



Thermal Conductivity of the Silicate Melts

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Agenda

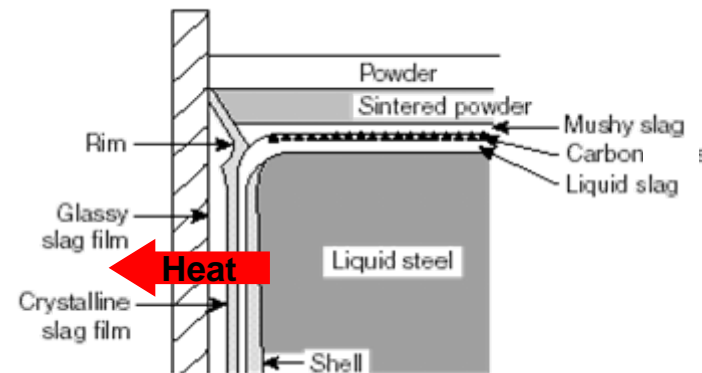


- Introduction
 - **Thermal conductivity of liquid oxide**
 - **Previous studies and Objectives**
- Experimental
 - **Apparatus, Experimental procedure, Sample preparation**
- Results and Discussion
 - **Temperature and Composition dependence**
 - **Amphoteric behavior of Al_2O_3**
 - **Relationship of thermal conductivity to silicate structure**

Thermal Conductivity of Liquid Oxides

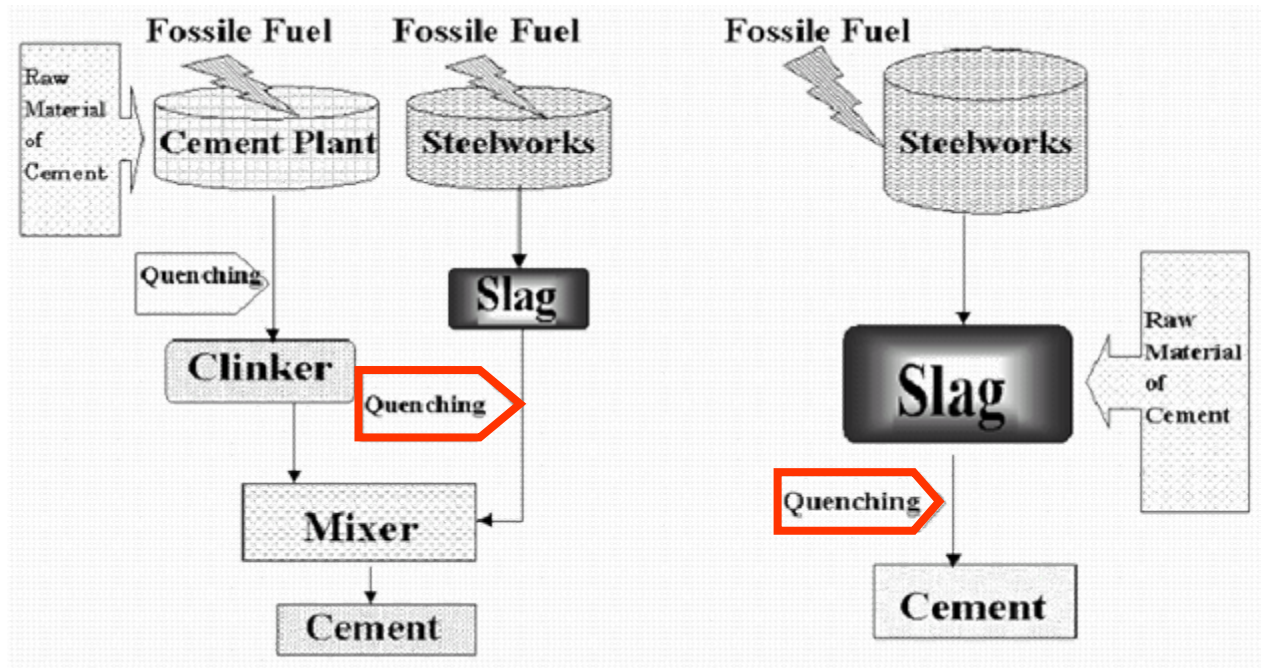
- An important physical property in material production processes
- Thermal conductivity of liquid oxide in iron- and steelmaking
 - Thermal conductivity of $\text{Na}_2\text{O-SiO}_2$ system (Nagata *et al.*)

Schematic representation of mold powder and slag film layer in continuous casting (M. Susa et al., Ironmaking and Steelmaking, 21(1994))



Thermal Application of Molten Slag

- Utilization of blast furnace slag and latent heat
- Optimization of BF slag recovery process



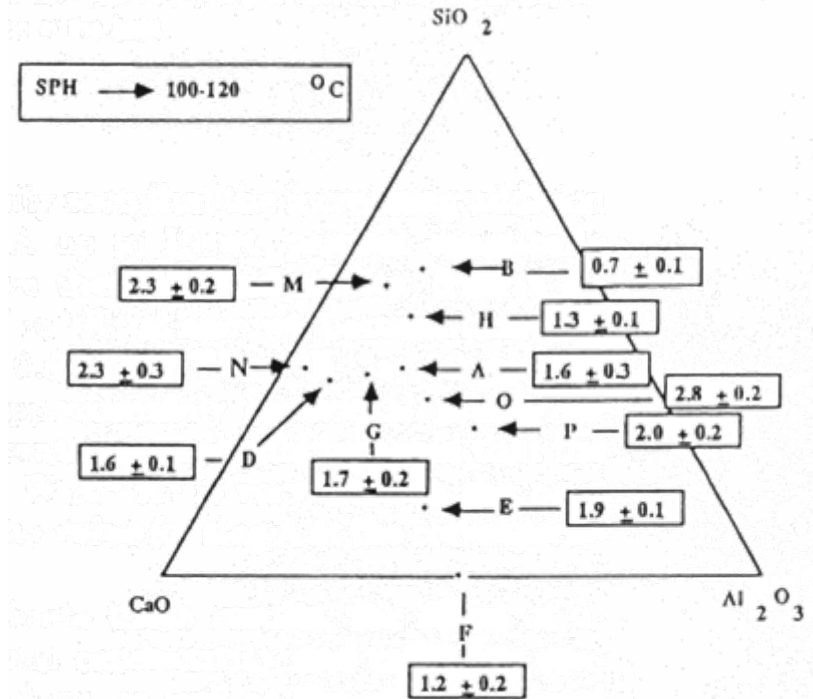
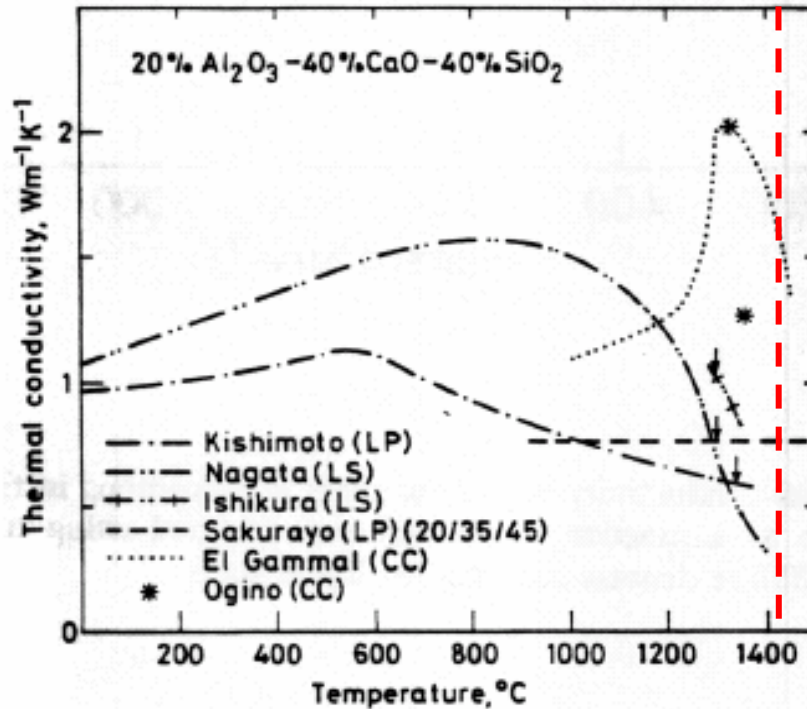
Previous Studies



COMPOSITION (mass%)	METHOD	TEMPERATURE RANGE (K)	THERMAL CONDUCTIVITY (W/mK)	AUTHORS
40CaO-20Al₂O₃-40SiO₂	hot wire method	373~1673	0.20~1.50	K. Nagata <i>et al.</i>
25CaO-15Al₂O₃-60SiO₂		373~1673	0.40~1.60	K. Nagata <i>et al.</i>
40CaO-20Al₂O₃-40SiO₂		1573	0.80~1.00	K. Nagata <i>et al.</i>
40CaO-20Al₂O₃-40SiO₂		373~1673	0.50~1.70	M. Susa <i>et al.</i>
40CaO-20Al₂O₃-40SiO₂	laser flash method	273~1623	0.70~1.20	M. Kishimoto <i>et al.</i>
45CaO-15Al₂O₃-40SiO₂		273~1673	0.60~1.20	M. Kishimoto <i>et al.</i>
50CaO-15Al₂O₃-35SiO₂		273~1673	0.50~1.00	M. Kishimoto <i>et al.</i>
50CaO-15Al₂O₃-35SiO₂		1273~1723	0.50	T. Sakuraya <i>et al.</i>
35CaO-20Al₂O₃-45SiO₂		1273~1723	0.70~0.80	T. Sakuraya <i>et al.</i>
40CaO-20Al₂O₃-40SiO₂	radial heat flow	1573~1623	1.10~2.00	K. Ogino <i>et al.</i>
40CaO-20Al₂O₃-40SiO₂		1273~1673	1.00~2.00	T. El Gammal <i>et al.</i>
CaO-Al₂O₃-SiO₂ system		m.p.+100	0.70~2.80	D. Sommerville <i>et al.</i>

→ limitation in the compositions and temperature

Previous Studies



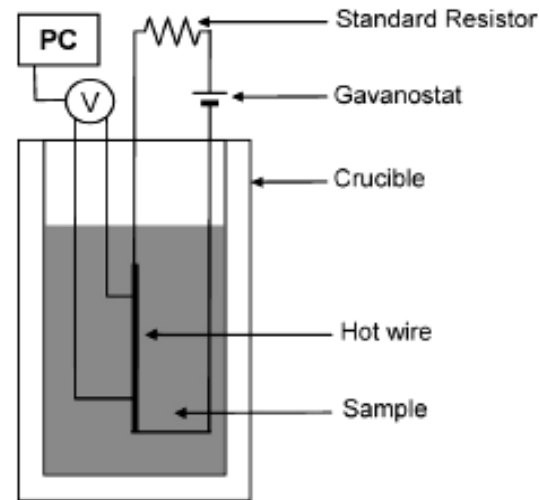
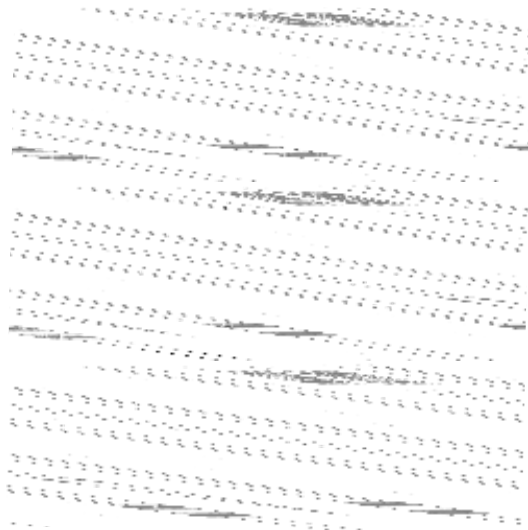
Results of thermal conductivity measurement of the CaO-Al₂O₃-SiO₂ system (left) after Slag Atlas and (right) by D.Sommerville et al, Trans. of the ISS,1991

→ reliable thermal conductivity data in pure liquid region: insufficient

Measurement of Thermal Conductivity



- Measurement methods for liquid oxide
 - Stationary methods
 - Non-stationary method
 - Laser flash method, **Hot-wire method**



Objectives



- Measurement the thermal conductivity of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system using hot-wire method from liquidus temperature to 1873K
- Better understanding on the relationship between the thermal conductivity and silicate structure from its temperature and composition dependences

Hot-wire Method



- Equation for thermal conductivity

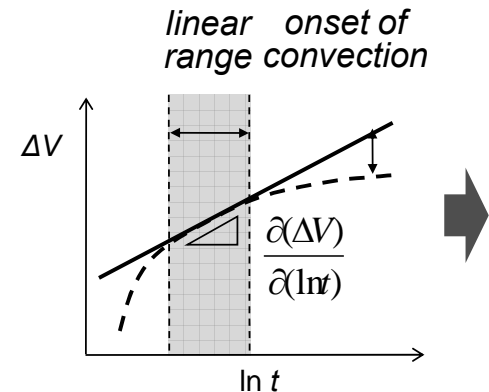
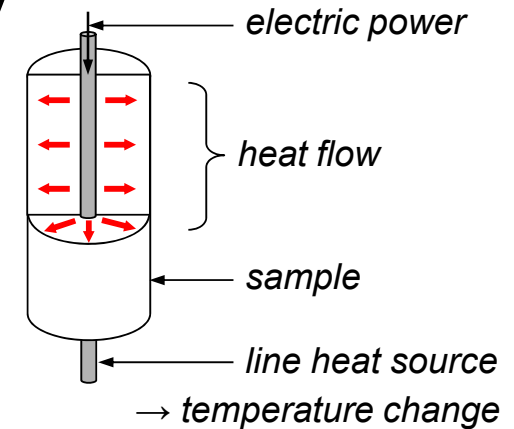
$$\lambda = \frac{Q}{4\pi} \frac{\partial(\Delta T)}{\partial(\ln t)}$$

Q : Heat generation of unit length of hot-wire

γ : Euler constant

– slope ΔT against $\ln t$

- Minimization of the effects of convection and radiation



Experimental Sample Preparation



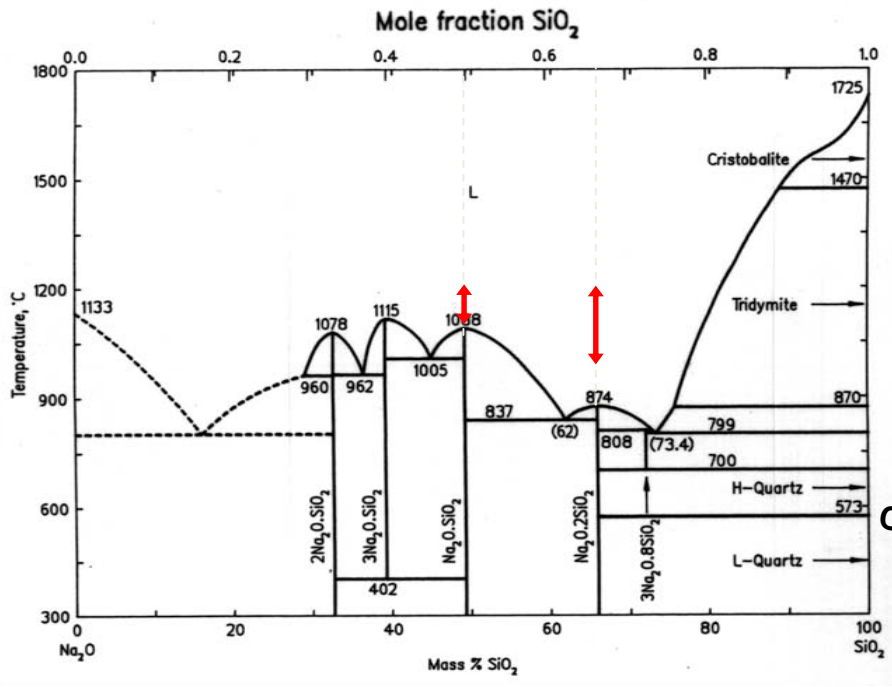
weighing,
mixing



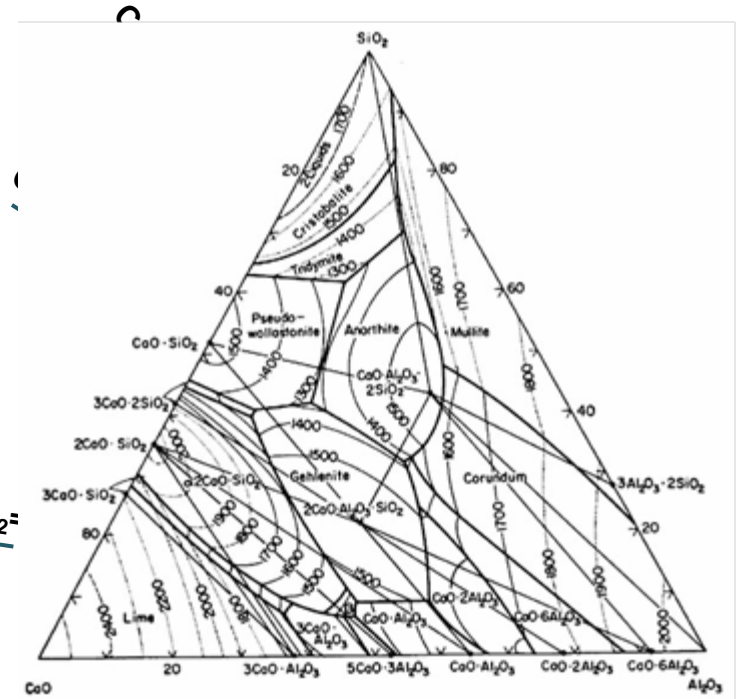
pre-melting
at 1873K for 20min.



crushing
to powder



Phase diagram of $\text{Na}_2\text{O}-\text{SiO}_2$ system and measurement range



ternary phase diagram of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system

Experimental Procedure



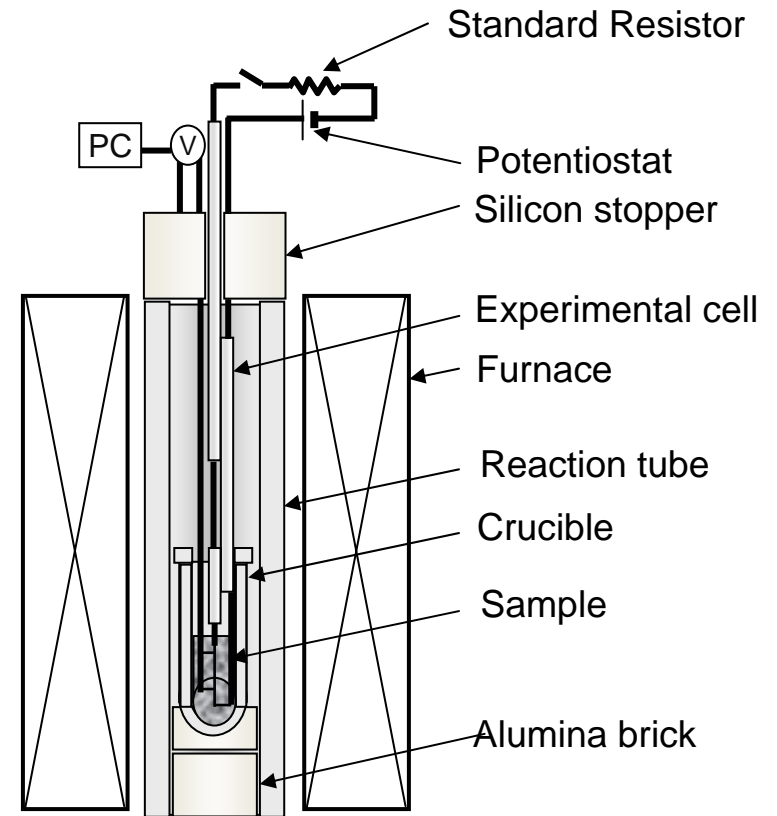
Measurement

- Supply constant power (1.5A) to hot-wire
- Measure temperature change of hot-wire
- Plot ΔT against $\ln t$
- Calculate thermal conductivity

Analysis

SiO₂: gravimetry., Others: ICP-AES

Crucible	Alumina or Pt-10%Rh
Temp.	L.T.~1873K, every 50K

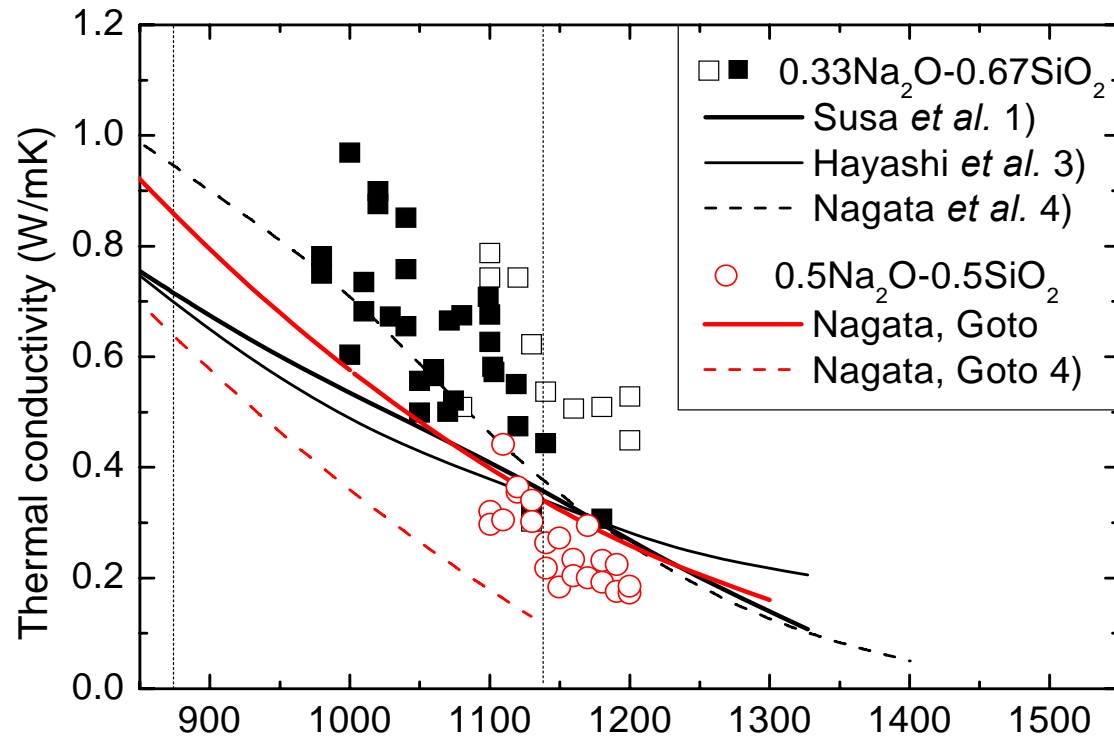


Schematic diagram of hot wire measurement apparatus

Thermal Conductivity and Temperature



- The $\text{Na}_2\text{O-SiO}_2$ system

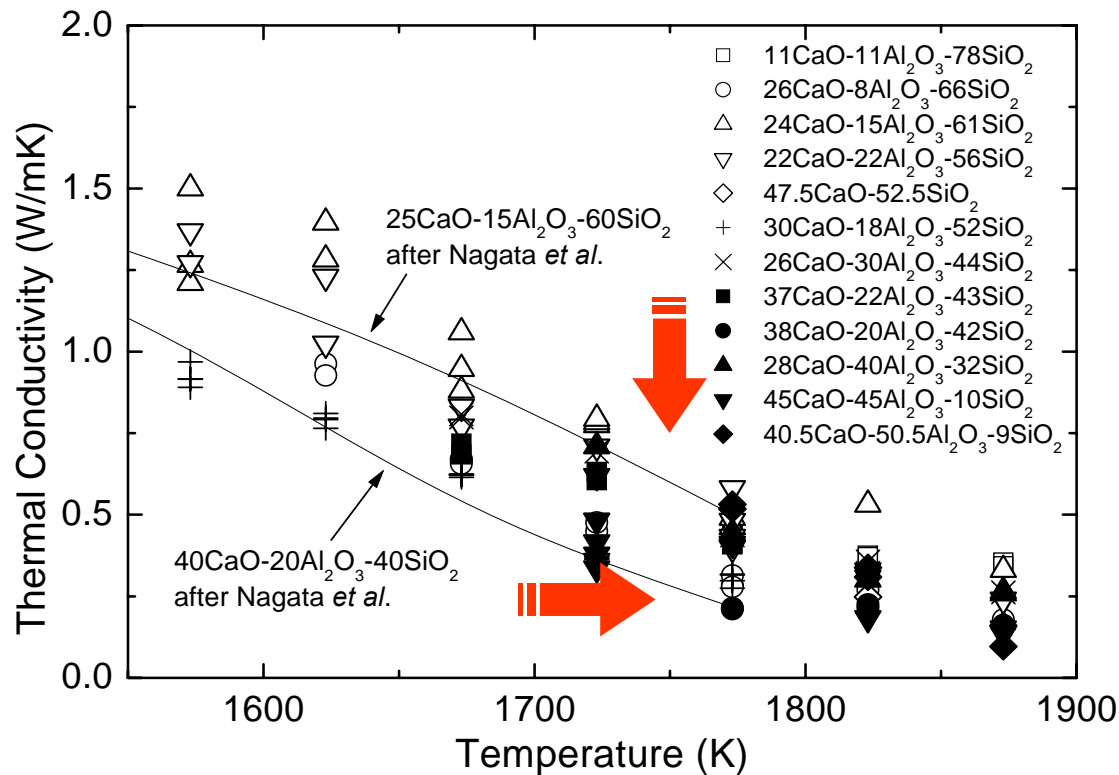


Thermal conductivities of the $\text{Na}_2\text{O-SiO}_2$ system as a function of temperature



Thermal Conductivity and Temperature

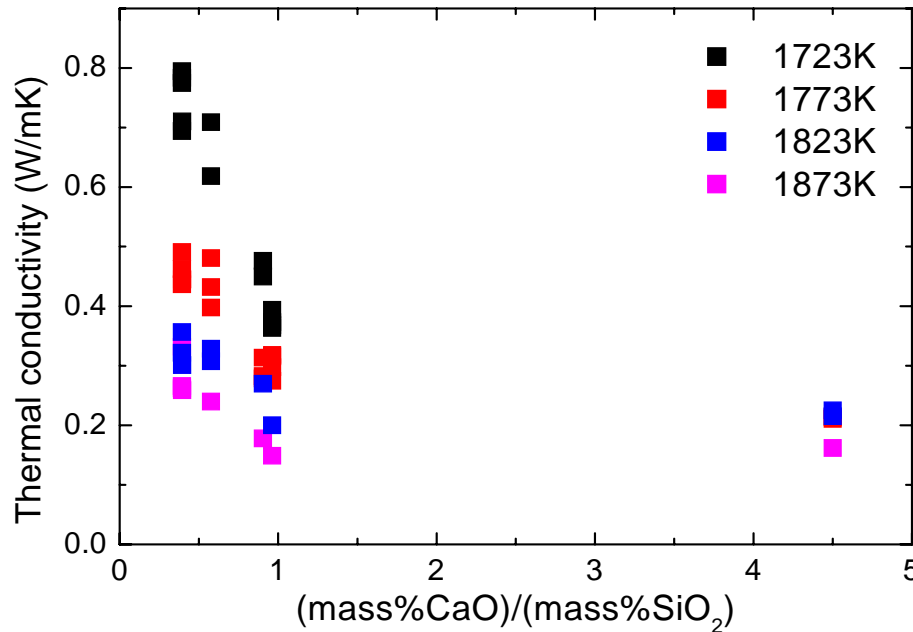
- The CaO-Al₂O₃-SiO₂ system



Thermal conductivities of the CaO-Al₂O₃-SiO₂ system as a function of temperature



Thermal Conductivity and Basicity



Relationship between thermal conductivity and CaO/SiO₂ ratio

$$\frac{\text{mass\%CaO}}{\text{mass\%SiO}_2} : \text{basicity}$$

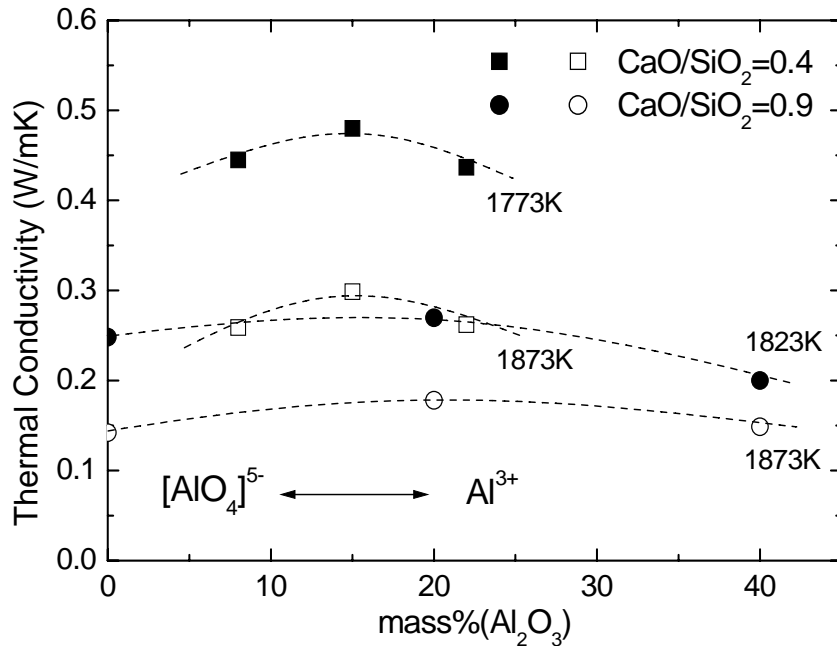
acid-side: basicity \propto thermal conductivity

basic-side: relatively high thermal conductivity

➔ influence of Al₂O₃ ?



Amphoteric Behavior of Al_2O_3



Dependence of thermal conductivity on Al_2O_3 content at constant CaO/SiO_2 ratios

- **Maximum value in thermal conductivity with Al_2O_3 addition**
- **Change in the role of Al_2O_3 between network former and network modifier**



Silicate Structure and Temperature

- Debye's expression for thermal conductivity

$$\lambda = \frac{Cv l}{3}$$

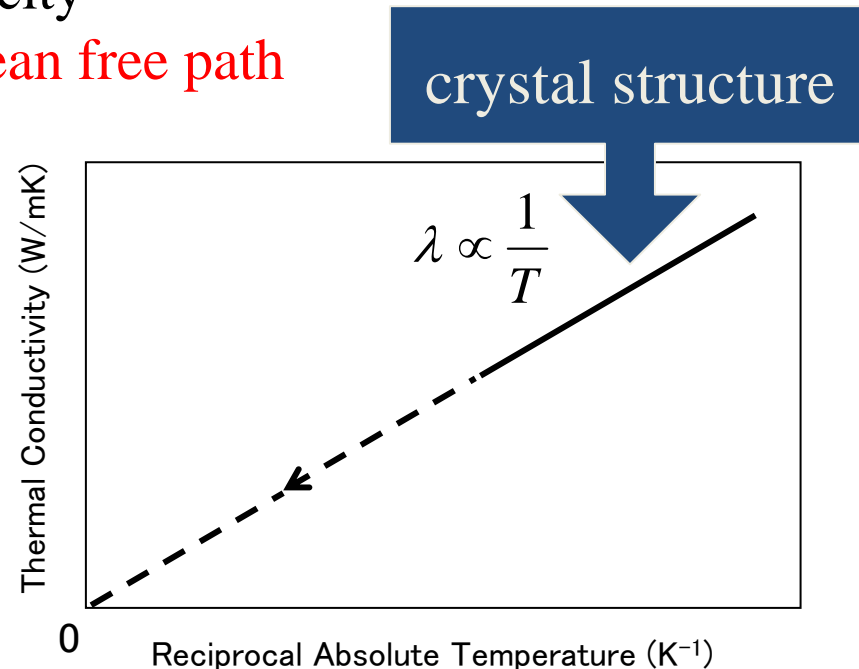
C : heat capacity

v : sound velocity

l : phonon mean free path

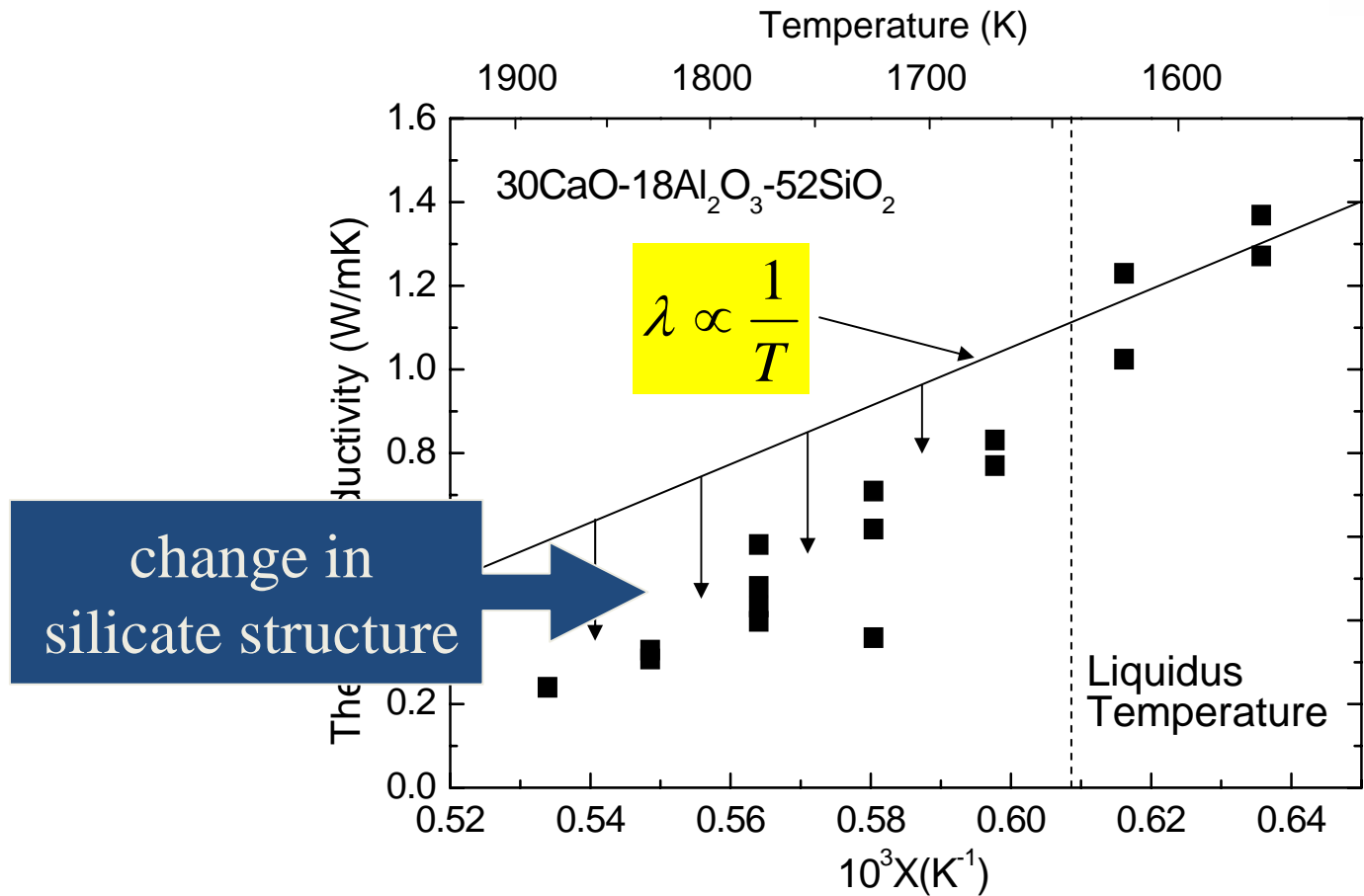
in crystalline materials

$$l \propto \frac{1}{T} \quad , \quad \lambda \propto \frac{1}{T}$$



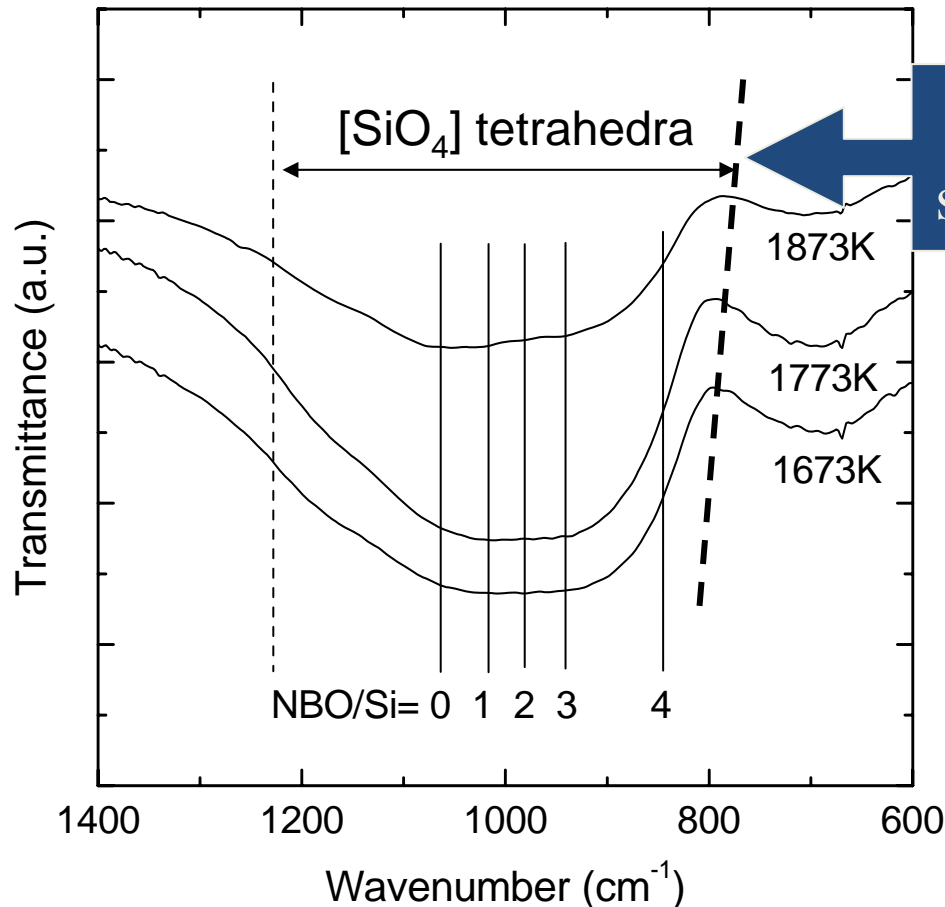


Silicate Structure and Temperature



Dependence of thermal conductivity of 30%CaO-18%Al₂O₃-52%SiO₂ on the inverse absolute temperature

Silicate Structure and Temperature

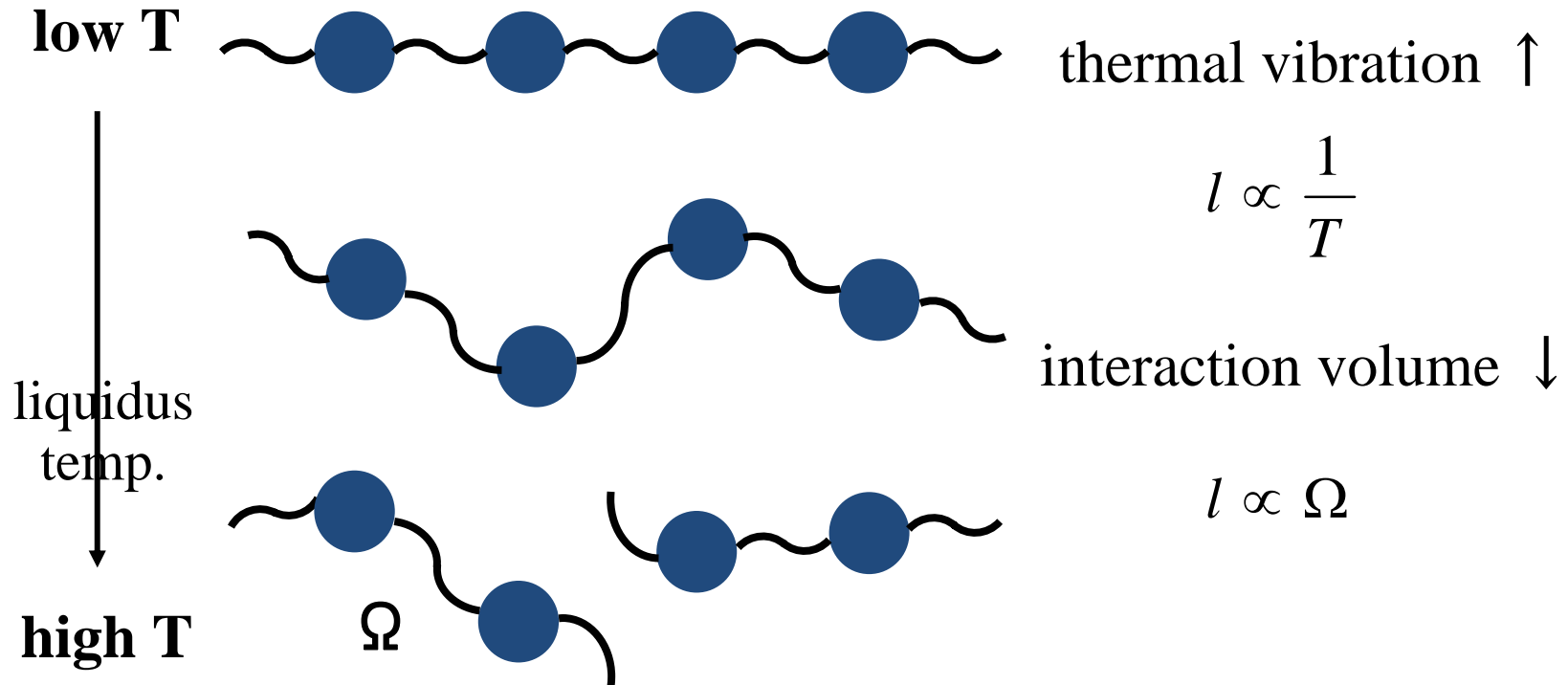


change in
silicate structure

IR transmittance of 30%CaO-18%Al₂O₃-52%SiO₂



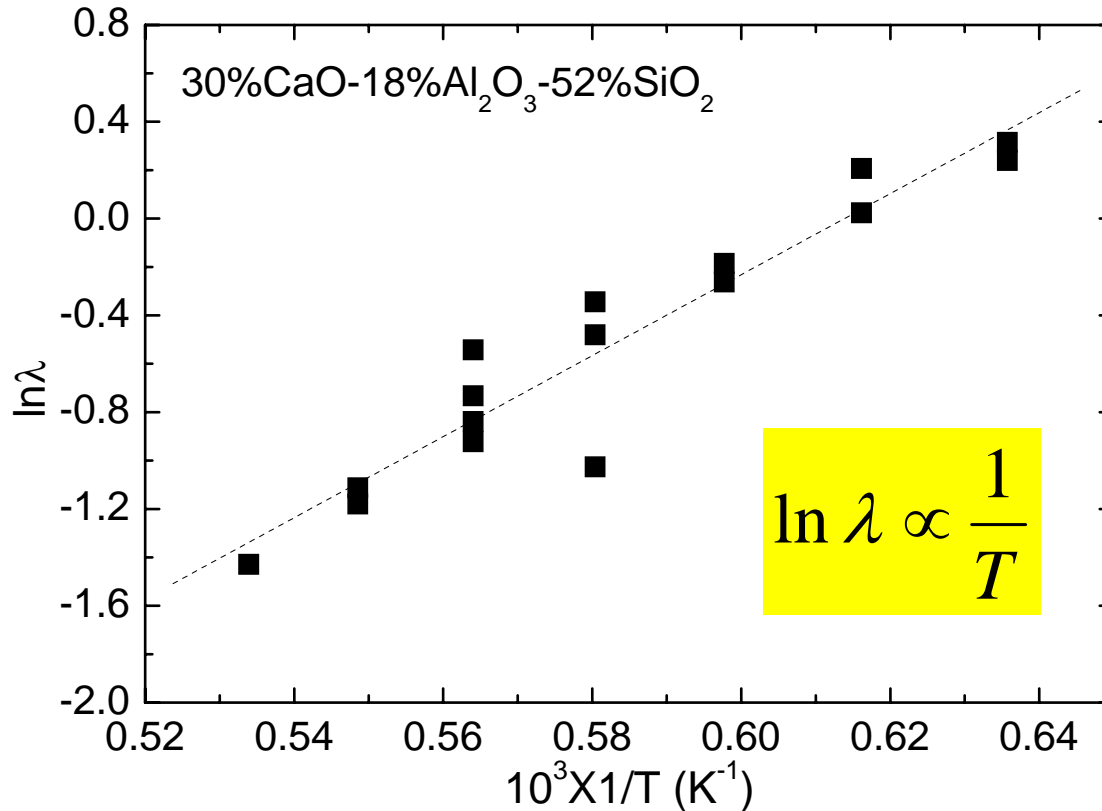
Silicate Structure and Temperature



- Bond breakage depends the bonding energy
- A broken bond divides the interaction volume

$$\lambda \propto \exp\left(\frac{1}{T}\right)$$

Silicate Structure and Temperature



Dependence of logarithm of thermal conductivity of 30%CaO-18%Al₂O₃-52%SiO₂ on the reciprocal absolute temperature

Conclusions



- **The thermal conductivity of the $\text{Na}_2\text{O-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system was measured by hot-wire method in their pure liquid region**
- **The thermal conductivity decrease in more basic silicate, and as temperature rises. And amphoteric behavior of Al_2O_3 was observed in the ternary system**
- **Temperature dependence deviates from the linearity at higher temperature than liquidus temperature. The change in silicate structure may cause this disagreement.**