Complete Characterization of Thermoelectric Materials by a Combined van der Pauw Approach and the Effect of Radiation Losses.

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Abstract

We have recently presented a novel method for a complete thermoelectric characterization [J. de Boor, V. Schmidt. Adv. Mater. 22:4303, (2010)]. This method is based on the well-known electrical van der Pauw method and allows measurement of the electrical and thermal conductivity, the Seebeck coefficient and the thermoelectric figure of merit. After a short review of this method we will discuss the systematic measurement errors of the method. It turns out that radiative heat loss can affect the thermal conductivity measurement significantly. We will give a simple estimation for the relative error due to radiation losses and discuss error minimizing strategies.

Introduction

Thermoelectric materials can convert heat directly into electrical energy. This can be used to enhance the energy efficiency of cars or solar cells by converting previously unused thermal energy into electricity, see [1] and references therein. Other applications include battery-less sensors and spacecrafts. Thermoelectric modules can also be used for precise and fast solid-state temperature control and are employed amongst others in laser cavities and life science laboratories. The efficiency of the heat to electrical energy conversion is governed by the thermoelectric figure of merit $ZT$, which is given by

$$ZT = \frac{\sigma S^2 T}{\kappa},$$

where $\sigma$ is the electrical conductivity, $\kappa$ the thermal conductivity, $S$ the Seebeck coefficient of the material and $T$ the absolute temperature. A good thermoelectric material must possess a good electrical conductivity and a high Seebeck coefficient but a low thermal conductivity. Unfortunately these three quantities are interdependent to some degree: High electrical conductivities increases the thermal conductivity since a fraction of the heat in a conductor is transported by the charge carriers. A further complication is that a high electrical conductivity is usually attended by a low Seebeck coefficient. Designing or optimizing thermoelectric materials is consequently a process that requires repeated measurements and adjusting of experimental parameters. Since thermoelectric characterization is a crucial step in this process it would be highly desirable to have a measurement method that can measure $\sigma$, $\kappa$, and $S$ simultaneously. Preferably all measurements are performed on the same sample since thermoelectric properties can vary within the same piece of material and measurements of single quantities on different pieces can therefore lead to erroneous results [1].

Measurement Method

We will discuss here a technique that allows the concurrent measurement of $\sigma$, $\kappa$, and $S$ and thus a complete characterization. It is based on the well-known electrical van der Pauw method [2], which will be introduced first. In his seminal papers van der Pauw showed that the electrical conductivity
of a sample with arbitrary shape can be determined from two four-point resistance measurements, provided that the sample has a uniform thickness, is without holes and insulated except for the contacts. Consider a sample with four electrical contacts, labeled \(E_1\)-\(E_4\). A current \(I\) is driven through the two contacts \(E_2\) and \(E_1\), and the resulting voltage \(U_{43}\) is measured across the other two contacts. Current and voltage can be used to calculate the first resistance: \(R_{21,43} = U_{43}/I_{21}\). Then, the leads to \(E_2\) and \(E_3\) are exchanged and the second resistance can be recorded likewise: \(R_{31,42} = U_{42}/I_{31}\). With these two values the electrical conductivity can be obtained by solving the van der Pauw equation

\[
\exp(-\pi\sigma d R_{21,43}) + \exp(-\pi\sigma d R_{31,42}) = 1,
\]

where \(d\) is the sample thickness.

Due to the fundamental analogy between electrical and thermal physics, this concept can be applied to thermal conductivity measurements. Instead of an electrical current a heat flow \(P\) is driven through the sample and temperature differences \(\Delta T\) are measured. From these the thermal resistances \(R_{21,43}^{th} = \Delta T_{43}/P_{21}\) and \(R_{31,42}^{th} = \Delta T_{42}/P_{31}\) can be determined and the thermal conductivity can be calculated from the thermal equivalent of (2) [3]. In order to perform these measurements we equipped the sample with three small resistors (Pt1000), that can be used both for heating and temperature measurements. To realize thermal insulation the sample was suspended as shown in Figure [1]. Thermal and mechanical contact to the environment is provided at one spot; this contact \(H_1\) therefore acts as heat sink.

![Figure 1: a) Photograph of the suspended sample and the sample holder; heat sink and resistors are indicated. b) Thermoelectric van der Pauw measurements, the color coding illustrates the temperature of the sample. The heater \(H_3\) creates a heat flow to \(H_1\) which causes a temperature difference between \(H_4\) and \(H_2\). Measuring both and performing a second measurement where \(H_2\) acts as heater and \(H_3\) as thermometer the thermal conductivity of the sample can be determined from the thermal van der Pauw equation. Likewise, using the electrical contacts \(E_1\) to \(E_4\) the electrical conductivity can be determined from the electrical van der Pauw equation. Additionally, the Seebeck coefficient can be calculated from the measured thermoelectric voltages and temperature differences.](image)
Figure 2: Complete thermoelectric characterization of an lightly doped InSb sample. a): Electrical conductivity, error bars 4%. b): Seebeck coefficient, error bars 10%. c): Thermal conductivity with reference data from [5], error bars increase with temperature from 13% to 25%. Subfigure d) shows the $ZT$ calculated from the measurement data (blue); the relative error is the sum of the relative errors of a)-c).

As shown in Figure 1 the sample is also equipped with four electrical contacts. These can be used to measure the electrical conductivity with the electrical van der Pauw method, as explained above. When driving a heat flow (but no current flow) through the sample the electrical contacts can also be used to measure the Seebeck voltage $U$ that arises due to the temperature gradient, see Figure 1. From this and the measured $\Delta T$ the Seebeck coefficient $S = -U/\Delta T$ can be calculated. This measurement can be performed simultaneously with the thermal conductivity measurement. With these three measurements $ZT$ can be calculated from (1) and the thermoelectric performance of the material under test can be evaluated.

**DISCUSSION**

The described method has been tested successfully on several materials as shown in [4]. In Figure 2 we show measurement data of a low doped InSb sample between 310 K and 430 K to motivate the error discussion. As expected for intrinsic or low doped InSb the electrical conductivity increases with temperature, while the Seebeck coefficient decreases. Exact comparison to literature data is difficult since the electrical properties depend sensitively on impurity concentration which can differ between samples. The thermal conductivity is not affected by low doping and the measurement results are compared to literature data from [5].
It can be seen that the deviation between measured thermal conductivity and reference data increases with increasing temperature. The van der Pauw equation requires insulation of the sample and while electrical insulation can be realized easily, a perfect thermal decoupling is not possible. The measurements were performed in high vacuum to prevent parasitic heat transport by convection or conduction through the surrounding gas, but heat loss by radiation and through the electrical connections cannot be avoided. Using long, thin wires the relative error due to heat loss through the wires can be kept below 1% \cite{4}, this leaves radiation as important error source. We shall now derive an analytical expression to estimate this error.

As a first step the temperature profile of the sample with side length $a$ and thickness $d$ has to be calculated. For this consider a cylindrical heater with diameter $\delta$ that is situated at $x = a/2$, $y = 0$ as $H_2$ in Figure 1. We assume that the temperature profile is symmetrical along $d$, this is a prerequisite of the van der Pauw equation. Disregarding the effect of the sample boundaries the problem exhibits cylindrical symmetry and the steady state heat equation can be written as

$$\kappa \Delta T_H(r) = \partial_r(r \partial_r T_H) = P_{\text{loss}},$$

(3)

where $T_H(r)$ is the temperature distribution of the sample. As a first order approximation, the temperature profile can be calculated for $P_{\text{loss}} = 0$. The boundary conditions are that sample temperature $T_H(r)$ is equal to the heater temperature $T_{H,0}$ at the intersection ($T_H(0.5\delta) = T_{H,0}$) and that a given $P$ flows uniformly from the heater with surface area $0.5\pi\delta d$ into the sample, i.e. $-P/(\pi\delta d) = \kappa \partial T_H(r)|_{r=0.5\delta}$. In this case the heat equation can be solved by simple integration. Inserting the boundary conditions yields a logarithmic temperature profile

$$T_H(r) = T_{H,0} - \frac{P}{\pi\kappa d} \ln \left( \frac{r}{0.5\delta} \right),$$

(4)

the slope of which increases with decreasing heater size and decreasing sample thickness at constant $P$. The above reasoning also holds for the case of a semi-cylindrical heat sink at $x = 0$, $y = a/2$ with a heat “generation” of $-P$. The temperature profile of such a sample is

$$T_S(r') = T_{S,0} + \frac{P}{\pi\kappa d} \ln \left( \frac{r'}{0.5\delta} \right),$$

(5)

where $T_{S,0}$ is the heat sink temperature. In the experiment we have a sample with both heater and sink and the resulting temperature profile is the superposition of source and sink profile

$$T(r, r') = T_M + \frac{P}{\pi\kappa d} \left( \ln \left( \frac{r'}{0.5\delta} \right) - \ln \left( \frac{r}{0.5\delta} \right) \right) = T_M + \frac{P}{\pi\kappa d} \left( \ln \left( \frac{r'}{r} \right) \right),$$

(6)

where $T_M = (T_{H,0} + T_{S,0})/2$ is the average temperature of the sample. In the actual experiment $T_{S,0}$ (the heat sink temperature) is set, while $T_M$ and $T_{H,0}$ depend on $P$. Setting

$$T(x = \delta/2, y = a/2) \overset{!}{=} T_{S,0}$$

(7)

and converting $r = \sqrt{(x-a/2)^2 + y^2}$ and $r' = \sqrt{x^2 + (y-a/2)^2}$ into Cartesian coordinates this
As shown theoretically and experimentally [8, 9] accurate van der Pauw measurements can be performed up to InSb. However, we also see that the error decreases with increasing side length to thickness ratio. This is unfortunate, since most thermoelectric materials have thermal conductivities lower than κ. This is indicated in Figure 2c, further information can be found in [8, 9].

At room temperature the systematic error is acceptable and similar to other techniques (3% at 100 K and 5% at 310 K and 3% at 300 K; ω ≈ 0.6 [7]. For these parameters Equation (12) yields ≈ 0.075 at 310 K and ≈ 0.2 at 430 K. This relative error plus another 5% accounting for finite contact size, thickness error, etc. is indicated in Figure 2c, further information can be found in [8, 9].

Using the parameters of the state-of-the-art material Bi$_2$Te$_3$ (κ ≈ 1 Wm$^{-1}$K$^{-1}$, ε = 0.6) and a still manageable sample with optimal side length thickness ratio (a = 5 mm, d = 2.5 mm, δ = 1 mm) the relative heat loss from (12) amounts to $P_{loss,rad}^{rel} = 0.3\%$ at 100 K and $P_{loss,rad}^{rel} = 6.9\%$ at 300 K;

\[
T_{S,0} = T_M + \frac{P}{\pi\kappa d} \ln \left( \frac{\sqrt{\delta/2} + (a/2 - a/2)^2}{\sqrt{(\delta/2 - a/2)^2 + (a/2)^2}} \right) \quad (8)
\]

\[
= T_M - \frac{P}{\pi\kappa d} \ln \left( \frac{\sqrt{2}a}{\delta} \right) \quad \text{for } \delta \ll a. \quad (9)
\]

Inserting in (6) yields the temperature profile of the sample:

\[
T(x,y) = T_{S,0} + \frac{P}{\pi\kappa d} \left[ \ln \left( \frac{\sqrt{2}a}{\delta} \right) + \ln \left( \frac{\sqrt{x^2 + (y-a/2)^2}}{\sqrt{(x-a/2)^2 + y^2}} \right) \right]. \quad (10)
\]

From this temperature profile the power lost by radiation $P_{loss,rad}$ can be calculated [6]:

\[
P_{loss,rad} = \varepsilon\sigma_B \int (T(x,y)^4 - T_0^4) dA \approx 4\varepsilon\sigma_B T_0^3 \int (T(x,y) - T_0) dA, \quad (11)
\]

where $T_0$ is the ambient temperature, ε is the sample emissivity, $\sigma_B = 5.67 \cdot 10^{-8}$ WK$^{-4}$ Stefan-Boltzmann’s constant, and $A$ the surface area of the sample. The heat sink temperature and the ambient temperature are identical, $T_0 = T_{S,0}$ if good thermal contact between the heat sink and the heat shield surrounding the sample is ensured. Since the sample temperature profile is symmetrical along $x = y$ the surface integral over the temperature profile can be replaced by total surface and mean temperature difference $T_M - T_{S,0}$ from (9). With $A = 2a(a + d)$ the radiation loss relative to the total heating power is thus

\[
P_{loss,rad}^{rel} = \frac{P_{loss,rad}}{P} = \frac{8a(a + d)\varepsilon\sigma_B T_0^3 \ln(\sqrt{2}a/\delta)}{\pi\kappa d}. \quad (12)
\]

The results shown in Figure 2 were obtained from a sample with $a = 1$ cm, $\delta = 1.25$ mm, $d = 0.5$ mm and $\varepsilon \approx 0.6$ [7]. For these parameters Equation (12) yields $\approx 0.075$ at 310 K and $\approx 0.2$ at 430 K. This relative error plus another 5% accounting for finite contact size, thickness error, etc. is indicated in Figure 2c, further information can be found in [8, 9].
i.e. up to room temperature the $\kappa$ measurement would be accurate and a complete thermoelectric characterization feasible.

Note that in the presented form the measurement method yields the in-plane properties of materials. In order to fully characterize anisotropic materials like $\text{Bi}_2\text{Te}_3$ two measurements on samples with different orientations have to be performed.

**CONCLUSIONS**

We have presented a method for the complete thermoelectric characterization of materials. Based on the electrical van der Pauw method it allows a concurrent measurement of $\sigma$, $S$, and $\kappa$ on a single sample. Furthermore we have analyzed the systematic errors of the measurement and identified radiative heat loss as the most severe one. A simple analytical expression to estimate this error was derived and strategies to minimize it have been discussed. Applying those, accurate measurements of state-of-the-art materials up to room temperature is feasible.

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**References**


