A simple differential steady-state method to measure the thermal conductivity of solid bulk materials with high accuracy

D. Kraemer and G. Chen
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

(Received 30 October 2013; accepted 25 January 2014; published online 20 February 2014)

Accurate measurements of thermal conductivity are of great importance for materials research and development. Steady-state methods determine thermal conductivity directly from the proportionality between heat flow and an applied temperature difference (Fourier Law). Although theoretically simple, in practice, achieving high accuracies with steady-state methods is challenging and requires rather complex experimental setups due to temperature sensor uncertainties and parasitic heat loss. We developed a simple differential steady-state method in which the sample is mounted between an electric heater and a temperature-controlled heat sink. Our method calibrates for parasitic heat losses from the electric heater during the measurement by maintaining a constant heater temperature close to the environmental temperature while varying the heat sink temperature. This enables a large signal-to-noise ratio which permits accurate measurements of samples with small thermal conductance values without an additional heater calibration measurement or sophisticated heater guards to eliminate parasitic heater losses. Additionally, the differential nature of the method largely eliminates the uncertainties of the temperature sensors, permitting measurements with small temperature differences, which is advantageous for samples with high thermal conductance values and/or with strongly temperature-dependent thermal conductivities. In order to accelerate measurements of more than one sample, the proposed method allows for measuring several samples consecutively at each temperature measurement point without adding significant error. We demonstrate the method by performing thermal conductivity measurements on commercial bulk thermoelectric Bi₂Te₃ samples in the temperature range of 30–150 °C with an error below 3%. © 2014 AIP Publishing LLC.

http://dx.doi.org/10.1063/1.4865111

I. INTRODUCTION

Thermal conductivity is the physical property of materials to conduct heat down a temperature gradient, as given by the Fourier Law of heat conduction,

\[ q = -k \nabla T, \tag{1} \]

where \( q \) is the heat flux, \( k \) is the thermal conductivity, and \( \nabla T \) is the gradient of the temperature. Static or dynamic methods can be used to obtain the thermal conductivity of a material experimentally. In dynamic methods, the temperature distribution throughout the sample varies with time, which requires solving the more involved time-dependent heat flow equation. The thermal energy is either supplied periodically,\(^{5,6,9}\) as a single step\(^{5,6,9}\) or as a pulse,\(^{5,6,9}\) resulting in periodic or transitory temperature changes in the sample, respectively. Dynamic methods are typically indirect, measuring thermal diffusivity, \( \alpha = kl/\rho c_p \), and calculating the thermal conductivity, \( k \), using the material’s specific heat, \( c_p \), and density, \( \rho \), which adds additional uncertainties. Besides the drawback of being indirect, the main advantages of these methods are that they neither require power input nor absolute temperature measurements.

Unlike dynamic methods, static methods rely on the accurate knowledge of absolute temperatures and power inputs, but have the advantage of measuring thermal conductivity directly based on the simple steady-state heat flow equation (Eq. (1)).\(^{10,11}\) Steady-state methods require planar, cylindrical, or spherical isotherms, and either measure the heat flow through the sample directly\(^{12,13}\) or mount a reference material with known and similar thermal conductivity in series with the sample.\(^{14,16}\) A critical challenge for an accurate heat flow measurement is to minimize parasitic heat losses, especially for samples with small thermal conductance values. Comparative methods with a reference sample minimize the error from the heat flow measurement, but the use of a reference adds additional uncertainties. Guarded heater methods measure the heat flow directly and address the parasitic heat losses from the heater by partially encapsulating the heater with the sample material and using very accurately controlled heated radiation shields.\(^{17,18}\) Similarly, hot wire methods minimize parasitic heat losses by embedding the heater wire within the sample material and using the radial heat flow equation to extract the thermal conductivity.\(^{19}\) For electrically conductive materials there are a variety of direct electrical heating methods, in which the developed temperature profile due to Joule heating within the sample is analyzed to obtain the thermal conductivity.\(^{20,22}\)

Another challenge of steady-state methods is the accurate measurement of the imposed temperature difference. Typical temperature sensors are thermocouples and resistance temperature detectors (RTDs). The latter usually have higher
accuracy standards and do not need an additional cold junction compensation measurement as required by thermocouples. However, RTDs are more complicated to attach to a sample and can have higher parasitic heat losses due to the sensor size, and current and voltage leads. In order to achieve an accurate temperature reading, the thermocouples should be in good thermal contact with the sample. Furthermore, the heat flow through the thermocouple junction needs to be minimized and the thermocouples are often calibrated. In order to reduce thermocouple uncertainties the applied temperature difference can directly be obtained with a differential thermocouple measurement. For the interested reader, more details on the mentioned thermal conductivity measurement techniques can be found in elaborate reviews in literature.

In this work we establish a simple differential steady-state method that due to its differential nature largely eliminates the uncertainties of the temperature sensors and calibrates for the parasitic heat losses of the electric heater during the measurement. This significantly simplifies the experiment while maintaining a high accuracy (error < 3%) in the thermal conductivity results. The method is demonstrated for 2 commercial thermoelectric bulk Bi$_2$Te$_3$ (p/n-type doped) samples measured consecutively in the temperature range of 30–150 °C.

II. METHODOLOGY

The main challenges for steady-state thermal conductivity measurements are to minimize the effect of parasitic heat losses and to measure the temperature difference across the sample accurately. There are various ways to minimize uncertainties in the temperature difference measurement as mentioned in Sec. I. However, in general, the uncertainty standards of temperature sensors put a lower limit on the required temperature difference ($\Delta T$) to achieve a target accuracy for the measurement (Fig. 1(a)): 

$$\text{required } \Delta T = \frac{\text{uncertainties from temperature sensors(°C)}}{\text{target accuracy of } \Delta T \text{ measurement}}.$$  

In order to achieve a 5% accuracy in the $\Delta T$ measurement with 2 standard (STD) K-type thermocouples (uncertainty: larger of $\pm2.2$ °C or $\pm0.0075$ T), a $\Delta T$ of at least 88 °C has to be established. Even for more sophisticated solutions such as the use of RTDs or a differential K-type special limits error (SLE) thermocouple, the minimum required $\Delta T$ is still around 10 °C and 20 °C, respectively. Even though the uncertainty of differential thermocouple measurements can be significantly reduced by choosing a T-type thermocouple, a simpler technique to largely eliminate these uncertainties is very much desirable especially if other material properties such as the electrical resistance and the Seebeck coefficient of the material are to be measured with the same setup.

There are several reasons to minimize the required $\Delta T$. (1) The parasitic heat flow through the temperature sensor can result in an unquantifiable offset in the temperature reading. However, these errors can also be minimized experimentally by making very good thermal contact and/or by thermally grounding the heat conducting sensor leads to minimize the parasitic heat flow through the sensor. (2) The material’s thermal conductivity can be a strong function of temperature. (3) The parasitic heat losses such as the heat loss due to radiation will increasingly affect the measurement with greater temperature differences and sample cold side temperatures, $T_{CJ}$. To illustrate this effect (Fig. 1(b)), the radiative heat transfer coefficient (HTC) is estimated for blackbody surfaces inside a radiation shield maintained at the temperature of the sample hot junction, $T_{HJ} = T_{CJ} + \Delta T$, with following equation:

$$\text{radiative HTC} = \sigma 4 \left( T_{HJ} + \frac{3}{4} \Delta T \right)^3,$$

where $\sigma$ is the Stefan-Boltzmann constant and $\Delta T$ is the required temperature difference (Eq. (2)).

A. Measurement concept

The basic idea of the proposed method is to perform a differential steady-state thermal conductivity measurement to largely eliminate the measurement uncertainties from the used thermocouples and to calibrate for the parasitic heat losses of

FIG. 1. The effect due to the error of various temperature sensors on the thermal conductivity measurement. (a) Calculations of the required temperature difference as a function of cold side temperature of the sample for a target accuracy in the temperature difference measurements of 5% for various temperature sensors with standard accuracies. Even for a differential thermocouple (special limits error (SLE) K-type) measurement method the required temperature difference is at least 20 °C (b) Calculations of the radiative heat transfer coefficient (HTC) for experiments with different temperature sensors assuming blackbody surfaces inside a heated radiation shield at the hot junction sample temperature surrounding the setup. The larger the required temperature difference due to errors in the temperature measurements and the larger the cold side sample temperature, the larger is the effect of the radiative HTC on the thermal conductivity measurement.
the top electric heater (Fig. 2). Consequently, the measurements can be performed with small temperature differences without additional calibration of the sensors. Additionally, the effect of the parasitic heat losses on the accuracy of the measurement is minimized as discussed earlier in this section. The heat flow through the sample is measured for several applied temperature differences, \( \Delta T \), and the thermal conductance of the sample is determined from the slope of the linear regression curve of the data points. The parasitic heat losses can be minimized by using a vacuum environment to suppress convection and air conduction. The temperature differences and the thermal conductance of the sample are determined from the slope of the linear regression curve (Fig. 2(a)) which defines this technique as a differential method.

Taking the derivative of the 1D Fourier Law with respect to the temperature difference and solving for the thermal conductivity, \( k \), leads to

\[
k = \frac{L}{A} \frac{dQ}{d(\Delta T)} \approx \frac{L}{A} \frac{dP_{el}}{d(\Delta T)},
\]

where \( L \) is the length, \( A \) is the cross-sectional area of the sample, and \( dQ \) and \( dP_{el} \) are the variations in heat flow and electric heater power input, respectively, resulting in a corresponding change in temperature difference, \( d(\Delta T) \).

As discussed earlier in this section, thermocouples measure small absolute temperature differences across a sample rather inaccurately, however, they are extremely accurate in measuring changes in temperature differences. Consequently, the uncertainties from the thermocouples are largely eliminated due to the differential nature of the measurement. In order to establish the temperature difference the sample is sandwiched between a top electrical heater at the hot junction and a temperature-controllable heat sink at the cold junction (Fig. 2(b)). In order to vary the temperature difference the heat sink is used to cool the cold junction to different temperatures, \( T_{CJ} \), while the top electric heater is maintained at a constant hot junction temperature, \( T_{HJ} \), by adjusting the electrical power input accordingly. Consequently, while the heat flow increases with an increasing temperature difference across the sample the parasitic heat losses from the top heater/hot junction assembly to the environment will stay the same. Therefore, these heat losses will not affect the linearity and slope of the heat flow dependence on \( \Delta T \) (Fig. 2(a)). Of course, this assumes that there is no change in the parasitic heat transfer between the top heater/hot junction assembly and the environment. The validity of this assumption and its effect on the systematic error of this measurement will be discussed in Sec. IV.

**B. Performed experiments**

In order to demonstrate the method, the thermal conductivities of two commercial thermoelectric bulk (p/n-type doped) \( \text{Bi}_2\text{Te}_3 \) samples (~1.64 mm cubes) from Marlow Industries, Inc. are measured in temperature increments of 10°C from 30°C to 150°C. The samples are soldered between cold and hot junction copper plates and soldered on top of 2 independently controlled thermoelectric coolers (TECs) (Figs. 3(a) and 3(b)). The solder joints provide excellent thermal contact leading to negligible temperature drops...
across the interfaces. The TECs are thermally attached to a ceramic-casted platinum heater (bottom heater) to perform measurements at elevated temperatures (Fig. 3(c)). The top heater assembly consists of a 100 Ω thin film platinum class B RTD (PT100) from Omega which is brazed into a milled slot of a small copper block (~3 mm cube) with a 3 mil insulated K-type (SLE) thermocouple from Omega. To ensure excellent thermal contact the fabricated top heater is then soldered to the hot junction (Fig. 3(c)). The electrical heater current is provided and measured by a source meter from Keithley (Model 2425) with μA resolution. The voltage across the top heater is measured with a digital multimeter (DMM) from Keithley (Model 2010) with nV resolution. In order to minimize parasitic heat losses the setup is suspended on a ceramic tube in an evacuated chamber and encapsulated by a copper radiation shield which is in good thermal contact with the bottom heater (Figs. 3(a) and 3(d)). The hot junction temperature is measured with the thermocouple embedded in the top heater assembly. There is a 3 mil insulated K-type (SLE) thermocouple embedded in each cold junction copper plate and attached to the heated radiation shield.

As mentioned, the cold junctions change temperature during the differential measurement, thus, to ensure excellent thermal contact and thermal grounding of the thermocouples with the cold junction copper plates for accurate temperature measurements, solder is used as the thermal potting material. The bottom heater is used to heat the setup including the copper radiation shield to the measurement set temperature. In order to perform the differential measurement for each sample at each set temperature the electrical input power to the top heater is measured for several temperature differences established across one of the samples by decreasing its cold junction temperature with the TEC. The hot junction temperature and the cold junction temperature of the other sample are maintained constant and close to the radiation shield temperature to minimize the parasitic heat losses from the heater, which maximizes the signal to noise ratio. After the measurement of the first sample the second sample is consecutively measured at the same set temperature with the same procedure. LabVIEW is used to control the experiment and to record the data.

III. EXPERIMENTAL RESULTS

A temperature difference of up to 5 °C in 1 °C increments is imposed across the sample to assure a satisfying linear fit for the data analysis. The electrical heater power and temperatures are recorded for 30 s (150 data points) after the established temperature difference and the setup reached equilibrium. The measured heater input power is linearly correlated with the temperature difference (Fig. 4(a)). This confirms that the changes in parasitic losses affecting the measurement are small with varying temperature difference. The thermal conductivity of each sample is obtained from the slopes of the linear regression curves at each set temperature from 30 °C to 150 °C in 10 °C increments (Fig. 4(b)). The measured thermal conductivity shows the typical temperature dependence of doped small bandgap semiconductor materials such as Bi₂Te₃. Typically the lattice thermal conductivity decreases with temperature due to increasing electron-phonon scattering. However, the increasing electronic contribution due to the additional energy carriers generated and the more dominant bipolar thermal-diffusion effect at elevated temperatures result in the observed positive temperature-dependence of the thermal conductivity.

Even though the differential method eliminates the uncertainties from the temperature difference measurement and calibrates for most of the parasitic heater losses, there are still possible systematic errors from the radiative heat transfer between the sample and its surrounding and between the hot and cold junction. During the differential measurement the hot junction/heater assembly and the heated copper radiation shield are maintained at the same temperature, while the temperature of the cold junction is reduced. Consequently, the parasitic heat transfer between sample and surrounding leads to an underestimation in the thermal conductivity while the parasitic heat transfer between the hot and cold junction leads to an overestimation (Fig. 5(a)). Even though the two systematic errors partially cancel each other, both errors...
are added to the reported error bars as an upper limit of the error (Fig. 4(b)). More details about the experimental errors are discussed in Sec. IV.

IV. UNCERTAINTY ANALYSIS

The proposed differential steady-state method has the potential to be very accurate even though the experimental setup is relatively simple compared to, for example, guarded heater methods that try to completely eliminate the parasitic heater losses. Due to the differential nature, the experiment not only minimizes the error from the temperature difference measurement but it also calibrates for the parasitic heater losses without an additional heater loss calibration step, which reduces the time for the experiment and increases the accuracy of the heat flow measurement. Even though not stringently required, the heater/hot junction assembly is kept close to the temperature of the surrounding copper radiation shield to maximize the signal-to-noise ratio, enabling accurate thermal conductivity measurements of samples with small thermal conductance values. The method also facilitates the measurement of samples with high thermal conductance due to the small required $\Delta T$. However, there are still several sources of error that put constraints on the sample geometry in order to perform the measurements with high accuracy.

A. Calculated systematic error

For a steady-state 1D axial-flow method plane isotherms perpendicular to the heat flow direction are crucial for the accuracy of the measurement. For the measured samples (≈1.64 mm cubes, $k \approx 1.5 \text{ W/m K}$), the Biot number is about 0.01, assuming a radiative HTC (Eq. (3)) of 10 W/m$^2$K. Thus, no significant error is introduced with the assumption of plane isotherms. However, the radiative heat transfer between the sample and the surrounding affects the temperature profile and the heat flow along the sample. This effect can be quantified by solving the following equation either numerically or algebraically with a linearized radiation term (2nd term on the right hand side):

$$0 = kA \frac{dT}{dx} - P \varepsilon (T^4 - T_{sh}^4),$$

where $\sigma$ is the Stefan Boltzmann constant, $T_{sh}$ is the temperature of the copper radiation shield which is assumed to be a blackbody surrounding, $P$ is the perimeter, $\varepsilon$ is the emittance, and $T$ is the local temperature of the sample. Consequently, the assumption of a linear temperature profile in the calculation of the thermal conductance using the measured electric top heater input power introduces a positive systematic error in the performed measurement which can be estimated with

$$\text{error} = \frac{\Delta T}{T} \cdot 100\%. \hspace{1cm} (6)$$

where $\Delta T$ is the temperature difference across a sample of length $L$. The actual temperature gradient $\left.\frac{dT}{dx}\right|_{HJ}$ of the sample at the hot junction is determined by solving Eq. (5) with fixed temperature boundary conditions, $T(x = 0) = T_{CJ}$, $T(x = L) = T_{HJ}$. For the measured samples with an emittance of 0.8 and an assumed blackbody surrounding at the hot junction temperature the error does not exceed 2% (Fig. 5(a)).

In addition to this positive systematic error, there is parasitic radiative heat transfer between the hot and cold junction which results in an overestimation in the thermal conductivity and, thus, introduces a maximum negative systematic error of $\sim-0.8\%$ (Fig. 5(a)). For the estimation of this systematic error the viewfactor between and the emittance of the hot and cold junction copper plates is assumed to be 1 and 0.3, respectively. Both systematic errors in the experiment increase with temperature and put constraints on the sample geometry (Fig. 5(b)). For example, in order to keep the systematic error for a sample below 5% at temperatures up to 500 °C, the value of $\Phi = \frac{SL}{A}$ needs to be below $\sim0.002 \text{ m² K/W}$, where $S$ is the surface, $L$ is the length, $A$ is the cross-sectional area, and $k$ is the thermal conductivity of the sample. The value of $\Phi$ of the measured samples up to 150 °C varies between 0.0036 m² K/W and 0.0046 m² K/W depending on the measured thermal conductivity of the samples. The same analysis can be conducted for the systematic error due to the parasitic radiative heat transfer between the hot and cold junction (red dashed lines in Fig. 5(b)).

B. Experimental measurement errors

Besides the estimated systematic errors of the experiment there are additional measurement errors such as the error in
the supplied and measured electrical top heater input power which does not exceed 0.25% in the experiments due to the use of a high precision source meter and DMM. Additionally, the statistical fluctuations in the temperature difference measurements and in the electrical power setting from the temperature controller (programmed in LabVIEW) add statistical errors to the experiment. The statistical error in the obtained thermal conductance is determined from the upper and lower limit of the slope of the 95% confidence linear regression curve of the measured top heater electrical power input versus $\Delta T$ data (Fig. 4(a)). The statistical error does not exceed 0.15% (Fig. 6) confirming that the parasitic heat losses, such as wire conduction, radiative heat loss from the heater, and conducted heat through the second sample, do not change significantly during the differential measurement. In order to obtain the thermal conductivity of the material from the measured sample conductance, the dimensions of the sample are measured with a digital caliper with an accuracy of ±0.005 mm adding an error of 0.9% to the thermal conductance data (Fig. 4(b)).

V. CONCLUSION

We developed a simple differential steady-state method to measure the thermal conductivity of solid bulk materials with high accuracy. The differential nature of the measurement eliminates the uncertainties of the temperature sensors, making it possible to perform high accuracy measurements with small temperature differences, simplifying the measurement of samples with high thermal conductance. The differential measurement also calibrates for the parasitic heat losses from the top heater assembly without an additional heater loss calibration step, which expedites the experiment and enables consecutive measurements of several samples. By minimizing the parasitic heat losses from the heater assembly, the signal to noise ratio is maximized, facilitating the measurement of samples with small thermal conductance. We demonstrate the method by measuring the thermal conductivity of 2 commercial thermolectric bulk ($p$-type doped) Bi$_2$Te$_3$ samples at temperatures from 30 $^\circ$C to 150 $^\circ$C. A conservative error analysis confirms a measurement error below 3%.

Whereas the discussed experimental system is limited to a maximum temperature of $\sim$200 $^\circ$C due to the used thermoelectric coolers, there is no inherent reason for this method not to be extended to higher temperatures with similar uncertainties.

ACKNOWLEDGMENTS

The authors would like to thank Kenneth McEnaney, Kimberlee Collins, and Sangeop Lee for discussions. This work was funded partially by “Solid State Solar-Thermal Energy Conversion Center (S$^3$TEC),” an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0001299/DE-FG02-09ER46577 (for experimental system) and by DOE EERE under Award No. DE-EE0005806 (for Bi$_2$Te$_3$ characterization).

3R. W. King, Phys. Rev. 6, 437 (1915).