NETZSCH

Analyzing & Testing

Thermoelectric Materials

Material Characterization, Phase Changes, Thermal Conductivity

Leading Thermal Analysis

Thermoelectricity – Figure of Merit (*ZT*), Thermoelectric Cooling and Generation

Thermoelectricity – Thermoelectric Materials and Devices

Thermoelectricity refers to a class of phenomena in which a temperature difference creates an electric potential or an electric potential creates a temperature difference. In modern technical usage, the term refers collectively to the Seebeck effect, Peltier effect, and the Thomson effect. Various metals and semiconductors are generally employed in these applications. One of the most commonly used materials in such applications is bismuth telluride (Bi_2Te_3).

Over recent decades, efforts have been made to improve the efficiency of thermal processes and the output energy of thermal engines. One approach is to generate electrical energy from heat which has been released to the environment. For such applications, thermoelectric materials with high working temperatures and optimized efficiency need to be developed.

Very often, accurate knowledge of certain thermal properties such as thermal stability, thermal diffusivity or thermal conductivity is of paramount importance in the application of these new materials. Measurements are necessary to resolve problems regarding a variety of issues, such as heat transfer within a given structure or the formation of thermally-induced stresses between two different materials which are in contact with each other.

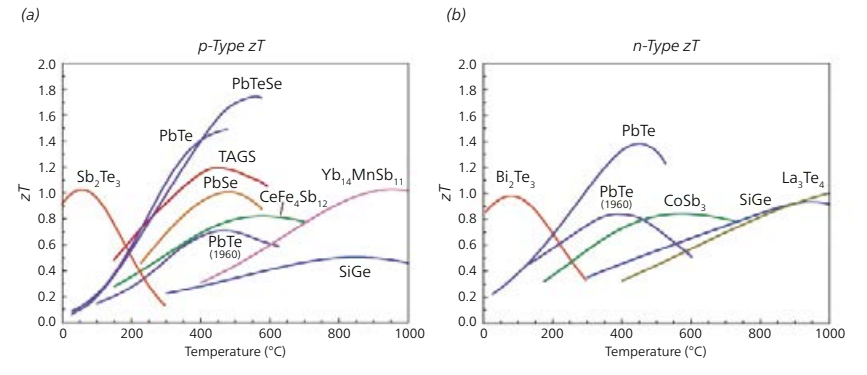
Figure of Merit

Beneficial thermoelectric materials should possess high Seebeck coefficients, high electrical conductivity and low thermal conductivity. A high electrical conductivity is necessary to minimize Joule heating, while a low thermal conductivity helps to retain heat at the junctions and maintain a high temperature gradient. These three properties all factor into what is known as the "figure of merit", *Z*. Since *Z* varies with temperature, a useful dimensionless figure of merit can be defined as *ZT*. The dimensionless figure of merit is calculated as follows:

$$ZT = \left(\frac{S^2\sigma}{\lambda}\right)T$$

where:
S = Seebeck coefficient or thermo power [μV/K]
σ = electrical conductivity [1/(Ωm)]
λ = total thermal conductivity [W/(m·K)].

ZT is a very convenient figure for comparing the potential efficiency of devices constructed of different materials. Values of *ZT* = 1 are considered good, but values in at least the 3-4 range would be considered essential in order to be competitive in terms of efficiency with regards to mechanical energy generation and refrigeration. To date, however, such values have not been achieved; the best reported *ZT* values have been in the 2-3 range.



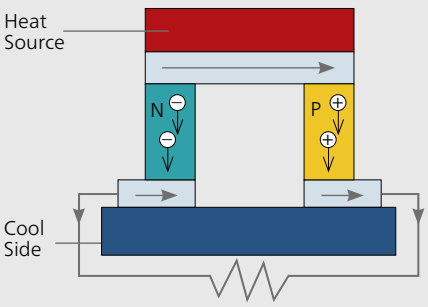
Approximate figure of merit (*ZT*) for various p-type and n-type thermoelectric materials.
Source: G. Jeffrey Snyder, California Institute of Technology
http://thermoelectrics.caltech.edu. Reproduced with permission.

Thermoelectric Generation

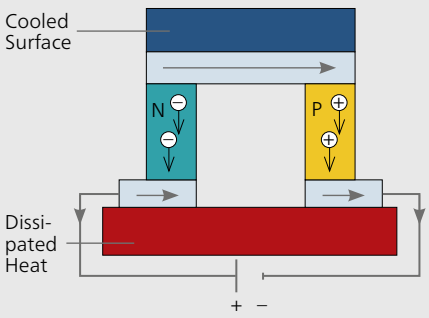
The simplest thermoelectric generator consists of a thermocouple (thermopile) comprising a p-type and an n-type semiconductor connected electrically in series and thermally in parallel. Heat is pumped into one side of the couple and discharged from the opposite side. An electrical current is produced which is proportional to the temperature gradient between the hot and cold junctions.

Thermoelectric Cooling

If an electric current is applied to the thermocouple as shown, heat is pumped from the cold junction to the hot junction. The cold junction will rapidly drop below ambient temperature provided heat is removed from the hot side. The temperature gradient will vary according to the magnitude of generation current applied (Seebeck effect).



Principle of thermoelectric generation
(Seebeck effect)



Principle of thermoelectric cooling
(Peltier effect)

Thermophysical Properties – Laser Flash Method and Models

Thermoelectric Materials – The Focal Point for Energy Savings

Novel thermoelectric materials have already resulted in a new consumer product: a simple, efficient way of cooling car seats in hot climates. The devices, similar to the more familiar car seat heaters, provide comfort directly to the individual rather than cooling the entire car, saving on air-conditioning and energy costs.

To optimize a thermoelectric device, its thermal properties must be known. The thermal conductivity (analyzed with LFA) is directly related to the efficiency of a thermoelectric material.

The thermal stability (analyzed with TGA or DSC) yields information on the maximum service temperature.

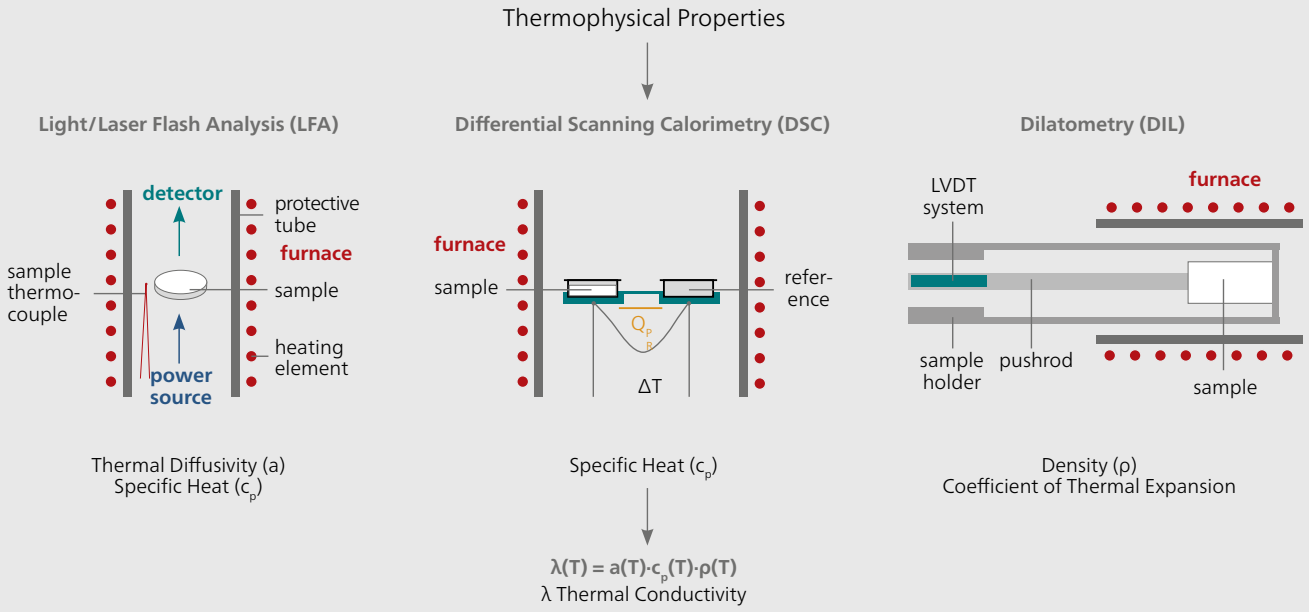
Differential scanning calorimetry (DSC) can further be used for the analysis of phase transitions or the specific heat capacity (c_p).

Finally, DIL or TMA methods are used to characterize the thermal and volumetric expansion of materials and their density change, allowing for the analysis and prediction of thermal stresses in a real device.

Determination of Thermophysical Properties

The world is turning its eye to the study of thermoelectric energy. Thermoelectric energy conversion is an environmentally friendly solid-state technology with many promising applications. One of the more straightforward of these lies in waste-heat recovery in cars and trucks; the energy now being lost from hot engines could save billions of dollars if captured and converted into electricity.

Research into the electrical and thermophysical properties of new materials could reduce the world's reliance and overdependence on fossil fuels and has shown promise with two classes of materials: low-dimensional systems for enhanced electrical properties and materials with increased phonon scattering which leads to inherently low thermal conductivity.



Light/Laser Flash Method

The LFA method is illustrated in the figure on page 4, on the left. The front surface of a plane-parallel sample is heated by a short light or laser pulse. The resulting temperature rise on the rear surface is measured versus time using an IR detector. The thermal diffusivity (a) and in most cases also the specific heat (c_p) can be determined from the measured signal.

If the density (ρ) is known, the thermal conductivity (λ) can be determined as follows:

$$\lambda(T) = a\,(T) \cdot c_p(T) \cdot \rho(T)$$

where:
λ = thermal conductivity [W/(m·K)]
ρ = bulk density [g/cm³]
c_p = specific heat [J/(g·K)].

LFA Analysis Information

The Laser Flash (LFA) technique is a fast, non-contact, absolute method for determining a complete set of thermophysical properties, including thermal diffusivity, specific heat capacity and thermal conductivity. This data can then be used:

- As input data for numerical simulations
- For optimization of thermoelectric materials with low lattice conductivity and a high figure of merit.

LFA 467 *HyperFlash*

The LFA 467 *HyperFlash* is a Xenon flash-based system with a compact design. It covers the temperature range from -100°C to 500°C. A variety of cooling options allow for measurements to be carried out across the full temperature range of the instrument without having to change either the furnace or the detector.

The integrated automatic sample changer allows for unattended analyses on up to 16 samples. The gas-tight design minimizes the risk of oxidation for measurements on oxygen-sensitive samples.

The very high sampling rate and the unmatched *ZoomOptics* make for a broad application range, even for thin samples.

LFA 467 *HyperFlash*

LFA for Fast and Reliable Thermal Diffusivity Measurements on Small and Thin Samples – LFA Software

LFA 457 *MicroFlash*®

LFA 457 *MicroFlash*®

The LFA 457 *MicroFlash*® incorporates the latest state-of-the-art technology for laser flash systems. This bench-top instrument allows for measurements from -125°C to 1100°C using two different interchangeable furnaces. The temperature increase on the back surface of the sample can be measured at very low sub-ambient temperatures thanks to the innovative infrared sensor technology.

The instrument accommodates both smaller and larger sample sizes (of up to 25.4 mm in diameter) and with the integrated sample changer, measurements can be run on several samples at the same time.

The vacuum-tight design allows for tests under defined atmospheres. The vertical arrangement of the sample holder, furnace and detector facilitates sample placement and simultaneously guarantees an optimum signal-to-noise ratio for the detector signal.

LFA 427

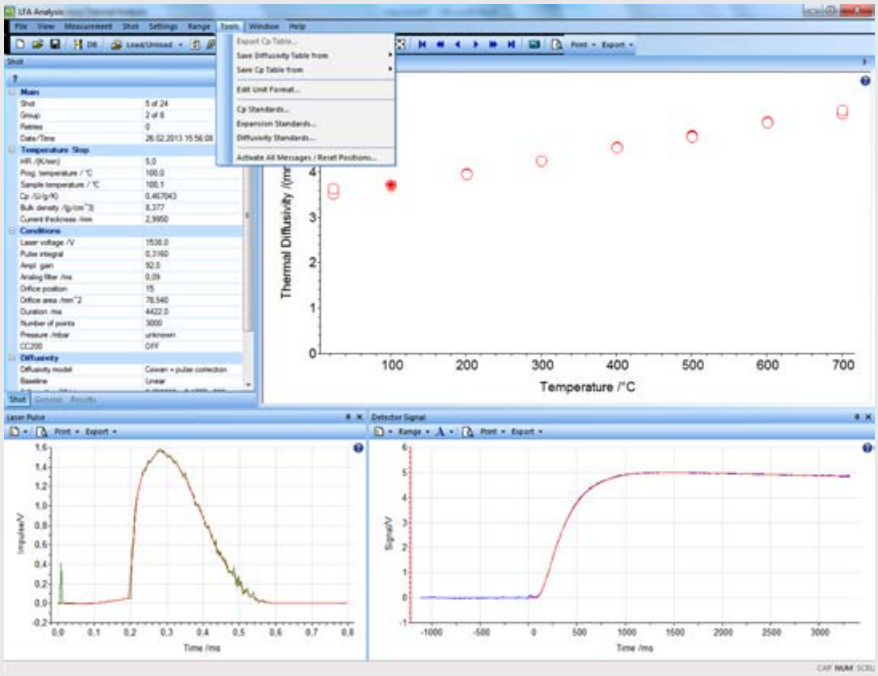
LFA 427

The vacuum-tight LFA 427 is our most powerful and versatile LFA system, ideal for any application involving the characterization of standard and high-performance materials. The LFA 427 guarantees high precision and reproducibility, short measurement times and defined atmospheres over the entire application range from -120°C to 2800°C. The laser, sample and detector are configured in such a way as to function without the use of any mirrors.

The laser power, pulse width, gas and vacuum functions can all be set variably over a wide range, making it possible to effectuate optimum measurement conditions for a great variety of sample properties.

LFA Software

The Laser Flash systems run under *Proteus*® software on a Windows® operating system. The combination of easy-to-understand menus and automated routines makes this software very user-friendly while still allowing for sophisticated analysis. The LFA software includes:



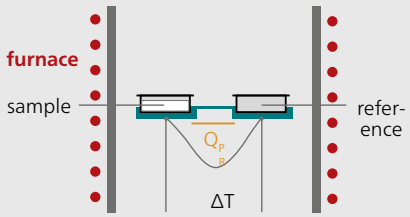
LFA software including heat loss and pulse length correction.

- Calculation models for thermal diffusivity:
  - Adiabatic
  - Cowan
  - Improved Cape-Lehman (via consideration of multi-dimensional heat loss and non-linear regression)
  - 2-/3-layer models (analysis by means of non-linear regression and consideration of heat loss)
  - In-plane
  - Radiation correction (for transparent and semi-transparent samples)
  - Heat-loss corrections
  - Accurate pulse length correction, patented pulse mapping (patent no.: US7038209B2; US20040079886; DE1024241)
  - Baseline correction
- Determination of contact resistance in multi-layer systems
- Ability to average shots at the same temperature level
- Approximation of shots as a curve via various mathematical functions (polynomials, splines, etc.)
- Model wizard for selecting the optimum evaluation model
- Definition of an arbitrary number of temperature levels and number of shots per level
- Determination of specific heat by means of a comparative method and standard samples
- Integrated database

Thermal Analysis – DSC and STA; Coupling to Evolved Gas Analysis

Heat Flow DSC Method

Based on a homogeneous temperature field in the DSC furnace, equal heat flows along the disc-shaped sensor are directed to the sample and reference crucibles. If the heat capacities on the sample and reference sides differ, or if the sample shows a changed heat absorption or resulting difference in heat flow causes temperature gradients at the sensor. Sensitive sensors record these temporary deviations, which are then depicted as either exothermal peaks, endothermal peaks or steps in the differential heat flow curves.



Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is one of the most frequently employed Thermal Analysis methods. It can be used to analyze nearly any energetic effect occurring in a solid or liquid during thermal treatment.

For standard applications between -180°C and 700°C, the easy-to-use DSC 204 ***F1*** *Phoenix*® can be used.

Our other models, the vacuum-tight DSC 404 ***F1/F3*** *Pegasus*® systems, are designed for the precise determination of the specific heat capacity of high-performance materials under defined atmospheres. They can be configured for different furnace and sensor types and are easily interchanged by the user to cover a broad temperature range from -150°C to 2000°C.

Thermogravimetric Analysis and Simultaneous Thermal Analysis

Simultaneous Thermal Analysis (STA) refers to the simultaneous application of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) to one and the same sample in a single instrument. The test conditions are of course identical for the two signals, since they share the same atmosphere, heating rate, thermal contact to the sample crucible, etc. The sample throughput is also improved, as more information is gathered from each test run.

The STA 449 ***F1/F3*** *Jupiter*® systems are designed for measurements in the temperature range from -150°C to 2400°C. Various interchangeable TGA, DTA and DSC sensors and furnaces make these vacuum-tight models to one of our most popular products.

DSC 204 ***F1*** *Phoenix*®

STA Analysis Information Combines Analysis Information from DSC and TGA

DSC Analysis Information

- Specific heat capacity (c_p)
- Melting/crystallization behavior
- Solid-solid transitions
- Polymorphism
- Degree of crystallinity
- Glass transitions
- Cross-linking reactions
- Oxidative stability
- *Purity Determination*
- DSC data as base for thermokinetic analysis (NETZSCH *Thermokinetics* software program)

TGA Analysis Information

- Mass changes
- Temperature stability
- Oxidation/reduction behavior
- Decomposition
- Corrosion studies
- Compositional analysis
- TGA data as base for thermokinetic analysis (NETZSCH *Thermokinetics* software program)

Standards

Our DSC and STA systems are designed in accordance with the majority of instrument and application standards for DSC and TGA systems, including: ISO 11357, ISO 11358, ASTM E967, ASTM E968, ASTM E793, ASTM D3895, DIN 51004, DIN 51006, DIN 51007.

Coupling to Evolved Gas Analysis

First-rate research and characterization can be achieved by coupling thermo-analytical instrumentation for TGA, DSC, STA, TMA or DIL to a mass spectrometer (MS), gas chromato-graph-mass spectrometer (GC-MS) or Fourier Transform Infrared spectrom-eter (FT-IR). These techniques can also include simultaneous coupling of the MS and FT-IR or GC-MS and FT-IR to the thermal analyzer. The unique adapter allows for coupling even when used in combination with an automatic sample changer.

For molecules which are highly condensable (e.g., metal vapors), the STA 409 CD with *SKIMMER*® system is available, which allows for maximum temperatures of either 1450°C or 2000°C.

Coupling Analysis Information

- Compositional analysis
- Evaporation/sublimation
- Decomposition/thermal stability
- Pyrolysis/combustion
- Solid-gas reactions
- Desorption/absorption

STA 449 ***F1*** *Jupiter*® coupled to QMS 403 C *Aëolos*®

STA 409 CD with *SKIMMER*®

Thermal Analysis – DIL and TMA

Dilatometry and Thermomechanical Analysis

Dilatometry (DIL) is used to measure the expansion or shrinkage of solids, powders, pastes or liquids under negligible load. It is closely related to thermomechanical analysis (TMA), which determines dimensional changes under a defined mechanical force.

We offer dilatometer systems for measurements in the temperature range between approx. -260°C and 2800°C.

For the investigation of thermoelectric materials, either our DIL 402 C or our dual/differential DIL 402 CD (-180°C to 2000°C) may be used. The specific needs of this application field are served by our interchangeable furnaces, protective tubes, and pushrods made of a variety of materials.

The TMA 402 ***F1*** and ***F3*** *Hyperion*® are based on a modular concept, with interchangeable furnaces covering the temperature range from -150°C to 1550°C. The broad range of force can be varied between -3 N and 3 N.

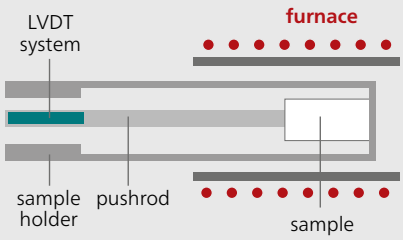
Dilatometer Method

In dilatometry, dimensional changes are determined versus temperature or time while the sample is subjected to a controlled temperature program. The degree of expansion divided by the change in temperature is called the material's coefficient of expansion (α) and generally varies with temperature.

$$\alpha = \frac{1}{L_0}\left(\frac{\Delta l}{\Delta T}\right)$$

where:
α = coefficient of expansion
L_0 = initial sample length
Δl = change in length
ΔT = change in temperature.

A pushrod is positioned directly against the sample and transmits the length change to a linear variable displacement transducer (LVDT). As the sample length changes during the temperature program, the LVDT core is moved, and an output signal proportional to the displacement is recorded. The temperature program is controlled using a thermocouple located either next to the heating element of the furnace or next to the sample.



Dilatometry (DIL)

DIL 402 C

TMA Method

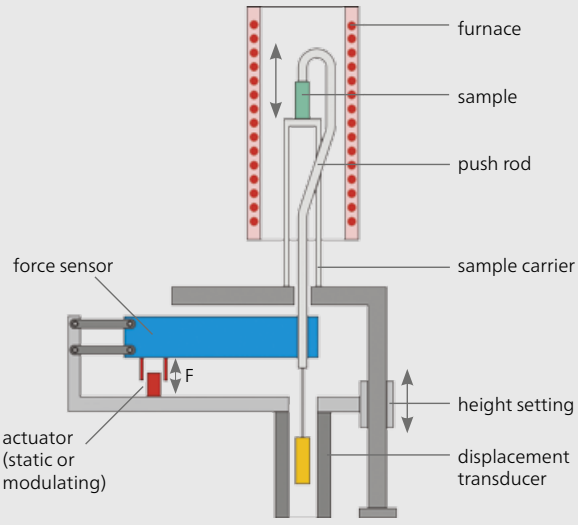
Irrespective of the selected type of deformation (expansion, compression, penetration, tension or bending), any length change in the sample is communicated to a highly sensitive inductive displacement transducer (LVDT) via a pushrod and transformed into a digital signal. The pushrod and corresponding sample holders of fused silica or aluminum oxide can be quickly and easily changed out to optimize the system to a given application.

DIL and TMA Analysis Information

- Linear thermal expansion
- Coefficient of thermal expansion (CTE)
- Volumetric expansion
- Shrinkage steps
- Glass transition temperature
- Phase transitions
- Sintering temperature/sintering step
- Density change
- Softening points
- Influence of additives/raw materials
- Decomposition temperature
- Anisotropic behavior
- Caloric effects by using c-*DTA*®
- DIL/TMA data as base for thermokinetic analysis (NETZSCH *Thermokinetics* software program)

Standards

All NETZSCH dilatometer and thermomechanical instruments are designed in accordance with standards such as DIN EN 821, DIN 51045, ASTM E831, ASTM E228, ASTM D696, ASTM D3386, ISO 11359 -Part 1 to 3.



Thermomechanical Analysis (TMA)

TMA 402 ***F1*** *Hyperion*®

Targeting Low-Lattice Conductivities for Increased Figure of Merit, *ZT*

Nanostructured bulk thermoelectrics have an enhanced thermoelectric figure of merit (*ZT*). The thermal conductivity is reduced due to phonon scattering at nanoscale interfaces.

The thermal diffusivity (a), density (ρ), and specific heat (c_p) are measured and used to calculate the total thermal conductivity using the formula:

$$\lambda = a \cdot \rho \cdot c_p.$$

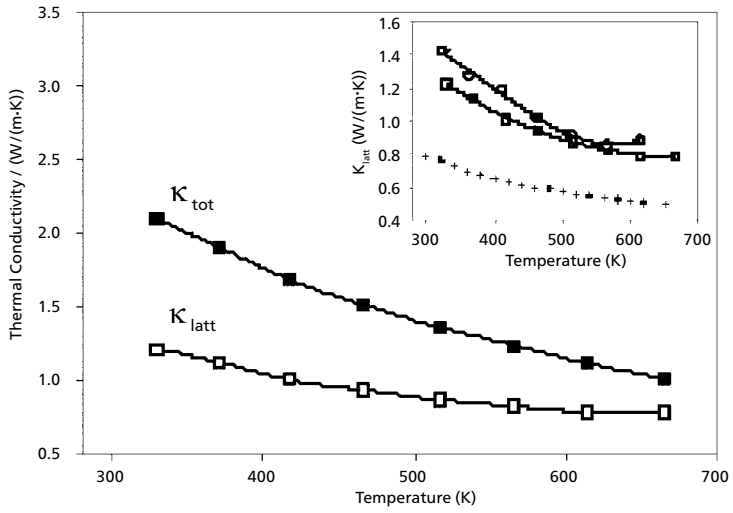
The lattice thermal conductivity is then calculated from:

$$\lambda_{lattice} = \lambda_{total} - \lambda_{elec}.$$

The contribution to thermal conductivity by charge carriers is described by the Wiedemann-Franz Law:

$$\lambda_{elec} = L_0 \cdot \sigma \cdot T$$

where L_0 is the Lorenz number and σ the electrical conductivity.



$Ag_{1-x}Pb_{18}MTe_{20}$ (M = Bi, Sb); published by Kanatzidis et al., Northwestern University, IL, USA [1]. Measurements were carried out using the NETZSCH LFA 457 *MicroFlash*®. The typical sample dimension with a diameter of 12.7 mm and thickness of 2 mm was used.

Thermal Conductivity and Separated Lattice Conductivity of $Ag_{1-x}Pb_{18}MTe_{20}$

This plot shows measurements carried out on $Ag_{1-x}PbMTe_{20}$ (M=Bi, Sb) in the temperature range from 150°C to 370°C. The lattice conductivity can be calculated from the measured thermal conductivity. Here, the temperature dependence of the total thermal conductivity (λ_{tot}, ■) and lattice thermal conductivity (λ_{latt}, □) of $AgPb_{18}BiTe_{20}$ is illustrated.

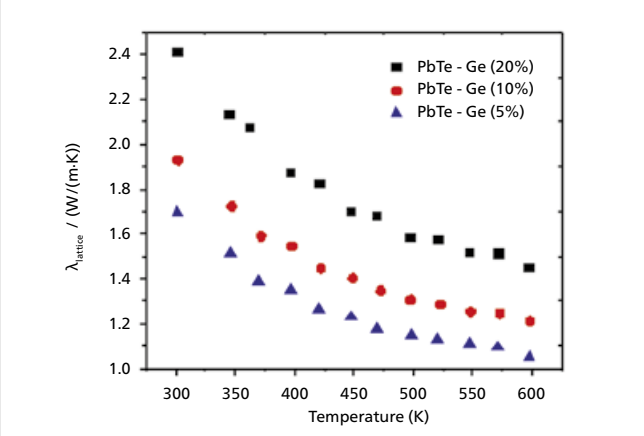
The inset indicates the temperature dependence of the lattice thermal conductivity of $Ag_{1-x}Pb_{18}BiTe_{20}$ (x = 0, 0.3), compared with the lattice thermal conductivity (λ_{latt}) of $AgPb_{18}BiTe_{20}$ (presented in + symbol).

[1] Han, M.K.; Hoang, K.; Kong, H.; Pcionek, R.T.; Uher, C.; Paraskevopoulos, K.M.; Mahanti, S.D.; Kanatzidis, M.G., Chemistry of Materials (2008), 20(10), 3512-3520

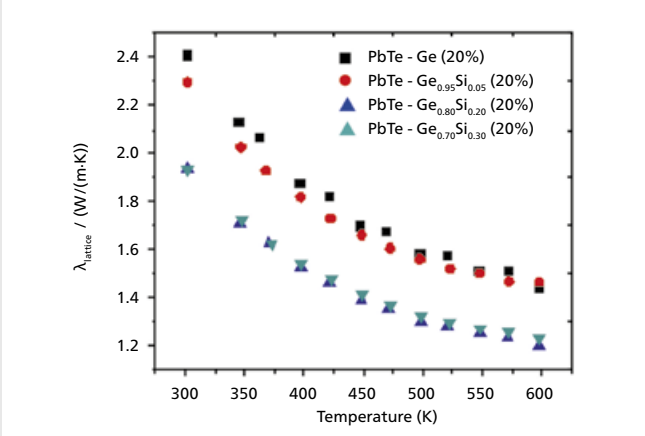
PbTe-Ge and PbTe-$Ge_{1-x}Si_x$

In the lead telluride materials PbTe-Ge and PbTe-$Ge_{1-x}Si_x$ the thermal conductivity is easily tuned by alloying Ge with Si and reducing the Ge content [2]. The results shown below are obtained in the temperature range between 25°C and 320°C.

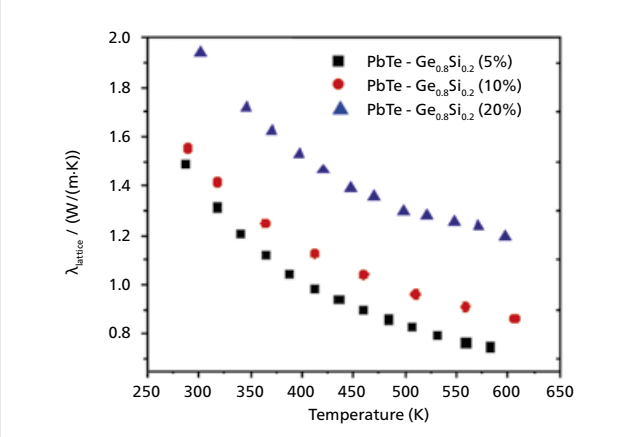
Plot A shows that Ge has a significant influence on the lattice conductivity of PbTe. With a decreasing Ge content, the lattice conductivity decreases over the entire temperature range. In addition, by alloying Ge with Si of the PbTe-Ge (20%) composition, a further reduction of the lattice conductivity can be observed (plot B). Similar behavior can be seen by keeping a constant mixing ratio of Ge and Si while decreasing $Ge_{0.8}Si_{0.2}$ content (plot C). Plot D shows that an amount of 5% Ge-/Ge-Si achieves an optimum lattice thermal conductivity.



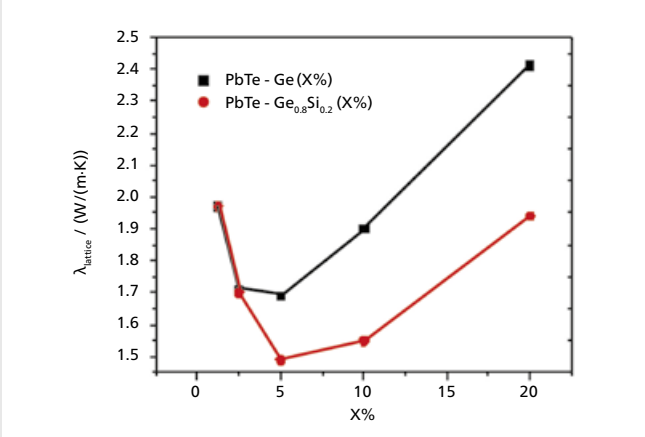
A) Lattice Thermal Conductivity of PbTe-Ge (5%, 10%, 20%); LFA 457 *MicroFlash*® measurements.



B) Lattice thermal conductivity of PbTe-$Ge_{1-x}Si_x$ (20%); LFA 457 *MicroFlash*® measurements.



C) Lattice Thermal Conductivity of PbTe-$Ge_{0.8}Si_{0.2}$; LFA 457 *MicroFlash*® measurements.



D) Lattice Thermal Conductivity of PbTe-Ge and PbTe-$Ge_{0.8}Si_{0.2}$ under increasing $Ge_{0.8}Si_{0.2}$ content; LFA 457 *MicroFlash*® measurements.

[2] Sootsman, Joseph R.; He, Jiaqing; Dravid, Vinayak P., Li, Chang-Peng; Uher, Ctirad; Kanatzidis, Mercouri G. High Thermoelectric Figure of Merit and Improved Mechanical Properties in Melt Quenched PbTe – Ge and PbTe – $Ge_{1-x}Si_x$ Eutectic and Hyper-eutectic Composites, J. Appl. Phys. (2009), 105, 083718.

Applications – Skutterudite with Nanoparticles, Thermal Expansion and Specific Heat of Bismuth Telluride

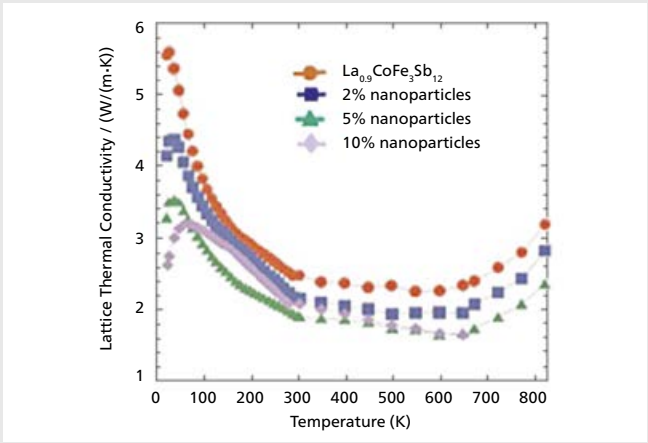
Skutterudite Thermoelectrics

Cubic skutterudite materials of the form $(Co,Ni,Fe)(P,Sb,As)_3$ have a potential for high *ZT* values due to their high electron mobility and high Seebeck coefficient. Unfilled $CoSb_3$-based skutterudites are disadvantaged by their inherently high thermal conductivity, which lowers their *ZT* value. However, these materials contain voids into which low-coordination ions (usually rare earth elements) can be inserted. These alter the thermal conductivity by producing sources for lattice phonon scattering and decrease thermal conductivity due to the lattice without reducing electrical conductivity. This makes these materials behave like a PGEC (phonon-glass, electron crystal). It is proposed that in order to optimize *ZT*, phonons which are responsible for thermal conductivity must experience the material as they would in a glass (high degree of phonon scattering – lowering the thermal conductivity) while electrons must experience it as they would in a crystal (very little scattering – maintaining the electrical conductivity).

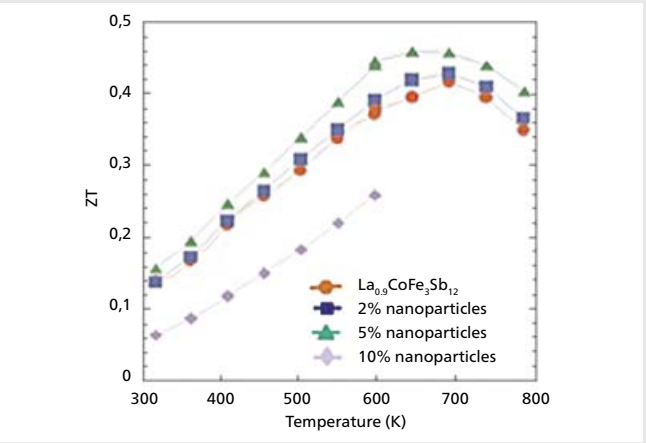
Lattice Thermal Conductivity and Figure of Merit of $La_{0.9}CoFe_3Sb_{12}$

The effect of introducing a nanoparticle layer in $La_{0.9}CoFe_3Sb_{12}$ in order to reduce the thermal conductivity was investigated up to 550°C in this example. The thermal conductivity (λ) was calculated by using the heat capacity (c_p), which was predetermined with the DSC 404 ***F1*** *Pegasus*®. The lattice thermal conductivity was found by calculating the electrical thermal conductivity using the Wiedemann-Franz relationship and subtracting it from λ_{total}.

At 452°C (725 K), the *ZT* exhibits its maximum, and the 5 wt.-% nanocomposite shows the highest *ZT* with an improvement of nearly 15% over that of the control sample which contains no nanoparticles (orange dots). These results show that nanoparticles introduced into skutterudite systems which are already optimized can further reduce the thermal conductivity and therefore improve *ZT* across a broad temperature range.



Systematic decrease of $\lambda_{lattice}$ with increasing the wt-% of nanoparticles (LFA 457 *MicroFlash*® measurements).

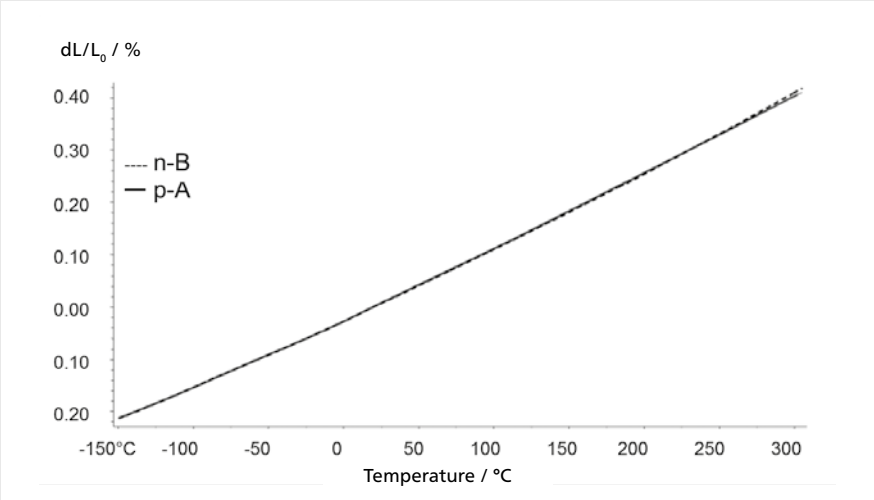


Clearly improved *ZT* by introduced nanoparticle layers up to 800K.

Lattice thermal conductivity and *ZT* of CoSb3-based skutterudites; P. N. Alboni, X. Ju, J. He, N. Gothard & Terry M. Tritt, J. Appl. Phys. 103, 113707_2008

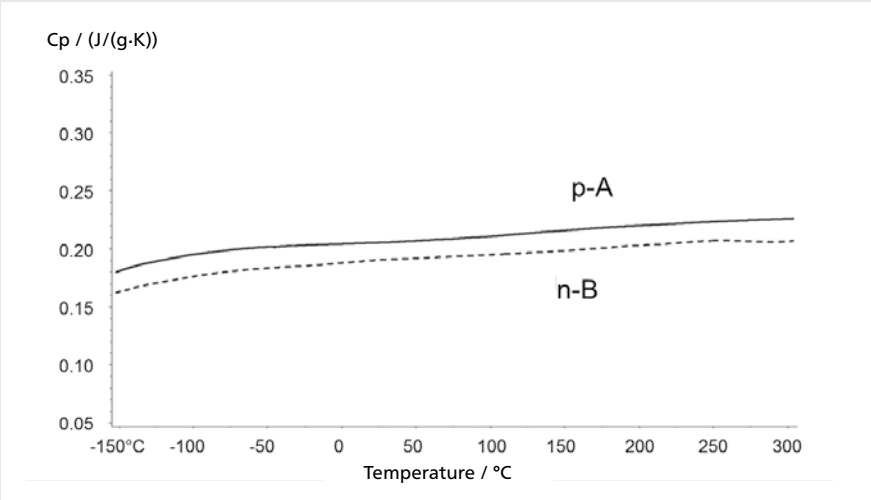
Bismuth Telluride – Thermal Expansion and Specific Heat

In this example, two bismuth telluride thermoelectric materials n-B ($Bi_2Se_{0.2}$ $Te_{2.8}$) and p-A ($Bi_{0.5}Se_{1.5}Te_3$) were analyzed with regard to their thermal expansion (dL/L_0, plot A) and specific heat (c_p, plot B) in the temperature range between -150°C and 300°C.



A) The thermal expansion measurements were carried out using the DIL 402 C equipped with a sample holder and pushrod made of fused silica along with a liquid nitrogen cooling device.

A) The dilatometer samples had an initial sample length of 20 mm. The room-temperature bulk densities of the samples were 7.824 g/cm³ (n-B) and 6.829 g/cm³ (p-A), respectively. Plot A clearly shows that samples n-B and p-A exhibit very similar thermal expansion behavior. This proves that the considerable differences in composition have no impact on the thermal expansion behavior.



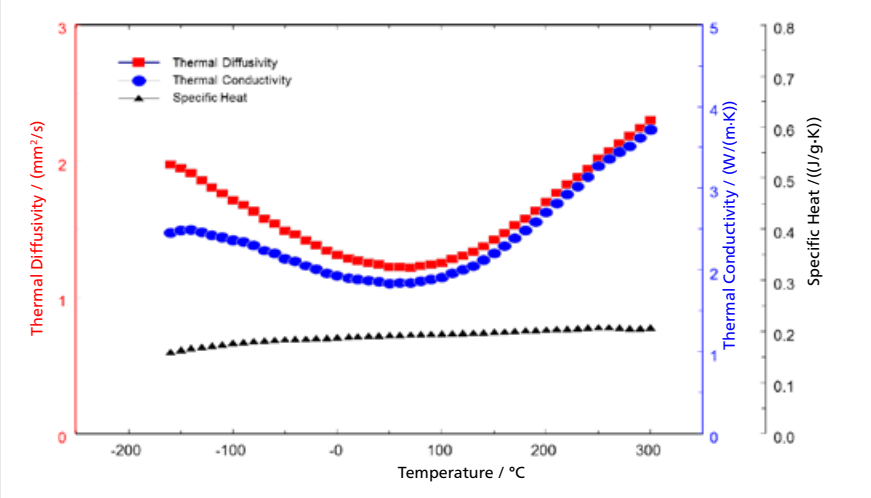
B) Specific heat (c_p) of two different bismuth tellurides (Ø 5 mm, 1 mm thick) measured at heating rates of 10 K/min in platinum crucibles in the DSC 204 ***F1*** *Phoenix®*

B) The evaluation of the specific heat was carried out using the ratio method. Plot B illustrates the specific heat capacities of two samples, n-B and p-A. Here, the antimonide content in p-A (solid line) results in a significantly higher specific heat than is the case for n-B (dashed line). The selenium content apparently results in a higher density and a lower specific heat. Furthermore, no phase transition can be observed in the two materials. This means that no structural changes can be estimated based on DSC tests.

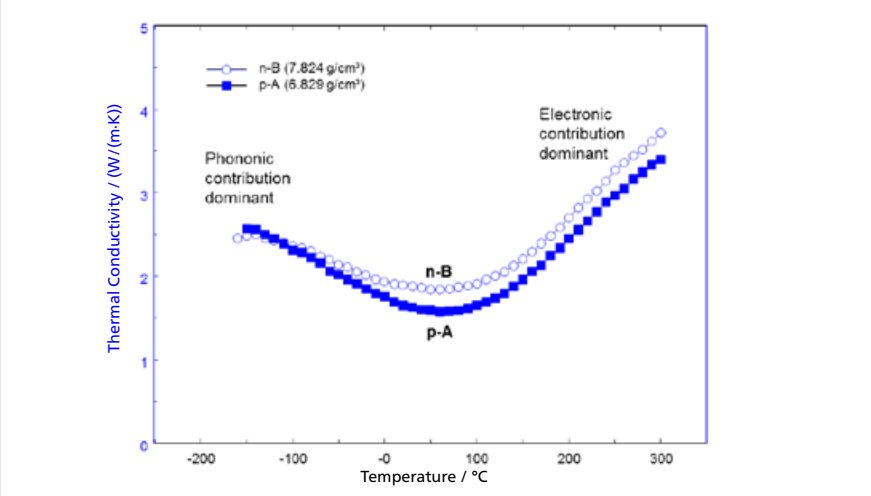
Applications – Thermal Diffusivity and Thermal Conductivity of Bismuth Telluride; Characterization of PbTe

Bismuth Telluride — Thermal Diffusivity and Thermal Conductivity

In this example, the thermal diffusivity of two bismuth telluride discs (Ø 12.60 mm, 2 mm thick), n-B ($Bi_2Se_{0.2}Te_{2.8}$) and p-A ($Bi_{0.5}Se_{1.5}Te_3$), were determined. The measurement results were used to calculate the thermal conductivity (λ).



A) Thermophysical properties of n-B determined at a heating rate of 10/Kmin in the DSC



B) Thermal conductivity of the two bismuth telluride thermoelectric materials.

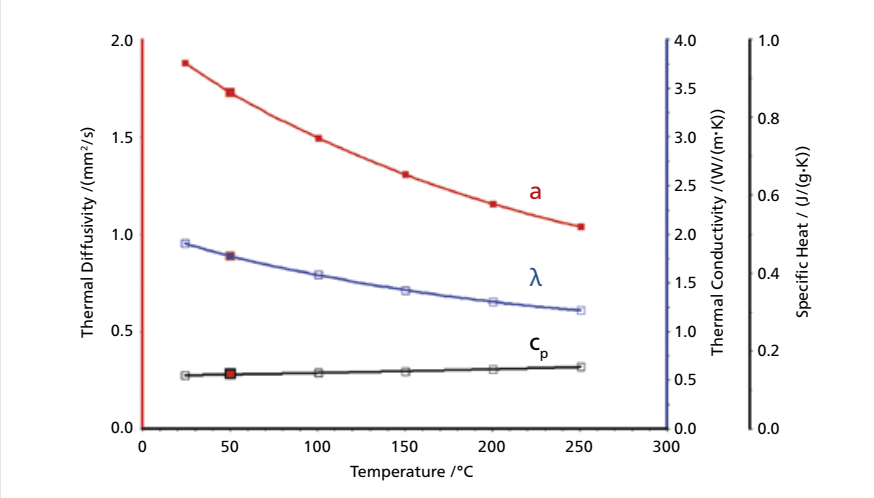
Plot A shows the thermal diffusivity (a), thermal conductivity and specific heat (DSC results, see page 15) of n-B. The specific heat increases slightly with temperature. The thermal diffusivity decreases versus temperature in the sub-ambient temperature range but increases sharply at high temperatures. This exemplifies a behavior which occurs in pure phonon-conducting materials at low temperatures. At high temperatures, the temperature dependence of the thermal diffusivity is dominated by free electrons which are generated at increasing temperatures. Their contribution to the heat transfer results in a sharp increase in thermal diffusivity. The thermal conductivity (λ) follows the temperature dependence of the thermal diffusivity.

In plot B, the thermal conductivities (λ) of n-B and p-A are compared. At -150°C, the thermal conductivities of the two materials are very similar. Up to 25°C, n-B exhibits less of a decrease in λ than p-A. Apparently the phonon contribution to λ decreases more sharply for p-A. The increase in λ at higher temperatures is almost parallel in the two materials. It can be assumed that the electron contribution to the thermal conductivity is nearly the same for both.

The sharp increase at higher temperatures is an indication for high electrical conductivity at elevated temperatures. Therefore, a high figure of merit can be expected.

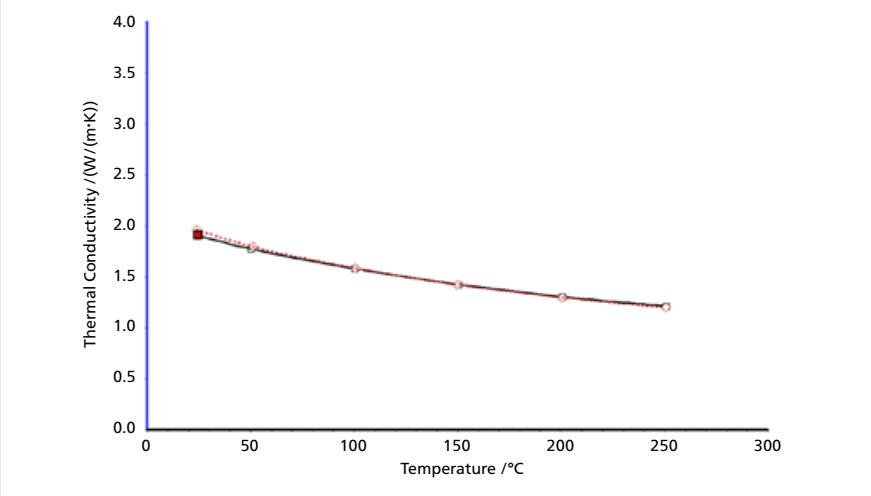
Characterization of PbTe

Due to its very low thermal conductivity, the variety of different doping materials which can be used, and the resulting high figure of merit, doped lead telluride (PbTe) is an important material in thermoelectric applications. Comprehensive characterization of the material is thus of paramount importance.



A) Thermophysical properties of PbTe determined in the LFA system (a, λ) and DSC 204 ***F1*** *Phoenix®* (c_p) between room temperature and 250°C.

Plot A shows the thermophysical properties of PbTe. The thermal diffusivity (a) and the calculated thermal conductivity (λ) decrease with increasing temperature. The specific heat capacity (c_p) exhibits only a small increase.



B) Thermal conductivity of two PbTe samples

Plot B depicts the thermal conductivity of two PbTe samples between room temperature and 250°C. Slight differences can only be observed around room temperature.

These measurements demonstrate the high reproducibility for determination of thermal diffusivity in the LFA system and specific heat in the DSC 204 ***F1*** *Phoenix®*.

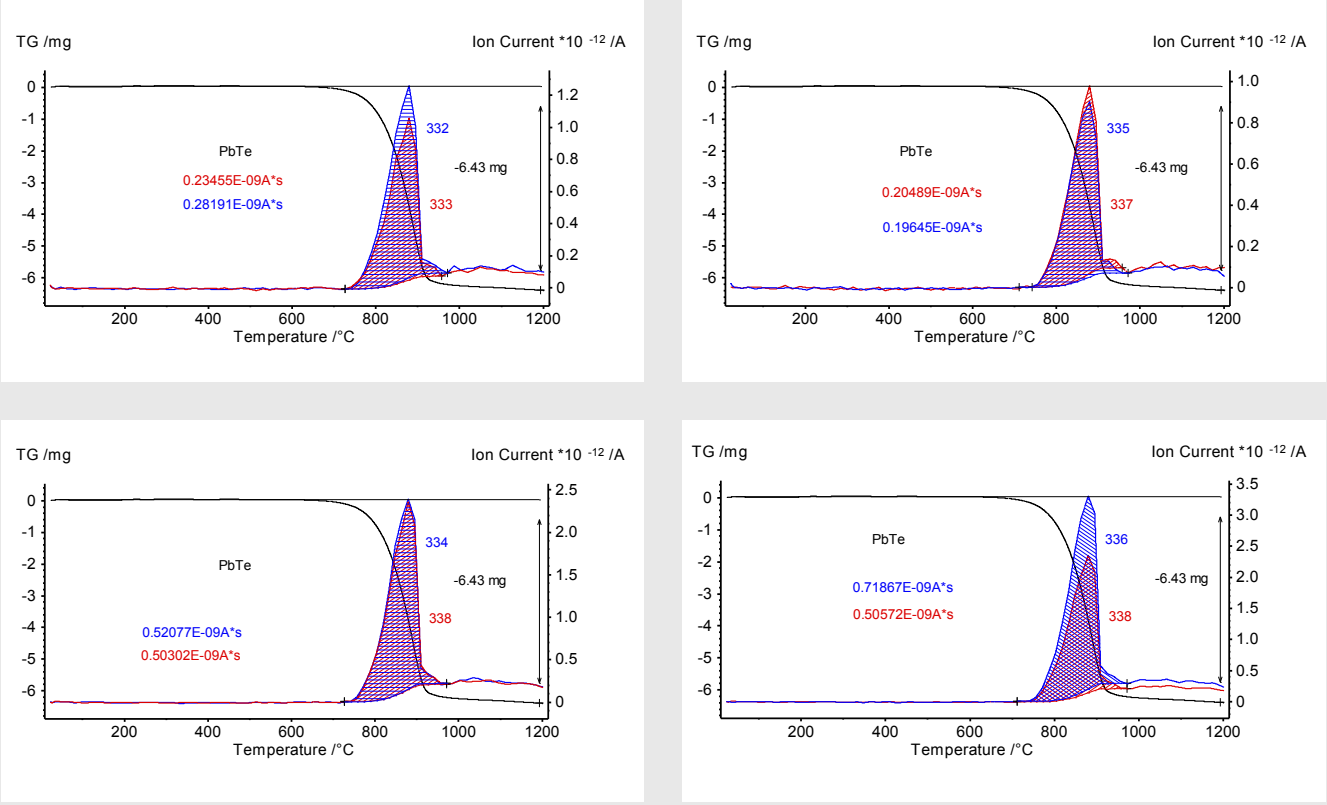
Applications – Characterization of PbTe

Thermal Stability of PbTe

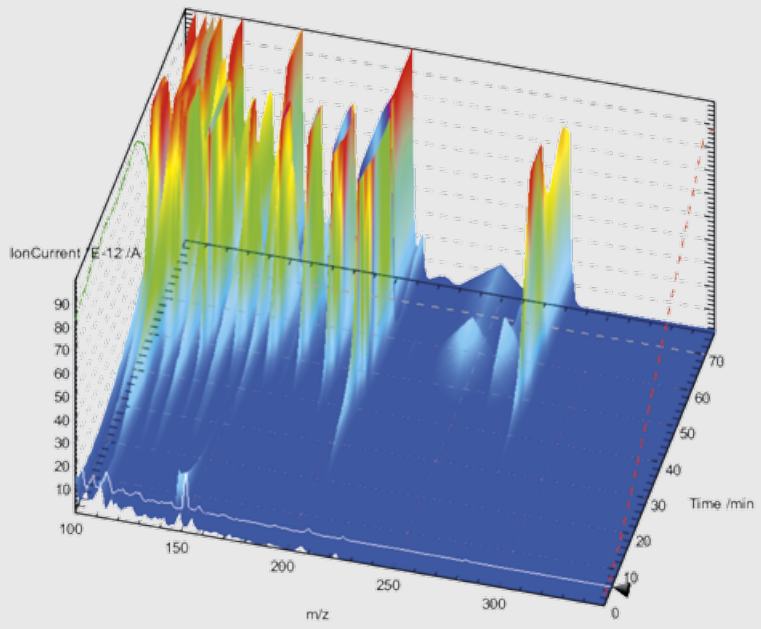
In this example, the thermal stability of PbTe was analyzed using the STA 409 CD coupled to a mass spectrometer via the *SKIMMER*® system. This sophisticated coupling system is specially designed to investigate the release of large molecules and highly condensable gases such as metal vapors.

Each plot shows the TGA curve of the PbTe sample but with different mass spectrometer results. PbTe starts decomposing at around 600°C. The plotted mass numbers represent the combination of the Pb and Te isotopes. The following gaseous products were detected:

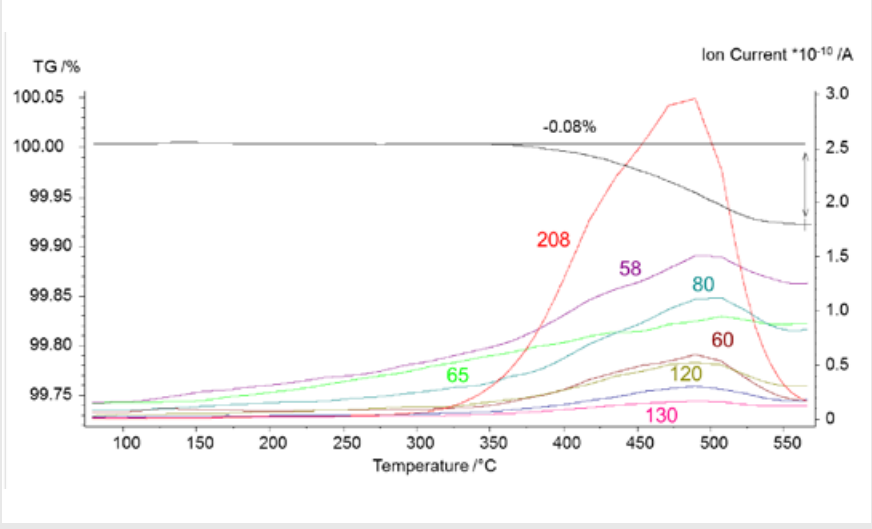
333 u: ^{208}Pb + ^{125}Te; ^{207}Pb + ^{126}Te
334 u: ^{208}Pb + ^{126}Te; ^{206}Pb + ^{128}Te
335 u: ^{207}Pb + ^{125}Te; ^{206}Pb + ^{126}Te
332 u: ^{207}Pb + ^{128}Te
336 u: ^{208}Pb + ^{128}Te
337 u: ^{207}Pb + ^{130}Te
338 u: ^{208}Pb and ^{130}Te.



STA-MS *SKIMMER*® measurements on PbTe; TGA curve in correlation with the detected metal vapors



STA-MS *SKIMMER*® measurements on a PbTe module deposited on a substrate; extract of the TGA curve and scan-bargraph in the mass number range from m/z 100 to 350.



STA-MS *SKIMMER*® measurements on a PbTe module deposited on a substrate; TGA curve in correlation with repeated MID curves for various mass numbers.

PbTe Thermoelectric Module on a Substrate

For a better overview, one can present the mass spectrometer data (obtained with the *SKIMMER*® coupling) along with the corresponding TGA, DTG and/or DSC curves in a 3D-plot. For a direct correlation, the mass numbers of interest were imported into the NETZSCH *Proteus*® software (instrument software) as continuous MID curves.

The PbTe sample was heated at a rate of 10 K/min across the temperature range from room temperature to 600°C. The MID curves selected here, which were directly imported from the coupled mass spectrometer, are in good correlation with the low mass loss of 0.08% (TGA signal). This low mass loss can be attributed in part to impurities but also to Pb and Te fragments of PbTe, such as Pb 208 u. Mass number 80 u can be attributed to the stable isotope ^{80}Se (natural abundance 49.6%).

The other mass numbers detected – e.g., 58 u, 60 u, etc. – can be attributed to organic impurities and the substrate material.

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