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Thermal Diffusivity and Conductivity Measurements in Diamond Anvil Cells

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FY06 LDRD Final Report

Thermal Diffusivity and Conductivity Measurements in Diamond Anvil Cells

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Abstract

We have undertaken a study of the feasibility of an innovative method for the determination of thermal properties of materials at extreme conditions. Our approach is essentiality an extension of the flash method to the geometry of the diamond-anvil cell and our ultimate goal is to greatly enlarge the pressure and temperature range over which thermal properties can be investigated. More specifically, we have performed test experiments to establish a technique for probing thermal diffusivity on samples of dimensions compatible with the physical constraints of the diamond anvil cell.

Introduction/Background

Without a doubt, the detailed understanding of the properties of condensed matter under extreme conditions is an increasingly important aspect of modern experimental and theoretical physics, with applications ranging from solid-state physics, engineering science, to Earth and planetary sciences. Indeed, both pressure and temperature can dramatically affect the structure, as well as the dynamical and electro-magnetic properties of materials. Consequently, based on recent technical advances in the application of high pressures and temperatures, a great deal of effort has been devoted to the experimental characterization and theoretical descriptions of materials at extreme conditions. However, while great advances have been made in the areas of mechanical properties (for instance elasticity, plasticity and phase stability) measurements of transport properties have greatly lagged behind.

More specifically, the study of heat transport properties is particularly crucial. Thermal properties place important constraints on several fundamental solid-state physical quantities, such as internal energy, kinetic properties, inter-atomic potentials and lattice dynamics. Furthermore, the knowledge of heat transfer mechanisms have important engineering and high-technology applications, for instance in the characterization of novel materials, for thin film manufacturing, laser diodes, radiation detectors, and more in general, for all the microelectronic devices that need to quickly evacuate the excess of heat. Thermal transport properties are also essential to address fundamental questions centered on the nature and style of heat and mass transfer within the interiors of the Earths and other planets. Indeed, heat transfer from the interior to the exterior of the Earth controls a number of fundamental processes within the planet. These include the thermal and chemical evolution of the core (and hence of the Earth's magnetic field), the style of convection within the asthenosphere, and movements of the lithosphere. Furthermore, most of the geophysical phenomena we experience at the surface, such as volcanism, earthquakes, orogenesis, metamorphism and plate tectonics are all, to a great degree, also controlled by the transfer of heat within the planet. As a matter of fact, irrespective of the ultimate source - be it radioactive heat, latent heat due to solidification of the inner core, gravitational energy released by segregation of crystals from the liquid outer core, friction related to the convection in the outer core, or just residual 'primordial heat' – the temporal evolution of the heat transfer has had a profound impact in the differentiation and habitability of the planet.

In the context of this LRDR-FS project, we proposed to address the heat transport properties of insulating materials at high pressure and high temperature. For hard solids, conventional measurements of thermal conductivity (involving physical contact with the sample) are problematic even at ambient conditions, strongly sample shape dependent [1], and experimental discrepancies commonly exceed 20% [2]. Furthermore, thermal diffusivity and conductivity have been measured up to now at high pressure mainly in large volume press (see for example [3-5]). This has limited the investigated pressure range to 20 GPa. This is a severe limitation and a critical problem for addressing the thermal properties of materials under extreme conditions. Diamond anvil cells (DAC) instead allow the exploration of pressures in the megabar range. Moreover, temperatures of the order of 1000 K can be investigated by resistively heated DAC, while, by laser heating, temperature as high as 5000 K can be obtained. However, the requirements on sample geometry and dimensions, together with the difficulties in the application of direct contact methods, have strongly limited the use of such high-pressure generating device for diffusivity and conductivity measurements.

Therefore we have undertaken the study of the feasibility a new and innovative method of determining thermal properties of materials of materials compressed into DAC, with the aim of significantly enlarging the pressure and temperature ranges over which these properties can be investigated. More specifically, we started the development of a novel technique, based on an extension of the flash method [6], capable of probing thermal diffusivity and eventually thermal conductivity in DAC. While this technique is applicable for studies on a wide range of materials, our main scientific motivation is to address the case of iron bearing oxide (Mg,Fe)O-ferropericlase and (Mg,Fe)SiO_3-perovskite, the two most important constituent of the mantle of terrestrial planets at megabar pressure.

Research Activities, Results and Technical Outcome

We have designed and implemented a novel method aimed at the measurements of thermal diffusivity and eventually thermal conductivity of materials at extreme conditions based upon an extension of the flash method [6]. This technique uses flat plate sample geometry, without the need of a direct thermal contact between the heating source and the specimen. This, coupled with the relatively straightforward data analysis, make the technique particularly appealing for use in the DAC. The basic principle can be summarized as follows: a pulse of radiant energy is instantaneously and uniformly absorbed at the front surface of the thermally insulated sample; the thermal diffusivity is then determined from the rear surface temperature history (see Figure 1).

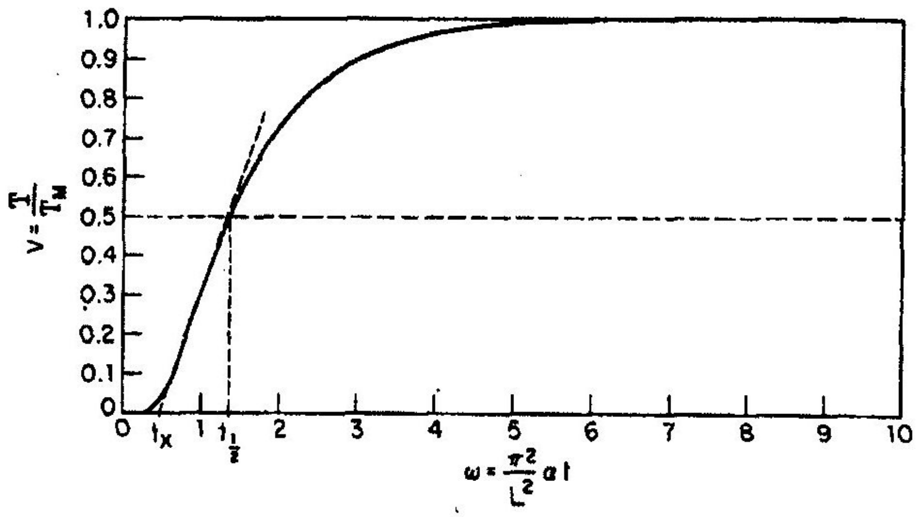

Figure 1: Dimensionless plot of the theoretically expected rear surface temperature history.

When the ratio between the effective temperature at the rear surface T and the maximum temperature T_M is equal to ½, the theoretical value for ω is 1.38, so that the thermal diffusivity α can be determined from the relation:

$\alpha=1.38L^2/\pi^2 t_{1/2}$

where L is the sample thickness and $t_{1/2}$ is the time required for the back surface to reach half of the maximum temperature rise. Moreover the time axis intercept of the extrapolated straight line portion of the curve in Figure 1 is at ω=0.48, which yields another possible way to derive α, according to:

$\alpha=0.48L^2/\pi^2 t_x$

If the amount of energy Q absorbed in the front surface is known, the thermal conductivity κ can be determined as well, without the input of the sample density and heat capacity according to the relation:

$\kappa= \alpha Q/V\Delta T$

where V is the sample volume and ΔT is the temperature raise of rear surface of the sample.

On the other hand, the input of the density ρ (derivable from the pressure according to sample equation of state) allows the determination of the heat capacity C:

$C= Q/\rho V\Delta T$

Another point important to stress is that with this method a total "effective" diffusivity, including both the lattice and electronic conduction is measured and the radiative term (heat transferred by photon through the sample) can be minimized by sample coating or explicitly considered in the experiment [7].

The main difficulties in applying this method arise from the severe constraints imposed by the DAC, and the success depends upon adequately meeting the boundary conditions of the theory [8]. In particular, the sample dimensions impose requirements on the flash heating duration (the flash duration must be short compared to the raising time of the temperature at the back surface), and scrupulous care is needed to ensure the measurement of the temperature of the sample and not the one of diamonds or gasket.

In our feasibility tests, we used an ultra-fast pulsed laser (~160 fs pulse width, rep. rate variable between 10 and 1000 Hz) as the heating source. This solution not only allowed the heating of the sample without direct contact between the heating source and the specimen, minimally affected by the presence of diamonds, but also provided a flash duration much shorter than the typical raising time of the temperature of samples of present interest ($t_{½}$~ $1x10^{-6}$÷$1x10^{-3}$ s for MgO or olivine at ambient conditions, with thickness between 10 and 100 μm). We have also implemented a capability to tune the wavelength for an optimal coupling of the heating source with different samples.

Figure 2 schematically illustrates the idea of the method when applied to samples compressed in DAC.

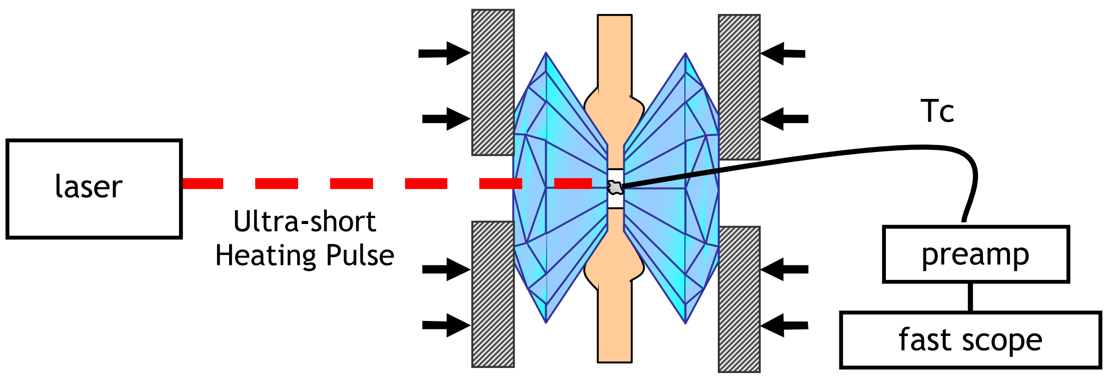

Figure 2: Schematic idea of the flash method applied to a sample compressed in a diamond anvil cell.

In FY 06 we have completed the set up of the laser, built the system, tested the optics and electronics necessary for the fast reading of the thermocouple signal and have begun test measurements of thermal diffusivity on samples of dimensions compatible with diamond anvil cell.

In these tests at ambient conditions we silver painted or evaporated a gold layer directly to the sample or on the front diamond, to ensure uniform heat transfer and to reduce diamond emissivity, obtaining good results.

The most challenging aspect concerned the reading of the thermocouple's signal. In our first tests we used a type K thermocouple. The laser line was operated at 10 Hz and the power tuned to obtained typical temperature increase of 4-5 K, which correspond to a variation of 160-200 μV on the thermocouple signal. Therefore a preamp was necessary. A differential pre-amplification ($5x10^4$) with a band pass 3-30 Hz, DC coupled to the oscilloscope, provided the best conditions. Nevertheless, a ~60 Hz noise and a higher frequency noise were still clearly visible in the signal. This did not prevent us from observing the overall shape of the temperature evolution, but did not allow a detailed analysis of the signal. We estimated the electronic of the fs laser itself to be he most likely source for the high frequency noise. This noise was also clearly present on the DC signal of the thermocouple, even when the laser was not coupled with the sample. A very careful shielding of the cables and oscilloscope, together with independent grounds for the electronics of the laser and of the preamp and oscilloscope have been envisaged as possible solutions to reduce this inconvenience. In any case, it is important to note that for the determination of the thermal diffusivity, only the temperature variations are necessary, not the absolute values. This also circumvents the problem of the calibration of the thermocouple under different stress when the method is applied to sample compressed in DAC.

Summary and Exit Plan

We have evaluated the feasibility and have estimated the potential capabilities of a new technique for measuring thermal transport properties in a diamond anvil cell. Our approach is essentiality an extension of the flash method to the geometry of the DAC and our ultimate goal is to greatly enlarge the pressure and temperature range over which thermal diffusivity and conductivity can be gathered. More specifically, we have performed test experiments to establish a technique for probing thermal diffusivity on samples of dimensions compatible with the physical constraints of the diamond anvil cell.

After six months of preliminary tests and considerations, despite some problems which still require better solutions, the proposed technique seems very promising. More specifically, the use of an ultra-short pulsed laser as heating source and the evaporation a gold layer on the front diamond, ensured uniform and controlled heat transfer without the need of a direct physical contact between the heating source and the sample. The electronic noise on the thermocouple signal is the main difficulty which remained to be solved.

When fully integrated into high pressure capabilities, this technique will allow experimental investigation of thermal properties in a pressure and temperature range much larger that what presently achievable. The measurements will lead to one publication on the technique itself, and ultimately to new knowledge and publications when applied to materials of interest to basic science and Laboratory programs. Along this line, once fully developed, this new method will add to our core competence in static high pressure and temperature experimentation. If successful, this will be a very useful technique for thermal properties measurements on a wide range of materials of basic science as well as of programmatic interest, including materials which might be available in only limited quantities.

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