4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

STRUCTURE OF Na_2O-B_2O_3 MELTS MEASURED BY PULSED NEUTRON TOTAL SCATTERING

Yoshifumi Kita1), Masakatsu Misawa2), Norimasa Umesaki3)
Tadashi Kirihara4), Toshiharu Fukunaga5) and Takamichi Iida1)

1) Department of Materials Science and Processing, Osaka University, Japan
2) National Laboratory for High Energy Physics, Japan
3) Material Physics Department, Government Industrial Research Institute, Japan
4) Graduate School, Osaka University, (Now, Nippon Steel Co., Ltd.), Japan
5) Department of Crystalline Materials Science, Nagoya University, Japan

Synopsis:

Pulsed neutron total scattering measurements have been carried out on 10 mol% Na_2O- and 30 mol% Na_2O- B_2O_3 melts at 1073K, in addition to the previous measurement on pure B_2O_3 melt. Molecular dynamics (MD) calculations have also been performed on pure B_2O_3 and 30 mol% Na_2O-B_2O_3 melts at 1073K.

The coordination number of O atoms around a reference B atom n_{B-O} increased from 3.0 to 3.5 with increase in Na_2O content. This increase in n_{B-O} could be explained by the simple assumption that two BO_3 triangle structure units are converted to two BO_4 tetrahedron units with the addition of one Na_2O molecule, in the same way as in Na_2O-B_2O_3 glasses. These n_{B-O} values also agreed well with those obtained by MD calculations.

Keywords:
Na_2O-B_2O_3 melt, sodium borate, ionic structure, structure unit, pulsed neutron scattering, molecular dynamics, MD calculation

1. Introduction

Alkali borate glasses have long been attractive to many investigators because of practical importance and fundamental interest concerning "borate anomaly" shown in some physical properties. Na_2O-B_2O_3 melts have also been attractive for its practical use in metallurgical processes. Therefore, the structure and properties of Na_2O-B_2O_3 glasses have been investigated extensively, for example, by means of x-ray diffraction1), Raman spectrscopy2,3), NMR4,5) and thermal expansion6). Regarding Na_2O-B_2O_3 melts, the physical properties such as the density7-9), viscosity10,11), surface tension12) and the velocity of sound13) have been measured widely.

Direct information on the structure of Na_2O-B_2O_3 melts at high temperatures is required for a clear understanding of these results. However, high temperature diffraction studies on the structure of Na_2O-B_2O_3 melts have not yet been reported, to the authors' knowledge, except for previous pulsed neutron scattering measurements by one of the authors14) and several diffraction studies15-18) on pure B_2O_3 melt. Recently, Derno et al19) have attempted to reveal the structure of Na_2O-B_2O_3 melts by comparing the X-ray diffraction data on rapidly quenched and normally cooled Na_2O-B_2O_3 glasses.

In the present study, pulsed neutron total scattering measurements have been carried out on Na_2O-B_2O_3 melts. Molecular dynamics (MD) caluculations have also been carried out on these melts. The structural change of Na_2O-B_2O_3 melts with addition of Na_2O is discussed from these diffraction results, in reference to the results of MD calculations.

2. Experimental

Pulsed neutron scattering experiments have been carried out on 10mol% Na_2O- and 30mol% Na_2O- B_2O_3 melts at 1073K with time-of-flight (TOF) method by using the high intensity total scattering spectrometer (HIT) installed at a pulsed neutron source at National

Laboratory for High Energy Physics (KEK) in Tsukuba. The temperatures and compositions of specimens measured are indicated in the phase diagram in Fig.1.

The total scattering spectrometer HIT used for the present measurements is shown in Fig.2. The incident neutrons, coming from the left-hand side of Fig.2, were scattered by the specimen and the scattered neutrons were detected by the ^{3}He counters. The time-of-flight spectra of scatered neutrons were recorded by a computer-controlled data-acquisition system. Since the time-of-flight corresponds to the wave length of a pulsed neutron, λ , the scattering intensity is obtained as a function of the magnitude of the scattering vector, $Q = 4\pi \sin\theta / \lambda$, where 2θ is the scattering angle.

The samples were prepared by the following procedure. B_2O_3 glass was prepared from boric acid (H_3BO_3) enriched with 99.61 at% ^{11}B, in order to avoide extremely high neutron absorption of ^{10}B. H_3BO_3 was melted and dehydrated in a platinum crucible in a vacuum furnace at 1073K under 10^{-3} Torr for more than 8 hours to produce B_2O_3 glass. The mixture of Na_2CO_3 (99.5%) and B_2O_3 with a given composition was heated and melted in a Pt crucible with a lid at 1373K for more than 4 hours, and then poured into cylindrical mould to form a cylindrical sample of 7 mm diameter.

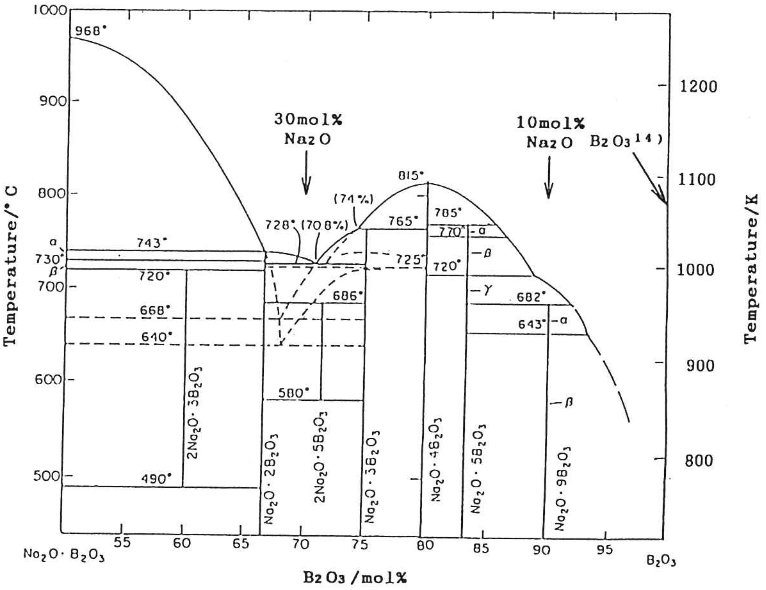

Fig.1. The phase diagram of Na_2O-B_2O_3 system. Allows show the temperatures and compositions of the specimens measured.

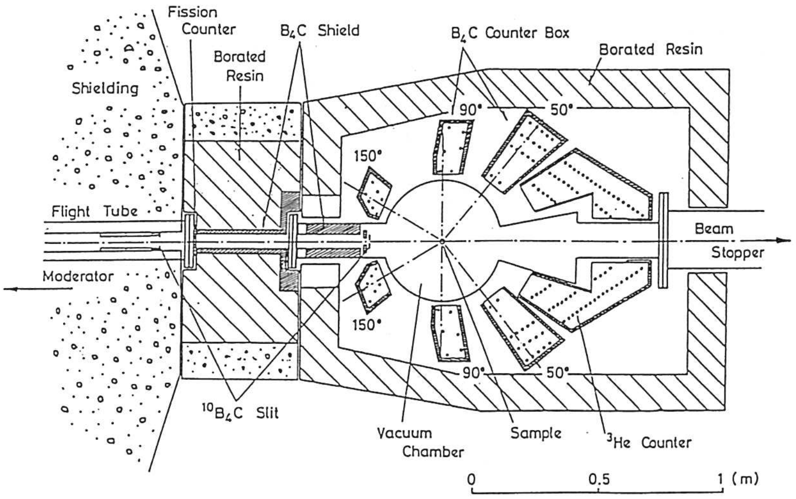

Fig.2. The total scattering spectrometer (HIT) used for pulsed neutron scattering experiments.

In the scattering experiment, the sample was contained in a thin-walled cylindrical Pt cell (8mm in inner diameter and 0.1 mm thick), and held at 1073K by heating with infrared image furnace at about 0.1 torr. The time-of-flight scattering intensity spectra were obtained for the sample in the Pt cell, and for the blank cell.

The scattering intensity for the sample in the Pt cell was corrected for the cell, background, absorption, and multiple and incoherent scatterings. The coherent scattering intensities I(Q) were normalized using the scattering intensities from the vanadium rod.

The interference function S(Q) is obtained as follows:

$$S(Q) = \frac{[\, I(Q) - \{ \Sigma\, (c_i b_i^2) - (\Sigma\, c_i b_i)^2 \}\,]}{(\Sigma\, c_i b_i)^2} \qquad (1)$$

where b_i is the coherent scattering length of the i-th nuclei, ($b_B = 6.65$, $b_O = 5.805$ and $b_{Na} = 3.63 \times 10^{-15}$m [20]) and c_i the atomic fraction. The radial distribution function RDF(r) is obtained by Fourier transform of the structure function Q(S(Q)-1):

$$\mathrm{RDF}(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi}\int_0^{Q_{max}} Q(S(Q)-1)\sin(Qr)dQ \qquad (2)$$

where the number density ρ_0 was evaluated from the density values[7)] of Na_2O-B_2O_3 melts. The pair distribution function g(r) is defined by: $\mathrm{RDF}(r) = 4\pi r^2 \rho_0 g(r)$.

3. Molecular Dynamics Calculation

Molecular dynamics (MD) calculations have been carried out on pure B_2O_3 melt and 30 mol% Na_2O-B_2O_3 melt at 1073K, as a reference to the findings in the pulsed neutron scatterind experiments.

The MD calculations were performed in a similar way to that used previously by one of the authors[21)]. The pair potential functions were assumed to consist of a simplified Coulombic and a repulsion terms:

$$\phi_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0(\beta_i + \beta_j)\exp\left[\frac{(a_i + a_j - r_{ij})}{(\beta_i + \beta_j)}\right] \qquad (3)$$

where, z_i : the formal charge number of ion i (e.g., +3 for B^{3+} ion
e : the unit charge
r_{ij} : the distance between ion i and j
f_0 : a force constant arbitrarily taken here to be 1 $\mathrm{kcal \cdot mol^{-1}\ A^{-1}}$ ($=6.948\times 10^{-6}$ dyn)
a_i, β_i : the crystal radius and compressibility of ion i, respectively.

The parameters used in the MD calculation are given in Table 1. The edge length of the basic cell (a cube) was calculated from the density[7)] of the melt. The number of particles (atoms) within the basic cell was about 1000 (B;400; O;600 for B_2O_3, and B:280; O:480; Na:120 for 30mol%Na_2O-B_2O_3). In evaluating the potential energy and the force, the Coulombic term was calculated by the Ewald method.

Table 1. Potential parameters used in MD calculations.

Atom	z	a/nm	β /nm
B	3	0.0720	0.0080
O	-2	0.1629	0.0085
Na	1	0.1260	0.0080

4. Results and Discussion

Figure 3 compares three Q(S(Q)-1) curves obtained from the experiments for B_2O_3[14)], 10mol% Na_2O- and 30mol% Na_2O-B_2O_3 melts at 1073K, in the wide range of Q up to 300 nm^{-1}. The first three peaks are located at 13.1, 29.4 and 57.0 nm^{-1} for B_2O_3, and these positions are almost unchanged with composition. The overall shapes of Q(S(Q)-1) curves also scarcely change with composition, and the oscillatory benavior in the high Q region is clearly observed, with appreciable damping in amplitude with increase in Na_2O content.

The radial distribution functions RDF(r) obtained by Fourier transform of the experimental Q(S(Q)-1) truncated at about 300 nm^{-1} are compared in Fig.4. The three peaks are

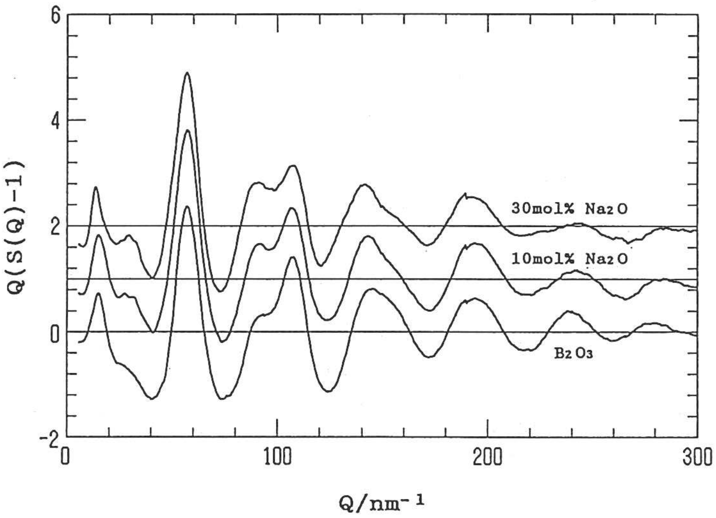

Fig.3. Experimental structure functions Q(S(Q)-1) for Na_2O-B_2O_3 melts at 1073K.

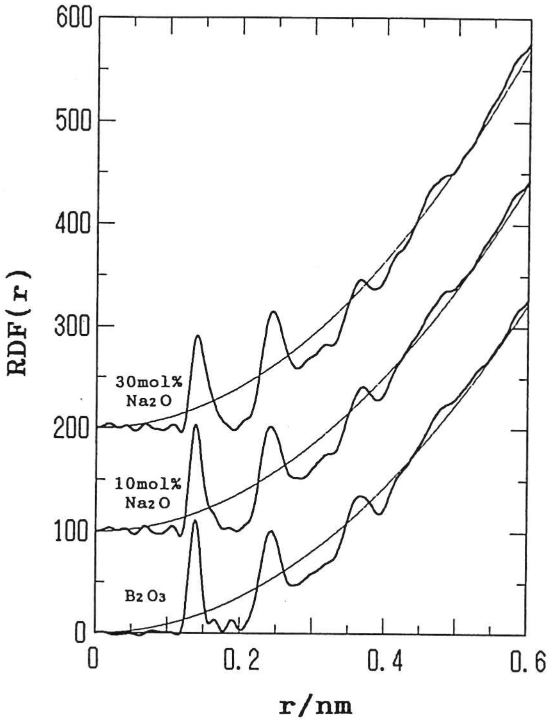

Fig.4. Radial distribution functions RDF(r) for Na_2O-B_2O_3 melts at 1073K.

Table 2. Peak positions of RDF(r).

Melt/mol%	1st/nm	2nd/nm	3rd/nm
B_2O_3	0.137	0.238	0.360
$10Na_2O$-$90B_2O_3$	0.138	0.241	0.370
$30Na_2O$-$70B_2O_3$	0.139	0.244	0.364

Table 3. Area under the first peak of RDF(r) A_1, and the experimental and calculated ooordination number n_{B-O}.

Melt/mol%	A_1	$n_{B-O(expt)}$	$n_{B-O(calc)}$
B_2O_3	2.43	3.0	3.0
$10Na_2O$-$90B_2O_3$	2.58	3.2	3.1
$30Na_2O$-$70B_2O_3$	2.59	3.5	3.4

Table 4. Area A_1 and the coordination number n_{O-B}.

Melt/mol%	A_1	$n_{O-B(expt)}$	$n_{O-B(calc)}$
B_2O_3	2.43	2.0	2.0
$10Na_2O$-$90B_2O_3$	2.58	2.0	2.0
$30Na_2O$-$70B_2O_3$	2.59	2.0	2.0

clearly observed for each of RDF(r). The peak positions are given in Table 3. With increase in Na_2O content from zero to 30 mol%, the first peak position of RDF(r), representing the atomic spacing of B-O, shifted gradually from 0.137 nm to 0.139 nm, and the first peak broadened asymmetrically, spreading to larger r side as shown in Fig.4.

As described in the previous paper on the structure of B_2O_3 melt[14], the first peak of RDF(r) is attributed to the B-O bond. The coordination number of O atoms around a reference B atom, n_{B-O}, is determined from the area, A_1, under the first peak of experimental RDF(r) using the following relationship:

$$A_1 = 2\frac{b_B b_O}{\langle b\rangle^2} c_B n_{B-O} \qquad (4)$$

The coordination number of B atoms around a reference O atom was evaluated from the relationship $c_O n_{O-B} = c_B n_{B-O}$. The experimental values of the coordination numbers $n_{B-O(expt)}$ and $n_{O-B(expt)}$ determined by eq.(4) are listed in Tables 3 and 4, respectively. With the addition of Na_2O to B_2O_3, the coordination number n_{B-O} increased from 3.0 to 3.5, showing variation of the configuration of O atoms around a reference B atom.

As regards the structure of alkali borate glasses, R_2O-B_2O_3, it has been confirmed from Raman[2,3] and NMR[4,5] spectroscopic study that the structure unit BO_3 triangle is converted to tetrahedron BO_4 by the addition of R_2O up to 33% into B_2O_3 as follows: On addition of one molecule of Na_2O to the B_2O_3 glass, two BO_3 units are converted into two BO_4 units. Assuming that the structure units in Na_2O-B_2O_3 melts are converted from BO_3 to BO_4 by the addition of Na_2O in the same way as in Na_2O-B_2O_3 glasses, we can express the fraction of three-coodinated and four-coordinated B atoms, N_3 and N_4 respectively, as follows:

$$N_3 = \frac{1-2x}{1-x}, \qquad N_4 = \frac{x}{1-x} \qquad (5)$$

where x is the mole fraction of Na_2O. Accordingly, the coordination number of O atoms around a reference B atom is:

$$n_{B-O} = 3N_3 + 4N_4 = 3 + \frac{x}{1-x} \qquad (6)$$

The coordination number of B atoms around a reference O atom is:

$$n_{O-B} = \frac{C_B}{C_O} n_{B-O} = 2 \tag{7}$$

The values of the coordination numbers $n_{B-O(calc)}$ and $n_{O-B(calc)}$ calculated from eqs.(6) and (7) are compared in Tables 3 and 4 with $n_{B-O(expt)}$ and $n_{O-B(expt)}$ determined from the experimental RDF(r). The values of n_{B-O} and n_{O-B} calculated from eq. (6) and (7) agreed well with experimental values, respectively. These results suggest that the structural change in Na_2O-B_2O_3 melts with the addition of Na_2O up to 30 mol% is similar to that in Na_2O-B_2O_3 glasses.

The total pair distribution functions g(r) obtained from the experimental Q(S(Q)-1) for B_2O_3 and 30 mol% Na_2O-B_2O_3 are compared in Figs.5 and 6 with the partial pair distribution function $g_{ij}(r)$ and the distribution of coordination numbers $n_{ij}(r)$ obtained from MD calculations. The experimental g(r) corresponds well to the calculated $g_{ij}(r)$ and $n_{ij}(r)$, which serve as a reference in attributing the peaks of RDF(r) to specific atomic bonds. The experimental and calculated n_{B-O} values correspond well to those of MD calculations shown in Figs.5 and 6 as a plateau of $n_{B-O}(r)$ curves (3.0 for B_2O_3 and 3.3 for 30 mol% Na_2O).

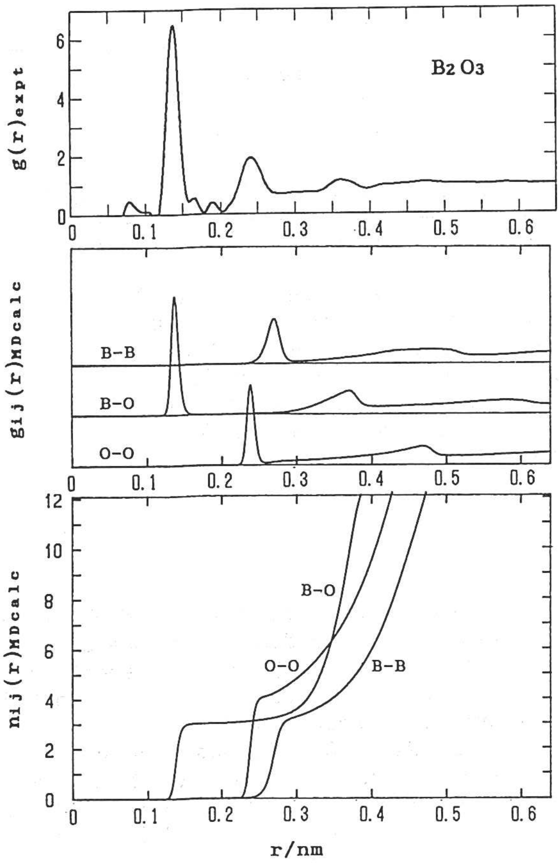

Fig.5. Experimental total pair distribution function $g(r)_{expt}$ compared with partial pair distribution function $g_{ij}(r)_{MDcalc}$ and distribution of coordination numbers $n_{ij}(r)_{MDcalc}$ by MD calculations. (B_2O_3 melt at 1073K)

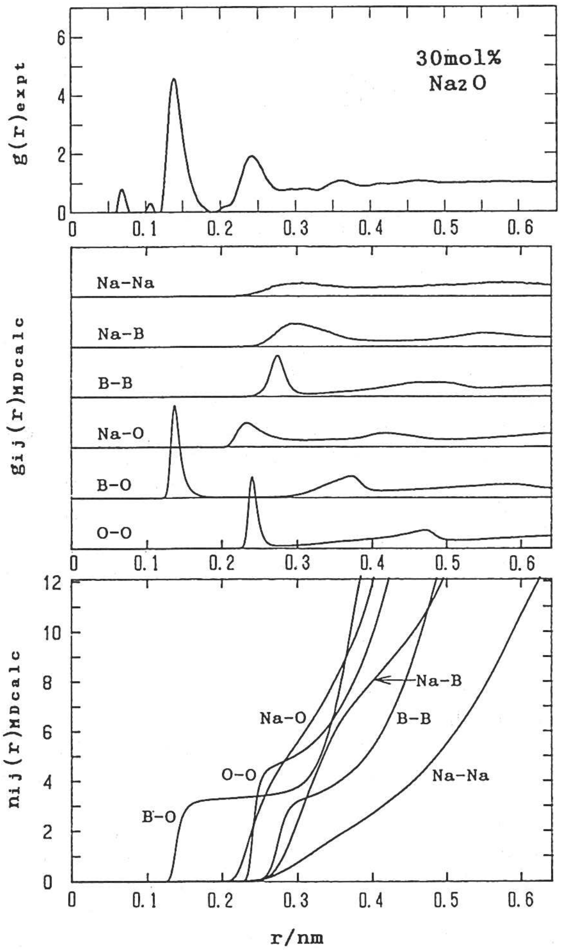

Fig.6. Experimental total pair distribution function $g(r)_{expt}$ compared with partial pair distribution function $g_{ij}(r)_{MDcalc}$ and distribution of coordination numbers $n_{ij}(r)_{MDcalc}$ by MD calculations. (30 mol% Na_2O-B_2O_3 melt at 1073K)

It can be safely deduced from the results mentioned above, that a part of the BO_3 triangle structure units is converted to BO_4 tetrahedron units with the addition of Na_2O to B_2O_3 melt in the same way as in Na_2O-B_2O_3 glasses.

5. Conclusions

Pulsed neutron total scattering measurements have been carried out on 10 mol% Na_2O- and 30 mol% Na_2O- B_2O_3 melts at 1073K. Data on pure B_2O_3 melt were used from the previous experiments at the same conditions. Molecular dynamics (MD) calculations were also carried out on pure B_2O_3 and 30 mol% Na_2O-B_2O_3 melts, for reference.

The first peak of RDF(r), attributed to B-O bond, spread asymmetrically to larger r side, and the coordination number of O atoms around a reference B atom n_{B-O} increased from 3.0 to 3.5 with increase in Na_2O content, showing the change of B-O correlation.

The experimental values of n_{B-O} agreed well with those calculated on the assumption that two triangle BO_3 units are converted to two BO_4 tetrahedron units with the addition of one Na_2O molecule as in Na_2O-B_2O_3 glasses.

The experimental g(r) corresponded well to $g_{ij}(r)$ of MD calculations. The experimental n_{B-O} was also agreed with taht of MD calcualtions.

From these results, it is deduced that a part of BO_3 triangle units in B_2O_3 melt is converted to BO_4 tetrahedron units with increase in Na_2O content up to 30 mol%, as in Na_2O-B_2O_3 glasses.

6. References

1) G.Herms et al : J.Non-Cryst.Solids, 88(1986), 381.
2) W.L.Konijnendijk and J.M.Stevels: J.Non-Cryst.Solids, 18(1975), 307.
3) W.L.Konijnendijk and J.M.Stevels: Borate Glasses (Mater.Sci. Res. Vol.12), ed. L.D.Pye, V.D.Frèchette and N.J.Kreidl, Plenum, New York, (1978), 259.
4) P.J.Bray and J.G.O'Keefe: Phys.Chem.Glasses, 4(1963), 37.
5) G.E.Jellison,Jr and P.J.Bray: J.Non-Cryst.Solids, 29(1978), 187.
6) J.E.Shelby: J.Am.Ceram.Soc., 66(1983),225.
7) L.Shartsis, W.Capps and S.Spinner: J.Am.Ceram.Soc., 36(1953), 35.
8) S.Takeuchi, T.Yamate and M.Kunugi: Zairyo (J.Soc.Mater.Sci.Jpn.), 14(1965), 59.
9) M.Kunugi, A.Konishi, S.Takeuchi and T.Yamate: Zairyo (J.Soc.Mater.Sci.Jpn.), 21(1972), 10.
10) L.Shartsis, W.Capps and S.Spinner: J.Am.Ceram.Soc., 36(1953), 319.
11) G.H.Kaiura and J.M.Toguri: Phys,Chem.Glasses, 17(1976), 62.
12) L.Shartsis and W.Capps: J.Am.Ceram.Soc., 35(1952), 169.
13) K.Nagata, K.Ohira, H.Yamada and K.S.Goto: Met.Trans.B, 18B(1987), 549.
14) M.Misawa : J.Non-cryst.Solids, 122(1990), 33.
15) F.Herre and H.Richter: Z.Naturforschg. 12a81957), 545.
16) J.Zarzycki: Borate Glasses (Mater.Sci.Res. Vol.12), ed. L.D.Pye, V.D.Frèchette and N.J.Kreidl, Plenum, New York, (1978), 201.
17) Y.Waseda: Can.Met.Quart., 20(1981), 57.
18) M.Miyake and T.Suzuki: J.Chem.Soc., Faraday.Trans. 1, 80(1984), 1925.
19) M.Derno, G.Herms and H.Steil: Phy.Stat.Sol., a93(1986), K5.
20) V.F.Sears: Atomic Energy of Canada Limited Report, No.AECL-8490, (1984).
21) N.Umesaki, N.Iwamoto, M.Takahashi, M.Tatsumisago, T.Minami and Y.Matsui: Trans.Iron Steel Inst. Jpn, 28(1988), 852.