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The effect of borate and silicate structure on thermal conductivity in the molten $Na_2O–B_2O_3–SiO_2$ system

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ABSTRACT

Thermal conductivity of molten $Na_2O–B_2O_3–SiO_2$ system was measured at various temperatures and for different compositions using the hot-wire method. It was observed that thermal conductivity decreases at higher temperatures. The calculated one-dimensional Debye temperature implies that the change of the phonon mean free path dominantly affects the thermal conductivity in the present measurements. Using solid state ^{11}B and ^{29}Si MAS NMR, the structure of the oxide system was confirmed. A conflicting effect of the R ratio (Na_2O/B_2O_3) on thermal conductivity was observed. For R below 0.5, owing to the increase in 4-coordinated boron, thermal conductivity increases with increasing R ratio. However, for R above 0.5, thermal conductivity decreases with increasing R ratio as a result of the depolymerization of silicate networks and the increase in non-bridging oxygen (NBO). Finally, the effect of the K ratio (SiO_2/B_2O_3) on thermal conductivity was considered. A higher K ratio causes an increase in thermal conductivity as a result of the increase in the total amount of the silicate structure and a more effective mixing between silicon and 4-coordinated boron.

1. Introduction

Owing to its low thermal expansion and excellent chemical durability, sodium borosilicate glass is widely used in laboratory apparatuses and household cookware [1]. However, it is also well-known for its complicated structural change, named as the “boron oxide anomaly”. The coordination number of boron initially changes from 3 to 4 at high concentrations of alkali oxides; further addition of alkali oxides results in the change of 4-coordinated boron into 3-coordinated boron with the formation of non-bridging oxygen (NBO) and depolymerization of the silicate network structure. Thus, a considerable amount of studies [2–14] have been carried out to understand the short- and intermediate-range order of the sodium borosilicate system by using nuclear magnetic resonance (NMR), Raman spectroscopy, and molecular dynamic (MD) simulations.

As a result of the complicated structural change, the physical properties of the sodium borosilicate system cannot be estimated by a simple linear approximation based on chemical compositions [15]. Several studies have been conducted to elucidate the relations between the structure of the sodium borosilicate system and the physical properties [16–21]. Shiraishi et al. [16] reported that the measured viscosity of glassy $Na_2O–B_2O_3–SiO_2$ systems initially increased with increasing B_2O_3 content until the Na_2O/B_2O_3 ratio reached the unity, and subsequently decreased. They attributed the dependence of the viscosity on the Na_2O/B_2O_3 ratio to the change of the boron coordination number. Such a conflicting effect of B_2O_3 on the viscosity of the $Na_2O–B_2O_3–SiO_2$ system was also reported by Zhang and Reddy [17], who measured the viscosity in the molten sodium borosilicate system. They observed that the addition of B_2O_3 resulted in an increase in viscosity at low SiO_2/Na_2O ratio, but in a decrease in viscosity at high SiO_2/Na_2O ratio. Ghoneim and Halawa [18] measured the thermal conductivity of the sodium borosilicate glass at room temperature and found that the formation of both the BO_4 and SiO_4 structure groups results in an increase in the thermal conductivity along with an extension of the phonon mean free path.

Even if other physical properties have been measured across various temperature ranges; from glass to melts, the thermal conductivity has been mainly studied in the glass state. Although understanding the thermal conductivity of the molten oxide is also important for the thermal processing of the glass [22], the thermal conductivity measurement in the molten oxide system has been limited because of the large convection and the radiation effects [23]. However, owing to the several modifications of the non-steady state method, the thermal conductivity has been successfully measured in the molten oxide system over the last few decades [24–33]. Similar to other physical properties of the molten oxide system, the thermal conductivity is closely related to the network structure (i.e., silicate, aluminate, and borate structure.)

Recently, Kim and Morita [25] measured the thermal conductivity in the molten $Na_2O–SiO_2$ and $Na_2O–B_2O_3$ system. In the $Na_2O–SiO_2$ binary system, a linear relationship between thermal conductivity and viscosity was obtained, indicating the dominant effect of the Q^4 unit, which is the SiO_4 tetrahedron with four bridging oxygen atoms and zero NBO

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atoms. In the Na_2O–B_2O_3 system, the positive relationship between thermal conductivity and the relative fraction of 4-coordinated boron was observed in the region where the tetraborate unit is dominant. However, the simultaneous effect on the thermal conductivity of both the relative fraction of 4-coordinated boron and silicate structures in the molten oxide system has not been reported yet.

Although Kim and Morita [26] measured thermal conductivity in the CaO–SiO_2–B_2O_3 mold flux system, it mainly consisted of the metaborate units formed by asymmetric 3-coordinated boron due to the high CaO concentration and the low B_2O_3 concentration. For this reason, the effect of 4-coordinated boron on thermal conductivity could not be appropriately evaluated along with silicate network structure.

Therefore, in the present work, the thermal conductivity of the molten Na_2O–B_2O_3–SiO_2 system was measured within the tetraborate or diborate dominant region in order to evaluate the effect of both relative fraction of 4-coordinate boron and silicate network structure. The thermal conductivity was measured by adopting a hot wire method. The structure of borate and silicate structure was evaluated using ^{11}B and ^{29}Si magic angle spinning (MAS) NMR.

2. Experimental procedures

2.1. Sample preparation

The experimental compositions of the present work are shown in Fig. 1. The samples were prepared with fixed K ratios (SiO_2/B_2O_3) of 0.5, 1.0, and 2.0, and various R ratios (Na_2O/B_2O_3). To investigate the glass structure of the present system, the experiments were performed outside the “No glass” region [34].

Reagent grade SiO_2, B_2O_3, and Na_2CO_3 were weighed and subsequently ground in an agate mortar for 20 min to obtain a homogeneously distributed mixture. The powder mixture was then transferred to a platinum crucible and kept in the temperature range of 1423–1573 K, depending on its melting temperature, to enable it to decarbonate, dehydrate, and homogenize. After 2 h, the melt was quenched on a water-cooled copper plate, and then it was finely crushed. The product was transferred to a Pt-10%Rh crucible (inner diameter (ID): 32 mm; outer diameter (OD): 38 mm; height: 70 mm), and the thermal conductivity was measured by the hot-wire method in the molten state.

After the measurement, the solidified sample was re-melted at 1373 K, quenched by pouring it onto a water-cooled copper plate, and then quickly covered with a copper block. The obtained glass was ground and sieved under 100 μm ϕ mesh. The final compositions of Na_2O and B_2O_3 were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7700, SII NanoTechnology, Tokyo, Japan), and the SiO_2 content was analyzed using a gravimetric analysis technique. The weighted initial and analyzed final compositions are listed in Table 1.

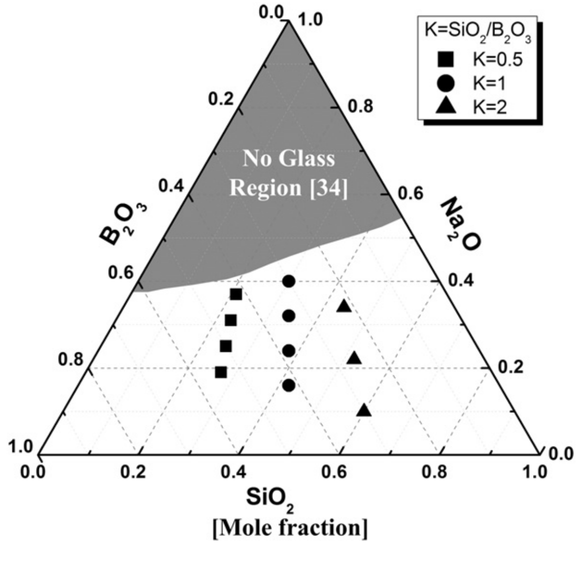

Fig. 1. Experimental compositions of the Na_2O–B_2O_3–SiO_2 system.

Table 1
Initial and final chemical compositions of the Na_2O–B_2O_3–SiO_2 systems used in the present work.

	Initial composition mol% (weighed)			R (Na_2O/B_2O_3)	K (SiO_2/B_2O_3)	Final composition mol% (analyzed)		
	Na_2O	SiO_2	B_2O_3			Na_2O	SiO_2	B_2O_3
1	37.0	21.0	42.0	0.88	0.5	35.2	19.8	45.0
2	31.0	23.0	46.0	0.67	0.5	30.6	23.0	46.4
3	25.0	25.0	50.0	0.50	0.5	24.3	23.2	52.5
4	19.0	27.0	54.0	0.35	0.5	18.1	25.4	56.5
5	40.0	30.0	30.0	1.33	1.0	37.4	30.6	32.0
6	32.0	34.0	34.0	0.94	1.0	29.6	34.9	35.5
7	24.0	38.0	38.0	0.63	1.0	23.4	37.9	38.7
8	16.0	42.0	42.0	0.38	1.0	15.2	42.3	42.5
9	34.0	44.0	22.0	1.55	2.0	32.8	44.5	22.7
10	22.0	52.0	26.0	0.85	2.0	21.1	52.2	26.7
11	10.0	60.0	30.0	0.33	2.0	9.4	59.8	30.8

For the ^{29}Si MAS NMR measurement, additional samples containing 0.1 mol% Fe_2O_3 to reduce the spin–lattice relaxation time were prepared [35]. The procedure followed to prepare the samples was the same as that described above.

2.2. Thermal conductivity measurement and error on the measurement

The Pt-10%Rh crucible, filled with approximately 90 g of the pre-melted sample, was placed in a vertical furnace equipped with a SiC heating element. The sample was held for 1 h at 1273 K to obtain a homogeneous phase, and then the thermal conductivity of the Na_2O–B_2O_3–SiO_2 system was measured from 1273 K to the liquidus temperature at intervals of 50 K. The temperature of sample was controlled by the PID (proportional integral differential) controller and calibrated B-type thermocouple (Pt-30%Rh/Pt-6%Rh) within ± 3 K. To ensure the thermal equilibrium of the system, the furnace temperature was reduced at a rate of 3 K/min and held for 15 min at the target temperature. At each temperature, the thermal conductivity was measured three times at intervals of 5 min to examine the reproducibility. The random error was determined by the standard deviation of the repetitive measurements [36], and it is displayed in the figures as error bar. During the thermal conductivity measurement, constant current, applied by galvanostat, was determined between the standard resistor of 0.1 Ω (Yokogawa 2792, Yokogawa, Tokyo, Japan); accuracy of 0.01%. Any voltage change between the potential leads at a four-terminal hot-wire sensor was recorded using digital multimeter (Keithley 2000, Keithley instruments, Cleveland, OH, USA); accuracy of 0.002%. It should be noted that the heat can be transferred by radiation from the Pt-13%Rh hot wire to the molten oxide, and contribution of radiation would be considerable due to the high temperature. Using the Stefan–Boltzmann law for gray-body radiation, the heat radiation at the surface of hot wire was estimated. During the calculation, emissivity of Pt-13%Rh wire was extrapolated on the basis of empirical equation of emissivity of Pt-10%Rh wire [37]. The calculation indicates that approximately 0.8% of total heat is transferred by radiation at 1273 K. In Table 2, systematic errors on present measurement are summarized.

Table 2
Estimation of the systematic errors on the thermal conductivity measurement.

Uncertainty component	Relative uncertainty
Temperature calibration	0.2%
Accuracy of standard resistor	0.01%
Resolution of digital multimeter	0.002%
Heat by radiation	0.8%