Effect of Oxidation State of Iron Ions on the Viscosity of Alkali Silicate Melts

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Understanding the changes in viscosity due to the different oxidation states of iron ions is important for simulating phenomena related to molten slags and also for understanding the structure of iron-oxide-containing silicate melts. However, these viscosity changes are not well understood. Here, we show the viscosity changes of $R_2O-SiO_2-Fe_xO$ ($R = Li, Na, \text{ or } K$) melts due to changes in the oxidation states of the iron ions by systematically varying the oxygen partial pressure using several Ar-based gases at 1773 K. The initial compositions of the samples were $30R_2O-60SiO_2-10Fe_2O_3$ (mol%), and the ratio of Fe^{3+} to Fe^{2+} in the $R_2O-SiO_2-Fe_xO$ melts increased with increasing oxygen partial pressure in all samples. Meanwhile, the viscosity of all the $R_2O-SiO_2-Fe_xO$ melts decreased with increasing Fe^{2+} to total-Fe ratio. The data indicate that the increase in the amount of Fe^{2+} ions, which behave as network modifiers, would result in depolymerization of the silicate melts. It should also be noted that the viscosity of the melts increased in the order of alkali cationic radius ($K > Na > Li$) when the ratios of Fe^{2+} to Fe^{3+} in the melts were comparable. This was due to the change in the coordination structure of Fe^{3+} in the melts. Not only the oxidation state of the iron ions but also the coordination structure of Fe^{3+} may be important for understanding the viscosity.

KEY WORDS: viscosity; alkali ferrosilicate melts; redox equilibria of Fe; oxygen partial pressure.

1. Introduction

Iron-oxide-containing silicate melts are important molten materials in various industrial processes carried out at elevated temperature, such as glass making and pyrometallurgical extraction (as slags). They are also major components in many geological processes in the Earth's mantle. In pyrometallurgical processes, the viscosity of the slag is an important physical property for estimating the fluidity of the molten slags and clarifying the reaction kinetics related to the slag at elevated temperature. Since the viscosity of the slag is a structure-sensitive property, viscosity is also important for understanding the microstructure of the slags at elevated temperature.

It is well known that the oxidation state of the iron ions (Fe^{2+} and Fe^{3+}) in silicate melts changes depending on the melting temperature, basicity of the melt, and the oxygen partial pressure.^{1–8)} In particular, the oxidation states of the iron ions in metallurgical slags can easily change depending on the conditions of the processes in which the slags are employed.⁹⁾ In addition, FeO (Fe^{2+}) is known to form octa-

hedra ($Fe^{2+}(6)$) and behaves as a network modifier,¹⁰⁾ while Fe_2O_3 (Fe^{3+}) plays an intermediate role between the network former and the network modifier^{10,11)} since it forms both tetrahedra ($Fe^{3+}(4)$) and octahedra ($Fe^{3+}(6)$). Therefore, the ratio of the Fe^{2+} content to the total amount of Fe ($Fe^{2+}/\text{total-Fe}$) in the melts should affect the viscosity. Viscosity data on iron-oxide-containing slags with different $Fe^{2+}/\text{total-Fe}$ values are important for optimizing the practical operation of high-temperature metallurgical processes.

From this background, several researchers^{12–15)} have studied the effect of $Fe^{2+}/\text{total-Fe}$ on the viscosity of iron-oxide-containing slags. **Table 1** shows a summary of the research works related to the effect of $Fe^{2+}/\text{total-Fe}$ on the viscosity. As shown in Table 1, different effects of $Fe^{2+}/\text{total-Fe}$ on the viscosity were reported by the different researchers. In these previous studies, all the researchers employed CO_2 -based gases to control the oxygen partial pressure. However, it is well known that CO_2 gas easily dissolves into oxide melts when the basicity of the melt is high. Hara *et al.*⁵⁾ mentioned that the $Fe^{2+}-Fe^{3+}$ equilibria of the $BaO-Fe_xO$ system were influenced by CO_2 gas dissolution into the melts. Moreover, Sumita *et al.*¹⁶⁾ reported that the viscosity of the $CaO-Fe_xO$ system increased as CO_2 gas dissolved into the melts. These

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Table 1. Summary of changes in viscosity of iron-oxide-containing melts for different oxidation states of iron ions reported by several researchers.

Authors (year)	System (contact material)	Atmosphere	Results
Kaiura <i>et al.</i> ⁽¹²⁾ (1977)	CaO–SiO ₂ –Fe _x O ternary system (Mo)	CO–CO ₂	Viscosity changed only slightly with Fe ²⁺ /total-Fe
Seki and Oeters ⁽¹³⁾ (1984)	CaO–SiO ₂ –Fe _x O ternary system (Pt–18Rh)	Air and CO ₂	Viscosity increased with Fe ²⁺ /total-Fe
Dingwell ⁽¹⁴⁾ (1991)	(R ₂ O or RO)–SiO ₂ –Fe _x O ternary system (Pt–20Rh)	CO–CO ₂	Viscosity decreased with Fe ²⁺ /total-Fe
Nowok ⁽¹⁵⁾ (1995)	CaO–SiO ₂ –Al ₂ O ₃ –Fe _x O based multicomponent system (Pt)	CO–CO ₂	Viscosity decreased with Fe ²⁺ /total-Fe

two previous reports indicate that utilization of CO₂ gas could make the viscosity change ambiguous.

In the present work, we selected an iron-oxide-containing alkali silicate system for a fundamental study of iron-oxide-containing slags. The effect of the oxygen partial pressure on the viscosity of the melts was examined using the rotating cylinder method. Ar-based gases, which are known to be slightly soluble to silicate melts,⁽¹⁷⁾ were employed to control the oxygen partial pressure when we examined the effect of Fe²⁺/total-Fe on the viscosity. Viscosity changes due to changes in the oxidation states of iron ions and in the kind of alkali oxides present were explored.

2. Experimental

2.1. Sample Preparation

Table 2 shows the initial compositions of the samples used for the viscosity measurements. The samples were prepared from reagent grade SiO₂, Fe₂O₃, Li₂CO₃, Na₂CO₃, and K₂CO₃ powders (supplier: Sigma Aldrich, Inc.). These reagents were precisely weighed to form the given compositions and were thoroughly mixed in a mullite mortar. The mixtures were placed in a Pt crucible and then melted at 1773 K in a resistance furnace for 30 minutes under air. Finally, the melts were quenched on a copper plate. Then, the quenched samples were crushed into powders, and these powders were employed for viscosity measurements. Since alkali carbonates were employed as the raw materials for the samples, there is a possibility that dissolved CO₂ can be present in the quenched samples. Richet and his coworkers^(18,19) have reported the effect of melting temperature on the dissolved CO₂ concentration in the potassium silicate glasses, which were made from K₂CO₃ and SiO₂. Bourgue and Richet⁽¹⁹⁾ reported that the concentration of dissolved CO₂ in the 56.9SiO₂–43.1K₂O (mol%) glass decreased with increasing melting temperature. In their study, dissolved CO₂ concentration in the glass after melting at 1773 K (melting time: 15–30 min) was reported as a small value of 0.22 wt%. In the present study, the samples were also made by melting the mixture of the reagents at 1773 K for 30 min. We believe that the dissolved CO₂ concentration in our samples could be low enough to have only slight influence on the viscosity of its melts.

Table 2. Initial compositions (mol%) of the samples for viscosity measurement.

Sample	SiO ₂	Fe ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O
LSF	60	10	30	–	–
NSF	60	10	–	30	–
KSF	60	10	–	–	30

Fig. 1. Schematic illustrations of (a) the apparatus for viscosity measurement and (b) the dimensions of the crucible and bob.

2.2. Viscosity Measurement

2.2.1. Apparatus

The viscosity of the samples was measured using the rotating cylinder method^(20,21) in the present study. **Figure 1(a)** shows schematic illustrations of a rotating-inner-cylinder viscometer with a gas-tight furnace, which allowed us to do the measurements under well-defined oxygen partial pressures. An electric resistance furnace with six U-shaped MoSi₂ heating elements was employed for heating. An acrylic box mounted on the top of the furnace, as shown in **Fig. 1(a)**, was used to isolate the system from the outside atmosphere during the measurements. The dimensions of the crucible and the bob are illustrated in **Fig. 1(b)**. The crucible and bob employed in the experiments were both of Pt-20 mass%Rh. The relative torque exerted on the inner cylinder (bob) was acquired using a commercial viscometer. The apparent viscosity of the sample was calculated based on the relationship between the viscosity and the relative torque value obtained beforehand using several kinds of silicone oil (viscosity range: 0.10–1.0 Pas) as a reference. After that, the measured apparent viscosity was corrected for the thermal expansion of the crucible and the bob using the following equation:

$$\eta = \frac{\eta'}{(1 + \alpha T)^3} \quad \dots \dots \dots (1)$$

where η , η' , α , and T are the viscosity, apparent viscosity, thermal expansion coefficient, and absolute temperature, respectively.

The viscometer was calibrated at high temperature using standard reference materials for high-temperature viscosity measurements (SRM2 type slags).⁽²²⁾ The chemical compo-

Table 3. Chemical compositions of standard reference materials for high-temperature viscosity measurements (mass%). We employed a standard material composed of the major components in the well-known SRM2.²²⁾

	SiO ₂	Al ₂ O ₃	Li ₂ O	K ₂ O	Na ₂ O	MgO	CaO	TiO ₂	P ₂ O ₅
SRM2	63.70	14.40	20.60	0.13	0.40	<0.10	0.40	<0.10	<0.01
Present study	63.95	14.45	20.67	0.13	0.40	—	0.40	—	—

Fig. 2. Temperature dependence of the viscosity of the standard reference material for high-temperature viscosity measurements. The dashed lines represent $\pm 10\%$ uncertainty from the recommended value²²⁾ for SRM2.

sitions of the standard reference materials are listed in **Table 3**. **Figure 2** shows the temperature dependence of the viscosity for the standard reference material. As shown in Fig. 2, the results of the high-temperature calibration values fit the recommended value well.²²⁾

2.2.2. Procedure

The atmospheres employed in the present study are listed in **Table 4**, including their oxygen partial pressures. The oxygen partial pressures were examined using a ZrO₂–CaO oxygen probe. We measured the viscosity under continuously varying oxygen partial pressures by changing the atmospheres in the sequence of air, Ar–1%O₂, Ar, high-purity Ar, and Ar–1%H₂.

The sample powders were placed in the Pt-20 mass%Rh crucible and heated up to 1 773 K under air. Then, the inner cylinder (Pt-20 mass%Rh bob) was immersed in the sample melts, after which we started turning the inner cylinder to monitor the relative torque. The viscosity of the sample melts could be continuously collected during the melting time. We changed the atmosphere after the viscosity of the samples melts became constant under each atmosphere. The experimental conditions used for the viscosity measurements are listed in **Table 5**. The errors in the viscosity measurements were within $\pm 5\%$.

After the viscosity measurements, the crucible was removed from the bottom of the furnace. Then the sample melt was poured on a copper plate and quenched to a glass by pressing with another copper plate. We chemically analyzed the quenched samples. **Table 6** shows the final compositions of the samples with analyzing method. The amount of each component changed only slightly during the

Table 4. Oxygen partial pressures of the atmospheres employed for the viscosity measurements. The oxygen partial pressures of the Ar-based gases were determined using a ZrO₂–CaO oxygen probe.

Atmosphere	Air	Ar–1%O ₂	Ar	High-purity Ar	Ar–1%H ₂
$p(\text{O}_2)/\text{atm}$	2.0×10^{-1}	1.3×10^{-2}	7.1×10^{-5}	3.2×10^{-6}	1.6×10^{-10}

Table 5. Experimental conditions for the viscosity measurements.

Temperature	1 773 K
Atmospheres	Air, Ar–1%O ₂ , Ar, high-purity Ar, Ar–1%H ₂
Sample weight	50.0–70.0 g
Immersion depth of inner cylinder	10.0 mm
Revolution speed of inner cylinder	30 rpm

Table 6. Chemical compositions (mol%) of the samples after the viscosity measurements. The samples were quenched from 1 773 K after the viscosity measurements.

Sample	SiO ₂ ^a	Fe ₂ O ₃ ^b	Li ₂ O ^c	Na ₂ O ^c	K ₂ O ^c
LSF	60.33	9.73	29.94	—	—
NSF	60.01	9.96	—	30.03	—
KSF	59.72	9.43	—	—	30.85

^a SiO₂ content was analyzed using gravimetry.

^b Iron oxide content was expressed as Fe₂O₃ content, which was calculated from the total Fe content. The total-Fe content in the samples was determined using a titration method with ethylenedinitrilo-tetraacetic acid (EDTA).

^c The alkali oxide content was determined using atomic absorption spectrometry.

experiments.

2.3. Analysis of the Oxidation States of Iron Ions in the Samples

We synthesized the samples for oxidation state analysis of iron ions by the same procedure as those for viscosity measurements as mentioned above. The samples were melted in a Pt-20 mass%Rh crucible (sample amount, 20 g; internal diameter of the crucible, 36 mm) for 270 min under each of the atmosphere (air, Ar–1%O₂, Ar, high-purity Ar or Ar–1%H₂) using the same furnace for the viscosity measurement (Fig. 1(a)). Since the viscosity of the sample melts became constant after 50–165 min of melting under each atmosphere (as described in the following section (**Fig. 3**)), a melting time of 270 min was sufficient for the sample to equilibrate with the oxygen in the gas phase at 1 773 K under each atmosphere. After that the crucible was removed from the bottom of the furnace. Then the sample melt was poured on a copper plate and quenched to a glass by pressing with another copper plate to enhance the cooling rate. In the previous study, one of the authors reported that the cooling rate of this method was estimated as 260 K/s.²³⁾ Wilke *et al.*²⁴⁾ reported that the oxidation state of iron ions were not affected by cooling rate when the cooling rate was higher than 2.5 K/s. Therefore, it is believed that cooling rate of 260 K/s does not affect the oxidation state of iron ions in the original melts.

The oxidation states of the iron ions for these quenched

Fig. 3. Changes in viscosity of the NSF melts with melting time at 1773 K. We changed the atmospheres after the viscosity of the melts became constant at each oxygen partial pressure.

vitreous samples were quantitatively determined by wet chemical analysis. In this analysis, the Fe^{2+} content was determined using a titration method with potassium dichromate. The Fe^{3+} content was calculated by subtracting the Fe^{2+} content from the initial total-Fe content.

3. Results and Discussion

3.1. An Example of Viscosity Change during the Measurements

Figure 3 shows the change in the viscosity of the NSF melt during the melting time at 1773 K as an example. As shown in Fig. 3, the viscosity of the melts decreased with melting time under each atmosphere. It should be noted that the viscosity of the NSF melt decreased with melting time even under air. In a previous paper,²⁵⁾ similar phenomena were observed in the $\text{CaO-SiO}_2\text{-Fe}_x\text{O}$ system. In that paper, we clarified that this phenomenon was due to an increase in the amount of octacoordinated Fe^{3+} ions ($\text{Fe}^{3+}(6)$) that behave as network modifiers. Therefore, the viscosity decrease during melting under air should also be due to an increase in $\text{Fe}^{3+}(6)$ in the present study. When the atmosphere was changed from air to $\text{Ar-1}\%\text{O}_2$, the viscosity started to decrease again during the melting time, and the viscosity became constant after 120 min of melting under $\text{Ar-1}\%\text{O}_2$ atmosphere. This indicates that it takes around 120 min to achieve $\text{Fe}^{2+}\text{-Fe}^{3+}$ equilibration. Similar phenomena were observed for all kinds of atmospheres and samples. However, the duration required for equilibration depends on the atmosphere and the composition and ranges from 50 to 165 min. There was a tendency for the duration to be shorter for the LSF samples than for the NSF and KSF samples, and the viscosity of the LSF samples was lower than for the other systems. The difference between the equilibration durations required for NSF and KSF was small. After the samples were melted until the viscosities became constant, the constant viscosity was employed as the equilibrated value under each atmosphere.

3.2. Oxidation State of Iron Ions in the Samples

Figure 4 shows the ratios of Fe^{3+} to Fe^{2+} ($\text{Fe}^{3+}/\text{Fe}^{2+}$) in the $\text{R}_2\text{O-SiO}_2\text{-Fe}_x\text{O}$ glasses quenched from 1773 K as a func-

Fig. 4. Effect of oxygen partial pressure, $p(\text{O}_2)$, on the ratio of Fe^{3+} to Fe^{2+} in the $\text{R}_2\text{O-SiO}_2\text{-Fe}_x\text{O}$ ($\text{R} = \text{Li, Na, K}$) glasses quenched from 1773 K. All samples were melted long enough to equilibrate with the oxygen in the gas phases before being quenched with copper plates. The dashed line represents the ideal slope of 0.25.

tion of the oxygen partial pressure. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ value increased with increasing oxygen partial pressure in all systems. In general, Fe^{3+} ions exist in several kinds of complex anions such as FeO^+ , $\text{Fe}_2\text{O}_5^{4-}$, FeO_3^{3-} , and FeO_4^{5-} in silicate melts.²⁶⁾ Morinaga *et al.*²⁶⁾ reported that Fe^{3+} ions mainly existed as FeO_3^{3-} or FeO_4^{5-} in the $\text{R}_2\text{O-SiO}_2\text{-Fe}_x\text{O}$ ($\text{R} = \text{Li, Na, K}$) glasses. If the Fe^{3+} ions in the present samples are assumed to exist in FeO_3^{3-} complex anions, the $\text{Fe}^{2+}\text{-Fe}^{3+}$ redox equation can be expressed as follows:²⁷⁾

As shown in Eq. (2), the value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ depends on the oxygen partial pressure of the gas phase and the activity of the O^{2-} ions in the liquid phase, namely, the basicity. The increase in $\text{Fe}^{3+}/\text{Fe}^{2+}$ indicates that reaction (2) shifts to the right with an increase in the oxygen partial pressure or the activity of O^{2-} . When the effect of O^{2-} ions on the redox state is neglected for simplicity, the reaction between iron oxides in the melts and oxygen can be expressed as follows:

From Eq. (3), the equilibrium constant K can be expressed by the following Eq. (4):

$$K = \frac{a_{\text{FeO}_{1.5}}}{a_{\text{FeO}} \cdot p(\text{O}_2)^{1/4}} \dots (4)$$

where a_i and $p(\text{O}_2)$ represent the activity of component i and the oxygen partial pressure, respectively. Equation (4) can be converted into Eq. (5) when the temperature is constant:

$$\log\left(\frac{a_{\text{FeO}_{1.5}}}{a_{\text{FeO}}}\right) = 0.25 \log(p(\text{O}_2)) + A \dots (5)$$

where A is constant. If we assume that the $\text{FeO}_{1.5}$ (Fe^{3+}) and FeO (Fe^{2+}) components mix ideally in the melts, a plot of $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ against $\log(p(\text{O}_2))$ will be linear with a slope of 0.250 (drawn as a dashed line in Fig. 4). In the present study, the relationship between $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ and $\log(p(\text{O}_2))$

shown in Fig. 4 was not consistent with the slope of the ideal relationship, especially in the lower oxygen partial pressure region. Similar phenomena were reported by Jimbo *et al.*¹⁾ They suggested there is a possibility that the observed oxygen partial pressure is different from that of the gas phase around the sample melts. Since we also employed the oxygen partial pressure of the exhaust gas from the furnace, there is the same possibility in this work.

As shown in Fig. 4, the value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the samples increased in the order of the cationic radius of the alkali cations ($\text{K} > \text{Na} > \text{Li}$) when the oxygen partial pressures were comparable. Since an increase in basicity corresponds to an increasing negative charge (electron density) on the oxygen atoms, basic oxides (network modifiers) have a greater tendency to liberate O^{2-} ions when they react with other species. The number of liberated O^{2-} ions, which is related to the electron-donor power of the oxygen atoms, should be positively correlated with the activity of the O^{2-} ions. It is difficult to directly observe the activity of O^{2-} in the melts. However, Duffy and Ingram²⁸⁾ established an optical basicity measurement that could be used to quantify the relative electron-donor power of the oxygen atoms in the system through the measurement of the wave number shift in the s - p absorption spectra of the probe ions (such as Pb^{2+}) in the solvent system. In other words, we can create a quantitative scale of activity of O^{2-} ions by using the optical basicity. Duffy²⁹⁾ calculated the theoretical optical basicity of the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) system, which is the solvent of the present $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ system, and the theoretical optical basicity was found to be in the order of $\text{K}_2\text{O} \cdot 2\text{SiO}_2 > \text{Na}_2\text{O} \cdot 2\text{SiO}_2 > \text{Li}_2\text{O} \cdot 2\text{SiO}_2$. Therefore, the increase in $\text{Fe}^{3+}/\text{Fe}^{2+}$ with increasing cationic radius of the alkali cation is due to the increase in the activity of O^{2-} in the silicate melts with increasing alkali cationic radius.

3.3. Viscosity Changes with $\text{Fe}^{2+}/\text{total-Fe}$

Figure 5 shows the effect of $\text{Fe}^{2+}/\text{total-Fe}$ on the viscosity (equilibrated value) of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ melts. The viscosity of the melts decreased with increasing $\text{Fe}^{2+}/\text{total-Fe}$ in all the melts. The data indicate that the increase in the amount of Fe^{2+} ions, which behave as network modifiers, would result in depolymerization of the silicate melts. It

Fig. 5. Viscosity variation of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) melts as a function of the ratio of Fe^{2+} to total-Fe at 1773 K.

should be also noted that the viscosity of the melts increased in the order of the alkali cationic radius ($\text{K} > \text{Na} > \text{Li}$) when the $\text{Fe}^{2+}/\text{total-Fe}$ in the melts was comparable. To make clear the effect of the kind of alkali cation on the viscosity, the viscosities of $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ melts with $\text{Fe}^{2+}/\text{total-Fe} = 0.3$ ($\text{Fe}^{3+}/\text{total-Fe} = 0.7$) were calculated based on interpolation of the data shown in Fig. 5. Figure 6 shows the relationship between the viscosity of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ melts and the cationic radius of the alkali cations at 1773 K, compared with that for the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) system measured by Bockris *et al.*³⁰⁾ The viscosity for both systems increased linearly with increasing cationic radius, while the viscosity variation against cationic radius of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ melts was larger than that for the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) system. In addition, the viscosity of the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) melts decreased upon the addition of Fe_xO because a part of iron ions act as the network modifier (Fe^{2+} and Fe^{3+} (6)). It was found that the decrease in the viscosity with increasing amount of Fe_xO is smaller in the larger alkali cation systems. Fe_2O_3 is known as an amphoteric oxide, and its behavior depends on the basicity of the system to which it is added. In a highly basic system (with a large alkali cation), Fe_2O_3 coordinates to four oxygen ions (Fe^{3+} (4)) and behaves as a network former, while it coordinates to six oxygen ions (Fe^{3+} (6)) and behaves as a network modifier when the basicity of the system is lower. Morinaga *et al.*²⁶⁾ examined the Fe^{3+} coordination in $30\text{R}_2\text{O}-60\text{SiO}_2-10\text{Fe}_2\text{O}_3$ (mol%) glasses using Mössbauer spectroscopy. Figure 7 shows the relationship between the ratio of Fe^{3+} (4) to total- Fe^{3+} in the $30\text{R}_2\text{O}-60\text{SiO}_2-10\text{Fe}_2\text{O}_3$ (mol%) glasses and the theoretical optical basicity of the solvent system,²⁹⁾

Fig. 6. Relationship between the viscosity of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) melts ($\text{Fe}^{2+}/\text{total-Fe} = 0.3$) and the cationic radius of the alkali ions at 1773 K, compared with that of the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) system,³⁰⁾ which is the solvent of the present $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ system. The viscosities of the $\text{R}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ melts with $\text{Fe}^{2+}/\text{total-Fe} = 0.3$ were calculated by interpolation of the relationship between the viscosity of the melts and the ratio of Fe^{2+} to total-Fe (shown in Fig. 5). Arrows in the figure represent rough measures of the decrease in viscosity upon addition of Fe_xO to the $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$) system. We employed the cationic radii of alkali cations reported by Shannon.³¹⁾

Fig. 7. Relationship between the ratio of $Fe^{3+}(4)$ to total- Fe^{3+} in the $30R_2O-60SiO_2-10Fe_2O_3$ (mol%) glasses and the theoretical optical basicity of the $R_2O \cdot 2SiO_2$ ($R = Li, Na, K$) system.²⁹⁾ Morinaga *et al.*²⁶⁾ determined the fractions of $Fe^{3+}(4)$ and $Fe^{3+}(6)$ ions using Mössbauer spectroscopy. In their study, no Fe^{2+} ions could be detected in glasses that were melted for 6 hours under air before quenching; the melting temperatures of the samples were not described in their paper.

namely, $R_2O \cdot 2SiO_2$ ($R = Li, Na, K$). The ratio of $Fe^{3+}(4)$ to total- Fe^{3+} increased with increasing optical basicity, as shown in Fig. 7. This is the reason why the decrease in the viscosity of $R_2O \cdot 2SiO_2$ ($R = Li, Na, K$) melts upon the addition of Fe_xO was the smaller in the systems containing larger alkali cations. It should be mentioned that the change in the viscosity of the silicate melts upon addition of Fe_xO is dominated not only by the oxidation state of the iron ions but also by the coordination structure of the Fe^{3+} ions. The coordination structure of Fe^{3+} is also strongly affected by the basicity of the system to which it is added.

Therefore, observations of the changes in the coordination structure of Fe^{3+} for different oxidation states of iron ions are strongly desired as future works in order to quantify the contribution of each Fe species on the viscosity.

4. Conclusion

We observed the viscosity changes for different oxidation states of iron ions in $R_2O-SiO_2-Fe_xO$ ($R = Li, Na, \text{ or } K$) melts using the rotating cylinder method. It was found that the ratio of Fe^{3+} to Fe^{2+} in the $R_2O-SiO_2-Fe_xO$ (mol%) glasses increased with increasing oxygen partial pressure for all samples. In addition, the ratio of Fe^{3+} to Fe^{2+} increased in the order of the alkali cationic radius ($K > Na > Li$) when the oxygen partial pressures were comparable. The viscosity

of all the $R_2O-SiO_2-Fe_xO$ melts decreased with increasing ratios of Fe^{2+} to total-Fe. The data indicate that Fe^{2+} ions behave as network modifiers in the silicate melts. In addition, the viscosity of the melts increased in the order of the alkali cationic radius ($K > Na > Li$) when the ratio of Fe^{2+} to Fe^{3+} in the melts was comparable. This is due to the change in the coordination structure of Fe^{3+} in these melts.

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