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# Thermal Conductivity Measurement of the Molten Oxide System in High Temperature

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## Abstract

In spite of practical importance in the pyro-metallurgy process, thermal conductivity of molten oxide system has not been sufficiently studied due to its notorious convection and radiation effects. By an aid of appropriate modification of measurement technique and evaluations for systematic errors, thermal conductivity measurement at high temperature becomes feasible. In this chapter, thermal conductivity measurement technique for high-temperature molten oxide system was discussed along with related experimental errors. In addition, thermal conduction mechanism by phonon was briefly introduced. The laser flash method and hot-wire method, which are representative measurement methods for high-temperature system, were compared. During the measurement by using hot-wire method, the convection and radiation effects on measurement results were evaluated. In the hot-wire method, both convection and radiation effects were found to be negligible within short measurement time. Finally, the effect of network structure of molten oxide system on thermal conductivity was discussed. The positive relationship between thermal conductivity and polymerization in the silicate and/or borate system was presented. In addition, the effect of cation expressed by function of ionization potential on thermal conductivity was also briefly introduced. This chapter is partially based on a dissertation submitted by Youngjae Kim in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of Tokyo, September 2015.

**Keywords:** thermal conductivity, hot-wire method, transient method, molten oxide, network structure

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## 1. Introduction

In the iron-making and steel-making field, understanding of thermal conductivity of the molten oxide system is significant because it is closely related with the operation conditions, quality of final products and recycling of slag.

For the recycle of blast furnace slag, the slag is slowly cooled down in the atmosphere or rapidly quenched by using rotary cup atomizer or air blast method. Highly crystallized slag can be recycled as cement concrete for road construction or fertilizer. On the other hand, noncrystalline blast furnace slag can be used as Portland cement for construction owing to its properties of cement when it is ground [1]. Therefore, in order to recycle the blast furnace slag as Portland cement, proper fineness and glass state should be achieved. Since the characteristic fine-granular shape and glass state are mainly determined by a cooling rate, understanding of thermal conductivity of blast furnace slag is important. For this reason, the thermal conductivity measurement in the molten  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system, which is the typical blast furnace slag system, has been carried out by using hot-wire method [2–4] and laser flash method [5].

During the steel-making process, understanding of thermal conductivity of the molten slag is closely related to the quality of final products and refractory lifetime. Recently, many works have been focused on the development of heat flow of the whole steel-making chain. However, due to the short information concerning about thermal conductivity of ladle slag, ladle slag is hardly considered during the simulation [6]. For the purpose of better understanding of heat flow, understanding of thermal conductivity of ladle slag is important. Glaser and Sichen [6] measured thermal conductivity of the conventional ladle slag system;  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  system, using the hot-wire method. Their results show the negative temperature dependence of thermal conductivity within the experimental region between 1773 and 1923 K. They reported that the formation of solid state in the slag results in the significant increase of thermal conductivity. On the other hand, Kang et al. [7], who measured thermal conductivity in the steel-making slag system of  $\text{CaO-SiO}_2\text{-FeO}_x$  system, reported that addition of  $\text{FeO}_x$  results in the decreasing of thermal conductivity due to the basic oxide behavior of  $\text{FeO}_x$ . Considering the structural information of  $\text{FeO}_x$  obtained by Mössbauer, they found the linear relationship between thermal conductivity and the  $\text{NBO}/T$ , which is the relative fraction of the number of nonbridging oxygen over total tetrahedral cation, implying the effect of network structure on thermal conductivity.

In addition, during the continuous casting process, irregular horizontal heat transfer through mold flux results in the “longitudinal cracking” and “star cracking” on the final product. Therefore, understanding of thermal conductivity of mold flux system is practically important in terms of quality control. Many studies [8–11] have been carried out in order to find out the relationship between structure of mold flux system and thermal conductivity at high temperature of molten state. These works [8–11] commonly observed the structure dependence of thermal conductivity. Addition of basic oxide, such as sodium oxide or calcium oxide, decreases thermal conductivity as a result of depolymerization of silicate network structure [8, 11]. Susa et al. [10] found that fluorides play a role of network modifier resulting in the lowering thermal conductivity. According to Mills [12], phonon transfer along silicate network

chain or ring has much lower thermal resistivity ( $1/\lambda$ ) than from chain to chain. Similarly, Susa et al. [10] observed that more ionic bonding has the greater thermal resistivity. Therefore, it can be concluded that the positive relationship between thermal conductivity and network structure is closely related to the formation of covalent bond which has low thermal resistivity.

Not only the steel-making process, but also other pyro-metallurgy process, understanding of thermal conductivity is significant. During the operation of submerged arc furnace (SAF) which is widely used in manganese ferroalloy producing, "freeze" lining is applied in order to insulate the refractory and prevent direct contact with molten metal and slag [13]. "Freeze" lining can enhance the refractory lifetime because it prevents the wear mechanism; such as alkali attack, thermal stress and dissolution of refractory. According to Steenkamp et al. [14], who measured thermal conductivity in the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnO}$  system, "freeze" lining becomes thicker with higher thermal conductivity indicating that thermal conductivity is the major factor determining the thickness of "freeze" lining.

The observed thermal conductivity, called effective thermal conductivity ( $\lambda_{\text{eff}}$ ), can be expressed by the summation of each different thermal conductivity such as lattice thermal conductivity ( $\lambda_L$ ), radiation thermal conductivity ( $\lambda_R$ ) and electronic thermal conductivity ( $\lambda_{\text{el}}$ ) [15]

$$\lambda_{\text{eff}} = \lambda_L + \lambda_R + \lambda_{\text{el}} \quad (1)$$

The lattice thermal conductivity ( $\lambda_L$ ) is based on the heat transfer by phonon. Because scattering of phonon results in the decrease in thermal conductivity, thermal conductivity by phonon is significantly influenced by the change of disordering of network structure in the glass and molten oxide system [16]. Over the 800 K, radiative heat transfer ( $\lambda_R$ ) in the clear glass becomes dominant factor [17]. At higher temperature of the transparent molten oxide system, more than 90% of heat is transferred by the radiation conduction. On the other hand, thermal conductivity by electron is insignificant in the molten oxide system as long as the composition of transition metallic oxide does not exceed 70% [15, 18].

In the molten oxide system, the radiative heat conduction can be simply predicted by assuming the steady state along with grey-body conditions. The radiative heat transfer through an optically thick sample can be calculated by a function of absorption coefficient and refractive index in the Stefan-Boltzmann law [15]. However, due to its tremendous radiative and convection effect, precise measurement of thermal conductivity by phonon in the molten oxide system was challenging. Recently, owing to the appropriate modifications [2, 4, 19] and evaluations for systematic error by simulation [20], thermal conductivity measurement technique in the molten oxide system has been improved.

In this chapter, transient hot-wire method that is one of the major thermal conductivity measurement techniques for molten oxide system is introduced comparing with laser flash method. The measurement principle is simply dealt with, and experimental errors are considered. In addition, thermal conduction mechanism in the amorphous system by phonon is discussed. Since the lattice thermal conduction is mainly determined by the structure of oxide system, the effect of structure such as silicate network or ionic bonding, and type of cation is briefly discussed.

## 2. Thermal conduction in glass and molten oxide system

Ziman [21] explained the transport of heat in terms of collective model instead of individual particle vibration. Namely, thermal energy is the distribution of normal modes of vibration. Owing to the collective model, the excitations that can be considered as the movement of particles in a gas, and kinetic theory is possibly adopted. In the case of glass and ceramic system, determination of a single Brillouin zone is impossible since there is no regular lattice. For this reason, not Umklapp scattering but irregular structure determines the phonon scattering in the glass system. Kingery [22] reported that the phonon interaction by discrete lattice is equivalent to random scattering in the ceramic and glass system. For convenience, he adopted mean free path concept and expressed thermal conductivity by phonon as the transport of energy by particle. As a result, thermal conductivity has been simply explained by the phonon gas model in various glass and ceramic systems [16, 23, 24].

$$\lambda = \frac{1}{3} C \bar{v} l \quad (2)$$

where  $\lambda$ ,  $C$ ,  $\bar{v}$  and  $l$  indicate thermal conductivity, heat capacity, mean particle velocity, and mean free path of collision.

However, the heat transfer mechanism in the liquid and molten oxide system is still controversial. In the liquid state, Zwanzig [25] proposed the collective dynamical variables having the similar characteristic of longitudinal and transverse phonon. The frequency of the elementary excitation is defined as approximate eigenvalue by an eigen function of the Liouville operator. In addition, he also calculated the lifetimes of elementary excitations reporting that it is determined by the elastic moduli and viscosities. As a result, in the molten oxide system which has enough viscosity coefficients, an elementary excitation has physical meaning. Recently, using *ab initio* molecular dynamics simulations, Iwashita et al. [26] showed that the local configurational excitations in the atomic connectivity network are the elementary excitations in molten metal at high temperature.

Turnbull [27] found that thermal conduction mechanism in the molten salts system is similar to the solid state. Due to the similar ionic spacing of salt system in the solid and liquid state along with the relatively small heat of fusion, he assumed that thermal motion would be similar in liquid and solid. In addition, according to his calculation, the diffusional contribution to thermal conductivity of liquids does not exceed 4%, indicating the major role of vibrational conduction in heat transfer. Similar to molten salt system, it can be inferred that heat is mainly transferred by vibrational excitations in the molten oxide system.

Recently, considering the similar thermal conduction mechanism in glass and molten oxide system, Kim and Morita [28] explained the effect of temperature on thermal conductivity following the same approach. Adopting the one-dimensional Debye temperature and phonon gas model, variables and effect of temperature on thermal conductivity were discussed. According to their work, thermal conductivity of glass initially increases with increasing temperature due to the increase of heat capacity. At one-dimensional Debye temperature where heat capacity becomes max, thermal conductivity reaches the maximum. Afterward, owing to the fluidity of molten state, mean particle velocity along with mean free path of collision decreases with increasing temperature. From physical viewpoint, as increasing

temperature, the required frequency of shear waves to propagate in molten oxide system increases. Since phonon is bosonic particle, the average number of particles follows Bose-Einstein distribution indicating that lower frequency modes have more phonons at a fixed temperature. As a result, negative temperature dependence of thermal conductivity can be found because lower number of shear wave with much higher frequency can propagate as temperature increases.

### **3. Thermal conductivity measurement technique and related experimental errors**

#### **3.1. Thermal conductivity measurement technique for high-temperature oxide melts**

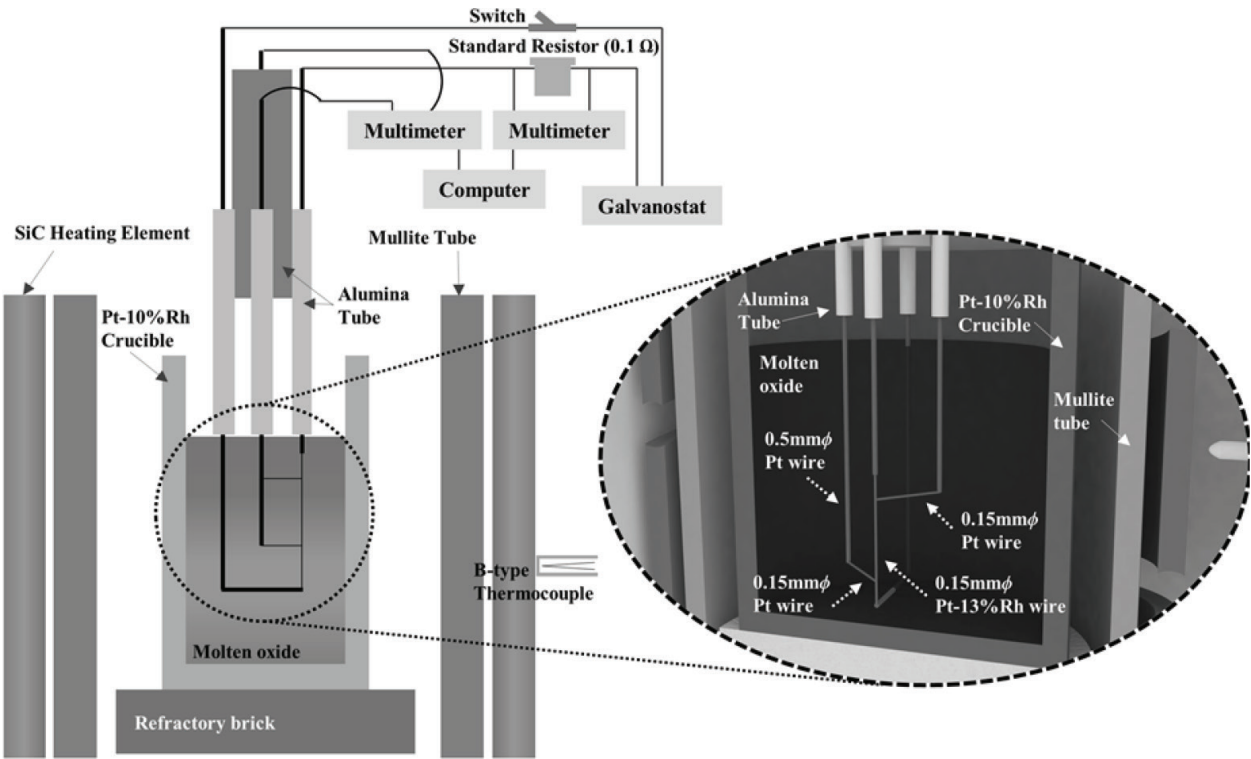
Although the understanding of thermal conductivity by phonon is significant for the process control in the iron-making and steel-making field, precise measurement of thermal conductivity by phonon is challenging due to the notorious radiation and convection effect at high temperature [29]. The measurement method of thermal conductivity by phonon can be classified into largely two groups: one is steady-state and another one is nonsteady-state method. In steady-state method, thermal conductivity is determined by the temperature profile across a sample contacting directly with a heat source [15]. However, steady-state method requires a relatively long measurement time in order to obtain the steady state of thermal profile across the sample [18]. In addition, during the measurement, contribution of radiation and convection becomes significant due to the long measurement time. For these reasons, at high temperature, thermal conductivity by phonon transfer cannot be precisely measured by using steady-state method.

In order to investigate the thermal conductivity of molten oxide system, nonsteady-state measurement method has been modified for the last few decades. For the measurement of molten oxide system, two measurement techniques have been widely adopted: one is laser flash method and another one is hot-wire method. Two techniques have in common that both two methods apply constant energy and monitor the temperature change with time. Because the thermal conductivity can be measured within approximately 10 s by nonsteady-state method, the effect of radiation and convection is insignificant as compared to the steady-state method.

Since the first introduction of laser flash method in 1961, this technique has been widely adopted for the purpose of measurement of thermal diffusivity and heat capacity in various materials [30]. During the measurement, the front surface is heated by a single pulse laser resulting in an increasing of temperature at the opposite surface. Then, thermal diffusivity is calculated from the increasing temperature. However, due to the leakage of heat from measurement sample, the sufficient accuracy cannot be achieved at high temperature. Several improvements of laser flash method have been introduced in order to overcome various problems occurred during the measurement. In the 1990s, Ogura et al. [31] developed three-layered laser flash method. Although it has the merit of relatively small heat leakage, calculation of thermal conductivity by phonon transfer requires various physical properties related with radiation such as absorption coefficient [32]. For this reason, recently, Ohta et al. [32, 33], revised the three-layered laser flash method and introduced new method,

called front heating-front-detection laser flash method. Distinct from previous laser flash methods, the laser pulse is irradiated on the bottom of platinum crucible during the front-heating front-detection technique. Assuming the one-dimensional heat flow along with semi-infinite thickness of liquid sample, [33] thermal conductivity is calculated by the measurement of the temperature decay at the bottom of surface. Since the thermal conductivity is measured within only 12 ms, front-heating front detection technique does not consider the additional process for distinguishing radiation effect from observed thermal conductivity data. However, although the front heating-front detection laser flash method has the merit of simple procedure and easy data processing, [34] the effect of radiation on thermal conductivity measurement is still controversial, especially at high temperature [18]. The three different laser flash methods, namely, conventional, three-layered and front heating-front detection laser flash method, have been adopted for the measurement of thermal conductivity, and more details can be found elsewhere [18].

**Figure 1** shows the schematic diagram of the hot-wire method for molten oxide system. The hot-wire method, also known as line-source method, is a nonsteady-state method. Because the hot-wire method uses a very thin metal wire, the effect of radiation is relatively insignificant even at high temperature [35]. Since transient hot-wire technique firstly introduced in the 1780s, this method has been widely used for the precise measurement of thermal conductivity of solid, liquid and even gas phases [36]. During the thermal conductivity measurement of molten oxide system, a thin Pt-13%Rh wire is placed in the middle of molten oxide sample and heated up by the applied constant current. The generated heat is transferred from hot-wire



**Figure 1.** Schematic diagram of the transient hot-wire method for molten oxide system.

into molten oxide system resulting in increasing temperature. If the hot-wire is long enough, the temperature change of molten oxide system resulting from constant heat flux  $Q$  can be expressed by a continuous line heat source solution [37].

$$\Delta T = \frac{Q}{4\pi\lambda} \left( \ln \frac{4\kappa t}{r^2} - \gamma \right) = \frac{Q}{4\pi\lambda} \left( \ln t + \ln \frac{4\kappa}{r^2 e^\gamma} \right) \quad (3)$$

Here,  $\Delta T$  is the temperature change of hot-wire,  $Q$  is the heat generation per unit length of hot-wire,  $\lambda$  is the thermal conductivity,  $\kappa$  is the thermal diffusivity,  $r$  is the radius of hot-wire,  $t$  is the time, and  $\gamma$  is the Euler's constant, 0.5772. The continuous line heat source solution can be adopted when the length and diameter ratio of hot-wire is larger than 30 [38]. Following the differentiation of Eq. (4), thermal conductivity can be expressed by Eq. (4).

$$\lambda = \left( \frac{Q}{4\pi} \right) / \left( \frac{dT}{d \ln t} \right) \quad (4)$$

Because a constant current is applied by galvanostat, heat generations per unit length of hot-wire ( $Q$ ) can be calculated by the following equation.

$$Q = \frac{VI}{m} = I^2 \frac{R_T}{m} \quad (5)$$

$$R_T = R_0(1 + AT + BT^2) \quad (6)$$

The abovementioned equation,  $V$ ,  $I$ ,  $m$ ,  $R_T$  and  $R_0$  represents the voltage, current, length of hot-wire, resistance per unit length at  $T^\circ\text{C}$ , and resistance per unit length at  $0^\circ\text{C}$ , respectively. Eq. (6) shows the empirical linear relationship between  $R_T$  and  $R_0$ . According to Kang and Morita [3], constant of  $A$  and  $B$  for Pt-13%Rh wire is  $1.557 \times 10^{-3}$  and  $-1.441 \times 10^{-7}$ , respectively. During the measurement,  $R_T$  is obtained by applying infinitely small current which could not heat up the experimental sample.

From the Ohm's law, the following equation can be obtained at the given temperature  $T$ .

$$\frac{dV}{dT} = I \frac{dR_T}{dT} = IR_0(A + 2BT) \quad (7)$$

From the Eqs. (4), (5) and (7), the thermal conductivity can be expressed as the function of voltage and time.

$$\lambda = \left( \frac{I^3 R_T R_0 (A + 2BT)}{4m\pi} \right) / \left( \frac{dV}{d \ln t} \right) \quad (8)$$

Using the four-terminal sensing, [11] the voltage change of hot-wire is recorded in real time. Therefore, thermal conductivity of the molten oxide system can be easily calculated by the slope of  $V$  versus  $\ln t$ .

Recently, Mills et al. [39] found that thermal conductivity of molten slag system measured by laser flash method is approximately 10 times than by hot-wire method implying the effect of radiation in the laser flash method. Therefore, it would be inferred that thermal conductivity of molten oxide system is precisely measured at high temperature by using the hot-wire method rather than using the laser flash method.

### 3.2. Evaluation of the experimental errors occurred during the thermal conductivity measurement by hot-wire method

According to Kwon and Lee [40] and Healy et al. [41] who studied about the errors occurred during the thermal conductivity measurement, appropriately designed hot-wire method can measure thermal conductivity of liquid with the error of less than 0.31%. Although they considered low temperature, below 100°C, effect of other variables such as convection and current leakage seems insignificant during the thermal conductivity measurement even at high temperature.

As previously mentioned, in order to reduce the radiative heat transfer, a thin Pt-13%Rh wire of 0.15 mm $\phi$  is used in the hot-wire method during the thermal conductivity measurement. However, although a hot-wire method uses extremely thin wire, the heat can be transferred from the surface of hot-wire by radiation and it becomes significant as temperature increases during the thermal conductivity measurement.

Using the Stefan–Boltzmann law for grey-body radiation, the radiation heat at the surface of hot wire was estimated.

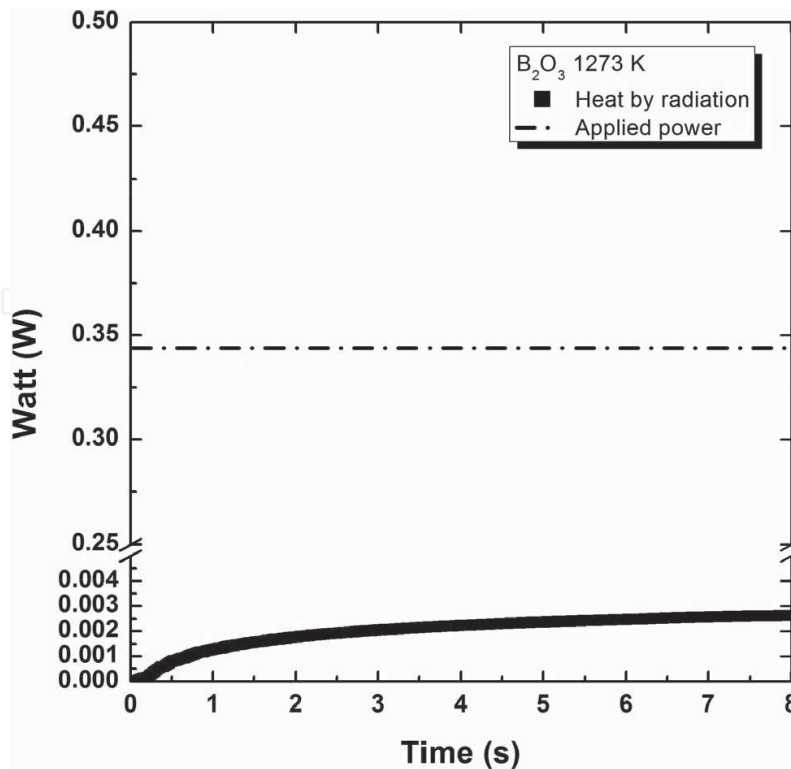
$$q = \varepsilon E_b = \varepsilon \sigma T_s^4 \quad (9)$$

where  $q$  is the radiated heat energy,  $\varepsilon$  is the emissivity,  $\sigma$  is the Stefan-Boltzmann constant,  $T_s$  is the surface temperature (K). During the calculation, emissivity of Pt-13%Rh wire was extrapolated on the basis of empirical equation of emissivity of Pt- 10%Rh wire [42]

$$\varepsilon = 0.751 (T\rho)^{0.5} - 0.632(T\rho) + 0.670 (T\rho)^{1.5} - 0.607 (T\rho)^2 \quad (10)$$

where  $\rho$  is the resistivity, and  $T$  is the temperature of hot-wire (°C). The temperature change of hot-wire along with heat generation was evaluated by the voltage change. Considering the resistivity of hot-wire, the radiation heat during the measurement was evaluated. In **Figure 2**, change of radiation heat along with applied power at 1273 K is presented. After 5 s of experiment, the ratio of radiation heat to the applied power, which is the net heat flow, becomes approximately 0.69% at 1273 K. This value is accordance with the previously calculated value of 1% in the transparent slag at 1273 K after 5 s of experiment [2]. Especially, within the thermal conductivity measurement region, which is 0.8–2 s, radiation heat takes less than 0.51% over total heat flow. Therefore, it can be concluded that radiation effect is not significant during the thermal conductivity measurement using a hot-wire method.

The effect of free convection can be reduced by placing the upper level of the sample in the highest temperature zone [4]. However, during the measurement, the heating up of hot-wire



**Figure 2.** Change of radiation heat (black rectangular) with varying time at a fixed temperature of 1273 K. Dashed dot line indicates the applied power.

results in the increase in temperature of molten oxide system along with partial temperature difference. Such temperature gradient would lead to the convection. In order to determine the effect of convection, the change of Rayleigh number with varying time was considered. **Figure 3** shows the schematic diagram of heat penetration during a hot-wire measurement.

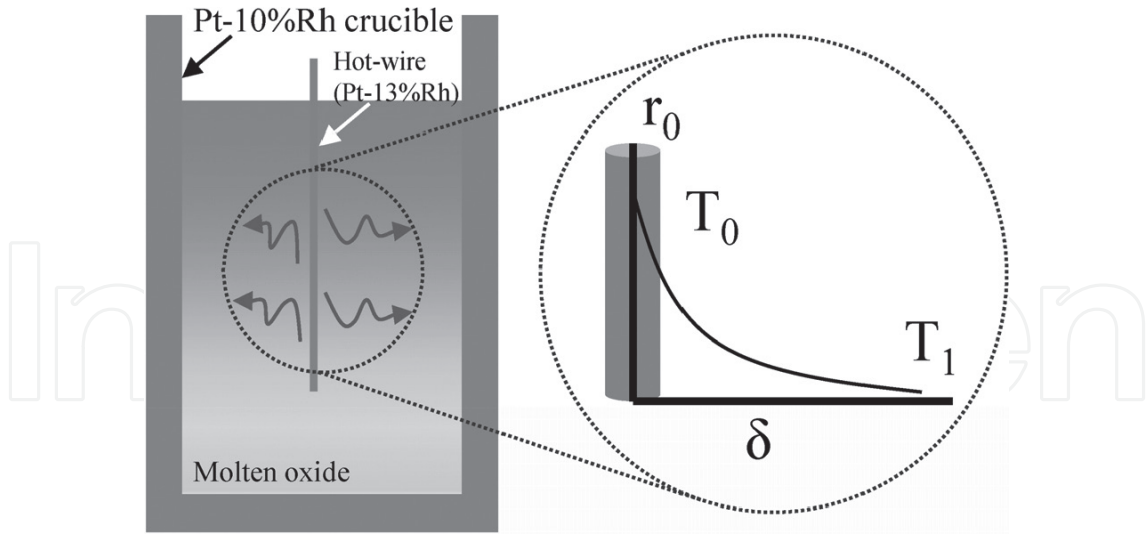
When a current is applied, heat is generated in a thin hot-wire; radius of  $r_0$ . Since it is a non-steady-state method, the heat penetration distance will be varying with time.  $\delta$  is the penetration distance.  $T_0$  and  $T_l$  is the temperature at the surface of hot-wire and the temperature at  $\delta$ , respectively. The heat penetration distance ( $\delta$ ) is a function of time ( $t$ ). Tokura et al. [43] reported that heat penetration distance from the hot-wire can be expressed by the following equation.

$$\delta \approx (24\alpha r_0 t)^{1/3} + r_0 \quad (11)$$

The abovementioned Eq. (11) is valid when  $(\delta - r_0) \gg 4r_0$ .  $\alpha$  represents the thermal diffusivity.

It has been reported that free convection is occurred when Rayleigh number ( $Ra$ ) is larger than 1000 [1]. Therefore, calculation of Rayleigh number in the present molten oxide system is significant in order to evaluate the effect of free convection during the experiment. Rayleigh number can be expressed by the following equation, which is the product of Grashof number and Prandtl number.

$$Ra = \frac{\beta \Delta T g L^3}{\nu \alpha} \quad (12)$$



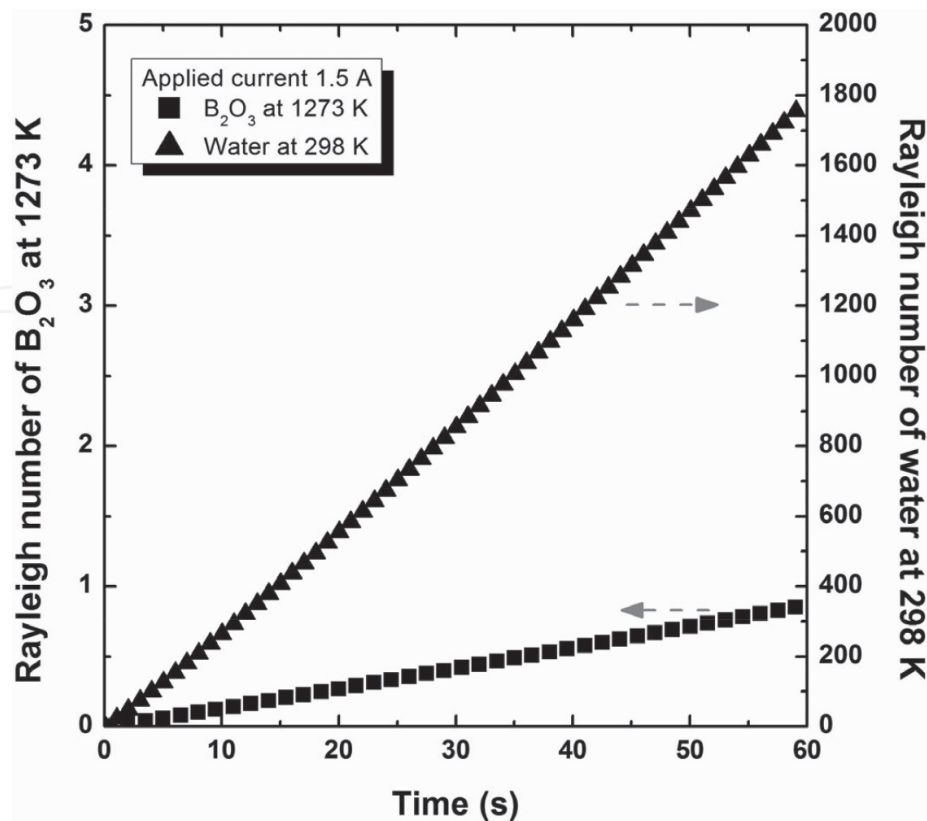
**Figure 3.** Schematic diagram of heat penetration during thermal conductivity measurement by hot-wire measurement.

where  $\beta$  is thermal expansion coefficient,  $\Delta T$  is temperature difference,  $g$  is gravitational acceleration,  $L$  is characteristic length,  $\nu$  is kinetic viscosity.  $L$  can be substituted with heat penetration distance ( $\delta$ ). Combine the Eqs. (3), (11) and (12), Rayleigh number can be deduced by the following equation, where  $C$  is the exponential of Euler's constant; 1.78.

$$Ra = \frac{\beta g Q}{4\pi \lambda \nu \alpha} [(24\alpha r_0 t)^{1/3} + r_0]^3 \ln\left(\frac{4\alpha t}{r_0^2 C}\right) \quad (13)$$

Using Eq. (13) along with following physical properties of molten  $B_2O_3$  system at 1273 K, Rayleigh number can be calculated. Thermal expansion coefficient ( $\beta$ ) of molten  $B_2O_3$  is 100 ppm/K at the temperature range between 1273 and 1473 K [44]. Thermal diffusivity ( $\alpha$ ) is  $4.325 \text{ cm}^2 \text{ s}^{-1}$  at 1273 K [31]. Kinematic viscosity, that is, the ratio of dynamic viscosity to density is  $0.0065 \text{ m}^2 \text{ s}^{-1}$  [45]. Rayleigh number is calculated, and it is shown in **Figure 4**. Compared to Rayleigh number of pure water at 298 K, molten  $B_2O_3$  system shows much lower Rayleigh number. Due to much higher kinematic viscosity and thermal diffusivity,  $B_2O_3$  shows much lower Rayleigh number even at high temperature of 1273 K. Therefore, it can be concluded that there is no free convection effect during the thermal conductivity measurement of molten oxide system within 10 s. In addition, if there is convection effect, the linearity between voltage and time could not be observed. As a result, the thermal conductivity by phonon transfer can be safely obtained within the region where the linear relationship between voltage and time exists.

Recently, several studies have evaluated the experimental conditions which affect precision of the measurement using hot-wire method [20, 46]. A computational fluid dynamics (CFD) calculation [20] revealed that determination of the resistivity and the temperature coefficient of resistance of the hot-wire is crucial in order to obtain precise thermal conductivity. In addition, Kang et al. [46] calculated the current leakage by semi-quantitative evaluation and reported that the current leakage is 2% (at most) in various silicate melts which contain less than 20 wt%  $FeO_x$ .

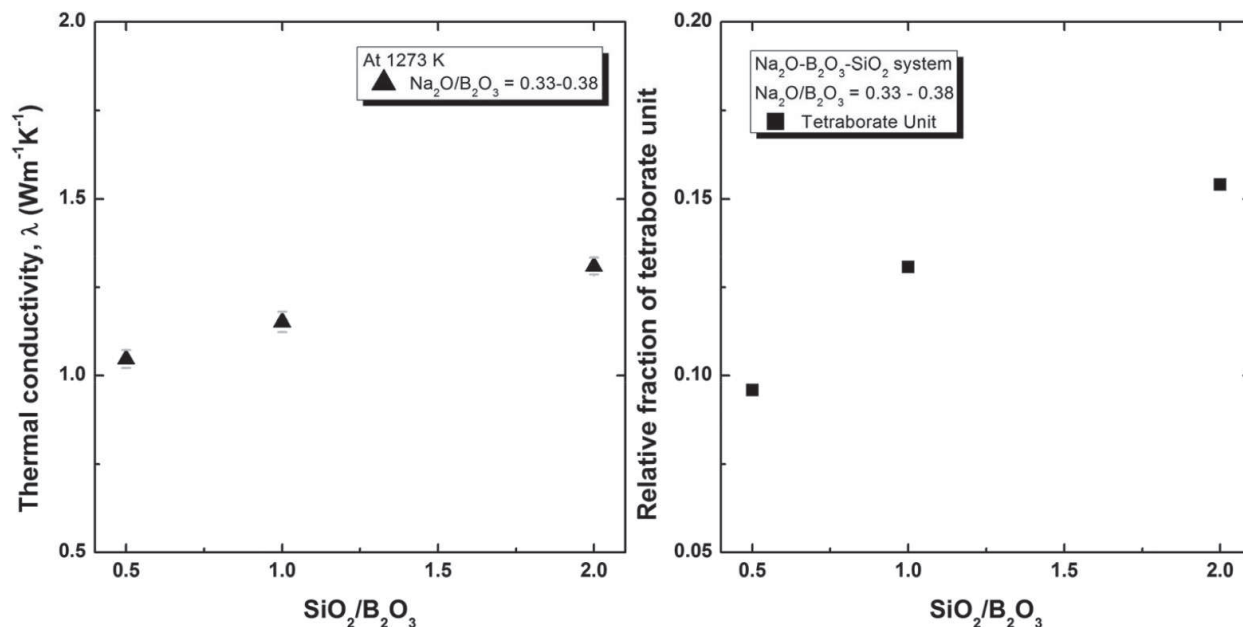


**Figure 4.** Calculated Rayleigh number of molten  $B_2O_3$  at 1273 K (left) and water at 298 K (right) with varying time.

#### 4. Effect of structure and cation on thermal conductivity of molten oxide system

Similar to other physical properties, such as density, thermal expansion, viscosity and electric conductivity, thermal conductivity of molten oxide system is affected by the network structure such as silicate, borate and aluminate network structures. It was known that formation of network structure in the glass and molten oxide system plays a role of limiting to the network randomness [47] resulting in the increase of thermal conductivity by reducing of phonon-phonon scattering. According to Kang and Morita [3], depolymerization of silicate network structure results in lowering thermal conductivity. In addition, amphoteric behavior of aluminum oxide related to aluminate structure leads to both increasing and decreasing of thermal conductivity depending on its compositions. Recently, Kim and Morita reported the effect of intermediate range order borate structure [48–52]. In case of borate structure, complicated super-structure units exist consisting of 3- and 4-coordinate boron ions associated with oxygen ions [53]. Depending on the compositions and oxide system, different borate super-structure can be formed resulting in different effects on thermal conductivity.

In **Figure 5**, thermal conductivity of molten  $Na_2O-B_2O_3-SiO_2$  system is shown with varying  $SiO_2/B_2O_3$  mole ratio [49]. At 1273 K, increasing of thermal conductivity with higher ratio of  $SiO_2/B_2O_3$  can be found. Although these systems show similar silicate network structures with



**Figure 5.** Relationship between  $\text{SiO}_2/\text{B}_2\text{O}_3$  ratio and the thermal conductivity (left),  $\text{SiO}_2/\text{B}_2\text{O}_3$  ratio and relative fraction of tetraborate unit (right).

analogous non-bridging oxygen (NBO) number [49]. On the right side of **Figure 5**, the effect of  $\text{SiO}_2/\text{B}_2\text{O}_3$  ratio on borate super-structure obtained by Raman spectroscopy is shown. It should be noted that the Raman spectra were identified by using Gaussian deconvolution from appropriate references. According to area ratio, the relative fraction of associated structures was calculated. The increase of relative fraction of associated structures can be found with higher concentration of  $\text{SiO}_2$ . Considering that tetraborate unit consisting of 3- and 4-coordinate boron forms three-dimensional network, thermal conductivity increases as a result of polymerization of the network structure. Similar effect can be found in another study reporting the increase of viscosity with formation of tetraborate unit in the  $\text{CaO-Al}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$  system [54].

Not only the polymerized network structure, but also cation affects thermal conductivity in the molten oxide system [8, 28, 51, 55]. The linear relationship between thermal conductivity and ionization potential ( $Z/r^2$ ); the ratio of the charge of the cation ( $Z$ ) to the square of the cation radius ( $r$ ), was observed in the alkali-borate system [28, 51]. In addition, the effect of ionization potential of cation on thermal conductivity is similar in both glass and molten oxide system. Recently, Crupi et al. [56] reported that intermediate range order borate structure, that is borate super-structure, is affected by the type of cations. As increasing of the ionic radius of cation, larger radius of void can be found. Since larger void has high flexibility with high configurations, thermal conductivity decreases as increasing of ionic radius [28].

## 5. Conclusions

In this chapter, the thermal conductivity measurement technique for high-temperature molten oxide system was reviewed along with heat conduction. Although phonon cannot be

defined in the molten oxide system, phonon-like excitation is elementary excitation having similar characteristic of longitudinal and transverse phonon. Recent studies revealed that local configurational excitation is a origin of phonon-like excitation. In addition, the effect of temperature on thermal conductivity in both glass and molten oxide system was reviewed. The laser flash method and hot-wire method, typical thermal conductivity measurement techniques for high temperature, were briefly reviewed. Compared to laser flash method, hot-wire method is relatively precise for measurement of molten oxide system by reducing radiation effect through small surface of heating source. The systematic errors probably occurred were considered. The radiation and convection effects were reviewed based on the simple modeling and mathematical calculations in the molten oxide system. Results showed that radiation effect and convection effect on thermal conductivity are insignificant at 1273 K. Especially, since the measurement is terminated within 5 s, its effect would be negligible. Finally, the effect of network structure and cations on thermal conductivity was discussed. Due to limiting its randomness, polymerization of glass and molten oxide system results in the increase of thermal conductivity. In addition, the effect of cation type on thermal conductivity in the molten oxide system was discussed through the ionization potential.

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