Infrared radiation, thermoelectricity and chaos

James Madison University, Harrisonburg VA, Wednesday June 17, 2015

Practical Realization of ZT>1 from the Materials Perspective

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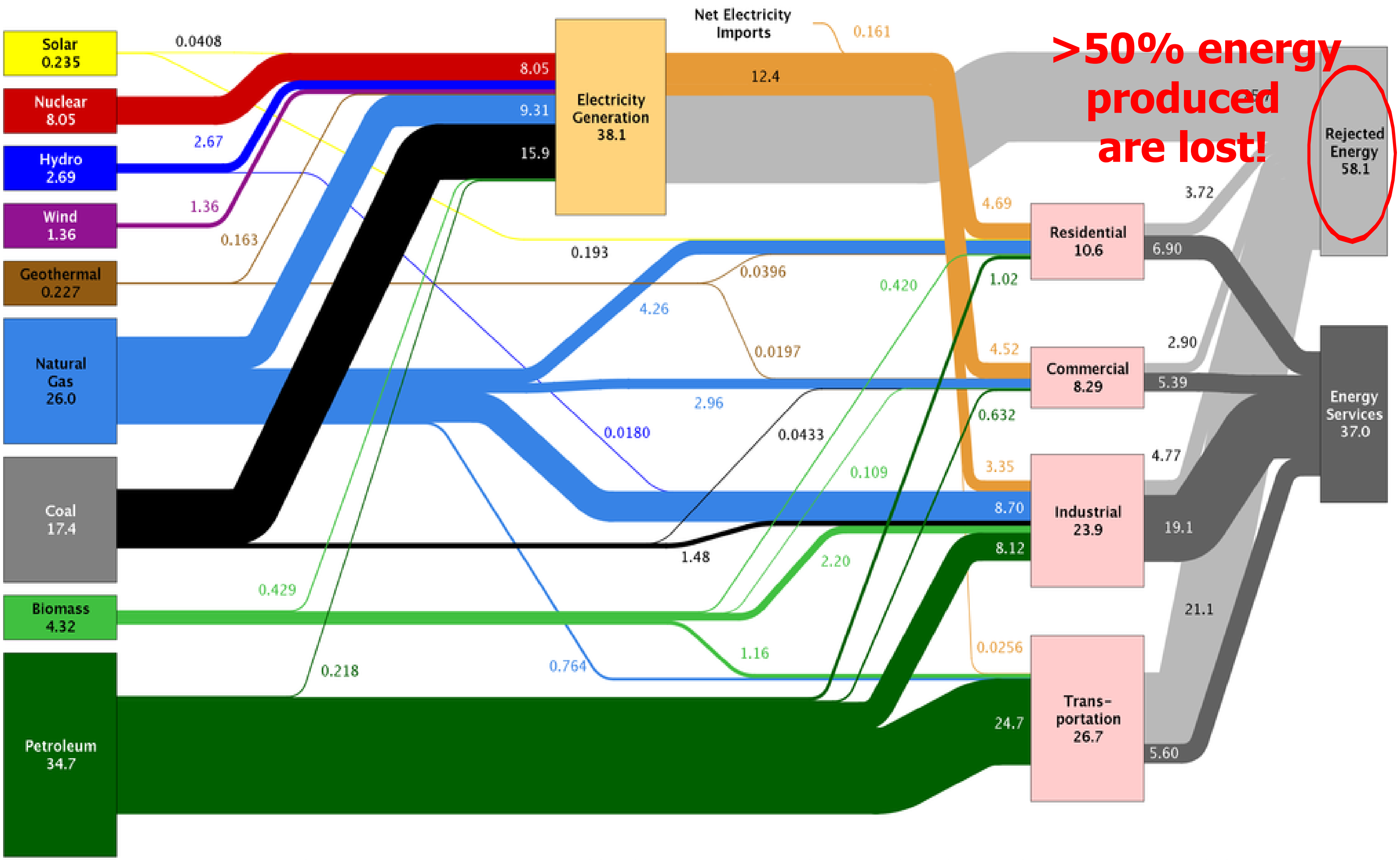
Lee Williams @ Nanosonic
Supported by DOE STTR *Phases 1 & 2*

Estimated U.S. Energy Use in 2012: ~95.1 Quads



Renewables

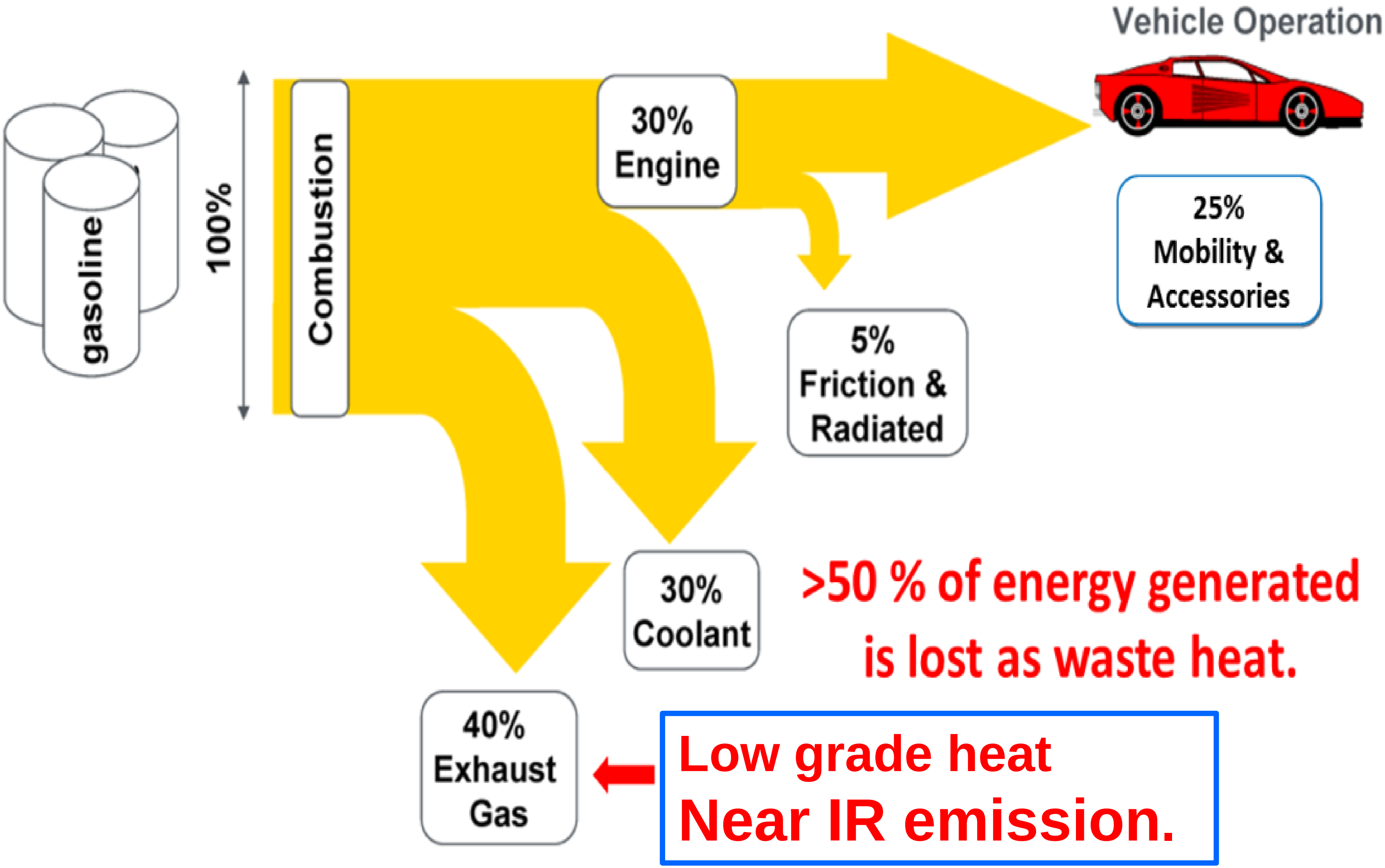
fuels

Fossil

>50% energy produced are lost!

Source: LLNL 2013. Data is based on DOE/EIA-0035(2013-05), May, 2013. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Major Source for Waste Heat Recovery



>50 % of energy generated is lost as waste heat.

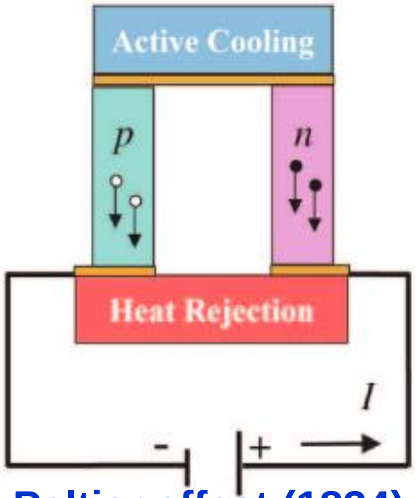
Low grade heat

Near IR emission.

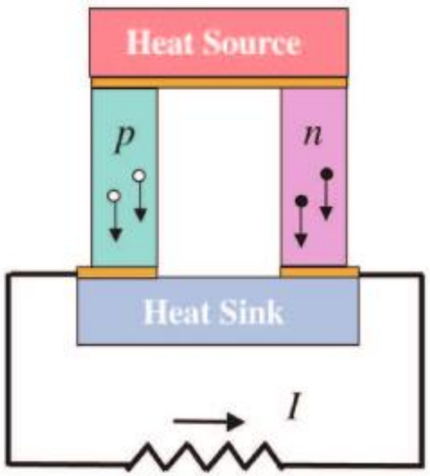
Spark Assisted Gasoline internal Combustion Engine (Light Truck or Passenger Vehicle)

Thermoelectric Effect

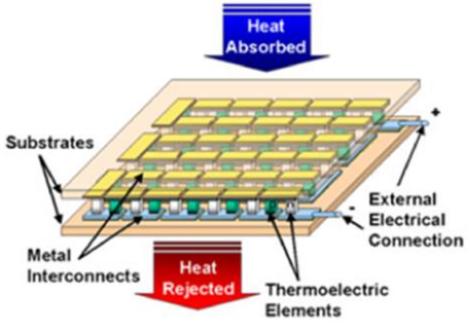
temperature difference ↔ electrical voltage



Peltier effect (1834)
Refrigeration Mode



Seebeck effect (1821)
Power-Generation Mode



No moving parts,
potentially green tech.

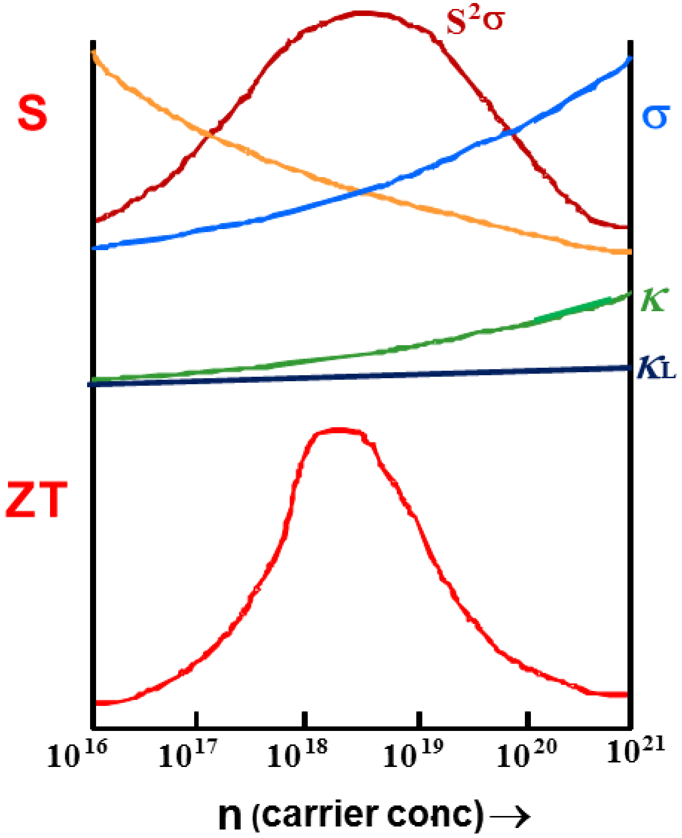
Areas that can benefit from thermoelectric include:
Transportation systems, power plants, and geothermal etc.
Cooling of computer chips, low noise amplifiers, IR detectors.

Thermoelectric Materials Performance

Figure-of-merit (Z), Dimensionless figure-of-merit (ZT)

$$Z = \frac{S^2}{\rho\kappa} \quad \text{or} \quad \frac{S^2\sigma}{\kappa}$$

S = Thermopower (Seebeck coeff.).
ρ= Electrical resistivity, σ = Electrical conductivity.
κ = Thermal conductivity (electronic κ_{el} + lattice κ_L)
Wiedermann-Franz Law $\kappa_{el} = L\sigma T$.



ZT optimization needed
due to conflicting factors

$$\frac{S^2\sigma \uparrow}{\kappa \downarrow}$$

Need independent tuning of S(σ,..) and κ_L

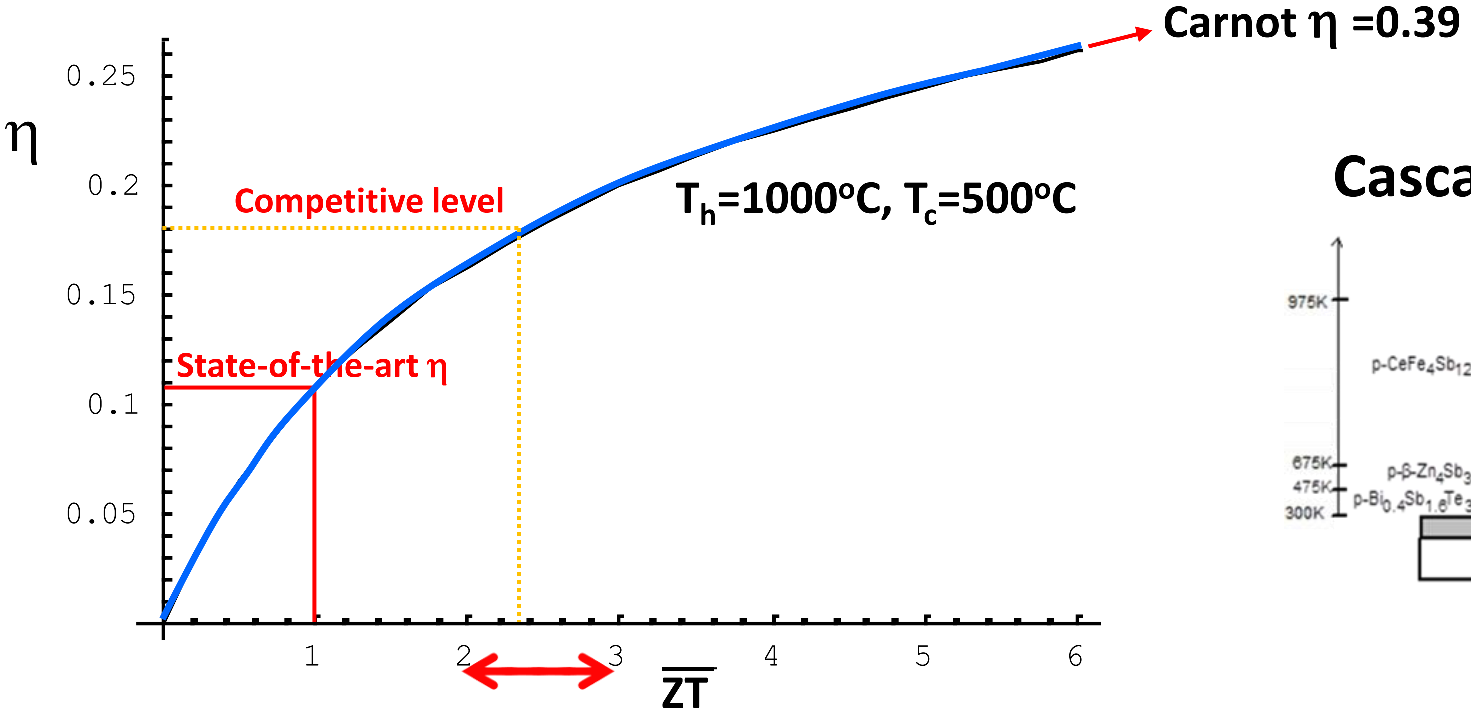
☹

$\sigma \sim \kappa_{el} \downarrow$

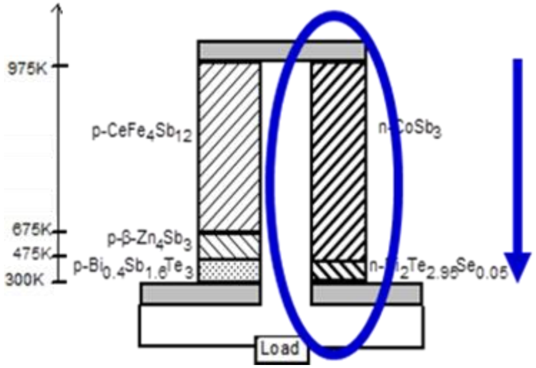
$\kappa = \kappa_{el} + \kappa_L \downarrow$

Device efficiency

$$\eta = \underbrace{\frac{T_h - T_c}{T_h}}_{\text{Carnot}} \frac{\sqrt{1+\overline{ZT}}-1}{\sqrt{1+\overline{ZT}}+1}$$



Cascade TE Device



Need ZT to be high along the legs of the device.

The rest of this talk will focus on

- **Materials consideration.**
- **TE properties enhancing mechanisms.**
- **Half Heusler alloys and nanostructuring results.**
- **Future opportunities.**

Nanostructured Thermoelectric Materials

Materials characterized by a high density of interfaces that provide

. Efficient thermal barrier and scattering of phonons. Less effect on electrical conductivity (mean free path $L_{electron} < L_{phonon}$).

. Efficient energy filtering effect leading to higher thermopower.

Materials Consideration

Locating high-ZT compositions is a challenge!

ZT is increasing function of *E(bandgap)* and parameter $B=N_v\tau(m)^{3/2}/m_i\kappa_L$

where m ***= band mass determined by electronic density of states***

m_i ***= band mass in direction of current (***$m_i=m$ ***in cubic crystal)***

N_v **= degeneracy of the band near Fermi level**

Several general guidelines: ***F. J. DiSalvo, Science 285, 703 (1999)***

Semiconductor can be doped to a high carrier density of ~$10^{19}/cm^3$ to give optimal S^2/ρ.

High symmetry crystal structure (high N_v) with a large number of heavy elements per unit cell (low κ_L). *Complex crystals can help*.

Small electronegativity differences between the elements favors high mobility.

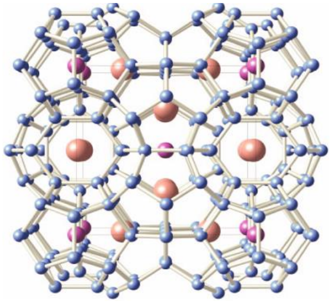
Alloying or "rattling" to further reduce the thermal conductivity.

A high effective mass.

Complex Crystal Systems (ZT>1 to 2.6)

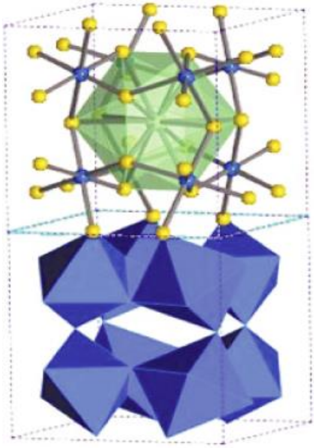
(Scatter phonons and enhance power factor)

Clathrate



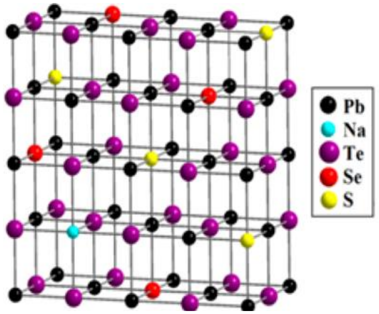
$Ba_8Ga_{16}Ge_{30}$

Skutterudite



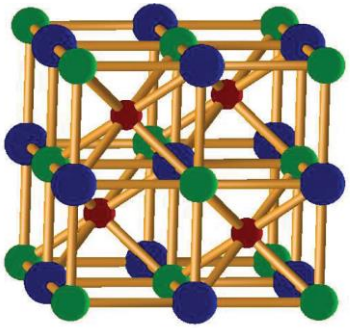
$LaCo_4Sb_{12}$

Lead Chalcogenide



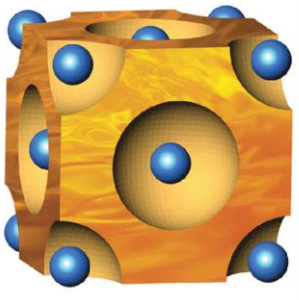
$(PbTe)_{1-2x}(PbSe)_x(PbS)_x$

Half-Heusler



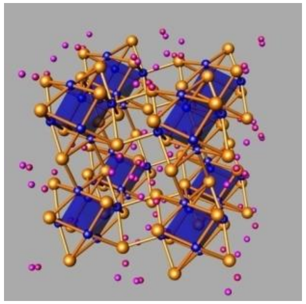
ZrNiSn

Chalcocite



Cu_2S

Chevrel Phase



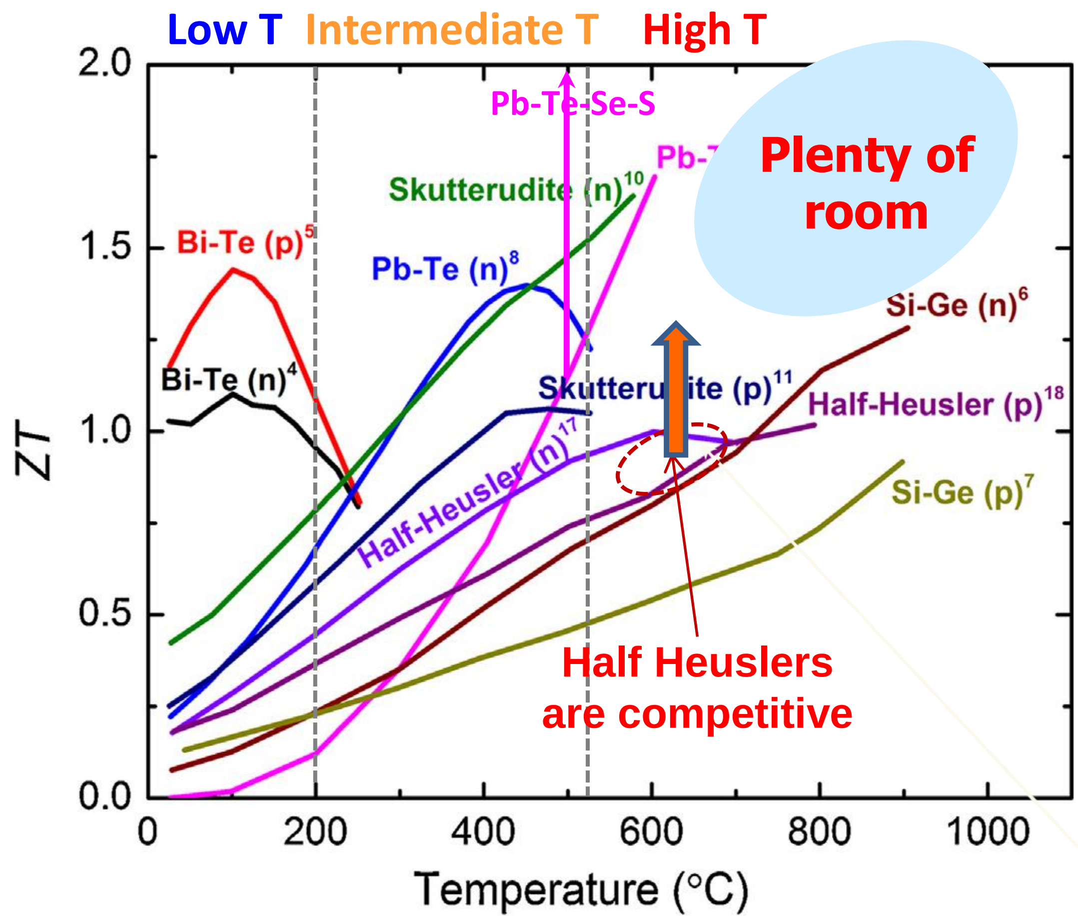
$Cu_4Mo_6Se_8$

G. Nolas, S. J. Poon, M. Kanatzidis, MRS Bull. 30, 199-205 (2006).

R.J. Korkosz , T.C. Chasapis, S.H. Lo, J.W. Doak, Y.J. Kim, C.I. Wu, E. Hatzikraniotis, T.P. Hogan, D.N. Seidman, C. Wolverton, V.P. Dravid, and M.G. Kanatzidis, J. Am. Chem. Soc. 136, 3225 (2014).

Y. He, T. Day, T. Zhang, H. Liu, X. Shi, L.D. Chen, and G.J. Snyder, Adv. Mater. 26, 3974 (2014).

Thermoelectric Materials with ZT ≥ 1



Overview of *ZT* vs temperature for different thermoelectric materials. The detailed compositions are Bi–Te (*n*): $Cu_{0.01}Bi_2Te_{2.7}Se_{0.3}$ [4]; Bi–Te (*p*): $Bi_xSb_{2-x}Te_3$ [5]; Pb–Te (*n*): $PbTe_{0.9988}I_{0.0012}$ [8]; Pb–Te (*p*): $K_{0.02}Pb_{0.98}Te_{0.15}Se_{0.85}$ [9]; skutterudite (*n*): $Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$ [10]; skutterudite (*p*): $Ce_{0.45}Nd_{0.45}Fe_{3.5}Co_{0.5}Sb_{12}$ [11]; half-Heusler (*n*): $Hf_{0.25}Zr_{0.75}NiSn_{0.99}Sb_{0.01}$ [17]; half-Heusler (*p*): $Hf_{0.44}Zr_{0.44}Ti_{0.12}CoSn_{0.8}Sb_{0.2}$ [18]; Si–Ge (*n*): $(Si_{95}Ge_5)_{0.65}(Si_{70}Ge_{30}P_{30})_{0.35}$ [6]; Si–Ge (*p*): $(Si_{80}Ge_{20})_{0.8}(Si_{100}P_3)_{0.2}$ [7].

S. Chen and Z. F. Ren, Mater. Today 16, 387 (2013).

Workhorse bulk materials
(ZT ≈ 1)

Cooling **Bi_2Te_3**

Power Generation **$Si_{1-X}Ge_X$**

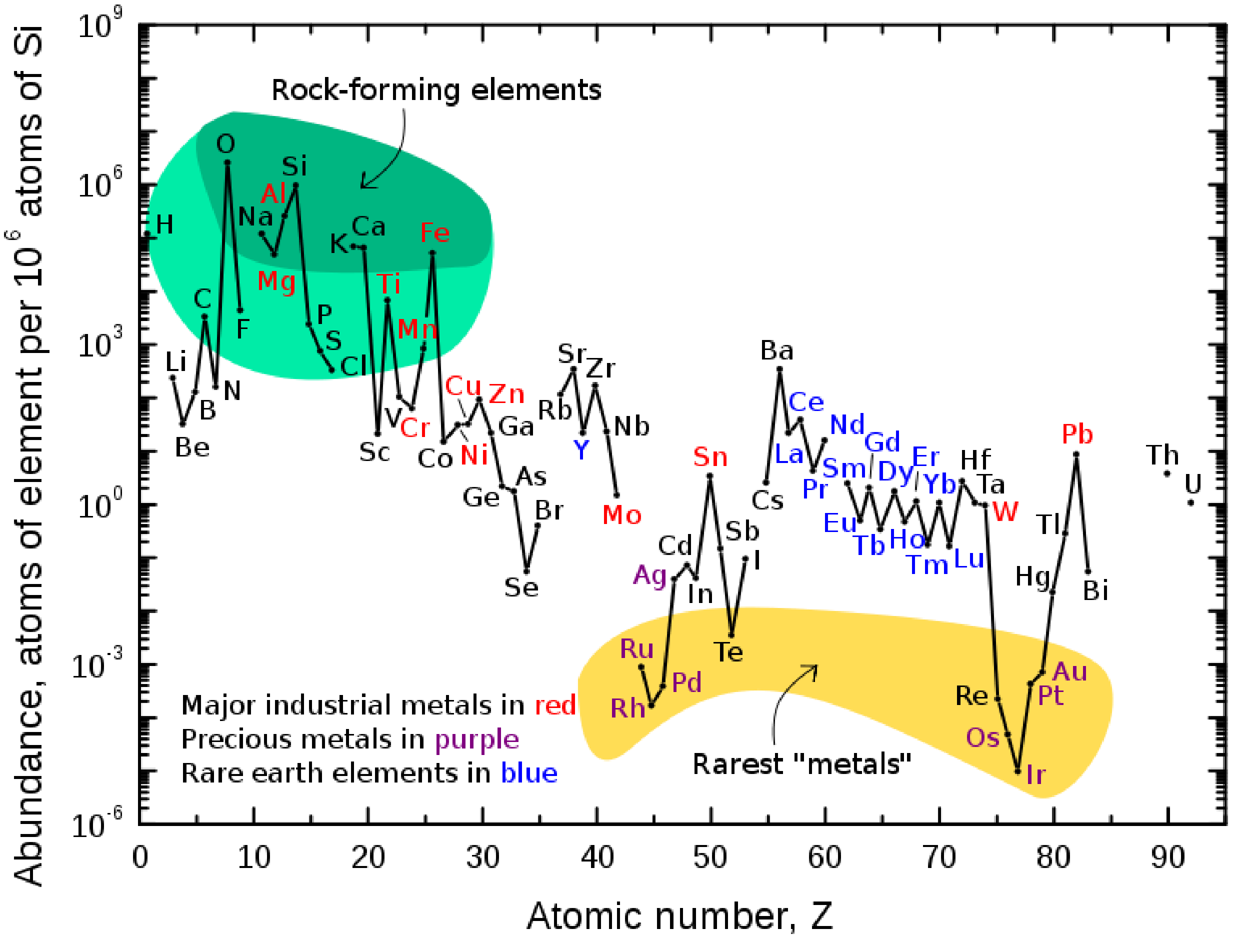
Half-Heusler Alloys (ZT~1)

N-type: S. J. Poon, D. Wu, S. Zhu, W. J. Xie, T. M. Tritt, P. Thomas, and R, Venkatasubramanian, J. Mater. Res. 26, 2795 (2011).

P-type: X. Yan, G. Joshi, W. Liu, Y. Lan, H. Wang, S. Lee, J.W. Simonson, S. J. Poon, T. M. Tritt, G. Chen, and Z. F. Ren, Nano Lett, DOI: 10.1021/n/104138t (2010).

Recently, we reported ZT~1.2 http://arxiv.org/abs/1505.07773.

Elemental Relative Abundance



Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. The rarest elements in the crust (shown in yellow) are not the heaviest, but are rather the siderophile (iron-loving) elements in the Goldschmidt classification of elements. These have been depleted by being relocated deeper into the Earth's core. Their abundance in meteroids materials is relatively higher. Additionally, tellurium and selenium have been depleted from the crust due to formation of volatile hydrides. [Wikipedia]

Materials Scarcity, Volatility, Toxicity

Material	ZT (high T)	Abundance in Earth's crust (ppm)	Volatility Toxicity
Skutterudites	P-type ~1.5 CeFe4Sb12, N-type ~0.9	Ce (60), other RE (~1), Fe (~10^5), Sb (0.2).	Sb (MAJOR element) Sb
Pb(Te,Se,S)	N-type ~1.4 P-type ~2	Pb (12), Se (0.05), Te (0.001).	Se, Te Pb, Te
Half Heuslers	N type ~1 HfZrNiSn(Sb), P-type ~1 HfZrCoSbSn.	e.g. Hf (3), Zr (180), Ti (6.10^3), Nb (20), V (150), Fe (~10^5), Ni (100), Co (25), Sn (2.2), Sb (0.2), Mg (~10^5), Ag (0.08).	Sb (non-major element)

Cu_2S chacocite with ZT~1.5-1.8 is promising: Cu and S are abundant.

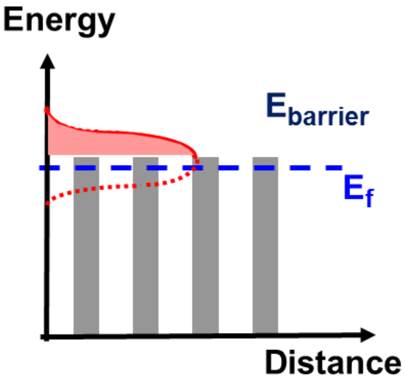
TE Properties Enhancement Mechanisms

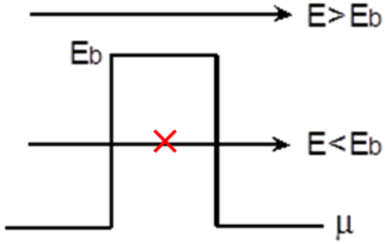
Examples Involving Nanostructuring

Electronic Effects Enhancing Seebeck Coeff.

Search for good thermoelectrics

Energy filtering





$$S = -(k/e\sigma)\int_{E_b}^{\infty} [(E-\mu)/kT]\sigma(E)\,dE$$

$$\sigma = \int_0^{\infty} \sigma(E)\,dE$$

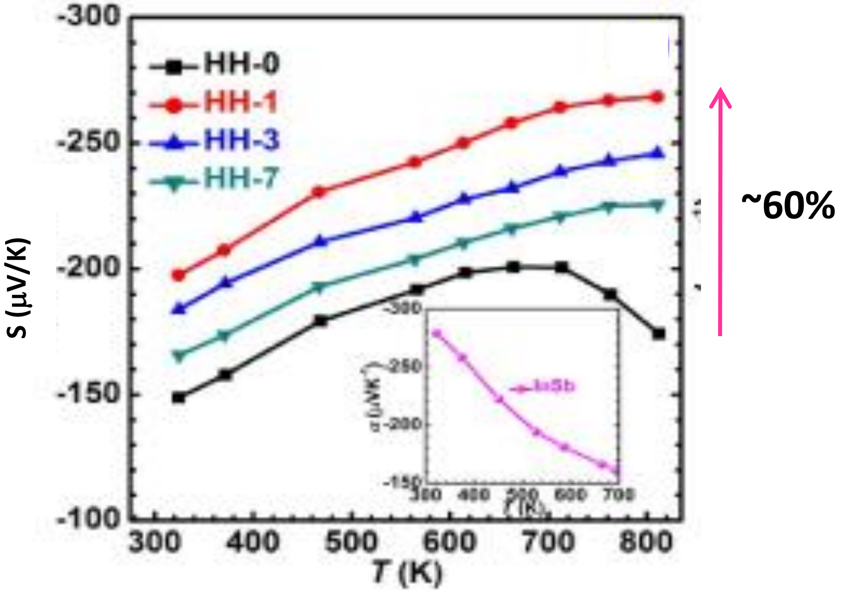
J. Martin, Li Wang, L. Chen, and G. S. Nolas, Phys. Rev. 79, 115311 (2009).
M. Zebarjadi *et al*, Appl. Phys. Lett. 94, 202105 (2009).
A. Popescu and L. M. Woods, Appl. Phys. Lett. 97, 052102 (2010).

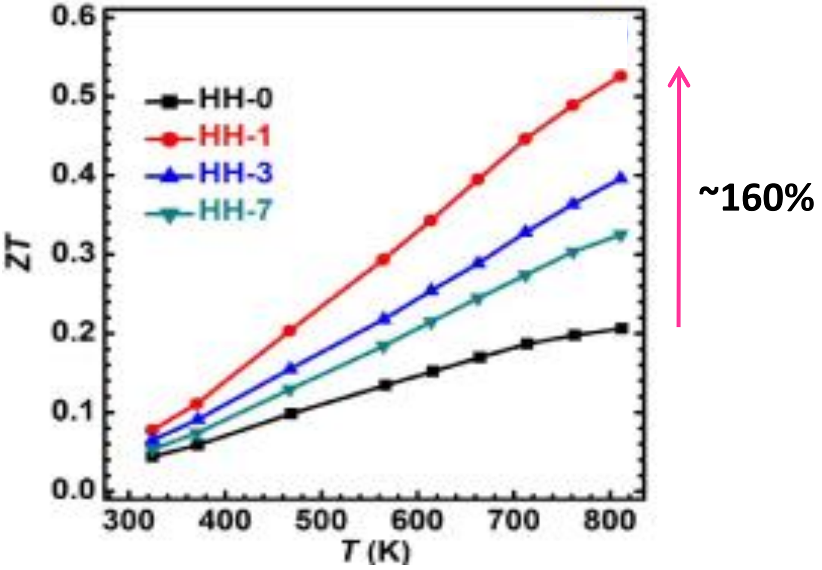
p-type (TiZrHf)CoSb

InSb-nanoinclusions result in Seebeck coeff. enhancement

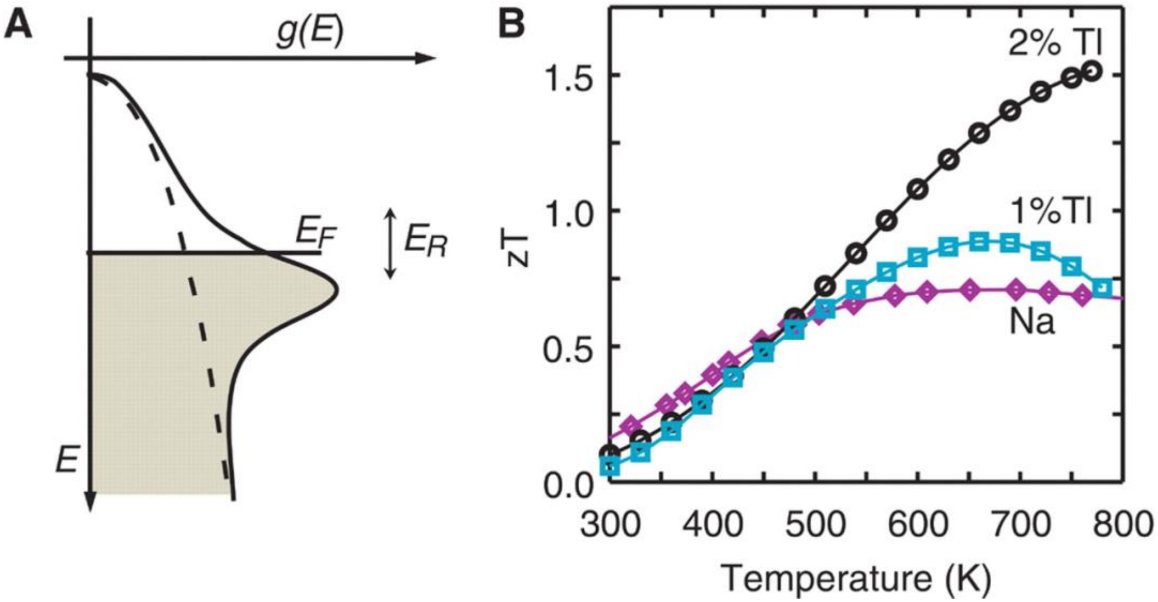
$$\boxed{ZT \sim S^2}$$

W. J. Xie, J. He, S. Zhu, X. Su, S. Wang, T. Holgate, J. W. Graff, V. Ponnambalam, S. J. Poon, X. Tang, Q. Zhang, and T. M. Tritt, Acta Mater. 58, 4705 (2010).





Non-Isoelectronic Resonant States (Orbitals Hybridization)

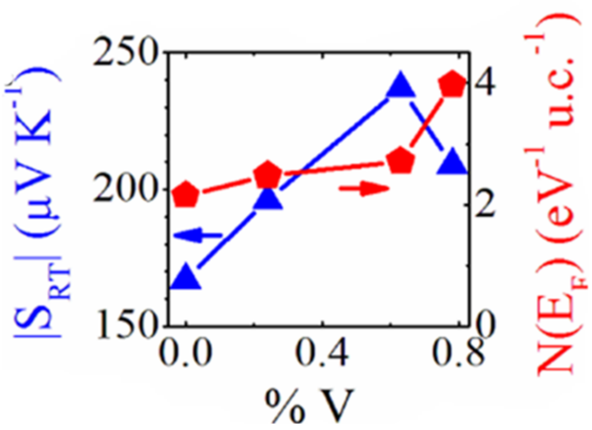


(A) Cartoon model of PbTe valence band with Tl doping. (B) Effect on ZT

J.P. Heremans, V. Jovovic, E.S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, and G.J. Snyder, Science 321, 554 (2008).

Dopant Resonant States

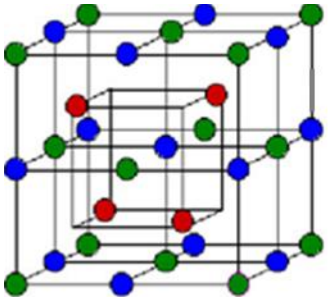
$Hf_{.75}Zr_{.25}V_xNiSn$



J. W. Simonson, D. Wu, W. J. Xie, T. M. Tritt, and S. J. Poon, Phys. Rev. B 83, 235211 (2011).

Resonant States in Half-Heusler alloys

Half Heusler Phases

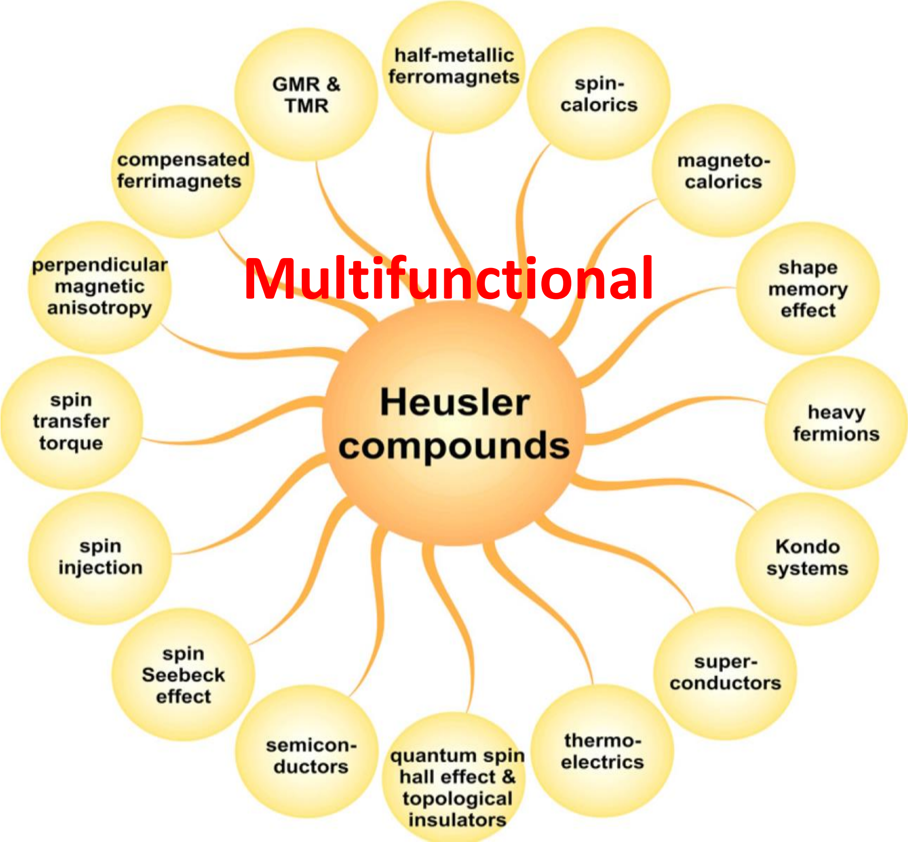


(MgAgAs-type, half filled GaAs)

🟢 Ti, Zr, Hf

🔴 Ni, Pd, Pt

🔵 Sn, Sb



Multifunctional

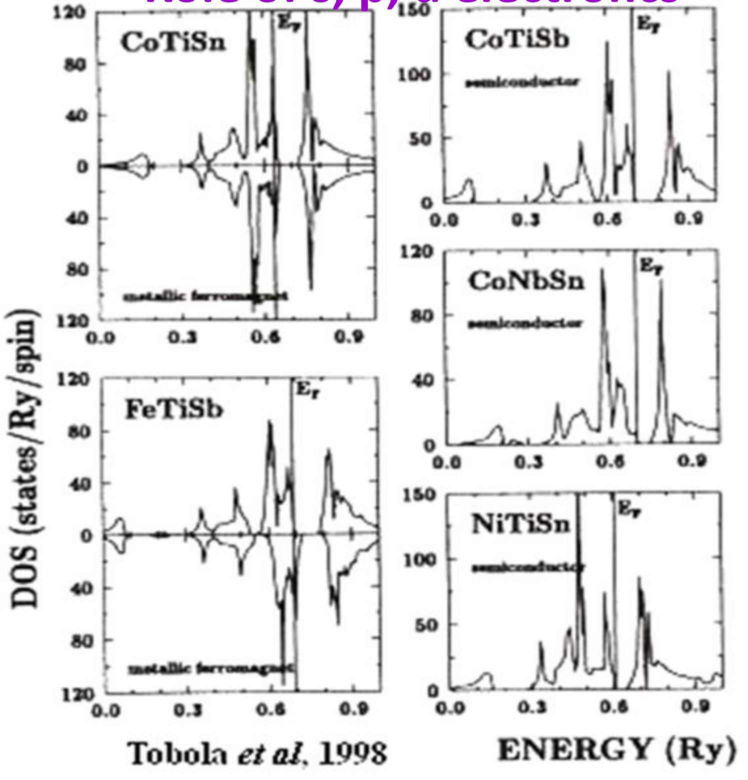
T. Graf, C. Felser, S. S. P. Parkin, Prog. Solid State Chem. 39, 1 (2011).

Valence electron count

$\neq 18$ — **Half metal**

$=18$ — **Semiconductor**

Role of s, p, d electroncs



Tobola *et al*, 1998

- **High Seebeck coefficient**

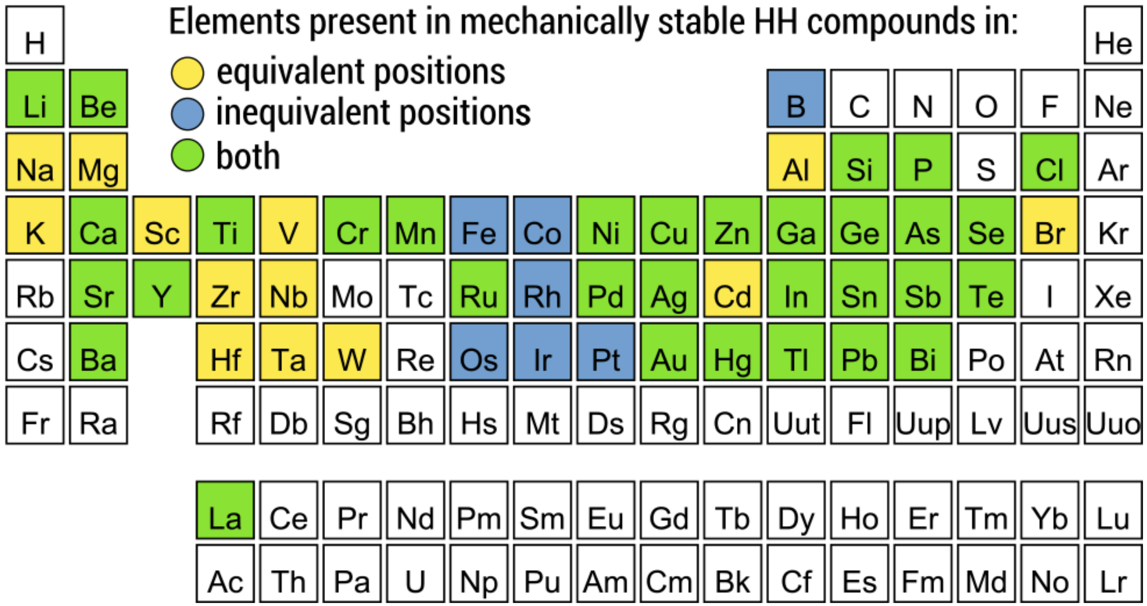
  S ~ 100-200 μV/K

- **Moderate electrical resistivity**

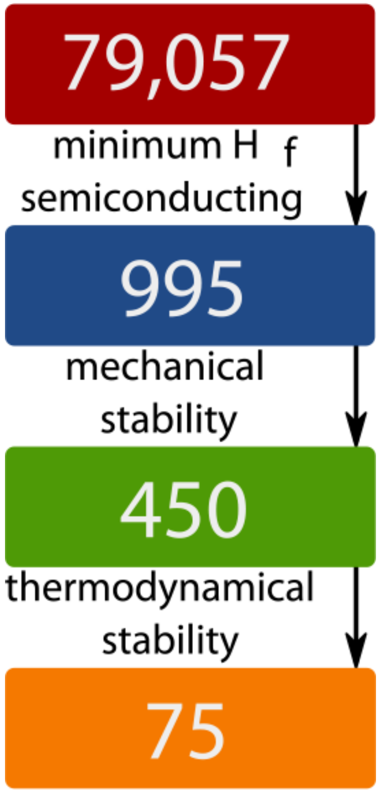
  ρ ~ 10^{-3}-10^{-4} Ω-cm

Finding low-thermal-conductivity half-Heusler semiconductors via high-throughput materials modeling

(Carrete, Li, Mingo, Wang, and Curtarolo, Phys. Rev. X 4, 011019 (2014)).



100s' compositions


79,057

minimum H_f semiconducting

995

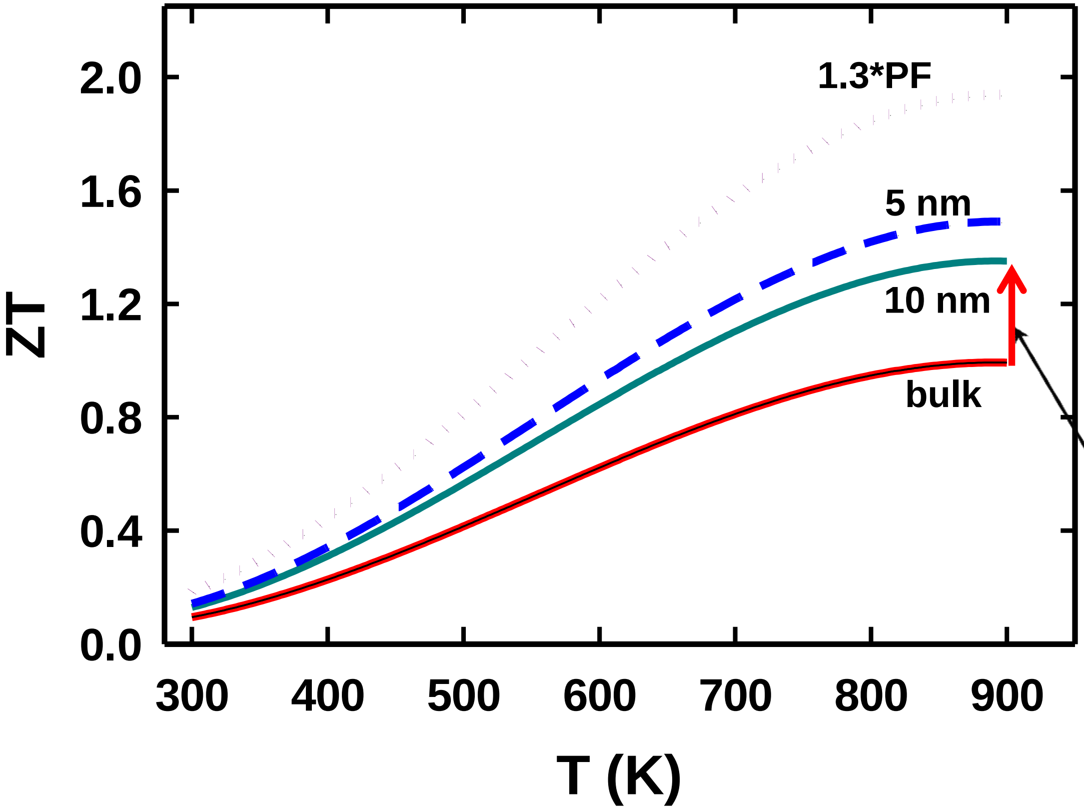
mechanical stability

450

thermodynamical stability

75

Reaching for ZT~2 in Half Heusler Alloys



Our computation modeling of thermal conductivity shows ZT increase as a function of grain size. Further ZT increase will come from the increase in power factor (thermopower and electrical conductivity). ZT of ~1.5 is possible.

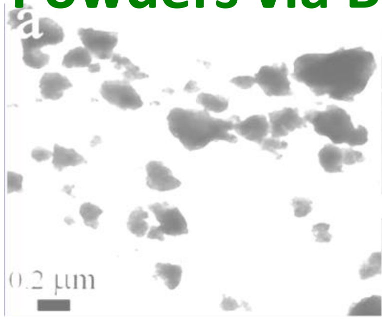
Our current HH alloys has ZT~1.3 without nanostructure.

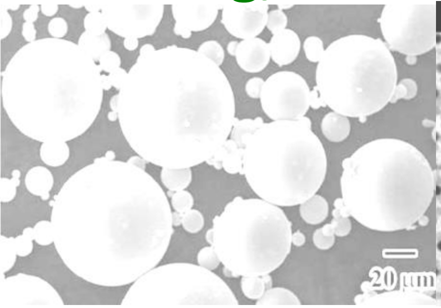
Even if such high ZT can be achieved in bulk-nano HH alloys, we still need to address the issue of grain growth as much as for any nanostructured systems!

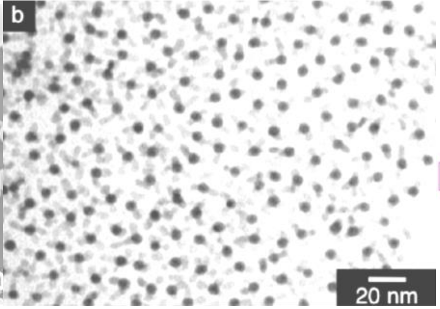
Refs. on effective medium modeling of lattice thermal conductivity: S. J. Poon, A. S. Petersen, and D. Wu, Appl. Phys. Lett. (2013); S. J. Poon and K. Limtragool, J. Appl. Phys. 110, 114306 (2011).

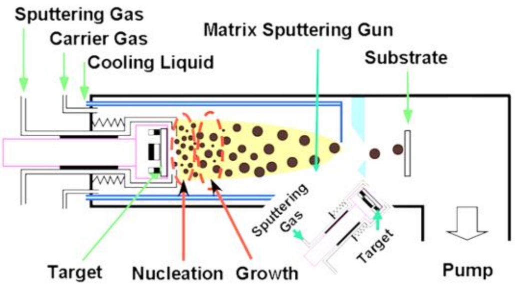
Nano-Bulk Synthesis by Spark Plasma Sintering, Hot Press, Shock Compaction, Extrusion.

Powders via Ball Milling, Atomization, Solution, Vapor Condensation.





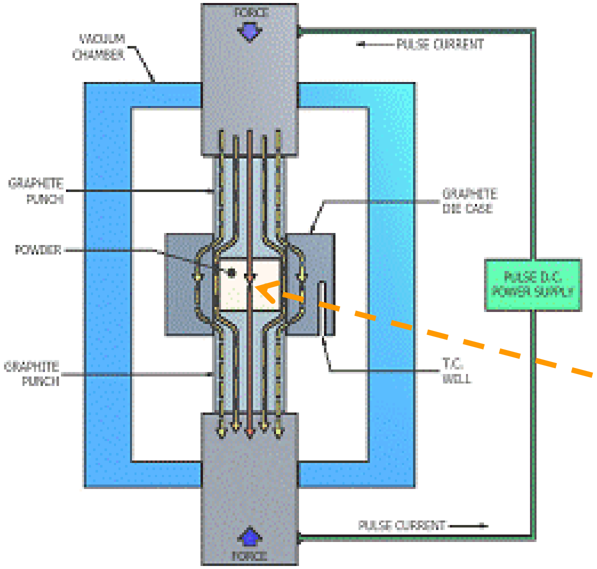




Spark Plasma Sintering (SPS)

(Electric Current Assisted Sintering, Direct Current Sintering)

Advanced Technologies



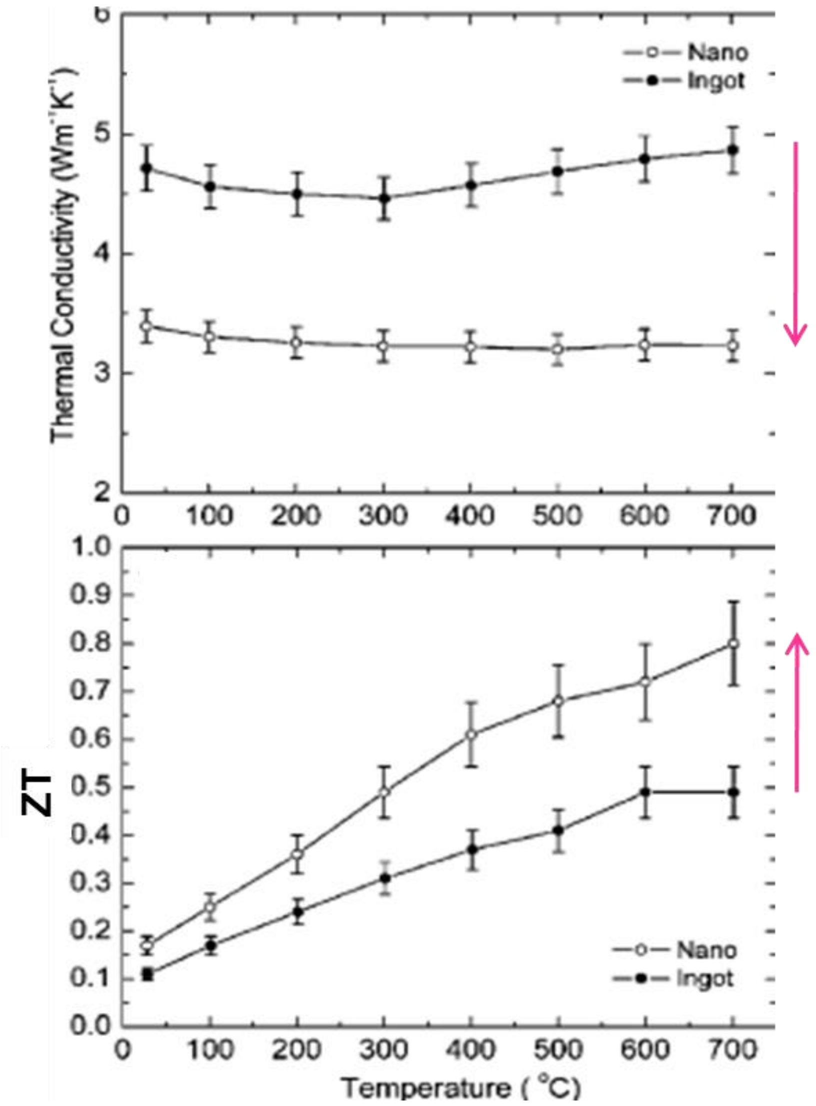
Nanostructuring Results

P-$Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}$

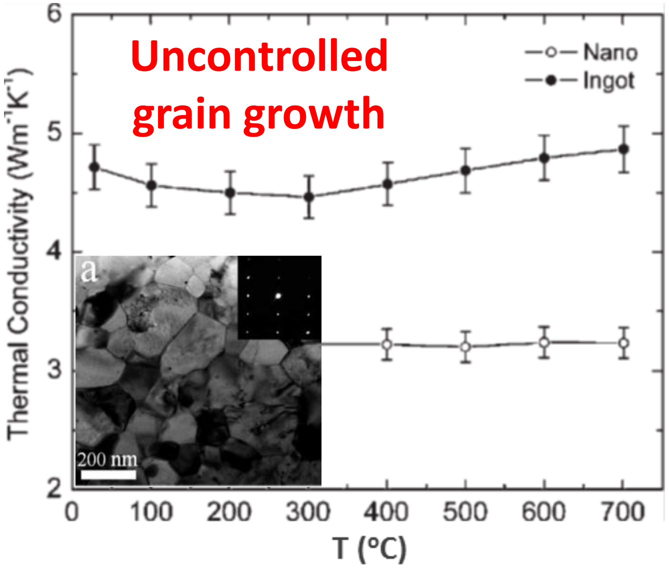
Nanostructuring results in thermal conductivity reduction

$$\boxed{ZT \sim \kappa^{-1}}$$

X. Yan, G. Joshi, W.S. Liu, Y.C. Lan, H. Wang, S.Y. Lee, J.W. Simonson, S.J. Poon, T.M. Tritt, G. Chen, and Z.F. Ren, Nano Lett. 11, 556 (2010).

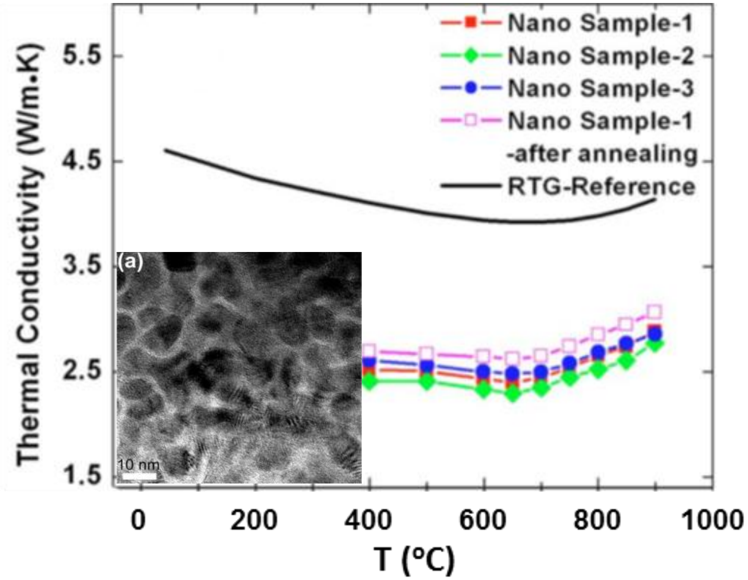


Barrier to Higher ZT



Half-Heusler alloy microstructure shows 100-200 nm grains with some 20-50 nm particulates. Yan *et al*, Nano Lett. 11, 556 (2010).

The uncontrolled grain growth is barrier to higher ZT.

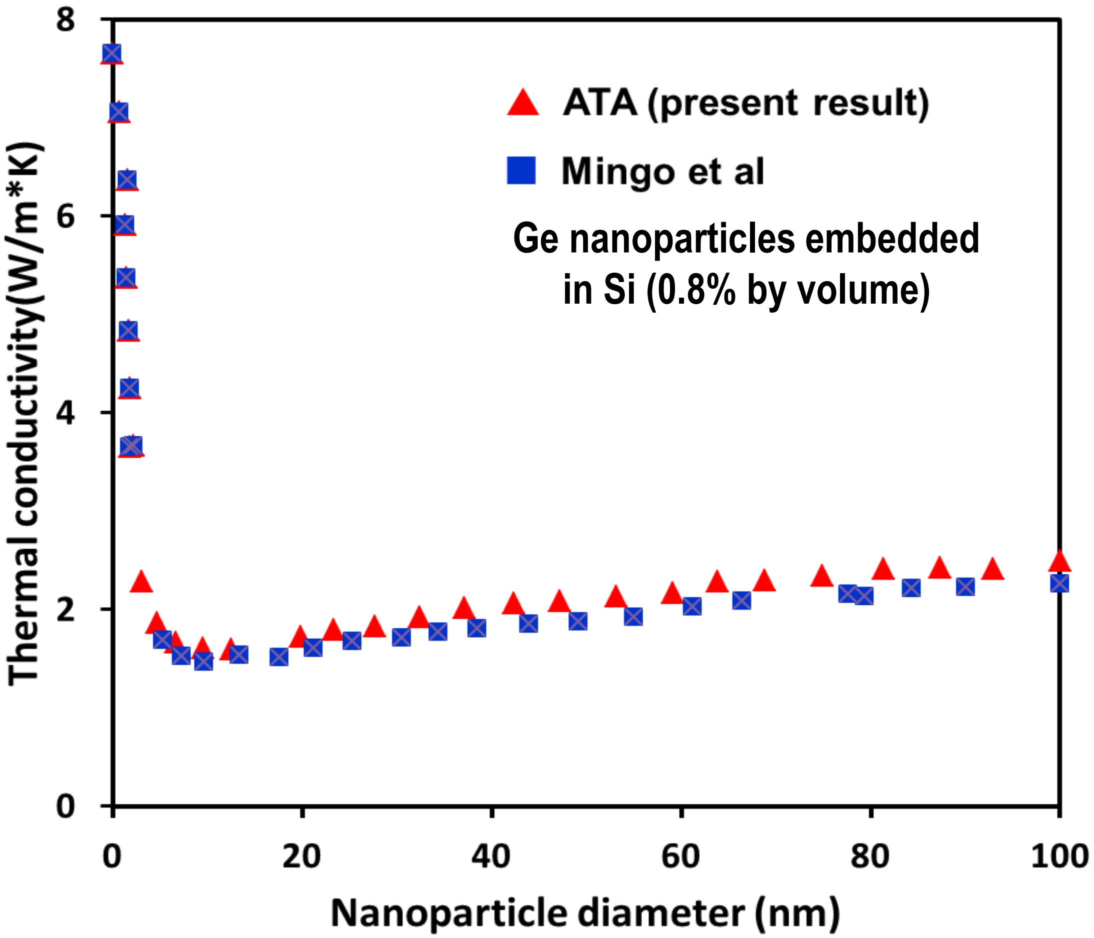


N-type nano-SiGe. Wang *et al*, Appl. Phys. Lett. 93, 193121 (2008).

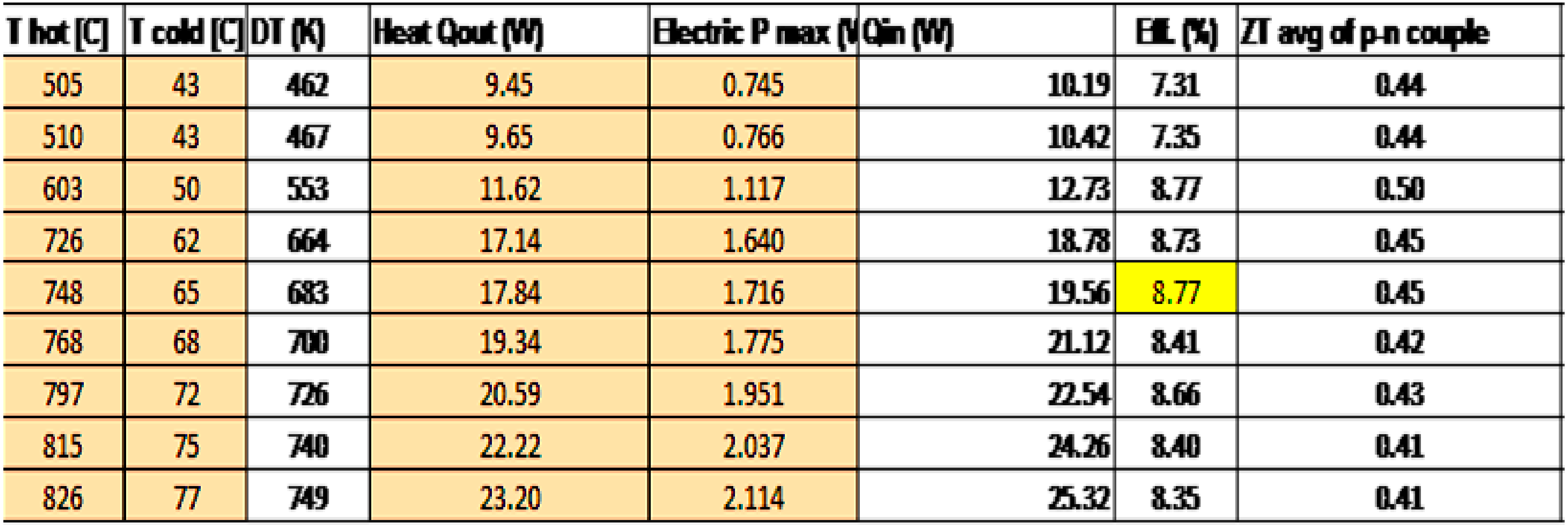
With further development of SPS processing, it is possible to produce the desirable nanostructure and structural order.

Can Nanostructures be Stable?

Particles-in-Matrix Approach



Devices Based on ZT~1 Half Heusler Materials



T hot [C]	T cold [C]	DT (K)	Heat Qout (W)	Electric P max (W	Qin (W)	Eff (%)	ZT avg of p-n couple
505	43	462	9.45	0.745	10.19	7.31	0.44
510	43	467	9.65	0.766	10.42	7.35	0.44
603	50	553	11.62	1.117	12.73	8.77	0.50
726	62	664	17.14	1.640	18.78	8.73	0.45
748	65	683	17.84	1.716	19.56	8.77	0.45
768	68	700	19.34	1.775	21.12	8.41	0.42
797	72	726	20.59	1.951	22.54	8.66	0.43
815	75	740	22.22	2.037	24.26	8.40	0.41
826	77	749	23.20	2.114	25.32	8.35	0.41

HH *n-p* couples based on ZT~0.8-1 led to device efficiency near 9%.

J. Poon, D. Wu, S. Zhu, W. Xie, T. Tritt, P. Thomas, and R, Venkatasubramanian, J. Mater. Res. 26, 2795 (2011).

High-performance three-stage cascade thermoelectric devices with 20% efficiency. B.A. Cook, T.E. Chan, G. Dezsi, P. Thomas, C.C. Koch, S.J. Poon, T.M. Tritt, R. Venkatasubramanian, J. Electr. Mater., DOI: 10.1007/s11664-014-3600-9 (2015).

Opportunities:

High throughput search of materials systems (data mining, properties prediction and screening, including doping…) has begun.

Particles-in-matrix approach for stability (phase separation, metal-ceramics…) may retain nanostructure.

Energy filtering approach needs to be better developed.

Challenges exist in transitioning from materials design to device implementation (e.g. electrical contact, materials compatibility..).

Great opportunities for cross-disciplinary R & D.