Report on the

Thermal Diffusivity, Specific Heat, and Thermal Conductivity of Aluminum Oxide and Pyroceram 9606

This report presents the results of phenol diffusivity, specific heat and calculated thermal conductivity measurements of samples of aluminum oxide (99.8% pure, polycrystalline) and pyroceram code 9606.

The samples tested were disks 2 mm thick by 12.7 mm in diameter. The samples were coated with approximately 0.1 um of gold and 5 J.l1D of graphite for testing.

Thermal diffusivity and specific heat of each sample were measured at 25, 100 and 200°C by the Laser Flash Method utilizing a Holometrix Thermaflash 2200 instrument. This instrument and method conform to ASTM E1461-92, "Standard Test Method for Thermal Diffusivity of Solids by the Flash Method" for the measurement of thermal diffusivity. The method for the measurement of specific heat by Laser Flash is described below.

The test results are given after a description of the experimental procedure.

Thermal Diffusivity
Transient heat transfer problems occur when the temperature distribution changes with time. The fundamental quantity that enters into heat transfer situations not at steady state is the thermal diffusivity. It is related to the steady-state thermal conductivity through the equation

$$D = \frac{\lambda}{C_p \rho}$$

where D is the thermal diffusivity, ? is the thermal conductivity, Cp is the specific heat, and ? is the density. The diffusivity is a measure of how quickly a body can change its temperature; it increases with the ability of a body to conduct heat (?) and it decreases with the amount of heat needed to change the temperature of a body (Cp). All three quantities on the right hand side of Equation (1), as well as the thermal diffusivity, can be functions of temperature.

Thermal properties of materials are measured by experimentally establishing a heat flow boundary value problem, solving the theoretical equations, and then measuring the necessary temperatures or heat fluxes to determine the thermal property by matching to

1

the theoretical solution. Thus the easiest theoretical way to measure the thermal conductivity is to set up a steady-state, linear flow of heat through the material and apply Fourier's equation. This approach has led to the development of a number of methods for measuring the thermal conductivity including the Guarded Hot Plate and Linear Rod methods. These methods are time consuming and can be susceptible to errors arising from non-realization of the assumed boundary or steady-state conditions. The flash methods of measuring thermal diffusivity remove the steady-state condition at the expense of measuring temperature as a varying function of time.

The measurement of the thermal diffusivity of a material is usually carried out by rapidly heating one side of a sample and measuring the temperature rise curve on the opposite side. The time that it takes for the heat to travel through the sample and cause the temperature to rise on the rear face can be used to measure the through-plane diffusivity and calculate the through-plane thermal conductivity if the specific heat and density are known. The through-plane measurement is depicted in Figure I.
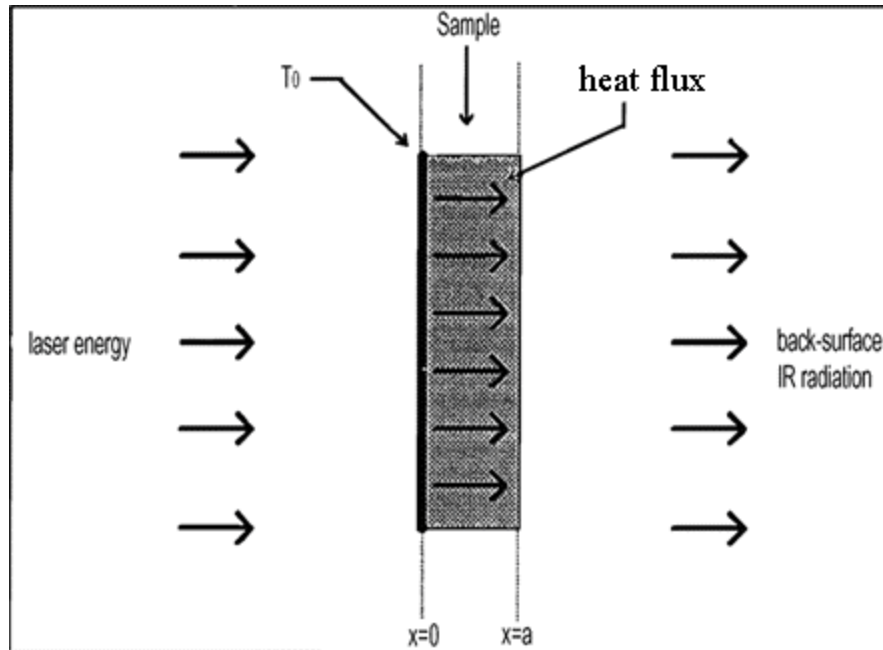

Figure 1

Through-Plane Method and Analysis
The basic method is sketched in Figure 2. The sample is a disk with a standard diameter of 12.7 mm and a thickness ranging from about 0.1 to 3 mm. With the Holometrix Thermaflash 2200 Laser Flash system, the sample disk is aligned between a neodymium glass laser (1.06 μm wavelength) and an indium antimonide (InSb) IR detector in a tantalum tube furnace. A Type C thermocouple in contact with the sample controls the sample and its surroundings at any temperature between 20 and 2000°C. Once the

sample has been stabilized at the desired temperature, the laser is fired several times over a span of a few minutes and the necessary data is recorded for each laser "shot". The laser beam energy strikes and is absorbed by the front surface of the sample, causing a heat pulse to travel through the samples' thickness. The resulting sample temperature rise is fairly small, ranging from about 0.5 to 2 degrees C. This temperature rise is kept in the optimum range by adjustable filters between the laser and the furnace. A lens focuses the back surface image of the sample onto the detector and the temperature rise signal vs. time is amplified and recorded with a high speed A/D converter. Figure 3 is an example of an actual temperature rise curve.
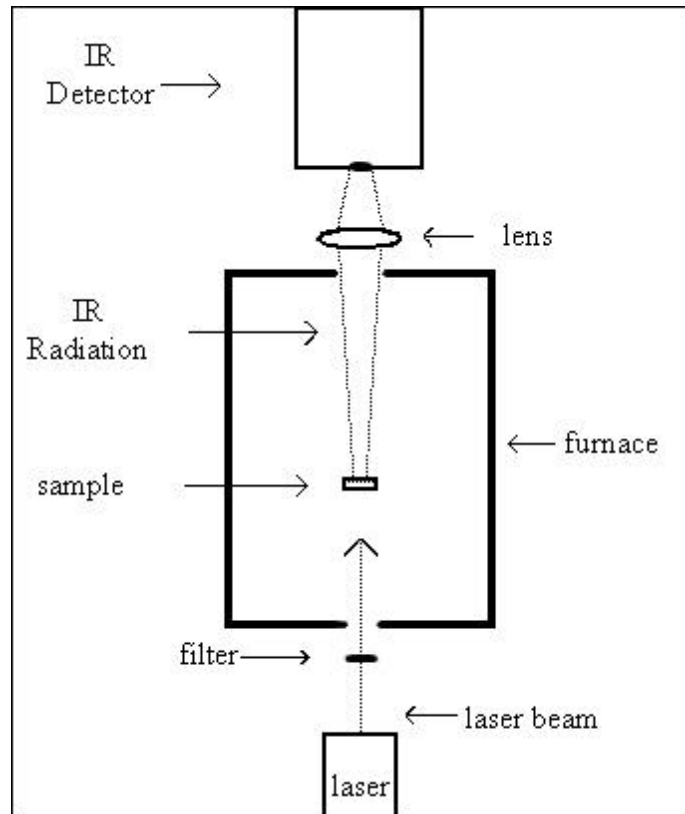

Figure 2

Testing is performed in a high vacuum or inert gas environment. The instrument is fully automated to control all systems and record, analyze and report the thermal diffusivity, specific heat and the calculated thermal conductivity.

The Holometrix Microflash system, designed for measurements from room temperature to 300°C, utilizes a lower temperature furnace design and lacks a vacuum system for controlling the furnace environment.

Samples that do not naturally have a high value of emissivity or absorbtivity are coated with a graphite film before testing. The graphite increases the energy absorbed on the laser side and increases the temperature signal on the backside of the sample. Some materials are transparent to infrared radiation and must be coated with a metal film on both sides. This prevents penetration of the laser beam into the sample on the front side, and on the backside it prevents the viewing of the IR detector into the sample. A 1000 Å gold film can be used as it constitutes many skin depths at the frequency of the laser or of the thermal radiation from the sample.
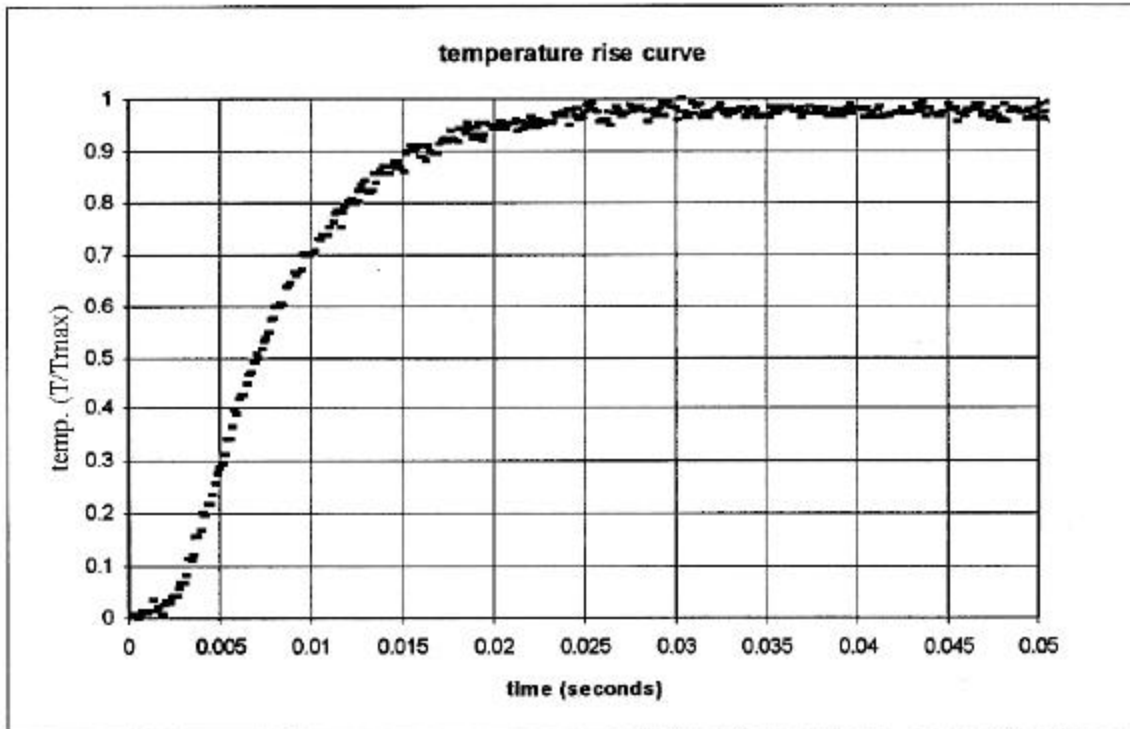

Figure 3

In the through-plane measurement depicted in Figure 1, the sample can be thought of as part of a sheet of material infinite in two dimensions but of finite thickness. Before the flash, the temperature of the sample and surroundings is at some uniform temperature that can be taken as zero. Immediately after the flash, the front surface of the sample is at some higher temperature, T_0. The heat flux lines are parallel and directed through the sample; there is no heat flow in the plane of the sample. The boundary conditions consist of radiation heat transfer from the front and rear faces into a surrounding space at the initial zero temperature. There have been many solutions of this boundary/initial value heat equation problem in different forms. The first to apply the solution to the flash diffusivity measurement was Parker et al.[1] Using the notation of Koski[2], the resulting equation for the rear face temperature as a function of time is

$$T(a,t)=2T_f \sum_{n=1}^{\infty} \frac{\gamma_n^2 (\gamma_n^2 + L^2) \cos \gamma_n}{\gamma_n^2 + L^2 + 2L} \exp(-\gamma_n^2 Dt / a^2) \qquad (2)$$

where

T_f =   the final sample temperature

D =   the thermal diffusivity

t =   time

a =   the sample thickness

L =   the heat loss factor

Each γ_n is found by solving the transcendental equation

$$\tan \gamma_n = \frac{2\gamma_n L}{\gamma_n^2 - L^2} \qquad (3)$$

The finite width of the laser pulse, t_p, can affect the measurement of thin and/or high diffusivity samples because the heating of the front surface can no longer be considered instantaneous relative to the time for the heat to diffuse through the sample. To include this effect in the analysis, the laser pulse width is folded into the results by convoluting Equation (2) with the pulse shape. If there is no heat loss, i.e. L=0, and the finite pulse can be ignored, then Equation (2) leads to the Parker expression

$$\alpha = \frac{0.139 a^2}{t_{50}} \qquad (4)$$

where, t_{50}, the half rise time, is the time for the back face temperature to reach 50% of its maximum value. Equation (4) is a very useful expression for calculating optimum sample thickness and expected rise times if the approximate diffusivity is known.

In the more general case, the approach used is that of Koski.[2] Equation (2) can be used to generate the temperature rise curve if the diffusivity and the bss factor are known. The analysis of the laser flash data requires the inverse of this operation; the temperature rise curve is known and the diffusivity is to be determined. The time required to perform real time analysis of the laser flash data can be reduced by pre-establishing the relationship between the diffusivity, loss factor and pulse width correction and the shape of the

temperature rise curve. Koski generated the temperature rise curves for a large range of diffusivity and heat loss and then analyzed the curves for their shapes. There are a number of parameters that can be used to describe the shape of the curve; Koski considers two approaches, that of Clark and Taylor[3] and that of Cowan[4]. Both use the ratio of the pulse width to the half rise time, $r_1 = t_p/t_{50}$ as one parameter. Cowan (as applied by Koski) uses as a measure of the heat loss a second parameter, r^2, the ratio of the temperature at five times t_{50} to the temperature at t_{50}. Clark and Taylor prefer to use only that part of the temperature rise curve before the peak. They noted that heat loss causes the curve to rise more steeply, so they use as r_2 the ratio of t_x to t_y, where x and y are percentages of the maximum temperature rise. Koski considers three ratios: t_{70}/t_{30}, t_{80}/t_{20}, t_{80}/t_{40}. One of these ratios is used along with r_1 as the two parameters that define the shape of the curve. Surface fits were made to the diffusivity and loss factor. The fits are a method of interpolating for shape parameters that do not correspond exactly to one of the temperature rise curves generated in the study.

The data is analyzed using both the Clark and Taylor method and the Cowan method. Because data taken on real samples does not conform exactly to the assumptions made in the theoretical analysis, either the Clark and Taylor method or the Cowan method may give better agreement with the data. After each laser shot the analyzed time rise curve is plotted and compared to the theoretical curve having the same value of diffusivity and heat loss. The software used in the analysis was verified by analyzing curves with known values of diffusivity and heat loss. All resultant values of diffusivity were within 1 % of the input values.

Specific Heat
The specific heat of a material is defined as the amount of energy required to raise a unit mass of material by one unit of temperature at constant pressure.

$$Cp = \frac{Q}{m\Delta T}$$

where:
        Cp = specific heat
         m = mass
         ΔT = change in temperature
         Q = energy

Specific heat can be measured with the Laser Flash Method by comparing the temperature rise of the sample to the temperature rise of a reference sample of known

specific heat tested under the same conditions[1]. This temperature (voltage) rise is recorded during the diffusivity measurement, so the specific heat can be calculated from the same data with a suitable calibration. Assuming that the laser pulse energy and its coupling to the sample remain essentially unchanged between samples,

$$Q = \text{absorbed energy} = (mCp\Delta T)_{ref} = (mCp\Delta T)_{sample}$$

and

$$Cp_{sample} = \frac{(mCp\Delta T)_{ref}}{(m\Delta T)_{sample}} \qquad (9)$$

A reference sample is measured at each temperature of interest to calibrate the change in output voltage of the IR detector (ΔV) resulting from the absorbed laser energy. The measured ΔV will be proportional to the temperature rise (ΔT), as long as the temperature rise is small. This calibration gives the absorbed energy in terms of the mass, specific heat and ΔV of the reference sample. When a sample of unknown specific heat is measured, the absorbed energy divided by the product of the mass and ΔV of the test sample, Equation 9, gives the test sample specific heat. Testing has shown that the laser pulse energy is stable from pulse to pulse within about 3%, so the average of several laser pulses at each temperature can be used in the calculations. The absorptive efficiency of the front surface of the samples to the laser pulse and the radiative efficiency of the back surface to the IR detector are controlled by coating the reference and test samples with the same thin layer of graphite.

Conductivity
The sample thermal conductivity can be calculated with Equation (1), after a measurement of the diffusivity and specific heat as described above, and with a measurement of the sample bulk density.

Test Results
The measured values of thermal diffusivity, specific heat, and bulk density and the calculated thermal conductivity for the samples tested here are given in Table 1. The aluminum oxide sample was used as the specific heat calibration sample, so its values of specific heat are reference values from the NIST certificate for SRM 720. Attachment 1 is a temperature rise curve for the aluminum oxide sample at 200°C. The measured conductivity values for the pyroceram 9606 are all within 4% of the recommended values established for this material through round robin testing.

References

1. W.J. Parker, R.J. Jenkins, C.P. Butler, and G.L. Abbott, "A Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity", J. Appl. Phys. **32**, 1679 (1961)

2. J .A. Koski, "Improved Data Reduction Methods for Laser Pulse Diffusivity Determination with the Use of Minicomputers", in Proc. Eighth Symp. Thermophysical Prop., Vol II, J. V. Sengers, Ed, Amer. Soc. Mech. Eng., New York (1981).

3. L.M. Clark III and R.E. Taylor, "Radiation loss in the flash method for thermal diffusivity", J. Appl. Phys. **46**, 714-719 (1975).

4. R.D. Cowan, "Pulse method of measuring thermal diffusivity at high temperature", J. Appl. Phys. **34**, 926-927 (1963).

Holometrix

Table 1

Laser Flash Thermal Conductivity Results

Sample	bulk density ρ @ 25°C (g/cm^3)	temperature (°C)	specifc heat Cp (J/gK)	diffusivity α (cm^2/s)	conductivity λ (W/mK)
aluminum oxide	3.89	25	0.775	0.105	31.8
		100	0.904	0.0659	23.2
		200	1.020	0.0450	17.9
Pyroceram 9606	2.60	25	0.787	0.0194	3.96
		100	0.893	0.0154	3.58
		200	0.990	0.0132	3.39

Holometrix

ALUM1 SAMPLE AT 200.0 C
FILE: ALUM1.DAT TRIAL 003:003:000

VOLTAGE (volts)

TIME (sec)

Thickness 2.
Gain 173