

A Universal Laser-Pulse Apparatus for Thermophysical Measurements in Refractory Materials at Very High Temperatures¹

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This paper presents a new experimental technique enabling thermophysical measurements to be carried out at very high temperatures in a very simple and small pressurized vessel in which the sample is heated by a continuous wave laser, and subsequently subjected to a short temperature pulse. The adopted method is essentially an extension of the "laser-flash" technique, widely used for thermal diffusivity measurements, whereby, in addition, the heat capacity and, hence, the thermal conductivity, λ , are simultaneously evaluated from the pulse analysis. Results are presented for the thermal diffusivity and heat capacity of graphite, zirconia, and uranium dioxide up to temperatures above 3000 K.

KEY WORDS: heat capacity; high-speed pyrometry; laser flash; laser heating; graphite; thermal conductivity; thermal diffusivity; uranium dioxide; zirconia.

1. INTRODUCTION

The idea of measuring the heat capacity of a sample from the temperature increase produced by an applied energy pulse of known intensity dates from 1961 when Parker et al. [1] published the first paper on the flash method for thermal diffusivity measurements. Yet the subsecond instrumentation available at that time was so unsophisticated that this seemed nearly impossible. Although, with progress in laser technology and fast pyrometry, the flash method became more and more precise, for nearly

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three decades any extension of this technique to calorimetric measurements was considered impracticable. Only at the end of the 1980s was a flash method successfully applied, using a xenon lamp, for heat capacity measurements up to 1300 K [2]. The method was, however, based on a comparative empirical procedure; moreover, the sample had to be sputtered with graphite in order to ensure a constant absorptance. The weak point of this setup was the sensitivity of the measurements to sample positioning within the light beam. In 1990, a feasibility study was carried out, in which a laser-flash device was successfully used to measure heat capacity [3]. Again, a comparative method was chosen; however, in order to avoid misalignments, the standard sample was permanently mounted in a separate holder and was thus acting as a rudimentary reference calorimeter.

A new experimental setup was recently constructed in our laboratory, using advanced pyrometric techniques in conjunction with high-quality lasers beams (obtained by optical fibers) and optical diagnostic equipment. An absolute calorimetric method was implemented, in which the maximum useful amount of experimental information is exploited to simultaneously obtain thermal diffusivity and heat capacity up to very high temperatures, and with good accuracy. Furthermore, with the same setup a very accurate determination of the phase transition parameters can be obtained with a precision better than 1 K; this aspect is, however, not treated in this paper.

2. MEASUREMENT PROCEDURE

The apparatus is shown schematically in Fig. 1. The sample, a disk of 5-mm diameter and ≈ 0.5 -mm thickness, is held by a three-pin mounting in a small autoclave. Two opposite CW Nd-YAG laser beams (of 300-W total power) heat the two faces of the sample up to the conditioning temperature. This is recorded on both faces of the disk by two rapid and precise pyrometers (settling time to 1% = 10 μ s; sensitivity, <0.1 K).

Because of the almost-flat radial profile of the laser beam power in the focal spot (5-mm diameter), and its stability with time, a homogeneous and constant surface temperature can be rapidly achieved within the illuminated spot. A temperature pulse of 1- to 2-ms duration and less than 0.5-J energy is then applied onto the front face of the sample with a YAG laser. The front-face temperature rise is detected above the steady-state level, while a similar pyrometer is viewing a spot of 0.3-mm diameter on the rear face of the sample. These signals are sent to a 14-bit A/D converter, providing a detection sensitivity of better than 0.05 K. The pulse power is measured as a function of time by a Si photodiode, which collects a fixed

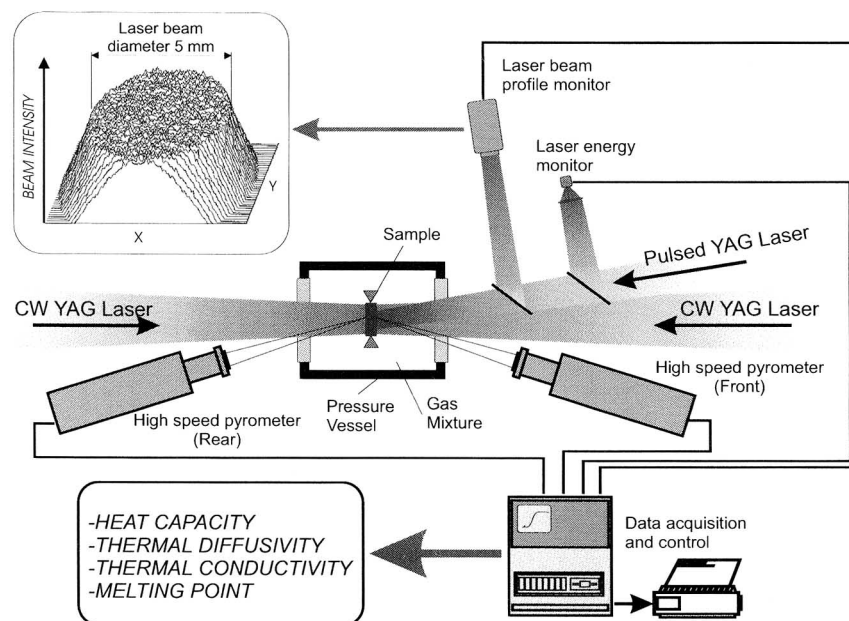


Fig. 1. Schematic of the apparatus for thermal diffusivity and heat capacity measurements.

fraction of the laser beam. The integral energy collected by the photodetector is calibrated with a disk calorimeter (SCIENTEC; precision, 3%). The absorbed surface power is calculated from the optical absorptance of the sample at the wavelength of the Nd-YAG laser and measured with an integrating sphere reflectometer with a precision of better than 5%. Finally, the probe-beam spatial profile in the focal point is measured, through a beam splitter, by a CCD camera.

3. ANALYTICAL

In the new apparatus, the homogeneity and symmetry of the heating conditions, in conjunction with the high precision and sensitivity of the instruments, enable sophisticated thermal diffusivity measurements to be performed (see Ref. 4 for details). In this paper, it is shown how the thermal diffusivity, a , and the heat capacity, C_p , can be evaluated simultaneously. The method is based on fitting the measured temperatures by the integral of the pulse diffusion equation, $\Delta T = \Delta T(t, \{C_p, a\})$, obtained for sufficiently realistic boundary conditions. This problem, which was investigated in the context of the thermal diffusivity measurements, presents

serious difficulties when large heat losses—unavoidable at high temperatures—or spatial variations of the applied power density are present during the pulse.

The adopted fitting function represents the general case of a pulse propagating into a platelet with the sole restriction of preserved cylindrical symmetry: for a disk of density ρ with axial coordinates $0 \leq z \leq l$ and radial coordinates $0 \leq r \leq R$, this function is approximated by the product of the pulse propagation function in an infinite slab of thickness l , and the radial propagation of a cylindrical surface source at $z=0$ of total energy Q , deposited with time dependence $\varphi(t)$ and radial dependence $f(r)$:

$$\begin{aligned} \Delta T(x, r, t) = & \frac{2}{\pi l^2 \rho C_p \tau} \frac{Q}{\tau} \sum_{n=1}^{\infty} \frac{\alpha_n (2\alpha_n^2 + Y_2^2) (\alpha_n \cos \alpha_n z + Y_1 \sin \alpha_n z)}{(\alpha_n^2 + Y_1^2) (\alpha_n^2 + Y_2^2 + Y_2) + Y_1 (\alpha_n^2 + Y_2^2)} \\ & \times \int_0^t \varphi(t') \sum_{j=1}^{\infty} \exp(-a \lambda_j^2 t') \frac{J_0(r \lambda_j)}{J_0^2(R \lambda_j) + J_1^2(R \lambda_j)} \\ & \times \int_0^R r' f(r') J_0(r' \lambda_j) \exp\left(\frac{-\alpha_n^2}{l^2} a t'\right) dr' dt' \quad (1) \end{aligned}$$

where α_n and λ_n ($n=1, \dots, \infty$) are, respectively, the roots of the equations:

$$(\alpha^2 - Y_1 Y_2) \operatorname{tg}(\alpha) = \alpha (Y_1 + Y_2), \quad R \lambda J_1(R \lambda) = Y_r J_0(R \lambda)$$

and Y_1 , Y_2 , and Y_r are, respectively, the Biot numbers on the front ($z=0$), rear ($z=l$), and lateral ($r=R$, $z=l/2$) surfaces of the sample. Finally, Eq. (1) depends on the five parameters: a , C_p , Y_1 , Y_2 , and Y_r . The experimental temperature function, $T_{\text{exp}}(t)$, is fitted with Eq. (1) by varying the parameters.

A five-parameter fit is only practicable if a fitting strategy is applied, based on the hierarchical rank of the variables, x_i . In fact, the thermal diffusivity, a , is by far the most important parameter, followed by C_p and the total heat-loss, while the partition of this latter into the three “top,” “bottom,” and “radial” directions represents a third-rank variable. Fitting is, therefore, started with the variables of the first and second rank, those of the third rank being previously assessed, for example, by calculation of the ratios of Y_2 and Y_r to Y_1 . A further optimization of the latter parameters can follow only if the N -dimensional nonlinear fitting (with $N \leq 5$) sufficiently provides “robust” solutions in the sense explained below.⁵ This condition depends mainly on the extent, range and quality of the specific experimental database.

⁵ Obviously, if one additional variable is introduced, all fitting variables are simultaneously recalculated.

If σ' is the MSQ residual fitting error, the errors of the fitted parameters, σ_i , are *approximately* expressed according to the linear regression formalisms as

$$\sigma_i = \sigma' \sqrt{\frac{M}{M-N} \frac{B_{ii}}{B}} \quad (2)$$

where B is the determinant of the matrix:

$$b_{rs} = \sum_{m=1}^M \frac{\partial T_m}{\partial x_r} \frac{\partial T_m}{\partial x_s} \quad (3)$$

and B_{ij} is the cofactor of the element b_{ij} .

In practice, with an experimental error of $\Delta T \leq 1\%$, a significant fitting of five parameters can be obtained if σ' is of the order of 0.5% or less. In our best experiments we obtained $\sigma_{C_p} \cong 3\%$, $\sigma_a \cong 0.5\%$, and $\sigma_{Y_1, Y_2, Y_j} \cong 10\%$. However, in most cases, a precision $\sigma_{C_p} < 5\%$ can also be obtained by fitting only three parameters, including the sum of the heat losses, and a previous reasonable estimation of the ratios of the Biot numbers, Y_j .

4. HEAT CAPACITY AND DIFFUSIVITY MEASUREMENTS

4.1. Graphite

POCO-5Q AMX graphite was measured as a reference material up to 3200 K. The best literature data (up to 2400 K) were obtained with the *direct electrical heating* technique. Figure 2 shows our results compared with these data. It can be seen that in the common temperature range, our measurements differ from the others by approximately 5%, whereas our error is 8%. It should be, however, remarked that our points correspond to individual measurements obtained from single pulses, while, for example, for the thermal conductivity, the three curves of points of Taylor and Groot represent the average of measurements on three nominally identical samples.

4.2. Uranium Dioxide

Since this material easily vaporizes at $T > 2000$ K, thermophysical measurements at high temperatures are rather difficult. The very short duration of our measurements is, therefore, of great advantage. In fact, the samples, stoichiometric ($10.5 \text{ g} \cdot \text{cm}^{-3}$ density) sintered pellets, did *not* show, after the measurements in Ar : 2% H₂, significant vaporization or stoichiometric changes up to 2600 K (post measurement $O/U = 1.995$). The

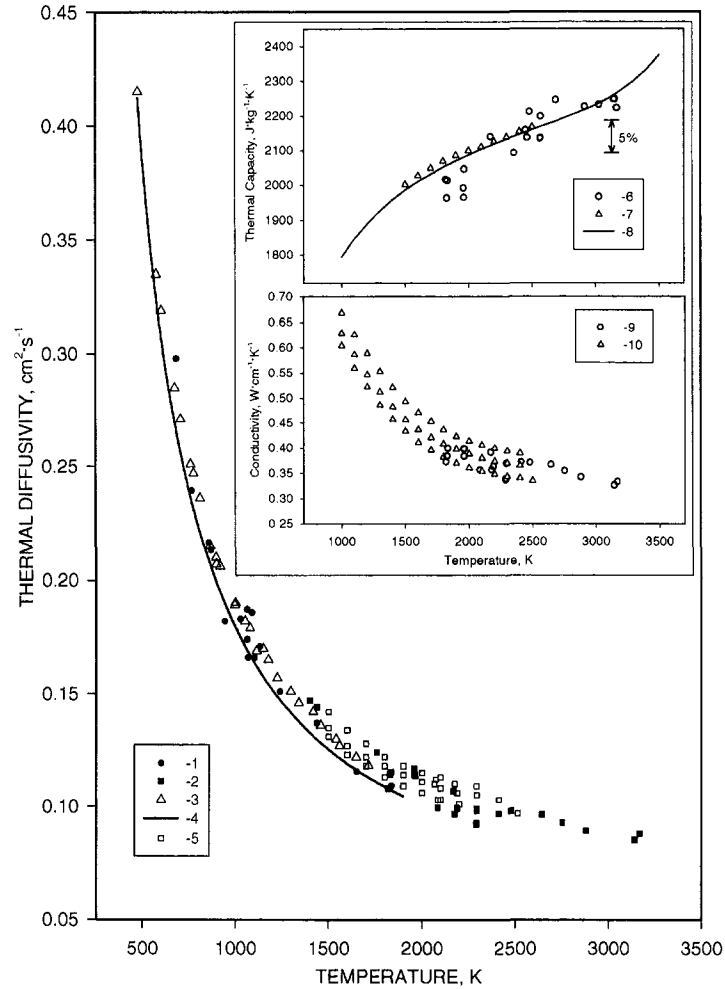


Fig. 2. Thermal diffusivity, heat capacity, and thermal conductivity of graphite: 1, ITU conventional laser-flash measurement in a furnace; 2, this work; 3, Ref. 18; 4, Ref. 5; 5, Ref. 6; 6, this work; 7, Ref. 7; 8, Ref. 8; 9, this work; 10, Ref. 6. The literature heat capacity values correspond to fits to spline functions, resulting in smooth curves while our points represent single, direct measurements. The same is true for the thermal conductivity, where the data of Taylor and Groot [6] are represented by smoothed curves obtained from three different samples.

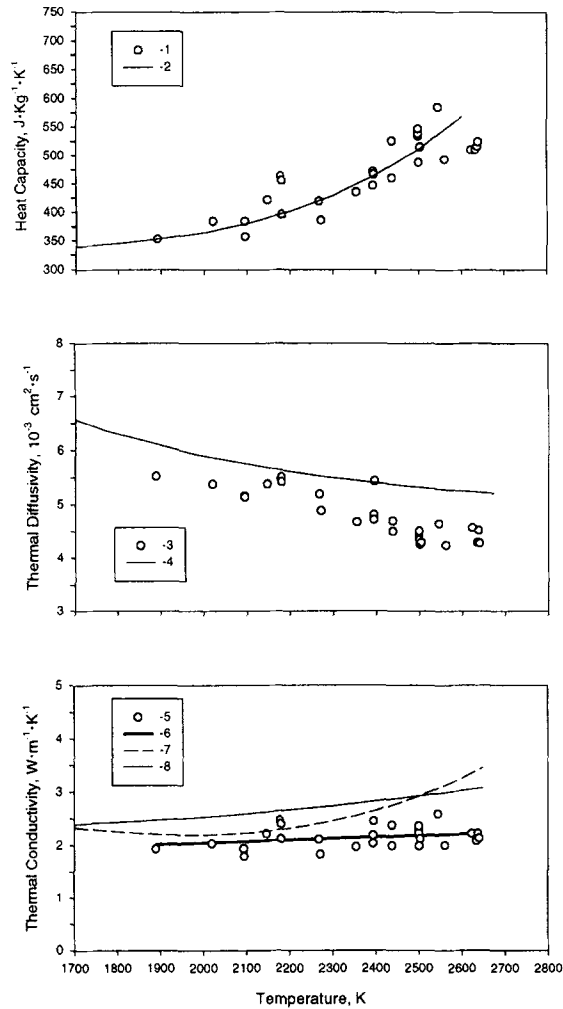


Fig. 3. Heat capacity, thermal diffusivity, and thermal conductivity of UO_2 : 1, this work; 2, Ref. 10; 3, this work; 4, Ref. 9; 5, this work; 6, linear fit of curve 5; 7, Ref. 10; 8, Ref. 11.

results are plotted in Fig. 3. Measurements above 2600 K are still in progress with a different laser pulse duration. The thermal diffusivity, in spite of a dramatic restructuring of the sample, exhibits a monotonic decrease up to 2500 K; at higher temperatures, the slope is significantly smaller. Particularly interesting are the measurements of the thermal

conductivity: after a pronounced decreasing stage at low temperatures, λ increases weakly in the interval 2000 to 2600 K. The trend of $\lambda(T)$ at high temperature seems to exclude a large increase of this quantity in the temperature interval preceding melting (3150 K), indicating a closer approach to the value of λ in the liquid [12] than predicted by the extrapolation curves of Fink et al. [10] and Hyland [11].

The measured heat capacity points lie within the $\pm 5\%$ error band of the curve reported in Ref. 10, obtained by differentiating the enthalpy measurements of Hein and Flagella [19]. Noteworthy is the large scatter of the data above 2500 K, probably due to the vicinity of the premelting transition [16], which starts affecting the front-surface layer.

4.3. Zirconia

Cubic-stabilized $\text{ZrO}_2 : 20\% \text{Y}_2\text{O}_3$ was measured. The samples were fabricated by plasma spraying and have a macroscopic density of $5.07 \text{ g} \cdot \text{cm}^{-3}$. The (textured) sintered porosity proved to be stable up to approximately 2500 K, though a permanent increase in thermal diffusivity is detected after heating above 1500 K, probably due to annealing of lattice defects and grain boundary restructuring. No changes in stoichiometry or color were observed after the measurements. While the sample is white at room temperature, above 1800 K, it exhibits a sufficiently high and stable absorptance (>0.65 at 1060 nm) to enable steady-state temperature stability of $< \pm 1 \text{ K}$ to be achieved.

The results for heat capacity are plotted in Fig. 4. As for the thermal diffusivity, whose thermal recovery is of little interest here, it can be seen that between 1850 and 2800 K the thermal diffusivity value is $4.2 \pm 0.5 \text{ cm}^2 \cdot \text{s}^{-1}$, and increases weakly with temperature. In the same temperature range, the measured heat capacity increases only from 620 to $700 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. The observed behavior of C_p , however, has important physical implications. In analogy with other *fcc* ionic dioxides, a marked increase in the heat capacity at high temperatures is normally expected, due to formation of oxygen Frenkel pairs, a thermal process in which a large amount of energy is expended.

The existing literature data are in disagreement: on one hand, in his samples Pears [13] (1% Ca-stabilized, supplied by Zirconium Corp. of America, where after exposure at high temperature both the oxygen-to-metal ratio and the Ca content decreased) measured a marked increase of C_p above 2000 K, corroborating the hypothesis of substantial oxygen defect formation at high temperatures; on the other hand, the measurements of Chekhovskoy et al. [14] on pure, nonstabilized zirconia exhibit a weak dependence of C_p with T up to 2750 K and no composition changes. Our

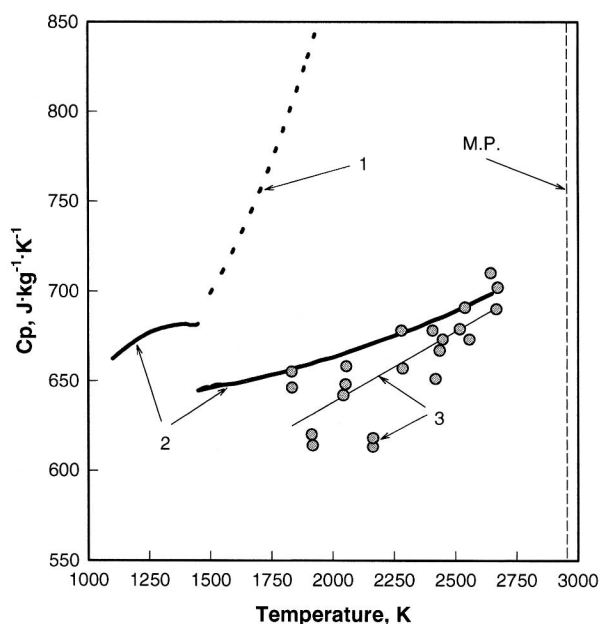


Fig. 4. Zirconia heat capacity as a function of temperature: 1, Ref. 13; 2, Ref. 14; 3, this work, data points and linear fit. The results for Pears [13] and Chekhovskoy et al. [14] were obtained by differentiating a spline curve of enthalpy vs. temperature. The zirconia used by Chekhovskoy et al. was not stabilized, and consequently, a discontinuity in C_p is found at the tetragonal-cubic phase transition at $T \cong 1450$ K.

measurements—on a doped but chemically stable material—are in agreement with the latter data. This should confirm that stoichiometric stability reduces intrinsic Frenkel defect formation. In fact, creation of oxygen Frenkel pairs requires a local charge rearrangement which is improbable in compounds like pure ZrO_2 , where all cations have a fixed valence (see, for example, the analogous behavior of ThO_2 [15]). On the other hand, in oxides where a valence disproportioning is possible—as, e.g., UO_2 —the oxygen defect concentration attains at sufficiently high temperatures fractional concentrations, of the order of magnitude of 10^{-1} , producing a marked increase in C_p [16].

As for the effect of yttrium doping, literature data [17] indicate that in Y_2O_3 the curve $C_p(T)$ reaches a plateau above 1600 K at $C_p/R \cong 15$, a value corresponding to the saturation of the vibrational modes of a *penta*-atomic crystal. Now, according to our data, the heat capacity in yttria-doped ZrO_2 above 1800 K stabilizes at $C_p/R \cong 9$, i.e., the saturation value

of a triatomic lattice. Since yttrium doping maintains C_p near the value corresponding to the perfect lattice of ZrO_2 , one can infer that the extrinsic excess oxygen of yttria indeed inhibits thermal Frenkel pair formation. Though perfectly plausible, these conclusions—which may be important for the refractory properties of the various types of zirconia—leave out of consideration the underlying dependence on dopant concentration of the effective free energy and entropy of formation of defects in the lattice, an aspect which may entail unexpected dramatic changes in the temperature dependence of C_p (see, e.g., Ref. 16). Therefore, extrapolations of these results to other types of stabilized zirconia must be considered with care.

5. CONCLUSIONS

It has been shown that the new laser-flash device presented in this paper can be used for *simultaneous* and *consistent* measurements of heat capacity and thermal diffusivity, providing insight into the dominant heat transport mechanisms. These features are demonstrated by the measurements on UO_2 and ZrO_2 .

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