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Estimation of thermal conductivity of silicate melts using three-dimensional thermal resistor network model

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ABSTRACT

The thermal conductivity of silicate melts was evaluated using a thermal resistor network model, which consisted of a diamond lattice. Based on the assumption that the mean free path of phonons is shorter than the interatomic distance, the thermal conductivity of the silicate melts was calculated through a Monte-Carlo simulation based on the non-bridging oxygens to tetrahedral cations (NBO/T) ratio and the ratio of the conductance of silicon with NBOs ($C_{Si\text{-}NBO}$) to that of silicon with bonding oxygens ($C_{Si\text{-}BO}$). For NBO/T < 1, the simulated thermal conductivity of the silicate melts was in good agreement with that reported in the literature. Thus, the proposed method and the three-dimensional thermal resistor network model used are suitable for estimating the thermal conductivity of silicate melts.

1. Introduction

The heat-transfer properties of silicate melts are of great importance for the design and control of solidification and refining processes of metals. Several studies have investigated the thermal conductivity of the silicates Al_2O_3-CaO-SiO_2 at high temperatures [1–5], and recently, the thermal diffusivity and conductivity of molten $NaAlSi_3O_8$, $CaMgSi_2O_6$, and Mg_2SiO_4 samples were also reported [6–8]. However, the thermal diffusivity and conductivity values in the latter studies exhibited a sharp negative temperature dependence. It can be presumed that the measured values vary with the experimental technique used because of the difficulty in performing measurements at elevated temperatures. Moreover, the effects of polymerization of the silicate network structure on the thermal conductivity have not been elucidated completely because of the poor reliability of thermal conductivity data for silicate melts obtained at elevated temperatures.

The objective of this study was to evaluate the thermal conductivity of Al_2O_3-CaO-Na_2O-SiO_2 silicate melts using a three-dimensional thermal resistor network model. The degree of polymerization of silicate melts was characterized by the ratio of non-bridging oxygens to tetrahedral cations, i.e., the NBO/T ratio, in which T represents Si or Al cations [9]. The chemical compositions of the samples were chosen systematically such that the thermal conductivities of silicate melts with a wide range of NBO/T ratios could be considered. In this study, given the actual structure of silicate melts, the three-dimensional thermal resistor network model was assumed to have a diamond lattice structure. In addition, since any differences in the measured values would depend on human error and the measurement technique used, among other factors, we used the front-heating and front-detection laser-flash method in this study [3,10,11].

2. Materials and methods

2.1. Silicate samples used

The chemical compositions of the investigated molten silicates are listed in Table 1. The NBO/T ratio has been used by many researchers as a descriptor of the degree of polymerization of silicate melts. In the case of the investigated molten silicates, the NBO/T ratios were calculated using the following relationship:

$$\mathrm{NBO/T} = \frac{2(X_{CaO} + X_{Na_2O}) - 2X_{Al_2O_3}}{X_{SiO_2} + 2X_{Al_2O_3}} \quad (1)$$

where X_{CaO}, X_{Na_2O}, X_{SiO_2}, and $X_{Al_2O_3}$ are the mole fractions of the melt in question of CaO, Na_2O, SiO_2, and Al_2O_3, respectively. The NBO/T ratios are also shown in Table 1. Mills et al. has previously suggested that the NBO/T ratios of slags are related to their thermal conductivities. Fig. 1 shows a two-dimensional network model to evaluate thermal conductivity. Unconnected points in the silicate network broken by alkaline or alkaline earth oxides act as barriers to phonon propagation, and the thermal conductivity thus increases with a decrease in NBO/T ratio. This model constitutes a resistor network model,

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Table 1
Chemical compositions (mol%) and NBO/T ratio values of silicate samples used [11].

Sample	Al_2O_3	CaO	Na_2O	SiO_2	NBO/T
A1	8.0	34.0	–	58.0	0.70
A2	13.1	31.5	–	55.4	0.45
A3	10.1	41.5	–	48.4	0.92
A4	16.0	39.0	–	45.0	0.60
A5	21.0	36.0	–	43.0	0.35
B1	–	–	45.0	55.0	1.64
B2	–	–	30.0	70.0	0.86
B3	7.0	–	27.9	65.1	0.53
C1	–	9.1	13.6	77.3	0.59
C2	–	18.4	12.2	69.4	0.88
C3	–	16.7	25.0	58.3	1.43
C4	–	10.1	40.5	49.4	2.05
C5	–	23.1	34.6	42.3	2.73

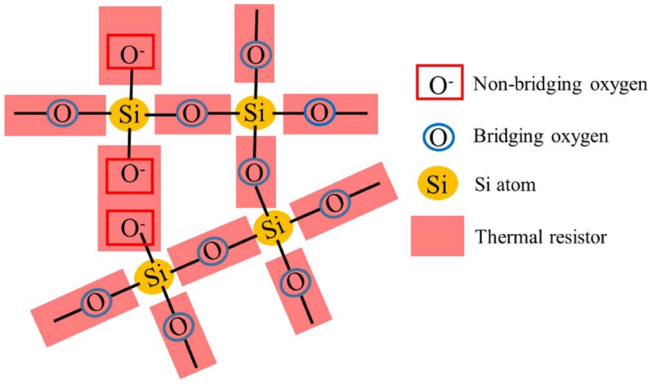

Fig. 1. Two-dimensional network model of molten silicates.

wherein the nodes and resistors correspond to the Si atoms and chemical bonds between the Si atoms, respectively. The bonds consist of one O atom shared between two Si atoms (bridging oxygen, BO) or a pair of ionized O^- atoms connected to one Si atom (NBO) [12–15]. This model has been successfully expanded to predict the thermal conductivity of alkali silicate melts containing fluorides, with bonds consisting of a pair of ionized F^- atoms connected to one Si atom acting as high resistors [16]. However, this two-dimensional model shown in Fig. 1 is qualitative estimation of thermal conductivity. This is because the resistor network model does not consider the spatial information related to the nodes and only connects information between neighboring nodes and the conductance, which is the reciprocal of the resistance between nodes. Therefore, we expanded the model to a three-dimensional one to estimate thermal conductivity and the effect of NBOs.

2.2. Three-dimensional resistor network model for estimating thermal conductivity

2.2.1. Model used

A silicon-oxygen tetrahedron is shown in Fig. 2. The three-dimensional network model was constructed by linking the tetrahedron on the corners that correspond to Si either with the adjacent Si or by inserting network-modifier cations between a pair of O^- ions to form a three-dimensional structure. The resulting tetrahedra had structures that were the same as that of diamond, in which tetrahedral units are formed by each C atom binding to four other C atoms. By positioning Si atoms at the locations of the C atoms instead, a three-dimensional resistor network is easily formed in this structure. Fig. 3(a) shows the unit connections corresponding to a crystallographic unit cell (unit cube) of the diamond structure. In this figure, the No. 3 Si atom is linked to the Si atoms labeled as No. 1, 2, 5, and 6. Hereinafter, Si atoms like No. 3 are referred to as nodes.

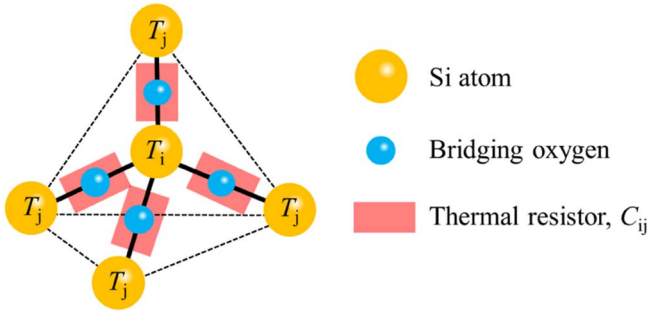

Fig. 2. Cluster used to model molten silicates.

Each of the 8 nodes has a list that contains the connections to the other four nodes to build the structure. For Node 3, this list is: Node 1, Node 2, Node 5, Node 6. All lists are shown below.

Node 1: Node 3, Node 4<$\bar{1}\bar{1}$0>, Node 7<$\bar{1}$01>, Node 8<0$\bar{1}$1>
Node 2: Node 3, Node 4, Node 7<001>, Node 8<001>
Node 3: Node 1, Node 2, Node 5, Node 6
Node 4: Node 1<110>, Node 2, Node 6<100>, Node 5<010>
Node 5: Node 3, Node 4<0$\bar{1}$0>, Node 8<0$\bar{1}$0>, Node 7
Node 6: Node 3, Node 4<$\bar{1}$10>, Node 7<$\bar{1}$10>, Node 8
Node 7: Node 1<10$\bar{1}$>, Node 2<00$\bar{1}$>, Node 5, Node 6<100>
Node 8: Node 1<01$\bar{1}$>, Node 2<00$\bar{1}$>, Node 5<1$\bar{1}$0>, Node 6

Here, the numbers with angle brackets denote the nodes of adjacent unit cells, which are connected in the same manner as the carbon atoms in the diamond structure. Fig. 3(b) shows the structure with 72 nodes formed by repeating the unit cell 27 times in a 3 × 3 × 3 structure. Only the conductance of the unit at the center of the structure is shown. The numbers in angle brackets indicate the direction from the central unit in terms of the crystallographic orientation. It should be noted that the spatial distribution of the nodes was not related to the results and only the topological configuration of the nodes determined the calculation procedure.

2.2.2. Calculation of thermal conductivity

The thermal conductivity was derived as the ratio of the net heat flow for a model consisting of NBOs and BOs to that for a model consisting only of NBOs.

Steady-state heat conduction was assumed when computing the effective thermal conductivity using the model.

A constant boundary temperature condition given by Eq. (2) was imposed at the top plane, while that given by Eq. (3) was imposed at the bottom plane in Fig. 3(b). The nodes on the top plane with top unit connections are 1 and 2, while those on the bottom plane with bottom unit connections are 7 and 8.

$$T_t = 1 \tag{2}$$

$$T_b = 0 \tag{3}$$

where T_t is the temperature of a node on the top plate and T_b is the temperature of a node on the bottom plate. The heat needed for the other nodes i to satisfy the energy conservation requirement when considering that the net heat flow is zero for any nodes connecting i in the steady state is as follows:

$$0 = \sum_{connecting\ i} C_{ij}(T_i - T_j) \tag{4}$$

where j is the connected node i and C_{ij} is the thermal conductance between nodes i and j. The conductance, C_{ij}, was fixed at 1 for the BOs. A total of 6 sets of calculations were performed for the conductance C_{ij} corresponding to the NBO pairs of 0, 0.2, 0.4, 0.6, 0.8, and 1.

The resulting simultaneous linear equations were solved