

Room temperature screening of thermal conductivity by means of thermal transient measurements

Jorge García-Cañadas^a, Shudan Cheng, Lourdes Márquez-García, Martin J. Prest, Ahmad Akbari-Rahimabadi^b and Gao Min^c

Cardiff School of Engineering, Cardiff University, Cardiff, CF24 3AA, UK

A proof of concept of the possibility to estimate thermal conductivity of bulk disc samples at room temperature by means of thermal decays is demonstrated. An experimental set-up was designed and fabricated, which is able to perform thermal transient measurements by using a specially designed *multifunctional* probe that has the ability to measure temperature at its tip. Initially, the probe is heated by a heater coil located in its interior until the tip temperature reaches a steady state. Then, the probe is contacted with a disc sample which produces a temperature decay until a new state is reached. The difference between the initial and final states temperatures shows a correlation with the thermal conductivity of the sample. Employing a calibration equation, obtained using reference materials, the thermal conductivity can be calculated. Reasonably good random and systematic errors (<13 % and ~9 % respectively) are obtained. Theoretical simulations performed using COMSOL show a good qualitative agreement with experimental results. This new method involves an inexpensive and simple set-up which can be especially useful for thermal conductivity screening and high-throughput measurements.

Keywords: Thermal conductivity, high-throughput, thermoelectric, screening.

^a Current address: Department of Industrial Systems Engineering and Design, Universitat Jaume I, Campus del Riu Sec, 12071 Castellón, Spain

^b Current address: Department of Mechanical Engineering, Kermanshah branch, Islamic Azad University, Kermanshah, Iran

^c Electronic mail: min@cardiff.ac.uk.

I. INTRODUCTION

Thermal conductivity (λ) is an important material property in a wide range of applications, such as polymer injection molding, materials for home insulation, heat shielding for space applications, thermal management in electronics and thermoelectric materials. Some of the most common methods to measure thermal conductivity include the guarded hot-plate [1], the laser flash method [2], the hot wire [3], the 3ω method [4] and the hot disk [5].

The high-throughput measurement of thermal conductivity is of significant importance in several fields. For example, for the discovery of new thermoelectric materials the variation of the thermoelectric properties (Seebeck coefficient, electrical resistivity and thermal conductivity) is frequently explored in compounds of different compositions and doping levels [6–8]. Examples of rapid methods to determine thermal conductivity in this field can be found in the literature [9,10]. A similar scenario also occurs in phase change composite materials [11].

In this paper we demonstrate the proof of concept of a new method to measure thermal conductivity using an inexpensive and simple set-up compared to well-established techniques. The method is based on the use of a *multifunctional* probe which serves to record thermal transients [12]. A description of the set-up is first provided, then the measurement procedure is described and finally COMSOL simulations are shown which provide theoretical support.

II. DESCRIPTION OF THE SET-UP

A *multifunctional* probe with the capabilities of measuring the temperature at its tip and having an integrated heater coil was designed. Fig. 1a shows a schematic diagram of the probe, which was fabricated using a Cu tube (30 mm long and 1.6 mm diameter) and an internal constantan wire which was welded to the tip of the tube [12]. The tip was sharpened and slightly flattened until a diameter of $\approx 150 \mu\text{m}$ was obtained. A heater coil (constantan wire) was installed inside the Cu tube to allow heating of the probe. The probe fabrication was performed by Physitemp Instruments Inc. (USA). Prior to its use, the probe was calibrated against a commercial thermocouple, as described in a previous work [12].

The probe was inserted into a plastic cylindrical holder (13 mm height and 8 mm diameter) and fixed by 2 plastic screws (see Fig. 1b). The cylinder was supported by a plastic enclosure screwed onto a top support with a spring placed inside the enclosure, which allows the displacement of the probe when pressed against the sample. At the base of the set-up, a movable stage was located. The stage was made of plastic and contains concentric circular stairs to locate sample discs of different diameters (5 to 15 mm). The height of each step of the stairs is 0.5 mm. In this way, the probe always contacts the disc

samples at their center and the samples have an air gap underneath. During the measurement, the probe was initially heated up to reach a steady-state temperature without being in contact with the sample. The contact to the sample was then achieved by raising the stage and monitoring the temperature change of the probe. The moment when the temperature of the probe start to decrease indicates that the initial contact has been made. To ensure a good and repeatable contact, the stage is lifted slightly further to a preset position. The zone around the sample was protected by a plastic enclosure and covered by insulating wool (not shown in Fig. 1b) to minimize the heat loss from the probe due to convection.

In order to power the heater coil and measure the voltage output of the probe, a DC power supply (Keithley 2230-30-1) and a multimeter (Keithley 2000) were employed respectively. All the apparatus and measurements were controlled and recorded by a computer using Labview.

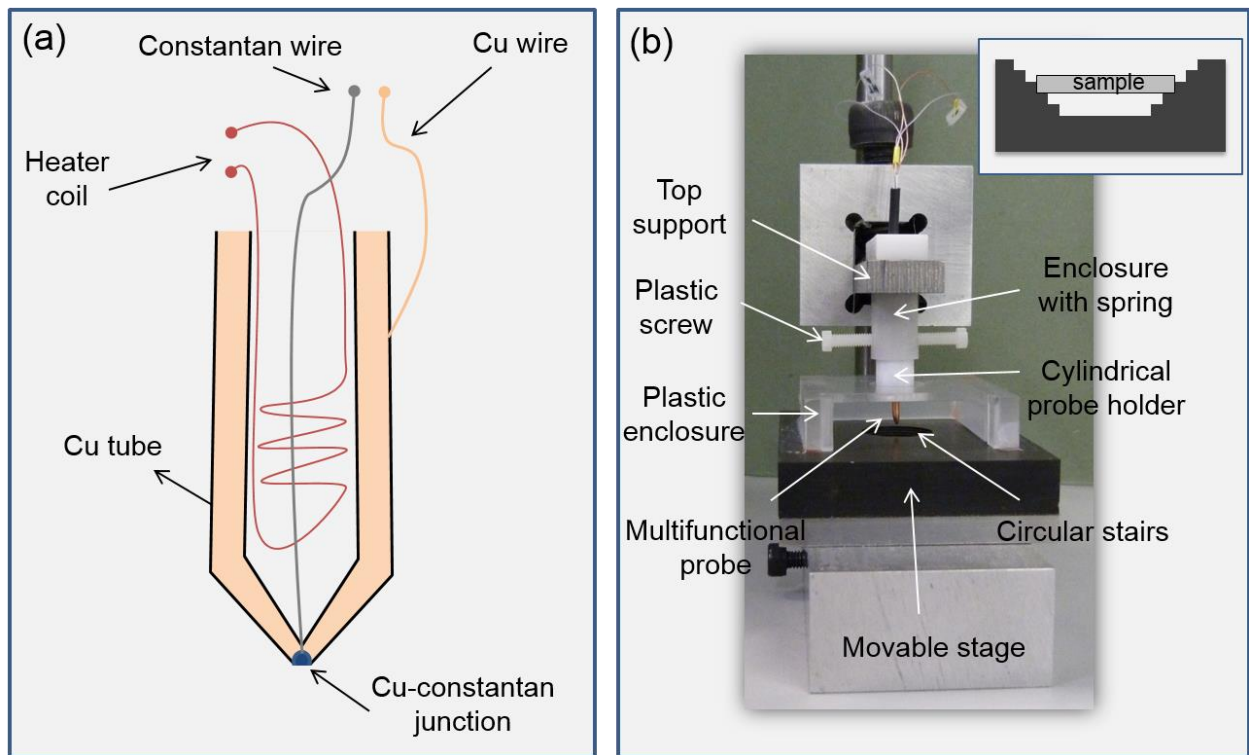


FIG. 1. Experimental set-up for room temperature thermal conductivity measurement: (a) Schematic diagram of the multifunctional probe with an internal heater coil; (b) a photograph of the actual set-up with a schematic of the cross-sectional view of the circular stairs in the inset.

III. MEASUREMENT PROCEDURE

The thermal conductivity is determined by identifying the correlation between the temperature change of the probe and the thermal conductivity of the sample. In this work, the correlation was determined using three disc-shaped reference samples of dimensions close to 13 mm diameter and 2 mm thickness. For each test, the probe was heated up with a constant current of 82 mA applied to its heater coil until a steady state temperature (usually between 68 to 74 °C) was reached. Then, the sample was brought into contact with the hot probe by lifting the sample stage, which resulted in a decrease of the tip temperature of the probe until it reaches a final state close to steady state. The temperature difference between the initial and final states, ΔT , can be obtained experimentally from the recorded temperature plots as shown in Fig. 2. The final state temperature was registered after 1100 s of contacting the probe to the sample. The 3 reference materials with different thermal conductivities selected for this study include a commercial PTFE disc (0.25 W/(m K)), a BCR-724A (4.06 W/(m K)) standard reference material (SRM) from LGC Standards (UK) and a Stainless Steel 1461 SRM (14.30 W/(m K)) from the National Bureau of Standards (USA, currently NIST). The certified uncertainties (k=1) provided by the suppliers are 3.25 % and 2 % for BCR-724A and the stainless steel SRM, respectively. Since no certified value was given for PTFE, the same value as BCR-724A (3.25 %) was assumed.

Fig. 2 shows the thermal transients recorded as a function of time t for the above-mentioned three reference materials. An initial steady state temperature is reached ($t < 30$ s) after applying the current to the heater coil when the input Joule heating is balanced by the heat losses from the probe. The slightly different initial temperatures between the different experiments (see values for $t < 30$ s) are due to fluctuations in the ambient conditions. It should be mentioned that during each experiment, the final room temperature (after completing the decay) typically experienced a variation of ± 0.2 °C with respect to the initial room temperature. In any case this variation was not higher than 0.6 °C. When the probe is brought into contact with the sample ($t > 30$ s), heat diffuses from the probe into the sample and a new steady state temperature is achieved ($t \gtrsim 1130$ s) when the total heat fluxes are again balanced. It is evident that a larger ΔT corresponds to a higher thermal conductivity of the sample because of its larger capability to remove heat from the probe. It is to be noted that the measurement can be performed in a reversed order - an initial steady-state is established with the probe in contact with the sample, while the final steady-state is achieved after the sample is detached to the probe (not included in this paper).

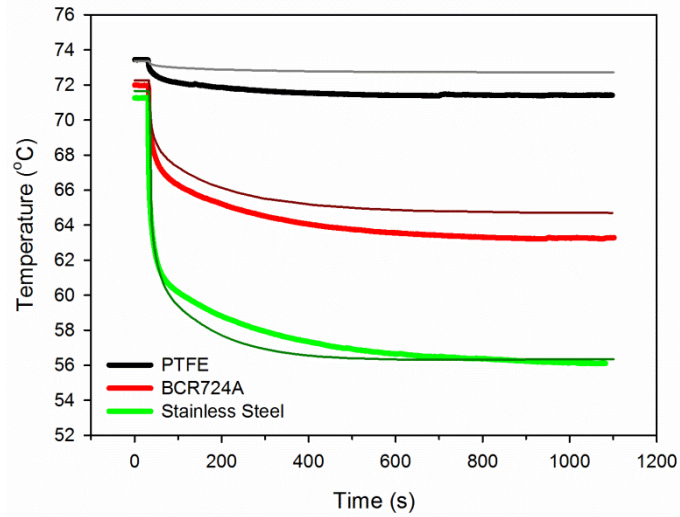


FIG. 2. Thermal transient experiments performed using PTFE (black), BCR724A (red) and Stainless Steel (green) reference materials. Simulation results for the same materials are represented by the grey, dark red and dark green lines respectively. Samples were contacted with the probe at $t \approx 30$ s.

The relation between the thermal conductivity of the samples and ΔT is shown in Fig. 3 (circles). A parabolic empirical relationship was observed for the range explored,

$$\lambda = 0.56 - 0.32\Delta T + 0.082\Delta T^2. \quad (1)$$

Based on this empirical equation, the thermal conductivity of a sample can be calculated using experimentally determined ΔT .

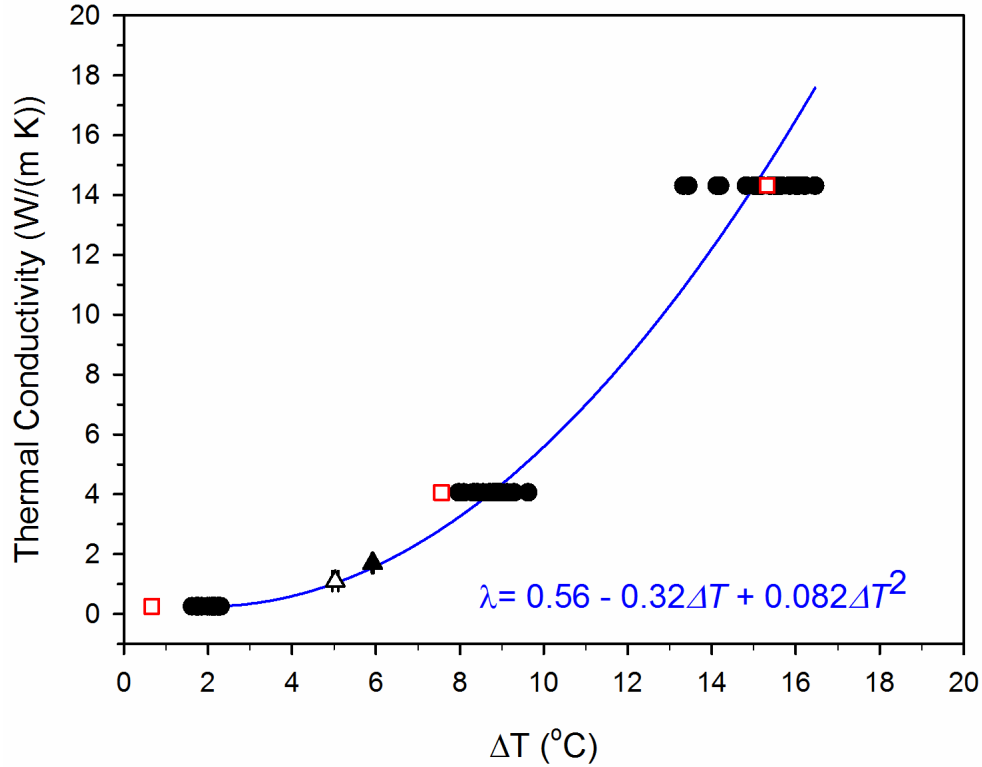


FIG. 3. Temperature differences between the initial and final states (ΔT) vs. the thermal conductivities for three reference samples (circles). The parabolic fit to these experimental points (line) and the resulting correlation equation are also shown. The triangles represent the ΔT obtained for Pyrex 7740 (white triangle) and the skutterudite sample (black triangle) vs. their true values of thermal conductivity. The red squares represent the simulated temperature differences.

Eq. 1 was obtained from a weighted fit (solid line in Fig. 3) to a total of 21 tests performed on each of the 3 reference samples. Table I shows the standard errors for each of the fitted parameters, which provides an indication of the repeatability of the technique. As observed in Fig. 3, a wider dispersion on the ΔT values can be observed for BCR724 (3.13 K) and stainless steel (1.66 K) compared to PTFE (0.68 K), which provides the main contribution to the standard errors $\sim 4\%$ in the fitted parameters a and b . Such dispersion variations may be due to the differences in thermal contact area. The surfaces of solids are not microscopically flat, which can result in randomness in the actual contact area at the solid/solid interface [13]. The amount of heat diffusing into the sample is expected to significantly depend on the contact area, which could be difficult to reproduce even for the same sample. Moreover, the reproducibility of the same contact area may differ for different materials. This explains the observed deviation in the ΔT dispersions for different materials.

TABLE I. Fitted parameters and their standard error from the empirical parabolic relationship between the thermal conductivity and ΔT .

$\lambda = a + b\Delta T + c\Delta T^2$	Fitted parameters	Standard error	Standard error (%)
a	0.55911	0.2137	3.82
b	-0.32031	0.01326	4.14
c	0.08226	0.00164	1.99

The accuracy of the technique was evaluated using Pyrex 7740 (Netzsch), which is a certified reference material for thermal conductivity, CRM 039, by the European Union Institute of Reference Materials and Measurements. The sample has the same dimension as the other reference samples. The measurements were repeated 7 times and the average thermal conductivity value and the standard deviation from the ΔT measurements were obtained (see Table II). The total combined random error u_c was calculated from the uncertainty contributions $u(x_i)$ of ΔT (standard deviation), the 3 fitted parameters, and their correlation $u(x_i, x_j)$ following the equation [14],

$$u_c^2 = \sum_{i=1}^N \left(\frac{\partial \lambda}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial \lambda}{\partial x_i} \frac{\partial \lambda}{\partial x_j} u(x_i, x_j). \quad (2)$$

A combined random error of 12.5 % results (see Table II), with a major contribution from the uncertainty of the empirical equation, which is mainly caused by the wide dispersions in the ΔT values (Fig. 3) of the reference samples (especially the stainless steel and the BCR-724A) produced by the thermal contact resistance.

The mean value ($\lambda_{average}$) obtained from the experiments shows a reasonably good agreement with the certified reference value (λ_{true}), which gives a systematic error of 6.2 %. The results demonstrate reasonable accuracy, providing a new method for rapid measurement of thermal conductivity. In addition, this method is simple and inexpensive, which makes it a suitable technique for high-throughput screening of the thermal conductivity in materials research.

TABLE II. Error analysis of the thermal transient measurements. Random error was obtained from the average thermal conductivity ($\lambda_{average}$) and the different uncertainty contributions. Systematic error was determined by comparing the average values with true values (λ_{true}), provided by the reference sample supplier or reference technique.

Sample	λ_{true} (W/(m K))	$\lambda_{average}$ (W/(m K))	St. Dev. for ΔT (K)	Random error (%)	Systematic error (%)
Pyrex 7740	1.10	1.03	0.070	12.5	6.2
Skutterudite	1.70	1.55	0.015	9.3	8.8

To further explore the application of the method in the field of thermoelectrics, a disc sample of a skutterudite material with the same dimensions of the reference samples used above was measured and the results compared with a Hot Disk apparatus (Model TPS 3500). The total combined random error, calculated using the same procedure employed above for Pyrex, is shown in Table II. A reasonably good repeatability, somewhat lower than that of Pyrex, was obtained. A systematic error of 8.8 % was also obtained (Table II), which is somewhat higher than the values identified for Pyrex.

It is to be noted that the heat conduction takes place in the radial directions during measurements using this novel technique. A careful interpretation of the results is needed for anisotropic materials such as Bi_2Te_3 . Also, the error estimations

shown in Table II can only be guaranteed for a specific sample shape (disc) and dimension (13 mm in diameter and 2 mm thickness). For samples with different shapes and sizes, new calibration is required for achieving the stated precision and accuracy.

On the other hand, it should be mentioned that the trend shown in Fig. 3 was not followed by samples with thermal conductivity larger than 60 W/(m K). At these larger values of λ the ΔT tends to a constant value and does not keep increasing with thermal conductivity as predicted by the parabolic trend. This could probably vary with different sample dimensions, but for the samples employed in this initial study it limits the method to the range covered by the 3 reference samples used (approximately from 0.2 to 15 W/(m K)).

IV. THEORETICAL SIMULATIONS

In order to obtain a theoretical framework to confirm the experimental results, thermal transients have been simulated using finite element modelling software (COMSOL Multiphysics 5). An axisymmetric model was adopted to reduce the computational demand, taking advantage of the radial symmetry of the probe set-up and sample. The time dependent heat equation was solved starting from an initial condition where all parts were at room temperature. The lower surfaces of the samples not in contact with the stage were considered as adiabatic and a room temperature boundary condition was applied at the lower edge of the stage. A domain heating of 0.3 W (approximately the electrical power input supplied to the heater) was applied within the probe, in substitute for the coiled wire heater. Heat loss to the surroundings of the probe and sample, either directly to the air or via the plastic support was calculated using a convective heat flux formula where the heat loss parameter $h_c=19$ W/(m²K). In the model, the contact between the probe tip and the sample was simulated using a block of material (10 μ m thickness) which had a thermal conductivity which stepped from a very low value ($\lambda=0.001$ W/(m K), so that it acted as though the probe and sample were not in contact) to a much higher value ($\lambda=18$ W/(m K)) at the contact time.

The simulated temperature-time profiles for the 3 reference materials employed in the calibration are shown in Fig. 2. A reasonably good qualitative agreement is observed with the experimental results, although significant differences appear, especially for PTFE. Since PTFE is a softer material we attribute the difference to the possible existence of a larger contact area. If the contact area is increased in the simulation a closer agreement is found. We would like to remark that our aim in this article is to simply obtain a qualitative agreement as theoretical framework for the method. More accurate simulations

could be performed by introducing a more detailed geometry and additional conditions, but this is out of the scope of this article. The ΔT values calculated from the simulations are compared with the experimental results in Fig. 3. A qualitative good match to the experimental results is also observed and the parabolic trend is also reproduced.

IV. CONCLUSIONS

A proof of concept of a new method to determine thermal conductivity of disc samples has been demonstrated. The technique consists in the determination of the temperature difference between the initial (no sample contacted) and final (after contacting the sample) state temperatures at the tip of a hot multifunctional probe. It was found that this temperature difference follows an empirical parabolic relationship with the thermal conductivity of the sample. A calibration equation, obtained using 3 reference materials, allows the direct determination of the thermal conductivity from the measured temperature difference. Random and systematic errors of around 12 % and 6 % were observed for a certified reference material. Main uncertainty contributions are attributed to the thermal contact, which causes wide dispersions of the measured temperature differences in some samples employed for obtaining the empirical calibration equation. Random and systematic errors around 9 % were obtained by comparison with well-established techniques. The method is simple and inexpensive compared to well-established techniques, which could be useful for the screening of the thermal conductivity and when high-throughput measurements are required. In addition, it can be readily integrated with a multifunctional probe system reported previously [12] to extend the measurement capability for all 3 key thermoelectric parameters.

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