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Temperature dependence and cation effects in the thermal conductivity of glassy and molten alkali borates

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ABSTRACT

The thermal conductivity of $\text{Li}_2\text{O-B}_2\text{O}_3$, $\text{Na}_2\text{O-B}_2\text{O}_3$ and $\text{K}_2\text{O-B}_2\text{O}_3$ glass systems was measured as a function of the temperature. As the temperature increases, the thermal conductivity of the glass phase initially increases and then reaches a plateau. Afterwards, in the liquid phases, a further increase in the temperature leads to a decrease in the thermal conductivity. The thermal conduction phenomenon can be better described by considering the glass and molten oxide systems as a one-dimensional continuum. It was found that the temperature corresponding to the highest thermal conductivity lies close to the one-dimensional Debye temperature (θ_{D1}). According to phonon gas model, the variables affecting the thermal conductivity were evaluated. Below θ_{D1} , the increase in heat capacity with the temperature leads to a corresponding increase in the thermal conductivity. The heat capacity then becomes constant above θ_{D1} leading to the observed plateau in the thermal conductivity of the glass phase. After melting the glass, the decrease in thermal conductivity with increasing temperature is due to changes in sound velocity and mean free path. The relative content of 3- and 4-coordinated boron was analyzed by ^{11}B MAS-NMR. The cation effect on the thermal conductivity of alkali borate glasses was evaluated through their ionization potentials.

1. Introduction

During the continuous casting process in the iron and steelmaking, the introduced synthetic oxides; termed mold flux, are located between the copper mold and molten steel, forming various glass, crystalline and liquid phases [1,2]. Since thermal conduction through the mold flux has a strong influence on the various defects; such as longitudinal crack and sticker break-out, found in the final products [1], understanding the thermal conductivity of the glass, crystalline, and liquid phases has high practical importance. Whereas the thermal conductivity of crystalline phases has been extensively reported, not many studies have focused on the thermal conductivity of glass and liquid phases over different ranges of temperature.

Nagata and Goto [3] measured the thermal conductivity of various slag systems from room to high (approximately 1673 K) temperature, and reported an interesting temperature dependence of the thermal conductivity. From room to a certain temperature; T_0 between approximately 773 and 1273 K, the thermal conductivity exhibits a positive temperature dependence which changes into a negative temperature dependence above T_0 . Such positive and negative temperature dependence is commonly observed for the thermal conductivity of the glass

and liquid phase, respectively. For instance, a positive temperature dependence has been found in various glass systems [4–6], whereas a negative dependence has been reported for a number of molten oxides [7–12]. Based on these studies, focused on the thermal conductivity of different phases, it can be inferred that the change in the temperature dependence of the thermal conductivity reported by Nagata and Goto [3] results from phase changing from glass to liquid.

Recently, a similar temperature dependence of the thermal conductivity in glass and molten oxide systems was reported by Ozawa and Susa [13], who measured the thermal conductivity in the $\text{CaO-SiO}_2\text{-Na}_2\text{O}$ system from room temperature (RT) to 1573 K. According to Ozawa and Susa's work, the thermal conductivity initially increases with increasing temperature, before reaching a maximum at approximately the glass transition temperature (T_g), followed by a negative temperature dependence. Although they attempted to separately determine the temperature dependence of the thermal conductivity in the glass and molten oxide systems, it was not clear whether a crystalline phase was formed or not during their measurements. In addition, the reason for the thermal conductivity reaching its maximum at the glass transition temperature is still unclear. Considering that glass and liquid phases coexist in the mold flux layer, understanding the changes in

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thermal conductivity over a wide temperature range, corresponding to both glass and liquid phases in the mold flux system, is thus a task of high practical importance.

The phonon spectrum of amorphous solids cannot be reduced to a single Brillouin zone due to the absence of a regular lattice. In addition, phonon scattering by Umklapp process is no longer valid [14]. The irregular structure of amorphous solids plays roles as not only thermal conduction medium but also defects resulting in phonon scattering. In the last few decades, several studies have reported the existence of phonon-like vibrational modes in molten systems and discussed their origin [15–18]. The structural similarity between glasses and highly viscous melts, in terms of intermediate range order periodicity, suggests that the mechanism of phonon thermal conduction in these systems is also similar.

In the majority of the previous studies, the thermal conductivities of glassy and molten states were investigated separately. However, in order to understand the thermal conduction through a mold flux layer consisting of different phases, along with its temperature dependence, the phonon thermal conduction in this system should be reviewed simultaneously for all phases.

Boron oxide is considered as one of the possible substitute in the CaF₂-free mold flux system for high Al containing ultra-lightweight steel [12]. In order to elucidate the relation between thermal conductivity and borate structure, thermal conductivity in the molten alkali-borate system has been investigated. In the previous studies [19,20], the thermal conductivity of molten alkali-borate system shows a negative temperature dependence in the higher temperature region. However, the slope of thermal conductivity-temperature relationship gradually decreases with decreasing temperature, until the thermal conductivity becomes constant near to the melting temperature. In the present study, the thermal conductivity of alkali borate glasses was measured with high accuracy through a transient hot-wire method. Based on the results of both the previous and the present study, the main variables affecting thermal conductivity in glass and liquid phases were qualitatively identified using the phonon gas model. In addition, the borate structure was investigated using MAS-NMR, with the purpose of elucidating the effect of cations on the thermal conductivity of the glass.

2. Experimental procedures

2.1. Sample preparation

The R₂O-B₂O₃ (R = Li, Na, and K) glass samples were prepared from reagent grade R₂CO₃ and B₂O₃. After grinding in an agate mortar, the powder mixture was transferred into a Pt crucible and melted at 1373 K in a muffle furnace. After 1 h, the molten sample was quenched on a copper plate and then, finely crushed in order to obtain a homogeneous mixture. The crushed powder was re-melted in the Pt crucible at 1373 K. After 1 h, the molten oxide was poured into a cylinder-shaped hole carved in the copper mold. Before pouring the molten oxide into the mold, a hot-wire (a Pt-13% Rh wire of 0.15 mm diameter) welded with Pt wires of 0.15 mm and 0.5 mm diameters was placed on a rectangular groove previously carved in the copper mold. In order to relax the thermal stress, the copper mold was heated at 603 K on the hot-plate. After pouring, the molten oxide remaining in the Pt crucible was quenched and then collected for further analysis.

After few hours, the solidified glass sample (with diameter and height of 15 and 10 mm, respectively) was transferred from the copper mold into an alumina holder. Finally, the holder was placed on an alumina plate hanging on an alumina lance equipped with Pt wires for the thermal conductivity measurements. The schematic diagram of the thermal conductivity measurement apparatus is shown in Fig. 1.

The alkali oxide and B₂O₃ contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS32350UV, SII NanoTechnology, Japan). The initial and final compositions are

listed in Table 1.

2.2. Determination of glass transition and crystallization temperatures

In order to determine the glass transition and crystallization temperature (T_g and T_c , respectively), thermogravimetry-differential thermal analysis (TG-DTA) experiments were carried out on a Thermo plus TG 8120 (Rigaku, Tokyo, Japan) unit. An approximate amount of 0.02 g of powdered sample was filled in a platinum pan (with inside and outside diameters of 5 and 5.5 mm, respectively, and 2.5 mm height) and placed on a platinum plate at the end of a ceramic rod. A similar quantity of reference sample (Al₂O₃) was filled in a platinum pan of the same size and placed on the platinum plate at the end of another ceramic rod. The samples were heated up under argon atmosphere from room temperature to the liquidus temperature, at a rate of 5 K/min. The temperature of the differential thermocouple was recorded as a function of time. After reaching the target temperature, the sample was cooled down at a rate of 20 K/min.

The glass transition temperature was determined from the heating curve according to the American Society for Testing Materials (ASTM) standard method E1356-08. The crystallization temperature was determined by the peak temperature corresponding to the maximum heat flow. Fig. 2 shows the DTA thermal curve for the present K₂O-B₂O₃ system, whose K₂O fraction was 10 mol%. The black dashed lines at 619 K and 785 K indicate the glass transition and crystallization temperature, respectively. The measured T_g and T_c of the present alkali borate system are listed in Table 2.

2.3. Thermal conductivity measurements and determination of the crystalline phase

The thermal conductivity of the glass system was measured using a transient hot-wire method. The prepared glass sample equipped with Pt wires was placed in an electric resistance furnace. The temperature was controlled using a PID (proportional integral differential) controller and a calibrated K-type thermocouple (chromel–alumel) within ± 2 K. The thermal conductivity was measured at 100 K intervals starting from room temperature. During these measurements, a constant current of 1.5 A was supplied to the hot-wire (a 0.15 mm diameter Pt-13% Rh wire) and the voltage change between the two terminals of the wire was recorded by a digital multimeter. At each temperature, the thermal conductivity was measured three times at intervals of 5 min in order to assess the reproducibility. According to the standard deviation of the repetitive measurements, the random error was determined and shown in the figures as error bar. The contribution of radiation from the Pt-13% Rh hot wire was estimated by using the Stefan-Boltzmann law for gray-body radiation. The calculation shows that approximately 0.2% of total heat is transferred by radiation at 873 K; the highest temperature of present measurement. In Table 3, systematic errors on present measurement are summarized. Further details about the procedures used to measure the thermal conductivity and the systematic errors can be found our previous papers [8,20].

A drastic increase of thermal conductivity was observed above T_c as a result of the formation of the crystal phase. After the thermal conductivity measurement, the crystalline phase of the opaque sample was determined by X-ray Diffraction (XRD; RINT 2500, Rigaku, Japan). Fig. 3 shows the XRD pattern of the amorphous and crystallized Li₂O-9B₂O₃ samples, before and after the thermal conductivity measurement. The crystal phases detected in the present alkali borate system are listed in Table 2.

2.4. Structure investigation

In order to characterize the structure of the alkali borate glass system, solid state ¹¹B magic angle spinning (MAS) spectra were recorded at 11.74 T using a Fourier Transform (FT) NMR spectrometer

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