The Effect of Fe$^{3+}$ Ions on the Anionic Structure of Iron-bearing Sodium Silicate Melts

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(Received on July 13, 2000; accepted in final form on September 11, 2000)

The effects of the coordination of iron ions on the anionic structure of molten iron-bearing sodium silicate slags at 1273 K have been investigated by Raman spectroscopy. The Raman spectra of Na$_2$O–SiO$_2$–FeO–Fe$_2$O$_3$ system equilibrated with various oxygen pressures (p$_{O_2}$) have been measured. The effect of the concentration of iron oxide on the Raman spectra of these systems has also been studied.

Under low p$_{O_2}$ conditions (CO$_2$/CO=10), the Raman spectra of Na$_2$O–2SiO$_2$–FeO–Fe$_2$O$_3$ are essentially the same as that of Na$_2$O–2SiO$_2$. However, under high p$_{O_2}$ conditions (CO$_2$/CO>54), a new Raman band of around 900 cm$^{-1}$ appears and its intensity increases with increase of p$_{O_2}$ and iron oxide content. The scattering intensity at low frequency region (<550 cm$^{-1}$) also becomes intense with increase of the iron oxide content.

It is confirmed that the near 900 cm$^{-1}$ band can be attributable to the network structure involving Fe$^{3+}$ ions. Fe$^{3+}$ ions in the metasilicate melts is found to conjugate the chain units and produce the sheet and monomer units. In the disilicate melts, it will conjugate the sheet units and produce the chain and three-dimensional network units.

KEY WORDS: Raman spectroscopy; molten sodium silicate; network; structure; tetrahedral coordination; three-dimensional network.

1. Introduction

Numerous studies$^{1-9}$ have used Raman spectroscopy to investigate the structure of silicate glasses and melts, and many of them have been applied to understand properties important in metallurgical and geochemical processes. Although there are extensive literature dealing with structures and properties of silicate glasses, most of studies have been restricted to systems not containing iron oxides in spite of the practical importance of iron oxide-containing slags. The influence of the redox ratio of iron ions on the Raman spectra of these systems has also been studied.

The coordination of iron ions on the properties of silicate melts is quite complex, because the iron ion may not respond simply to variations in melt structure; rather it may affect the melt structure itself. Furthermore, iron in a melt can play a dual role because iron ions can be both tetrahedrally and octahedrally coordinated. The coordination of the iron ions is controlled by an involved interrelationship between the degree of polymerization of the silicate, the types of cation present, the amount of iron ion present and the oxygen potential.

Depending on the coordination states of iron ions, the amount of oxygen coordinated by iron ions or that of free oxygen will be changed. As a result, variation of redox ratios of iron will change the degree of polymerization of the melt and therefore the viscosity, the cation diffusion coefficients and the reactivity of slags. Therefore, understanding of the role of iron ions in silicate melts is very important for fundamental reasons and for practical uses, since commercial steelmaking slags always contain iron ions.

The study of the Fe ions in the molten silicate have been mainly concerned with the coordination of the Fe ions. Hirao et al.$^{10}$ investigated the Fe$^{3+}$ coordination in alkali iron silicate glasses using Mössbauer spectroscopy and they confirmed that Fe$^{3+}$ ions in silicate glasses tetrahedrally coordinated, which agreed with the conclusion reported by Kurkjian and Sigety$^{11}$ who studied the coordination of Fe$^{3+}$ in silica glasses with low iron contents. Iwamoto et al.$^{12}$ studied the coordination of Fe ions in CaO–SiO$_2$–10mol%Fe$_2$O$_3$ glasses using Mössbauer spectroscopy. Fe$^{2+}$ was found to be always present in octahedral sites, while Fe$^{3+}$ occupied both octahedral and tetrahedral sites. The same conclusion was reached by Pargamin et al.$^{13}$ Mysen et al.$^{14}$ measured the redox equilibrium and the coordination states of iron in alkali silicates under different oxygen potentials and alkaline-earth silicate melts with different cation ratios of Ca/Mg in air using Mössbauer spectroscopy. Their Mössbauer spectroscopic results indicated that, in the system Na$_2$O–FeO–Fe$_2$O$_3$–SiO$_2$, Fe$^{3+}$ iron was in tetrahedral coordination, and the Fe$^{2+}$ was octahedrally coordinated with oxygen ions. In the system CaO–MgO–FeO–Fe$_2$O$_3$–SiO$_2$, however, both Fe$^{3+}$ and Fe$^{2+}$ were octahedrally coord-
dinated. Based on these results they suggested that only alkali ions can stabilize Fe\textsuperscript{3+} iron in tetrahedral coordination, but not alkaline-earth.

Mössbauer spectroscopic results can provide the coordination state of iron ions in silicate melts, but the technique is not suitable for correlating the coordination state of iron ions with the framework of silicate structure or degree of polymerization. For this purpose, Raman spectroscopy is very suitable. Mysen et al.\textsuperscript{3} used Raman spectroscopy to study the anionic structure of alkali silicate melts on the join Na\textsubscript{2}SiO\textsubscript{3}–NaFeSi\textsubscript{2}O\textsubscript{6} at 1 400 K in air. As they measured Raman spectra along the join Na\textsubscript{2}SiO\textsubscript{3}–NaFeSi\textsubscript{2}O\textsubscript{6}, each measured sample has different Na/Si ratio and total Fe content. In this case, the change of Raman spectra was contributed from several factors. Thus it is not easy to evaluate the role of Fe ion precisely. Namely, to study the effect of Fe ions on the structure of melts, it is preferable to study the melts of constant composition in which only the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio is varied.

The present work was undertaken to investigate the role of iron ions on the framework of molten alkali silicate structures by applying Raman spectroscopy. This has been achieved for a quenched Na\textsubscript{2}O·2SiO\textsubscript{2}–FeO–Fe\textsubscript{2}O\textsubscript{3} melts containing up to about 9 mol\% Fe\textsubscript{2}O\textsubscript{3} with varying oxygen potential from about 10–12 to 0.025 MPa and on the join Na\textsubscript{2}O·2SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}·2SiO\textsubscript{2} system (constant SiO\textsubscript{2} of 50 mol\%) with varying Na\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3} ratio with air.

2. Experimental Detail

2.1. Sample Preparation

Na\textsubscript{2}O–SiO\textsubscript{2}–FeO–Fe\textsubscript{2}O\textsubscript{3} glasses for this study were made in two stages. Appropriate portions of reagent grade Na\textsubscript{2}CO\textsubscript{3}, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} were ground together in an agate mortar in air and placed in a Pt crucible. The mixture was heated at 1 073 K for 3 h, and then fired in a muffle furnace at 1 273 K for 2 h. The melted mixture was quenched into a water-cooled copper flat mold and then ground to form a powder. This treatment was repeated twice to ensure homogeneity.

The initial compositions of Na\textsubscript{2}O–SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3} system are presented in Table 1. The silicate melts in the present study actually contained FeO or Fe\textsuperscript{2+} ion. But the slag compositions are represented by initial compositions for convenience.

2.2. Equilibration

The Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio in the Na\textsubscript{2}O·2SiO\textsubscript{2}–FeO–Fe\textsubscript{2}O\textsubscript{3} sample was fixed by controlling the CO\subscript{2}/CO ratio. CO\subscript{2} and CO gas were dried by passage through silica gel and magnesium perchlorate, and the CO was passed through ascalete to remove any residual CO\subscript{2}. The gases were mixed in the required ratios using mass flow controllers and passed at the rate of 500 ml/min into the equilibration furnace. The Pt crucible (ID=5 mm, height=5 mm) containing about 50 mg of sample was suspended by means of a Pt suspension wire in the hot zone of the resistance furnace, controlled to ±5 K.

The Na\textsubscript{2}O·2SiO\textsubscript{2}–FeO–Fe\textsubscript{2}O\textsubscript{3} sample was equilibrated with CO–CO\subscript{2} gas mixtures of CO\subscript{2}/CO ratio ranging from 1 to 800 and in air at 1 273 K for 24 h in the resistance furnace and then the Pt crucible was quenched by rapidly lowering the Pt wire onto the water-cooled endcap. This equilibrated quenched sample was immediately used for the Raman spectroscopy measurements to avoid the absorption of water from the atmosphere. As a preliminary experiment, Raman spectra were measured by varying the equilibrating period of 1, 2, 6, 24 hrs. It was observed that the Raman spectra did not change after 2 hrs. Based on this result, all samples were equilibrated for 24 hrs. Premixed cylinder gas (Ar–10%CO–15%CO\subscript{2}) was used directly for the equilibration.

2.3. Raman Spectroscopy Measurement

Raman spectra of quenched glasses were obtained with an automatic micro-Raman system (JASCO NRS-2000). Silicate samples in the Pt crucibles were excited by the 514.5 nm line of a coherent Ar laser (NEC GLG-2162) operating at 100 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 spectra were measured for all samples and several spectra from each sample were measured for each composition. No detectable change in Raman spectra occurred for the same composition. All spots used for micro-Raman analysis were examined for laser damage immediately following the runs and detectable damages were not observed.

3. Results

3.1. The Effect of Oxygen Potential

Observed Raman spectra from Na\textsubscript{2}O·2SiO\textsubscript{2}–4.0 mol% Fe\textsubscript{2}O\textsubscript{3} (as an initial composition) samples equilibrated with various oxygen potentials (pO\textsubscript{2}) from about 0.25 to 10\textsuperscript{−12} MPa at 1 273 K are shown in Fig. 1. These melts differ only in Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio. In Fig. 1, the spectrum of Na\textsubscript{2}O·2SiO\textsubscript{2} is also shown as a reference. In each spectrum, there are intense slightly asymmetric bands near 1 100 and 600 cm\textsuperscript{−1} and a relatively weak band in the region of 950 cm\textsuperscript{−1}. The frequencies of these bands are virtually independent of the CO\subscript{2}/CO ratio. With increasing of

| Composition | Na\textsubscript{2}O | SiO\textsubscript{2} | Fe\textsubscript{2}O\textsubscript{3} |
|-------------|----------------|----------------|----------------|
| 25.0        | 75.0           | 0.0            |               |
| 33.3        | 66.6           | 0.0            |               |
| 39.0        | 61.0           | 0.0            |               |
| 50.0        | 50.0           | 0.0            |               |
| 33.2        | 66.4           | 0.4            |               |
| 32.6        | 65.4           | 2.0            |               |
| 32.0        | 64.0           | 4.0            |               |
| 30.4        | 60.9           | 8.7            |               |
| 27.7        | 66.6           | 5.5            |               |
| 22.2        | 66.6           | 11.1           |               |
| 50.0        | 50.0           | 0.0            |               |
| 46.8        | 50.0           | 3.2            |               |
| 43.7        | 50.0           | 6.3            |               |
| 37.5        | 50.0           | 12.5           |               |
pO₂ (CO₂/CO >10), the 600 cm⁻¹ band is skewed and the peak position of 600 cm⁻¹ band shifts to lower frequency. This may be due to the development of unresolved other bands near 600 cm⁻¹ with increase of CO₂/CO ratio. The most notable change with CO₂/CO ratio is the appearance of a new band of around 900 cm⁻¹ at CO₂/CO ratio >56 and the intensity of which increases with CO₂/CO ratio. At CO₂/CO ratio <10, the relative intensities of the bands of each sample are only slightly changed, and these spectra are qualitatively the same as that of the binary Na₂O·2SiO₂. It suggests that the distribution of consisted anions in these melts (at CO₂/CO ratio<10) is not much different from each other.

3.2. The Effect of Iron Oxide Content

The Raman spectra of Na₂O·2SiO₂–Fe₂O₃ system containing from 0.4 to 8.7 mol%Fe₂O₃ equilibrated with air are shown in Fig. 2. In these samples, their basicities are almost constant. In Fig. 2, the 900 cm⁻¹ band is not seen in the Na₂O·2SiO₂–0.4 mol%Fe₂O₃. In the Na₂O·2SiO₂–2.0 mol%Fe₂O₃ system, the 900 cm⁻¹ band is observed as a shoulder, and it becomes dominant with increase of Fe₂O₃ content. These results strongly suggest that near 900 cm⁻¹ band is closely related to the existence of Fe³⁺ ions. It is also found that the 900 cm⁻¹ band observed in Na₂O·2SiO₂–2 mol%Fe₂O₃ and 4 mol%Fe₂O₃ has shifted to 920 cm⁻¹ in Na₂O·2SiO₂–8.7 mol%Fe₂O₃. The scattering intensity at low frequency region (<550 cm⁻¹) also becomes intense with increase in the iron oxide content.

4. Discussion

4.1. Assignments of Bands

As shown in Fig. 1, the spectra of Na₂O·2SiO₂–4.0 mol%Fe₂O₃ under reduced condition (CO₂/CO ratio< 10) are almost the same as that of the Na₂O·2SiO₂ system. They have the same major bands of 1100, 950 and 600 cm⁻¹, although their relative intensities are slightly changed. It means that the complex anions in these melts are essentially the same, although the amount of complex anions may be slightly different. Thus the introduction of Fe²⁺ in the melt basically doesn’t change the framework of
Table 2. Raman frequencies of the stretching vibrations of specific anionic structural units in silicate melts.

| Silicate anions | NBO/Si | Frequency (cm⁻¹) | Structural unit |
|-----------------|--------|------------------|-----------------|
| SiO₄²⁻           | 4      | 850-880          | monomer         |
| Si₂O₅²⁻          | 3      | 900-920          | dimmer          |
| Si₃O₇⁴⁻          | 2      | 950-980          | chain           |
| Si₄O₉⁴⁻          | 1      | 1050-1100        | sheet           |
| Si₂O₅²⁻          | 0      | 1060, 1190       | 3-D network     |

Na₂O·2SiO₂ system.

Figure 3 shows the measured Raman spectra of the Na₂O·SiO₂ binary system as a function of Na₂O content up to metasilicate composition. The Raman spectra of the Na₂O·SiO₂ binary system have been widely investigated and the present measured results are essentially the same as those already reported.²,⁴,⁵ Assignments of main bands are the most generally accepted in the literature.¹,⁸,¹⁴ Namely, the 1100, 950 and 850 cm⁻¹ bands are due to symmetric "O-Si-O" (e.g., Sheet structure), "O-Si-O" (e.g., chain structure) and Si-O²⁻ (monomer unit) stretch vibration respectively. NBO(Non bonding oxygen)/Si of simple ring structure will be 2, and that of branched chain may vary from 2 to 1. The existence of ring and branched chain is still uncertain. Presumably these units did not exist at least in significant amount.¹¹ Therefore, just as a convenience, the structure units with NBO/Si=1 and 2 have been referred to as a sheet and chain in the present study. The band around 600 cm⁻¹ is assigned to the bending motion of Si–O–Si. In Table 2, the major band corresponding to the anionic units are shown on the basis of the average NBO/Si by summarizing the published data.¹,⁸,¹⁴ For some weak peaks, however, assignments are still ambiguous. In this study, however, we do not examine the assignments of weak bands.

The most interesting aspect of compared the Raman spectra in Fig. 1 with those of Fig. 3 is that there is no band at around 900 cm⁻¹ in the binary Na₂O·SiO₂ system that is observed in the Na₂O·2SiO₂·FeO·Fe₂O₃ system under high pO₂ conditions (CO₂/CO ratio>56). There have been several studies of the pO₂ dependence of Fe³⁺/Fe²⁺ ratio in Na₂O·Si₂O₅·FeO·Fe₂O₃ system.¹³,¹⁵-¹⁷ From all these results, it can be safely estimated that the iron ions in Na₂O·Si₂O₅·FeO·Fe₂O₃ system equilibrated with air are mostly Fe²⁺. As shown in Fig. 1, the near 900 cm⁻¹ band in Na₂O·Si₂O₅·FeO·Fe₂O₃ system becomes dominant under oxidizing condition (CO₂/CO>56). Therefore, the near 900 cm⁻¹ band can be related to Fe³⁺ ion. Thus, differed from the case of Fe²⁺ ions, the introduction of Fe³⁺ ions seems to change the anionic structure significantly. However, it is not certain whether the near 900 cm⁻¹ band is attributed to the Fe³⁺ contained units themselves or newly produced silicate units due to the Fe³⁺ ion introduction.

It has been well known that the major band of 900 cm⁻¹ was not observed in alkali silicate system, but has only been explicitly observed for the alkaline earth silicate²,³,¹⁴ and is interpreted as being due to the presence of dimmer structural units (Si₃O₉²⁻) in the melt. The 900 cm⁻¹ band is maximized in relative intensity near the pyrosilicate composition of the alkaline earth silicates²,³,¹⁴ and is only resolved for a narrow range of compositions near the pyrosilicate. The presence of 900 cm⁻¹ band in higher silica glass spectra was deduced from band deconvolutions,²⁹ and is first recognized by this method between the metasilicate and disilicate. The Si₂O⁷⁻ ions may also exist in Na₂O–SiO₂–FeO–Fe₂O₃ melts, but it does not exist in significant amount and only possible in compositions closed to the pyrosilicate composition. Namely, there is least possibility that 900 cm⁻¹ band in the composition of the present study is directly related to Si₂O⁷⁻ ions.

If the dimmer units are produced by the increase of Fe³⁺, the degree of the polymerization in the melt must be decreased with Fe³⁺ and consequently the viscosity of the melt can be decreased. Digwell and Virgo¹⁸ measured the viscosity of Na₂O·Si₂O₅·FeO·Fe₂O₃ melts with varying pO₂, and found that the viscosity increased with Fe³⁺ content. Their result¹⁸ suggests that the introduction of Fe³⁺ does not produce the dimmer units in the melt. Furthermore, as already mentioned, all Mössbauer spectroscopic results¹,¹⁰-¹³ indicated that Fe³⁺ ion in Na₂O·FeO·Fe₂O₃–SiO₂ system was in tetrahedral coordination. The tetrahedral coordination of Fe³⁺ generally means that Fe³⁺ ion behaves as a network former, but not network modifier. Therefore, in the present study, the dimmer units do not exist enough amounts to produce the 900 cm⁻¹ band. Combined all these results, it can be confirmed that the near 900 cm⁻¹ band in the present study is not originated from the dimmer units, but can be attributed to the network structure unit involving Fe³⁺ ions.

4.2. Three-dimensional Network Structure

Another interesting aspect in the present study is the increase in the scattering intensity at the low frequency region with pO₂ and Fe₂O₃ content (see Figs. 1 and 2). A three-dimensional array of SiO₂ tetrahedra causes a strong broad band near 430 cm⁻¹ and a sharp band near 480 cm⁻¹.¹³,¹⁹-²⁰ These bands between 400 to 500 cm⁻¹ are due to the vibration of Si–O¹⁰ bond (O¹⁰ is bridging oxygen). The broad band around 500 cm⁻¹ is also observed in melts with a three-dimensional network structure on the join CaAl₂O₄–SiO₂ and NaAl₂O₄–SiO₂, and is considered characteristic of melts with a three-dimensional network unit.²⁰ Therefore, the increase in the intensity in the low frequency region in the present work implies that the Fe³⁺ introduction may develop a Si–O¹⁰ bonds or a three-dimensional network structure involving Fe³⁺ ions.

Hirao et al.¹⁹ measured the coordination state of Fe³⁺ in leucite type iron silicate glasses on the join Na₂O·2SiO₂·FeO·Fe₂O₃ (⁵(Na₂O)₈·(Fe₂O₃)₄·2SiO₂))) x=0.15-0.65) and crystals by using Mössbauer technique. Crystalline KFeSi₂O₆ (iron leucite), CsFeSi₂O₆ (iron polleucite) and KFeSi₂O₆ (iron feldspar) are known to contain Fe³⁺ in tetrahedral coordination,²¹ whereas NaFeSi₂O₆ (acmite) crystalline contains Fe³⁺ in octahedral coordination.²²,²³ They found that the isomer shift and quadrupole splitting values for the alkali iron silicate glasses were unlike those of crystalline NaFeSi₂O₆, but were similar to that of cubic crystalline CsFeSi₂O₆. The cubic crystalline CsFeSi₂O₆ has a complete three-dimensional network of linked tetrahedra similar to those of the various forms of silica, but involving
Fe$^{3+}$ ions with coordination number 4 as well as silicon ions. Therefore, their results also strongly suggests that the state of Fe$^{3+}$ in the alkali iron silicate glasses is very similar to that of Fe$^{3+}$ in the cubic lattice of a crystalline compound having a three-dimensional network structure and the alkali iron silicate glasses will have the three-dimensional network structure involving Fe$^{3+}$.

Their results suggest that the Raman spectra of CsFeSi$_2$O$_6$ polycrystalline involving Fe$^{3+}$ ions will be the same to that of alkali iron silicate glasses. To confirm this, the Raman spectra of CsFeSi$_2$O$_6$ polycrystalline and quenched alkali iron silicate glasses are measured and results are shown in Fig. 4. CsFeSi$_2$O$_6$ polycrystalline was prepared by mixing the reagent grade Cs$_2$CO$_3$, SiO$_2$, Fe$_2$O$_3$ powder and heated the mixtures at 1 073 K for 3 h, and then fired in a muffle furnace at 1 523 K for 4 h. The sintered mixture was ground to form powder and heated again to ensure homogeneity.

It is clearly shown that they have the same band of around 920 cm$^{-1}$ band that is supposed to originate from the Fe$^{3+}$ ion involving network structure. This is another strong evidence that the quenched alkali iron silicate glasses also have the three-dimensional network structure. Compared with the Raman spectra of these two samples, the band corresponding to the three-dimensional network structure involving Fe$^{3+}$ can be the band of 920 cm$^{-1}$. Namely the 920 cm$^{-1}$ band is asymmetric and has a shoulder at about 900 cm$^{-1}$.

As already shown in Fig. 3, the 900 cm$^{-1}$ band seems to shift to 920 cm$^{-1}$ with increase of Fe$_2$O$_3$ content. If this shift is associated to the change of the Si/Fe ratio in the three-dimensional network structural unit, the 900 cm$^{-1}$ band may be corresponding to the (Fe, Si)--O$^{0}$ stretching of low Fe content three-dimensional network structural unit, or close to the Si--O$^0$ stretching. In pure SiO$_2$ glass, however, the band around 900 cm$^{-1}$ has not been observed. Mysen et al. also observed 900 cm$^{-1}$ Raman band on the join Na$_2$SiO$_3$–NaFeSi$_2$O$_6$ at 1 400 K in air and it was interpreted to be consisted of two bands of the (Fe, Si)--O$^0$ stretch (920 cm$^{-1}$) and highly coupled O--(Fe, Si)--O$^0$ stretch vibration (880 cm$^{-1}$). There is no doubt that 900 cm$^{-1}$ is related to the units involving Fe$^{3+}$, but there has been no clear evidence to determine the origin of 900 cm$^{-1}$ at this moment. Tentatively we also accept their interpretation as a most plausible one, but further work is necessary to firmly establish the origin of 900 cm$^{-1}$. If so, the O--(Fe, Si)--O$^0$ stretch vibration will be governing with increase of Fe$_2$O$_3$.

As shown in Fig. 2, relative intensity of 1 100 cm$^{-1}$ band seems to decrease with increase of Fe$_2$O$_3$. Since the SiO$_2$ content was also decreased with increase of Fe$_2$O$_3$ content, it is not certain whether the decrease of 1 100 cm$^{-1}$ band is attributable to the decrease of SiO$_2$ content or the effects of Fe$_2$O$_3$. To confirm this, Raman spectra of the melts on the join Na$_2$O·2SiO$_2$–Fe$_2$O$_3$·2SiO$_2$ with constant SiO$_2$ of 66 mol% in air at 1 373 K as a function of Fe$_2$O$_3$ are measured and results are shown in Fig. 5.

From Fig. 5, the intensity of 1 100 cm$^{-1}$ band is found to significantly decrease with Fe$_2$O$_3$ content, but that of 950 cm$^{-1}$ seems to increase. Since the 950 cm$^{-1}$ bands are asymmetric and has a shoulder at about 900 cm$^{-1}$, the 950 cm$^{-1}$ band may be consisted of 950 and near 900 cm$^{-1}$ bands. To evaluate the increase of 950 cm$^{-1}$ quantitatively,
the bands in the high frequency region (800 to 1 200 cm$^{-1}$) of $5\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{SiO}_2$, $2\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ systems are deconvoluted with the assumption that the line shape is Gaussian, the background in this region is horizontal and all bands are symmetric. To carry out the deconvolution, tentatively 5 bands of near 1 100, 1 050, 950, 920 and 850 cm$^{-1}$ band are used as initial values to fit inside the high frequency envelope of the spectra. The Raman spectra in the high frequency region of these systems are well reproduced by the combination of these bands. As shown in Fig. 6, near 900 cm$^{-1}$ band (880 and 920 cm$^{-1}$) increases with Fe$_2$O$_3$ just as expected and the 950 cm$^{-1}$ band also increases with Fe$_2$O$_3$.

It means that the amount of sheet units in the melt decreases with Fe$_2$O$_3$ but the chain units may increase, since 1 100 and 950 cm$^{-1}$ band is mainly corresponded to the vibration of sheet and chain structure of silicate anions respectively as indicated in Table 2. The growth of the broad bands at low frequency region (less than 550 cm$^{-1}$) with Fe$_2$O$_3$ is also observed in Fig. 5, and means the development of a Si–O$^0$ bond or a three-dimensional network structure with Fe$_2$O$_3$. Based on these results, it can be confirmed that the three-dimensional and chain structural units are increased but the sheet structural unit is decreased by the introduction of Fe$^{3+}$ ions.

In the melts of around disilicate composition, there will be three major silicate units of chain, sheet and three-dimensional network and they can be related each other with the following equation.

$$2\text{Si}_2\text{O}_5^2^- = \text{Si}_2\text{O}_6^{4+} + \text{2SiO}_2$$

or in the form of

$$2\text{O}^-\text{Si}–\text{O}^0 = \text{O}–\text{Si}–\text{O}^- + 2\text{Si}–\text{O}^0$$

From the results in Fig. 5, the three-dimensional units in the melts may increase but sheet units decrease with increase of Fe$_2$O$_3$. Most plausible explanation of these changes is that Fe$^{3+}$ ions do conjugate the sheet silicate units and create the three-dimensional network units. This reaction may be expressed by arranging the Eq. (1),

$$5^-\text{O}–\text{Si}–\text{O}^0 + \text{Fe}^{3+} \rightarrow \text{O}–\text{Si}–\text{O}^- + 5(\text{Si, Fe})–\text{O}^0$$

In this disproportionation process, to maintain the local charge-balance, the chain units ("O–Si–O") also must be produced along with the production of three-dimensional structure units. The measured and deconvoluted results of Raman spectra with Fe$_2$O$_3$ simply support this disproportionation process. Accordingly, the assumption that the role of Fe$^{3+}$ in the disilicate melts is to conjugate sheet units and produce the three-dimensional network structure appears to be fully consistent with all the results.

From the Raman data for sodium metasilicate melt shown in Fig. 3, there will be two major silicate units of monomer, chain and small amount of sheet units and they can be related each other with the following equation.

$$3\text{Si}_2\text{O}_5^2^- = 2\text{SiO}_4^{2+} + 2\text{Si}_2\text{O}_3^-$$

Assuming the similar reaction mechanism with Fe$^{3+}$ for the sodium metasilicate melt, it can be expected that the sheet unit and monomer will be increased with Fe$^{3+}$, but chain unit may decrease. To investigate this speculation, Raman spectra of the melts on the join Na$_2$O–SiO$_2$–Fe$_2$O$_3$–SiO$_2$ with constant SiO$_2$ of 50 mol% in air at 1 373 K as a function of Fe$_2$O$_3$ were measured and results are shown in Fig. 7. For the Raman spectra of Na$_2$O–SiO$_2$ system, the 950 cm$^{-1}$ band corresponded to the chain unit is shifted to about 970 cm$^{-1}$. From Fig. 7, the intensities of 1 050 and 850 cm$^{-1}$ bands are likely to increase with Fe$_2$O$_3$ content,
but that of 970 cm\(^{-1}\) seems to decrease. It is known that the frequency of the band corresponded to the sheet structural unit changes from 1 100 to 1 050 cm\(^{-1}\) depend on the silicate composition.\(^{5)}\) Take into account of the electric charge and ionic radius of Fe\(^{3+}\) and Si\(^{4+}\), the force constant of Fe–O bond is lower than those of Si–O bond. Since the frequency of Raman bands corresponding to the Fe–O bonds will therefore be lower than those of Si–O bonds, the frequency corresponded to the sheet structural unit will shift from 1 100 to 1 050 cm\(^{-1}\) when some Fe\(^{3+}\) ions entering the silicate sheet unit. Namely, the 1 050 cm\(^{-1}\) band observed in Fig. 7 will correspond to the vibration of sheet unit contains Fe\(^{3+}\) ions. Therefore, the increases of the intensity of 1 050 and 850 cm\(^{-1}\) bands with Fe\(_2\)O\(_3\) content means that the sheet structural units and monomers increase with the increase of Fe\(_2\)O\(_3\). Thus, just as expected, Fe\(^{3+}\) ions in the metasilicate melts are likely to conjugate the chain units and produce the sheet and monomer units.

From these results, it is confirmed that the role of Fe\(^{3+}\) in the molten sodium silicate is to conjugate the consisted silicate anions and consequently produce much larger silicate anion structures. Namely the Fe\(^{3+}\) in silicate melts rearranges the degree of polymerization of the melt and therefore it will significantly influence the viscosity, the cation diffusion coefficients and the reactivity of molten silicate melts. From thermodynamic view point, the role of Fe\(^{3+}\) in the silicate melts can be interpreted as that Fe\(^{3+}\) ion make larger the equilibrium constants of reaction (1) and (3).

5. Conclusions

The Raman spectra of Na\(_2\)O–SiO\(_2\)–FeO–Fe\(_2\)O\(_3\) system at 1273 K have been measured by varying oxygen potential and Fe\(_2\)O\(_3\) content to investigate the effects of iron ions on the anionic structures of molten silicates.

1) The most notable feature of the observed Raman spectra is the appearance of a new band 900–920 cm\(^{-1}\) at above the CO\(_2\)/CO ratio of 56 and its intensity increases with CO\(_2\)/CO ratio and Fe\(_2\)O\(_3\) content. It is also found that the scattering intensity at the low frequency region (<600 cm\(^{-1}\)) is increased with P\(_2\)O\(_5\) and Fe\(_2\)O\(_3\) content.

2) The observed band 900–920 cm\(^{-1}\) is determined to be related to the network structure involving Fe\(^{3+}\) and the 900 cm\(^{-1}\) band is found to shift to 920 cm\(^{-1}\) with increase of Fe\(_2\)O\(_3\) content.

3) The band observed at around 900 cm\(^{-1}\) band may result from the superposition of two bands of the (Fe, Si)–O\(^{-}\) stretch vibration (920 cm\(^{-1}\)) and the O–(Fe, Si)–O\(^{-}\) stretch vibration (880 cm\(^{-1}\)).

4) The main role of Fe\(^{3+}\) ions in the disilicate melts, such as Na\(_2\)O–2SiO\(_2\)–Fe\(_2\)O\(_3\) system, is most likely to conjugate the silicate sheet units and create the three-dimensional network units. In the metasilicate, Fe\(^{3+}\) ion conjugates chain units and produces sheet units.

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