Viscosity of Binary Borate and Ternary Borosilicate Melts

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ABSTRACT

An outer cylinder rotating viscometer has been built, and tested at room temperature as well as at high temperature. The viscometer is utilized in the measurement of the viscosity range from 10^{-2} to 10^{2} Pa·s, and at a temperature up to 1600℃.

Viscosities of R_2O-B_2O_3-SiO_2 (R; Na and K) and RO-B_2O_3-SiO_2 (R; Ba and Ca) systems have been measured by the viscometer. The binary borate melts exhibit an anomalous behavior of viscosity isotherms with the continuous variation of B_2O_3 content. The iso-viscosity curves of ternary borosilicate melts have been provided. The characteristic features of viscosity for these binary and ternary systems have been discussed on the basis of the structural changes of the melts.

1. INTRODUCTION

Borosilicate based ternary glasses are used for sealing glasses of hybrid IC, HID lamp and TV tube[1], and for protective lubricants for hotworking of metals and alloys[2]. In these industrial processes, viscosity of molten oxides is one of the important physical properties since this property has a decisive influence on fluid flow. On the other hand, binary alkali borate glasses are of particular interest because they exhibit a different trend of physical properties with the continuous variation in B_2O_3 content.

Viscosity of molten oxides is a structure related property. To study viscosity behavior of molten oxides, the understanding of ionic distribution in molten oxides is of considerable importance. Although, numerous viscosity measurements in the slag systems have been carried out, the data available in literature are still too few to meet the technological demands. This is particularly true in the case of complex molten oxides system, for which, experimental data are very often found to be available only for a few temperatures and cover small composition ranges.

In the present study, viscosities of R_2O-B_2O_3-SiO_2 (R; Na and K) and RO-B_2O_3-SiO_2 (R; Ca and Ba) systems have been measured by the outer cylinder rotating viscometer built in our laboratory. The isotherm viscosity curves for binary borate systems and for ternary borosilicate systems have been provided. The characteristic features of viscosity of these systems have been discussed on the basis of the network structures of the melts.

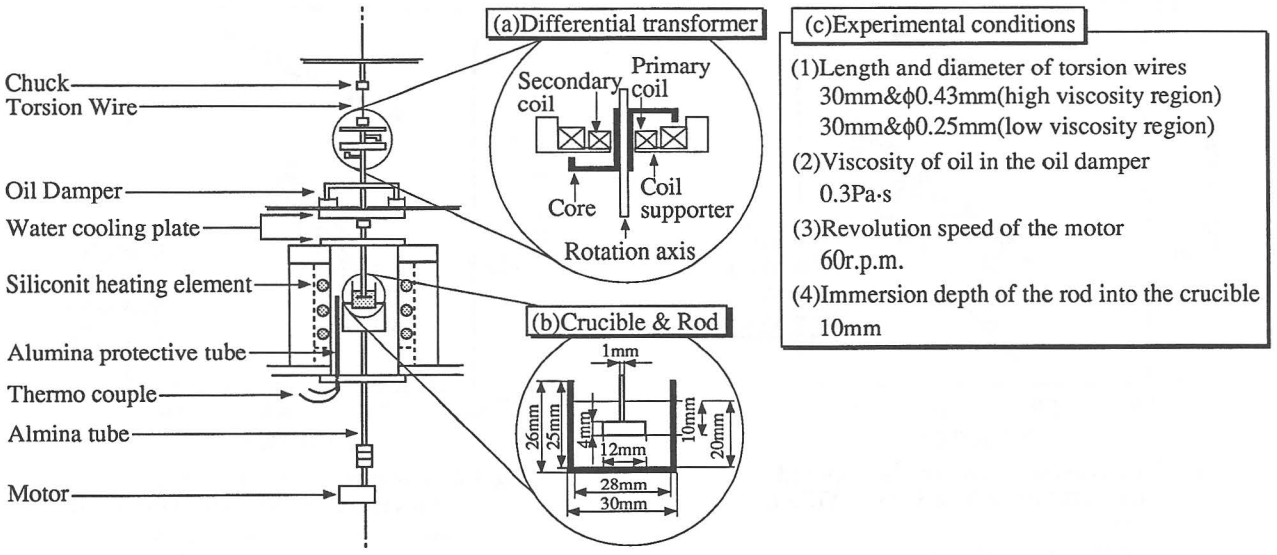

Fig.1 Apparatus for viscosity measurement

2. EXPERIMENTS

2. 1 Apparatus for viscosity measurement

Figure 1 presents the schematic diagram of the outer cylinder rotating viscometer, which comprises a rotating system, a heating system and a measuring system. An electric resistance furnace with 12 cylindrical SiC heating elements was employed for heating and melting. The latest style differential transformer, as shown in Fig. 1-(a), was developed by improving a commercially available rotation angle detector. The adjustment of the center axis and the range of the detectable rotation angle became easier and wider than the former type differential transformer[3]. The Pt-20wt%Rh crucible and rod, as shown in Fig. 1-(b), were employed in this study. Calibration of the viscometer, i.e. the optimizations of (1) the length and the diameter of the torsion wire, (2) the viscosity of the oil in the oil damper, (3) the revolution speed of the motor, and (4) the immersion depth of the rod into the crucible, were done by using 8 kinds of silicon oil with a known viscosity (Shinetsu Chemical Co. Ltd., KF96, Standard Viscosity; 0.01~10 Pa•s)[4]. The experimental conditions of (1), (2), (3) and (4) determined are summarized in Fig.1-(c). After the calibration, the linear relationship[3] between the known viscosity of the silicon oil and the potential difference of the differential transformer was measured for two kinds of torsion wires, which are valid in the different viscosity ranges, as the reference relationship of them. The temperature was measured with a thermocouple placed just outside the crucible as shown in Fig.1 and was held constant within ± 5°C.

2. 2 Preparation of sample

Special-grade B_2O_3, SiO_2, Na_2CO_3, K_2CO_3, $CaCO_3$ and $BaCO_3$ were used for the preparation of samples. These reagents were precisely weighed to form given compositions (cf.Tables 1~4), and mixed thoroughly. The mixtures were placed in a platinum crucible, and melted at the temperature about 100°C higher than the melting point for decomposition of carbonate and homogenization, and then quenched on a Pt plate.

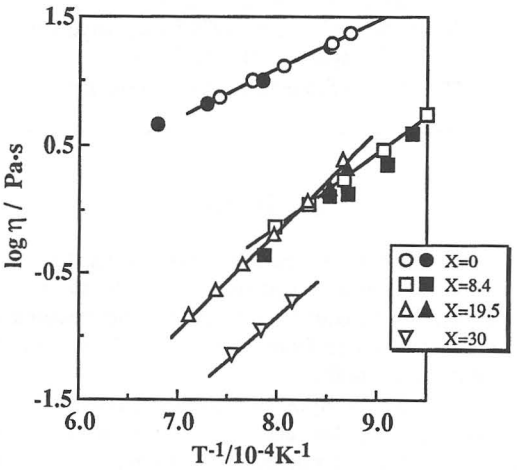

Fig.3 Relationship between viscosity and temperature in XK2O-(100-X)B2O3 melts
Open marks;present work
● ■ ▲ ;L.Shartsis *et al.* (ref.6)

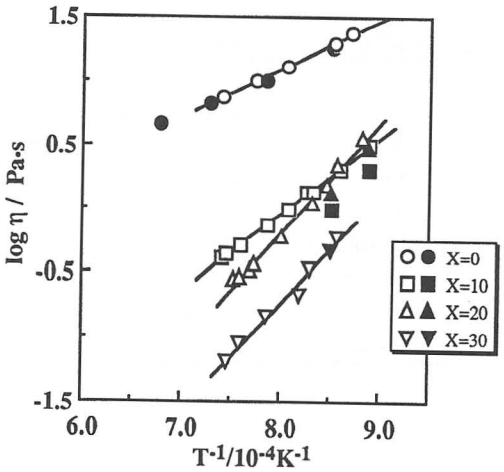

Fig.2 Relationship between viscosity and temperature in XNa2O-(100-X)B2O3 melts
Open marks:present work
● ;J.Boow (ref.5)
■ ▲ ▼ ;L.Shartsis *et al.* (ref.6)

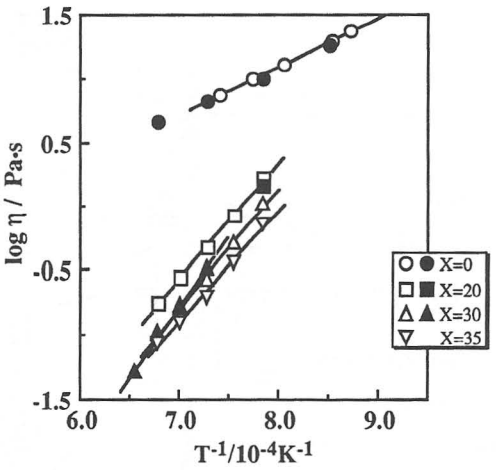

Fig.4 Relationship between viscosity and temperature in XRO-(100-X)B2O3 melts
Open marks;present work for BaO-B2O3 melts
▲ ;present work for CaO-B2O3 melt
● ■ ;L.Shartsis *et al.* (ref.6)

2. 3 Procedure

The sample was melted at the temperature well above the melting temperature. Then, the measurements were carried out 2 times at every 25°C or 50°C after keeping at each temperature for 20 min on cooling to the temperature about 100°C higher than the melting point of each composition. Thereafter, the measurements were repeated at the same temperatures on heating to the initial temperature. The average value of these 4 measurements was used for the measured potential difference. An apparent viscosity was calculated by using the reference relationship between the viscosity and the potential difference measured beforehand. The viscosity of each composition was obtained from the apparent viscosity by considering the thermal expansions of the crucible and the rod at each temperature of measurements[4]. The scatter of the measured values between on cooling and on heating, and the repetitive error of measurements were both within ± 3%.

3. RESULTS AND DISCUSSIONS

The temperature dependences of the viscosity in binary borate melts investigated are presented in Figures 2~4 as examples. The present results agreed well with those of literature measured in molten state[5, 6], and the viscosity data can be described by an Arrhenius equation over the entire temperature region.

Table1 Compotition of samples and viscosity of Na_2O -B_2O_3 - SiO_2 melts

Na_2O (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)	Temp. range(℃)	A	$B \times 10^4$
100	0	0	900-1070	-1.930	0.378
90	10	0	850-1070	-4.938	0.610
80	10	10	840-1170	-5.039	0.655
70	10	20	850-1140	-5.379	0.731
60	10	30	880-1130	-5.927	0.840
50	10	40	960-1140	-5.573	0.847
40	10	50	1040-1180	-5.693	0.904
80	20	0	860-1050	-7.284	0.883
70	20	10	860-1080	-7.625	0.946
60	20	20	860-1050	-9.388	1.172
50	20	30	860-1060	-8.610	1.116
40	20	40	900-1100	-8.139	1.078
30	20	50	910-1090	-6.737	0.925
70	30	0	890-1070	-7.316	0.820
60	30	10	870-1060	-7.375	0.842
50	30	20	870-1060	-7.515	0.868
40	30	30	860-1080	-6.959	0.832
30	30	40	910-1060	-6.316	0.793
20	30	50	880-1060	-6.348	0.863
10	30	60	950-1070	-4.932	0.762
30	40	30	880-1060	-5.733	0.634
20	40	40	880-1050	-5.376	0.624
10	40	50	900-1070	-4.368	0.597

Table2 Compotition of samples and viscosity of K_2O -B_2O_3 - SiO_2 melts

K_2O (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)	Temp. range(℃)	A	$B \times 10^4$
90	10	0	800-1050	-4.938	0.600
80	10	10	900-1150	-5.039	0.651
70	10	20	850-1150	-5.379	0.680
60	10	30	900-1150	-5.927	0.776
50	10	40	950-1150	-5.573	0.876
40	10	50	1050-1150	-5.693	1.044
80	20	0	850-1050	-7.284	0.896
70	20	10	850-1050	-7.625	0.991
60	20	20	850-1150	-9.388	1.023
50	20	30	900-1150	-8.610	0.994
40	20	40	950-1150	-8.139	1.061
70	30	0	950-1050	-7.316	0.820
60	30	10	850-1000	-7.375	0.777
50	30	20	800-1000	-7.515	0.917
40	30	30	800-1000	-6.959	0.909
30	30	40	850-1000	-6.316	0.871
20	30	50	900-1000	-6.348	0.857

Table3 Compotition of samples and viscosity of CaO -B_2O_3 - SiO_2 melts

CaO (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)	Temp. range(℃)	A	$B \times 10^4$
30	70	0	1100-1300	-8.405	1.087
50	25	25	1150-1350	-7.401	0.968
50	16.7	33.3	1350-1500	-5.130	0.685
50	10	40	1450-1550	-5.491	0.794

Table4 Compotition of samples and viscosity of BaO -B_2O_3 - SiO_2 melts

BaO (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)	Temp. range(℃)	A	$B \times 10^4$
20	80	0	1000-1200	-7.008	0.918
30	70	0	1000-1200	-7.403	0.941
35	65	0	1000-1200	-6.956	0.863
40	60	0	1100-1300	-5.076	0.590
10	72	18	1430-1530	-3.649	0.639
20	64	16	1100-1300	-5.888	0.801
30	56	14	1050-1250	-6.257	0.822
40	48	12	1100-1300	-5.554	0.673
10	60	30	1450-1500	-4.185	0.682
20	53.3	26.7	1150-1300	-5.458	0.769
30	46.7	23.3	1100-1300	-6.351	0.849
40	40	20	1150-1350	-4.741	0.576
10	45	45	1500-1550	-3.653	0.677
20	40	40	1300-1450	-4.085	0.590
30	35	35	1100-1250	-6.676	0.951
40	30	30	1100-1300	-5.647	0.748
50	25	25	1150-1300	-6.709	0.792
20	26.7	53.3	1400-1500	-4.269	0.702
30	23.3	46.7	1200-1350	-6.374	0.952
40	20	40	1200-1400	-4.832	0.696
50	16.7	33.3	1300-1500	-5.074	0.701
30	14	56	1300-1410	-3.661	0.614
40	12	48	1350-1550	-4.048	0.622

$$\log\eta = A + B/T \qquad (1)$$

Where A and B are constants, and T is the absolute temperature. The Arrhenius relationship shown by equation (1) holds for entire compositions investigated in this study. The viscosity data for entire compositions are given in Tables 1 ~ 4 as the Arrhenius relationship. Binary alkaline earth borate and ternary alkaline earth borosilicate systems have two immicsible liquid region[7,8]. The two immicsible liquid region is wide, and its critical temperature is high for CaO containing system[7,8]. Therefore, viscosities of four compositions as shown in Table 3 were measured in the CaO containing systems.

3. 1 Viscosity of binary borate melts

The viscosity isotherms for Na_2O-B_2O_3, K_2O-B_2O_3, and BaO-B_2O_3 are presented in Figures 5~7 together with the results of literature[6,9,10]. The viscosity data at the region of low BaO content for BaO-B_2O_3 melts contained 3 mol% K_2O[9]. The viscosity isotherms for Na_2O-B_2O_3, K_2O-B_2O_3 systems show a minimum at alkali content of ≈10 mol% and a maximum at those of ≈20 mol% at 800°C[6,10]. With an increase in temperature, the maximum tends to become less prominent. The maximum and the minimum almost disappear at around 900°C, and a rather smooth curve is obtained at higher temperature.

The shape of viscosity isotherms for borate glasses is quite different from that for silicate glasses. The so called " boron anomaly " can be explain by the results of the structural changes obtained from NMR experiments[11] and Raman spectral studie[12], and by the calculation[13] of ionic distribution in binary borate melts. According to P. J. Bray[11], the fractions of boron atoms in four coordination in alkali borate glasses increase linearly with increasing the alkali contents up to about 30 mol%. Moreover, the fraction of tetraborate units, which is the largest structural units in alakli borate glasses, increases with an increase in alkali content , and shows maximum values at the alkali content of ≈20 mol%. B.N. Meera *et al*[12] suggested that the structure of vitreous B_2O_3 is a continuous random network of broxol rings, and addition of alkali oxides

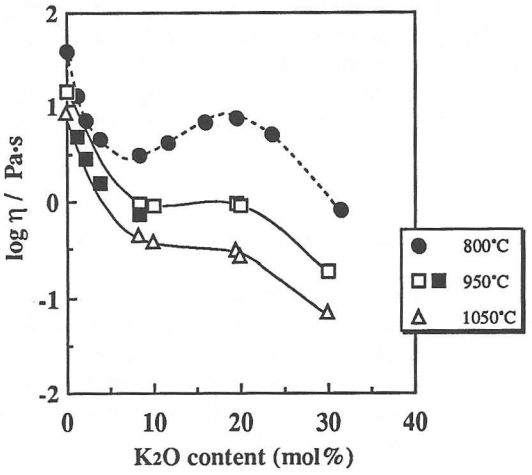

Fig.6 Relationship between viscosity and K_2O content in K_2O-B_2O_3 systems
□ △ ;present work
● ■ ;L.Shartsis *et al.*(ref.6)

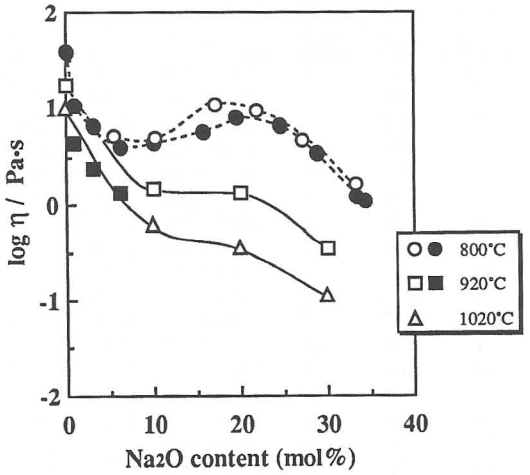

Fig.5 Relationship between viscosity and Na_2O content in Na_2O-B_2O_3 systems
□ △ ;present work
○ ;G.H.Kaiura *et al.*(ref.10)
● ■ ;L.Shartsis *et al.*(ref.6)

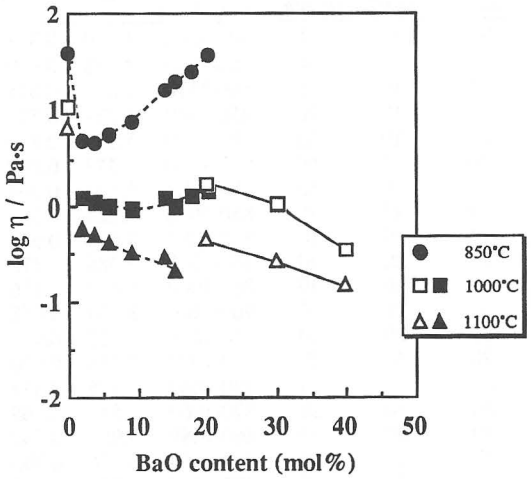

Fig.7 Relationship between viscosity and BaO content in BaO-B_2O_3 systems
□ △ ;present work
● ■ ▲ ;L.W.Coughanour *et al.*(ref.9)

results in the formation of polyborate group. Moreover, with the addition of alkali oxides, broxol rings are initially converted to pentaborate units and not tetraborate or triborate groups.

On the basis of the structural change of alkali borate glasses mentioned above, viscosities of alkali borate melts decrease in the range of alkali content of 0 to 10 mol% by the network breakdown and the formation of triangular structure. For alkali content of ≥10 mol%, viscosities start to increase by the formation of large structural units, such as pentaborate, tetraborate or triborate. Above the alkali content of 20 mol%, such large structural units start to decrease, thus viscosity also start to decrease. However, the maximum values seen in the molten state are small compared with those of glassy state.

The similar variation of viscosity isotherm with an increase in alkaline earth content and in temperature is observed for BaO-B_2O_3 melts as shown in Fig. 7, and for 3 mol% CaO containing BaO-B_2O_3 system[9]. Therefore, it is possible to consider that the similar structural change with the addition of alkaline earth oxides could occur in this melts.

3. 2 Viscosity of ternary borosilicate melts

The iso-viscosity curves of ternary borosilicate melts are shown in Figure 8 ~ 10. The viscosity data for CaO-B_2O_3-SiO_2 melts are plotted in Fig. 10 together with those for BaO-B_2O_3-SiO_2 melts. The dotted line in these figures shows the line of R_2O/B_2O_3 =1 or RO/B_2O_3 =1 lines. The viscosity of these systems decreases with increasing the content of alkali and alkaline earth oxides, and increases with an increase in SiO_2 content.

A density study of relatively fluid B_2O_3-rich ternary liquid in the sodium brosilicate system concluded that BO_4 tetrahedra exist in most compositions that contain between 15 and 45 mol% Na_2O[14]. The iso-expansion coefficient contours for sodium brosilicate melts show the same trend to the iso-viscosity curves measured in this stud[15]. The structural change of Na_2O-B_2O_3-SiO_2 glasses was also explained by NMR[16] and Raman spectral[11] studies.

The boron coordination conversion would dominantly occur in the region of higher B_2O_3 content than R_2O/B_2O_3=1. The variation of the iso-viscosity curves of alkali borosilicate melts corresponds to the boron coordination conversion and the change of the structural

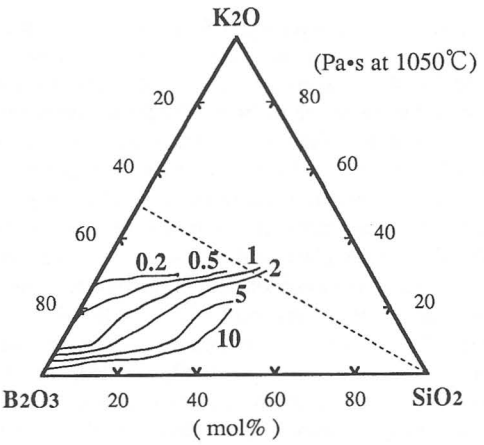

Fig.9 Iso-viscosity curves of K_2O-B_2O_3-SiO_2 melts

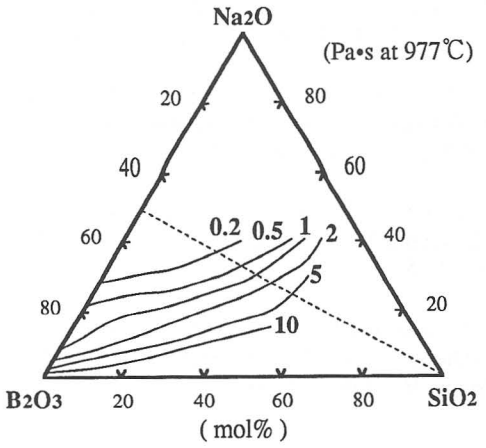

Fig.8 Iso-viscosity curves of Na_2O-B_2O_3-SiO_2 melts

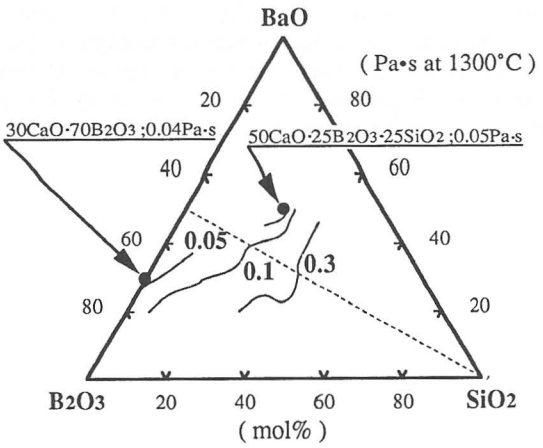

Fig.10 Iso-viscosity curves of BaO-B_2O_3-SiO_2 melts

units which takes place in these ternary borosilicate melts depending on the change in composition[16]. For BaO-B_2O_3-SiO_2 melts, the similar trend of the iso-viscosity curves was obtained as shown in Fig. 10. The viscosity data for CaO-B_2O_3-SiO_2 melts are almost same as those for BaO-B_2O_3-SiO_2 melts at the same compositions. It is possible to consider that the similar structural change could also occur in this melt. However, available measurements on alkaline earth borosilicate systems are limited and, it is difficult to draw a definite and a systematic consideration.

Clearly further study will be required to identify the relationship between the structural change and the viscosity or the other physical properties in binary borate and ternary borosilicate systems.

4. CONCLUSIONS

Viscosities of R_2O-B_2O_3-SiO_2 (R; Na and K) and RO-B_2O_3-SiO_2 (R; Ba and Ca) systems have been measured by the viscometer built in the present study. Viscosity of binary borate melts exhibit the so called "boron anomaly" where a minimum and a maximum is observed in the viscosity isotherms with a continuous B_2O_3 content. On increasing the temperature, the minimum and the maximum disappear. This anomaly is attributed to the structural changes which takes place in these borate melts depending on the change in composition and temperature. The iso-viscosity curves of ternary borosilicate melts have been provided. The boron coordination conversion would dominantly occur in the high B_2O_3 content, and the variation of the iso-viscosity curves corresponds to the structural change which takes place in these ternary borosilicate melts depending on the change in composition.

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