Viscosities of CaO–SiO$_2$–Al$_2$O$_3$–(R$_2$O or RO) Melts

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The effect of adding R$_2$O (R=Li, Na and K) or RO (R=Ba, Mg) on the viscosities of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) melts has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al and ^{29}Si MAS-NMR spectra.

The viscosities of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O quaternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O. However, the viscosity of the melts increased with increasing the additive content of K$_2$O. In the case of CaO–SiO$_2$–Al$_2$O$_3$–RO quaternary melts, the viscosities of the melts with CaO/SiO$_2$=0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO$_2$=1.00 and 1.22 increased with increasing the additive content of BaO.

In the case of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O, the analysis of ^{27}Al MAS-NMR spectra and ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate anions in the glasses decreased with the addition of Li$_2$O or Na$_2$O, and that the degree of polymerization of aluminosilicate anions in the glasses increased with the addition of K$_2$O. It was estimated from the results that the increase in viscosities of CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts was dependent on increase of aluminosilicate anions in the melts with the addition of K$_2$O.

In the case of CaO–SiO$_2$–Al$_2$O$_3$–RO, the analysis of ^{27}Al MAS-NMR spectra and ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate and aluminosilicate anions in the glasses decreased with the addition of MgO. The degree of polymerization of aluminosilicate anions in the glasses increased with the addition BaO. It was estimated from the results that the increase in viscosities of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts was dependent on increase of aluminosilicate anions in the melts with the addition of BaO.

KEY WORDS: CaO–SiO$_2$–Al$_2$O$_3$–(R$_2$O or RO); viscosity; ^{27}Al MAS-NMR; ^{29}Si MAS-NMR.

1. Introduction

Viscosity of molten slag changes in wide range depending on temperature and composition. Several of factors not only in a blast furnace but also melting furnace of waste or refuse incineration residue process, such as the rate of various reactions and the fluid flows, are affected by the properties of molten slag. It is well known that the viscosity is an important physical property for understanding the network structure of slag melts and for simulating the rate of various phenomena in high temperature processes. Numerous viscosity measurements have been carried out for binary or ternary slag in last decades.[1–7] Although practical slags related to the processes mentioned above are multi-component systems, there are few data available on their viscosities. Furthermore, errors in the values of viscosity depending on published data range within ±25–50%.[8] Thus, the accuracy of measurements in viscosity for multi-component slag and flux is strongly required for understanding of the reaction behavior in high temperature processes.

The slag obtained not only in iron- and steel-making process but also in melting treatments of the incineration residuals are mainly composed of CaO, SiO$_2$ and Al$_2$O$_3$.[9] Here, the effect of adding R$_2$O (R=Li, Na and K) or RO (R=Ba and Mg) on the viscosity of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) slag has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al and ^{29}Si MAS-NMR spectra.

2. Experimental Procedures

2.1. Apparatus for Viscosity Measurement

Figure 1 presents the schematic diagram of the rotating crucible viscometer, which consists of a rotating system, a heating system and a measuring system.[10–12] An electric resistance furnace with six U-shape MoSi$_2$ heating elements was employed for heating and melting. The differential transformer, as shown in Fig. 1(a), was developed by improving a commercially available rotation angle detector. A crucible and a bob, both with Pt–20Rh mass%, were used in the experiments. The dimensions of the crucible and the bob are given in Fig. 1(b).

The viscometer was calibrated using several kinds of silicone oil standards with viscosities of 0.001–10 Pa·s at room temperature before the each measurement.[11,12] The calibration of the viscometer at high temperature were also

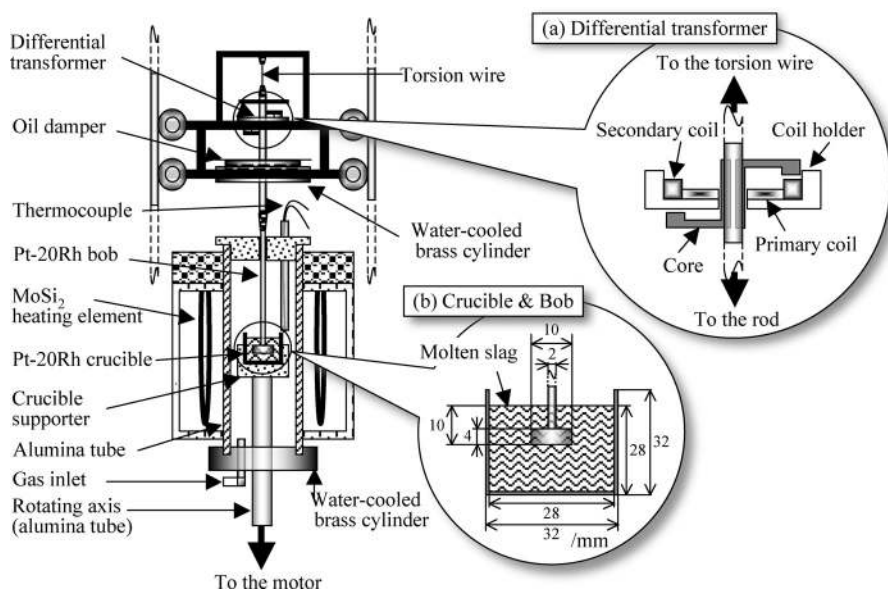**Fig. 1.** Schematic illustration of the apparatus for viscosity measurement.

Table 1. Chemical compositions of slags (mass%).

Atmosphere	Air
Temperature range	~1873 K
Diameter & length of torsion wire	$\phi\,0.20{\sim}0.26 \times 40$ mm
Sample weight	40 g
Immersion depth	10 mm
Revolution speed	60 rpm

Table 2. Experimental conditions for viscosity measurement.

Initial Compositions (mass%)			
CaO	SiO₂	Al₂O₃	R₂O or RO
32.0	48.0		-
30.0	45.0	20	5
28.0	42.0		10
26.0	39.0		15
40.0	40.0		-
37.5	37.5	20	5
35.0	35.0		10
32.5	32.5		15
44.0	36.0		-
41.2	33.8	20	5
38.5	31.5		10
35.7	29.3		15

($R_2O=$ Li₂O, Na₂O, K₂O   RO= MgO, BaO)

made by using reference slag (SRM2 type slag).[8,11,12] The experimental conditions used in this study are summarized in **Table 1**.

2.2. Sample preparation

Samples for viscosity measurement were prepared from reagent grade SiO_2, Al_2O_3, $CaCO_3$, Li_2CO_3, Na_2CO_3, K_2CO_3, $BaCO_3$ and MgO powders (Sigma-Aldrich Japan). These reagents were precisely weighed to form given compositions (*cf.* **Table 2**), and mixed in an alumina mortar thoroughly. The sample was pre-melted in a resistance furnace using Pt crucible for an hour under air. The sample was crushed into powder and then used for measurements.

2.3. Viscosity Measurements

The crucible filled with slag powder was placed in a crucible supporter in the furnace and heated up to 1 873 K. After then, the molten slag was kept at that temperature until the detected voltage value (Viscosity) became constant.

The measurements were carried out three times at every 50 K interval on cooling. Thereafter, the measurements were repeated at the same temperature on heating. The thermal equilibration time at each temperature setting point was chosen to be 30 min. The average value of these six measurements was used for the measured potential difference. An apparent viscosity was calculated based on the reference relationship between the viscosity and the potential difference, which was obtained by using various silicone oils beforehand.[11,12] Thereafter, these values were corrected for the thermal expansions of the crucible and the bob using

following equation.

$$\eta = \eta'/(1+\alpha T)^3 \quad \text{.............................(1)}$$

Where η, η', α and T are viscosity, apparent viscosity, thermal expansion coefficient and absolute temperature, respectively. The scatter of the measured values between on cooling and on heating, and the repetitive error of measurements were both within $\pm3\%$. After the viscosity measurements, the quenched slags were used for chemical analysis.

2.4. ²⁷Al and ²⁹Si MAS-NMR Spectroscopy

The aluminum or silicon environment was investigated by solid-state magic angle spinning-nuclear magnetic resonance (MAS-NMR) of ²⁷Al or ²⁹Si on a high-resolution apparatus (CMX300, JEOL, Japan). This corresponds to ²⁷Al and ²⁹Si frequencies of 78.1 and 59.5 KHz, respectively. Powdered glass samples were packed in zirconia rotors, and ²⁷Al and ²⁹Si spectra were obtained using MAS rates of 12 and 3 KHz. The chemical shifts of ²⁷Al and ²⁹Si spectra were referenced using aqueous $Al_2(SO_4)_3$ solution and poly-dimethyl-silane (PDMS) as standards.

3. Results and Discussion

3.1. Viscosity of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O Quaternary Melts

Figures 2–4 show the temperature dependence of the viscosity in CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O (R=Li, Na and K, CaO/SiO$_2$=1.00, Al$_2$O$_3$=20 mass%) quaternary melts, as examples. The present result for 40CaO–40SiO$_2$–20Al$_2$O$_3$
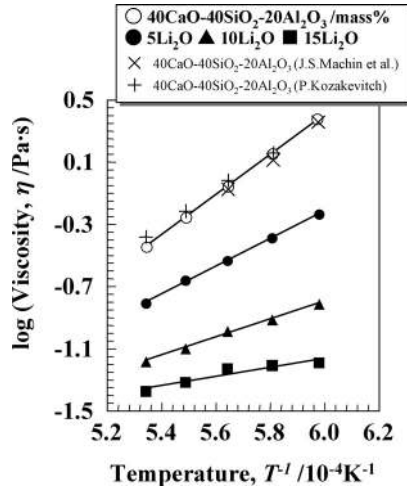
Fig. 2. Temperature dependence of the viscosity of (40CaO–40SiO$_2$–20Al$_2$O$_3$)–Li$_2$O melts.
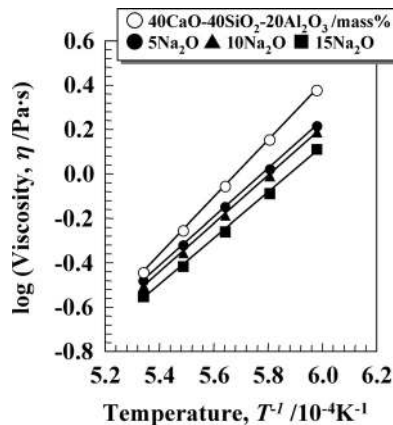

Fig. 3. Temperature dependence of the viscosity of (40CaO–40SiO$_2$–20Al$_2$O$_3$)–Na$_2$O melts.
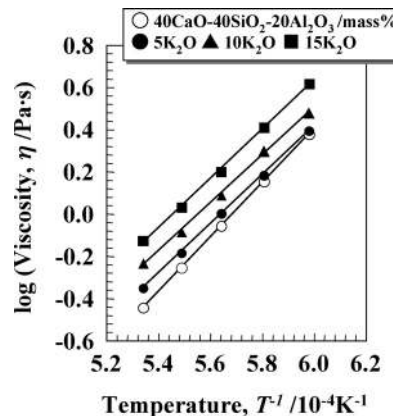

Fig. 4. Temperature dependence of the viscosity of (40CaO–40SiO$_2$–20Al$_2$O$_3$)–K$_2$O melts.

(mass%) melts shown in Fig. 2 was in good agreement with the results reported by Machin *et al.*[13] and Kozakevitch.[14] The viscosity of this ternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O. However, the viscosity of this ternary melts increased with increasing the additive content of K$_2$O.

Figure 5 illustrates the effect of adding oxide (Li$_2$O, Na$_2$O and K$_2$O) on the viscosity of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) ternary melts at 1 873 K. The horizontal axis shows the molar concentration of additive oxides by using the analyzed compositions. The viscosity of CaO–SiO$_2$–Al$_2$O$_3$ ternary melts was found to decrease in order of increasing the basicity (CaO/SiO$_2$). It was clearly found from Fig. 5 that the viscosities of these quaternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O, however, the viscosities of the melts increased with increasing the additive content of K$_2$O.

3.2. Viscosity of CaO–SiO$_2$–Al$_2$O$_3$–RO Quaternary Melts

Figures 6 and **7** show the temperature dependence of the viscosity in CaO–SiO$_2$–Al$_2$O$_3$–RO (R=Ba and Mg, CaO/SiO$_2$=1.00, Al$_2$O$_3$=20 mass%) quaternary melts, as
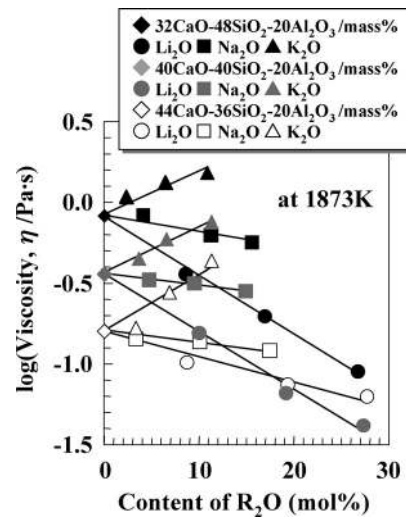

Fig. 5. Effect of adding alkali oxide on the viscosity of CaO–SiO$_2$–Al$_2$O$_3$ melts at 1 873 K.
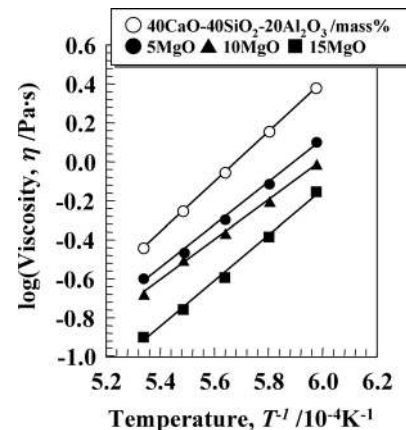

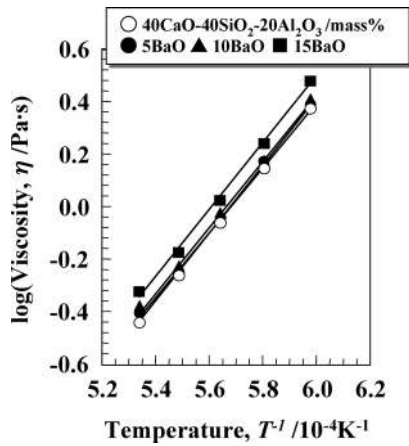**Fig. 6.** Temperature dependence of the viscosity of (40CaO–40SiO$_2$–20Al$_2$O$_3$)–MgO melts.

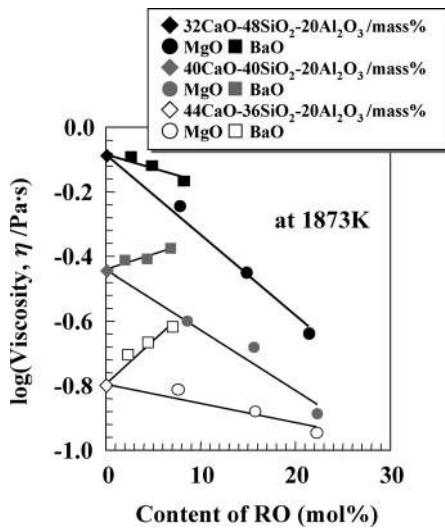**Fig. 7.** Temperature dependence of the viscosity of (32CaO–48SiO$_2$–20Al$_2$O$_3$)–K$_2$O melts.

Fig. 8. Effect of adding alkaline-earth oxide on the viscosity of CaO–SiO$_2$–Al$_2$O$_3$ slags at 1 873 K.

Fig. 9. ^{27}Al MAS-NMR spectra of (32CaO–48SiO$_2$–20Al$_2$O$_3$)–R$_2$O glasses.

Fig. 10. ^{27}Al MAS-NMR spectra of (44CaO–36SiO$_2$–20Al$_2$O$_3$)–RO glasses.

examples. The viscosity of this ternary melts decreased with increasing the additive content of MgO. However, in the case of BaO, the viscosity of the melts increased with increasing the addition content.

Figure 8 illustrates the effect of adding oxide (BaO and MgO) on the viscosity of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$= 0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) ternary melts at 1 873 K. The horizontal axis also shows the molar concentration of additive oxides by using the analyzed compositions. It was clearly found from Fig. 8 that the viscosities of the quaternary melts with CaO/SiO$_2$=0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO$_2$=1.00 and 1.22 increased by the increasing the additive content of BaO.

It is well known that Al$_2$O$_3$ is amphoteric oxide[15,16] and its behavior depends on the basicity of melts to which it is added. In the case of the mole ratio Al$_2$O$_3$/RO<1 (RO: basic oxide), Al$_2$O$_3$ would behave as acid oxide (network former), as described in references.[15–17] Moreover, the viscosity of 50CaO–50SiO$_2$ (mass%) slag increased linearly with increasing Al$_2$O$_3$ content.[10] These results suggest that the behavior of Al$_2$O$_3$ will affect the viscosity of CaO–SiO$_2$–Al$_2$O$_3$–(R$_2$O or RO) quaternary melts.
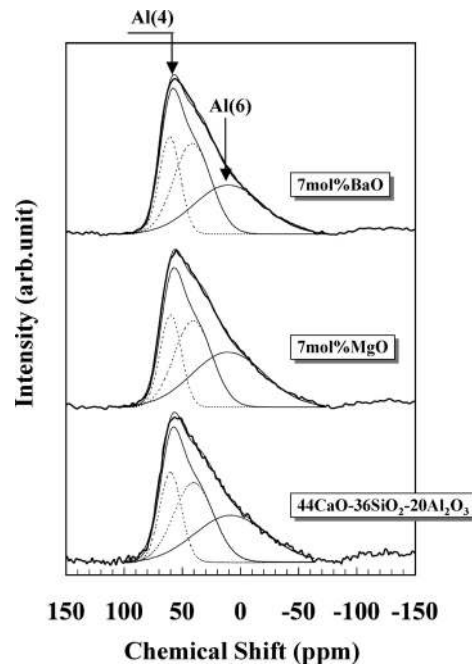
3.3. Structural Characterizations by ^{27}Al and ^{29}Si MAS-NMR

In this study, ^{27}Al and ^{29}Si MAS-NMR spectra have been measured for CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, Al$_2$O$_3$= 20 mass%)–R$_2$O (R=Li, Na and K) and CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=1.22, Al$_2$O$_3$=20 mass%)–RO (R=Ba and Mg) quaternary glasses. To make clear the effect of the kinds of adding R$_2$O or RO on the structure of glasses, the content of adding R$_2$O or RO in these glasses was kept the constant value of 10.8 mol% or 7.0 mol%. The occurrence and relative amount of different units was obtained by deconvolution of ^{27}Al and ^{29}Si MAS-NMR spectra.[18,19]

3.3.1. ^{27}Al MAS-NMR Spectra

Figures 9 and **10** show ^{27}Al NMR spectra of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O (CaO/SiO$_2$=0.67, Al$_2$O$_3$=20 mass%) glasses, and that of CaO–SiO$_2$–Al$_2$O$_3$–RO (CaO/SiO$_2$= 1.22, Al$_2$O$_3$=20 mass%) glasses. It is reported that ^{27}Al MAS-NMR spectra of aluminosilicate glasses shows three different signals at −10–+20 ppm, at 37 ppm and at +50–+80 ppm, and that the signals at −10–+20 ppm, and at +50–+80 ppm are attributed to octahedrally (Al(6)) and tetrahedrally (Al(4)) coordinated Al, and the signal at 37 ppm is attributed to distorted tricluster-forming Al–O$_4$ tetrahedra.[20] In this study, ^{27}Al NMR spectra were reproduced two peaks for Al(6) and Al(4) as drawn with solid lines in Figs. 9 and 10.

From Fig. 9, the resonance position of spectra is shifted from ≈50 ppm of the mother glasses to a downfield with the addition of R$_2$O. It is also found that the peak for Al(6) of the mother glasses decrease, and the peak for Al(4) of the glasses increase with the addition of R$_2$O. No significant difference of the relative areas of Al(6) (34.6±0.7%) or Al(4) (65.4±0.7%) for the glasses with adding the different kinds of R$_2$O is observed. These results suggest that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts shown in Fig. 5 is not dependent on the increase of Al(4) in the glasses with adding of K$_2$O.

From Fig. 10, the resonance position of spectra of the glasses with adding of RO is found at ≈60 ppm, and is not change from that of the mother glasses. Compared with the mother glasses, the deconvolution analysis indicated that no significant difference of the relative areas of Al(6) (40.1±2.0%) or Al(4) (59.9±2.0%) for the glasses with the addition of MgO or BaO is observed. These results suggest that the increase of Al(4) in the glasses is not a major factor in the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts shown in Fig. 8.

3.3.2. ^{29}Si MAS-NMR Spectra

In aluminosilicates, ^{29}Si MAS-NMR can provide quantitative information on the fractions of silicon present in different tetrahedral environments. According to widespread use, SiO$_4^{4-}$ units are identified according to their mutual connectivity as Q^n(mAl), where n is the number of bridging oxygen (BO) atoms, and m is the number of neighbor aluminate groups.[21,22] In general, silicon chemical shift becomes less negative with the number of bridging oxygen (BO) decreasing from four to zero.[23] Adjacent aluminum tetrahedra (Al(4)) also affect the silicon chemical shift. Namely, silicon nuclei are deshielded and d value (ppm) becomes less negative as the number of neighboring aluminum atoms increases from zero to four. **Table 3** lists the experimentally determined chemical shift ranges associated with species.[23–25]

Figure 11 shows ^{29}Si NMR spectra of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O (CaO/SiO$_2$=0.67, Al$_2$O$_3$=20 mass%) glasses. It is found from Fig. 11 that the resonance position of spectra is shifted from ≈−85 ppm of the mother glasses to a downfield with the addition of R$_2$O. It is also found that the peak of spectra of the glasses with Li$_2$O or Na$_2$O become sharp, and that with K$_2$O become broad. The ^{29}Si NMR spectra of these glasses resolved four peaks, and relative areas of the

Table 3. Isotropic ^{29}Si chemical shift ranges for Q^1–Q^4 units in crystalline silicates and aluminosilicates.

SiO$_4$−nAl	Q^1 units (ppm)	Q^2 units (ppm)	Q^3 units (ppm)	Q^4 units (ppm)
n = 0	−68 ⁓ −97	−75 ⁓ −102	−88 ⁓ −99	−102 ⁓ −114
n = 1	−63 ⁓ −92	−70 ⁓ −97	−85 ⁓ −99	−96 ⁓ −107
n = 2			−84 ⁓ −86	−93 ⁓ −102
n = 3			−76 ⁓	−88 ⁓ −97
n = 4				−80 ⁓ −89
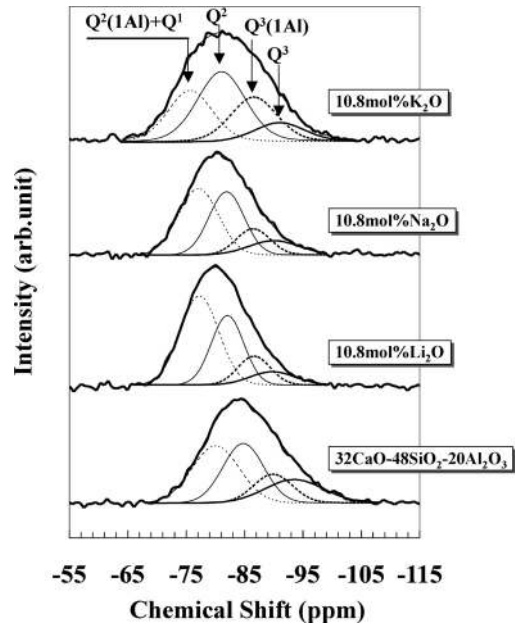
Fig. 11. ^{29}Si MAS-NMR spectra of (32CaO–48SiO$_2$–20Al$_2$O$_3$)–R$_2$O glasses.

Table 4. Deconvolution results of ^{29}Si MAS-NMR spectra of (32CaO–48SiO$_2$–20Al$_2$O$_3$)–R$_2$O glasses.

R$_2$O	Chemical shift (ppm)				Relative area (%)			
	Q^3	Q^3(1Al)	Q^2	Q^2(1Al)+Q^1	Q^3	Q^3(1Al)	Q^2	Q^2(1Al)+Q^1
Mother	-93.5	-89.9	-84.8	-80.0	17.8	14.6	32.0	35.6
Li$_2$O	-89.8	-86.6	-82.1	-77.3	8.3	12.9	31.1	47.7
Na$_2$O	-90.0	-86.5	-81.9	-77.1	11.0	13.6	34.2	41.2
K$_2$O	-91.0	-86.6	-81.0	-75.7	11.0	23.6	38.9	26.4

peaks were calculated by spectra deconvolution. In the deconvolution analysis, the peak of Q^2(1Al) and the peak of Q^1 overlapped each other so that the peak at −75–−80 ppm showed as Q^2(1Al)+Q^1. The summary of the deconvolution results is listed in **Table 4**. It is found that the ^{29}Si NMR spectra of the mother glasses and that of the glasses with the addition of R$_2$O consist of Q^2, Q^3, Q^2(1Al)+Q^1 and Q^3(1Al). It is estimated that the peaks at ≈−75–−80 ppm in Table 4 mainly consist of Q^2(1Al).[16,26] From the deconvolution analysis (Table 4), the degree of polymerization of silicate anions decrease with the addition of Li$_2$O or Na$_2$O, namely the relative area of Q^3 decrease in Li$_2$O- and Na$_2$O-containing glasses compared with the mother glasses as shown in Table 4. On the other hand, the degree of polymerization of aluminosilicate anions increase, namely the relative area of Q^3(1Al) increase in K$_2$O-containing glasses compared with the mother glasses as shown in Table 4. It is estimated from the results that the increase in viscosity of
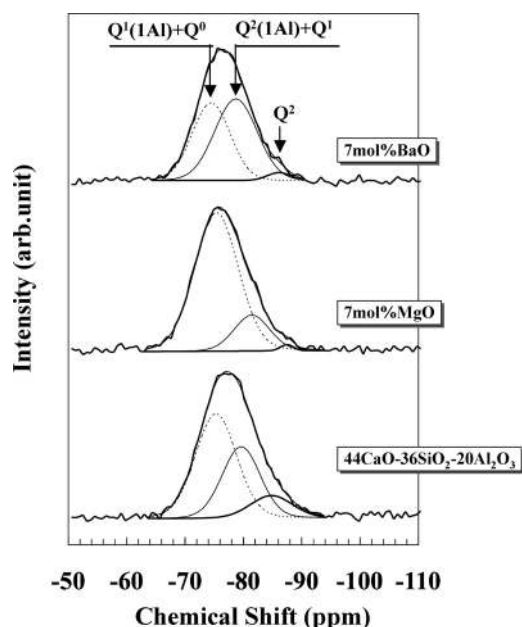
Fig. 12. ^{29}Si MAS-NMR spectra of (44CaO–36SiO$_2$–20Al$_2$O$_3$)– RO glasses.

Table 5. Deconvolution results of ^{29}Si MAS-NMR spectra of (44CaO–36SiO$_2$–20Al$_2$O$_3$)–RO glasses.

RO	Chemical shift (ppm)			Relative area (%)		
	Q^2	$Q^2(1Al)+Q^1$	$Q^1(1Al)+Q^0$	Q^2	$Q^2(1Al)+Q^1$	$Q^1(1Al)+Q^0$
Mother	-84.8	-79.6	-75.3	11.9	34.1	54.0
MgO	-87.5	-81.5	-75.4	1.1	17.3	81.6
BaO	-86.1	-78.7	-74.5	2.8	52.5	44.8

CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts shown in Fig. 5 is dependent on increase of aluminosilicate anions (Q^3(1Al)) in the melts with the addition of K$_2$O.

Figure 12 shows ^{29}Si NMR spectra of CaO–SiO$_2$– Al$_2$O$_3$–RO (CaO/SiO$_2$=1.22, Al$_2$O$_3$=20 mass%) glasses. It is found that the resonance position of spectra is found at ≈ -80 ppm, and is not change from that of the mother glasses. The ^{29}Si NMR spectra of these glasses resolved three peaks, and relative areas of the peaks were calculated by spectra deconvolution. In the deconvolution analysis, the peaks of Q^1(1Al) and Q^0 or that of Q^2(1Al) and Q^1 overlapped each other so that the peak at ≈ -75 ppm or at ≈ -80 ppm showed as Q^1(1Al)+Q^0 or Q^2(1Al)+Q^1. The summary of the deconvolution results is listed in **Table 5**. It is estimated that the peaks at ≈ -75 ppm or at ≈ -80 ppm in Table 5 mainly consist of Q^1(1Al) or Q^2(1Al).[16,26] From these considerations, the degree of polymerization of silicate and aluminosilicate anions decrease in the glasses with MgO, namely the relative area of Q^2 and of Q^2(1Al) decrease, and the relative area of Q^1(1Al) increase in this glasses compared with the mother glasses as shown in Table 5. On the other hand, the degree of polymerization of aluminosilicate anions increase in the glasses with BaO, namely the relative area of Q^2(1Al) increase in this glasses compared with the mother glasses as shown in Table 5. It is estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts shown in Fig. 8 is dependent

on increase of aluminosilicate anions (Q^2(1Al)) in the melts with the addition of BaO.

4. Conclusions

The effect of adding R$_2$O (R=Li, Na and K) or RO (R=Ba, Mg) on the viscosities of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) melts has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al and ^{29}Si MAS-NMR spectra.

(1) The viscosities of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O quaternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O. However, the viscosities of the melts increased with increasing the addition content of K$_2$O.

(2) ^{27}Al MAS-NMR spectra indicated that the population of (Al(4)) in the glasses increased with adding of R$_2$O, however, that of Al(4) was independent of the kinds of adding R$_2$O.

(3) ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate anions in the glasses decreased with the addition of Li$_2$O or Na$_2$O, and that the degree of polymerization of aluminosilicate anions in the glasses increased with the addition of K$_2$O. It was estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts was dependent on increase of aluminosilicate anions in the melts with the addition of K$_2$O.

(4) The viscosities of CaO–SiO$_2$–Al$_2$O$_3$–RO quaternary melts with CaO/SiO$_2$=0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO$_2$=1.00 and 1.22 increased with increasing the additive content of BaO.

(5) ^{27}Al MAS-NMR spectra indicated that no significant difference of the population of Al(6) or Al(4) for the glasses with the addition of MgO or BaO was observed.

(6) ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate and aluminosilicate anions in the glasses decreased with the addition of MgO. The degree of polymerization of aluminosilicate anions increased in the glasses with BaO. It was estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts was dependent on increase of aluminosilicate anions in the melts with the addition of BaO.

REFERENCES

1) J. O'M. Bockris and D. C. Lowe: *Proc. R. Soc.* (*London*) *A*, **A226** (1954), 423.
2) Handbook of Physico-chemical Properties at High Temperatures, Ed. by Y. Kawai and Y. Shiraishi, ISIJ, Tokyo, (1988), 121.
3) S. Sumita, T. Mimori, K. Morinaga and T. Yanagase: *J. Jpn. Inst. Met.*, **44** (1980), 94.
4) H. Schenk and M. G. Frohberg: *Arch. Eisenhüttenwes.*, **33** (1961), 421.
5) E. T. Turkdogan and P. M. Bills: *Am. Ceram. Soc. Bull.*, **39** (1960), 682.
6) E. E. Hoffmann and K. Nabin: *Arch. Eisenhüttenwes.*, **32** (1961), 199.
7) Y. Shiraishi and T. Saito: *J. Jpn. Inst. Met.*, **29** (1965), 614.
8) T. Iida and Y. Kita: *Boundary*, **10** (1996), 34.
9) T.Sato, N. Saitou, K. Nakashima, K. Mori and T. Hiraaki: *Shigen-Syorigijyutu*, **49** (2002), 128.
10) T. Yasukouchi, K. Nakashima and K. Mori: *Tetsu-to-Hagané*, **85**

(1999), 571.

11) N. Saitou, N. Hori, K. Nakashima and K. Mori: *High Temp. Mater. Process.*, **22** (2003), 129.

12) N. Saitou, N. Hori, K. Nakashima and K. Mori: *Metall. Mater. Trans. B*, **34B** (2003), 509.

13) J. S. Machin, T. B. Yee and D. C. Hanna: *J. Am. Ceram. Soc.*, **35** (1952), 322.

14) P. Kozakevitch: *Rev. Metall.*, **57** (1960), 149.

15) K. Morinaga, Y. Suginohara and T. Yanagase: *Tech. Rep. Kyushu Univ.*, **48** (1975), 859.

16) T. Kou, K. Mizoguchi and Y. Suginohara: *J. Jpn. Inst. Met.*, **41** (1978), 775.

17) H. Ikeda, Y. Murayama, Y. Ohoka, K. Morinaga and T. Yanagase: *J. Jpn. Inst. Met.*, **41** (1983), 1063.

18) W. Storek, R. Muller and G. Kunath-Fandrei: *Solid State Nuclear Magnetic Resonance*, **9** (1997), 227.

19) N. Kashii, H. Maekawa and Y, Hinatsu: *J. Am. Ceram. Soc.*, **82** (1999), 1844.

20) M. Schmucker, K. J. D. MacKenzie, H. Schneider and R. Meinhold: *J. Non-Cryst. Solids*, **217** (1997), 99.

21) I. G. Richardson, A. R. Brough, R. Brydson, G. W. Groves and C. M. Dobson: *J. Am. Ceram. Soc.*, **76** (1993), 2285.

22) J. Schneider, M. A. Cincotto and H. Panepucci: *Cem. Concr. Res.*, **31** (2001), 993.

23) H. Maekawa, T. Maekawa, K. Kawamura and T. Yokokawa: *J. Non-Cryst. Solids*, **127** (1991), 53.

24) R. J. Kirkpatrick, K. A. Smith, S. Schramm, G. Turmer and W.-H. Yang: *Ann. Rev. Earth Planet. Sci.*, **13** (1985), 29.

25) P. J. Schilling, L. G. Butler, A. Roy and H. C. Eaton: *J. Am. Ceram. Soc.*, **77** (1994), 2363.

26) P. McMillan, B. Piriou and A. Navrotsky: *Geochim. Cosmochim. Acta*, **46** (1982), 2021.