Comparative Roles of Al$^{3+}$ and Fe$^{3+}$ Ions for Network Construction in Sodium Silicate Melts

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The Raman spectra of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system with different Al$_2$O$_3$ contents (up to 25 mol%) and with Na$_2$O/SiO$_2$ ratio from 1 to 2 have been measured at 1673 K.

In the disilicate systems, the Raman spectra do not change significantly with increasing of Al$_2$O$_3$ content except the development of the 500 cm$^{-1}$ band which is assigned to the three-dimensional network structural unit consisted of Si$^{4+}$ and Al$^{3+}$ ions. Also it is found that Al$^{3+}$ ions possibly interact with monomers and form three-dimensional structures.

In the metasilicate systems, intensities of 950 and 850 cm$^{-1}$ bands gradually decrease while that of 1100 cm$^{-1}$ band increases with the increase of Al$_2$O$_3$ content. According to the following equilibrium reaction in the metasilicate composition,

\[ \text{O–Si–O} \text{(chain-like unit)} \leftrightarrow \text{Si–O}^2 \text{(monomer)} + \text{O–Si–O} \text{(sheet-like unit)} \]

it is confirmed that Al$^{3+}$ ions in the metasilicate systems do not interact with the polymerized silicate anions, such as chain-like or sheet-like structural units. On the other hand, it has a high tendency to interact with SiO$_4^{4–}$ and construct three-dimensional network units involving Al$^{3+}$ and Si$^{4+}$ ions randomly. So it is obvious that the role of Al$^{3+}$ ions for constructing the network structure is found to be quite different from that of Fe$^{3+}$.

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

1. Introduction

Sasaki et al.$^{1}$ studied the role of Fe$^{3+}$ for constructing network structures in the sodium silicate melts. They found that the main role of Fe$^{3+}$ ions in the sodium silicate melts is to conjugate the consisted silicate anion units and created more polymerized network units, such as a three-dimensional network structure. Also it is known that Al$^{3+}$ ion has a high ability as a network former. Since Al$_2$O$_3$ is a major constituent of iron and steelmaking slags, the effect of Al$^{3+}$ on the physical and chemical properties of slags has been extensively studied.$^{2–6}$ Riebling$^{3}$ examined the effect of Al$^{3+}$ on the viscosity and molar volume by varying composition of sodium aluminosilicate and concluded that the formation of the three-dimensional cristobalitlike network structure mainly consisted of Al$^{3+}$ ions. Mysen et al.$^{4}$ confirmed the three-dimensional network structure of Al$^{3+}$ tetrahedra in aluminosilicate melts based on the Raman spectroscopy. Sugino$^{5}$ et al.$^{6}$ also studied the structure of Na$_2$O–Al$_2$O$_3$–SiO$_2$ systems by using IR absorption measurement, and confirmed that there was three-dimensional network structure of Al$^{3+}$ tetrahedra.

Based on the previous results,$^{2–7}$ Al$^{3+}$ in the silicate melts is expected to have a similar role of Fe$^{3+}$ in silicate melts. Also it is well known that the viscosity of silicate melts strongly related to the anionic structures.$^{2–4,6–9}$ Fe$^{3+}$ and Al$^{3+}$ ions will have a high efficiency to enhance the viscosity of melts since they work as network formers just as mentioned. The iso-viscosity contours in the Na$_2$O–Fe$_2$O$_3$–SiO$_2$ system at 1573 K$^{10,11}$ and Na$_2$O–Al$_2$O$_3$–SiO$_2$ system at 1773 K$^{12–14}$ are approximately reproduced respectively in Figs. 1(a) and 1(b), and they are qualitatively quite different. This result suggests that the anionic struc-
tures of these melts will be different. In other words, the role of Al$^{3+}$ as a network former in the silicate melts may be qualitatively different from that of Fe$^{3+}$, although both act as network formers.

From this point of view, in the present study, the direct or indirect effects of Al$^{3+}$ ions on the anionic structure of molten silicate slags have been investigated by carrying out the Raman spectroscopy measurement of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system in air with varying the content of Al$_2$O$_3$ and then compared with those of Na$_2$O–Fe$_2$O$_3$–SiO$_2$ system$^{1}$ If the local charge balance is not attained, it will indicate that Al$^{3+}$ may not be in tetrahedral coordination.$^{3-5}$ Therefore, all Raman spectra measurements are dealt with the samples having Na/Al ratio more than 1.

2. Experimental

2.1. Sample Preparation

Sample preparation was described in detail earlier.$^1$ Na$_2$O–Al$_2$O$_3$–SiO$_2$ samples for this study were made in two stages. Appropriate portions of reagent grade Na$_2$CO$_3$, SiO$_2$ and Al$_2$O$_3$ were ground together in an agate mortar in air and poured in a Pt crucible. The mixture was heated at 1 073 K for 10.8 ks and then fired in a muffle furnace at 1 673 K for 7.2 ks. The melted mixture was quenched into a water-cooled copper flat mold and then ground to a powder form. This treatment was repeated twice to ensure homogeneity of samples.

Quenching process of silicate melts was carried out by using hot thermocouple method$^{15}$ to enhance quenching rates. The ground powder was melted as a bead (about 5 mg) at 1 673 K on a Pt–Pt alloy thermocouple wire loop in air and quenched by switching off the power to the hot thermocouple. This procedure produced transparent glassy samples. Details of the hot thermocouple method are given elsewhere.$^{15}$ The initial compositions of the Na$_2$O–Al$_2$O$_3$–SiO$_2$ system are presented in Table 1.

2.2. Raman Spectroscopy Measurement

Raman spectra of quenched 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$^+$ laser (NEC GLG-2162) operating at 300 mW. All the Raman spectra measurements for the samples were made at room temperature. Unpolarized spectra were measured for all the samples and several spectra from each sample were also measured for each composition.

3. Results

3.1. Spectra in Disilicate Composition

The measured Raman spectra of quenched sodium aluminosilicate melts with varying Al$_2$O$_3$ content (up to 11.1 mol%) equilibrated in air at 1 673 K are shown in Figs. 2(b) and 2(c). At the same figure, the spectrum of Na$_2$O–2SiO$_2$ is also shown as a reference (Fig. 2(a)). It can be seen that, in each spectrum, there are intense bands near 1 100 and 600 cm$^{-1}$ and a relatively weak band in the region of 950 cm$^{-1}$. The frequencies of the bands of 1 100, 950 and 600 cm$^{-1}$ are almost independent of the Al$_2$O$_3$ content. The change of the relative intensities of 1 100, 950 and 600 cm$^{-1}$ bands due to the addition of Al$_2$O$_3$ is not so significant, but at the same time the widths of 1 100 and 950 cm$^{-1}$ bands become broader on increasing the Al$_2$O$_3$ content and merge together to some extent. The most notable change with the increase of the Al$_2$O$_3$ content is the appearance of a new band near 500 cm$^{-1}$ and its intensity increases with the Al$_2$O$_3$ content and finally becomes dominant in 2Na$_2$O·Al$_2$O$_3$·6SiO$_2$ system (Fig. 2(c)).

3.2. Spectra in Metasilicate Composition

The Raman spectra of the quenched sodium aluminosilicate melts with varying Al$_2$O$_3$ content equilibrated in air at 1 673 K are shown in Fig. 3. It is noticed that with the increasing of Al$_2$O$_3$ content, the intensity of 950 cm$^{-1}$ band gradually decreases while that of the 1 100 cm$^{-1}$ band increases and finally merge together to form an envelope in the high frequency region.

Also, another notable change is obtained by replacement 1/6 of Na$_2$O by Al$_2$O$_3$ in the Na$_2$O–SiO$_2$ system, the new
band of 570 cm\(^{-1}\) is produced as shown in 5Na\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\) system (Fig. 3(b)). With further increase of Al\(_2\)O\(_3\) to 16.6 mol%, the intensity of 570 cm\(^{-1}\) band increases moreover and another new band of 520 cm\(^{-1}\) band comes appear (Fig. 3(c)). Furthermore, the intensity of 850 cm\(^{-1}\) band decreases with the increasing of Al\(_2\)O\(_3\). On the other hand, the intensity of 620 cm\(^{-1}\) band that is dominant in the Na\(_2\)O·SiO\(_2\) system decreases and it remains only as a shoulder.

4. Discussion

4.1. Assignment of 500 cm\(^{-1}\) Band in Aluminosilicate System

Assignments of main bands in silicate melts are basically established.\(^5,16\) Namely, the 1 100, 950 and 850 cm\(^{-1}\) bands are due to symmetric O–Si–O\(^0\) (e.g., sheet-like structural unit), O–Si–O\(^-\) (e.g., chain-like structural unit) and Si–O\(^2\) (SiO\(_4\)\(^-\) monomer unit) stretch vibration respectively. As a convenience, the bands corresponded to the O–Si–O\(^0\), O–Si–O\(^-\) and Si–O\(^2\) stretch vibrations are referred as those of sheet-like, chain-like and monomer units respectively. In Table 2, the major bands corresponded to the anionic units are shown on the basis of the average NBO (Non bridging oxygen)/Si by summarizing the published data.\(^5,16\)

The 500 cm\(^{-1}\) band observed in Fig. 2 and Fig. 3 has not been observed in the sodium silicate binary system. It can be related to the structures involving Al\(^{3+}\) ions, because its intensity increases with the increase of Al\(_2\)O\(_3\) content.

It is well known that the Al\(^{3+}\) ion plays a key role to construct the three-dimensional (referred as 3-D) structures of aluminosilicate systems, such as albite (Na\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\)) and carnegite (Na\(_2\)O·Al\(_2\)O\(_3\)·2SiO\(_2\)) crystals.\(^5\) They have the complete framework of linked tetrahedra similar to the forms of silica, but randomly involving Al\(^{3+}\) ions with the coordination number 4 as well as Si\(^{4+}\) ions.\(^17\)

It is reasonable to assume that molten albite may have the three-dimensional tetrahedral framework. By using X-ray diffraction, Taylor and Brown\(^19\) investigated the structures of molten and crystal albite and confirmed the presence of similarities between the structures of molten and crystal albite.

Enthalpy and entropy of fusion for albite is relatively high up to 63 kJ/mol and 46 J/(mol · K), respectively.\(^19\) It suggests that the structural difference between molten and crystal albite is not negligible. Therefore, the molten albite may not have the near complete tetrahedral framework, but possibly small amount of chain-like and sheet-like units may be incorporated to the melts with the three-dimensional structure in the main.

In order to investigate silicate structural units in the melt of albite composition, the Raman spectra of quenched Na\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\) glass were measured and the result is shown in Fig. 4. There are very dominant 500 cm\(^{-1}\) band and a weak broad envelope around 1 050 cm\(^{-1}\). The band around 1 050 cm\(^{-1}\) can be attributed to the overlapping of 1 100 and 950 cm\(^{-1}\) band. Just as mentioned, the melt of albite composition will be consisted of the three-dimensional structure in the main and small amount of sheet-like and chain-like units may be incorporated to the melts with the three-dimensional structure in the main.

Based on this result, the dominant 500 cm\(^{-1}\) band observed for the alumino-silicate system as shown in Fig. 2, Fig. 3 can be also attributed to the three-dimensional network structure consisted of Si\(^{4+}\) and Al\(^{3+}\) ions.

![Fig. 3. Raman spectra of quenched sodium alumino-metasilicate melts in air at 1 673 K.](image)

![Fig. 4. Raman spectra of quenched Na\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\) melts at 1 673 K.](image)

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| Silicate anions | NBO/Si | Frequency (cm\(^{-1}\)) | Structural unit |
|---------------|--------|------------------------|-----------------|
| SiO\(_4\)^+   | 4      | 850-880                | monomer         |
| Si\(_2\)O\(_6\)^- | 3      | 900-920                | dimmer          |
| Si\(_3\)O\(_8\)^- | 2      | 950-980                | chain           |
| Si\(_4\)O\(_8\)^- | 1      | 1050-1100              | sheet           |
| SiO\(_2\)     | 0      | 1060, 1190             | 3-Dimensional   |

Table 2. Raman frequencies of the stretching vibrations of specific anionic structural units in silicate melts.\(^1,8,14\)
4.2. Role of Al\textsuperscript{3+} in Disilicate Composition

In the previous study,\textsuperscript{1) Raman spectra of iron bearing sodium disilicate system containing from 0.55 to 11.1 mol\% Fe\textsubscript{2}O\textsubscript{3} equilibrated in air were measured and they are reproduced in Fig. 5. It indicates that the intensity of 900 cm\textsuperscript{-1} band and that of the broad band at low frequency region (<600 cm\textsuperscript{-1}) increased with Fe\textsubscript{2}O\textsubscript{3}, while that of 1 100 cm\textsuperscript{-1} band decreased. Based on these results, it was concluded that the role of Fe\textsuperscript{3+} ions in the disilicate melts was to conjugate the silicate sheet-like units and created the three-dimensional network units.\textsuperscript{1) From the comparison between the Raman spectra of the Na\textsubscript{2}O · 2Al\textsubscript{2}O\textsubscript{3} · 6SiO\textsubscript{2} system (Fig. 2(c)) and that of Na\textsubscript{2}O · 2Fe\textsubscript{2}O\textsubscript{3} · 6SiO\textsubscript{2} system (Fig. 5(c)), it is obvious that they are quite different. The Raman spectra in the high frequency region (from 800 to 1 200 cm\textsuperscript{-1}) for the sodium aluminosilicate system are not significantly changed with increasing of Al\textsubscript{2}O\textsubscript{3} content, and the dominant change is only observed as the appearance of 500 cm\textsuperscript{-1} band with the increase of Al\textsubscript{2}O\textsubscript{3} content. On the contrary, the relative intensities of 1 050 and 950 cm\textsuperscript{-1} bands in the iron bearing sodium-disilicate system changed drastically with the increase of Fe\textsubscript{2}O\textsubscript{3} content.\textsuperscript{1)}

Very small changes in the intensities of 1 100 and 950 cm\textsuperscript{-1} bands of sodium aluminosilicate system with the increase of Al\textsubscript{2}O\textsubscript{3} content (Fig. 2) means that the amount of sheet-like and chain-like structural units practically do not change with the addition of Al\textsubscript{2}O\textsubscript{3}. This result suggests that Al\textsuperscript{3+} ions in the disilicate composition do not effectively interact with the silicate chain-like or sheet-like units at least up to 11.1 mol\% Al\textsubscript{2}O\textsubscript{3} content which is differed from the case of Fe\textsuperscript{3+}. However, Al\textsuperscript{3+} ions must be interacted with another silicate units, such as monomers or the small three-dimensional clusters, to construct the three-dimensional network. This is due to the increasing in the intensity of 500 cm\textsuperscript{-1} band of the three-dimensional network structural unit involving Si\textsuperscript{4+} and Al\textsuperscript{3+} with the increase of Al\textsubscript{2}O\textsubscript{3} content.

It is reasonable to assume that Al\textsuperscript{3+} ions do not prefer to interact with the small three-dimensional clusters, because the surface structure of the small three-dimensional clusters can be close to that of sheet-like unit. Therefore, Al\textsuperscript{3+} ions possibly interact with monomers, which is not shown by the Raman spectra of Na\textsubscript{2}O · 2SiO\textsubscript{2} system. But such unit must be present in order to maintain the mass balance, although its amount is small.

4.3. Role of Al\textsuperscript{3+} in Metasilicate Composition

Raman spectra of the quenched iron oxide contained sodium-disilicate melts with various content of Fe\textsubscript{2}O\textsubscript{3} equilibrated in air were measured in the previous study,\textsuperscript{1) and were reproduced as in Fig. 6. By comparing the spectra in Fig. 3 and Fig. 6, it is found that the Raman spectra of the quenched sodium alumino-metasilicate and iron bearing sodium metasilicate melts are almost similar to each other. In both systems, the 950 cm\textsuperscript{-1} band gradually decreases and the 1 100 cm\textsuperscript{-1} band increases with the increase of Al\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{2}O\textsubscript{3} content. For the low frequency region, the similar changes of spectra, such as increasing the intensity of 570 cm\textsuperscript{-1} and also the 520 cm\textsuperscript{-1} bands, are observed with the increase of Al\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{2}O\textsubscript{3} content.

Very small changes in the intensities of 850 cm\textsuperscript{-1} band with increasing of Al\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{2}O\textsubscript{3} in these two melts are totally different as shown in the following observations. With the increase of Al\textsubscript{2}O\textsubscript{3} content, the intensity of 850 cm\textsuperscript{-1} band in the sodium alumino-metasilicate system decreases, while in the iron bearing sodium metasilicate system increases. Therefore,

![Fig. 5. Raman spectra of quenched iron bearing sodium disilicate melts in air at 1 573 K.](image1)

![Fig. 6. Raman spectra of quenched iron bearing sodium metasilicate melts on in air at 1 573 K.](image2)
the different roles of Al$^{3+}$ and Fe$^{3+}$ ions on interactions with silicate anions are expected. The mechanism for the intensity increasing of the 850 cm$^{-1}$ band with the increase of Fe$_2$O$_3$ content in the iron-bearing sodium metasilicate system was explained by the interaction between Fe$^{3+}$ ions and chain-like units which was already discussed in the previous study.$^{11}$ Judging from the Raman spectra for sodium metasilicate melts shown in Fig. 3(a), there will be two major silicate units of monomer and chain-like units with a small amount of sheet-like unit (observed as a shoulder) in the sodium metasilicate melt. These silicate anions can be qualitatively related to each other with the following equilibrium reaction,$^{23}$

\[
3\text{Si}_2\text{O}_6^-(\text{chain-like unit}) \rightleftharpoons 2\text{SiO}_4^{2-}(\text{monomer}) + 2\text{Si}_2\text{O}_5^-(\text{sheet-like unit})
\]

or in the form of

\[
\text{\text{-O-Si-O\text{-}}} \rightleftharpoons \text{\text{-O-Si-O\text{-}}} + \text{\text{-O-Si-O\text{-}}} \quad \ldots \ldots \ldots (1)
\]

The decrease in the intensity of 850 cm$^{-1}$ band in the alumino-metasilicate system with the increase of Al$_2$O$_3$ content shown in Fig. 3 means that the amount of monomers in the melt is decreased with increasing Al$_2$O$_3$ content. It implies that the Al$^{3+}$ ions interact with monomers and consume monomers for constructing the three-dimensional structure in the melt. Since the intensity of 1 100 cm$^{-1}$ also increased, it can be reflected that Al$^{3+}$ may interact with chain-like units and form sheet-like units instead of the three-dimensional structure. If so, the amount of monomers must be increased based on reaction (1) as observed in the iron-bearing sodium metasilicate. As shown in Fig. 3, however, the amount of monomers decreases. So it can be said that Al$^{3+}$ ions in the alumino-metasilicate system do not interact with chain-like units.

Once the amount of monomers decrease, the equilibrium reaction (1) will shift to the right hand side and so the chain-like units will be decreased while the sheet-like units will be produced at the same time. This is just the variation of Raman spectra of the quenched sodium alumino-metasilicate melts with increasing of Al$_2$O$_3$ content as shown in Fig. 4.

Thus, the variation of intensities of 850, 950 and 1 100 cm$^{-1}$ bands in alumino-metasilicate melt shown in Fig. 3 can be well explained on the assumption that Al$^{3+}$ ions preferentially interact with monomers and construct the three-dimensional structures just as like in disilicate melts. Mysen et al.$^{21}$ measured the Raman spectra of the join Na$_2$Si$_2$O$_5$–Na$_2$SiO$_3$ melts and concluded that all Al$^{3+}$ entered the three-dimensional network structural unit with up to 10 mol% Al$_2$O$_3$. These conclusions are qualitatively agreed with the present results, although they did not discuss the interaction mechanism of Al$^{3+}$ with silicate anions.

5. Conclusions

To investigate the effects of Al$_2$O$_3$ ions on the anionic structures of molten silicates, the Raman spectra of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system at 1 673 K have been measured by varying Al$_2$O$_3$ content and Na$_2$O/SiO$_2$ ratio. The most notable change of Raman spectra with the increase of the Al$_2$O$_3$ content is the appearance of a new band of 500 cm$^{-1}$ which is related to the three-dimensional network structure involving Al$^{3+}$ and Si$^{4+}$ randomly. Also it is found that Al$^{3+}$ ions in the Na$_2$O–Al$_2$O$_3$–SiO$_2$ system have the preference to interact with monomers and construct the three-dimensional network structures, while as shown previously,$^{11}$ Fe$^{3+}$ ion was found to interact with chain-like or sheet-like units but not with monomers.$^{11}$ Therefore, the roles of Al$^{3+}$ and Fe$^{3+}$ in sodium silicate melts for the network construction are totally different.

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Appendix. Spectroscopic Structural Model of Molten Silicates

Reaction (1) is deduced based on the spectroscopic model$^{2,4,5}$ of molten silicates. A wide range of structural models for molten silicates, such as Bockris model,$^{2}$ the thermodynamic model,$^{20}$ quasicrystalline model$^{21}$ and theoretical model,$^{22}$ have been developed for metal oxide–silica
melts. Such models often rely on several assumptions. Direct determination of local structural geometries and distribution of cations between structural units now can be conducted with considerable confidence. From various spectroscopic methods currently available, it is possible to determine melt and glass structure directly. In principle, this approach is far superior over any other methods as it is the only way which is model-independent, and also, no assumption are needed to describe the atomic structure of materials.

The most important observation made from the assignment of the Raman and IR spectra is that there is a unique set of coexisting anionic structural units for special range of NBO/Si ratio. Observed anionic structural units are already shown in Table 1. The spectroscopic model is developed based on these observations. In comparison to some models of melt structure, this spectroscopic structural model is strikingly simple. Namely it proposes that the silicate melts are mainly consisted of only 5 anionic structural units that are classified by NBO/Si (Table 1).

Based on these observations, the equilibria relating the coexisting anionic units in silicate melts can be expressed with the following equations:

\[
3\text{Si}_4\text{O}_{10}^{5-} \rightleftharpoons 2\text{SiO}_4^{4-} + 2\text{Si}_2\text{O}_5^{3-} \quad \text{(sheet-like)}
\]

and for \(\text{NBO} / \text{Si} > 0\)

\[
2\text{Si}_2\text{O}_5^{3-} \rightleftharpoons \text{Si}_2\text{O}_6^{4-} + 2\text{SiO}_2 \quad \text{(3-dimentional)}
\]

Equivalent relations also have been established by using high temperature NMR spectroscopic results. Previous models of melt structures such as the polymer theory include complex anions such as trimers, tetramers, pentamers, etc., in addition to rings and branched chains. This theory predicts that there is a positive correlation between number of Si in the polymers, proportion of various silicate polymers and bulk NBO/Si of the melt. In Raman spectroscopic studies, such as a correlation would result in a successive increase of the frequency of Si–O stretch bands as the number of Si\(^{4+}\) cations in the polymers increases. On this basis, it would be expected that if anionic structural units between chains and dimmers were formed in the melts, new bands would occur between 900 and 970 cm\(^{-1}\) or bands such as that at 900 cm\(^{-1}\) would shift to higher frequency as a function of NBO/Si of the melt. No such spectroscopic evidence is present in any related published data, and so it can be concluded that structural units between that of a dimmer and that of a chain-like unit do not exist in significant amounts in silicate melts. For ring and branched chain units, there have been no reliable experimental results to confirm their existence.