



Aalto University
School of Chemical
Engineering

Functional Inorganic Materials

Lecture 8: Thermoelectricity

Fall 2022

Antti Karttunen (antti.karttunen@aalto.fi)
Department of Chemistry and Materials Science

Lecture Exercise 8 is a MyCourses Quiz

Contents

- Introduction to thermoelectricity
 - Thermoelectric figure-of-merit ZT
 - Electronic properties
 - Lattice thermal conductivity
- Materials perspective
 - Brief review of existing thermoelectrics
 - Current trends
- Applications
 - Thermoelectric generators for solid-state heat-to-electricity conversion
 - Peltier elements for solid-state cooling

Figure: Unknown

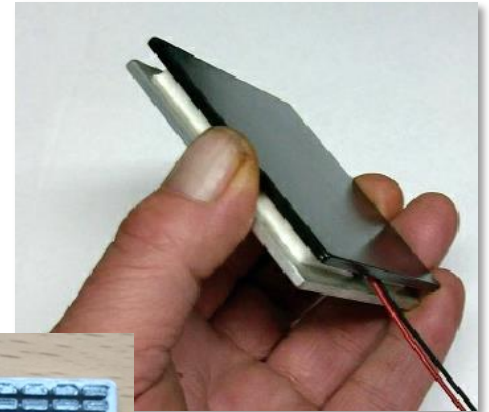


Figure: Taneli Tiittanen / Aalto

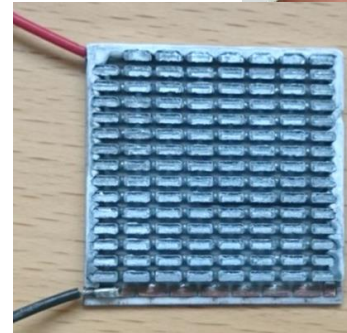
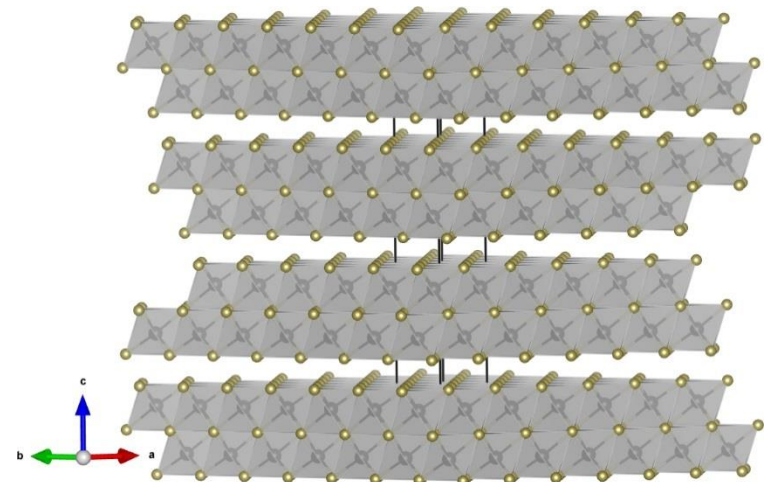


Figure: AJK



Thermoelectric effect

- Direct conversion of temperature differences into electric voltage: "Seebeck effect"
- Discovered by Thomas Seebeck already in 1821 using metal junctions
 - He called the effect "thermomagnetic effect" (effect on compass needle)
 - Hans Ørsted realized that electric current was involved -> "thermoelectric"
- Direct conversion of electric voltage into temperature differences: "Peltier effect"
 - Discovered by Jean Peltier in 1834

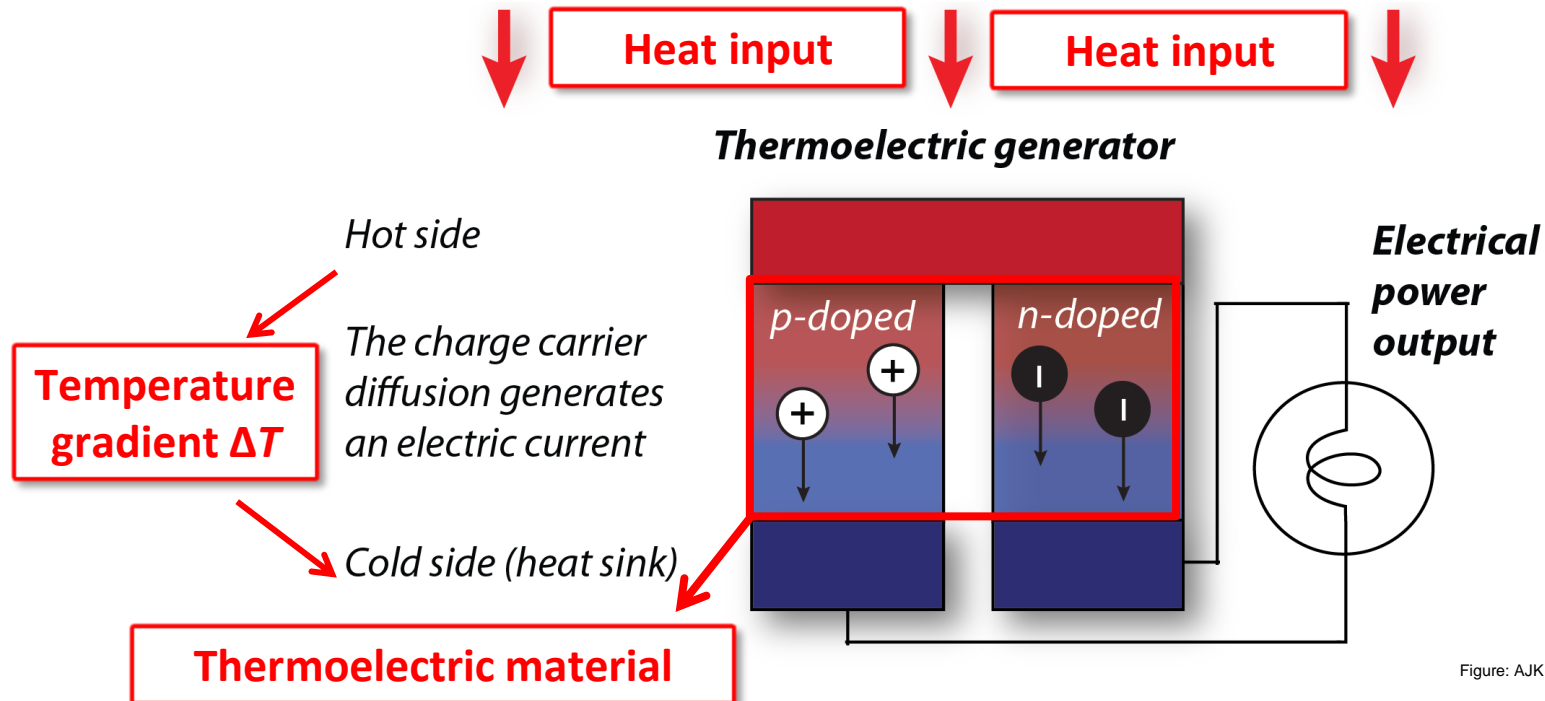


Figure: AJK

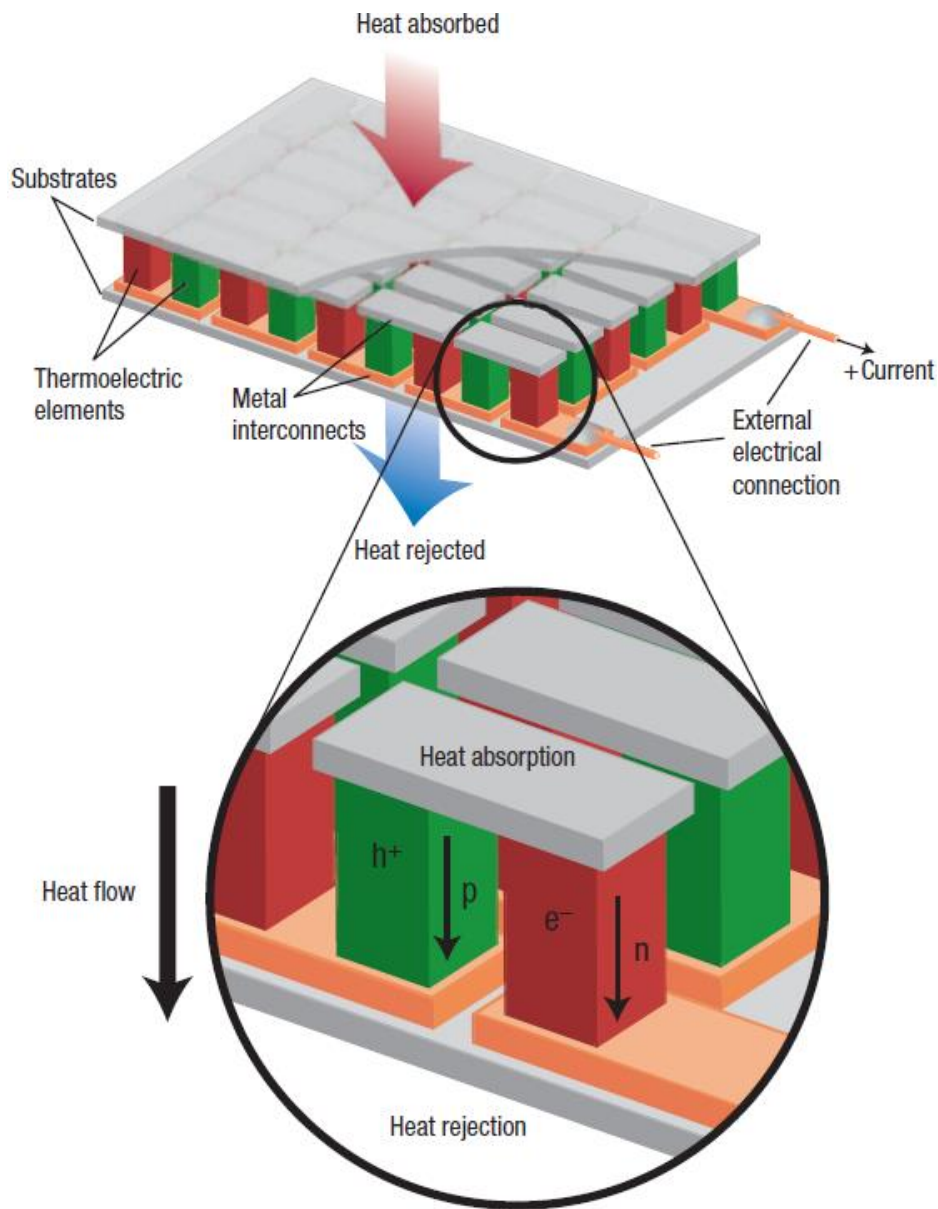


Figure B1 Thermoelectric module showing the direction of charge flow on both cooling and power generation.

Thermoelectric module

G. J. Snyder, E. S. Toberer, *Nature Mater.* **2008**, 7, 105.

Commercial modules typically in cm size range

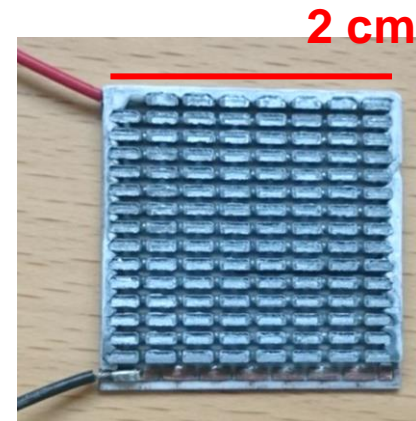


Figure: Taneli Tiittanen / Aalto

Sub-cm generators are also possible (thin-film technology)

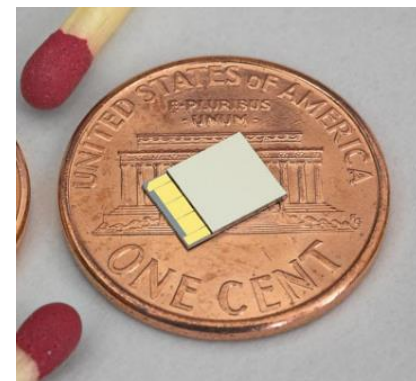
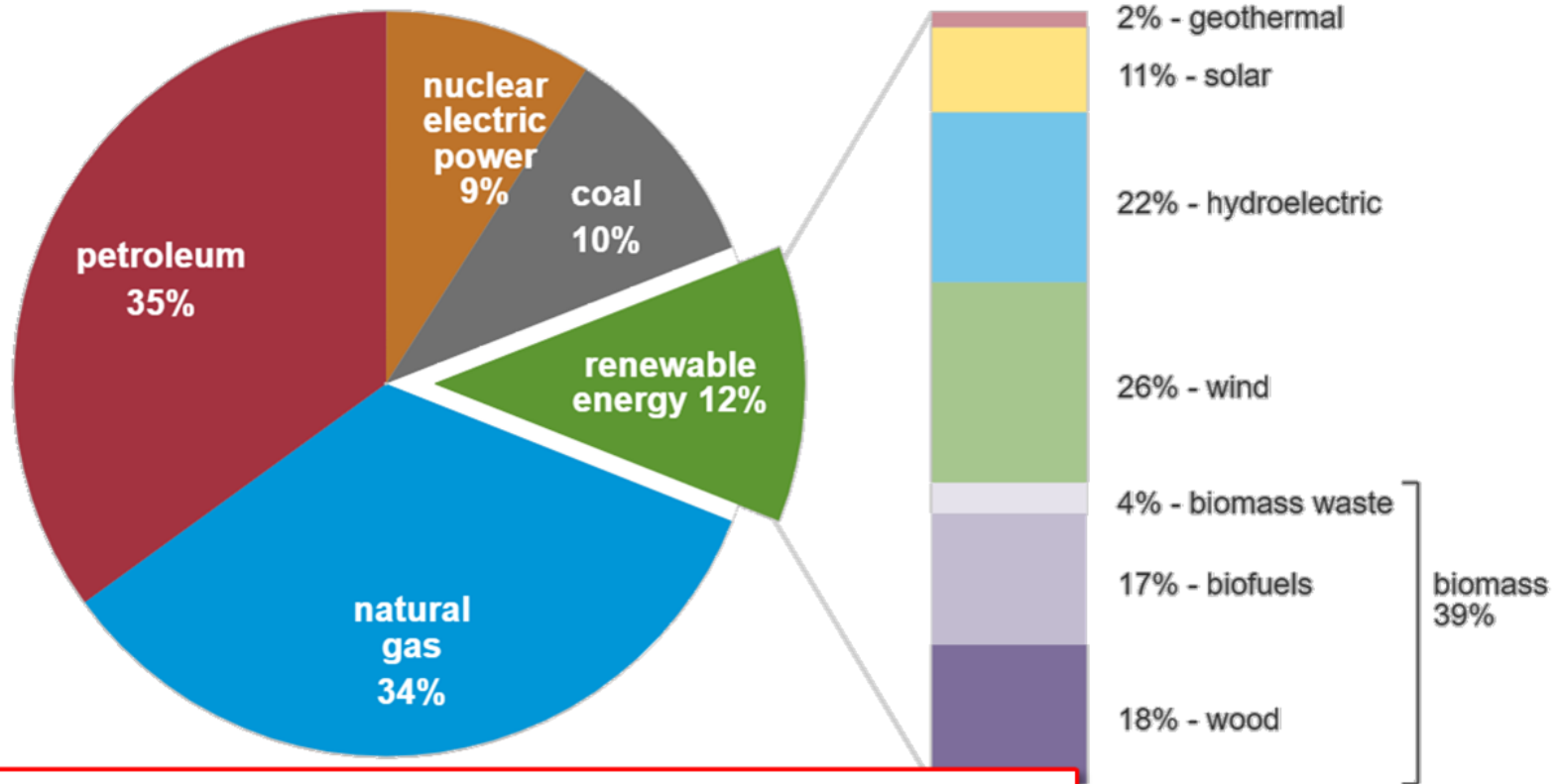


Figure: Micropelt

Waste heat harvesting

U.S. primary energy consumption by energy source, 2020



Over 50% of the consumed primary energy is actually rejected as waste heat!

Figure: [U.S. Energy Information Administration](#)

Convert waste heat into electrical energy using thermoelectrics?

An inconvenient truth about thermoelectrics

Cronin B. Vining

More numbers on this later

Despite recent advances, thermoelectric energy conversion will never be as efficient as steam engines. That means thermoelectrics will remain limited to applications served poorly or not at all by existing technology. Bad news for thermoelectricians, but the climate crisis requires that we face bad news head on.

- **Despite this, thermoelectric generators do have some clear advantages:**
 - Scalability: solid-state thermoelectric generators can be made very small
 - Reliability: There are no moving parts, so TE generators are maintenance-free
 - Possible breakthrough area: (flexible) small-scale, low temperature devices
 - We will see real-world examples of TE generators running over 40 years without maintenance!

Thermoelectric watch: Utilize body heat



Bulova Thermatron (1982). Unreliable technology. The company went bankrupt.

<http://www.watchonista.com/2914/watchonista-blog/news/bulova-thermatron-%E2%80%93-thermal-revolution>



Seiko Thermic

Seiko Thermic (1998). This one actually worked. The watch still needs a battery.

TE watches refuse to die:
MATRIX PowerWatch
Crowdfunded in 2016 and
shipped in 2017

Still in business in 2022!



<https://www.powerwatch.com/>

Thermoelectrics in cars



Figure 1 | Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

The poor conversion efficiency ($\sim 3\text{-}7\%$) with currently available TE materials, lots of engineering required for integration. Electric vehicles made the whole idea obsolete.

Radioisotope thermoelectric generator

- RTGs are an example of a very successful application of thermoelectric generators
- Convert the heat released by the decay of a radioactive material into electricity
- Invented in the 1950s, first RTG launched to space in 1961 (US)
- RTGs have been used as power sources in satellites, space probes, and unmanned remote facilities such as lighthouses

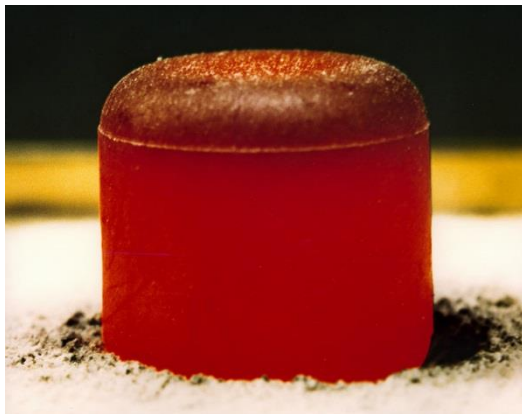
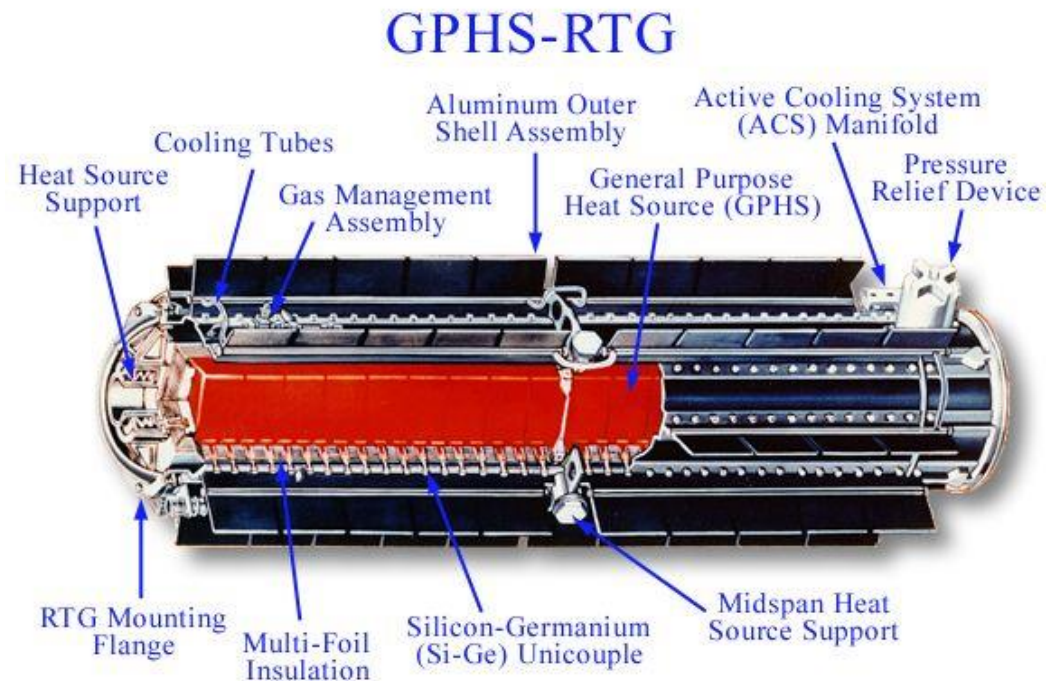


Figure: US DOE / Wikipedia

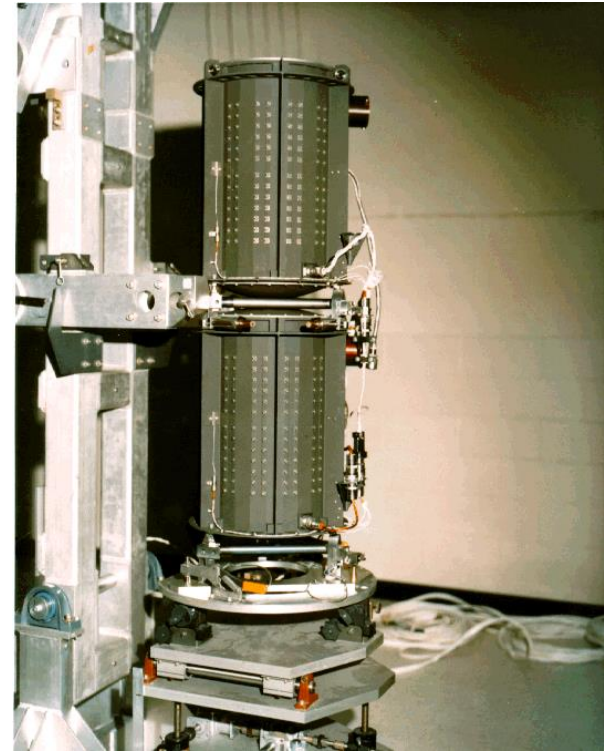
A pellet of $^{238}\text{PuO}_2$ RTG fuel. Photo taken after insulating the pellet under a graphite blanket for several minutes and then removing the blanket. The pellet is glowing red hot because of the heat generated by radioactive decay (primarily α). The initial output is 62 watts.



Radioisotope thermoelectric generator

- Voyager 1 and 2 probes launched in 1977 are powered by three RTGs (Multihundred-Watt RTG)
- Each RTG had a total weight of 37.7 kg including about 4.5 kg of Pu-238 (half-life 87.7 years)
- Each RTG generated about 2400 W of thermal power
 - 157 W of electrical power (6.5% efficiency)
- **SiGe** thermoelectric generator
 - $T_{hot} = 1273 \text{ K}$, $T_{cold} = 573 \text{ K}$
- Over 40 years of operation, have left the solar system
- Power density 4.2 W / kg
 - Typical Li-ion battery ~200-300 W / kg
- Pu-238 supply about to run out
 - Production restart costs: \$150 M
 - Expected Pu-238 price: ~ \$10-15 M/kg

Figure: NASA / Wikipedia



Voyager MWH-RTG

Current trend: Wearable thermoelectrics

- The idea is to harvest the heat emitted by the human body.
- Power levels would probably be in the 10-1000 μW range. However, this is already enough to drive most energy-efficient electronics (even CPUs)

Woven-Yarn Thermoelectric Textiles

Jae Ah Lee, Ali E. Aliev, Julia S. Bykova, Mônica Jung de Andrade, Daeyoung Kim, Hyeon Jun Sim, Xavier Lepró, Anvar A. Zakhidov, Jeong-Bong Lee, Geoffrey M. Spinks, Siegmund Roth, Seon Jeong Kim,* and Ray H. Baughman*

Adv. Mater. **2016**, *28*, 5038.

Thermoelectric Fabrics: Toward Power Generating Clothing

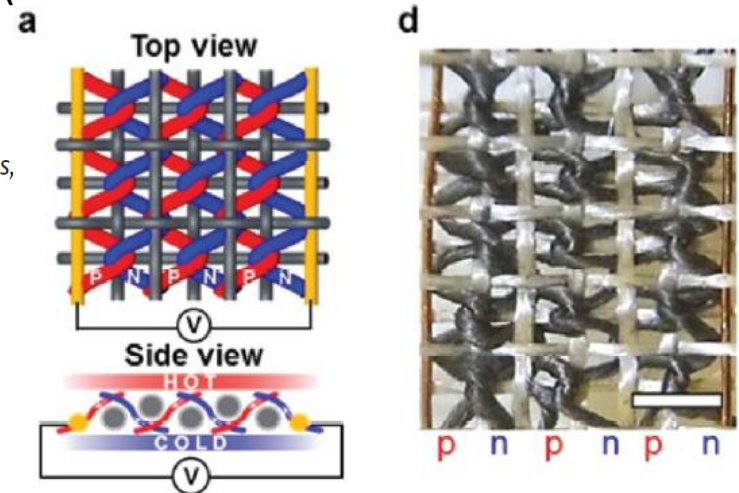
Yong Du¹, Kefeng Cai², Song Chen², Hongxia Wang¹, Shirley Z. Shen³, Richard Donelson³ & Tong Lin¹

SCIENTIFIC REPORTS | 5 : 6411 | DOI: 10.1038/srep06411

Flexible thermoelectric materials and device optimization for wearable energy harvesting

Je-Hyeong Bahk,^{†*} Haiyu Fang,^b Kazuaki Yazawa^a and Ali Shakouri^a

J. Mater. Chem. C, 2015, **3**, 10362–10374



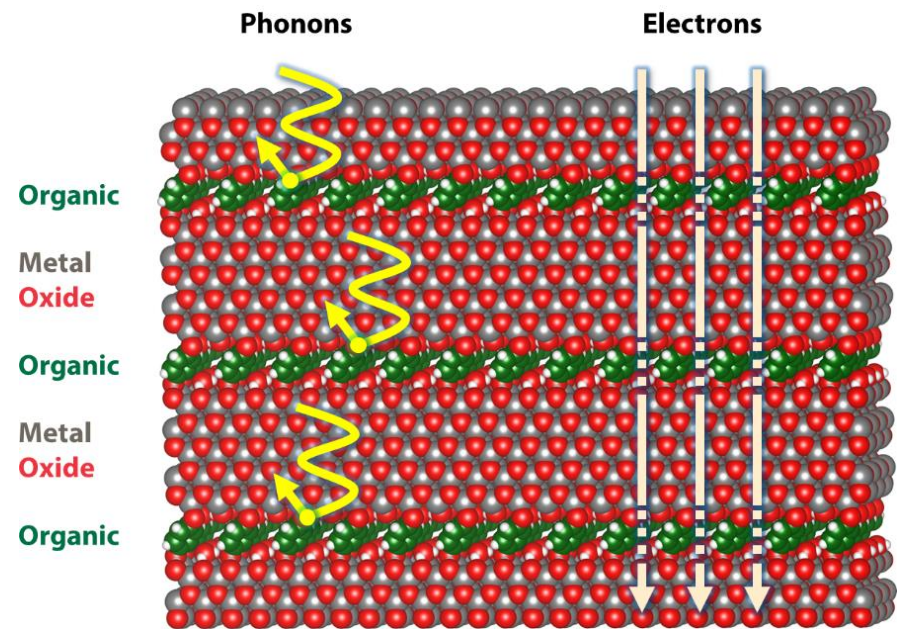
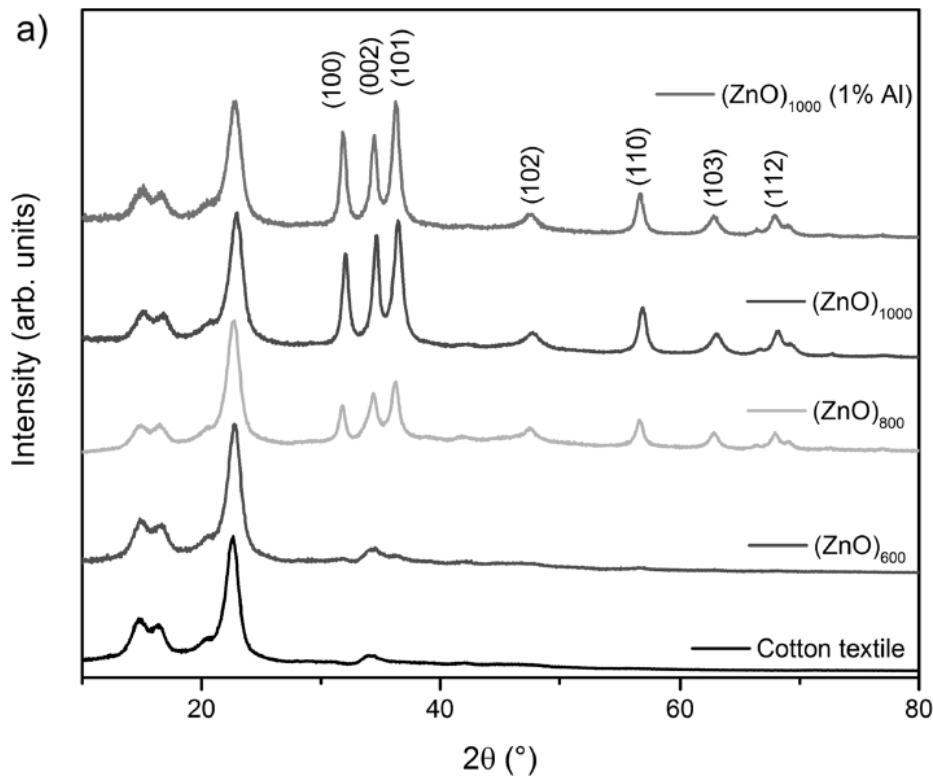
TE material: Bi_2Te_3

TE modules based on bulk materials are not flexible. New materials are required for flexibility!

Flexible Thermoelectric ZnO–Organic Superlattices on Cotton Textile Substrates by ALD/MLD

Antti J. Karttunen,* Liisa Sarnes, Riikka Townsend, Jussi Mikkonen, and Maarit Karppinen

Adv. Electron. Mater. **2017**, 3, 1600459



XRD patterns for ZnO thin films deposited directly on a cotton textile substrate using 600, 800, and 1000 diethylzinc + H₂O cycles. Peak indices for bulk ZnO (*P6₃mc*)

Thermoelectric refrigerators

- The reverse Seebeck effect is called the **Peltier effect**
- Electric current generates a temperature gradient
 - Can be used for cooling (or heating!)
- Thin-film Peltier coolers do actually possess high cooling power densities
- They can be utilized in scenarios where compressor-based cooling is impossible
- Cooling in microelectronics



Figure: blog.novaeletronica.com.br

Figure: alphageek.fi



USB-powered Peltier refrigerator

Thermoelectric figure-of-merit ZT

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T$$

$ZT < 1 \rightarrow$ very specialized applications

$ZT > 1 \rightarrow$ small-scale applications

$ZT > 3 \rightarrow$ large-scale applications (currently, $ZT < 2$)

$S \rightarrow$ Seebeck coefficient (depends on band structure)

$\sigma \rightarrow$ Electrical conductivity (depends on band structure)

$\kappa_e \rightarrow$ Thermal conductivity due to electrons ($\approx LT\sigma$)

$\kappa_l \rightarrow$ Thermal conductivity due to lattice vibrations

$$S = \frac{\pi^2 k^2 T}{3e} \left. \frac{d \ln \sigma(E)}{dE} \right|_{E=E_f}$$

Density of states (DOS)

Metals

- Low S
- High σ
- High κ_e
- Low ZT

Insulators/non-doped semiconductors

- High S
- Zero σ
- High/low κ_l
- Low ZT

Heavily doped semiconductors

- High S
- Low/moderate σ
- High $\kappa_l \rightarrow$ Low ZT
- Low $\kappa_l \rightarrow$ High ZT

Target: Phonon-glass / electron crystal materials (PGEC)

TE generator performance

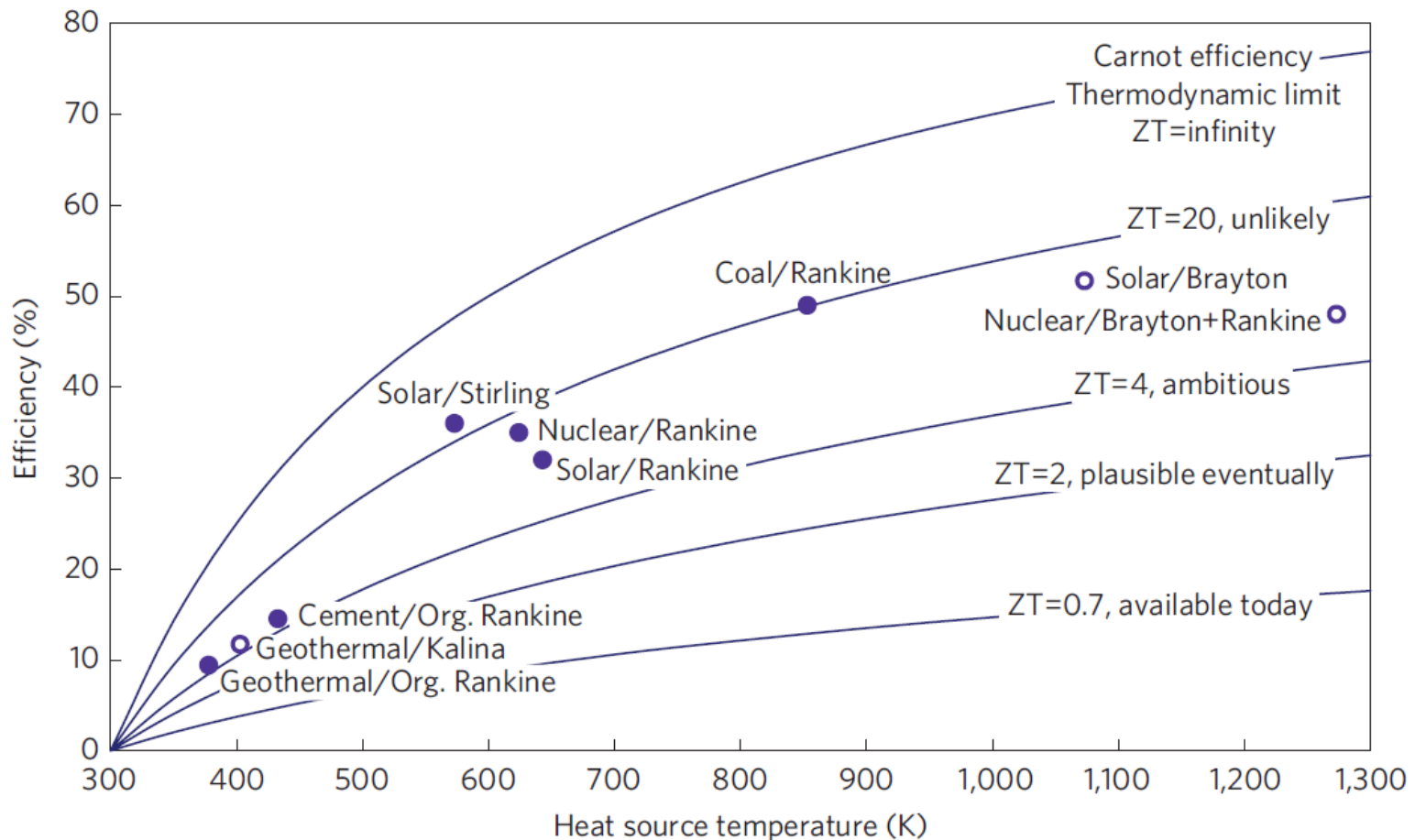


Figure 2 | Assessing thermoelectrics. Efficiency of 'best practice' mechanical heat engines compared with an optimistic thermoelectric estimate (see main text for description).

C. B. Vining, *Nature Mater.* **2009**, *8*, 83.

One big advantage of TE generators: scalability

TE cooling performance

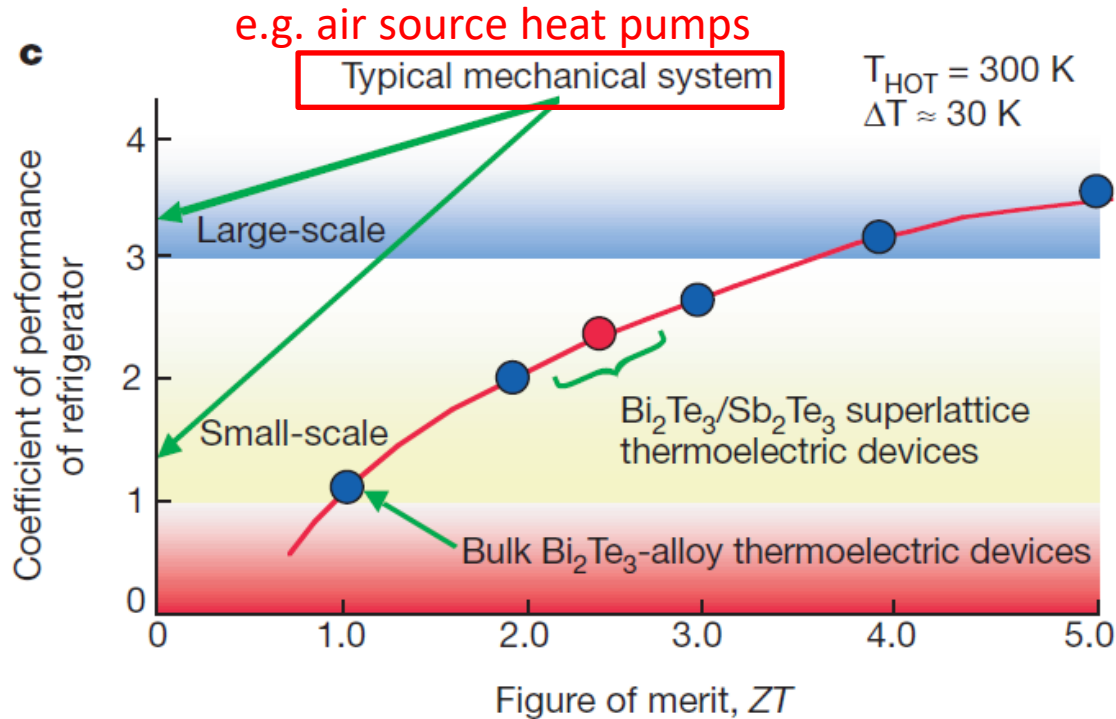
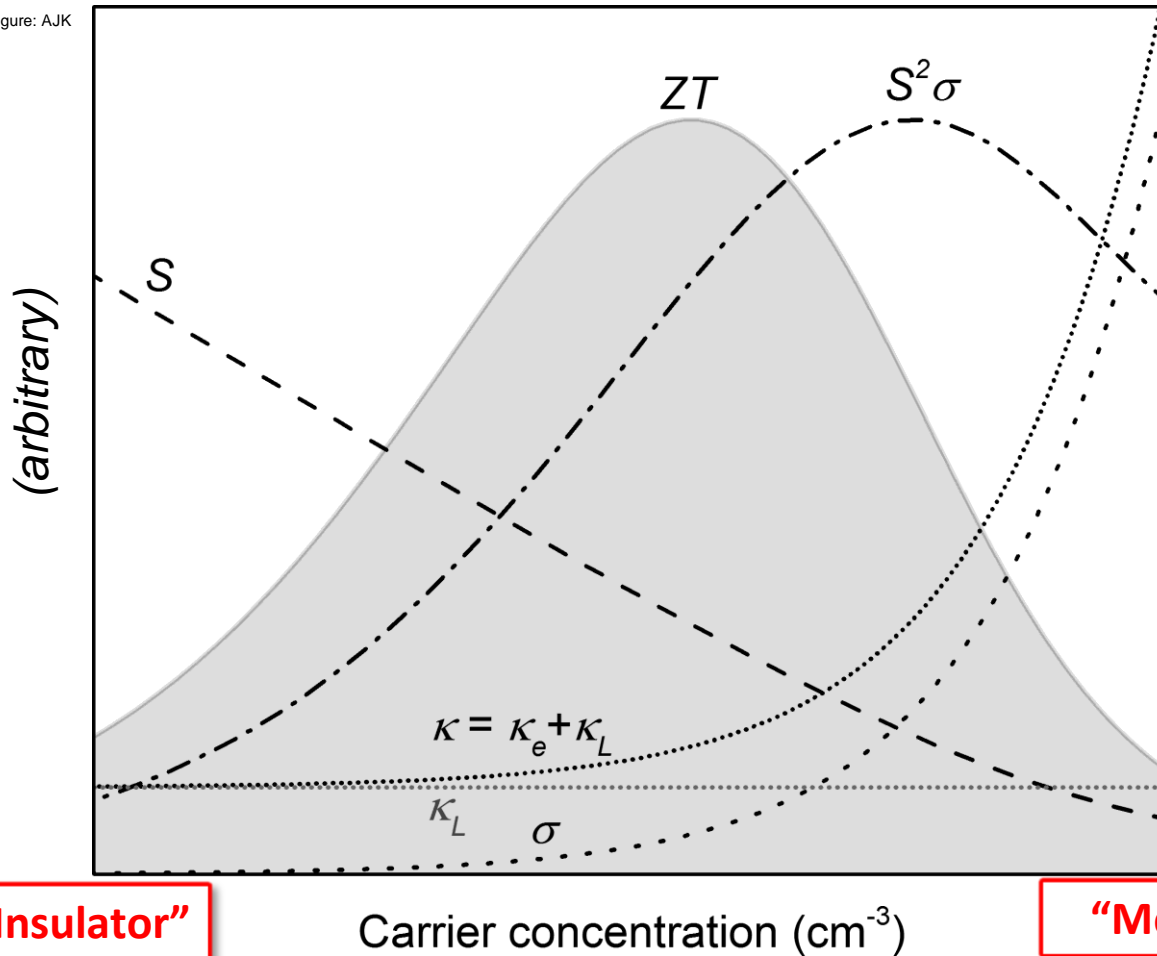


Figure 4 Cooling properties. **a**, Observed cooling as a function of current in a 150- μm circular device made from a p-type superlattice (data shown for hot side at 298 K (blue triangles) and 353 K (red diamonds)) is compared with that of a bulk device (hot side at 298 K, purple circles). **b**, Estimated cooling power density for superlattice devices as a function of current; blue triangles, hot side at 298 K, red diamonds, hot side at 353 K). **c**, Potential COP as a function of ZT with various technologies. T_{HOT} refers to the heat-sink temperature.

It is not easy to increase ZT

The quantities in the thermoelectric figure-of-merit ZT depend on each other.

Figure: AJK



$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_l} T$$

κ_l does decrease as a function of doping, here assumed to stay constant

“Insulator”

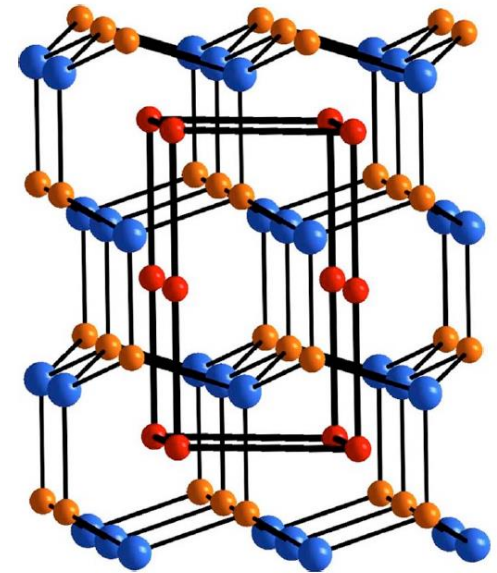
Carrier concentration (cm⁻³)

“Metal”

= doping level

High-throughput screening for thermoelectric materials

- In a pioneering high-throughput screening study (**2006**), Madsen studied ~ 600 Sb-containing materials with Density Functional Theory (DFT)¹
- *n*-doped LiZnSb was predicted to be an excellent thermoelectric material ($ZT \sim 2$ at 600 K, carrier concentration $n = 0.01 e^-$ per unit cell)
- Experimentalists confirmed the accuracy of the predictions for *p*-type LiZnSb, but they could not prepare *n*-type LiZnSb²



LiZnSb: Zn-Sb wurtzite structure ($P6_3mc$) with interstitial lithium ions drawn in red

¹ Madsen, G. K. H. Automated Search for New Thermoelectric Materials: The Case of LiZnSb *J. Am. Chem. Soc.* **2006**, *128*, 12140–12146.

² Toberer, E. S. *et al.* Thermoelectric properties of *p*-type LiZnSb: Assessment of *ab initio* calculations *J. Appl. Phys.* **2009**, *105*, 063701.

State-of-the-art thermoelectric materials

Recent developments (2019)

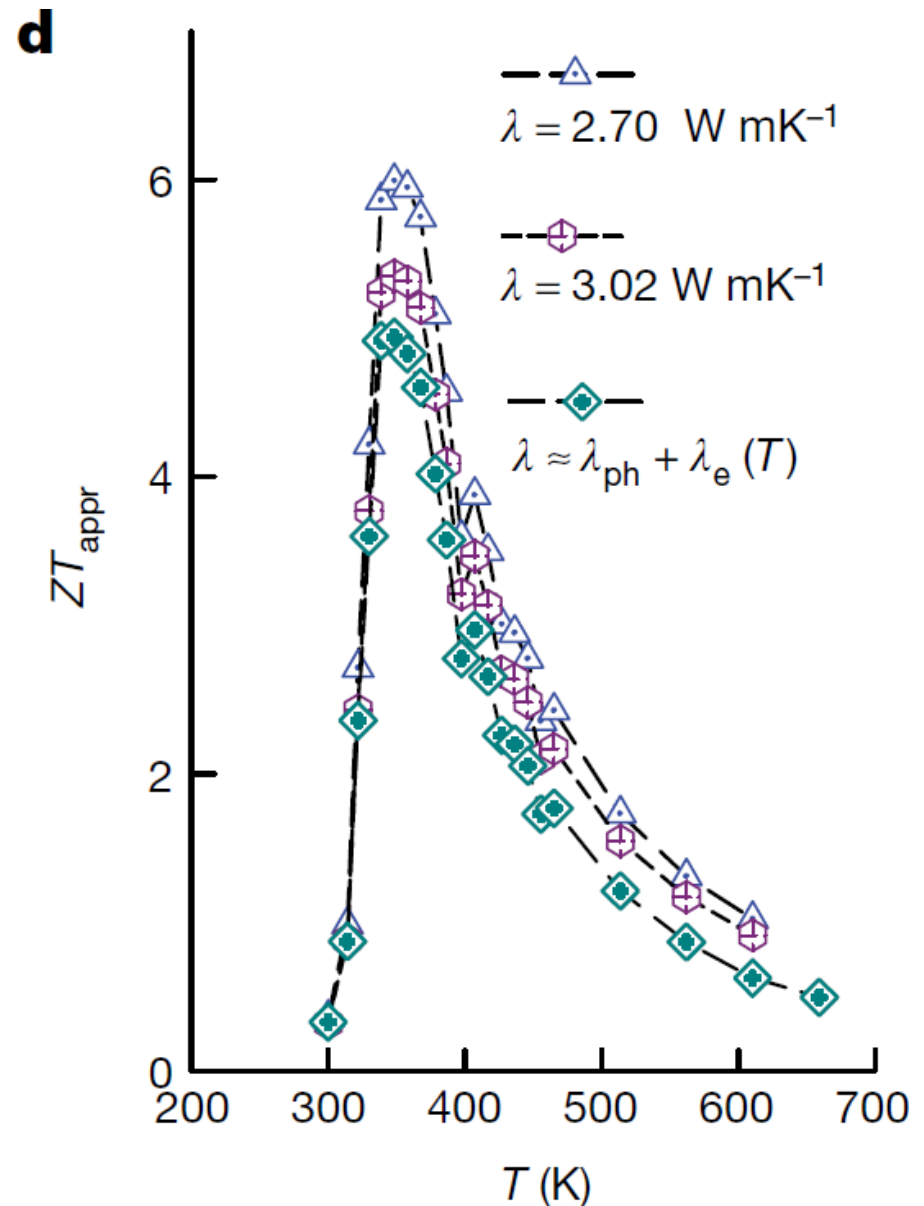
Hinterleitner, B., Knapp, I.,
Poneder, M. *et al.*

Thermoelectric performance of a
metastable thin-film Heusler
alloy.

Nature **576**, 85–90 (2019).

<https://doi.org/10.1038/s41586-019-1751-9>

Thin-film $\text{Fe}_2\text{V}_{0.8}\text{W}_{0.2}\text{Al}$



Two recent reviews

APPLIED PHYSICS REVIEWS 5, 021303 (2018)



APPLIED PHYSICS REVIEWS

<https://doi.org/10.1063/1.5021094>

A practical field guide to thermoelectrics: Fundamentals, synthesis, and characterization

Alex Zevalkink,¹ David M. Smiadak,¹ Jeff L. Blackburn,² Andrew J. Ferguson,² Michael L. Chabinyk,³ Olivier Delaire,^{4,5} Jian Wang,^{6,7} Kirill Kovnir,^{6,7} Joshua Martin,⁸ Laura T. Schelhas,⁹ Taylor D. Sparks,¹⁰ Stephen D. Kang,¹¹ Maxwell T. Dylla,¹¹ G. Jeffrey Snyder,¹¹ Brenden R. Ortiz,¹² and Eric S. Toberer¹²

Fundamentals, exp. methods

CHEMICAL REVIEWS

<https://doi.org/10.1021/acs.chemrev.0c00026>

pubs.acs.org/CR

Review

Advanced Thermoelectric Design: From Materials and Structures to Devices

Xiao-Lei Shi, Jin Zou,* and Zhi-Gang Chen*

Large survey of materials



Cite This: *Chem. Rev.* 2020, 120, 7399–7515



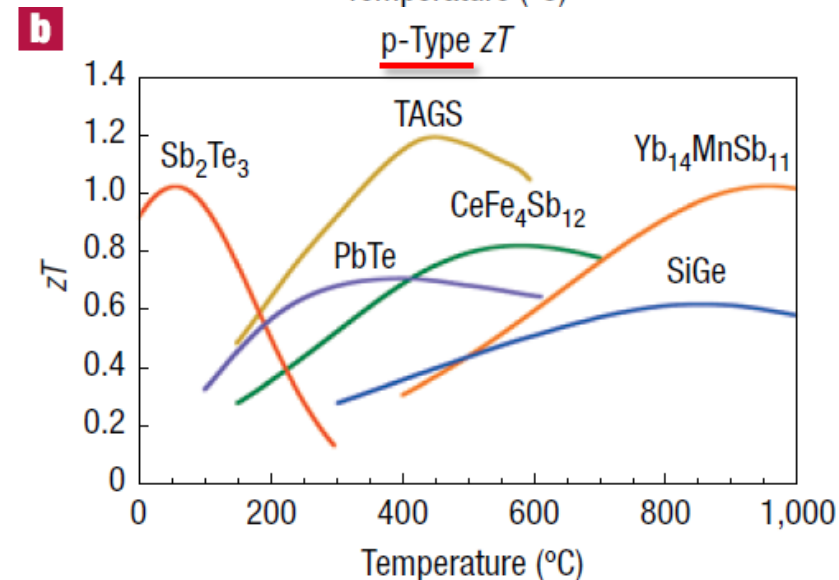
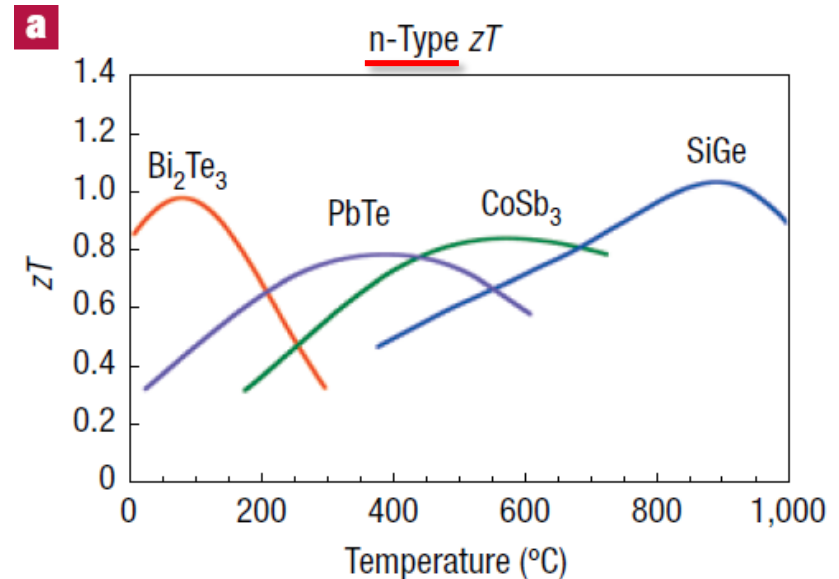
Read Online

Overview on thermoelectric materials

- Bulk tellurides
- Nanostructured materials
 - Superlattices
- SiGe
- Metal oxides
- Zintl phases, group 14 clathrates
- Half-Heuslers
- Skutterudites

For more details, see:
Kutt, L.; Millar, J.; Karttunen, A. J.; Lehtonen, M.;
Karppinen, M.; *Renew. Sustainable Energy Rev.* **2018**, *98*,
519–544.

Figures: G. J. Snyder, E. S. Toberer, *Nature Mater.* **2008**, *7*, 105.

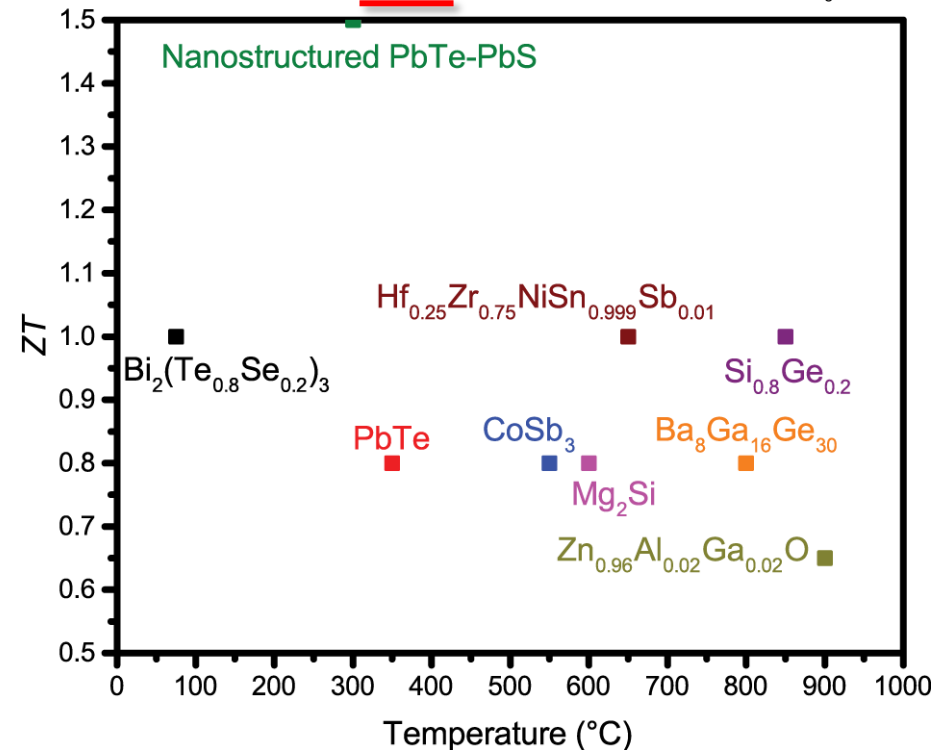
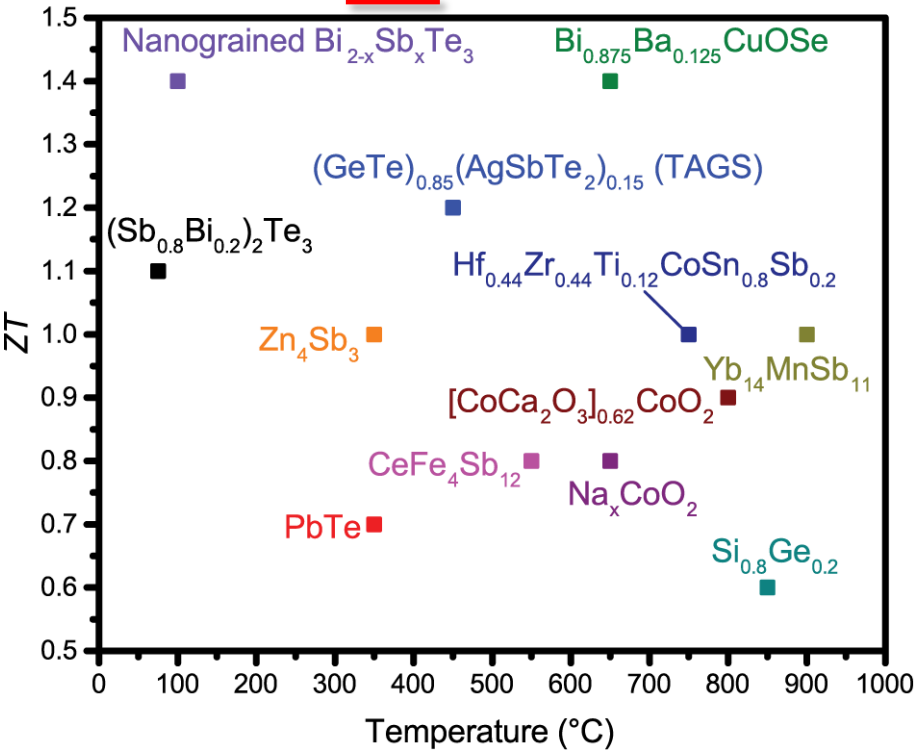


Highest reported ZT values for some thermoelectric materials

p-type TE materials

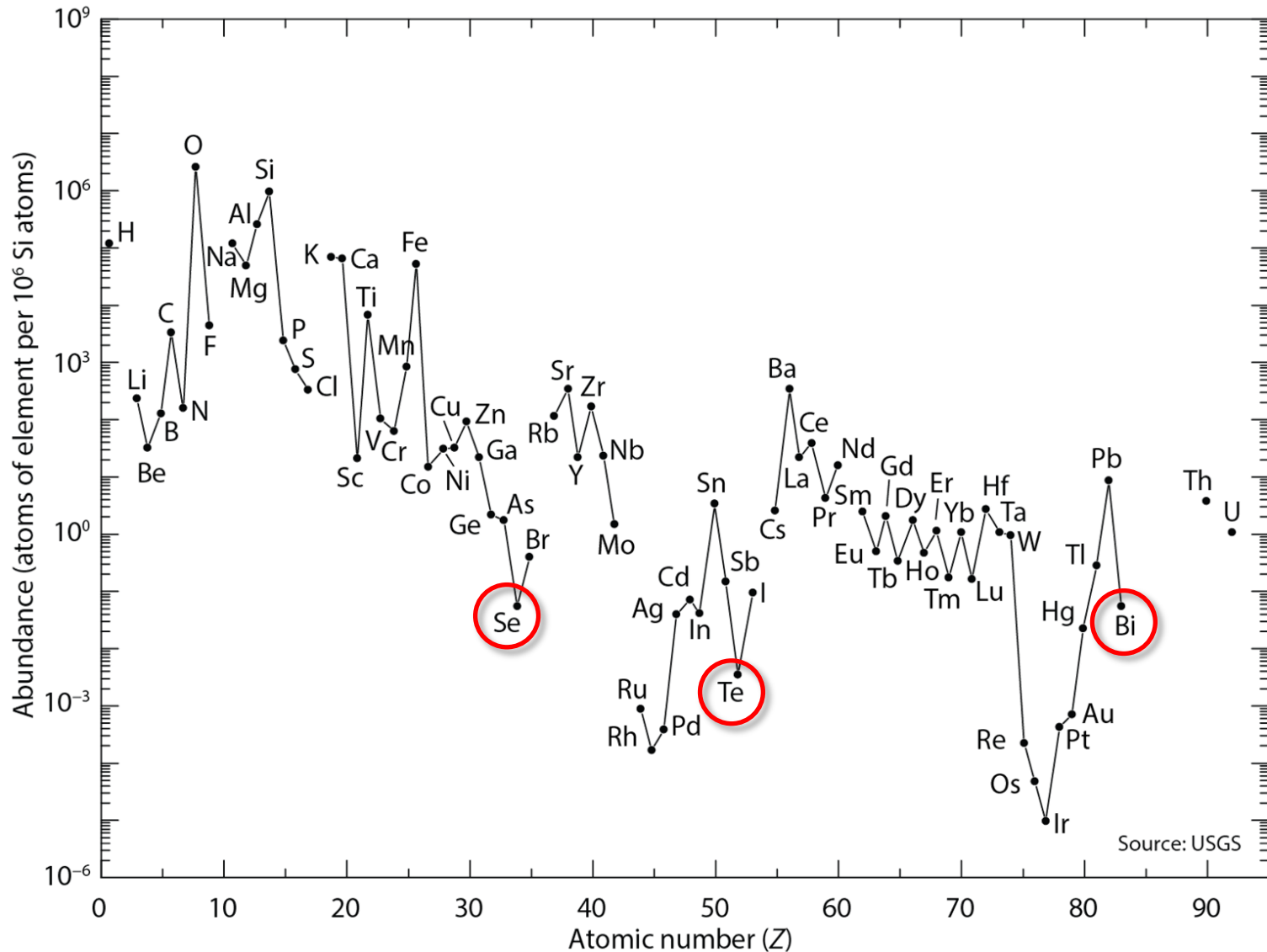
n-type TE materials

Figure: AJK



Data from: Karppinen, M.; Karttunen, A. J. *ALD of thermoelectric materials*, in *Atomic layer deposition in energy conversion applications*, Bachmann J. (Ed.), Wiley, 2017 ([link](#)).

Abundances of the elements in the Earth's crust

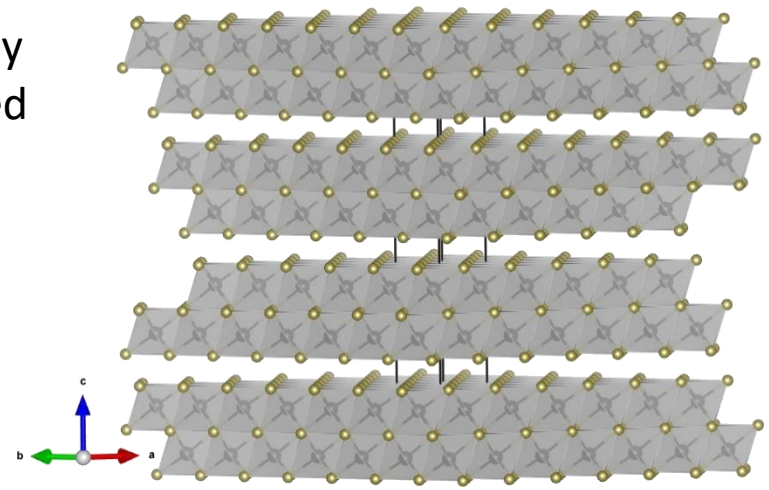


Source: USGS

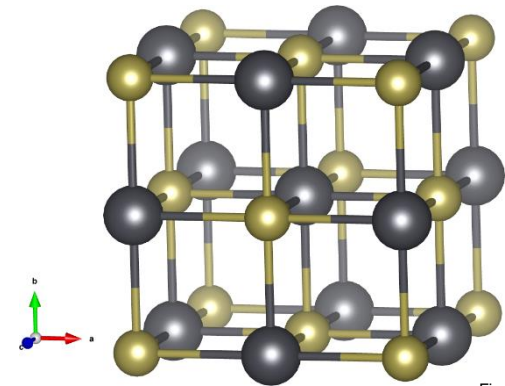
Figure: AJK

Bulk tellurides (1)

- Alloys of bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) are by far the most widely used thermoelectric materials ($\kappa \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$)
- Discovered and optimized in 1950s and 1960s
- $ZT \approx 1$ for near-room-temperature applications
- Have been utilized for decades in solid-state refrigeration applications
- Bismuth tellurides are not very efficient in applications involving temperatures $> 200^\circ\text{C}$, and for higher temperatures (up to 600°C), the telluride material of choice is lead telluride (PbTe)
- ZT values of the telluride materials can be further enhanced by nanostructuring
- The huge downside of the telluride materials is the low abundance of tellurium
- Another significant downside: toxicity (Te, Pb).



Bi_2Te_3 ($R\text{-}3m$)



PbTe ($Fm\text{-}3m$)

Figures: AJK

Bulk tellurides (2)

Material	n/p	ZT_{MAX}	Typical operating T (°C)	Max operating T (°C)
$(Sb_{0.8}Bi_{0.2})_2 Te_3$	p	1.1	50–100	300
$Bi_2(Te_{0.8}Se_{0.2})_3$	n	1.0	50–100	300
PbTe	p	0.7	300–400	600
PbTe	n	0.8	300–400	600
$(GeTe)_{0.85}(AgSbTe_2)_{0.15}$ (TAGS)	p	1.2	400–500	600

SnSe

Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals

Li-Dong Zhao¹, Shih-Han Lo², Yongsheng Zhang², Hui Sun³, Gangjian Tan¹, Ctirad Uher³, C. Wolverton², Vinayak P. Dravid² & Mercouri G. Kanatzidis¹

17 APRIL 2014 | VOL 508 | NATURE | 373

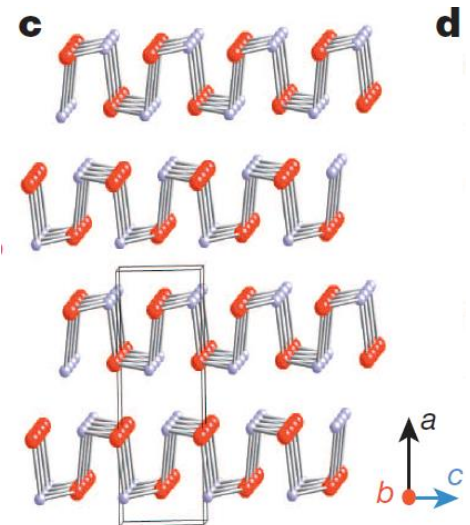
***ZT = 2.6 at room temperature (b-axis)?
Others have had problems reproducing this
(Wei et al. Nature 2016, 539, E1–E2)***

Science 2016, 351, 141.

Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe

Li-Dong Zhao,^{1,2*} Gangjian Tan,² Shiqiang Hao,³ Jiaqing He,⁴ Yanling Pei,¹ Hang Chi,⁵ Heng Wang,⁶ Shengkai Gong,¹ Huibin Xu,¹ Vinayak P. Dravid,³ Ctirad Uher,⁵ G. Jeffrey Snyder,³ Chris Wolverton,³ Mercouri G. Kanatzidis^{2*}

Thermoelectric technology, harvesting electric power directly from heat, is a promising environmentally friendly means of energy savings and power generation. The thermoelectric efficiency is determined by the device dimensionless figure of merit ZT_{dev} , and optimizing this efficiency requires maximizing ZT values over a broad temperature range. Here, we report a record high $ZT_{\text{dev}} \sim 1.34$, with ZT ranging from 0.7 to 2.0 at 300 to 773 kelvin, realized in hole-doped tin selenide (SnSe) crystals. The exceptional performance arises from the ultrahigh power factor, which comes from a high electrical conductivity and a strongly enhanced Seebeck coefficient enabled by the contribution of multiple electronic valence bands present in SnSe. SnSe is a robust thermoelectric candidate for energy conversion applications in the low and moderate temperature range.



SnSe (*Pnma*, #62)

Nanostructured TE materials (1)

- Nanostructured TE materials have gained huge attention during the past 20 years due to the possible efficiency improvements arising from
 - Nanostructure-induced quantum confinement effects (**higher S**)
 - **Increased phonon scattering** from nanometer-scale structural features
- Nanograined $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and nanostructured PbTe–PbS alloys show 50% and 100% increase in ZT values in comparison to their bulk counterparts
- The key question for the actual application is long-term-stability: the material might be degraded more easily in comparison to bulk materials.
- A highly controllable strategy for producing novel nanostructured TE materials is to create superlattices with artificial interfaces between material layers
- $\text{SrTiO}_3/\text{SrTiO}_3:\text{Nb}$ superlattice, where the internal ZT value of the two-dimensional nanostructure was estimated to be as high as 2.4, even though in actual devices the ZT would be limited to around 0.24

Material	n/p	ZT_{MAX}	Typical T (°C)	Max T (°C)
Nanograined $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$	p	1.4	50–150	250
PbTe–PbS	n	1.5	250–350	450
$\text{SrTiO}_3/\text{SrTiO}_3:\text{Nb}$ superlattice	n	2.4 / 0.24	300	

Nanostructured TE materials (2)

Adv. Energy Mater. 2011, 1, 713–731

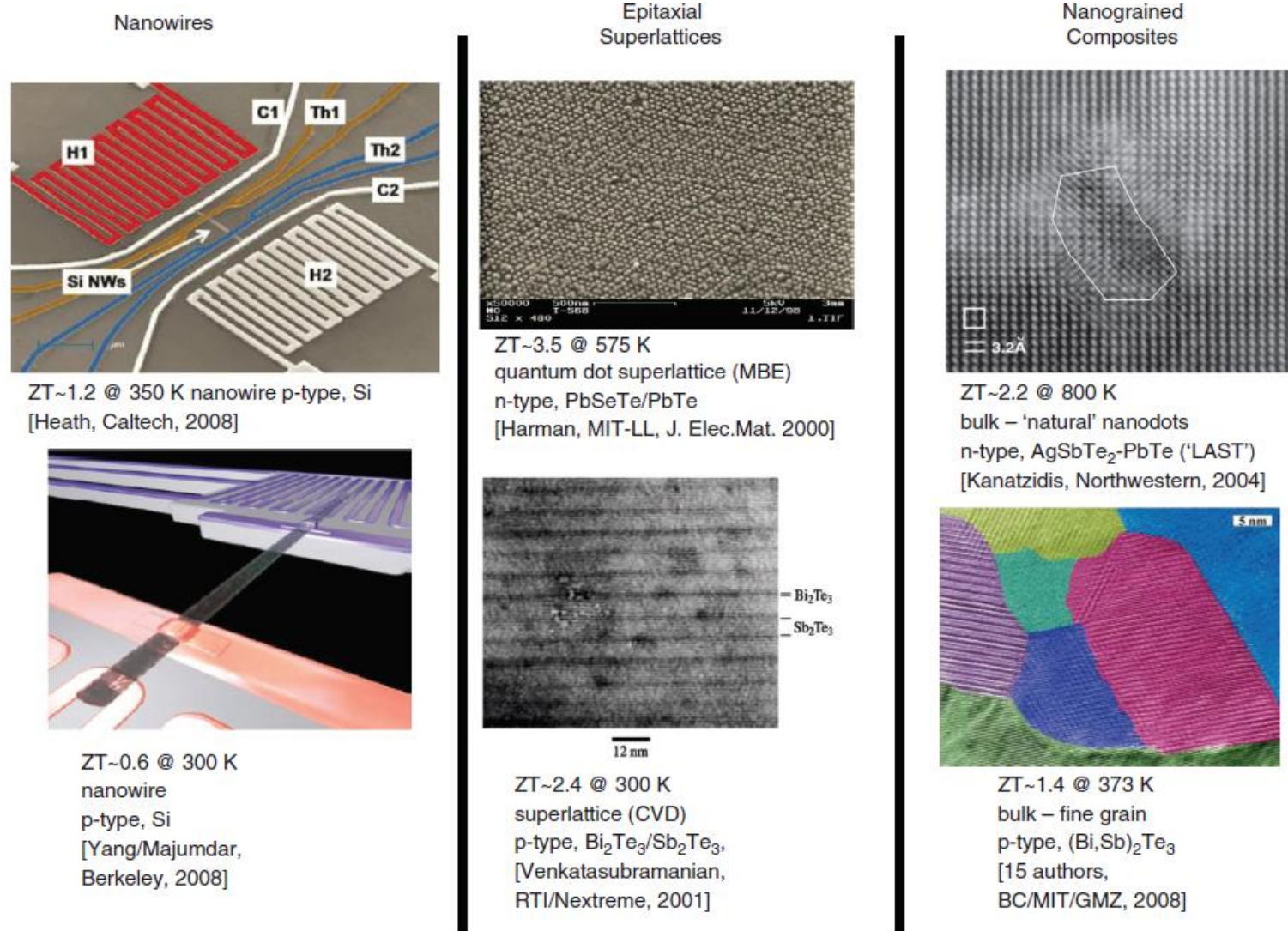


Figure 2. Research highlights on the development of thermoelectric nanostructure and their figure of merit *ZT* of the past decade (2001–2010). Reproduced with permission.^[6–8,10,62] Copyright 2000, Springer; 2004, Science; and 2008, Nature Publishing Group, respectively.

Silicon-germanium alloy

- Silicon-germanium alloy, $\text{Si}_x\text{Ge}_{1-x}$, is the traditional TE material of choice for high temperatures ($> 800^\circ\text{C}$)
- $\text{Si}_x\text{Ge}_{1-x}$ can be doped to function both as n- and p-type material, enabling complete TE devices using one material platform
- While silicon is highly abundant element, germanium is much more expensive, making large-scale application of $\text{Si}_x\text{Ge}_{1-x}$ TE devices unlikely
 - The efficiency is low, as well

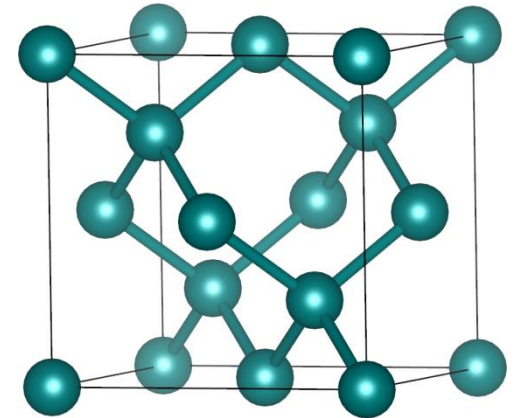


Figure: AJK

$\text{Si} / \text{Ge} (Fd-3m)$

Material	n/p	ZT_{MAX}	Typical operating T ($^\circ\text{C}$)	Max operating T ($^\circ\text{C}$)
$\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.2$)	n	1.0	800–900	1000
$\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.2$)	p	0.6	800–900	1000

Metal oxides (1)

- Metal oxides are in general environmentally benign and thermally stable
- Due to their low carrier mobility and high lattice thermal conductivity values they were not seriously considered for thermoelectrics until the discovery of unexpectedly high electrical conductivity and Seebeck coefficient values for the layered Na_xCoO_2 compound in late 1990s
- Since then a number of other oxide thermoelectrics have been identified as promising TE material candidates particularly for high-temperature applications.
- An advantage of these materials is that they are composed of abundant and relatively cheap elements. However, the TE performance of the currently available oxide materials is not yet up to the level of the best conventional TE materials.

Material	n/p	ZT_{MAX}	Typical operating T (°C)	Max operating T (°C)
$\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$	n	0.65	> 900	> 1000
Na_xCoO_2	p	0.8	600–700	800
$[\text{CoCa}_2\text{O}_3]_{0.62}\text{CoO}_2 / \text{Ca}_3\text{Co}_4\text{O}_9$	p	0.9	700–900	1000
$(\text{Bi}_{0.875}\text{Ba}_{0.125})\text{CuOSe}$ (oxyselenide)	p	1.4	350–650	650

Metal oxides (2)

- Currently, the most intensively investigated oxide materials are probably the p-type misfit-layered cobalt oxide $[\text{CoCa}_2\text{O}_3]_{0.62}\text{CoO}_2$ (low thermal conductivity) and the n-type Al-doped or Al/Ga-dual-doped ZnO (high- T operation ($> 1000^\circ\text{C}$))
- In the first all-oxide TE modules, $[\text{CoCa}_2\text{O}_3]_{0.62}\text{CoO}_2$ is combined with n-type CaMnO_3 perovskite
 - The operation temperature range extends up to *ca.* 800°C

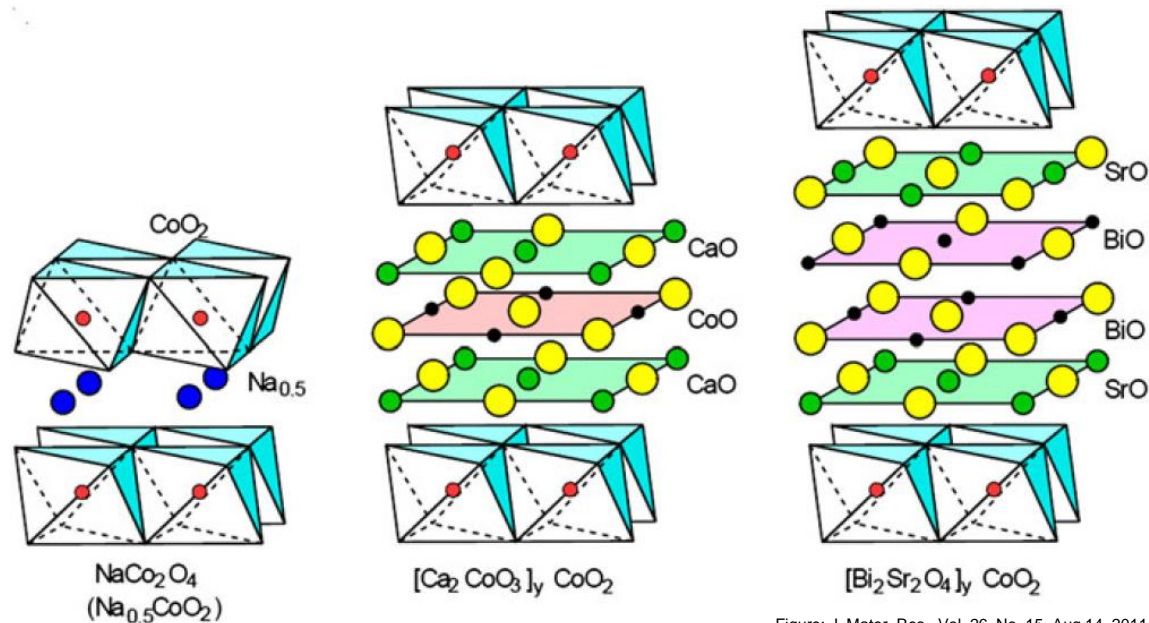


Figure: J. Mater. Res., Vol. 26, No. 15, Aug 14, 2011

Layered cobalt oxides

Zintl phases

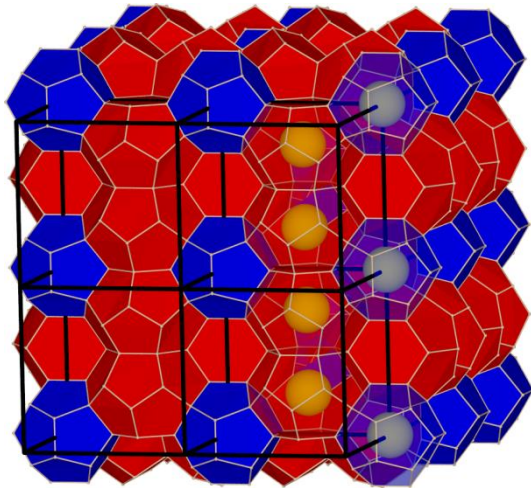
- Zintl phases are a very diverse group of materials and a number of known Zintl phases possess several beneficial properties for thermoelectric applications
- Typically Group 1-2 elements with group 13-16 elements (but not limited to these)
- Zintl phases are typically semiconductors and their atomic-level composition can often be tuned very flexibly, enabling the optimization of TE properties
- Zintl phases often possess rather **complex unit cell**, which leads to low lattice thermal conductivity
- Many thermoelectric Zintl phases are composed of earth-abundant and relatively cheap elements, which is a significant advantage in comparison to traditional TE materials such as bulk tellurides

Material	n/p	ZT_{MAX}	Typical operating T (°C)	Max operating T (°C)
Zn_4Sb_3	p	1.0	300–400	500
$Ba_8Ga_{16}Ge_{30}$ (BGG clathrate)	n	0.8	750–850	950
$Yb_{14}MnSb_{11}$	p	1.0	850–950	1000
Mg_2Si	n	0.8	550–650	800

Zintl Phases: Group 14 clathrates

- Microporous group 14 framework with polyhedral cages (Si, Ge, Sn)
- Charge transfer occurs between the guest and the framework
- The charge is (usually) balanced by heteroatoms in the framework
 - Metallic systems such as $\text{Na}_{24}\text{Si}_{136}$ are also known
- The atomic composition and properties are highly tunable

Clathrate-I ($Pm-3n$, 46 framework atoms in the unit cell)



- $\text{Ba}_8[\text{Ga}_{16}\text{Ge}_{30}]$ (**anionic** framework)
- Each Ba atom donates $2e^-$
- Ga atoms have $1e^-$ less than Ge, so the 4-coordinated framework needs $16e^-$

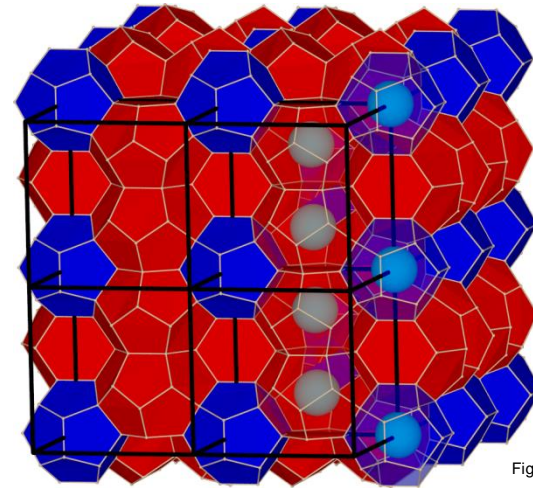
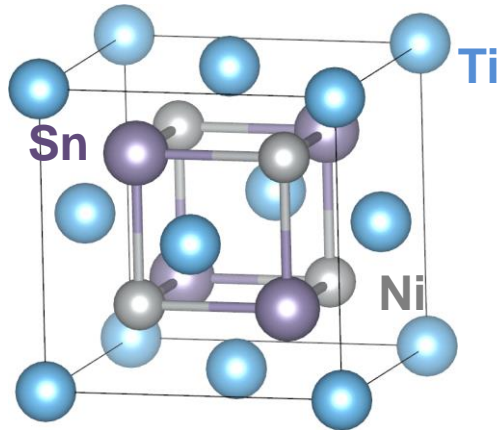


Figure: AJK

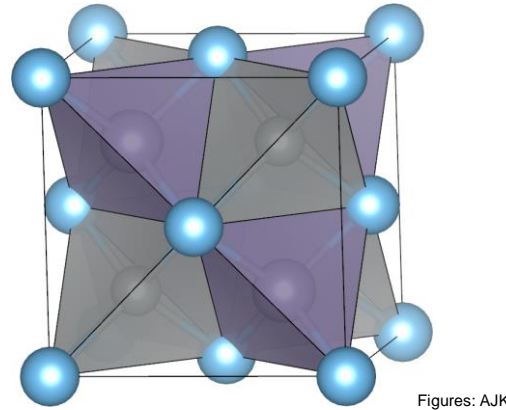
- $\text{I}_8[\text{As}_8\text{Ge}_{38}]$ (**cationic** framework!)
- Each I atom accepts $1e^-$
- As atoms have $1e^-$ more than Ge, these extra electrons are donated to the I atoms

Half-Heuslers

- FCC crystal structure and composition XYZ (Aalto Solid State Chemistry, lecture 12)
- Semiconductors, when they have **8** or **18** valence electrons



TiSnNi (F-43m)
Semiconductor with 18 VE)
(Sn-Ni contacts drawn for clarity,
not bonds)



Another view, Sn and Ni
4-coord., Ti 8-coord.

Figures: AJK

Material	n/p	ZT_{MAX}	Typical operating T (°C)	Max operating T (°C)
$Hf_{0.25}Zr_{0.75}NiSn_{0.99}Sb_{0.01}$	n	1.0	600–700	800
$Hf_{0.44}Zr_{0.44}Ti_{0.12}CoSn_{0.8}Sb_{0.2}$	p	1.0	700–800	800

Skutterudites

- Similar to telluride materials, skutterudites are a well-explored class of thermoelectric materials, which are already being applied in long-life TE generators
- Fundamentally, skutterudites are binary compounds with a composition of MX_3 , where M is a Group 9 *d*-metal (Co, Rh, and Ir) and X is a Group 15 nonmetal (P, As, and Sb)
- The skutterudite structure involves voids, which can be filled by additional atoms, leading into compositions such as cerium-iron-antimony ($CeFe_4Sb_{12}$)
- Expected to fulfil the PGEC-concept, as the additional guest atom reduces the thermal conductivity of the material by scattering heat-carrying phonons

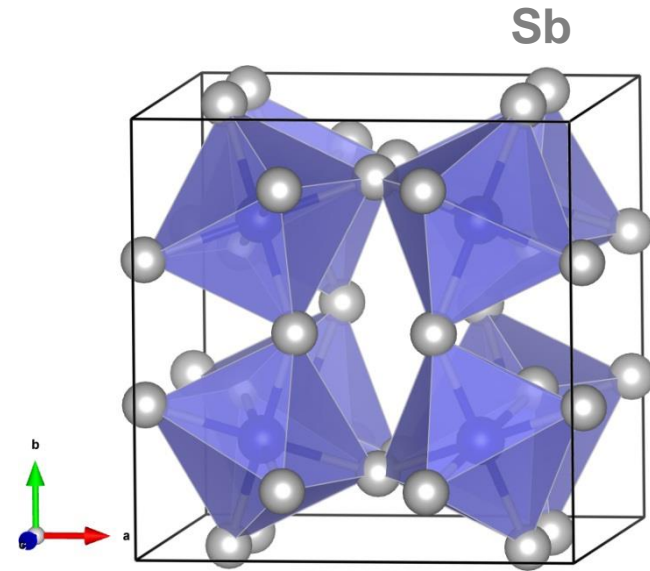
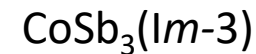


Figure: AJK



Material	n/p	ZT_{MAX}	Typical operating T (°C)	Max operating T (°C)
$CoSb_3$	n	0.8	500–600	700
$CeFe_4Sb_{12}$	p	0.8	500–600	700