

Thermoelectric Materials

Material Characterization, Phase Changes, Thermal Conductivity



Thermoelectric Materials – Historical Background



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).

Small devices without moving parts!

A thermoelectric (TE) device can capture waste heat. It produces electrical power just like conventional heat engines, steam, gas or diesel engines that are coupled to electrical generators, but it uses electrons instead of water or gases as the working fluids and makes electricity directly.

Currently there are two primary areas in which thermoelectric devices can be used to increase

energy efficiency and/or decrease pollutants: conversion of waste heat into usable energy, and refrigeration.

History

The discovery of thermoelectricity dates back to Thomas Johann **Seebeck** (1770-1831). In 1821, he discovered that a compass needle deflected when placed in the vicinity of a closed loop formed from two dissimilar metal conductors if the junctions were maintained at different temperatures. The magnitude of the deflection was proportional to the temperature difference and depended on the type of conducting material.

The **Seebeck coefficient** is defined as the open circuit voltage produced between two points on a conductor, where a uniform temperature difference of 1 K exists between those points.

Later Jean **Peltier** described thermal effects at the junctions of dissimilar conductors when an electrical

current flows between the materials (1834).

In 1851, William **Thomson** (later **Lord Kelvin**) observed the cooling or heating of a homogeneous conductor resulting from the flow of an electrical current in the presence of a temperature gradient. This is known as the **Thomson effect** and is defined as the rate of heat generated or absorbed in a single current carrying conductor subjected to a temperature gradient.

In 1909 and 1911, **Altenkirch** showed that good thermoelectric materials should possess large Seebeck coefficients, high electrical conductivity and low thermal conductivity. A high electrical conductivity is necessary to minimize Joule heating, whilst a low thermal conductivity helps to retain heat at the junctions and maintain a large temperature gradient. These three properties were later embodied in the so-called 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 defined as:

$$ZT = (S^2 \sigma \lambda^{-1})T *$$

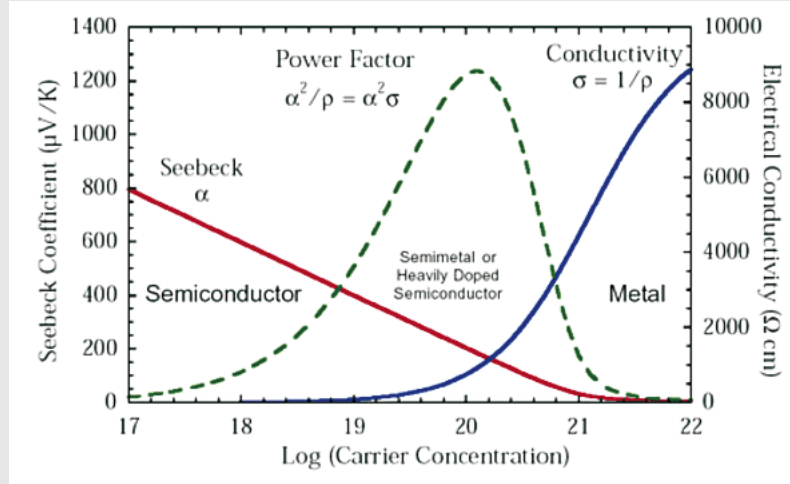
* where
S is the Seebeck coefficient or thermopower of the material (measured in $\mu\text{V/K}$)
 σ is the electrical conductivity of the material (measured in $1/\Omega\text{m}$) and
 λ is the total thermal conductivity of the material (measured in W/mK).

Basic Parameters, Figure of Merit

Metals – Semiconductors

Although the properties associated with good thermoelectric materials were known, the advantages of semiconductors as thermoelectric materials were largely overlooked for many years and research continued to focus on metals and metal alloys. Most of these materials, however, have a nearly constant ratio of electrical to thermal conductivity (Wiedemann-Franz law), so it is not possible to increase one without increasing the other. Metals best suited to thermoelectric applications should therefore possess a high Seebeck coefficient. Unfortunately, most metals show Seebeck coefficients in the order of 10 $\mu\text{V/K}$, which generate efficiencies of only fractions of a percent.

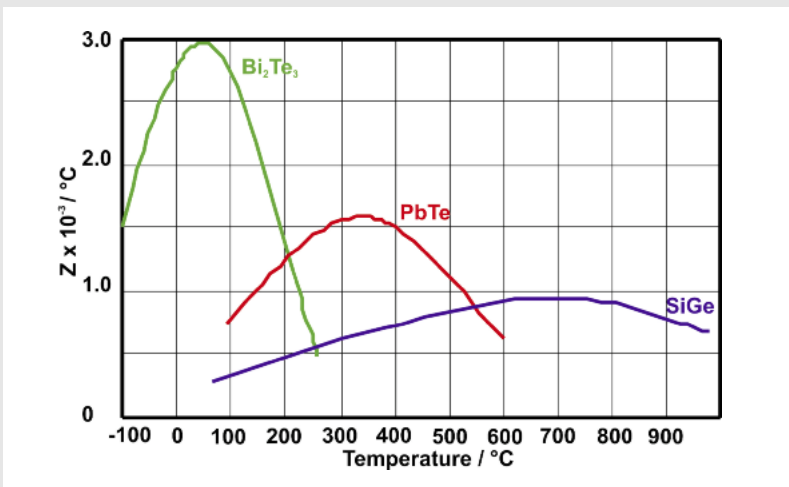
In the 1920s, the development of synthetic semiconductors with



Thermoelectric behavior of metals and semiconductors F.D. Rosi Solid State Electronics, **11**, 833-868, (1968). T.M. Tritt, M.A. Subramanian MRS Bul. **31**, 188 (2006)

Seebeck coefficients in excess of 100 $\mu\text{V/K}$ increased interest in thermoelectricity. At that time it was not apparent that semiconductors would be superior thermoelectric

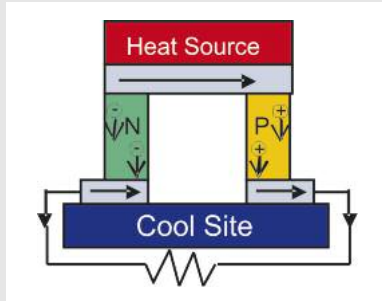
materials due to their higher ratio of electrical conductivity to thermal conductivity in comparison with metals.



Approximate figure of merit (Z) for various TE materials

The larger the Z value, the greater the thermodynamic. Z is therefore a very convenient figure for comparing the potential efficiency of devices using different materials. Values of $Z=1$ are considered good, and values of at least the 3-4 range are considered to be essential for thermoelectrics to compete with mechanical energy generation and refrigeration in efficiency. To date, the best reported Z values have been in the 2-3 range.

Thermoelectric Devices



Principle of thermoelectric generation (Seebeck effect)

In 1929, Abram F. **Ioffe** showed that a thermoelectric generator utilizing semiconductors could achieve a conversion efficiency of 4% (the ratio between the useful output of an energy machine and the input, in energy terms $\eta = P_{out}/P_{in}$. Generally, conversion efficiency is a dimensionless number between 0 and 1.0 or 0 to 100%). The thermoelectric generator shows further possible improvement in his performance. He had developed the theory of thermoelectric conversion, which forms the basis of all modern thermoelectric theory.

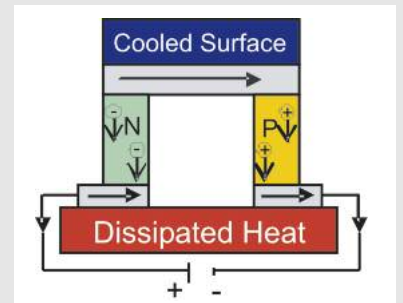
Thermoelectric Generation

The simplest thermoelectric generator consists of a thermocouple (thermopile) comprising a p-type and n-type semiconductor connected electrically in series and thermally in parallel. Heat is pumped into one side of the couple and rejected from the opposite side. An electrical current is produced, 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 cooling (Peltier effect)

The Thermoelectric Module

A typical thermoelectric module consists of pairs of p-type and n-type semiconductor thermoelements forming thermocouples which are connected electrically in series and thermally in parallel. They can be used in cooling or electricity-generating mode.

Thermoelectric modules offer many advantages including:

- No moving parts
- Small and lightweight
- Maintenance-free
- Acoustically silent and electrically "quiet"
- Heating and cooling with the same module (including temperature cycling)

- Wide operating temperature range
- Highly precise temperature control (to within $\pm 0.1^\circ\text{C}$)
- Operation in any orientation, at zero gravity and high G-levels
- Environmentally friendly
- Cooling to very low temperatures (-80°C)

Thermophysical Properties of Thermoelectric Materials

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.

For optimization of thermoelectric devices, the thermal properties must be known. The thermal conductivity has a direct impact on the efficiency of a thermoelectric material.

The thermal stability (analyzed with TG 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.

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

Determination of the 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 billion 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 that leads to inherently low thermal conductivity.



LaserFlash Technique

LaserFlash Technique

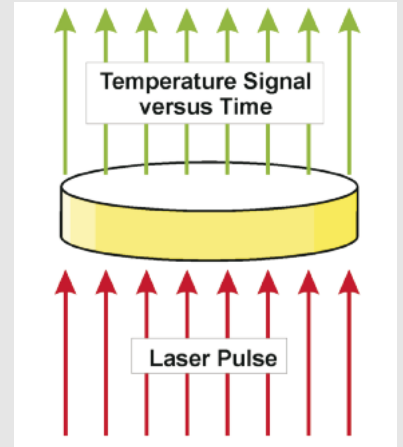
For the precise measurement of thermal diffusivity, specific heat and thermal conductivity, the LaserFlash technique (LFA) has proven itself as a fast, versatile and exact absolute method.

The front surface of a plane-parallel sample is heated by a short light or laser pulse. The temperature rise on the rear surface is measured versus time using an IR detector. The thermal diffusivity (a) and in most cases 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:

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



LFA measurement principle introduced by Parker et al. 1961

NETZSCH offers three LFA models, covering the entire spectrum of possible materials and temperatures:

LFA 447 NanoFlash®

The LFA 447 NanoFlash® is a Xenon flash-based system with a compact design. It covers the temperature range between RT and 300°C. The integrated automatic sample changer allows unattended analysis of up to 4 samples.

The flash method is a non-contact, non-destructive technique for determining the thermal diffusivity.

The light flash is created by the Xenon flash lamp and the temperature response on the rear surface is measured using an IR detector.

A wide range of different sample dimensions can be measured. The optional MTX extension allows the



characterization of 5 cm x 5 cm sample areas and shows the local

distribution of the thermal diffusivity/conductivity in high resolution.

Flash Methods – Fast and Reliable Thermal Conductivity Measurements on Small and Thin Samples

LFA 457 *MicroFlash*®

The LFA 457 *MicroFlash*® embodies the latest technology for modern laser flash systems. This table-top instrument allows for measurements from -125°C to 1100°C using two different user-interchangeable furnaces.

The innovative infrared sensor technology employed in the system enables measurement of the temperature increase on the back surface of the sample, even at temperatures of -125°C.

The instrument accommodated 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 enables tests under defined atmospheres.

The vertical arrangement of the sample holder, furnace and detector

simplifies sample placement and, at the same time, guarantees an optimum signal-to-noise ratio for the detector signal.

LFA 427

The LFA 427 is the most powerful and versatile LFA system for research and development as well as all applications involving the characterization of standard and high-performance materials in automobile manufacturing, aeronautics, astronautics and energy technology.

The LFA 427 guarantees high precision and reproducibility, short measurement times and defined atmospheres over the entire application range from -70°C to 2000°C. Various sample holders are available.

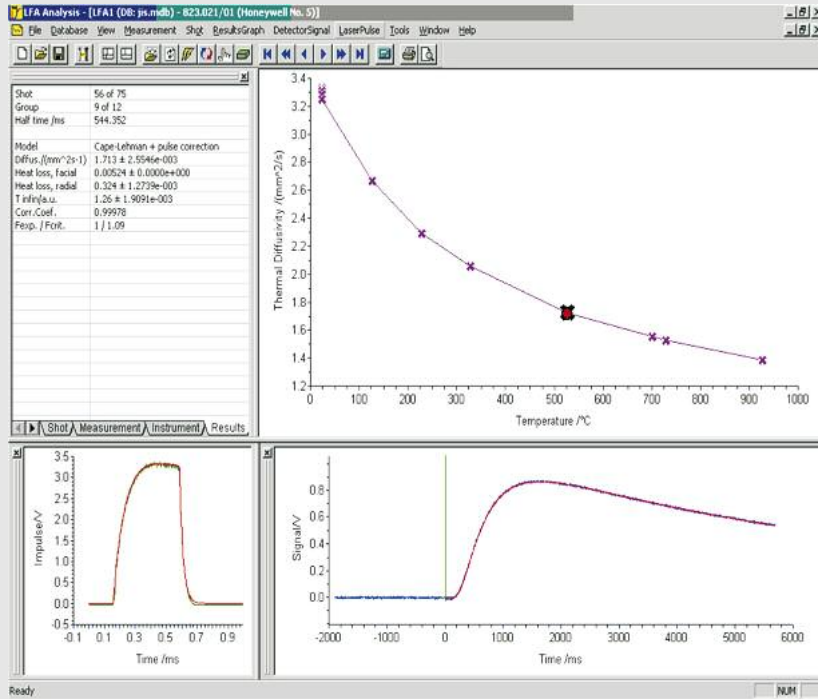
The system is highly vacuum-tight by design. The laser, sample and detector configured (no mirrors



are used). The laser power, pulse width, gas and vacuum functions are variable over a wide range, making it possible to set the

optimum measurement conditions for a great variety of sample properties.

Software



LFA software including heat loss and pulse length correction

LFA Software

The LFA systems run under *Proteus*® Software on MS Windows . The combination of easy-to-under-

stand menus and auto-mated routines makes this software very user-friendly while still allowing

for sophisticated analysis. The LFA software includes:

- Accurate pulse length correction, pulse mapping
- Heat-loss corrections
- Non-linear regression for Cowan fit
- Improved Cape-Lehmann model through consideration of multi-dimensional heat loss and non-linear regression
- Radiation correction for semi-transparent samples
- 2- or 3-layers systems: analysis by means of non-linear regression and consideration of heat loss
- Determination of contact resistance in multi-layer systems
- Model wizard for selecting the optimum evaluation model
- Determination of specific heat by means of a comparative method and standard samples
- Integrated database

Thermal Analysis – DSC and STA

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

For standard applications, the DSC 204 **F1 Phoenix**[®] can be used. The system is easy to handle and can be operated from -180°C to 700°C. Another model, the DSC 404 **F1 Pegasus**[®], can be configured for up to five different furnace types, easily interchangeable by the user, to cover a broad temperature range from -150°C to 2000°C.

DSC Analysis Possibilities

- Specific heat
- Melting/crystallization behavior
- Solid-solid transitions
- Polymorphism
- Degree of crystallinity
- Glass transitions
- Cross-linking reactions
- Oxidative stability
- Purity determination
- *Thermokinetics*

Important hardware extensions like automatic sample changers (ASC), as well as software features such as BeFlat[®] for an optimized baseline or for the optional temperature modulation of the DSC signal (TM-DSC) make the DSC 404 **F1 Pegasus**[®] and STA 449 **F1 Jupiter**[®] the most versatile DSC and STA system available for research & development, quality assurance, failure analysis and process optimization.

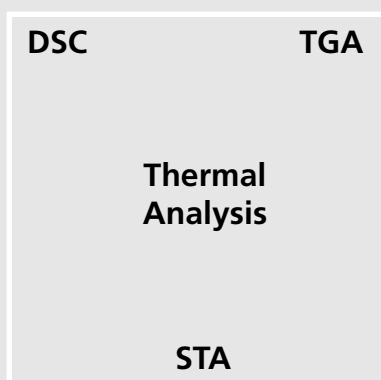
For evolved gas analysis, the systems can be coupled to a QMS and/or FTIR system, even if equipped with an automatic sample changer.

The vacuum-tight design (up to 10⁻⁴ mbar) ensures the exact determination of the specific heat of high-performance materials in the temperature range from -150°C to 1400°C under highly pure atmospheres.

Simultaneous Thermal Analysis generally refers to the simultaneous application of Thermogravimetry (TG) and DSC to one and the same sample in a single instrument. The test conditions are perfectly identical for the TG and DSC signals (same atmosphere, gas flow rate, vapor pressure of the sample,

heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.). Furthermore, sample throughput is improved as more information is gathered from each test run.

The DSC and STA systems all meet most of the respective instrument and application standards for DSC and TGA systems, including: ISO 11357, ISO 11358, ASTM E 967, ASTM E 968, ASTM E 793, ASTM D 3895, DIN 51004, DIN 51006, DIN 51007.



TG Analysis Possibilities

- Mass changes
- Temperature stability
- Oxidation/reduction behavior
- Decomposition
- Corrosion studies
- Compositional analysis
- *Thermokinetics*



STA 449 **F1 Jupiter**[®] coupled to QMS Aeolos[®] and FTIR

Applications

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

The measurements shown below are carried out with the LFA 457 *MicroFlash*[®] in the temperature range from 150°C to 370°C. The

typical sample dimension with a diameter of 12.7 mm and thickness of 2 mm is used.

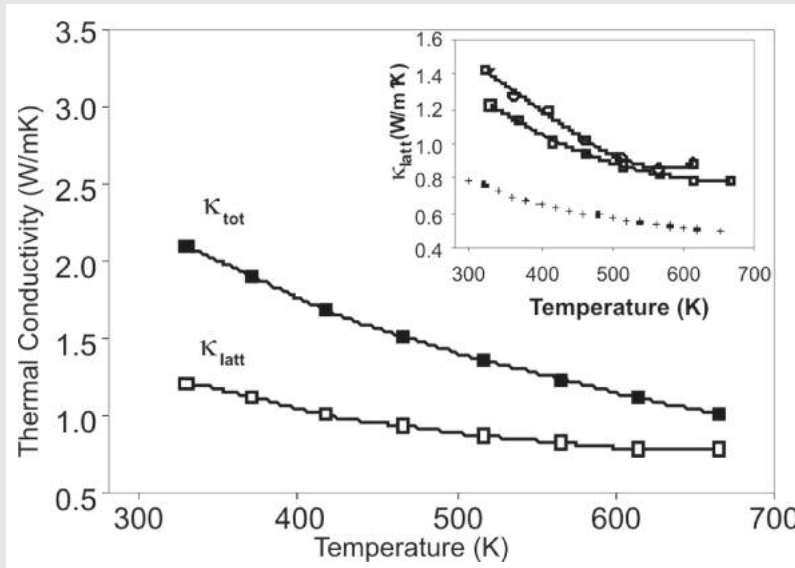
The thermal diffusivity (a), density (ρ), and specific heat (c_p) are measured and used to calculate the total thermal conductivity using the formula

$$\lambda = a \times \rho \times c_p$$

The lattice thermal conductivity was then calculated from

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

The contribution to thermal conductivity by charge carriers is described by the Wiedemann-Franz law.

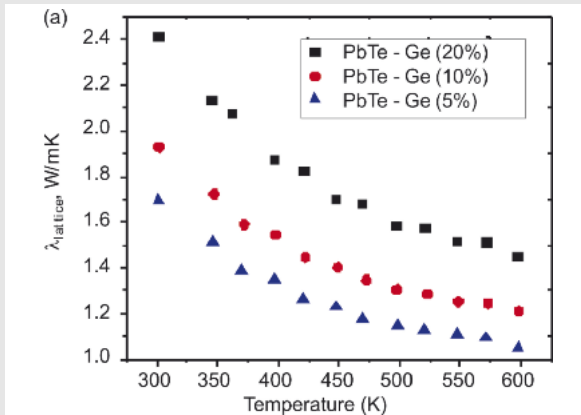


$\text{Ag}_{1-x}\text{Pb}_{18}\text{MTe}_{20}$ (M = Bi, Sb); published by Kanatzidis et al. Northwestern University, IL, USA

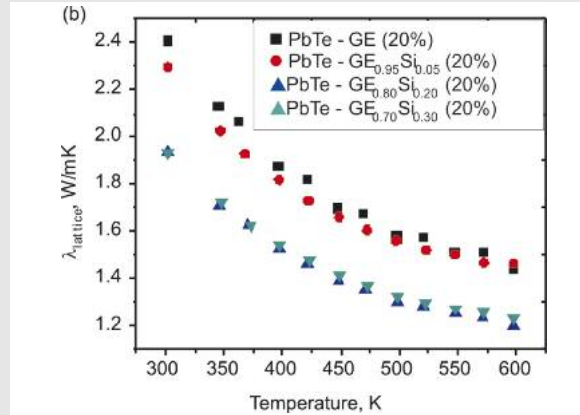
Temperature dependence of the total thermal conductivity (λ_{tot} , ■) and lattice thermal conductivity (λ_{latt} , □) of $\text{AgPb}_{18}\text{BiTe}_{20}$ is demonstrated. The inset indicates the temperature dependence of the lattice thermal conductivity of $\text{Ag}_{1-x}\text{Pb}_{18}\text{BiTe}_{20}$ ($x = 0, 0.3$), compared with the lattice thermal conductivity (λ_{latt}) of $\text{AgPb}_{18}\text{BiTe}_{20}$ (presented in + symbol).

Applications

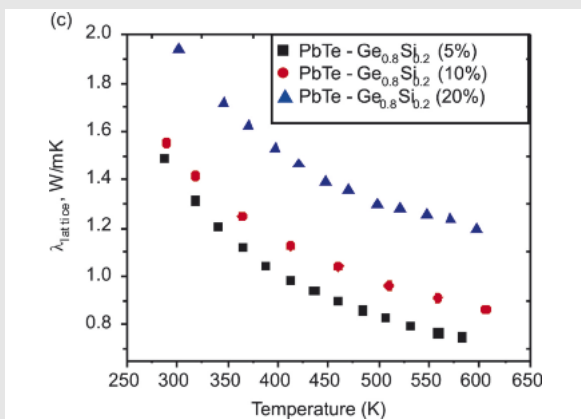
In PbTe-Ge and PbTe-Ge_{1-x}Si_x the thermal conductivity is easily tuned by alloying Ge with Si and reducing the Ge content.



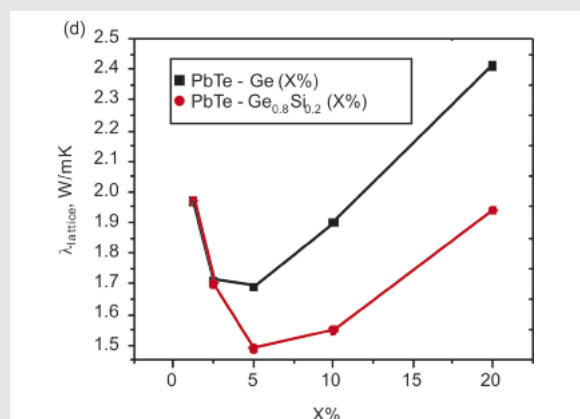
Lattice Thermal Conductivity of PbTe-Ge (5%, 10%, 20%)



Lattice Thermal Conductivity of PbTe-Ge_{1-x}Si_x (20%)



Lattice Thermal Conductivity of PbTe-Ge_{0.8}Si_{0.2}



Lattice Thermal Conductivity of PbTe-Ge and PbTe-Ge_{0.8}Si_{0.2} at increasing Ge_{0.8}Si_{0.2} content

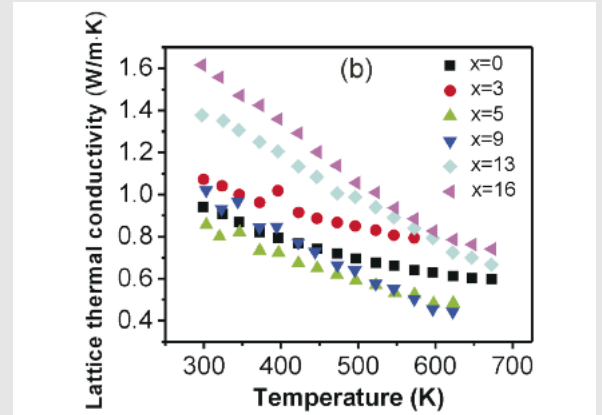
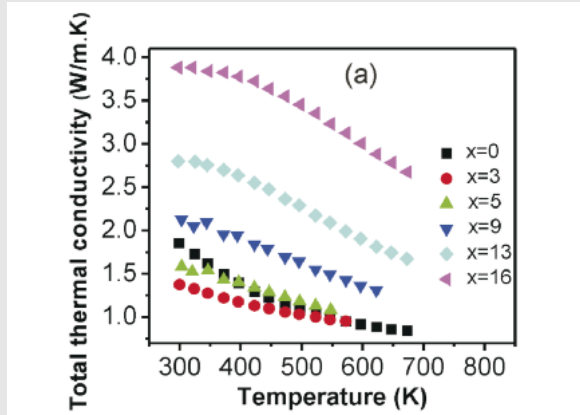
Sootsman, Joseph R.; He, Jiaqing; David, Vinayak P., Li, Chang-Peng; Uher, Ctirad; Kanatzidis, Mercouri G. High Thermoelectric Figure of Merit and Improved Mechanical Properties in Melt Quenched PbTe – Ge and PbTe – Ge_{1-x}Si_x Eutectic and Hyper-eutectic Composites *J. Appl. Phys.* (2009), 105, 083718.

Applications

In $\text{NaPb}_{18-x}\text{Sn}_x\text{SbTe}_{20}$ the Pb and Sn ratio varies for different x-values between

0 and 16. It can be clearly seen that the total and lattice thermal

conductivity is tuned by the Pb-Sn ratio.



Total thermal conductivity and lattice thermal conductivity of $\text{NaPb}_{18-x}\text{Sn}_x\text{SbTe}_{20}$ published by Kanatzidis et al. Northwestern University, IL, USA

Skutterudite Thermoelectrics

Recently, cubic skutterudite materials of the form $(\text{Co,Ni,Fe})(\text{P,Sb,As})_3$, have sparked interest in the search for new thermoelectrics. They 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 large thermal conductivity, which lowers their ZT value.

However, these materials contain voids into which low-coordination ions (usually rare earth elements) can be inserted in order to alter thermal conductivity by producing sources for lattice phonon scattering and decrease thermal conductivity due to the lattice without reducing electrical conductivity. Such qualities make these materials behave like a PGEC (phonon-glass, electron-crystal).

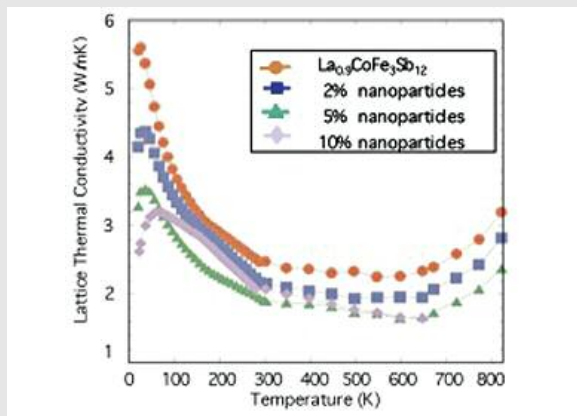
It is proposed that in order to optimize the figure of merit (ZT), phonons which are responsible for thermal conductivity must experience the material as they would in a glass (experiencing a high degree of phonon scattering – lowering the thermal conductivity) while electrons must experience it as a crystal (experiencing very little scattering – maintaining the electrical conductivity). It is through the adjustment of each of these properties independently of the other that the ZT can be improved.

The effect of introducing a nanoparticle layer in CoSb_3 -based skutterudites in order to reduce the thermal conductivity is investigated with high-temperature thermal diffusivity measurements in the LFA 457 *MicroFlash*® in the temperature range to 825 K. The thermal conductivity is calculated using $\lambda = a \times \rho \times c_p$ where heat capacity (c_p) was

predetermined in the DSC 404 *Pegasus*®. The lattice thermal conductivity was found by calculating the electrical thermal conductivity using the Wiedemann-Franz relationship and subtracting it from the total thermal conductivity.

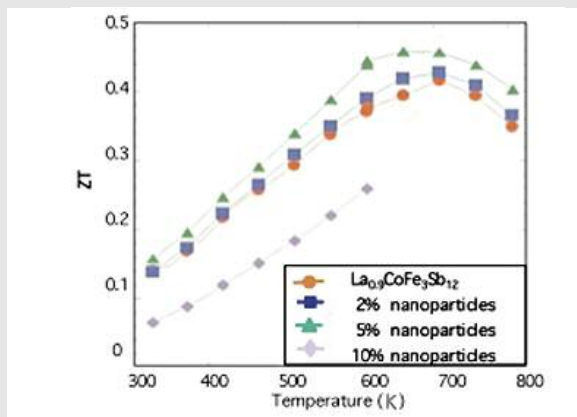
Applications

The lattice thermal conductivity shows a systematic decrease with an increase in the wt % of nanoparticles across the entire temperature range.



Lattice thermal conductivity and ZT of CoSb_3 -based skutterudites; published by Tritt et al., Clemson University, USA P. N. Alboni, X. Ju, J. He, N. Gothard & Terry M. Tritt *Jour of Appl. Phys.* 103, 113707_2008_

At 725 K, the ZT exhibits its maximum, and the 5 wt % nano-composite shows the highest ZT with an improvement of almost 15% over that of the control sample that contains no nanoparticles. These results show that nanoparticles can be used in conjunction with already optimized skutterudite systems in order to further reduce the thermal conductivity and therefore improve ZT within a broad temperature range.

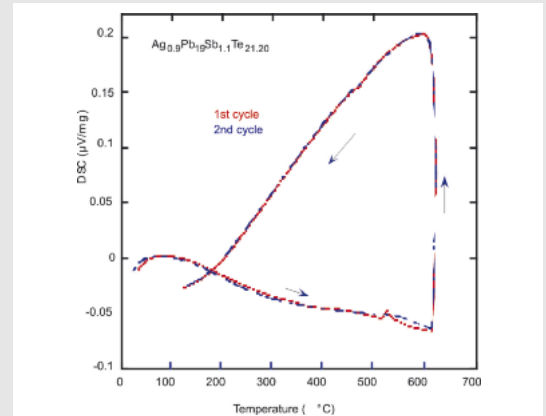
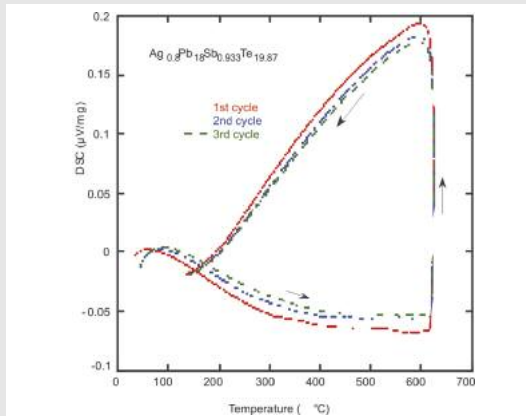


Applications

In thermoelectric research, it is not uncommon to observe a phase affecting the electrical properties, such as electrical conductivity.

With a well-designed DSC analysis, researchers can record phase changes occurring during the thermal cycles.

The thermal stability and any phase changes that might repeat are examined with temperature cycling.



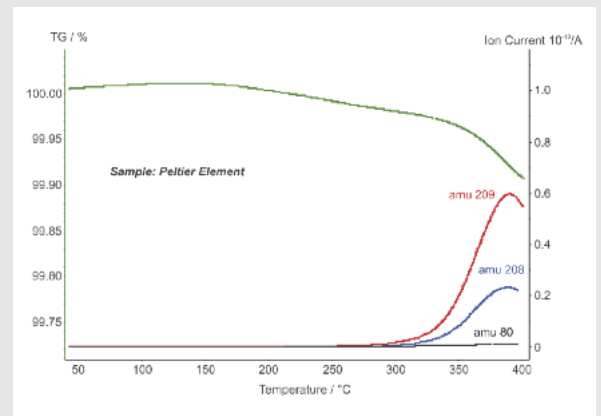
$Ag_xPb_yTe_z$ DSC measurements were carried out at Michigan State University, Depart. of ECE, T. Hogan & C. Wu

The thermal stability and phase changes of two different $Ag_xPb_yTe_z$ materials were here investigated with the STA 449 *Jupiter*® in the

temperature range from RT to 620°C at a heating rate of 20 K/min. While $Ag_{0.9}Pb_{19}Sb_{1.1}Te_{21.20}$ is stable, $Ag_{0.8}Pb_{18}Sb_{0.933}Te_{19.87}$

shows a continuous slope change in DSC with every heating cycle indicating a continuous thermally-induced structural change.

STA-MS measurements are ideal for understanding the thermal stability of thermoelectric components. Presented here are the results on a complete thermoelectric module. Evaporation of humidity causes a slight mass loss between 100 and 300°C (not shown in the MS traces). At temperatures above 300°C, bismuth, lead and selenium evaporate from the sample. This effect is due to the decomposition of parts of the structure.



During the mass loss of the sample, the mass spectrometer detected signals for mass numbers 209, 208 and 80 which are most probably due to Bi-209, Pb-208 and Se-80.

NETZSCH Analyzing & Testing

specializes in the development of versatile, reliable and sensitive instruments for material research, development, quality control and

failure analysis. We transmit our broad application knowledge to our customers by means of demonstration or contract testing, application books for different materials or

industrial branches, or directly and personally through seminars, workshops and users' meetings.



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We kindly thank TEC Microsystems GmbH for providing us with the cover picture.

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