An Apparatus for Concurrent Measurement of Thermoelectric Material Parameters

R.L. Kallaher, C.A. Latham, and F. Sharifi

Center for Nanoscale Science and Technology
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-6204

We describe an apparatus which concurrently and independently measures the parameters determining thermoelectric material conversion efficiency: the Seebeck coefficient, thermal conductivity, and electrical resistivity. The apparatus is designed to characterize thermoelectric materials which are technologically relevant for waste heat energy conversion, and may operate from room temperature to 400 °C. It is configured so the heat flux is axially confined along two boron nitride rods of known thermal conductance. The Seebeck coefficient and thermal conductivity are obtained in steady-state using a differential technique, while the electrical resistivity is obtained using a four-point lock-in amplification method. Measurements on the newly developed NIST Seebeck Standard Reference Material are presented in the temperature range from 50 °C to 250 °C.

fred.sharifi@nist.gov

Introduction

Thermoelectric devices may reversibly convert thermal and electric energy [1,2]. Although conversion efficiencies of known thermoelectric material are currently too low to be economically viable for widespread implementation [3], recent reports of improved materials with complex morphology [4-8] open the possibility for future higher efficiency devices. For power generation, the material's conversion efficiency at a temperature, T, is characterized by a dimensionless figure of merit $ZT=S^2T/\rho k$, where S, ρ, and k are the material's Seebeck coefficient, electrical resistivity, and thermal conductivity. The overall conversion efficiency increases with ZT, but is ultimately bound by Carnot efficiency, as with any device operating on the principal of a temperature difference. A complete assessment of a material's figure of merit requires measurements of S, k, and ρ over the temperature range of interest.

Thermoelectric material properties are usually measured with separate instruments: those that measure S and ρ, and those that measure k. Of these, characterization of thermal conductivity is most challenging; in contrast to electrical conductivity measurements where the flow of charge may be confined to a specific conducting path, in heat flow measurements the removal of parasitic heat conduction paths is extremely difficult [9]. Consequently, thermal conductivity characterization often involves separate measurements of material parameters, such as heat capacity and thermal diffusivity [10]. There are reports of direct measurements of thermal conductivity employing heat rods [11-13], though most primarily operate below room temperature, precluding them from characterizing thermoelectric materials whose material efficiencies are optimized at waste heat temperatures. Finally, the only currently available and widely used technique for directly obtaining ZT (as a whole) is due to Harman [14], where ZT is measured by relating the Peltier effect to changes in the potential difference across the sample under an applied current [14,15]. In this report, we describe an instrument comprised of a pair of boron nitride (BN) rods in which the heat flows axially, and where the heat is confined to the rods. The instrument is capable of concurrent measurements of all three parameters comprising the thermoelectric figure of merit at elevated temperatures. We hope the design serves as a basis for future instruments, where thermal and electronic material properties may be measured more efficiently and precisely.

The instrument described here is comprised of a pair of thermally conducting BN rods containing thermometry and electrical leads, and measures S, k, and ρ. It is designed to operate

at temperatures to a maximum range of approximately 400 °C, above which errors in thermometry become significant. Its capability to measure thermal properties is due to features that minimize thermal losses occurring through conductive, convective, and radiative processes. Data is acquired in steady-state [16] as opposed to transient mode [17,18], and the Seebeck coefficient and thermal conductance are concurrently obtained through a differential technique whereby small (constant) temperature gradients are produced across the sample [19-21]. The sample stage is segmented, yielding four electrical probes for Seebeck and electrical resistivity measurements; the latter is obtained through ac lock-in amplification methods so as to avoid spurious results due to thermopower voltages [17]. The thermal conductance of the BN rods is calibrated using a NIST thermal conductivity reference material (RM8424). Fundamentally, the instrument is designed to confine heat flow to the rods to the extent that is possible, with a data acquisition and analysis procedure which accounts for systematic errors, including small temperature differences between the sample face and thermometers in the sample stage.

Currently, there is no thermoelectric standard which provides validation for all of the individual parameters comprising the figure of merit. As such, the newly developed NIST Seebeck Coefficient Standard Reference Material (SRM3451) was used to validate S, and comparison to literature reports were used for validations of ρ and k.

Description and Operation

<u>Apparatus Construction</u>

The thermoelectric measurement system is shown in Figure 1a. The instrument is constructed in axial flow geometry where the sample is pressed between two identical boron nitride (BN) cylindrical rods, of approximate lengths and diameters of 10 cm and 1 cm respectively. Each rod has a thermometer comprised of a platinum resistance temperature detector (Pt RTD) embedded half-way along its length, and a heater attached at one end. At the opposite end is the sample stage, which can accommodate samples with thicknesses ranging from 1 cm to as low as 0.5 mm. The stage is made of two high purity Cu pieces, each semi-circular in shape shown in Figure 1b. A narrow (less than 200 μm) separation exists between the two semi-circular parts to yield four total electrical contacts. On each side, a thermometer is embedded just below the contact face in the Cu body, and spans both semi-circular pieces. The Cu pieces are polished to ensure a large contact area and minimize thermal contact resistance

with the sample. Finally, each BN rod is thermally decoupled from the structural support by being attached with a high thermal resistance zirconia rod (k ≈ 2 W/m·K, 3 mm diameter, 4 cm length). These structural supports are heat sunk to water cooled platforms, creating constant temperature attachment points for the BN rod assemblies, and allowing for timely stabilization of temperature.

Platinum RTDs were chosen for thermometry because of their high precision and reliability over the apparatus' designed operational temperature range. Their basic operation relies on the stability of platinum's resistivity temperature coefficient over a large temperature range. It is in fact, the temperature at which the deviations of this coefficient become significant that sets the upper operation range of the apparatus. As shown in Figure 1a, each rod has two thermometers located at the center of the BN rod and in the Cu body at the sample platform stage. In the absence of heat losses, the temperature difference across a segment of the BN rod (of known thermal conductance) yields the heat flow, and in conjunction with the temperature difference and induced thermopower voltage across the sample, yields both the Seebeck coefficient and the thermal conductance of the sample. Cu wiring, 50 μm in diameter, is used for connecting the thermometers and semi-circular stage pieces. Cu is chosen because of it has a very low Seebeck coefficient, reducing this source of error in the measurements. To assure the wires are isothermal with the BN rod, they are embedded in grooves running the length of the rod and attached with high temperature cement. Each BN rod has an independently controlled heater, made of 100 μm diameter Ni-Cr alloy wire wrapped at its end, enclosing both the rod and the wiring. This configuration again ensures the end assembly of the rod, consisting of the BN and the wiring, is isothermal, as both the wires and the BN rod are surrounded by the heater. Each rod heater is independently controlled by a temperature controller using either the body or the stage thermometer as a reference. Finally, a spring under a compressive force of approximately 90 N, located on one side of the assembly, continuously presses the BN rods, with the sample inserted in between, sustaining the integrity of the Cu contacts during measurements.

To address radiative losses, each BN rod assembly is surrounded by a cylindrical heated radiation shield, made of Cu foil of 127 μm thickness, and wrapped with insulated Ni-Cr alloy heater wire, 270 μm diameter, along its entire length. The heater wire is again attached with high temperature cement. Further, each shield has a thermometer attached at it center, allowing for independent temperature control. Finally, the entire assembly is surrounded by a passive

radiation shield, also made of Cu foil of the same thickness. The apparatus is permanently mounted to a stainless steel vacuum flange and is inserted into a spherical vacuum chamber whose outer wall temperatures are controlled to within 0.2 °C. The base pressure of the vacuum chamber is below 1 x 10^{-5} Pa, minimizing convective heat transfer.

Thermal Measurements

Heat Losses

A primary motivation in constructing this apparatus is to enable concurrent thermal and electrical characterization. The former is a significant challenge as the design of the apparatus must be consistent with one dimensional heat flow to high precision. As such, heat losses from convective, conductive, and radiative paths must be minimized as much as possible so as to ensure the heat flux is effectively constrained to the rods.

Convective heat losses are the simplest to address as the measurements are performed inside a vacuum chamber at pressures below 1 x 10^{-3} Pa. At this pressure, the mean free path of the gas molecules is approximately 8 m, and an estimate of residual gas conduction may be obtained by calculating the heat transported between the Cu ends comprising the sample stage [22]. For the dimension of the sample platforms in the apparatus and the respective temperature difference of the platforms during measurement, a conservative estimate of $Q_{gas} \approx 10^{-7}$ W is obtained. As shown later, this value is roughly 4 orders of magnitude smaller than the heat conduction through the BN rods during measurements, and thus can be ignored.

Conductive heat losses through the connecting wires are addressed through design and construction of the apparatus. As previously mentioned, the electrical leads to the thermometers and the sample stage are embedded along the length of the BN rods, and heat sunk at the end of the rods by being surrounded with the heater assembly. This design ensures that the temperature gradient across the ends of each rod is the same as the temperature gradient across the connecting wires embedded in the rod.

Radiation losses are the most problematic and manifest themselves at temperature differences of less than one degree between the BN rods and the external environment, leading to anomalous differences in temperature between the two thermometers in the rod. Radiation heat loss scales as $(T^4 - T_{env}^4)$ where T and T_{env} are the temperatures of the BN rods and the surrounding environment. Passive radiation shielding inserted between the BN rods and walls of

the vacuum chamber can decrease these losses by a factor $(n+1)^{-1}$ where n is the number of independent radiation shields [23]. Heated radiation shield are more efficient, however, and were used here. The shields are made of polished copper so as to have low emissivity. The temperature for each shield is independently set so as to minimize the radiative heat losses from the corresponding BN rod. Ideally the temperature profile along the length of each shield should match the profile in the respective BN rod. However, matching the profiles is quite difficult as it would require creating axial temperature gradients in both the heated and passive radiation shields. Consequently, the heat shields are isothermal and are set to average temperature of the rods. During measurement, the temperature gradients along the length of the BN rods are kept small (below 0.6 °C), and the uncertainties resulting from the minor radiative heat losses are discussed below.

Temperature Calibration

The sample stage is designed so that the thermometer embedded in the Cu body is as isothermal as possible with the sample face. Nevertheless, there are unavoidable remnant thermal resistances between the thermometer and the sample face. For a sample of thermal resistance R_s, the heat flow through the rods may be written as

$$Q = \frac{T_{1,2}}{R_{BN}} = \frac{T_{2,3}}{R_0 + R_s} = \frac{T_{3,4}}{R_{BN}},$$

where R_0 is the total remnant thermal resistance, and $T_{i,j} \equiv T_i - T_j$. Here, R_0 is obtained by replacing the thermoelectric sample with a high purity thin Au foil (100 μm thickness). Au was chosen as at this thickness, its high thermal conductivity (320 W/m·K) yields negligible thermal resistance, leading to $R_s \cong 0$. Thus,

$$Q = \frac{T_{1,2}}{R_{BN}} = \frac{T_{2,3}}{R_0} = \frac{T_{3,4}}{R_{BN}}.$$

The remnant resistance can then be obtained with respect to R_{BN}:

$$\frac{R_0}{R_{BN}} = \frac{T_{2,3}}{T_{1,2}} = \frac{T_{2,3}}{T_{3,4}}.$$

The experimental procedure consists of measuring the temperature difference between the thermometers embedded in the opposing Cu platforms, $T_{2,3}$, as the heat flux is varied through the rods. Specifically, $T_{1,4}$ is varied from +0.6 °C to -0.6 °C in 0.2 °C intervals and the temperature difference across the platform, and $T_{2,3}$ is recorded as a function of the temperature

difference in each BN rod ($T_{1,2}$ and $T_{3,4}$). This procedure is performed from room temperature to the maximum characterization temperature of the sample, and slope of the resulting line at each temperature yields the remnant resistance as a percentage of the thermal resistance of each BN rod.

We believe there are three major contributions to the remnant resistance R_0: 1) The thermal resistance of the Cu body, 2) the thermal resistance of the cement used for attachments of the parts, and 3) the interfacial contact resistance between the Au foil and the Cu face. The first contribution arises as a consequence of design requirements for structural integrity between the Cu stage and the BN rod, and leads to a small offset in temperature. Since the dimensions and material properties are known, this contribution may be realistically modeled and yields an estimate of 1 % correction, shown in Figure 1c. As for contributions from the thermal resistance of the cements used for assembly, this is more difficult to model since the exact properties and thicknesses may only be estimated. The cement is silica-based with low thermal conductivity, and therefore this contribution may be significant and dominate with rising temperature, due to the reduction in the thermal conductivity of silica with increasing temperature. The third, interfacial contact resistance between the Au foil and the Cu stage, is made negligible through the choice of Au: the thermal conductivity of both Au and Cu is due mostly from an electronic contribution and this interface would not impede charge flow. One additional factor in the analysis is that over the operational temperature range of the apparatus, the thermal conductivity of BN increases with increasing temperature and peaks at roughly 100 ºC, after which it slowly drops [24]. Thus for a given value of $T_{1,2}$ ($T_{3,4}$), the heat flow through the rods varies with temperature, and is accounted for in subsequent analysis.

The results of the measurements are shown in Figure 2, which show the thermal resistance between the two thermometers embedded in the Cu stages ranges from 2 % to 5 % of the thermal resistance of (half) the length of a BN rod. In this procedure, the spring loading was increased until this ratio was minimized and no longer changed with increasing load. The correction initially increases with rising temperature, partly due to the increased thermal conductance of BN. Past roughly 150 ºC, the correction increases and may be caused by the increasing thermal resistance of the silica-based cement. Further, the magnitude of the total correction indicates the cement thermal resistance contributes more than resistance of the Cu

body (Fig. 1c). This correction is subsequently incorporated in the data analysis of the Seebeck coefficient and thermal conductivity at each measurement temperature.

Thermal Conductivity Calibration

The thermal conductivity of the BN rods is obtained by using a NIST thermal conductivity reference material (RM8424) as a sample. The reference material is composed of graphite of known thermal conductivity over the temperature range of interest, and its soft composition, along with its high electrical conductivity, again minimize thermal contact resistance. Here,

$$Q = \frac{T_{1,2}}{R_{BN}} = \frac{T_{2,3}}{R_0 + R_{std}} = \frac{T_{3,4}}{R_{BN}},$$

where R_{std} is the thermal resistance of the graphite sample, resulting in

$$R_{BN} = (R_0 + R_{std})\frac{T_{2,3}}{T_{1,2}} = (R_0 + R_{std})\frac{T_{2,3}}{T_{3,4}}.$$

As before, $T_{1,4}$ is varied and the temperature difference across the platform, $T_{2,3}$, is measured as a function of heat flow through a BN rod, $T_{1,2}$. The data is corrected for the temperature offset caused by the residual thermal resistance R_0. Figure 3 displays the values for the extracted thermal conductivity of a BN rod, using the above procedure over the temperature range of interest, along with the corresponding polynomial fit. The results are consistent in both magnitude and temperature dependence with literature measurements for thermal conductivity of BN [24].

Electrical Measurements

Thermopower

Seebeck measurements are obtained through the differential technique by measuring the induced thermopower voltage resulting from the temperature difference across the sample. This method has the advantage of not incorporating offset voltage values that may be present in the electronic instrumentation. As each face of the sample stage contains two contacts, two simultaneous values of the Seebeck parameter are obtained. This feature allows for a check on measurement consistency, and additionally also identify any potential sample inhomogeneity. Using the same measurement procedure, the induced thermopower voltage and the temperature difference across the sample, $T_{2,3}$, are measured concurrently for several values of $T_{1,2}$ ($T_{3,4}$).

Subsequently, $T_{2,3}$ is again corrected for the temperature drop due to R_0, and the slope of the resulting linear plot of thermopower voltage vs. the temperature difference across the sample yields the Seebeck coefficient. For all measurements, the temperature differences are deliberately kept small to ensure the thermopower voltage changes are in the linear regime; further, the reversal of the temperature difference checks for any systematic errors that may arise from contact potential in the leads.

Resistivity

The electrical resistivity poses the fewest challenges in the measurements as thermoelectrics are usually highly doped narrow band gap semiconductors with resistivities that are relatively insensitive to change with variations of about one degree in temperature. Consequently, it is possible to concurrently perform Seebeck and resistivity measurements where the latter is performed using an ac modulation current and lock-in amplification techniques, so as to avoid dc thermopower voltages. The temperature dependence of the sample resistance is obtained in a straight-forward manner by changing the temperature of the apparatus. However, the extraction of an absolute resistivity value is problematic due to an unavoidable feature in the design of this apparatus. The uncertainty results from the large area and geometry of the electrical contacts of the sample stage (Fig. 1a). Unfortunately, this configuration is necessary to minimize thermal resistance and ensure the sample face is isothermal, a critical requirement for both the Seebeck and thermal conductivity measurement. Because of this large area contact, it is difficult to accurately determine the geometric correction factor so as to absolutely directly relate the measured resistance to resistivity through the van der Pauw formulism [25]. This issue can be straightforwardly resolved with a one-time *ex-situ* bench measurement using standard small-contact microprobes, which readily yields the geometric factor. The room temperature value is then used to scale the temperature dependence of the resistivity, yielding the absolute resistivity value over the entire temperature range.

Apparatus Validation

<u>Measurements on Bi_2Te_3</u>

Measurements on the newly developed NIST Seebeck Coefficient Standard Reference Material (SRM3451) were performed in order to test the performance of the apparatus. This

Standard is a specimen of Te-rich (n-type) Bi_2Te_3 having dimensions of 8.0 mm x 2.5 mm x 3.5 mm.

Using the previously described procedures, the Seebeck values were obtained at 25 °C intervals from 50 °C to 250 °C and the results are displayed in Figure 4. (The measurements did not exceed 250 °C, due to concerns regarding the stability of Bi_2Te_3 at elevated temperatures.) For comparison, the solid line represents the expected values, which are certified to a maximum temperature of 120 °C, and which has an uncertainty of approximately ± 2.7 % over this temperature range.

The measured temperature dependence of electrical resistivity is shown in Figures 5. This material has a complex band structure and a negative temperature coefficient of its band gap, and consequently its resistivity is dominated both by the usual transport scattering processes and by the Fermi level crossing bands in a multi-valley band structure [26]. The small band gap of this material mostly limits the transport studies of this material to below room temperature, and higher temperature data is sparse. Nevertheless, the resistivity data shown [Fig. 5] agree with those previously reported, in both magnitude and temperature dependence [27, 28].

The thermal conductivity of the Bi_2Te_3 sample is obtained through the ratio of the temperature drop across the sample and the temperature drop (heat flow) across a BN segment, shown in Figure 6. (We note the maximum heat flow through the structure is approximately 3 mW.) Due to its high electrical conductivity, at above room temperature, ambipolar thermo-diffusion dominates the electronic contribution to the thermal conductivity [29, 30], resulting in a thermal conductivity that scales inversely with electronic resistivity [Fig. 5]. The results shown [Fig. 6] agree both in magnitude and temperature dependence with previous reports [31].

The independent measurements of S, ρ, and k, are subsequently used to calculate the resulting figure of merit, ZT, of the Bi_2Te_3 sample, as shown in Figure 7. The small band gap of this material leads to a peak in the figure of merit at temperatures slightly below room temperature [1,2], consistent with the results presented here.

Uncertainty Analysis

A systematic uncertainty analysis (at 1σ level) has been undertaken throughout these measurements, consisting of determining errors at each step of the data analysis and their propagation to the final result, ZT.

For the temperature corrections arising from thermal resistance (Figure 2), the primary error source is the precision of the Pt RTD thermometry. This type of thermometer is essentially a resistor whose nominal resistance can modeled as $R_{Pt} = R_c + \alpha T$. As the measurement is done differentially, the uncertainty in the temperature coefficient, α, is the dominant error and amounts to a maximum of $\pm$ 1.2 mK for the temperature differences used here. The resulting uncertainty is shown in Figure 2.

There are three dominant sources of uncertainty in the thermal conductivity of the BN, shown in Figure 3. The first is the uncertainty in the thermal resistance corrections [Fig. 2]. The second source is heat losses that arise between the isothermal radiation heated shield and the BN rods containing a 0.6 °C temperature gradient. To ascertain the corresponding correction due to this heat loss, the temperature difference between the middle and Cu sample stage thermometer was measured with a cold radiation shield as a function of temperature, and amounted to 0.47 % heat loss in the BN rod per degree temperature difference. The last source, and largest, uncertainty is from the accuracy of the graphite thermal conductivity standard, which is 3 %. The net propagated uncertainty is shown in Figure 3. Similarly, this uncertainty is used to calculate the (propagated) uncertainty in the thermal conductivity of the Bi_2Te_3 sample, shown in Figure 6.

Two sources contribute to the uncertainty in the Seebeck coefficient shown in Figure 4: the Seebeck coefficient of the Cu wire connections, and the intrinsic accuracy of the electronics. Over the temperature range of interest, the first source results in a maximum error of $\pm$ 3 μV [1], while the second is insignificant and contributes less than $\pm$ 0.02 μV. The intrinsic uncertainty in the Seebeck coefficient of the SRM is similar, being approximately $\pm$ 2.7 %. As for the resistivity measurements, the uncertainty arises from the signal to noise ratio of the lock-in measurement, and is dependent on the excitation current. This current must be kept at a level to ensure no local heating occurs. For this measurement, a 10 μA excitation current produces power dissipation at an insignificant level ($\approx 10^{-11}$ W). The electronic noise fluctuations are shown in Figure 5.

Finally, the uncertainty in *ZT* at each temperature, arising from the propagation of uncertainties in the above parameters, is shown in Figure 7. The fractional uncertainty is shown in Figure 8, rising slightly with increasing temperature, and reaching approximately 5.6 % at

250 °C. This increase is primarily due to the temperature dependence of the errors in the thermal conductivity measurements.

Summary

An apparatus for simultaneously measuring the properties of thermoelectric materials has been described. As progress is made toward the development of a high temperature thermoelectric standard, we expect to further validate this apparatus and provide a means for consensus in metrology of thermoelectric materials.

References

[1] D.M. Rowe, ed., CRC Handbook of Thermoelectrics (CRC Press, Boca Raton, 1995).
[2] D.M. Rowe, ed., Thermoelectrics Handbook: Macro to Nano (CRC Press, Boca Raton, 2006).
[3] L.E. Bell, Science **321**, 1457 (2008).
[4] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature **413**, 597 (2001).
[5] T.C. Harman, P.J. Taylor, M.P. Walsh, and B.E. LaForge, Science **297**, 2229 (2002).
[6] K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis, and M.G. Kanatzidis, Science. **303**, 818 (2004).
[7] J.P. Heremans, V. Jovovic, E. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, and G.J. Snyder, Science **321**, 554 (2008).
[8] Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, and G.J. Snyder, Nature **473**, 66 (2011).
[9] C. Uher, Nav. Res. Rev., TE Mater. **XLVIII**, 44 (1996).
[10] R. Taylor, CRC Handbook of Thermoelectrics, edited by D. M. Rowe (CRC Press, Boca Raton, 1995), ch 16.
[11] M.J. Laubitz, Thermal Conductivity, Vol. 1, edited by R.P. Tye (Academic Press, New York, 1969) p111.
[12] T.M. Tritt, Thermoelectrics Handbook: Macro to Nano, edited by D.M. Rowe (CRC, Boca Raton, 2006), ch. 23, and references within.
[13] C. Xing, C. Jensen, H. Ban, and J. Phillips, Meas. Sci. Technol. **22**, 075702 (2011).
[14] T.C. Harman, J. Appl. Phys. **29**, 1373 (1958).
[15] A.E. Bowley, L.E.J. Cowles, G.J. Williams, and H.J. Goldsmid, J. Sci. Instrum. **38**, 433 (1961).
[16] J. Martin, T. Tritt, and C. Uher, J. Appl. Phys. **108**, 121101 (2010).
[17] A.T. Burkov, Thermoelectrics Handbook: Macro to Nano, edited by D.M. Rowe (CRC, Boca Raton, FL, 2006), ch. 22.
[18] C. Wood, A. Chmielewski, and D. Zoltan, Rev. Sci. Instrum. **59**, 951 (1988).
[19] A.T. Burkov, A. Heinrich, P.P. Konstantinov, T. Nakama, and K. Yagasaki, Meas. Sci. Technol. **12**, 264 (2001).
[20] Z. Zhou and C. Uher, Rev. Sci. Instrum. **76**, 023901 (2005).
[21] V. Ponnambalam, S. Lindsey, N.S. Hickman, and T.M. Tritt, Rev. Sci. Instrum. **77**, 073904 (2006).
[22] R.J. Corruccini, Vacuum **7-8**, 19 (1959).
[23] J.P. Holman, Heat Transfer, seventh ed. (McGraw-Hill, New York, 1990).
[24] G.A. Slack, J. Phys. Chem. Solids **34**, 321 (1973).
[25] L.J. van der Pauw, Philips Res. Repts **13**, 1 (1958).
[26] H. J. Goldsmid, J. Appl. Phys. **32**, 2198 (1956).
[27] P. P. Konorov, Zhur. Tekh. Fiz. **25**, 1400 (1956).
[28] P. W. Erickson, Thesis, United States Naval Postgraduate School, p26 (1961).
[29] P. J. Price, Phil. Mag **46**, 1252 (1955).
[30] H.J. Goldsmid, Proc. Phys. Soc. **72**, 17 (1958).
[31] C.B. Satterthwaite and R.W. Ure, Phys. Rev. **108**, 1164 (1957).

Figure captions

Figure 1a. Schematic of the TE measurement system, not drawn to scale. The sample is pressed between two independently heated BN rods; here the rods are shown separated for viewing the sample placement. The temperature in the BN rods is measured at the four positions indicated in the Figure. The Cu sample stage capping the end of each BN rod provides electrical contacts to the sample. The active and passive radiation shields are denoted by dashed lines.

Figure 1b. Top and side views of the sample stage. Each side of the stage consists of two semi-circular Cu pieces, with a 200 μm gap in between. A thermometer is inserted in the thermometer housing, spanning both semi-circular pieces. Each of the four Cu pieces has an electrical connection for Seebeck and resistivity measurements.

Figure 1c. Simulation of isothermal lines indicating the temperature offset arising from the contribution of thermal resistance of the Cu body to R_0. Each isotherm represents 1 mk, for a temperature gradient $T_{1,2}$ ($T_{3,4}$) of 300 mK. The model predicts an offset temperature difference, $T_{2,3}$ of 3 mK, or 1 % of the net temperature drop along a BN rod. This difference constitutes roughly 1/3 of the measured temperature offset, as the model ignores thermal resistance of the silica-based cement used for assembly.

Figure 2. Temperature correction arising from thermal resistance between the stage thermometer and the sample as a function of temperature, measured using a thin Au foil as a sample. The plot shows the symmetry between both BN rods, and correction ranging from approximately 2 % to 5 %.

Figure 3. The extracted thermal conductivity of a BN rod, obtained using NIST SRM8424 as a sample as a function of temperature. The polynomial fit is subsequently used to obtain the thermal conductivity of samples.

Figure 4. Measured Seebeck coefficient of NIST SRM 3451 Seebeck Standard as a function of temperature. The certified reference data for the SRM is depicted by the solid line, which has an uncertainty of ± 2.7 % and is shown as dashed lines, in agreement with the measured data.

Figure 5. Measured electrical resistivity of NIST SRM 3451 Seebeck Standard as a function of temperature. Due to its multi-valley band structure, Bi_2Te_3 has a complex temperature dependent resistivity, as the chemical potential level crosses specific bands with changing temperature.

Figure 6. Measured thermal conductivity of NIST SRM 3451 Seebeck Standard as a function of temperature. Due to the high electrical conductivity of Bi_2Te_3, the electronic thermal conductivity dominates at these temperatures.

Figure 7. Extracted figure of merit, *ZT*, of NIST SRM 3451 Seebeck Standard as a function of temperature. This figure is calculated from the measurements of the Seebeck coefficient, electrical resistivity, and thermal conductivity.

Figure 8. Relative uncertainty in the figure of merit of NIST SRM 3451 Seebeck Standard as a function of temperature, obtained from propagation of the uncertainties in the individual material parameters. The increase in relative uncertainty primarily arises from the increased uncertainty in the thermal conductivity as the temperature increases.