

Measurement of thermal diffusivity at high pressure using a transient heating technique

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Abstract:

We describe a flash-heating procedure designed to measure thermal diffusivity of materials at high pressure and temperature in diamond anvil cells. This technique involves time-resolved radiometry combined with a pulsed IR laser source. Results for MgO, NaCl and KCl are presented (to $P=32$ GPa and $T=2600$ K). These measurements agree with previous studies at low pressure and high temperature and enable to test models for the combined P-T dependence of thermal conductivity. This technique can be extended to a broader range of pressures and can be used to address a variety of problems in geoscience, planetary sciences, and materials science.

Main text:

At the macroscopic level, heat transport is characterized by thermal conductivity k (W/mK), as given by the heat transport equation $\rho C_p \frac{dT}{dt} = k \Delta T$ (where ρ is the material density and C_p is the heat capacity). In non-metallic crystals, conductive heat transport originates from lattice vibrations through multiple phonon interactions, which are difficult to predict theoretically¹. Measurements of thermal conductivity usually involve determination of the temperature gradient across the sample subjected to a steady heat flow², or a phase shift in a thermal signal with regard to a periodic perturbation³. Recently, a pulsed plane-wave technique⁴ was developed that improves the accuracy of thermal conductivity measurements. Nevertheless, there are strong limitations because of geometrical constraints and the presence of materials that have thermal conductivity which is strongly dependent on pressure and temperature. These constraints become even more severe at higher pressure, because of increased spatial limitations and inaccuracies in temperature determination. To date, accurate measurements of the thermophysical properties have been reported up to a few gigapascal^{1,4} pressures using these conventional methods. Simple predictive models for P - T dependence of the thermal diffusivity have been developed instead (*e.g.*, Ref.¹) which are useful for certain applications; predictions related to changes in the crystal structure⁵, to spin transitions, or disorder effects need to be better developed.

Static experiments at substantially higher pressure (>20 GPa) require the use of diamond anvil cell (DAC) techniques. Only one pulse heating thermal diffusivity study was performed in the gem anvil cell⁶. It was limited to 2 GPa and close to room temperature. Impulsively stimulated light scattering (ISLS) enables to study the relaxation of a periodic

heat wave on the surface of a sample. This technique was adapted to the DAC⁷, but measurements to pressure above 10-20 GPa were restricted by sample size consideration. Similar to ambient pressure flash-heating approach, the experiment we present is a non steady state method, in which time resolved temperature variations are measured. The technique is inspired by the plane wave technique⁴ and has been adapted to match the size constraints required by conventional diamond-anvil cell (DAC) studies.

In these experiments, thin iridium foils (40x40x0.1 μm) were loaded in symmetrical DACs. The pressure transmitting media was chosen as the material of study, in our case KCl, NaCl or MgO. Platelets (~100x100x10 μm) of the solid media were obtained by compacting a powder in a moissanite anvil-cell (MAC) and were positioned on the tip of each diamond anvil. This procedure avoids deformation of the Ir foil upon compression and ensures to have a substantial amount of the material between the metallic coupler and the diamond. The Ir coupler was heated by absorption of 8 ns IR laser pulse (1064 nm, YAG) with the 10-20 kHz repetition rate. The laser is focused into the sample by a special aberration-corrected long-focal length lens (120 mm) to a Gaussian spot of approximately 30 micrometers diameter. The laser power and the repetition rate must be chosen in such a way that the coupler temperature must go back to the initial temperature (or sufficiently low steady temperature) after each shot. The thermal emission of the Ir surface is then collected by an all-reflective microscope and transferred by a relay optics (two off-axis paraboloids) to the entrance slit of an imaging spectrograph (ANDOR SHAMROCK, 300 g/mm grating) equipped with a multichannel gated CCD (ANDOR iStar Intensified), typically using a 10 ns gate.

Unlike previous studies using pulsed laser DAC methods⁸, our use of a gated detector enables to monitor thermal emission in the time domain with as small as 5 ns time resolution. The delay time between the laser arrival and probe window is controlled electronically by using a delay generator triggering the detector, and the measurements

correspond to averaging over approximately 20,000 cycles. The thermal emission spectra were corrected to the spectrometer transfer function (determined by measuring the emission spectrum of a standard spectral irradiance ribbon-filament lamp) and converted into absolute temperature using Wien's law. The accuracy of temperature measurements was tested by measuring platinum melting point and is within 50 K (a current was applied to a Pt wire located on the focal point of the microscope, and melting was diagnosed as a discontinuity in the current/temperature curve). The temperature profile across the heating spot was determined by analyzing the variation of spectra along the vertical (nondispersive) spectrograph direction, and the temperature distribution was found to be flat in at least a 20 μm area, no broadening of the hot spot with delay was detected. Varying detector delay enables one to study the foil surface temperature in the time domain. Since the absorber is thin, its temperature will equilibrate over a short time scale (of the order of a nanosecond). Heat loss will then be only controlled by diffusive exchange with the surrounding media and can be considered as 1D.

Typical experimental results for KCl and MgO are presented in Figure 1. We measured temperatures until the samples were cooling down to about 1500 K. Variations of the thermal diffusivity with pressure are clearly seen for KCl since the typical temperature relaxation time varies by a factor of 3 between 3 and 15 GPa (Fig. 1). The effect is reduced for MgO. From these curves, thermal diffusivity was inferred by modeling the measured temperature-time profiles using a finite difference method. These calculations solve the one dimensional diffusion equation⁹. The thinness of the foil with regard to our heating spot size (1/200 ratio) enables use of the planar approximation in solving the diffusion equation¹⁰. This hypothesis was tested by comparing with a set of 3D calculations. Our model assumes a temperature independent thermal diffusivity coefficient D ($D=k/\rho C_p$) since temperature variation of thermal diffusivity in our temperature range is limited (see for instance

Hofmeister compilation¹¹), and below our analytical uncertainty. Since the typical diffusion length scale is $L \sim 1 \mu\text{m}$ ($L \sim \sqrt{Dt}$, with $D=10^{-6} \text{ m}^2\text{s}^{-1}$ and $t=1000 \text{ ns}$), our measurements are unlikely to be affected by the foil position inside the DAC. The errors in Figs 1 to 4 are estimated from the reproducibility of the measurement (i.e. if the same sample at the same power at the same delay is measured many times in a row and standard deviation is calculated). The estimates for D at the lowest pressure studied here are compared with published data for NaCl, KCl and MgO^{12,13} as a function of temperature at ambient pressure in Fig. 2. For MgO, we observe a fair agreement between our measured value at 6 GPa and 2500 K, and a previous room pressure extrapolation to high temperature¹¹. For NaCl and KCl, at the lowest pressure studied, D was estimated in the melt region. The value we obtained is slightly higher than the ambient pressure high-temperature measurements for molten NaCl and KCl¹⁴; the difference could be due to the effects of pressure (see Fig. 3). Although upon crystallization latent heat should be released and a temperature plateau may occur around the melting point, it was not observed in our temperature-time profiles. The duration of the plateau is unknown and its observation would probably require improved time-resolution ($\sim 1 \text{ ns}$).

Different models have been proposed to express variations of k with compression. Details on the models described below can be found in the literature (i.e. Ross et al., 1984; Hofmeister, 2001). One should remark that those models are over-simplified since they do not take into account the full phonon spectra, and then phonon branches crossing upon compression (scattering channels can be opened or closed as pressure increases leading to complex behaviour).

A convenient way is to define the density dependence through the g parameter:

$$g = \left(\frac{\partial \ln k^{latt}}{\partial \ln \rho} \right)_T \quad (\text{eq. 1})$$

According to Ross et al. (1984) g for non-metallic solids can be as approximated by:

$$g = 3\gamma + 2q - \frac{1}{3} \quad (\text{eq. 2})$$

γ can be approximated as the thermodynamic Grüneisen parameter and q is its density dependence $q = \left(\frac{\partial \ln \gamma}{\partial \ln \rho} \right)_T$ which may be considered a measure of bulk anharmonic effects.

For the three materials we studied, the photon mean free path is much larger than the sample size. We can thus reasonably neglect the radiative contribution to thermal diffusivity ($k^{\text{rad}} \ll k^{\text{latt}}$)¹⁵. Then:

$$g = \left(\frac{\partial \ln k^{\text{latt}}}{\partial \ln \rho} \right)_T \approx \left(\frac{\partial \ln k^{\text{Tot}}}{\partial \ln \rho} \right)_T$$

The results obtained for g are presented in Fig. 3 and the values are significantly lower than measurements obtained up to 2 GPa for a variety of crystal structures, including our materials of study ($g=6-12$)¹. This difference can be explained by a decrease in anharmonic effects with pressure ($q \rightarrow 0$), in which case g should decrease to $3\gamma - 1/3$ for solids. Although measurements of g performed in liquids typically showed lower values than for solids ($g \approx 3$), this difference could not be resolved between molten and crystalline KCl within our experimental uncertainty.

Finally, our measurements enabled us to test the validity of models that have been proposed for the density dependence of lattice thermal conductivity. Hofmeister (2001) included optical phonon contributions and considered the following pressure dependence of k ,

$$\frac{d \ln(k^{\text{Latt}})}{dP} = \frac{\frac{1}{3} + 4\gamma}{K_0 + K_0' P} \quad (\text{eq. 3})$$

Neglecting the volume dependence of γ ($q \approx 0$) the pressure dependence of k can be expressed as:

$$k_{(P,T_0)}^{Latt} = k_{P_0,T_0} \left(1 + \frac{K_0' P}{K_0} \right)^{\frac{1+4\gamma}{3}}, \quad (\text{eq. 4})$$

Since $4\gamma+1/3 \sim K_0'$, equation 4 simplifies into a linear dependence of k^{Latt} with pressure:

$$k_{(P,T_0)}^{Latt} = k_{P_0,T_0} \left(1 + \frac{K_0' P}{K_0}\right). \quad (\text{eq. 5})$$

The Ross¹ and Hofmeister¹¹ models were applied to MgO using the measured equation of state¹⁶ (Fig. 4). We calculated the expected density dependence of thermal diffusivity using Hofmeister eq. 4 (model 1), and eq. 5 (model 2). We note that Hofmeister (2001) approximation that $4\gamma+1/3 \sim K_0'$ implies a difference in thermal diffusivity of ~50 % at 40 GPa using the values obtained from the experimental K_0' and γ (though there are uncertainties in those two parameters). We also calculated the density dependence of thermal diffusivity expected using Eq. 1 and two values of g . The first g value is chosen to be equal to experimental measurements up to 5 GPa ($g=9.5$)¹⁷. The second value corresponds to $g=3\gamma-1/3=4.3$ which refers to quasi-harmonic behavior. Extrapolation of the Ross *et al.*¹ model using values of g measured at low pressure overestimates the pressure variation of D . This suggests that the simple extrapolation of eq. 1 with the low pressure value of g (0-5 GPa) is not valid, at least in the case of MgO. Our results are consistent with the simplified model of Hofmeister¹¹ or the use of Ross *et al.* formalism with $q=0$.

In conclusion, we have presented a straightforward approach that enables the measurements of thermal diffusivity at high pressure-temperature conditions with the accuracy sufficient to validate the available theoretical models. Our results are in agreement with the lower P - T experimental data available from the literature. Future improvement includes the use of a shorter laser pulse (~1 ns), and detector gate (~1 ns). This technique can be in principle applied to up to megabar pressures allowing thermal diffusivity measurements in previously

unreachable P-T domains and enabling unique insights into the thermal state of planets.

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FIGURE CAPTION

Figure 1 Time-resolved surface temperature of the iridium foil embedded in KCl (up) and MgO media. The insert shows a typical thermal emission spectra and the corresponding fit to Planck's law. The red dashed curve on the upper panel corresponds is a set of 3D calculations which confirms the validity of 1D approximation. The small black dots and gray shaded area of the lower panel show the IR pulse temporal shape.

Figure 2: Measured thermal diffusivity at low pressure and high-temperature for MgO, KCl and NaCl compared with literature data (see Ref. 12). Modelled temperature dependence are also presented and were calculated using Hofmeister (2001) formalism.

Fig.3: Compression dependence of thermal diffusivities measured for MgO, KCl and NaCl. Volumes were obtained from literature equation of state for MgO and B2 KCl, and molecular dynamics calculations for molten NaCl and KCl. Solid lines are the best fits to Ross model (eq. 1) while dashed line is calculated using Hofmeister (2001) model for MgO (eq. 5).

Figure 4: Pressure dependence of MgO thermal conductivity ($T=2000$ K).







