Thermal Conductivitiy of Oxides and Silicates Relevant to Geophysics

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Abstract

Thermal diffusivities of polycrystalline rocksal-tstructure oxides, rutile-structure oxides, orthopyroxenes, olivines, silicate spinels, and garnets have been measured on sintered samples, using a modified Ångström method in the temperature range from 300 K to 600 K at the normal pressure. The calculated thermal conductivities from the measured thermal diffusivities are compared in order to examine systematical relationships among them due to the crystal structure and the chemical composition. Unlike the olivines and spinels, a plain relationship for the simple oxides cannot be found among the thermal conductivities with reference to the mollar volume or the density.

1. Introduction

Heat transfer in the earth's mantle is one of the important factors for dynamic aspects of the Earth which acts as a heat engine due to the temperature difference between the hot interior and the cold surface. Heat energy in the Earth is transported by conduction and convection. Convection, which entrains heat on material flow, could operate both in the Earth's mantle and core, and would be the most efficient way of radial heat transport where upwelling or downgoing flows occur. On the other hand, conduction would have mostly negligible contribution at these sites, however, this is also vital to the thermal state of the earth because heat can be transported only by this way in the radial direction within the thermal boundary layers which exist at least at three depths, the surface of the earth, the mantle-core boundary and the bottom of the outer core (another possible one is advocated to exist at the seismic transition layer in the mantle). In addition, the criterion for occurrence of convective motion includes the magnitude of thermal conduction, *i. e.* thermal conductivity or thermal diffusivity.

The heat conduction in the earth consist of individual mechanisms. So far two possible mechanisms are known: phonon conductivity, *i. e.* heat conduction by lattice vibration and photon conductivity, *i. e.* that by radiation. Radiative heat transfer would be effective at higher temperatures (Clark, 1957), thereby, it could be dominant in the deep interior of the earth. On the other hand, lattice heat conduction is crucial in the upper part of the solid Earth. Moreover, it might compete with the radiative

transfer even in the lower mantle (Mao, 1973). From now on, a term of thermal conduction or thermal conductivity is used only for those meaning the lattice conduction, as the conventional expression.

The thermal conductivity is controlled by temperature, pressure, chemical composition and structure of material. Many authors reported experimental results of thermal conductivities of various rocks and minerals. Birch and Clark (1940) measured on may rocks and some single crystal minerals. The temperature range was from 0°C to 500°C. Kawada (1964) extended the temperature up to 600°C. He obtained the thermal coductivities of some igneous and ultramafic rocks. The typical value of thermal conductivity of these rocks at the room temperature is 2 or 3 W/m K.

Pressure dependence of thermal conductivity or thermal diffusivity of minerals and/or rocks has been studied by Bridgman (1924), Hughs and Sawin (1967), Fujisawa et al. (1968), Yukutake and Shimada (1978), Schloessin and Dvorak (1972), MacPherson and Schloessin (1982), Susaki et al. (1990) and so forth. They found that the phonon thermal conductivity or thermal diffusivity increases as pressure increases. Fujisawa et al. (1968) found that the thermal diffusivity of fayalite composition leaps up with the phase transition from the olivine to the spinel structure.

Horai (1972) measured the thermal conductivity of about hundred of minerals which were mostly separated from aggregates or rocks. He discussed relationships of the thermal conductivity of minerals to the density, the elastic wave velocities, the crystal structure and the chemical composition.

This stuby deals the phonon thermal conductivity of the mantle minerals which are thought to be constituents of the upper mantle and the transition zone and the materials which are not components of the Earth but have the same crystal structure as these minerals. Comparing the thermal conductivities calculated from the thermal diffusivities, systematic relationships among them are examined in view of the crystal structure and the chemical composition.

2. Experimental procedures

(1) Samples

The materials investigated here were selected among mantle candidate minerals and those of which crystal structures are the same as the mantle minerals. Of course, they are restricted to those which are stable under the one atmospheric condition or recoverable into the room condition as a metastable phase by quenching method.

Table 1 shows the samples used in this study. They are classified into two groups: silicates and simple oxides. The silicates are three olivines (α-Fe_2SiO_4; fayalite, α-Co_2SiO_4, and α-Ni_2SiO_4), two silicate spinels (γ-Fe_2SiO_4 and γ-Ni_2SiO_4), two orthopyroxenes ($MgSiO_3$; enstatite, $FeSiO_3$; ferrosilite) and two garnets ($Mg_3Al_2Si_3O_{12}$; pyrope and $Fe_3Al_2Si_3O_{12}$; almandine). The solid solutions of these Fe-Mg bearing

Table 1. Samples

Samples	Synthetic or hot-pressing conditions of pressure, temperature and duration	Edge length or hight for thermal diffusivity measurement (mm)	Porosity (%)
Rocksalt structure oxides			
MnO	2.8 GPa, 1100°C, 30 min	3.01	2.8
FeO	2.9 GPa, 800°C, 60 min	2.10	
CoO	3.0 GPa, 870°C, 60 min	2.78	
NiO	3.0 GPa, 700°C, 90 min	2.13	
Rutile structure oxides			
CrO$_2$	3.0 GPa, 750°C, 75 min	1.81	3.6
MnO$_2$	3.0 GPa, 800°C, 75 min	2.73	4.4
GeO$_2$	3.5 GPa, 800°C, 90 min	2.88	0.5
SnO$_2$	2.5 GPa, 900°C, 60 min	3.98	
Orthopyroxenes			
MgSiO$_3$	3.0 GPa, 1000°C, 60 min	4.86	0.9
FeSiO$_3$	3.6 GPa, 1100°C, 20 min	1.96	6.1
Olivines			
α-Fe$_2$SiO$_4$		1.54	1.2
α-Co$_2$SiO$_4$	3.0 GPa, 960°C, 40 min	2.93	4.2
α-Ni$_2$SiO$_4$		1.50	2.2
Spinels			
γ-Fe$_2$SiO$_4$		1.90	1.5
γ-Ni$_2$SiO$_4$		1.50	3.2
Garnets			
Mg$_3$Al$_2$Si$_3$O$_{12}$	3.5 GPa, 1200°C, 35 min	1.75	5.3
Fe$_3$Al$_2$Si$_3$O$_{12}$	3.0 GPa, 900°C, 60 min	2.94	2.6

The samples MnO, CoO, NiO, CrO$_2$, MnO$_2$, FeSiO$_3$, α-Fe$_2$SiO$_4$, γ-Fe$_2$SiO$_4$, α-Ni$_2$SiO$_4$ and γ-Ni$_2$SiO$_4$ were used for the elastic wave velocity measurements by Mizutani (1971) and Hamano (1972). Synthetic conditions for the samples α-Fe$_2$SiO$_4$, γ-Fe$_2$SiO$_4$, α-Ni$_2$SiO$_4$ and γ-Ni$_2$SiO$_4$ were not reported.

silicates are thought to be the major constituents of the upper mantle and the seismic transition layer of the mantle. The oxides are simple compounds of MnO, FeO (wüstite), CoO and NiO with rocksalt structure, and GeO$_2$, SnO$_2$, CrO$_2$ and MnO$_2$ with rutile structue. Oxides of these structures have oxygen atoms cited to make nearly close-packed structure, and could be secondary components of the lower mantle. These silicate and oxide samples are the end members of solid solution series.

Of the samples in Table 1, MnO (p), MnO$_2$, CrO$_2$, α-Fe$_2$SiO$_4$, α-Co$_2$SiO$_4$, α-Ni$_2$SiO$_4$, γ-Fe$_2$SiO$_4$, γ-Ni$_2$SiO$_4$ and FeSiO$_3$ specimens are the same as those used for elastic wave velocity measurements by Mizutani (1971) and Hamano (1972).

Preparation of the samples for this time are described in the following. All these polycrystalline samples were prepared using a tetrahedral-anvil high-pressure appratus. They were sintered and/or synthesized at temperatures of 600°C or 1100°C and at pressures of 3Gpa or 8Gpa. The enstatite sample was converted at 3Gpa and 1000°C in one hour from protoenstatite which was solidified

from equimoller mixture melt of MgO and SiO_2 in carbon arc. Coarse-grained almandine was obtained from a mixture of Fe_2SiO_2 and Al $(OH)_3$. The latter component of starting material makes the environment in a heater capsle to hydro-thermal condition due to the OH-radical. The synthesized almandine was ground and hot-pressed again. The pyrope sample was crystallized and hot-pressed from quench-ed glass of pyrope composition fused in an arc-image furnace. Alpha-Co_2SiO_4 was synthesized in air at 1300°C in one hour, then a sintered sample was made under high pressure. Commercial regents were used for preparing the samples of GeO_2 and SnO_2. Hot pressing was made under the conditions of 3Gpa, 800°C and one hour. Germanium dioxide reagent is usually of the α-quartz structure, however, it was converted to the rutile structure after hot pressing. Polycrystalline wüstite prepared in a furnace by controlling oxygen fugacity was installed in an iron capsule, then it was hot-pressed at 2.9GPa and 800°C and in one hour. All of these recovered samples were of cylindrical shape, however, they often have plain cracks parallel to the end surface of cylinder. Therefore, cutting out specimen of free cracks makes it small. Of these materials, ferrosilite, γ-Fe_2SiO_4, γ-Ni_2SiO_4, and pyrope are of metastable phase under the ambient condition.

The samples were used in cylindrical shape or rectangular parallelepiped. The height or the edge length was 1 mm to 5 mm. The bulk densities were measured by a torsion balance specific gravity meter. The porosity is determined from differ-ence between the X-ray density from lattice parameter(s) and the bulk density.

(2) Measurement

The thermal diffusivity a relates with the thermal conductivity λ as,

$$a = \lambda/c\rho \qquad (1)$$

where c is the heat capacity per unit mass and ρ is the density. The thermal diffusivity is measured by the unit of diffusion coefficient, $m^2 s^{-1}$. While determination of thermal conductivity usually require the value of heat or heat flux of the sample, thermal diffusivity can be determined without the amount of heat flow through the sample. This makes the sample assembly simple; measurement can be made in a small, mm-sized samples. For the study on the thermal conduction of the mantle materials, the thermal diffusivity measurement is more convenient than that of thermal conductivity.

An Ångström method modified by Kanamori et al. (1969) was used for the thermal diffusivity measurement. Figure 1 shows the schematic drawing of the sample and the heater of this method. The temperature at one end of the sample $x=0$ is varying as $A + A_1 \cos \omega t$ by a heater current periodically switched on and off. Higher frequen-cy modes of the temperature variation decay rapidly in the heater; only a sinusoidal temperature change with the fundamental frequency arrives at the interface between the heater and the sample. At the opposite end of the sample ($x=L$) no heat flows out of the sample, namely $\partial T/\partial x=0$. The thermal diffusivity is obtained as
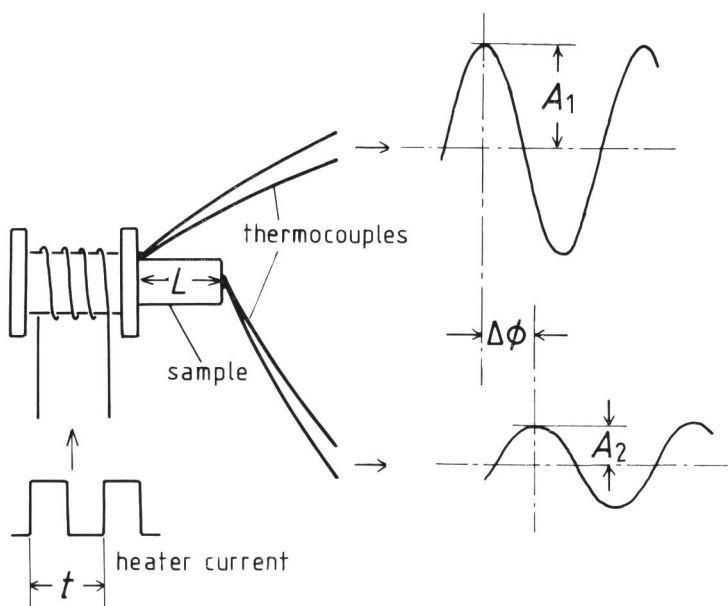
$$a = \omega/2qq' . \qquad (2)$$

Fig. 1. Schematic drawing of thermal diffusivity measurement by a modified Angström method. Thermal diffusivity a is obtained as: $a = (\pi L^2/t)\{\ln(2A_1/A_2) \times \Delta\phi\}$.

In this expression q and q' are defined as $q = \ln\{(A_1/A_2) \times L^{-1}\}$ and $q' = \Delta\phi/L$, where A_2 is the amplitude of the temperature variation at $x = L$, and $\Delta\phi$ is the phase difference at the two end surface of the sample with a length of L.

In the case of the ordinary Ångström method using a semi-infinite sample, the equation of heat conduction is exactly solved, *i. e.*, thermal diffusivity a can be expressed analytically. On the other hand, for the modified method using a sample with a finite or rather short length, no exact solution for thermal diffusivity is obtained. Hence it should be calculated approximately. When $A_1/A_2 > 2$, a is determined within a error of 10%, by substituting $(2A_1/A_2)$ for (A_1/A_2) in $q = \ln\{(A_1/A_2)L^{-1}\}$ (Kanamori *et al.*, 1969).

The minerals and silicate or oxide compounds in this study have a small length, a few mm. The minimum frequency of periodic heating is from 2 Hz to 0.2 Hz, to ensure a sufficient amplitude ratio $2A_1/A_2$ for diminishing errors as mentioned above. We have to detect the reducing amplitudes A_1 and A_2 with increasing the frequency. For this purpose, a metal base of the heater was made of material with high thermal conductivity, copper, and a heater wire was covered with cement to cut the loss of heat by radiation. Two thermocouples were attached on both ends of the sample to measure the temperature variation and the ambient temperature. Heat conducting away along the thermocouples will disturb the measurement. To minimize this effect, thin alumel-chromel thermocouple leads with a diameter of 0.1 mm were used.

Masahiro OSAKO

Table 2. Thermal diffusivities, heat capacities and theraml conductivities of oxides and silicates. Thermal diffusivity, a in $10^{-6}m^2s^{-1}$, heat capacity at constant pressure C_p in $10^6 Jm^3K^{-1}$ and thermal conductivity λ in $Wm^{-1}K^{-1}$. Heat capacities by Watanabe (1982), otherwise noted.

					T (K)				
		300	350	400	450	500	550	600	error (%)
MnO	a		1.43	1.30	1.16	1.06	0.98		5
	C_p		3.49	3.54	3.59	3.62	3.66		
	λ		5.0	4.6	4.2	3.8	3.6		
FeO	a	0.50	0.51	0.53					5
	$C_p^{1)}$	3.97	4.06	4.16					
	λ	2.0	2.1	2.2					
CoO	a	1.72	1.71	1.59	1.49	1.39	1.34	1.32	5
	C_p	4.54	4.56	4.57	4.58	4.58	4.60	4.64	
	λ	7.8	7.8	7.3	6.8	6.4	6.2	6.1	
NiO	a		5.0	4.2	3.26	2.47	2.58	2.4	5
	$C_p^{1)}$		4.42	4.84	5.62	5.79	5.30	4.99	
	λ		22	20	18.3	14.7	13.7	12	
CrO_2	a		1.67	1.48	1.39	1.34			7
	$C_p^{2)}$		3.5	4.0					
	λ		5.8	5.9					
MnO_2	a		4.8	4.1	3.7	3.4	3.1	2.9	5
	$C_p^{1)}$		3.60	3.88	4.01	4.10	4.19	4.27	
	λ		17	16	15	14	13	12	
GeO_2	a	7.4	6.0	5.2	4.5	4.0	3.6	3.2	5
	$C_p^{3)}$	3.13	3.39						
	λ	23	20						
SnO_2	a		10.8	9.1	7.8	6.7	6.0		7
	$C_p^{4)}$		2.77	2.99	3.14	3.26	3.35		
	λ		30	27	24	22	20		
$MgSiO_3$ (Enstatite)	a		2.1	1.9	1.7	1.5			5
	$C_p^{5)}$		2.87	3.10	3.26	3.39			
	λ		6.0	5.9	5.5	5.1			
$FeSiO_3$ (Ferrosilite)	a		1.7	1.5	1.3	1.2			7
	$C_p^{5)}$		3.06	3.29	3.43	3.54			
	λ		5.2	4.9	4.5	4.2			
α-Fe_2SiO_4 (Fayalite)	a	1.21	0.97	0.83	0.74	0.68	0.63	0.59	5
	C_p	2.96	3.14	3.27	3.39	3.49	3.57	3.65	
	λ	3.6	3.3	2.7	2.5	2.4	2.3	2.2	
α-Co_2SiO_4	a		1.19	1.07	0.97	0.89	0.81		5
	C_p		3.31	3.52	3.67	3.78	3.88		
	λ		4.0	3.9	3.6	3.3	3.2		

Table 2. (Continued)

		300	350	400	450	500	550	600	error (%)
α-Ni$_2$SiO$_4$	a	2.44	2.02	1.75	1.57	1.44			7
	C_p	3.10	3.30	3.53	3.69	3.81			
	λ	7.6	6.7	6.2	5.8	5.5			
γ-Fe$_2$SiO$_4$	a		1.51	1.29	1.14	1.04	0.97	0.92	7
	C_p		3.32	3.48	3.61	3.73	3.83	3.88	
	λ		5.0	4.5	4.1	3.9	3.7	3.6	
γ-Ni$_2$SiO$_4$	a		2.85	2.51	2.26	2.08	1.94	1.82	7
	C_p		3.45	3.68	3.84	3.96	4.06	4.13	
	λ		10	9.6	8.8	8.3	7.9	7.5	
Mg$_3$Al$_2$Si$_3$O$_{12}$	a	1.36	1.21	1.10	1.02	0.95	0.90	0.86	5
(Pyrope)	C_p	3.02	3.28	3.49	3.68	3.85			
	λ	4.1	4.0	3.8	3.8	3.7	3.4	3.4	
Fe$_3$Al$_2$Si$_3$O$_{13}$	a	1.31	1.16	1.06	0.99	0.94	0.89	0.86	5
(Almandine)	C_p	2.90	3.19	3.39	3.56	3.69	3.78	3.86	
	λ	3.8	3.7	3.6	3.5	3.5	3.4	3.3	

1) Touloukian et al., 1970
2) Osako, 1980
3) Touloukian et al., 1970, extrapolated from 300 K to 350 K
4) Auer, 1961
5) heat capacities for clinopyroxenes

3. Results and discussion

Figures 2, 3, 4, 5, 6, 7 and 8 illustrate plotting the observed thermal diffusivities. The thermal diffusivities of these oxides and minerals except NiO, CoO and FeO decrease with increasing temperature. Table 2 shows the smoothed values of thermal diffusivities and their errors representing the extent of scattering data points. The temperature of the measurements ranged from 300 K to 550 K. For several materials the temperature range was restricted shorter, from 350 K or up to 500 K. At these temperatures almost of all heat can be transported by lattice vibrations in solids. Contribution from radiative conductivity, proportional to T^3 could be negligible because of the relative low temperature of measurements (Kanamori et al., 1969). Electron thermal conductivity does not occur because these materials are insulators except SnO$_2$ (with still low electrical conductivity compared to metals).

Table 2 also shows the thermal conductivity calculated from the thermal diffusivity by the relation (1). Heat capacity data cannot necessarily cover the complete temperature range of the present measurements of thermal diffusivity. Therefore, in some cases they were extrapolated to high or low temperatures by 50 K, to overlap the temperature range of thermal diffusivities.
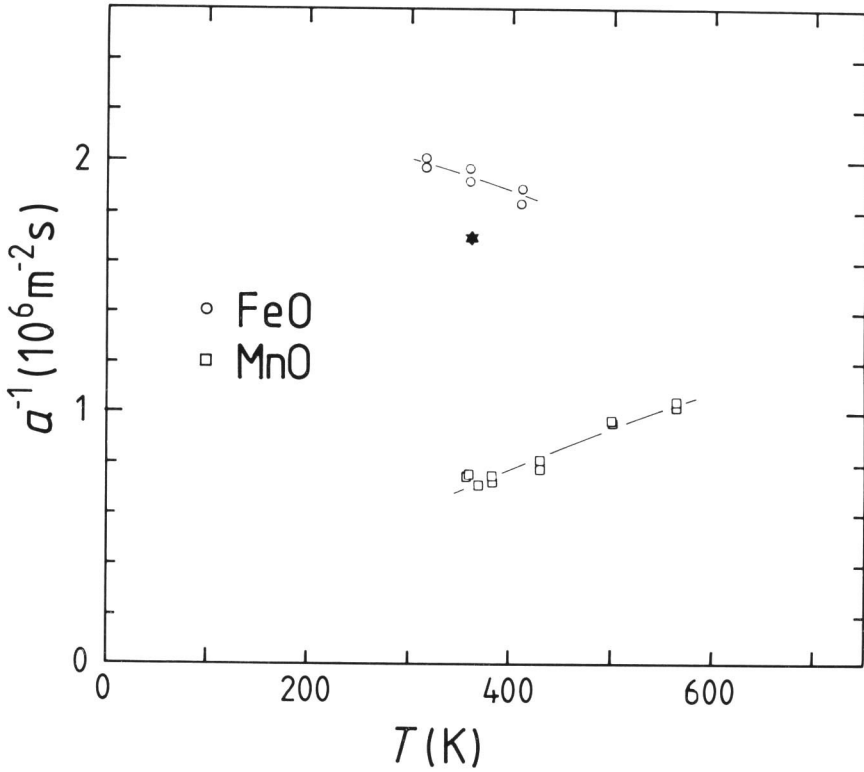
Masahiro Osako

Fig. 2.   Thermal diffusivities (a) of MnO and FeO versus absolute temperature (T).   The star shows the thermal diffusivity of FeO after heating up to 450 K.

Although the polycrystalline samples for present experiments have a little fraction of pores, the intrinsic thermal conductivity could be determined only by multiplying the thermal diffusivity by the density and the heat capacity.   The presence of pores affect the apparent thermal conductivity, however, the observed thermal diffusivity can be same to that for no pores when porosity is small.   The thermal conductivity of a material with a small porosity η is related to that of no pores, intrinsic polycrystal as (Kingery et $al.$, 1954),

$$\lambda_\eta = \lambda(1-\eta) \tag{3}$$

On the other hand, the thermal diffusivity as (1) leads to,

$$a_\eta = \lambda_\eta/(\rho_\eta c) = \lambda(1-\eta)/\{\rho(1-\eta)c\} = \lambda/\rho c = a , \tag{4}$$

where suffix η denotes quantities with pores.   Hence the thermal diffusivitiy values of present study for a small porosity would be eqaul to those free from pores.
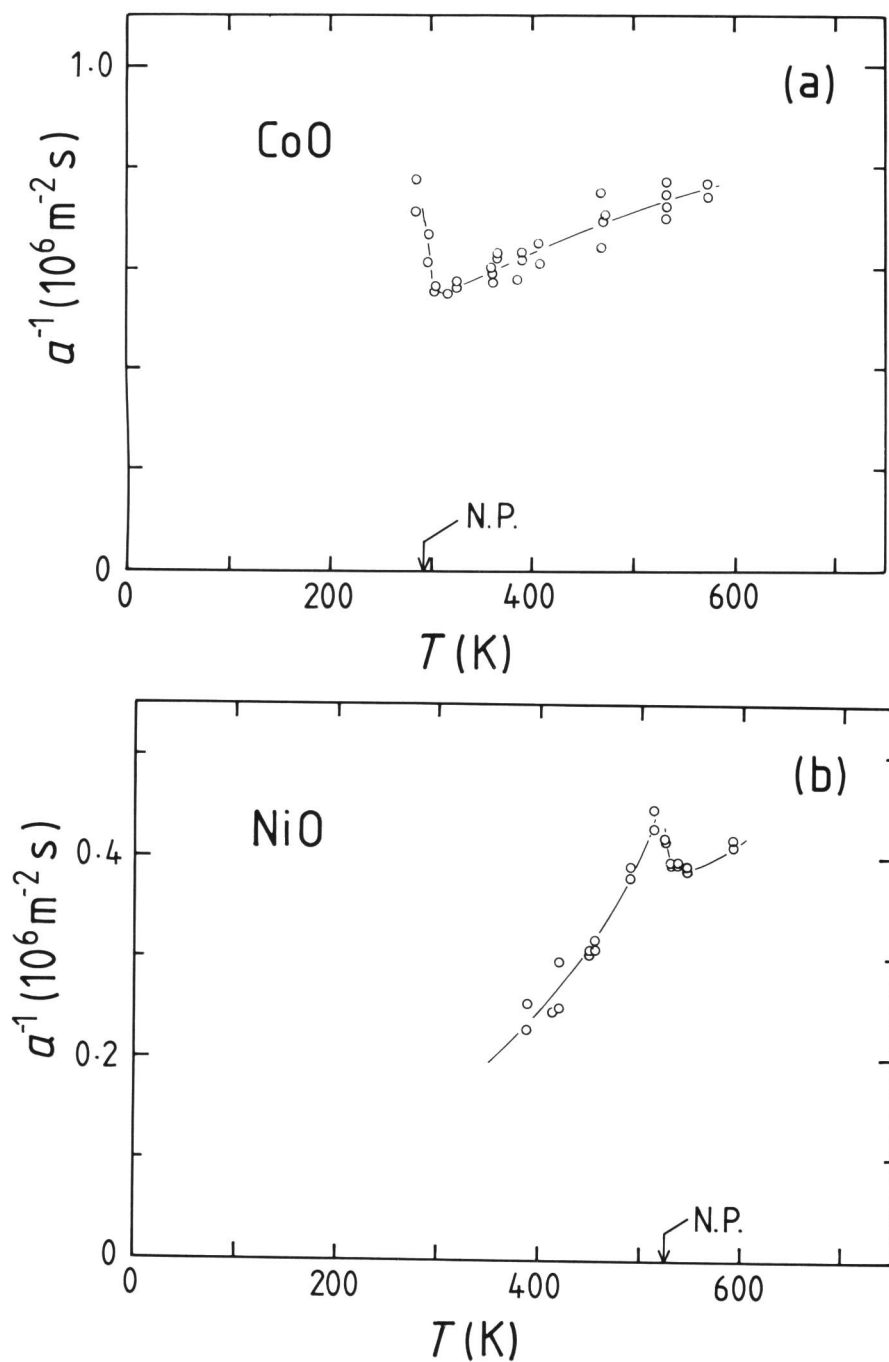
Fig. 3.   Thermal Diffusivities of (a) CoO and (b) NiO.   Neel temperatures are shown by an arrows described N. P..
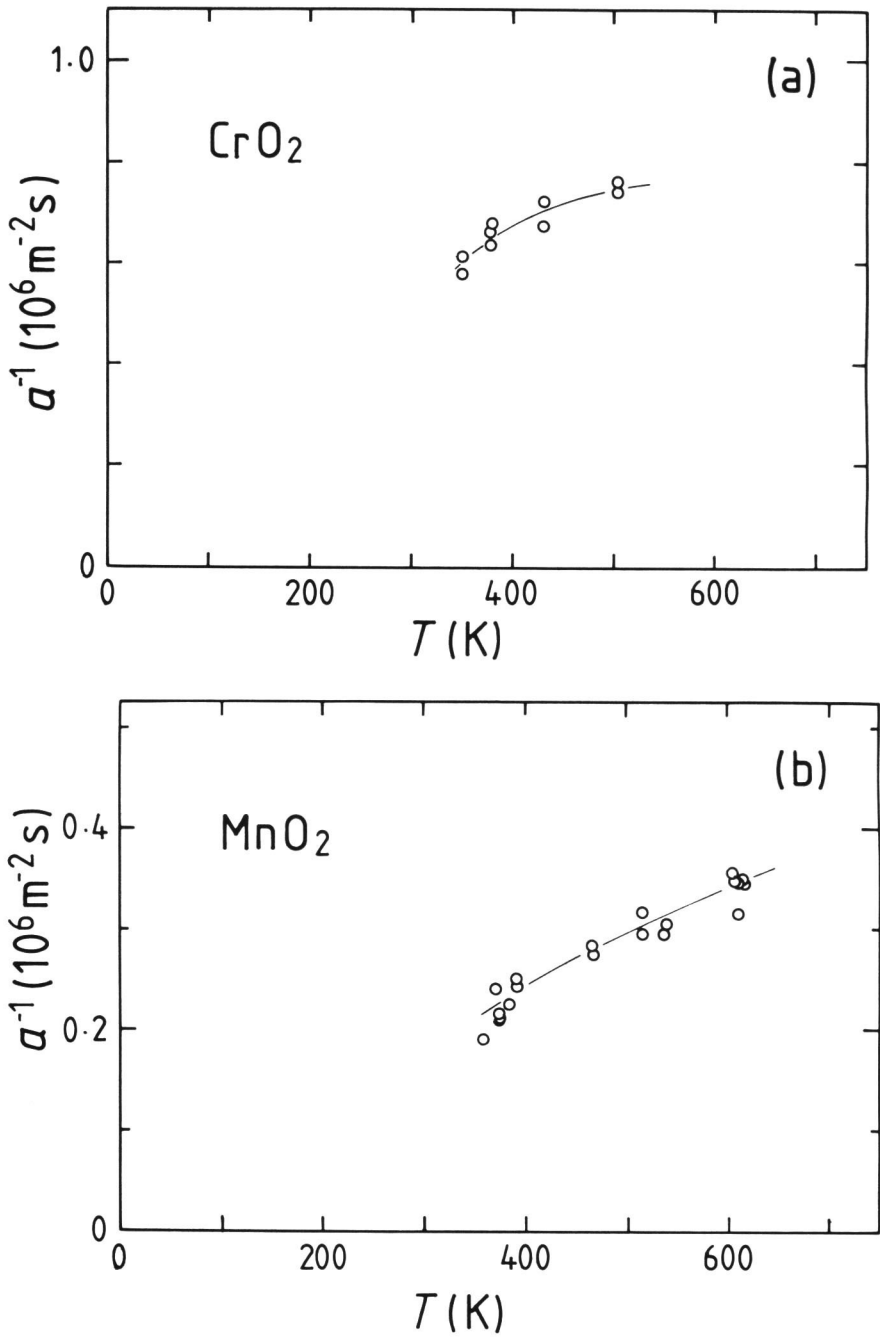
Fig. 4. Thermal diffusivities of (a) CrO_2 and (b) MnO_2. The thermal diffusivity of CrO_2 sample reveals irreversible effect after measurements at high temperatures, 500 K (not shown).
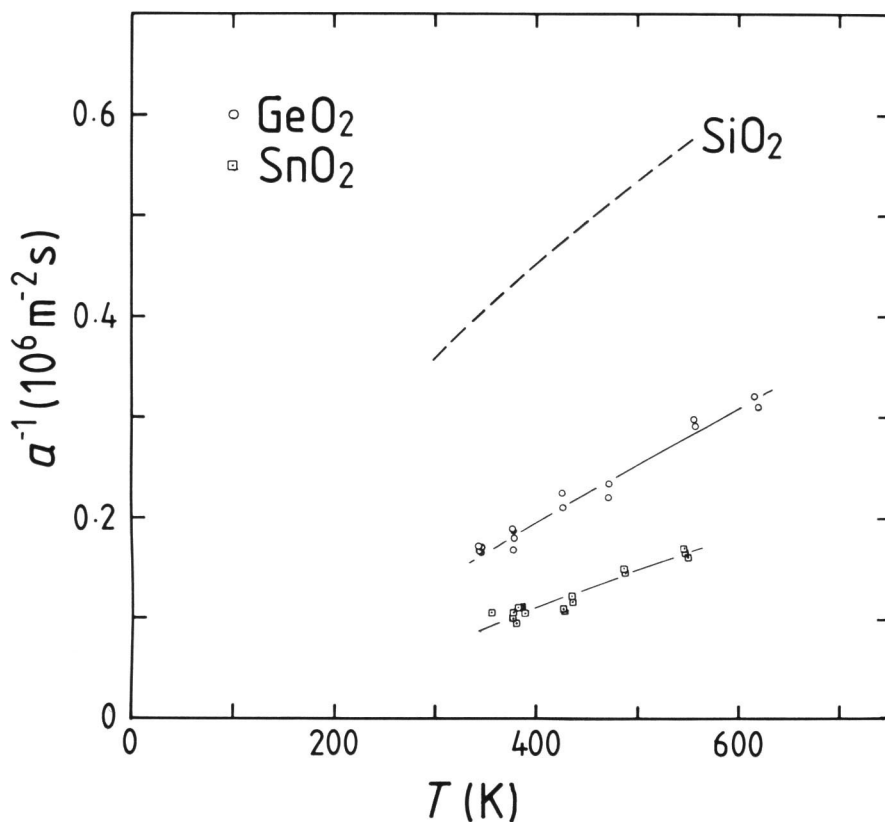
Fig. 5. Thermal diffusivities of rutile type GeO_2 and SnO_2. The dashed line shows thermal diffusivity of stishovite (after Osako and Kobayashi, 1979).

The thermal diffusivities of CoO and NiO reveal a remarkable depression at 290 K and 520 K, respectively. These temperature are known as the Neel points where the magnetic change occurs between antiferro magnetism at the lower temperature and para magnetism at the higher temperature. The heat capacity has a peak value at this point; the thermal diffusivity (1) coincidentally falls its value sharp.

The iron monoxide, FeO shows a little change of its thermal diffusivity with temperature as compared with the other oxides and silicates. Moreover the values markedly small among the other iron group monoxides, MnO, CoO, and NiO. It is well known that the iron monoxide, FeO is not a stoichiometry. The numbers of iron atoms and oxygen atoms are not equal, namely iron content is short for making the ideal chemical formula of FeO. This oxide is rather expressed as $Fe_{1-x}O$. Disorder of lattice due to the high density of point defects would reduce the thermal conductivity or thermal diffusivity, as those in glassy materials do so.
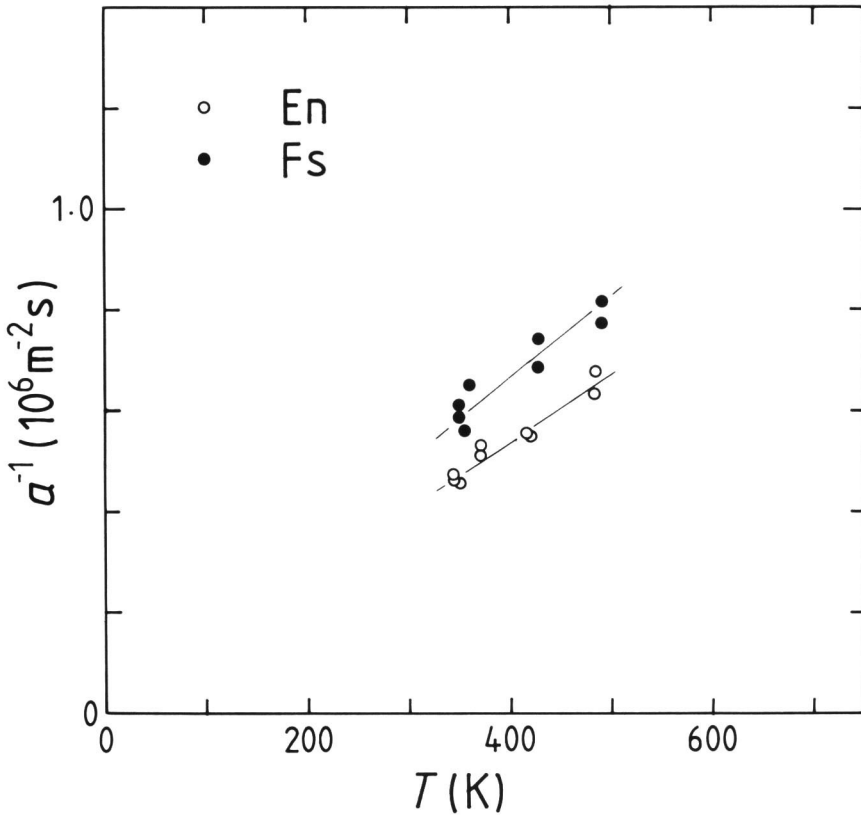
Fig. 6. Thermal diffusivities of orthopyroxenes. Open circles represents $MgSiO_3$ (Enstatite:
En) and solid circles for $FeSiO_3$ (Ferrosilite: Fs).

Figure 9 shows the plotting of the thermal conductivities of the rocksalt-structure
oxides and the rutile-structure oxides at 373 K versus the molar volumes V. Al-
though in the case of olivines and spinels a fairly good systematical relationship reveals
on this diagram (Osako, 1989), the simple oxides, in particular those of rutile-structure,
show a chaotic aspect. The systematics as in olivine and spinel cannot be applied
to these compounds which have wide range of mean atomic weight, especially in
rutile-structure oxides. Only the monoxides of the iron group elements, MnO,
CoO and NiO show a fairly good relation to the mollar volume. The iron monoxide
seems to run off the line, however, this could be explained by the presence of high
density of point defect, utmost over ten precent of vacancy at the Fe^{2+} site for the NaCl
structure. The thermal conductivity of the stoichiometric FeO (with little defects)
is predicted to be about 8 W/m K at 373 K on this λ-V diagram.
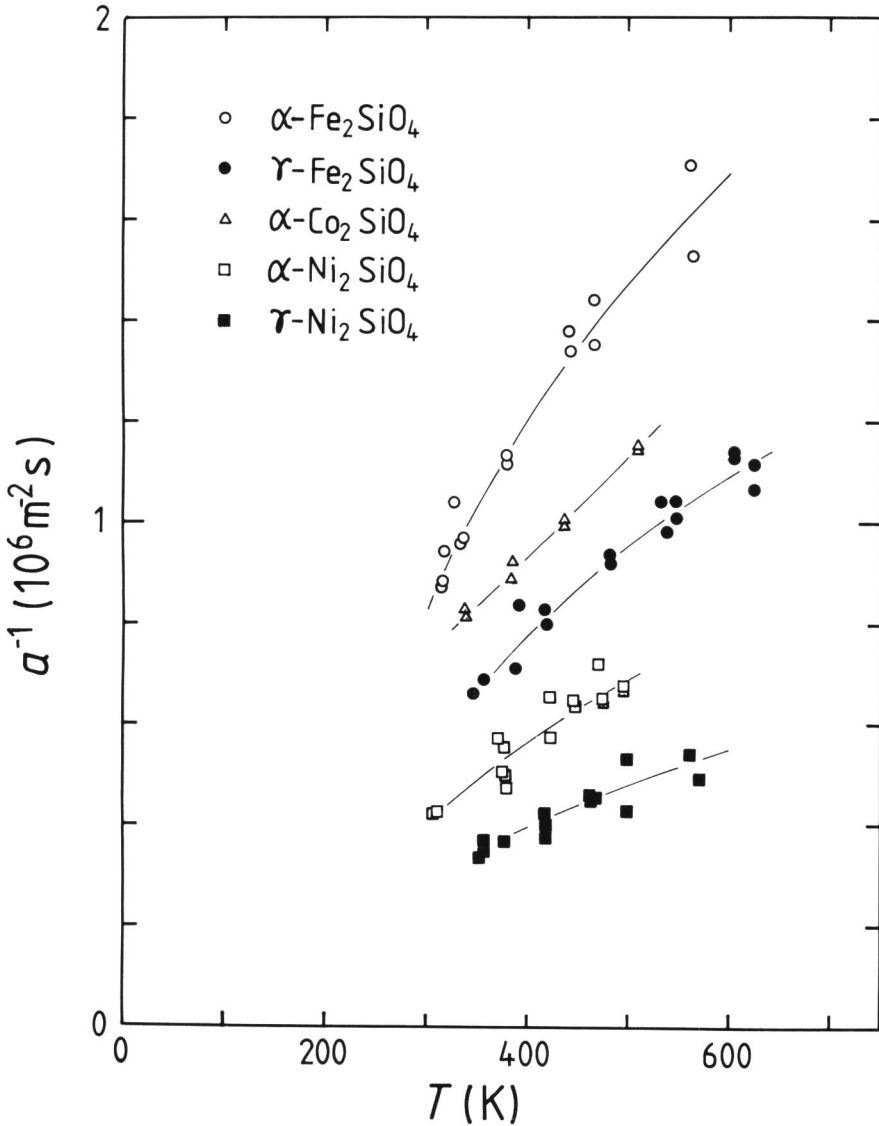
Fig. 7. Thermal diffusivities of olivines and spinels (high-pressure form of olivine).

4. Concluding remarks

The rutile-structure and rocksalt-structure oxides seem to have no systematical relationship among their thermal conductivities with reference to the mollar volume, while the olivines and the spinels reveal a fairly good systematics. However, it should be considered whether the comparison at the same temperature has any physical
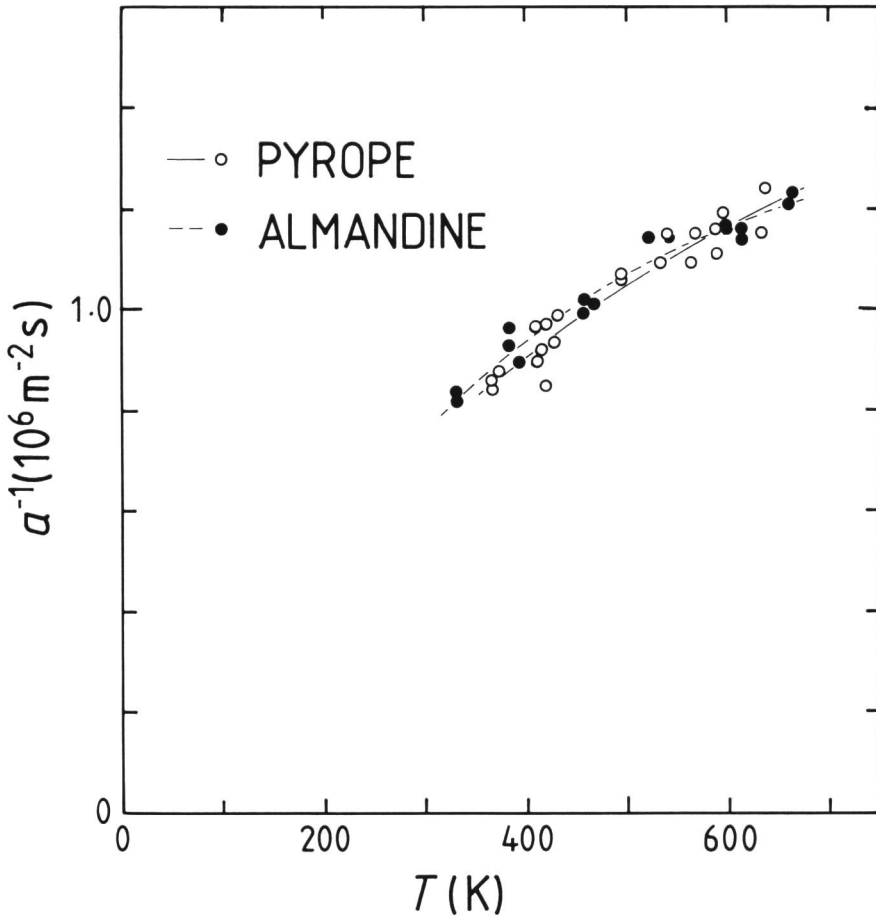
Masahiro Osako

Fig. 8. Thermal diffusivities of garnets: $Mg_3Al_2Si_3O_{12}$ (pyrope) and $Fe_3Al_2Si_3O_{12}$ (Almandine).

pertinent, because the thermal conductivity of oxides and silicates has strong tempera-
ture dependence. Since the thermal conductivity is due to lattice vibrations, com-
paring at a characteristic temperature, *e. g.* Debye temperature of individual materials
may be more convenient than at a fixed temperature.
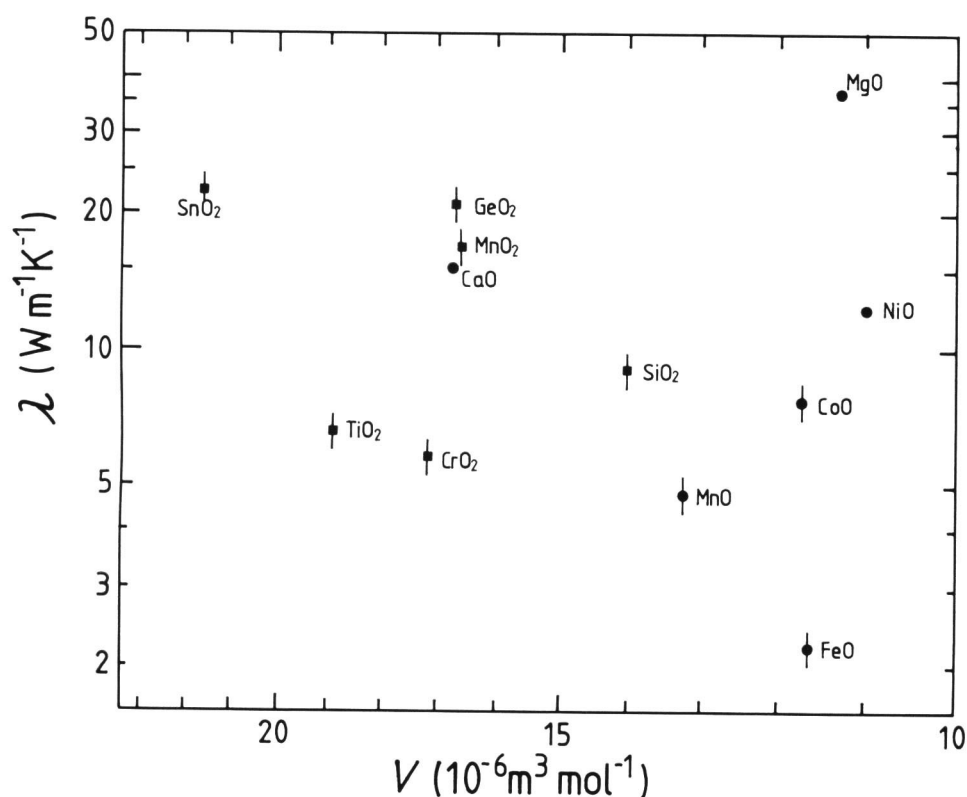
Acknowledgments

Fig. 9.   Thermal conductivities (λ) of rocksalt-structure oxides and rutilestructure oxides versus molar volume (V) at 373 K.   Data for MgO, CaO and TiO_2 are from Kingary *et al.* (1954)

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