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Measurement of Thermal Conductivity Using Steady-State Isothermal Conditions and Validation by Comparison with Thermoelectric Device Performance

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A new technique for measuring thermal conductivity with significantly improved accuracy is presented. By using the Peltier effect to counterbalance an imposed temperature difference, a completely isothermal, steady-state condition can be obtained across a sample. In this condition, extraneous parasitic heat flows that would otherwise cause error can be eliminated entirely. The technique is used to determine the thermal conductivity of p-type and n-type samples of $(Bi,Sb)_2(Te,Se)_3$ materials, and thermal conductivity values of 1.47 W/m K and 1.48 W/m K are obtained respectively. To validate this technique, those samples were assembled into a Peltier cooling device. The agreement between the Seebeck coefficient measured individually and from the assembled device were within 0.5%, and the corresponding thermal conductivity was consistent with the individual measurements with less than 2% error.

Key words: Thermoelectric power generation, thermal conductivity, Seebeck coefficient

INTRODUCTION

Thermoelectric (TE) power generation can contribute towards meeting the future demand for electricity by converting sources of otherwise wasted heat energy into useful electricity. Applications that are specifically enabled by TE power generation include scavenging electrical power from vehicular waste heat, or large adventitious, perhaps industrial temperature differences. The efficiency with which TE power generation can convert heat energy to electricity is determined, in part, by the thermal conductivity, κ, of the materials used for fabricating TE devices. Experimental measurement of that property usually results in significant error, $>\pm 10\%$.[1] Because of the increasing application space for TE technologies, thermal conductivity measurements having greater simplicity and improved accuracy are desired.

The measurement of κ can be made by quantifying the flow of thermally conducted heat, Q_κ, across an imposed temperature difference, ΔT. For materials having low κ, such as TE materials, that measurement can be a challenge. This is because κ for TE materials is typically quite low, and other "parasitic" heat flows can be similar in magnitude to Q_κ and cause significant error. Despite this challenge, TE materials offer a unique, special opportunity for incorporating an independent, electrically controlled internal heat source: Peltier heat, $\pm Q_\Pi$. Peltier heat is liberated ($+Q_\Pi$) or absorbed ($-Q_\Pi$) at the junction between the thermoelectric material and electrical contact metal by the application of electrical current, $\pm I$.

Q_Π was first employed to roughly estimate κ by Putley.[2] In Putley's experiment, one side of a sample suspended in air was heated and the opposite was cooled by the application of Q_Π. In Putley's

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simple experiment, convective, parasitic, and nonsymmetric heat flows required correction factors larger than 20%. Harman and colleagues laid out the general framework whereby routine measurements of κ using Q_{Π} can be obtained.[3] Harman dramatically improved upon Putley's demonstration by performing the measurements in vacuum, and by reducing other parasitic heat flows. Despite these improvements, error is still obtained because the parasitic heat flows are nonzero.

In these past studies, the principal parasitic heat flows causing error are: conduction along lead wires, conduction along thermocouples, Joule heating within the lead wires, and radiation. Based on prior descriptions, the magnitudes of these parasitic heat flows can be estimated[3] and can range to within 30% of the Peltier heat. A further complication with that prior work is that the ends of the sample are respectively cooled and heated, making the heat flows into and out of the sample nonsymmetric, which means that the incoming parasitic heat on one end and outgoing heat on the other are not necessarily equal.

Penn[4] quantified the significance of the parasitic heat flows in Harman's technique, and showed that they can cause error for κ that is at least 10%. Penn described the need for experiment-specific correction factors by substituting wires of alternate metallurgy, as well as making radiation corrections. Bowley and Goldsmid,[5] as well as Buist[6] reported that significant experiment-specific correction factors are required to account for parasitic heat flows, or some error will result, possibly as large as 20%.

The focus of the present work is the development and description of a new, correctionless method to measure κ by introducing two different, independently controlled heat sources: Q_{Π}, and radiatively coupled input heat as per the Stefan–Boltzmann law, Q_{SB}. In this new method, Q_{Π} and Q_{SB} can be independently adjusted and exactly balanced to force a steady-state isothermal condition, leaving the steady-state temperature of the sample exactly equal to that of the surroundings, T_e. Because there is no ΔT, parasitic heat flows that would otherwise cause error, such as those along lead wires/thermocouples (Q_{wires}) and radiative heat loss ($Q_{radiation\text{-}error}$), converge exactly to zero.

Assume a sample having the temperature of one end anchored by a large heat sink and the opposite end having small thermal mass and capable of temperature diversion by the application of Q_{SB}. A vacuum is used to obviate convective heat flow, and Q_{SB} is applied by a small heater that has approximately the same subtended area as that of the cross-sectional area (A) of the sample, such that Q_{SB} is localized to the top and there is no direct line of sight along the sample's length (ℓ). Thermocouples are attached to each end to determine the temperature difference across the sample, and electrical leads are used to apply $\pm I$ to control Q_{Π}.

When Q_{SB} is applied, the temperature of the heated contact will increase with respect to T_e and some magnitude of Q_κ will be conducted through the sample. At the heated contact, the contributing heat flows include Q_{SB}, Q_κ, $Q_{radiation\text{-}error}$, and Q_{wires}. The radiation error is governed by the emissivity (ε), Stefan–Boltzmann constant (σ), sidewall temperature ($T_{sidewall}$), and exposed sidewall area ($A_{sidewall}$) of the sample. Q_{wires} follows the usual Fourier law description where, for simplicity, the aspect ratio (A_{wires}/ℓ_{wires}) and thermal conductivity (κ_{wires}) of all wires and thermocouples are combined into one lumped parasitic term. When electrical current flows through the sample, Q_{Π} is absorbed at the heated contact, where the first Kelvin relation gives $Q_{\Pi} = (\alpha I T)$, α is the sum of the Seebeck coefficients of the sample and the contact metal; T is the temperature of the heated contact. While an equal but opposite Q_{Π} is liberated at the contact between the sample and the large heat sink, it is too small to cause any measurable temperature change of the heat sink, and so is unimportant. Including Q_{Π} at the heated contact yields Eq. 1, which must sum to zero at steady state:

$$\sum Q = Q_{SB} - Q_{\Pi} - Q_\kappa - Q_{radiation-error} - Q_{wires} = 0. \tag{1}$$

To quantify the magnitude of Q_κ, a range of electrical currents can be passed which enables Q_{Π} to absorb a corresponding range of Q_{SB} at the contact, so

$$Q_{SB} = (\alpha I T) + \left[\kappa\left(\frac{A}{\ell}\right)\Delta T\right] + \varepsilon\sigma A_{sidewall}\left(T_{sidewall}^4 - T_e^4\right) + \left[\kappa_{wires}\left(\frac{A_{wires}}{\ell_{wires}}\right)\Delta T\right]. \tag{2}$$

For progressively larger I, Q_{Π} absorbs increasingly more of the Q_{SB} and the temperature of the heated contact begins to converge to T_e such that the overall ΔT across the sample goes to zero. As ΔT becomes smaller with increasing I, the only relevant heat flows are Q_{SB}, Q_{Π}, and Q_κ because $Q_{radiation\text{-}error}$, and Q_{wires} are only statistically significant[7] for larger ΔT, say >10 K, and all parasitic heat flows converge to zero. Therefore, under these conditions at any given I, the ΔT across the sample is required to satisfy Eq. 3:

$$Q_{SB} = (\alpha I T) + \left[\kappa\left(\frac{A}{\ell}\right)\Delta T\right]. \tag{3}$$

From the requirement imposed by Eq. 3, a new method for measuring κ is obtained. Equation 3 is solved to show the dependence of ΔT on I. By taking the derivative of Eq. 3, prior knowledge of Q_{SB} is not required,* and the analysis yields the following:

$$\frac{\partial \Delta T}{\partial I} = -\left[\frac{\alpha T}{\kappa\left(\frac{A}{\ell}\right)}\right]. \tag{4}$$

To determine κ, Eq. 4 is solved using the slope at $\Delta T = 0$ of the steady-state ΔT as a function of I, and that slope is combined with α as well as the geometrical aspect ratio (A/ℓ) of the sample.

A series of p-type and n-type samples having defined alloy compositions[8] with a range of extrinsic doping were selected for study. Crystalline $(Bi,Sb)_2(Te,Se)_3$ materials grown by the Bridgman technique were chosen so as to avoid the complications from polycrystalline structure including the effects of grain boundaries as well as the effects from the ensemble averaging of the highly anisotropic thermal conductivity.[8,9] The samples were oriented such that the directions of heat flow and of κ measurement were along the cleavage planes. The rectangular parallelepiped samples had A = 0.09 cm^2 and ℓ = 0.3 cm.

Before the Seebeck coefficient and thermal conductivity were determined, the electrical resistivity was measured by both four-point probe and two-point probe methods. As per Ohm's law, the slope of the current–voltage curve together with the A/ℓ ratio gives the electrical resistivity. The four-point measurement indicates the inherent resistivity of the material, and the two-point measurement includes contributions from both the inherent resistivity and the electrical contact resistance. The two-point and four-point probe electrical resistivity measurements were performed using alternating current to eliminate Seebeck voltage error, and pulsed direct current where the time-gated pulse of 100 mA is kept below 10 ms to negate the voltage error from the Seebeck effect. The two-point probe measurement was also used as an index of the thermal contact resistance of the soldered contact. Because the electrical contact resistance is small, the thermal contact resistance must also be small, so all subsequent κ measurements have negligible effects from thermal contact resistance.

To facilitate uniform, linear heat flow through the samples, solid copper tabs having small thermal mass were soldered onto the exposed end, as well as the opposite end. The tab on the opposite end is then thermally secured onto a large brass heat sink.

*It should be noted that Q_{SB} should have some small dependence on the temperature difference between the radiant heater and the heated contact. However, for the technique described here, the heater temperature is close to 350 K and the temperature divergence during measurement is usually within 2 K from ambient, as shown in Figs. 1 and 2, so the change in Q_{SB} during measurement is on the order of 1%, usually less, and therefore the change is on the order of 10^{-5} W, which cannot cause any significant error in temperature at the contact.

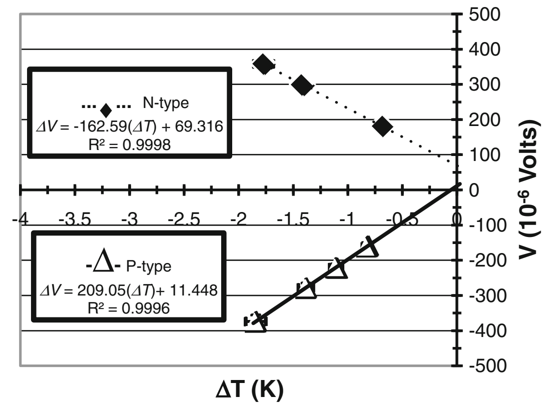

Fig. 1. ΔV_{oc} as a function of ΔT for n-type and p-type $(Bi,Sb)_2(Te,Se)_3$.

Thermocouples (0.003 inch diameter) and Cu lead wires (8.5 mΩ/cm) were soldered directly onto the copper tabs. Q_{SB} is applied by a small-form-factor, noncontact heater placed 2–3 mm above the sample. Because accurate α is required for this measurement method, it is premeasured independently as the slope of the open-circuit voltage as a function of a range of ΔT values as imposed by Q_{SB}.

The results from the Seebeck coefficient measurements from an n-type and a p-type sample are presented in Fig. 1. By using the slope of the ΔV and ΔT data, the offset voltages of 69.3 μV and 11.4 μV, respectively, are eliminated. A small +1.8 × 10^{-6}/K correction is required to account for the copper lead wires, so the absolute Seebeck coefficients are -163.8×10^{-6}/K and 207.2×10^{-6}/K, respectively. The small temperature difference used to obtain the data ranges from the heat sink temperature of 298 K to the heated contact temperature of 300 K.

The thermal conductivity was then determined by passing electrical current to apply Q_{Π}. The dependence of ΔT on I for both the n-type and p-type samples is presented in Fig. 2. For I = 0, the steady-state open-circuit ΔT values are obtained as the y-intercepts. As I is progressively increased, ΔT decreases, and at electrical currents of 63.4 mA for the n-type and 58.5 mA for the p-type, the steady-state isothermal condition is respectively obtained. At those currents, the temperature differences across the sample, the lead wires, and thermocouples are all zero. So too are the respective heat flows that would otherwise contribute to measurement error. To determine the thermal conductivity at the isothermal condition, the slope at the x-intercept is used. The isothermal temperature is that of the heat sink and corresponding ambient, 298 K. The slopes are linear throughout the range of spanned ΔT and electrical current. For the n-type sample, the slope at the x-intercept is -0.011 K/mA, and from that, the thermal conductivity is determined to be 1.48 W/m K. Similarly for the p-type sample, the slope at the x-intercept is -0.014 K/mA and the thermal conductivity is 1.47 W/m K.

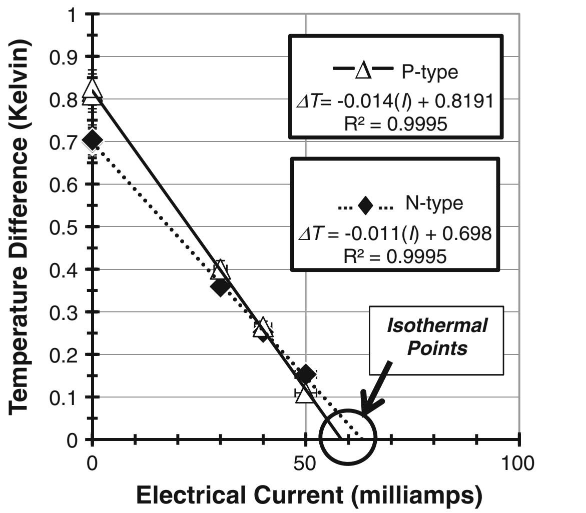

Fig. 2. ΔT as a function of I for individual n-type and p-type $(Bi,Sb)_2(Te,Se)_3$ samples.

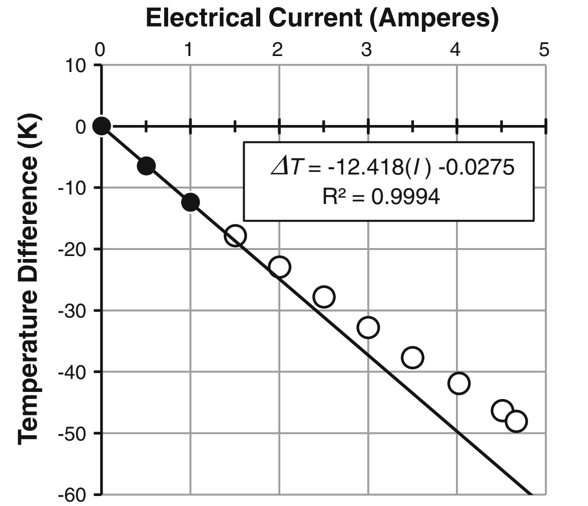

Fig. 4. ΔS as a function of electrical current up to the 5 A equipment limit for fully assembled Peltier cooling device.

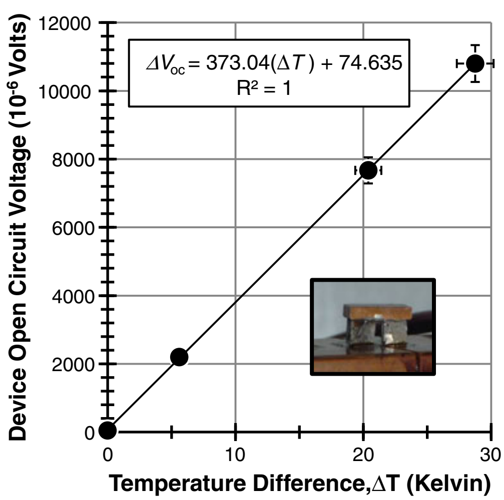

Fig. 3. ΔV_{oc} as a function of ΔT for the fully assembled device.

Independent confirmation of the validity and accuracy of this method for determining κ was obtained by fabricating a device from these specific samples and comparing the experimental device performance with the theoretical device performance based on the individually measured properties. To validate the Seebeck coefficient measurement, the open-circuit voltage of the device can be measured because the slope of the open-circuit voltage as a function of temperature difference should equal the sum of the Seebeck coefficients. The open-circuit device data are presented in Fig. 3, and the obtained slope, 373.0×10^{-6}V/K, is nearly exactly equal to the sum of the individually measured Seebeck coefficients, 371.0×10^{-6} V/K.

To confirm the thermal conductivity measurements, this device was tested in thermoelectric cooling mode and the Peltier cooling performance was measured as a function of applied electrical current up to the equipment limit of 5 A and compared with the theoretical performance calculated using the measured properties. The slope of the Peltier cooling curve is determined by the sum of the thermal conductivities of the device components. Pure copper was chosen as the interconnect between the two active TE components because its thermal conductivity, 395 W/m K, is more than two orders of magnitude larger than that of the active TE components, so the thermal resistance across the copper is negligible compared with that of the TE materials and the measurement error of T_{cold} is minimized. As shown in Fig. 4, the Peltier cooling performance is linear for approximately $<\pm 10$ K temperature difference values (closed symbols), but for larger values there is a deviation from linearity (open circles) with applied current. This nonlinearity is primarily due to the emergence of Joule heating, which increases as the square of current, from negligible to significant levels. To a lesser extent, the deviation results from the increasing significance of parasitic heat flows (e.g., radiative heat, heat flow down the sensing thermocouple, etc.) as well as the temperature-dependent properties physically changing with temperature. However, in the approximately $<\pm 20$ K window where ΔT is linear with I, the slope of the device data can yield the sum of the thermal conductivities of the components. As shown in Fig. 4, the present device was tested within the 20 K window, and the slope for <20 K yields the sum of 2.90 W/m K. This is within 2% of the equivalent sum of the thermal conductivity values obtained from the individually measured thermal conductivity values, 2.95 W/m K. As summarized in Table I, the agreement between individually measured properties and those extracted from device performance are in agreement to within 2% over a broad range.

Table I. Comparison between properties measured individually and extracted from a device

Physical Property	Individually Measured	Extracted from Device	Agreement
Thermal Conductivity (Sum)	2.95 W/m K	2.90 W/m K	1.70%
Seebeck Coefficient (Sum)	371.0 μV/K	373.0 μV/K	0.5%

The significance of this work is that the accuracy of thermal conductivity measurements for thermoelectric materials can be significantly improved to within about 2% in an extremely fast and simple experiment. The improved accuracy is obtained because the parasitic heat flows, which are probably equipment specific and likely sample specific, can be eliminated entirely by measuring under isothermal conditions. The use of differential measurements eliminates offsets in voltage and temperature, and improves accuracy. It should be noted that, because Peltier terms are linear with current and Joule heating increases as the square, only the Peltier term dominates at small I, so for samples where slope linearity persists across a large spanned temperature and electrical current range, the thermal conductivity can probably be extracted even under nonisothermal conditions.

Extending this κ measurement to higher and lower temperatures would seem to require only a simple cylindrically symmetric radiation shield having temperature equivalent to the isothermal temperature. Because all other parasitic heat flows can be made negligible, such a radiation shield would ensure that radiation losses would be eliminated.

There is likely a practical limit to employing this technique to generally determine κ of any given, arbitrary material. The primary criterion that should be satisfied is that Joule heat should be negligible compared with the Peltier heat. As an example, for the samples of this study, the percent ratio of the Joule heat to the Peltier heat at the isothermal condition is 0.36% for the p-type and 0.38% for the n-type material. In this small range of electrical current, these respective Joule heat flows are more than two orders of magnitude smaller than the Peltier heat, so they have negligible influence for determining κ. For other materials, if that ratio is, say, 1% or larger, then consideration should probably be given to including a Joule heat term and resolving for Eq. 4. However, it may be possible that alternate sample sizes, where different (A/ℓ) could be investigated, may present a path to experimentally satisfy this primary criterion without including the Joule term. Another criterion is that the electrical contact resistance should also be small relative to the electrical resistance of the bulk.[10] If the electrical contact resistance is small, so too should the thermal contact resistance.

Measurement of κ is classically open-circuit (laser-flash, Angstrom method, comparison method, etc.), so coupling the presently described technique with a classical one would conceivably facilitate (1) understanding between electron–phonon coupling, if present, and (2) investigating the electric field dependence of the electronic contribution to the total κ. Lastly, it should be recognized that some measurement systems capable of determining the Seebeck coefficient[11] that employ a conductive heat-source input instead of a radiative one could readily be adapted to directly measure thermal conductivity by simply incorporating a small electrical current source to apply Q_{Π}, forcing the isothermal condition across the sample and substituting a thermally conducted heat input term for the radiative heat input term.

CONCLUSIONS

A new technique to determine thermal conductivity that simultaneously uses Peltier heat and radiatively coupled heat to counterbalance and cancel an imposed temperature difference is presented. By counterbalancing the respective heats, a steady-state isothermal condition is obtained across the sample. In that condition, extraneous parasitic heat flows that would otherwise cause error are eliminated entirely. The technique is validated by measuring individual samples which were then assembled into a thermoelectric device. The agreement between the Seebeck coefficients measured individually and those values from the assembled device was within 0.5%, and thermal conductivities were consistent with the individual measurements with less than 2% error.

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