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THERMOELECTRIC MATERIALS

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THERMOELECTRICITY

Thermoelectricity describes the reciprocal interaction of temperature and electricity and their conversion into one another. There are three different effects the Seebeck-Effect (Thermoelectric-Effect), the Peltier-Effect and the Thomson-Effect, which describe a reversible interaction between the both values. Nearly always these effects appear together.

Seebeck-Effect

With the Seebeck-Effect, a temperature difference creates an electrical potential along an electric conductor.

The voltage was induced through thermo diffusion currents. With other words, The Seebeck effect is the conversion of temperature differences directly into electricity.

$$U_{\text{Seebeck}} = S \cdot \Delta T$$

S: Seebeck-Koeffizient T: Temperaturdifferenz

$$[U_{\text{Seebeck}}] = \text{V/K}$$

Thomas Johann Seebeck was the discoverer of this effect. He incidentally detected, that between two ends of a metal rod an electric voltage appears, if in the rod is a temperature gradient. With the connecting of both ends an electric current flows, whose magnetic field he detected with a compass needle. 1821 he used this effect for working as a thermoelement.

Peltier-Effect

The Peltier-Effect is the inverted effect as the Seebeck-Effect. An exterior current produce a change of heat transport. This discovery was made 13 years after the Seebeck-Effect from Jean Peltier (1834). This effect appears, if two conductors with different electric heat capacity get in contact with each other and with an exterior current, electrons flow from one conductor to the other.

Thomson-Effect

The Thomson-Effect describes the heating or cooling of a current-carrying conductor with a temperature

gradient. William Thomson (1856) developed this Effect. Any current-carrying conductor (except for a superconductor), with a temperature gradient between two points, will either absorb or emit heat, depending on the material. This effect superposes with the heating of the electric conductor through the current based on the resistivity. Therefore this effect is difficult to detect.

Field of Application

In recent years, thermoelectricity has been increasingly used in applications such as portable refrigerators, beverage coolers, electronic component coolers, and metal alloy sorting devices. Furthermore it is used in thermoelectric generators for waste heat recovery (for example in cars to decrease CO2 emission) and solid state cooling or peltier-elements. Thermoelectric generators (TEG) are available since the early 1960s with a power output range from 10 to 550 W. Some advantages of the TEGs are a high reliability, long service intervals, low maintenance and a long durability. One of the most commonly used materials for such applications is Bismuth telluride (Bi_2Te_3), a chemical compound of bismuth and tellurium.

Thermoelectric Generators

Thermoelectric generators (also called thermogenerators) are devices which convert heat (temperature differences) directly into electrical energy, using a phenomenon called the „Seebeck effect“ (or „thermoelectric effect“). Their typical efficiencies are around 5-10%.

Early thermocouples were metallic, but many more recently developed thermoelectric devices are made from alternating p-type and n-type semiconductor elements connected by metallic interconnects as pictured in the figures below. Semiconductor junctions are especially common in power generation devices, while metallic junctions are more common in temperature measurement. Charge flows through the n-type element, crosses a metallic interconnect, and passes into the p-type element. If a power source is provided, the thermoelectric device may act as a cooler, as in the figure to the left below. This is the Peltier effect, described below. Electrons in the n-type element will move opposite the

direction of current and holes in the p-type element will move in the direction of current, both removing heat from one side of the device. If a heat source is provided, the thermoelectric device may function as a power generator, as in the figure to the right below. The heat source will drive electrons in the n-type element toward the cooler region, thus creating a current through the circuit. Holes in the p-type element will then flow in the direction of the current. The current can then be used to power a load, thus converting the thermal energy into electrical energy.

Figure of Merit

Altinkirch (1909, 1911) showed that good thermoelectric materials should possess large Seebeck coefficients, high electrical conductivity and low thermal conductivity. With this three values were later generated the so called figure of Merit, ZT . ZT is a dimensionless value and is defined as:

$$ZT = \frac{S^2 \cdot \sigma \cdot T}{\lambda}$$

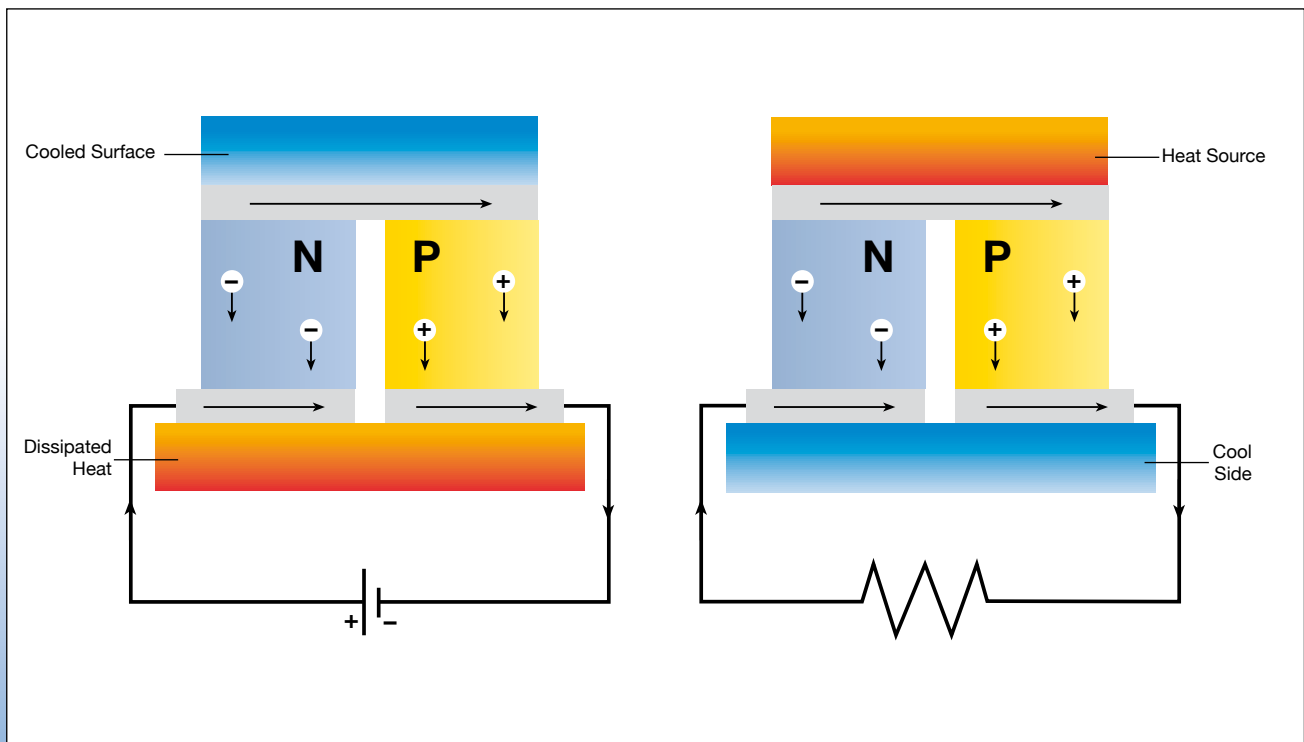
S : Seebeck Coefficient; $[S] = \mu V/K$

σ : Electrical Conductivity; $[\sigma] = 1/\Omega m$

λ : Thermal Conductivity; $[\lambda] = W/mK$

The Figure of Merit is a value for comparing the potential efficiency of devices using different materials.

Actually, the highest value of Z is between 2 to 3. The range of 3 to 4 was considered as a competition to mechanical energy generators.



General

The function of figure of merit shows a physical dilemma: The electric and thermal conductivity can not optimized independent of each other: In metals exclusively the electrons account for the heat transport ($\kappa = \kappa_{el}$). The thermal and the electric conductivity are direct proportional. This shows the Wiedemann-Franz-Law:

$$\kappa = T \cdot L \cdot \sigma$$

L is the Lorenz-constant $(\pi^2/3) \cdot (k_B/e)^2 = 2,45 \cdot 10^{-8} V^2 / K^2$

In an isolator the Heat transport is exclusively determined through the lattice vibrations (phonons) ($\kappa_{ges} = \kappa_{Ph}$). In Semiconductor free charge carrier (p-holes and electrons) and phonons causes the heat transport ($\kappa_{ges} = \kappa_{el} + \kappa_{Ph}$). The input of the phonons to the heat transport is uncoupled from the electrical conductivity.

Materials of interest

For low temperatures:

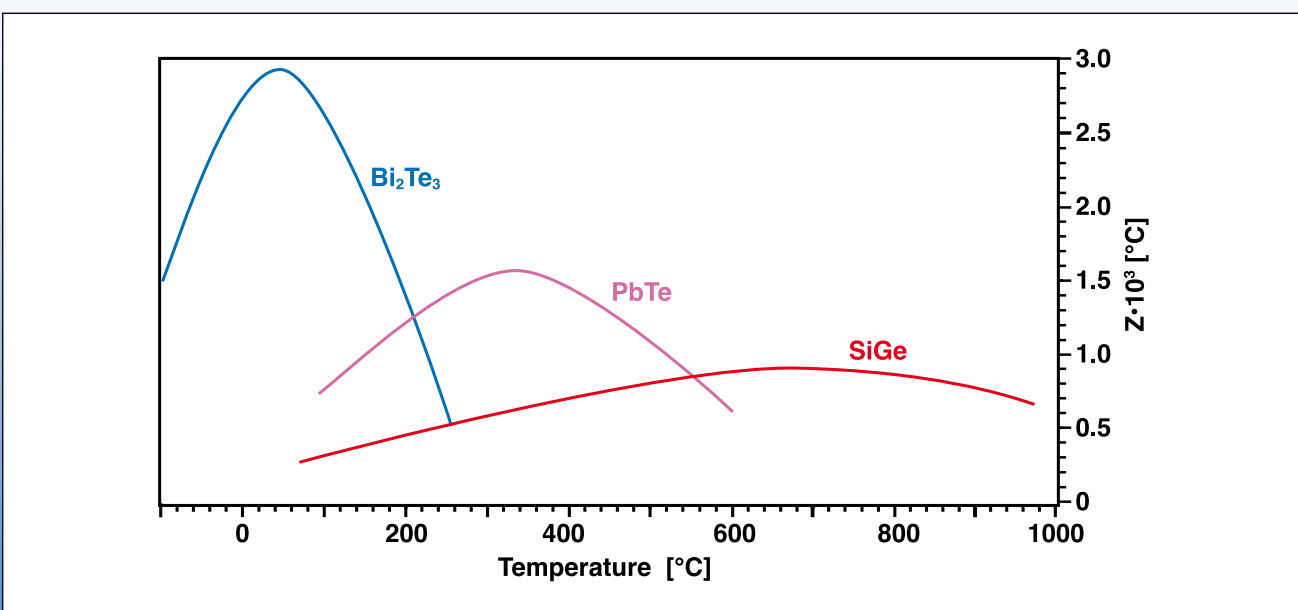
For the operation with low temperatures elements of the V. main group and their alloys (Bi, Sb) are qualified. Bi in the elementary state is a semi-metal. The alloy BiSb is a semiconductor. The optimum $Bi_{0,88}Sb_{0,12}$ has a figure of merit of circa 0.88 to 1.

For room temperature:

For applications around room temperature predominantly V-IV-combinations on the basis of Bi_2Te_3 are used. Bi_2Te_3 is a p-type with Bi overplus and n-type with Te overplus. Bi_2Te_3 - Bi_2Se_3 - Sb_2Te_3 the combinations $Bi_2(Te_{0,9}Se_{0,1})_3$ for n-type and $(Bi_{0,25}Sb_{0,75/2})Te_3$ for p-type are the optimal combinations for a thermoelectric material. This materials offer the best thermoelectric characteristic at room temperature with a temperature independent figure of merit between 0,8 and 1,0.

For high temperature:

For temperatures between 600 and 1200 K PbTe respectively SiGe-alloys are used. PbTe (550 to 800 K) can be easily doped with alkali metals (acceptor, for example Na) respectively halogens (donator, for example I). Also the PbTe shows that solid solutions offer better thermoelectric properties compared with PbTe alone. Within the solid solutions two material groups were developed in the last years: TAGS are compounds from the typ $(AgSbTe_2)_{1-x}(GeTe)_x$ and LAST from the Typ $Ag_{1-x}PbmSbTe_{2+m}$. Materials on the basis of SiGe-alloys (especially $Si_{0,8}Ge_{0,2}$ and $Si_{0,7}Ge_{0,3}$) are used up to 1300 K. Alongside there are more materials developed for the usage as thermoelectric material, for example the skutteride thermoelectrics with the form $(Co, Ni, Fe)(P, Sb, As)_3$. They have a potential for high ZT values due to their high Seebeck-Coefficient and their high electron



To enable advanced research in Thermoelectrics, LINSEIS offers a complete range of instruments for this demanding task. The instruments available involve Seebeck and Electric Resistivity - LSR, Thermal Diffusivity and Thermal Conductivity - LFA, Thermal Expansion and Density - Dilatometer, Specific Heat - DSC.

$$ZT = \frac{S^2 \cdot \sigma \cdot T}{\lambda}$$

S: Seebeck Coefficient; [*S*] = $\mu V/K$

I: Electrical Conductivity; [σ] = $1/\Omega m$

K: Thermal Conductivity; [λ] = W/mK

With the LSR measurement the Seebeck Coefficient can be measured directly. The LSR device can also determine the electric resistivity Q . With the formula $\sigma = 1/\rho$ follows the electrical conductivity ρ .

The thermal conductivity is arranged as followed equation:

$$\lambda = \alpha \cdot \rho_{(density)} \cdot C_p$$

λ : Thermal Conductivity; [λ] = W/mK

α : Thermal Diffusivity; [α] = cm^2/s

$\rho_{(density)}$: Density; [ρ] = g/cm^3

C_p : Specific Heat Capacity; [C_p] = J/gK

With the LFA device the thermal diffusivity R can be directly measured. The density Q follows from the Dilatometer measurement and the value of the specific heat capacity C_p from the DSC measurement.

LSR

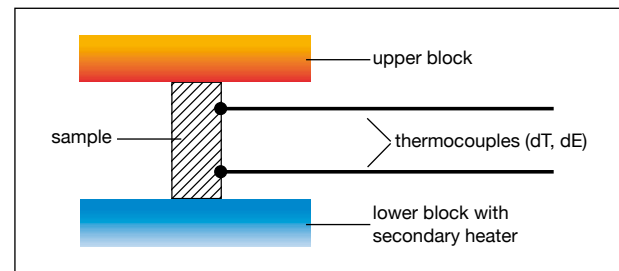
Principal of Measurement

The following picture shows the design of the LSR measurement system. The sample is in a vertical way between the upper and the lower block. The lower block includes a secondary heater that causes a temperature gradient. For the determination of the Seebeck-Coefficient the temperature difference and the thermo-electromotoric force dE (voltage) will be measured. The Seebeck-Coefficient can now be calculated with this formula:

$$S = \frac{dE}{dT}$$

dE : thermo-electromotoric force (Voltage)

dT : temperature difference



Simultaneously the electric resistivity can be measured. Therefore a constant current at both side of the sample is applied. The voltage drop dV minus the thermo-electromotoric force dE subtracted by the current show the resistance.

$$R = \frac{dV - dE}{I}$$

R: Resistance

dV : voltage drop

dE : thermo-electromotoric force

I: current

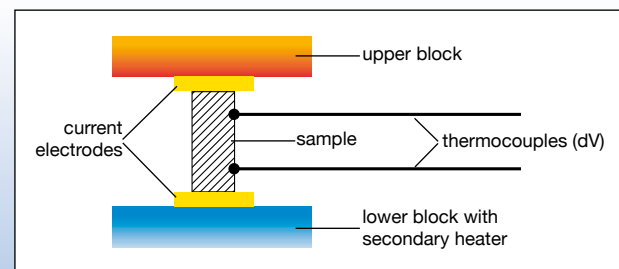
With determination of the sample geometry and the distance of the thermocouples the electric resistivity can be calculated.

$$\rho = R \cdot \frac{A}{d}$$

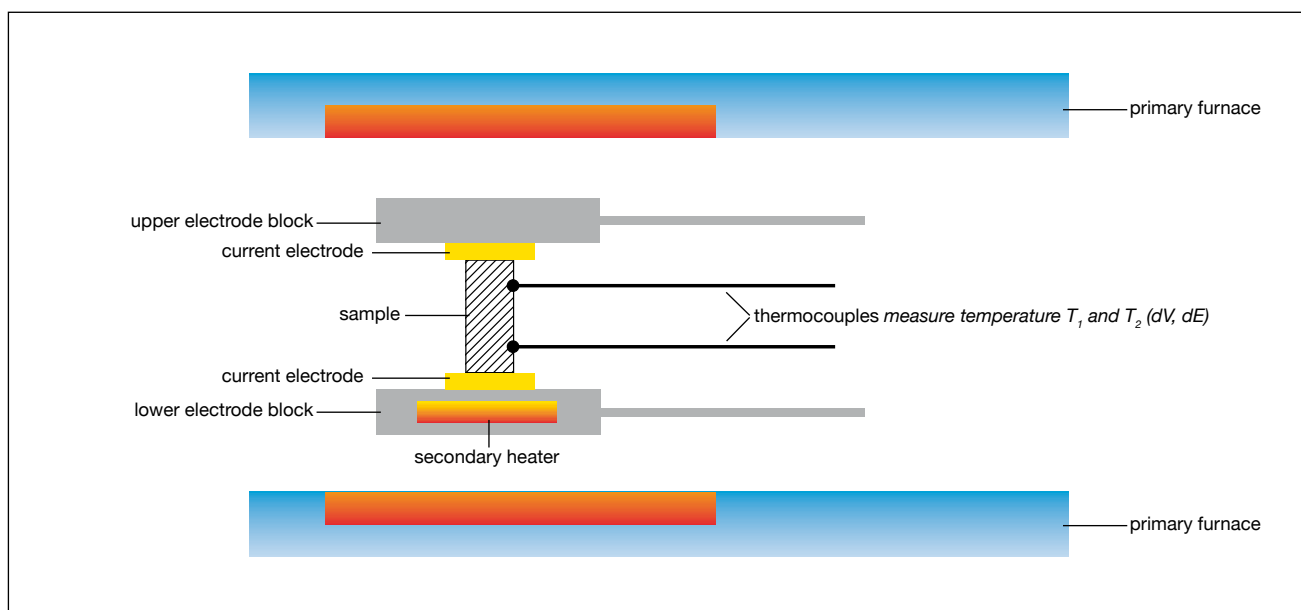
Q: resistivity

A: sample geometry

d: distance of the thermocouples



Therefore the design of the measurement includes the thermocouples the current electrodes, a constant current power supply the upper and lower block. The lower block includes a secondary heater and the whole installation is in a primary furnace.



Specifications

The LINSEIS LSR measures the Seebeck coefficient and the electric Resistivity of a specimen simultaneously. The system can be equipped with either a resistance of an infrared furnace. The entire measurement procedure runs automatically after defining the temperature / measurement steps in the software interface. Measurement Data can be easily exported. State of the art 32-Bit software enables automatic measurement procedures. The design of the sample holder guarantees highest

measurement reproducibility. Wires and Foils can be analyzed with a unique measurement adapter.



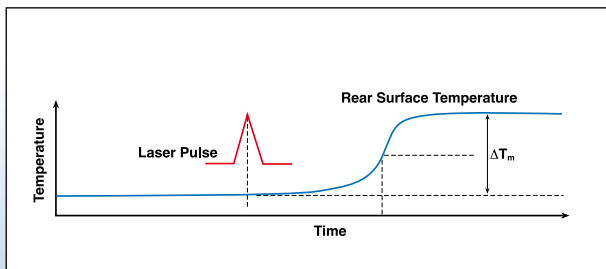
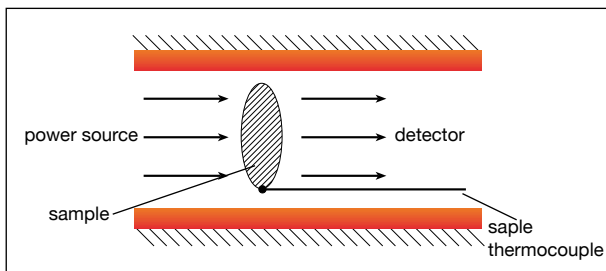
Measurement method	Seebeck-Coefficient: Static dc method Electric Resistance: Four-terminal method
Sample size	2 to 4 mm square or diameter 6 to 22mm long (maximum)
Specimen holder	Horizontal sandwiched between two electrodes
Electrodes	Nickel, Pt/Rh
Atmosphere	Inert, oxid., red., vacuum
Lead intervall	4,6,8 mm
Temperature range	RT to 800 °C; RT to 1100 °C RT to 1500 °C -100 °C to 500 °C
Current source	0 to 160 mA
Accuracy	Seebeck: $\pm 7 \%$ Electric Resistivity: $\pm 10 \%$

LFA

Principal of Measurement

The sample is positioned on a sample robot, located in a furnace. The furnace is then held at a predetermined temperature. At this temperature the sample surface is then irradiated with a programmed energy pulse (laser or xenon flash). This energy pulse results in a homogeneous temperature rise at the sample surface. The resulting temperature rise of the rear surface of the sample is measured by a high speed IR detector and thermal diffusivity values are computed from the temperature rise versus time data. The resulting measuring signal computes the thermal diffusivity, and in most cases the specific heat (C_p) data. If the density (ρ) is identified, the thermal conductivity can be calculated:

$$k(T) = a(T) \cdot c_p(T) \cdot \rho(T)$$

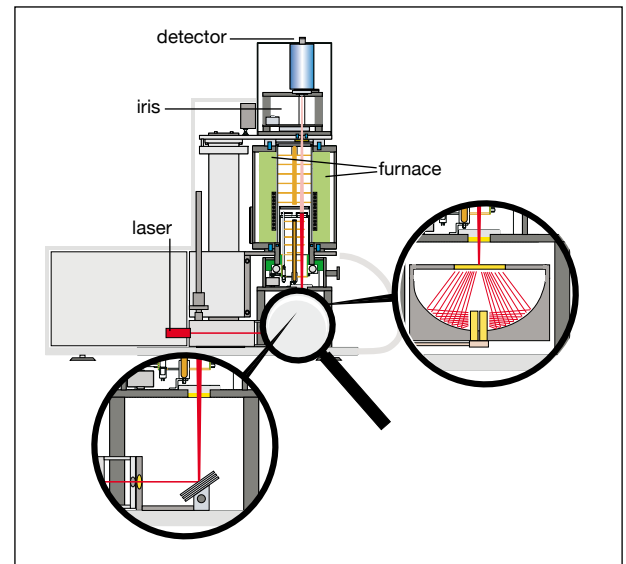


Correspondence with International Standards. The LINSEIS LFA and XFA operate in agreement with national and international standards such as: ASTM E-1461, DIN 30905 and DIN EN 821.

LINSEIS is offering an unparalleled modular system design for this Thermophysical properties Analyzer. It is possible to upgrade the temperature range (exchangeable furnaces/ measuring system) and the detector (InSb/

MCT). This enables the user to start with a cost effective solution and upgrade the system whenever the budget allows or the measurement task requires it.

The whole design of the LFA device is showing in the following picture:



DSC

Differential Scanning Calorimetry (DSC) is most popular thermal analysis technique it measures endothermic and exothermic transitions as a function of temperature. The heat capacity is the amount of the heat required to raise or lower the temperature of a material. Specific heat capacity refers to a specific mass and temperature change for the material (J/g K). With a special test series the specific heat capacity can directly measured.

The instrument is used to characterize polymers, pharmaceuticals, foods/biologicals, organic chemicals and inorganics. Transitions measured include T_g, melting, crystallization, curing and cure kinetics, onset of oxidation and heat capacity.

The LINSEIS Differential Scanning Calorimeters (DSC) operate in agreement with national and international standards such as: ASTM C 351, D 3417, D 3418, D 3895, D 4565, E 793, E 794, DIN 51004, 51007, 53765, 65467, DIN EN 728, ISO 10837, 11357, 11409



DIL

Dilatometry (DIL) is a technique in which a dimension of a substance under negligible load is measured as a function of temperature while the substance is subjected to a controlled temperature program in a specified atmosphere.

Certainly LINSEIS Dilatometers comply with all national and international standards related to thermal expansion measurements, such as: ASTM E228, E289, E831, D696, D3386, DIN ISO 7991, DIN EN 821, DIN 51045



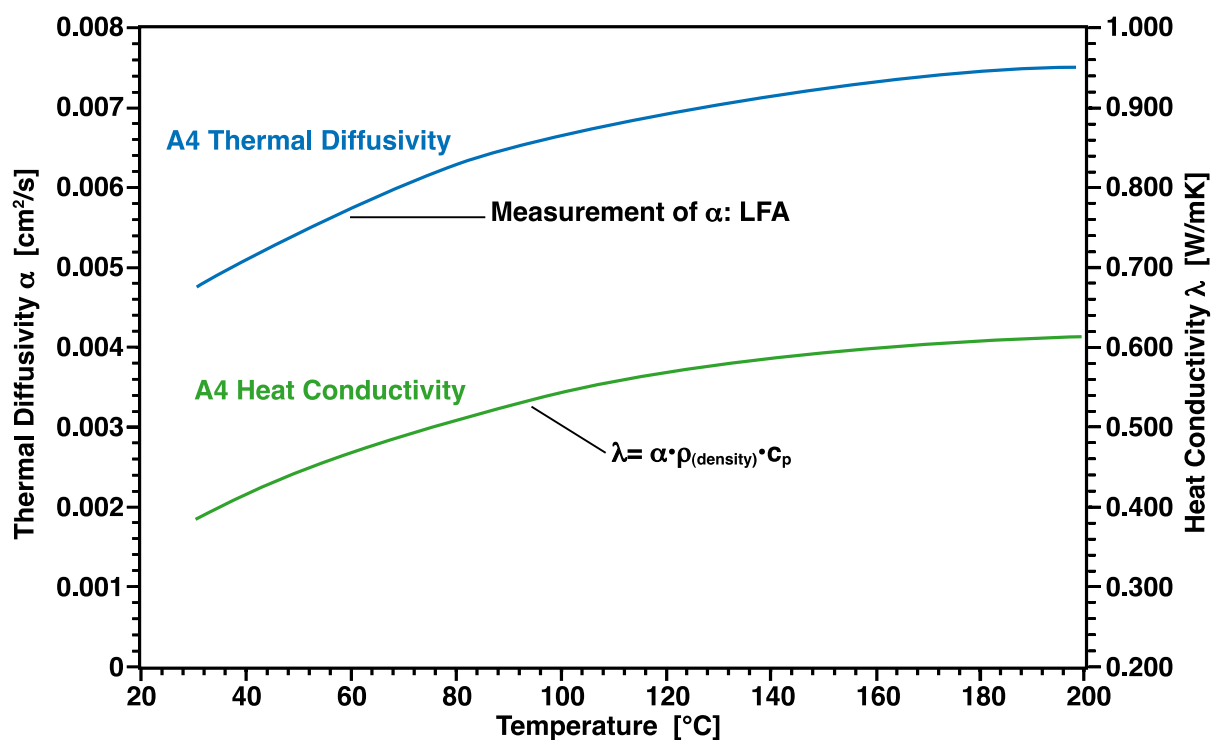
EXAMPLE

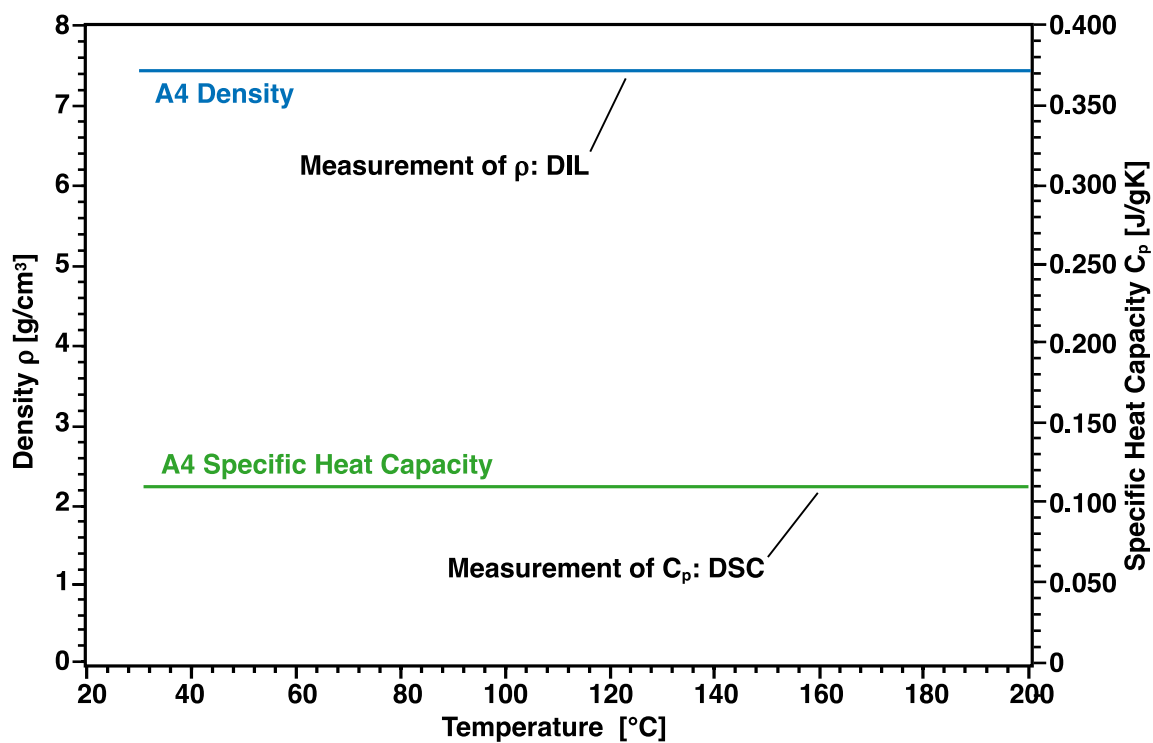
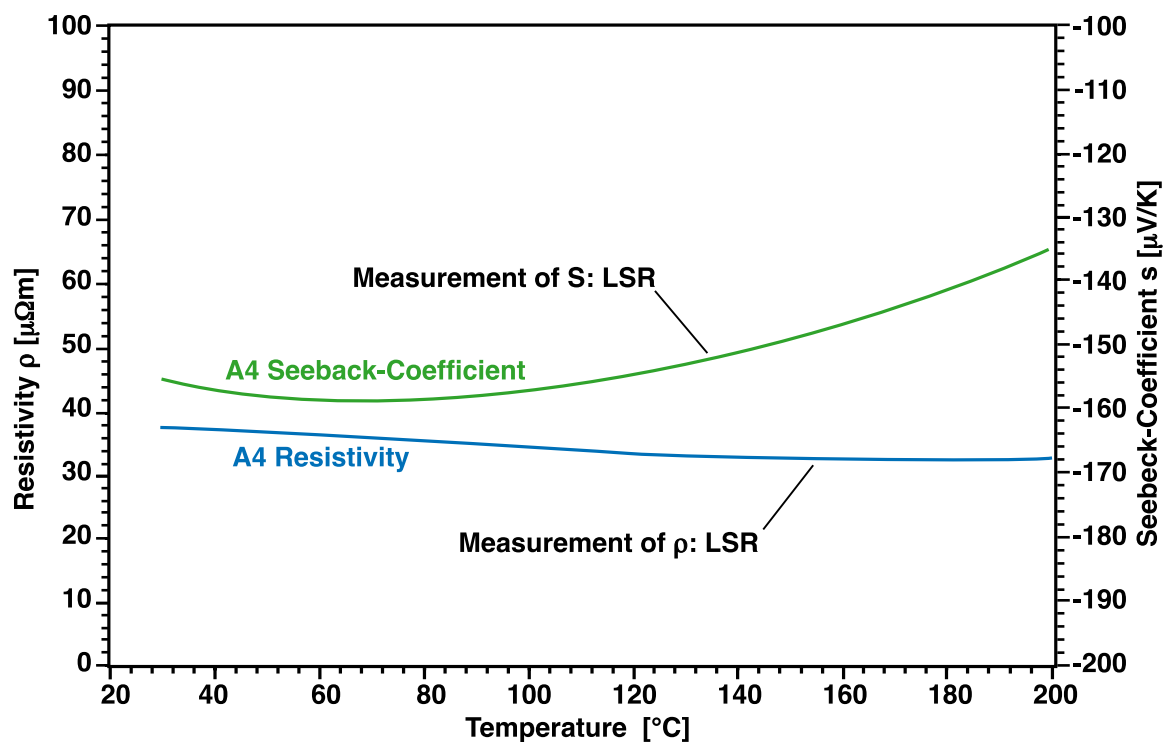
Measurement of a sample of the tellur family

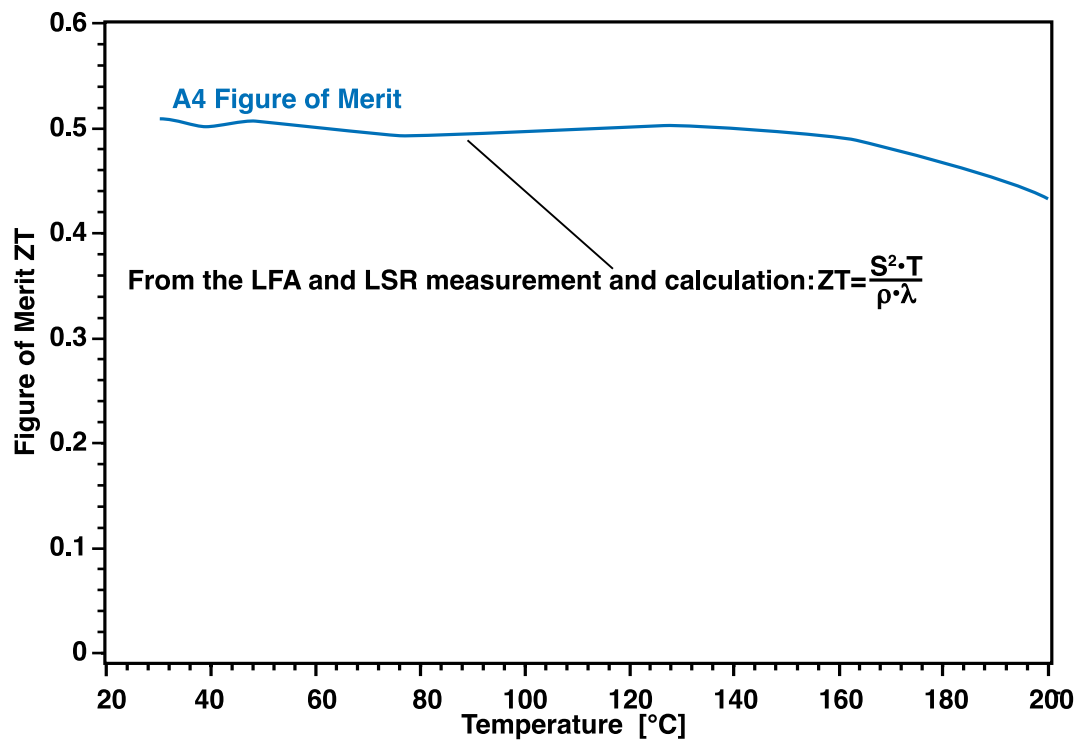
A batch of samples of the tellur family enriched with bismuth and antimony ($(\text{BiSb})_2\text{Te}_3$) was evaluated. As an example this can be a test series with changes in the chemical mixture and changes in the way the samples are manufactured. With the determination of the figure of merit one can evaluate which change of chemical mixture or which change in the production process generates the best figure of merit. The first diagram shows the thermal diffusivity R and the heat conductivity K

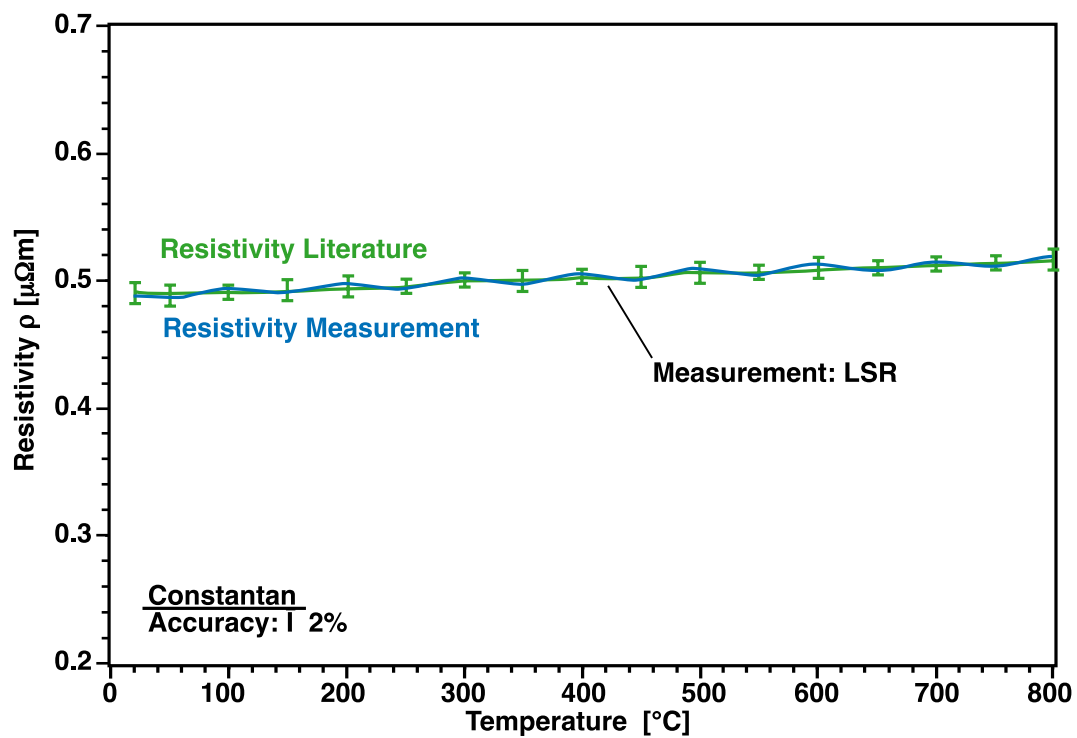
in relation to temperature. The thermal diffusivity can directly be measured with the LFA (Laser Flash system), and with the density (from the Dilatometer measurement) and the specific heat C_p (from the DSC measurement) the heat conductivity λ can be calculated.

The second diagram shows the resistivity ρ and the Seebeck-Coefficient S of the LSR measurement. In the third diagram the results of the Dilatometer measurement (density) and of the DSC Measurement (C_p) are displayed. And in the fourth diagram the figure of merit is calculated.





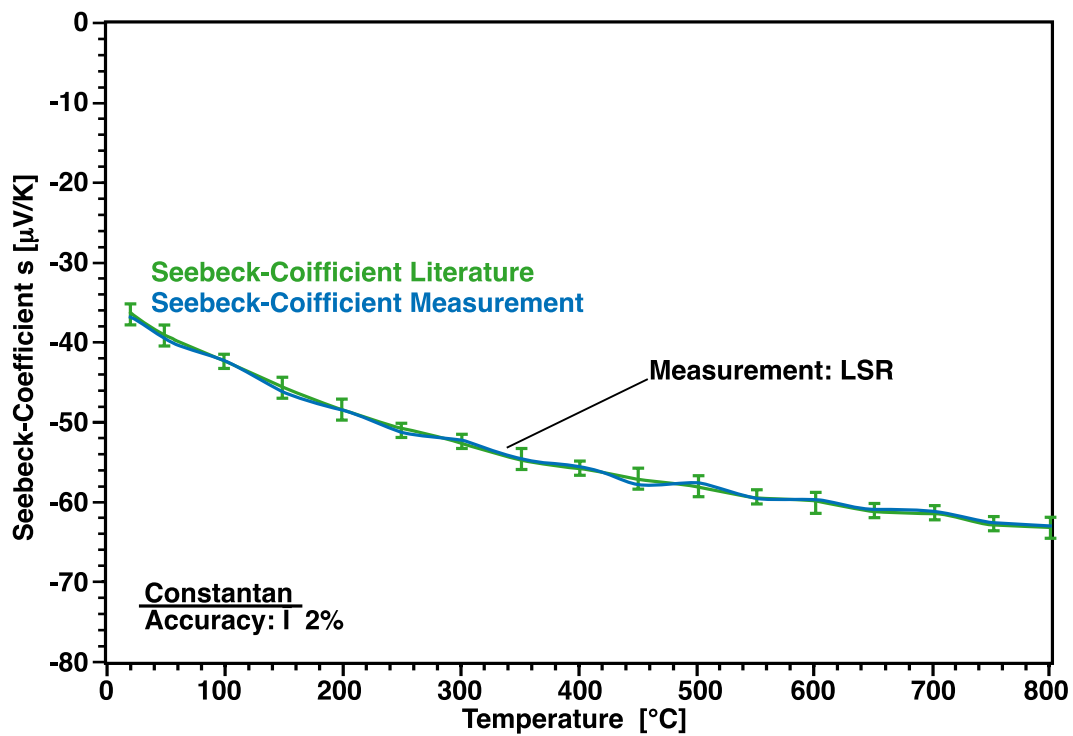




Accuracy Resistivity: Constantan Sample

Presented here is the Electric Resistivity measurement result from a Constantan Sample, measured with an

LSR-3/800. Additionally shown are literature values for this material. It can clearly be seen that the measurement results is in agreement with the corresponding literature data within 2%.



Accuracy Seebeck: Constantan Sample

Presented here is the Seebeck measurement result from a Constantan Sample, measured with an

LSR-3/800. Additionally shown are literature values for this material. It can clearly be seen that the measurement results is in agreement with the corresponding literature data within 2%.



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