</sub> -7Na <sub>2</sub> O-3Na <sub>2</sub> F <sub>2</sub>	50.00	35.00	15.00
10SiO <sub>2</sub> -6Na <sub>2</sub> O-4Na <sub>2</sub> F <sub>2</sub>	50.00	30.00	20.00
9(Na <sub>2</sub> O·SiO <sub>2</sub> )-0.5 Na <sub>2</sub> F <sub>2</sub>	48.65	48.65	2.70
8(Na <sub>2</sub> O·SiO <sub>2</sub> )-Na <sub>2</sub> F <sub>2</sub>	47.06	44.45	5.88

spectra were measured for all samples and several spectra from each sample were measured for each composition. All spots used for micro-Raman analysis were examined for laser damage immediately following the runs and detectable damages were not observed.

### Molecular dynamic simulation method

The molecular dynamics simulations were applied to the same compositions as measured by Raman spectroscopy and high F content compositions. The MD calculations were carried out by using the MXDORTHO program<sup>4</sup>. The pair potential used in these molecular dynamics simulations was the Busing approximation of Born-Mayer-Huggins form<sup>5</sup> of

$$U_{ij}(r) = Z_i Z_j e^2 / R_{ij} + f_o (b_i + b_j) \exp\left(\frac{a_i + a_j - R_{ij}}{b_i + b_j}\right) \quad [1]$$

where  $R_{ij}$  is the distance between ions  $i$  and  $j$ ,  $Z_i$  is the charge of ion  $i$ ,  $f_o = 6.9472 \times 10^{-11}$  N.  $a_i$  and  $b_i$  are potential parameters that are related to the size and softness of the  $i$ th atom, respectively. The potential parameters of each atom were empirically determined to reproduce crystal structures and their melting points. The reliability of the molecular dynamics simulation results largely depended on the parameters employed. The reliability of parameter sets for the Born-Mayer-Huggins potential was well discussed by Sangster and Dixon<sup>18</sup>. The values of the parameter set that was used in this calculation are shown in Table II<sup>6</sup>. Hirao and Kawamura<sup>17</sup> established these values that satisfied the reproduction of various stable crystal structures of 30 compounds. These parameters so far have been successfully used by many workers to simulate molten oxide and fluorides.

For the calculation, three-dimensional periodic boundary conditions were applied to the basic cells containing about 3 000 atoms. The long-range Coulombic forces were calculated by the Edwald summation within the uncertainty of 0.01%. The equation of motion was integrated by the Verlet algorithm with the time step of 2.0 fs. All the calculation was carried out at constant pressure of 101 kPa. The initial temperature was set to 4000 K to agitate the atoms and eliminate the effect of the initial distribution on the final structure. Namely, the distribution of the constituent atoms in the basic cells was set to be statistically random at the start of calculation. The temperature was then decreased to 3000, 2000, 1800 and finally 1673 K. The calculation process of changing temperature from one to another was carried out for 10 000 steps. The setting of temperature decreasing rate was 1 K

per 10 steps. It was confirmed that about 3 000 steps were enough to reach another equilibrium state by changing temperature. However, just to be safe, 10 000 steps calculation was adapted. All the calculated structural data were accumulated at each temperature. Based on these calculated data, cumulative coordination numbers, average distances between atoms, pair correlation functions and the anionic structural unit distributions (cf. 'Linkage between silicate tetrahedras' below) were calculated.

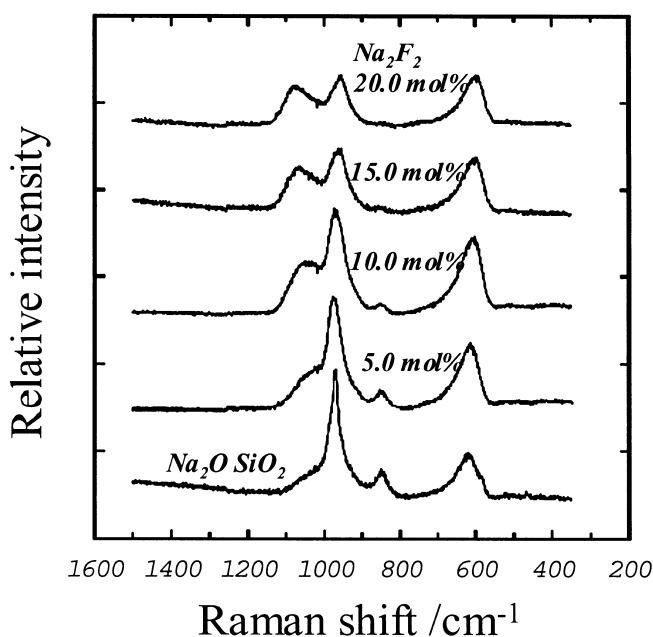
## Results

### Raman spectra

The change in Raman spectra of joins Na<sub>2</sub>O·SiO<sub>2</sub>-Na<sub>2</sub>F<sub>2</sub>·SiO<sub>2</sub> quenched melts with varying Na<sub>2</sub>O/Na<sub>2</sub>F<sub>2</sub> ratios are shown in Figure 1. There were an intense band of 950 cm<sup>-1</sup> and a relatively weak band of 850 cm<sup>-1</sup> in the Na<sub>2</sub>O·SiO<sub>2</sub> system without F. With an increase of F content, the intensity of about 1075 cm<sup>-1</sup> band gradually developed and also slightly shifted to higher frequency but that of 950 cm<sup>-1</sup> was gradually decreased. The band 850 cm<sup>-1</sup> also gradually decreased and finally disappeared. Assignments of main Raman bands in silicate melts have been basically established<sup>1,7,8</sup>: namely, the bands near 1100, 950 and 850 cm<sup>-1</sup> are due to symmetric  $\bar{\nu}_1$  O-Si-O<sup>0</sup> (e.g., sheet structural unit),  $\bar{\nu}_2$  O-Si-O<sup>-</sup> (e.g., chain structural unit) and Si-O<sup>2-</sup> (monomer unit) stretch vibration respectively. The observed bands were essentially the same as that observed in binary silicate systems: namely, new bands did not appear due to

**Table II**  
Parameter set used in the present calculations

	Z	a (10 nm)	b (10 nm)
Si	4	1.102	0.080
Na	1	1.260	0.080
F	-1	1.565	0.085
O	-2	1.626	0.085



**Figure 1.** Raman spectra along the join Na<sub>2</sub>O·SiO<sub>2</sub>-Na<sub>2</sub>F<sub>2</sub>·SiO<sub>2</sub>

the F substitution. This means that F in these melts had a negligible effect on the vibration between Si-O. In other words, F ions might not be coordinated to the Si tetrahedral.

Thus, the spectra change due to the F substitution shown in Figure 1 simply means that the number of the sheet structural unit was increased, but that of the monomer unit was decreased. To examine the effect of F on the polymerization quantitatively, the intensity ratio of 1100 and 950  $\text{cm}^{-1}$  bands ( $I_{1100}/I_{950}$ ) of the melts is plotted as a function of NaF content in Figure 2. The  $I_{1100}/I_{950}$  increased almost lineally with  $\text{Na}_2\text{F}_2$  content within the experimental scatters. Based on these results, it can be said that the polymerization was enhanced with an increase of F for the  $\text{Na}_2\text{O}$ -NaF- $\text{SiO}_2$  melts, at least within the present experimental compositions.

### Molecular dynamics simulation

Information about O and F coordination for Si and Na ions in the simulated melts can be obtained from the pair correlation function (PCF) between ions  $i$  and  $j$ ,  $g_{ij}(r)$ , and the cumulative coordination number (CCN) curve  $N(r)$  given<sup>8</sup> by

$$g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \frac{\langle n_{ij}(r) \rangle}{4\pi r^2 \Delta r} \quad [2]$$

$$N(r) = 4\pi \delta_j \int_0^r r^2 g_{ij}(r) dr \quad [3]$$

where  $N$  is the number of ions in the box,  $V$  is the volume of the box,  $n_{ij}$  is the number of ions  $j$  about ion  $i$  in the shell within distances  $r \pm \Delta r/2$ ,  $\langle \rangle$  is the time average, and  $\delta$  is the particle density of an ion.

The individual calculated correlation functions for the Si-O and Si-F pairs and cumulative coordination numbers of O and F around Si at 1473 K in the simulated  $\text{Na}_2\text{O}$ - $\text{SiO}_2$ - $\text{Na}_2\text{F}_2$ - $\text{SiO}_2$  (20 mol%) melt are shown in Figure 3 and Figure 4 respectively. The peak of PCF for Si-F pairs at around 0.172 nm was slightly asymmetric and had a small tail at longer distance. It suggests that the coordination of F around Si was not so tight or loosely bounded and differed from the case of Si-O bond. The Si-O and Si-F pair correlation functions yielded only the first peak at about 0.162 and that for the Si-F pair was found at 0.172 nm, and there was no other distinct peak at longer distance. This implies that, in the  $\text{Na}_2\text{O}$ - $\text{SiO}_2$ - $\text{Na}_2\text{F}_2$ - $\text{SiO}_2$  (20 mol%) melt,

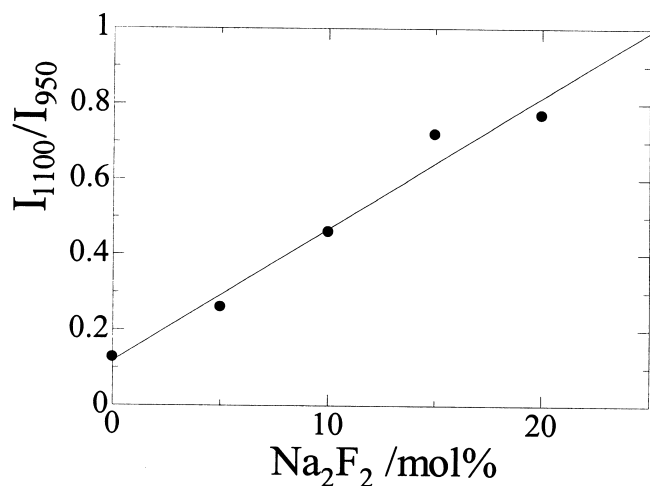


Figure 2.  $I_{1100}/I_{950}$  ratio as function of  $\text{Na}_2\text{F}_2$

only the first coordination sphere was distinguishable. In this first coordination sphere the O coordination number of Si ions was found to be 4 and that of F ions was about 0.1 from the cumulative coordination number curves. The coordination number of 4 for the Si-O pair simply indicated the Si tetrahedral formation. The coordination number of about 0.1 for the Si-F pair means that there exists one Si tetrahedral with an F ion coordinated per 10 Si tetrahedrals, if F plays a non-bridging role.

### Linkage between Si tetrahedrals

Binary silicate melts are known to consist of mixtures of five distinct types of structural units that have NBO/Si = 0, 1, 2, 3 and 4 (NBO/Si; nonbridging oxygens per silicon<sup>1</sup>). In terms of a stoichiometric expression, these units were described as  $\text{SiO}_4^{4-}$  (monomer),  $\text{Si}_2\text{O}_7^{6-}$  (dimer),  $\text{Si}_2\text{O}_6^{4-}$  (chain unit),  $\text{Si}_2\text{O}_5^{2-}$  (sheet unit) and  $\text{SiO}_2$  units. In the terminology commonly employed in NMR spectroscopy, these structures were referred to as  $Q^0$ ,  $Q^1$ ,  $Q^2$ ,  $Q^3$  and  $Q^4$  where the superscript referred to the number of bridging oxygen atom in a given structural unit. Thus  $\text{SiO}_4^{4-}$  is a  $Q^0$ ,  $\text{Si}_2\text{O}_7^{6-}$  is a  $Q^1$ ,  $\text{Si}_2\text{O}_6^{4-}$  is a  $Q^2$ ,  $\text{Si}_2\text{O}_5^{2-}$  is a  $Q^3$ , and  $\text{SiO}_2$  is a  $Q^4$ .

When oxygen atoms were found to exist within a separation of the first-nearest neighbour of a silicon, within  $0.165 \pm 0.2$  nm as shown in Figure 3, then it was assumed

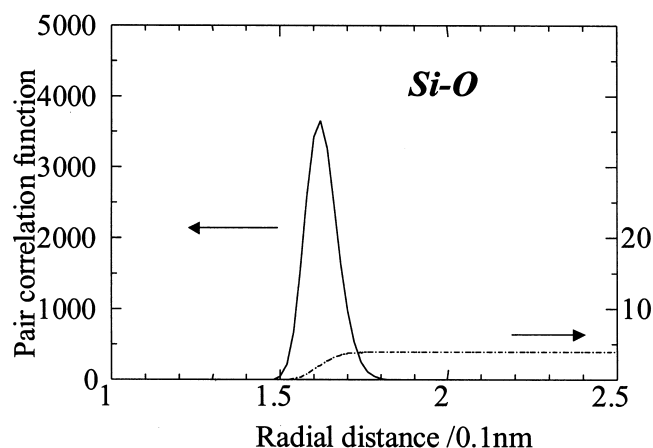


Figure 3. Pair correlation function for Si-O and cumulative O coordination numbers for Si

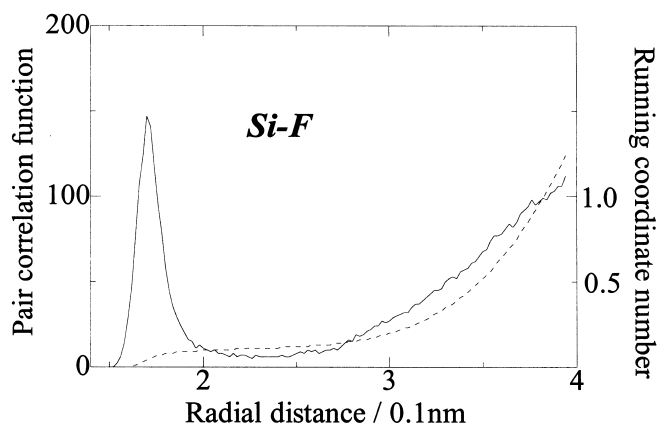


Figure 4. Pair correlation function for Si-F and cumulative F coordination numbers for Si

that Si-O bonds were formed, namely these oxygen atoms were determined to belong to the Si tetrahedral in the MD simulation. The interconnected relations between the Si tetrahedrals were evaluated based on the number of bridging oxygen atoms of each tetrahedral and consequently each Si tetrahedral was classified into five types of structural units ( $Q^0$  to  $Q^4$ ). In this evaluation of the interconnected relation between Si tetrahedrals, the existence of F was neglected, since F was confirmed to play a nonbridging role.

Based on their classified types, their relative distribution ratios were calculated. The calculated distribution of  $Q^i$  ( $i=1$  to  $4$ ) as a function of NaF content are shown in Figure 5. With an increase of F content, the fractions of  $Q^3$  and  $Q^4$  increased, whereas  $Q^2$  and  $Q^1$  decreased. Namely, the polymerization was promoted with increasing of F content just as observed in Raman spectra change. From the results of the Raman spectra measurements and MD simulations, within the present experimental condition, it can be said that the substitution of F for O in the sodium silicate melts enhanced the polymerization of silicate complex anions.

### Discussion

From the Raman spectroscopic results and molecular dynamics simulation, it was confirmed that the substitution of F for O enhanced the degree of the polymerization of melts, at least with the composition of basicity of less than 1 and with NaF content of less than 30 mol%. Luth<sup>9</sup> also found the same tendency for the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system and discussed the mechanism to enhance the polymerization by F substitution. His discussed mechanism is possibly applied to the Na<sub>2</sub>O-NaF-SiO<sub>2</sub> system. Namely, the mechanism consistent with polymerization accompanying the substitution of F for O was formation of loosely bounded Na-F complexes. Formation of such complexes would remove Na<sup>+</sup> from a network-modifying role so that the degree of polymerization was enhanced.

In other words, NaF in the sodium silicate melts worked just as a diluter so that the existence of NaF did not influence the relative distribution of the complex anions of silicate melts. Then, this mechanism predicts that melts along a join from NaF to a point on the Na<sub>2</sub>O-SiO<sub>2</sub> join have the same distribution ratio of the silicate network units, except the relative amount of Na-F complexes. Consequently, the Raman spectra of the silicate melts on

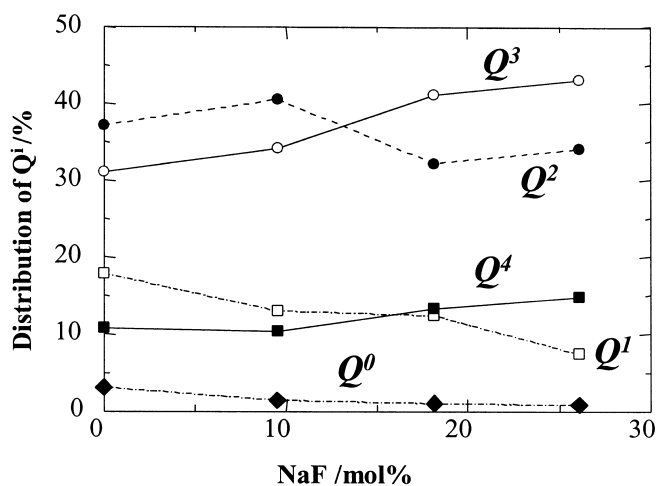


Figure 5. Distribution of  $Q^i$  as a function of NaF

this line can be the same. To confirm this, Raman spectroscopic measurements were carried out for the Na<sub>2</sub>O-SiO<sub>2</sub>-NaF system as a function of NaF. The change in Raman spectra of join Na<sub>2</sub>O-SiO<sub>2</sub>-NaF with different NaF content is shown in Figure 6. Although the relative heights of bands were a little bit different from each other, it can be said that they were basically the same. The distribution of  $Q^i$  ( $i=1$  to  $4$ ) for the Na<sub>2</sub>O-SiO<sub>2</sub>-NaF system as a function of NaF was also calculated and shown in Figure 7. The relative amount of  $Q^i$  was reasonably independent from the increase of NaF content. These results support the previously mentioned polymerization mechanism.

### Conclusions

Based on the investigation of the effect of F ions on the structure of molten Na<sub>2</sub>O-SiO<sub>2</sub>-NaF systems by Raman spectroscopy and molecular dynamics simulation, the following conclusions can be drawn:

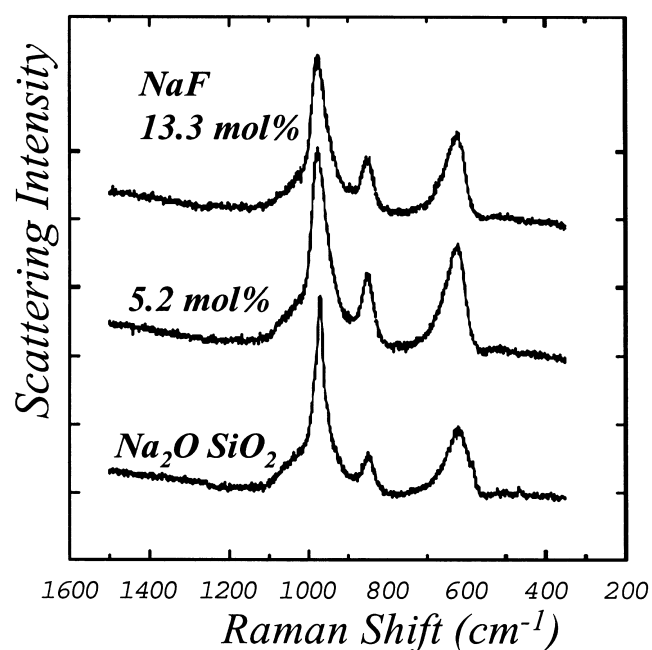


Figure 6. Raman spectra along the join Na<sub>2</sub>O-SiO<sub>2</sub>-NaF

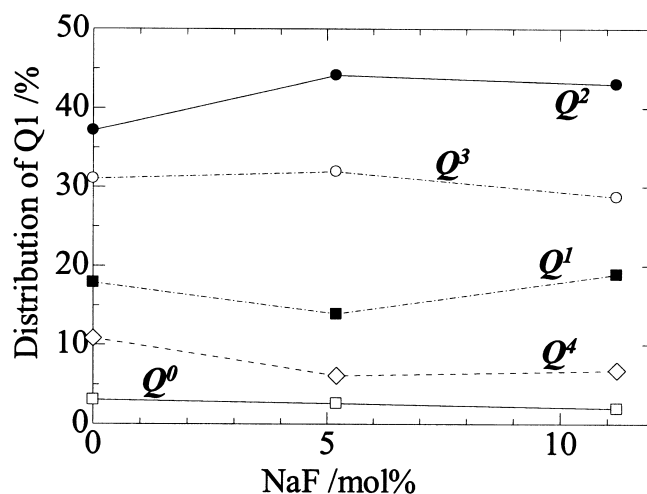


Figure 7. Distribution of  $Q^i$  as a function of NaF for the melts along the join Na<sub>2</sub>O-SiO<sub>2</sub>-NaF

- The intensity of 1100 cm<sup>-1</sup> band in the Raman spectra, corresponding to highly polymerized silicate unit, was increased by the replacement of F for O
- Most of substituted F was found to be mainly coordinated to Na<sup>+</sup> ions but not Si<sup>4+</sup> ions from the molecular dynamic simulation
- From the molecular dynamic simulation, a small amount of F was found to be coordinated to Si and the cumulative coordination number was found to be about 0.1
- From the molecular dynamics simulation and the change of Raman spectra, it was confirmed that the polymerization of melts was enhanced by the substitution of F
- The mechanism consistent with the polymerization development accompanying the substitution of F for O is formation of loosely bounded Na-F complexes.

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### References

1. MYSEN, B.O. *Structure and Properties of Silicate Melts*, Elsevier, New York, 1988, pp. 247–253.
2. TSUNAWAKI, Y., IWAMOTO, N., HATTORI, T., and MITSUISHI, A.J. Analysis of CaO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> glasses by Raman spectroscopy. *Non-Crystal. Solids*, vol. 44 1981, pp. 369–378.
3. MOHRI, M., SASAKI, Y., and ISHII, K. Cooperative roles of Al<sup>3+</sup> and Fe<sup>2+</sup> ions for network construction in sodium silicate melts. *ISIJ Int.*, vol. 41 2001, pp. 410–415.
4. KAWAMURA, K. MXDORTH program. Japan Chemistry Program Exchange, No. 076.
5. BUSING, W.R. Interpretation of the crystal structure of Li<sub>2</sub>BeF<sub>4</sub> in terms of the Born-Mayer-Huggind model. *J. Chem. Phys.*, vol. 57 1972, pp. 3008–3010.
6. HIRAO, K. and KAWAMURA, K. *Material Design using Personal Computer*, Shokabo, Tokyo, 1994, pp. 52–54.
7. MCMILLAN, P. Structural studies of silicate glasses and melts-applications and limitations of Raman spectroscopy. *Amer. Miner.*, vol. 69 1984, pp. 622–644.
8. KAWAMOTO, K., HORISAKA, T., HIRAO, K., and SOGA, N. A molecular dynamics study of barium meta-fluorozirconate glass. *J. Chem. Phys.*, vol. 83 1985, pp. 2398–2404.
9. LUTH, R.W. Raman spectroscopic study of solubility mechanism of F in glasses in the system CO-CaF<sub>2</sub>-SiO<sub>2</sub>. *Amer. Mineral.*, vol. 73 1988, pp. 297–305.

