

High temperature measurement of Seebeck coefficient and electrical conductivity

J. de Boor^{1*}, C. Stiewe¹, P. Ziolkowski¹, T. Dasgupta¹, G. Karpinski¹, E. Lenz², F. Edler², E. Mueller¹

¹ German Aerospace Center, Institute of Materials Research, Linder Höhe, 51147 Köln, Germany

² Physikalisch-Technische Bundesanstalt, Abbestraße 2-12, 10587 Berlin, Germany

Phone: +49-2203-6014037

Fax: +49-2203-696480

Email: johannes.deboor@dlr.de

Article note: presented at ICT

Abstract:

We have developed a system for the simultaneous measurement of the electrical conductivity and the Seebeck coefficient for thermoelectric samples in the temperature region of 300 K to 1000 K. The system features flexibility in sample dimensions and easy sample exchange. In order to verify the accuracy of the setup we have referenced our system against the NIST standard reference material 3451 and other setups and can show good agreement. The developed system has been used in the search for a possible high temperature Seebeck standard material. FeSi₂ emerges as a possible candidate as this material combines properties typical for thermoelectric materials with large scale fabrication, good spatial homogeneity, and thermal stability up to 1000 K.

Keywords: thermoelectrics, measurement technique, measurement of Seebeck coefficient, Seebeck coefficient reference material

Introduction

Thermoelectrics deals with the direct conversion of heat into electrical energy and can therefore be a valuable contribution to the solution of the energy crisis of the 21st century. Thermoelectric generators can utilize the waste heat of various sources like combustion engines to generate electrical power and thus increase the energy efficiency of such devices. This form of energy recuperation has various implemented and potential applications in the field of space flight, traffic and aviation [1,2].

The efficiency of the waste heat to electrical energy conversion is governed by the thermoelectric figure of merit ZT , which is given by basic material properties:

$$ZT = \frac{\sigma S^2}{\kappa} T. \quad (1)$$

A good thermoelectric material thus has a high electrical conductivity σ , a large Seebeck coefficient S , and a low thermal conductivity κ ; T is the absolute temperature. The

identification and especially the optimization of thermoelectric materials requires repeated measurement of σ, S and κ , as these three quantities are strongly interdependent and the optimization of ZT cannot be achieved by simple optimization of the individual quantities [2]. This is particularly true for the Seebeck coefficient and the electrical conductivity, which are coupled via the charge carrier concentration of the material: a high charge carrier concentration usually increases σ and decreases S . For a better understanding of the measurement results and in order to reduce the measurement time and sample count it is highly advantageous to employ a system that can measure σ and S simultaneously. This is particularly interesting for materials that are unstable under heat treatment, as sequential measurements on the same sample would give misleading results in this case. Although there are some systems for the measurement of σ and S commercially available, we decided to set up a custom designed system. These are more flexible in measurement routines and measurement data analysis; furthermore we wanted an apparatus that is applicable up to 1000 K.

In this manuscript we will first describe the hardware of the setup and its advantages compared to commercially available systems. In the second section we will discuss the accuracy of the system and discuss the comparison with other setups. Although strongly needed, there is yet no available standard material for the measurement of the Seebeck coefficient above 400 K. We will shortly discuss requirements of such a material and present initial results on FeSi_2 which emerges as one possible candidate.

Setup

The Seebeck coefficient is the constant of proportionality of the temperature difference ΔT across a sample and the voltage U that arises due to this temperature gradient:

$$S = -\frac{U}{\Delta T} = -\frac{U}{T_2 - T_1}, \quad (2)$$

in the limit of a vanishing temperature gradient. For the determination of S a temperature gradient is applied across the sample and the resulting voltage is measured. It is highly advantageous to determine S from a variable temperature gradient, therefore our sample holder is equipped with two gradient heaters, see Figure 1. One heater is sufficient for a variable temperature gradient, but two have the additional advantage that one can vary the gradient in both directions. The heaters are bifilar wound filaments that are heated by supplying electrical power. The temperatures T_1, T_2 and the thermally induced voltage U are measured using two sheathed type N thermocouples. Sheathed thermocouples are superior to thermocouples inserted into ceramic tubes (see e.g. [3]) as they possess some mechanical flexibility that facilitates thermocouple assembly and exchange. The individual thermocouple wires are surrounded by ceramic filling and insulated from each other, while the sheath made from Inconel protects the measuring junction from chemical contamination and provides the mechanical strength that allows for pressing the thermocouples onto the sample. We employ flat springs made from tungsten-rhenium to press the thermocouples onto the sample. Tungsten-rhenium has a large Young's modulus even at elevated temperatures and causes a good thermal coupling between the sample and the tips of the thermocouples [4]. This is a prerequisite for an accurate measurement of the

Seebeck coefficient since otherwise thermal contact resistances will lead to an erroneous temperature reading and thus an incorrect result for S . The sample itself is pressed onto the sample holder using a headless screw and a “T”-piece that can be plugged into a hole drilled into the headless screw. The head of the “T”-piece is rotatable and can therefore also be used for samples with non-parallel surfaces.

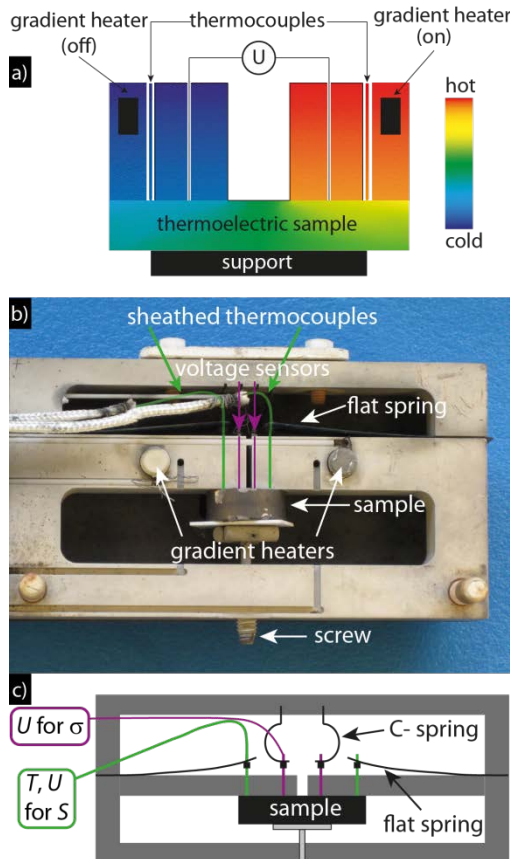


Figure 1: Sample holder for σ and S measurement. Two gradient heaters can be used to create a temperature gradient across the sample which results in Seebeck voltages. The scheme in a) displays the temperature profile during a measurement of the Seebeck coefficient. The photograph in b) shows the sample holder with a mounted sample, while the scheme in c) illustrates the mechanical and electrical connections (only left half shown for clarity). The sheathed thermocouples are used to measure the sample temperatures and the thermoelectric voltages; from these the Seebeck coefficient S of the sample under test can be calculated. For the measurement of σ a current is driven through the sample using the thermocouples for current supply. Additional voltage sensors in line with the thermocouples are used to record the Ohmic voltage drop.

The electrical conductivity is determined in a four probe in-line arrangement. The sheath of the thermocouples is used to drive a current through the sample while two additional probes are used to measure the resulting voltage; from the magnitude of the current, the voltage, the spacing of the tips, and the sample geometry the electrical conductivity of the sample can be calculated. The voltage probes are made from tungsten carbide and are pressed onto the sample using C-springs made from tungsten rhenium.

Electrical connection in the hot temperature region (e.g. from platinum wires to the tungsten carbide voltage probes) are made employing laser spot welding. The sample holder itself is made from Shapal (AlN), a ceramic with good mechanical properties and a relatively high thermal conductivity. The components of the sample holder are chosen on the basis of their thermo-mechanical properties and while the maximum operating

temperature of all parts is way above 1300 K, the maximum operation temperature of the setup is currently restricted to 1000 K as the Young's modulus of the tungsten rhenium springs reduces significantly above 1050 K.

The sample holder is covered on both sides by graphite semi-cylinders that are attached to the sample holder using ceramic screws. The semi-cylinders homogenize the thermal environment and serve as radiation shields. The sample holder is connected to a vacuum flange by a molybdenum rod; the flange covers a quartz glass tube which contains the sample holder. The glass tube is connected to a vacuum pump and can be operated under vacuum ($p \approx 10^{-5}$ mbar) or inert gas atmosphere. The glass tube plus sample holder is inserted into a tube furnace (Thermconcept) that is used to regulate the ambient temperature. Furnace, gradient heater power supply as well as measurement electronics (Agilent 33210A, Keithley 2700 + switch card 7700) are connected to a PC via a GPIB interface and are operated using a custom made Visual Basic program. There have been several reports on setups for the measurement of S and σ [5-11]. Compared to these our measurement system distinguishes itself by a large flexibility in sample dimensions ($10 \text{ mm} < \text{length} < 30 \text{ mm}$, $0.1 \text{ mm} < \text{thickness} < 8 \text{ mm}$), very little required maintenance and a very easy sample exchange: since all electrical connections are made with pressure contacts, exchanging the sample requires only mounting the sample on the T-piece and fastening the screw. The system accommodates parallelepiped and cylindrical samples. The latter one is crucial as this is the typical geometry for thermal conductivity measurement with the frequently employed laser flash method.

We will now briefly describe the measurement procedure for σ and S . At first the desired temperature is set in the furnace and stabilized. Then an alternating current I is passed through the sheath of the thermocouples and the resulting voltage U between the tungsten carbide probes is recorded. The sample conductivity is then calculated from

$$\sigma = \frac{I}{2\pi s U C} , \quad (3)$$

where s is the spacing between the tips and C a geometrical correction factor. This correction factor accounts for the finite size of the sample, its geometry and the spacing between the tips. For typical geometries like bar-shaped or cylindrical samples, correction factors have been reported in the literature. We have employed the values reported in Ref [12-15].

The Seebeck coefficient can in principle be determined from

$$S = -\frac{U_A}{T_2 - T_1} + S_A, \quad (4)$$

where U_A is the voltage measured across the two thermocouple wires of type A (in our case A: Nisil, B: Nicrosil) and S_A the Seebeck coefficient of the wire material; the equivalent equation holds true for U_B . However, determination of S from a single temperature-voltage pair can be highly inaccurate due to spurious thermal voltages within the measurement system and imperfections of the employed thermocouples. To record the voltages and temperatures for a number of data points we first run heater1 for a short time, typical 60 s. A temperature difference arises, see Figure 2.

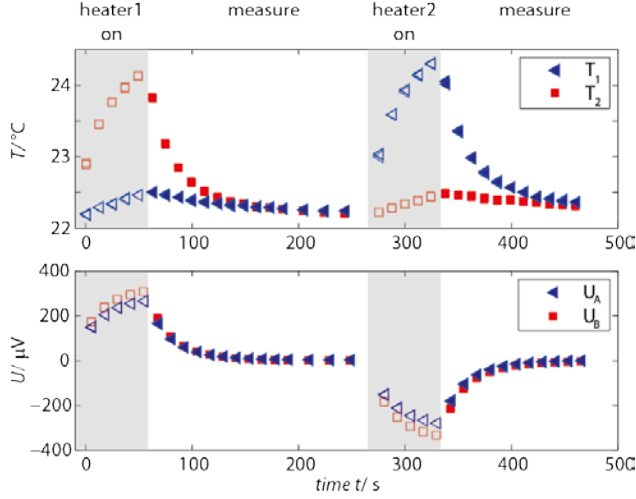


Figure 2: Measurement routine for the determination of the Seebeck coefficient. At first heater1 is switched on and a temperature gradient arises. After a short time the heater is switched off and the system relaxes; finally the step is repeated with heater2. Temperatures and voltages are recorded for the complete measurement cycle, but only the data acquired during relaxation is used for the calculation of S .

The heater is switched off and the system relaxes, during this time T_1, T_2 and U_A, U_B are recorded and used for the later analysis. The step is repeated for heater2. Instead of using single voltage-temperature pairs we can now employ the slope of U_A vs. U_B to calculate S .

The two recorded voltages U_A and U_B are given by

$$U_A = -(S - S_A)\Delta T; \quad U_B = -(S - S_B)\Delta T, \quad (5)$$

which can be rewritten as

$$\frac{\partial U_A}{\partial \Delta T} = -S + S_A; \quad \frac{\partial U_B}{\partial \Delta T} = -S + S_B. \quad (6)$$

Combining these two equations to replace ΔT yields after some math

$$S(\bar{T}) = \frac{S_{TC}(\bar{T})}{1 - \frac{\partial U_B}{\partial U_A}} + S_A(\bar{T}), \quad (7)$$

with the mean temperature \bar{T} and $S_{TC} = S_B - S_A$, where S_{TC} is the Seebeck coefficient of the thermocouple as tabulated and S_A is the wire with the more negative Seebeck coefficient. Employing Eq. (7) instead of Eq. (4) is highly advantageous for several reasons. Firstly spurious thermal offset voltages from the system are cancelled since only the slope and no absolute values are used. In contrast to the equation used in Ref. [5] Eq. (7) does not require the thermal offset voltages of U_A and U_B to be the same with respect to ΔT , the offsets just have to be constant. Secondly the equation requires no direct temperature measurements which tend to be less accurate than voltage measurements. Temperatures are only required for the calculation of the mean temperature \bar{T} , where accuracy is less important. Finally by taking the slope from a large number of data points statistical errors in the voltage readings of the individual points are of less significance as they are averaged. A representative plot of U_B vs. U_A is shown in Figure 3. Also given in the figure is the linear correlation coefficient R of the linear fit, which can be used to judge the quality of the measurement and to check for errors.

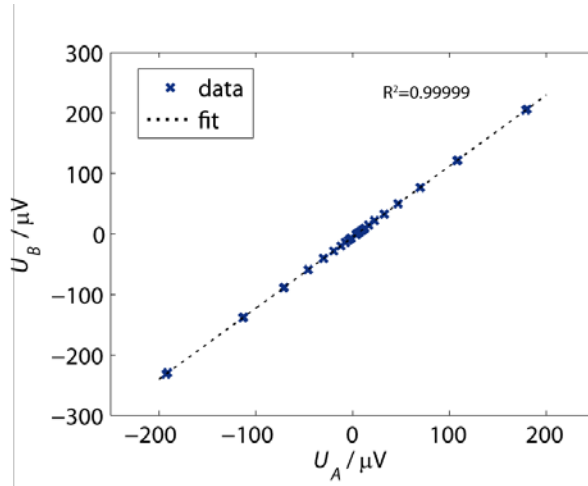


Figure 3: Plot of U_B vs. U_A . The slope of U_B vs. U_A is used to determine the Seebeck coefficient, see Eq. (7). The linear fit is excellent as can be deduced from the correlation coefficient R .

Measurement uncertainty analysis and comparison with reference data

We will begin with a discussion of the uncertainties of the σ measurement. It is calculated from Eq. (3) and thus uncertainties can stem from noisy voltage readings affecting R or from geometrical uncertainties of sample or probe spacing, affecting s or the geometrical correction factor C . The voltage probes are rigid and have an allowance for clearance of less than $50 \mu\text{m}$ and the distance between both can be measured using optical microscopy with high accuracy. The thermocouples have a larger allowance for clearance and show a variation of $\approx 100 \mu\text{m}$, which can lead to an uncertainty in σ of some percent. Additional uncertainties arise from incorrect measurements of the sample dimensions which affect the calculation of C and improper positioning of the sample with respect to the tips. Most calculations of C either assume a sample symmetrical with respect to the tips [12] or a known distance from tips to sample edge [14]. Nevertheless, comparison with a different setup in house that determines the electrical conductivity based on the van der Pauw method [16] shows an agreement better than 5%, typically better than 3%.

The error of environment temperature in the σ and S measurement is governed by the accuracy of the thermocouples, which are class 1 in our case. The Seebeck coefficient measurement is necessarily obtained from a temperature interval, in our case the temperature $S(\bar{T})$ is taken as the average over all recorded temperatures in one measurement cycle, see Figure 2. The temperature interval over which the measurement is taken is usually $< 2 \text{ K}$ which is small compared to the typical spacing of the temperature points where measurements are taken.

The uncertainties of the Seebeck coefficient measurement itself stem from several sources. First there are inaccuracies of the voltage readings used to determine S . Since the recorded voltages are usually small $250 \mu\text{V} < U_A, U_B < 2 \mu\text{V}$ the noise can have some effect on the measurement result. Another possible source of uncertainty is the

interpolation of the recorded voltages with respect to time which is necessary as Eq. (7) (and also Eq. (4)) requires the respective quantities to be recorded simultaneously. While Eq. (7) is not affected by thermal offset voltages (like $U_A \neq 0$ for $U_B = 0$) it nevertheless requires an offset which is constant over the measurement time. A changing offset voltage will tamper with the result for S but can be identified by a correlation coefficient not close to unity, see Figure 3.

The potentially most severe uncertainty stems from thermal contact resistances between the sample, the thermocouples, and the part of the sample holder pressed on the sample. These can cause a discrepancy between the Seebeck voltage reading and the temperature reading and therefore an incorrectly determined Seebeck coefficient [8]. Eq. (7), which is used in our setup, does not require the temperatures to determine S , but the voltages U_A and U_B are affected in the same manner as the temperatures by thermal contact resistances.

The statistical errors due to electrical noise, the effect of the data interpolation as well as a varying offset can be estimated by a variation of measurement parameters and are found to cause an error of $< 4\%$ for the presented setup. The effect of the thermal contact resistances depends on various physical parameters (sample hardness, surface roughness, temperature, pressure of the sample against the sample holder, pressure of thermocouples against sample, pressure and type of surrounding atmosphere, etc.) that are partially poorly accessible and controllable in the experiment. To get an estimation for the absolute accuracy of the developed setup it is therefore necessary to compare the measurement results with known references or the results of other setups.

Up to now, there is no standard reference material for the Seebeck coefficient above 400 K, although research in this direction is under way [17,18]. We have therefore used a two-fold strategy to proof the accuracy of our setup, labeled HTS σ in the following. First we have used a different custom-build setup "CTEM" to measure the recently published NIST standard reference material for low temperature Seebeck coefficient measurements (SRM 3451) [19]. The results for the NIST reference material are presented in Figure 4 and show excellent agreement with the measured data. We cannot measure the NIST standard reference material in the presented HTS σ -setup as the length of the SRM 3451 is only 8 mm, and thus too small.

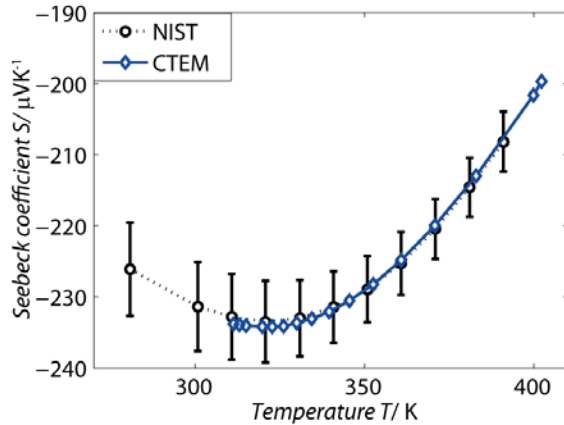


Figure 4: Comparison of the Seebeck coefficient from the NIST SRM 3451 with the custom-built system CTEM (blue). The black points indicate the published data from NIST, while the error bars indicate the stated measurement uncertainty. The black and the blue curve show excellent agreement with maximal deviations of 1%.

After proofing accurateness of the CTEM we can now in a second step compare the measurement results between CTEM and HTS σ . Results for a CoSb₃ skutterudite sample are plotted in Figure 5 and show very good agreement between CTEM and HTS σ results up to \approx 550 K which is the current maximum operation temperature for the CTEM-setup.

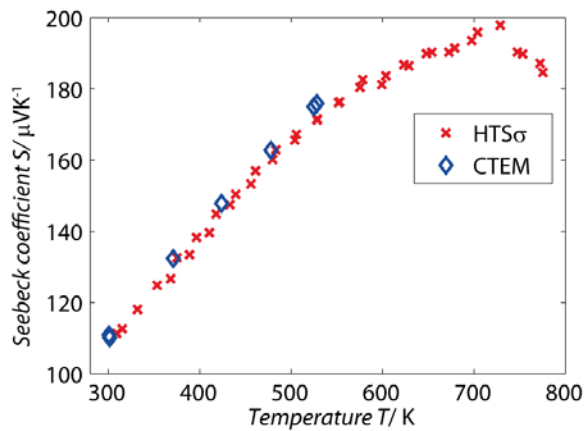


Figure 5: Comparison of the measurement results for the Seebeck coefficient between the CTEM and the HTS σ . A hot-pressed skutterudite was used as sample. Both data sets show good agreement.

Apart from this indirect comparison with the NIST reference material we checked the accuracy of the presented HTS σ -setup by comparative measurements of two further samples in different setups. Traditionally pure metals like Ni are often used as reference materials [4,10]. Here we use two commercially available Ni-based alloys as reference materials because the material properties are closer to that of actual thermoelectric materials. The results shown in Figure 6 are related to the first sample with an approximate composition of Cu₄₅Ni₅₅ and the dimensions 17 mm*10 mm* 1.0 mm (Silverin 404, Auerhammer Metallwerk GmbH). The Measurements were performed with CTEM, HTS σ , and an apparatus situated at the Physikalisch-Technische Bundesanstalt (PTB), the German Metrology Institute. Their system [20] is an improved

version of the apparatus presented in [5]. It can be seen that all three systems show good agreement over the whole temperature range, with a maximal deviation of less than 4%.

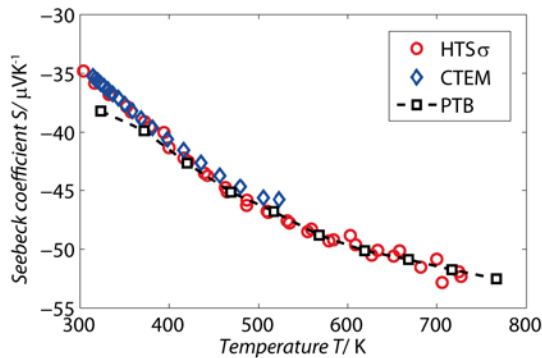


Figure 6: Comparison of Seebeck coefficient of $\text{Cu}_{45}\text{Ni}_{55}$ measured with three different setups: HTS σ and CTEM in-house as well as an apparatus from the PTB. The agreement between all three data sets is very good.

The results for the second sample ($\text{Cu}_{54}\text{Ni}_{44}\text{Mn}_1$, 24 mm*11 mm*0.3 mm, ISOTAN from Isabellenhütte Heusler GmbH & Co. KG, Germany) are shown in Figure 7 together with the measurement results for the electrical conductivity. The magnitude of the sample's Seebeck coefficient is around $-37 \mu\text{V}/\text{K}$ at room and increases with temperature. The data sets for both samples compare very well and show a maximum deviation of $< 4\%$ from each other. The electrical conductivity of the second sample shows weak temperature dependence. This is not surprising as the alloy has a similar composition as constantan.

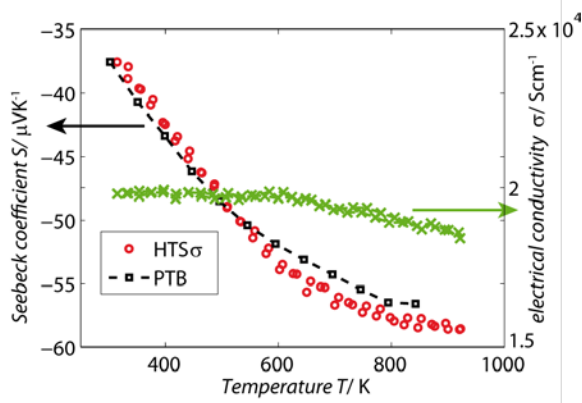


Figure 7: Seebeck coefficient and electrical conductivity of $\text{Cu}_{54}\text{Ni}_{44}\text{Mn}_1$. Also shown is the comparative measurement of the Seebeck coefficient of the PTB which again confirms the measurement data of the HTS σ .

All presented measurements were taken in a helium atmosphere with a pressure of $p \approx 1$ bar. Compared to vacuum a He atmosphere decreases the thermal contact resistances between sample, thermocouple, and sample holder and can improve the measurement accuracy [4]; outgassing from the samples is also reduced. From the discussion of the measurement errors, the comparison with reference data and with

results from different setups we can deduce that the Seebeck coefficient can be measured with an accuracy of around 5% in the temperature regime from 300 K to 1000 K.

Towards a high temperature Seebeck standard

For the realization of various thermoelectric applications material identification and optimization is required. This process includes systematic studies of fabrication parameter variation and accurate measurements of the thermoelectric properties are indispensable for the evaluation of these studies and thus for efficient material optimization. This is particularly true for the Seebeck coefficient which enters the thermoelectric figure of merit squared and thus governs the conversion efficiency of materials to a large extent. For trustworthy and meaningful measurements comparison of the employed setup with references is necessary. Such a standard material has recently been presented for the low temperature regime [19]. For the high temperature regime above 400 K, where many attractive applications exist, no standard material yet exists. This hinders the comparison between different thermoelectric measurement setups and slows down the material development process. A possible high temperature standard material has to fulfill a number of requirements: it must be mechanically and thermally stable in the required temperature regime, the fabrication must be reproducible, and the sample properties must be spatially homogeneous and typical for thermoelectric materials; the material should furthermore be chemically inert. An inexpensive material that is non-toxic and fulfills environmental regulations is advantageous as this simplifies handling and facilitates the establishment of the standard.

Among the many materials under investigation β -FeSi₂ is one possible candidate. We have employed the presented setup for the evaluation of the Seebeck coefficient of several FeSi₂ samples. These were produced from a gas atomized powder with a nominal composition of Fe_{0.95}Co_{0.05}Si₂. The compaction by a direct current assisted short term sintering process at 1173 K for 30 min using a heating rate of 60 K/s and a mechanical load of 50 MPa. This compaction was followed by 24h annealing at approximately 1100 K in order to form the desired semiconducting β -FeSi₂ [21]. The detailed fabrication parameters will be the subject of a future publication, we will focus here on the suitability of the material as high temperature Seebeck reference material.

The spatial homogeneity of the samples can be investigated using a Potential-Seebeck-Microprobe [22]. The results of the local Seebeck coefficient of one sample are presented in Figure 8. The sample shows a very narrow distribution of the Seebeck coefficient with a full-width half maximum of 2.5 μ V/K, which equals 1.7% of the statistical mean value.

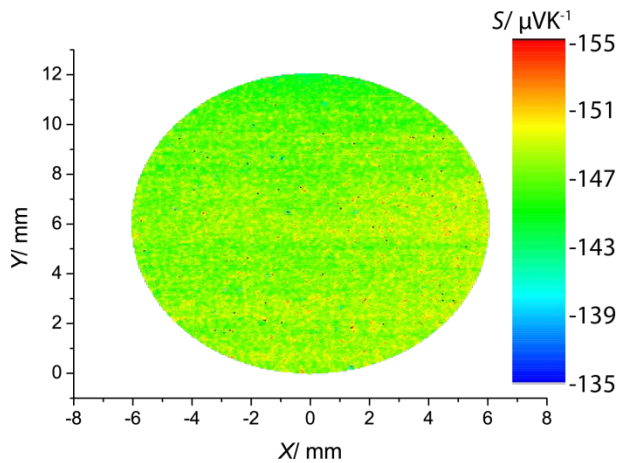


Figure 8: Spatial scan of the Seebeck coefficient of a β -FeSi₂ sample. It can be seen that the sample is very homogeneous; the full width half maximum of the Seebeck coefficient distribution is only 1.7% of the mean value.

We have investigated the thermal stability of FeSi₂ samples employing the presented setup. We have therefore exposed one of the samples to several thermal cycles up to 1000 K as shown in Figure 9a. The corresponding results for the Seebeck coefficient are presented in Figure 9b. For clarity polynomial fits of the measurement data are plotted together with the raw measurement results. The maximum deviation of the polynomial fits from each other is $\approx 2\%$ of the absolute value and shows no systematic drift with temperature. We can therefore deduce that the prepared FeSi₂ is thermally stable up to 1000 K, which is one crucial requirement for a high temperature standard material.

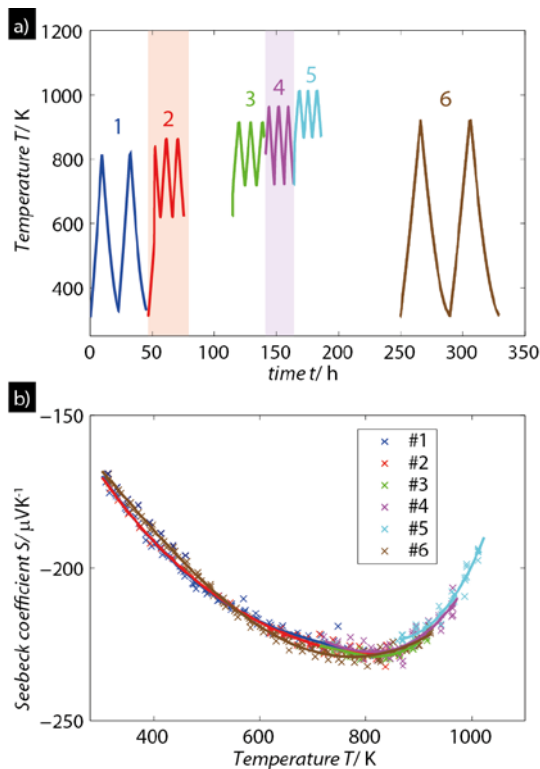


Figure 9: Thermal cycling program (a) and corresponding results for the Seebeck coefficient. In b) the corresponding raw measurement data is shown together with polynomial fits for better clarity. No significant change of the Seebeck coefficient can be seen after repeated thermal cycling of the sample, partially above 1000 K.

Another important criterion for a reference material is the reproducibility of the samples. Figure 10 compares the measurement results of the first sample with a further sample that is not from the same batch but fabricated under the same conditions. The measurement results are very close to each other as exemplified by the polynomial fits that are plotted for clarity. These fits differ by less than 2% over the whole temperature range, which is less than the measurement uncertainty. Comparison of two samples is clearly not sufficient to prove reproducibility, but it indicates that the fabrication process is well understood and a consistent production of samples is feasible.

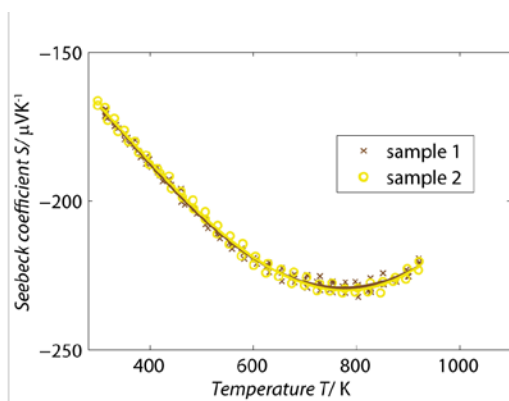


Figure 10: Comparison of the Seebeck coefficient of two FeSi₂ samples. The two samples show very similar values which indicate a reproducible sample fabrication.

It can be concluded that FeSi₂ fulfills several requirements of a high temperature Seebeck standard: good spatial homogeneity over a relatively large sample size, thermoelectric properties in a typical range, mechanical stability, low price, non-toxicity as well as thermal stability for the Seebeck coefficient; reproducible fabrication is indicated.

Despite the shown encouraging results for FeSi₂ further experiments are necessary to decide whether the material will be used as high temperature standard material. These include further comparisons between different samples, long-time thermal cycling experiments as well as round-robin measurements.

Summary

We have presented a setup for the concurrent measurement of the electrical conductivity and the Seebeck coefficient. The setup features a large operating temperature regime (300 K – 1000 K), a flexibility in sample geometry as well as easy and fast sample exchange. We have presented details on the hardware of the system as well as the employed data analysis for the determination of the Seebeck coefficient. In order to verify the accuracy of the presented setup we have compared measurement results on the NIST low temperature standard sample as well as other materials in different setups in two different laboratories and can show very good agreement. The system was employed in the search for a possible high temperature standard reference material for the Seebeck coefficient. We have investigated the thermoelectric properties

of β -FeSi₂ and could show good spatial homogeneity as well as thermal stability for the Seebeck coefficient which makes the material a suitable choice as future reference material. A readily available Seebeck standard will increase the trustworthiness of measurement results from thermoelectric materials and thus facilitate progress in material optimization.

Acknowledgements

H. Kolb is acknowledged for the comparative electrical conductivity measurements. Financial support from the BMBF projects INTEG (03X3555A) as well as TEST (03X3550B) is gratefully acknowledged.

Bibliography

- [1] L. E. Bell, *Science* 321, 1457 (2008)
- [2] G. S. Snyder and E. S. Toberer, *Nat. Mater.* 7, 105, (2008)
- [3] S. Iwanaga, E. S. Toberer, A. LaLonde, and G. J. Snyder, *Rev. Sci. Instrum.* 82, (2011)
- [4] A. T. Burkov, A. Heinrich, P. P. Konstantinov, T. Nakama, and K. Yagasaki, *Meas. Sci. Technol.* 12, (2001)
- [5] O. Boffoue, A. Jacquot, A. Dauscher, B. Lenoir, and M. Stölzer, *Rev. Sci. Instrum* 76, 053907, (2005)
- [6] C. Byl, D. Bérardan and N. Dragoe, *Meas. Sci. Technol.* 23, 035603, (2012)
- [7] J. Martin, *Rev. Sci. Instrum.* 83, 065101, (2012)
- [8] P. H. Michael, E. Flage-Larsen, O. B. Karlsen, and T. G. Finstad, *Rev. Sci. Instrum.* 83, 025101, (2012).
- [9] V. Ponnambalam, S. Lindsey, N. S. Hickman, and T. M. Tritt, *Rev. Sci. Instrum.* 77, 073904, (2006)
- [10] J. de Boor and V. Schmidt, *Adv. Mater.* 22, 4303, (2010)
- [11] J. de Boor and V. Schmidt, *Appl. Phys. Lett.* 99, 022102, (2011)
- [12] E. Hansen, *Appl. Sci. Res.* 8, 93, (1960)
- [13] A. Uhlir, *Bell Labs Tech. J* 105, (1955)
- [14] L. Valdes, *P. IRE* 42, 420, (1954)

- [15] F. Smits, *Bell Labs Tech. J* 37, 711, (1958)
- [16] L. J. van der Pauw, *Philips Res. Rep.* 13, 1, (1958)
- [17] N. W. Wong-Ng, NIST, *personal communication*
- [18] P. Ziolkowski, P. Blaschkewitz, G. Karpinski, C. Stiewe, and E. Müller, *European Conference on Thermoelectrics – ECT*, (2011)
- [19] N. D. Lowhorn, W. Wong-Ng, Z.-Q. Lu, J. Martin, M. L. Green, J. E. Bonevich, E. L. Thomas, N. R. Dilley, and J. Sharp, *J. Mater. Res.* 26,1983, (2011)
- [20] E. Lenz, S. Haupt, F. Edler, P. Ziolkowski and H. F. Pernau, „Traceable measurements of electrical conductivity and Seebeck coefficient of Fe_{0.95}Co_{0.05}Si₂ and Ge in the temperature range from 300 K to 850 K,“ *Phys. Stat. Sol.*, 2012, available online, DOI: 10.1002/pssc.201200305
- [21] Z. He, D. Platzek, C. Stiewe, H. Chen, G. Karpinski, and E. Mueller, *J. Alloys Compd.* 438, 303, (2007)
- [22] P. Ziolkowski, G. Karpinski, D. Platzek, C. Stiewe, and E. Mueller ICT 2006, 25th Int. Conf. Thermoelect., 684, (2006)
- [23] J. Martin, T. Tritt, and C. Uher, *J. Appl. Phys* 108, (2010)