

Climate Crisis & Science Priorities: A Case Study on Thermoelectric Technology

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Carbon Neutral

Climate change is all around
Creeping on us, makes no sound
Always something else to do
The cars, the wars, a bank or two

The answer: easy! has been found!
Leave that carbon in the ground.
Can we resist these fuels so useful?
And live each day carbon neutral?

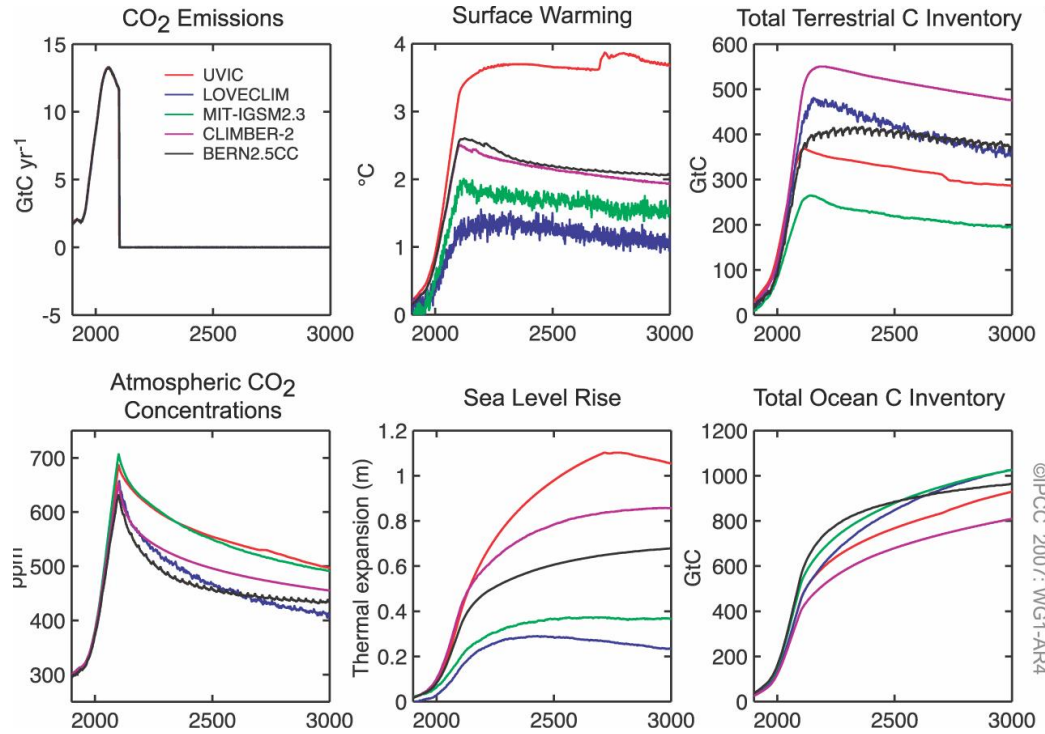
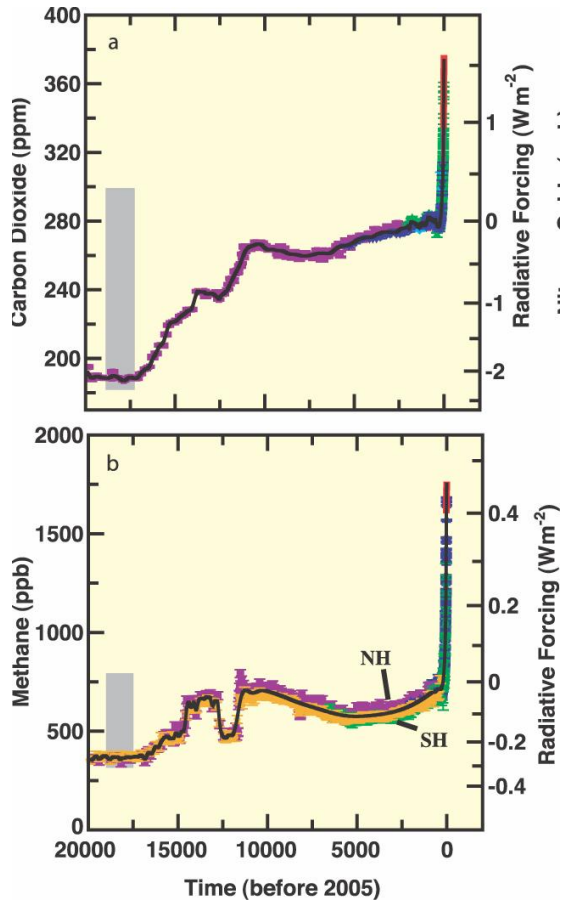
Musings

- The Climate Crisis requires reevaluation of priorities and long term planning beyond anything ever attempted.
- 40 years ago we put men on the moon.
- By about 40 years from now, we need to replace practically everything about how we use resources on earth with sustainable technologies.
- Business-as-usual science and technology priorities won't get us there
 - only a sustained, focused global effort will.
- Scientists particularly need to reevaluate their own specialties with respect to the global scale of the problem and the timescales involved.

This Talk

- Focuses on thermoelectric technology
 - A case study in the context of the Climate Crisis.
- The basic principles and capabilities of thermoelectric technology will be discussed
- Thermoelectric technology has been discussed as a possible player in solar-thermal electricity generation, waste heat recovery in automobiles and other power generation applications.
- These findings were presented to former Vice President Al Gore at one of his Solutions Summits in 2008.

Persistence of Damage



- Human Damage is Fast
- Earth Response is Slow
- From **IPCC Fourth Assessment Report, 2007**

Scale Of The Energy Problem

Totals	Energy			Electricity			CO2
	Total TW	FF TW	FF/Total %	Total TW	FF TW	FF/Total %	Total Billion Metric Tons
World	16.9	14.4	85.5%	2.31	1.54	66.7%	30.4
US	3.3	2.8	84.0%	0.47	0.34	72.0%	6.1
US/World (%)	19.6%	19.2%		20.4%	22.0%		20.0%
Per Capita	W	W		W	W		Metric Tons
World	2485	2125		341	227		4.48
US	10752	9034		1540	1109		19.78
Human Metabolism	109						0.19
US/Metabolism:	99						107

- Americans use energy and produce CO₂ at rates 100x evolutionary requirements
- Build a new emission-free 1 GW electric power plant every week, it will take 30 years to replace present fossil fuel capacity
- China is said to be building a new coal plant every 4 days.

TE & the Climate Crisis

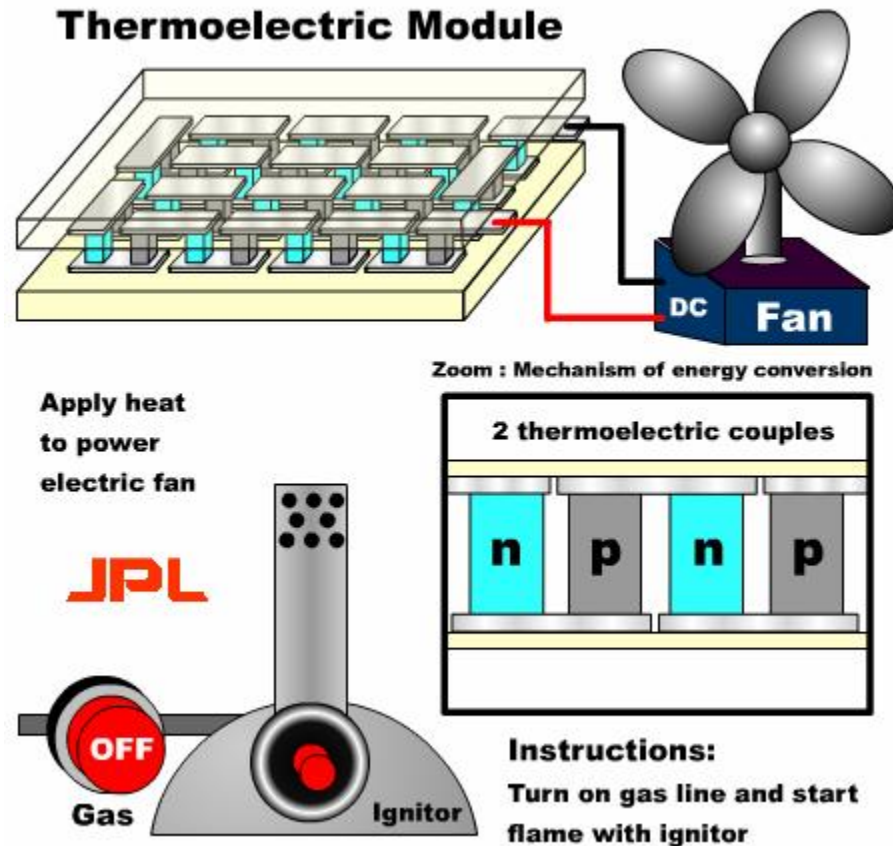
- In 2007 the *International Thermoelectric Society* adopted new goal:
 - ***“To promote an understanding of the role thermoelectric technology may play in environmental impact and mitigating global climate change.”***
- If thermoelectricity can contribute, it is imperative that we do so.
- Alternatively, if it can be determined that TE has little to offer then we must not act as advocates of thermoelectric technology.
 - Instead, resources must re-directed to technologies that may help.
 - The stakes are simply too high for anything less.

“It doesn't matter if a cat is black or white, so long as it catches mice.”

Deng Xiaoping, 1961

This presentation contains my current thoughts on what thermoelectrics can, can't and might offer

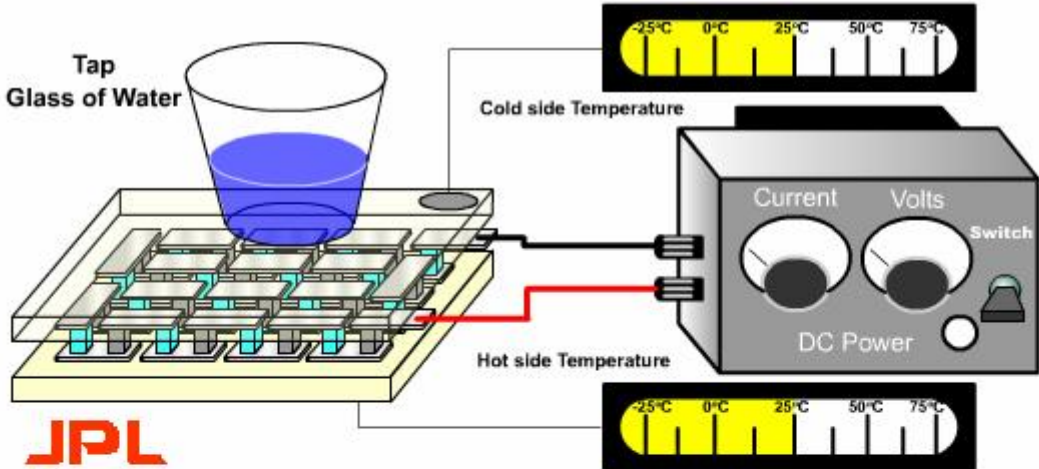
Introduction



One p-n pair is a 'thermocouple'
Also works as cooler

Courtesy J. Snyder, CalTech/JPL
<http://thermoelectrics.caltech.edu/>

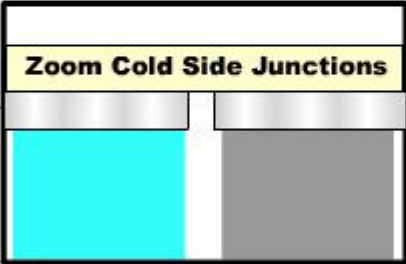
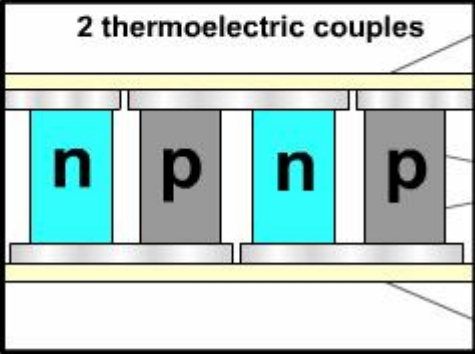
TE Cooler



JPL

Thermoelectric Module

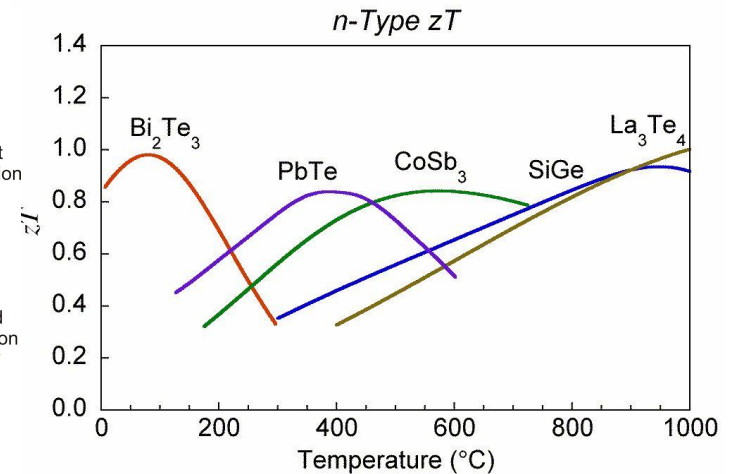
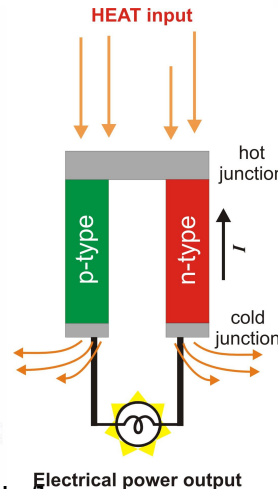
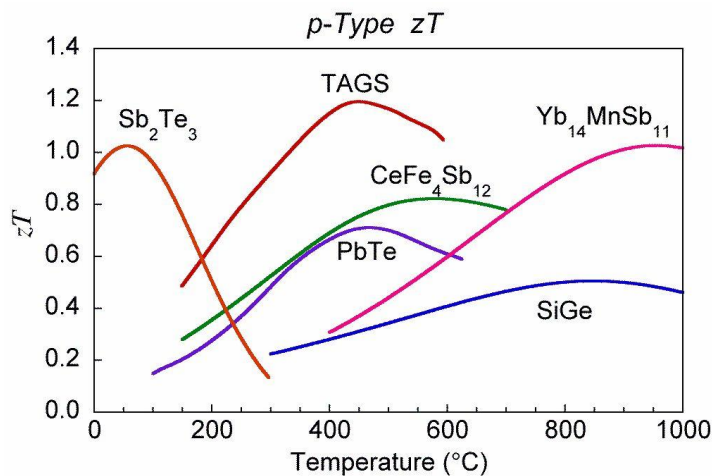
Zoom : Mechanism of energy conversion



Instructions:
Turn on DC power to drive heat pump
and freeze glass of water

Courtesy J. Snyder, CalTech/JPL
<http://thermoelectrics.caltech.edu/>

ZT Determines Efficiency

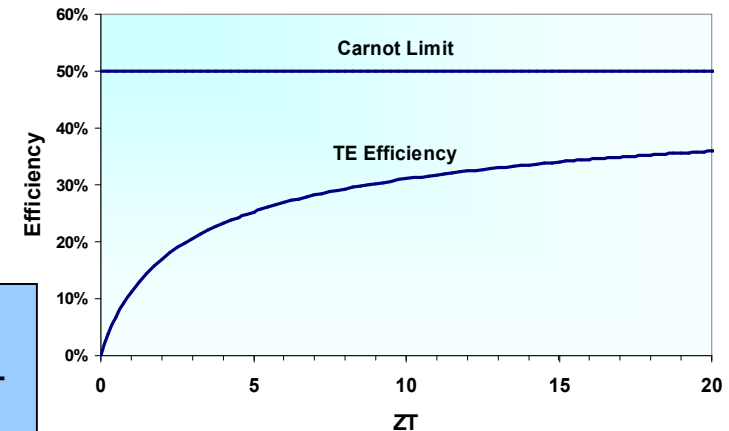


[Snyder, Caltech, <http://thermoelectrics.caltech.edu/>]

[Snyder, Caltech, <http://thermoelectrics.caltech.edu/>]

$$ZT = \frac{S^2 T}{kr} = \frac{(\text{Seebeck Coefficient})^2 \times (\text{Temperature})}{(\text{thermal conductivity}) \times (\text{electrical resistivity})}$$

$$h = \frac{T_{hot} - T_{cold}}{T_{hot}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_{cold}/T_{hot}}$$



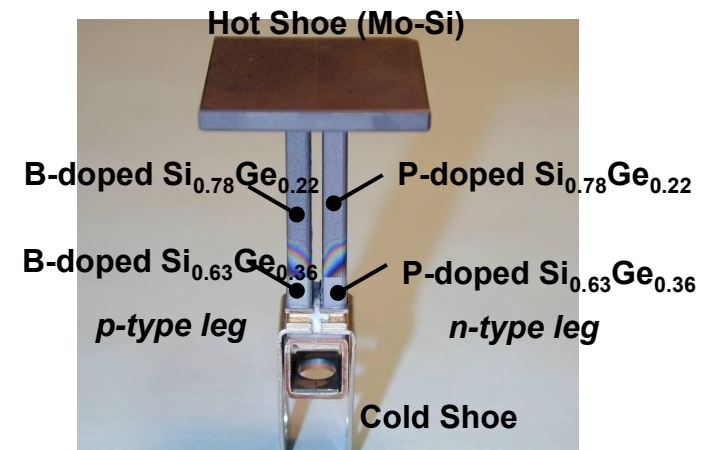
- ZT is a property of the material used
- Efficiency improves asymptotically with ZT
- Increase ZT = more useful

RTG: Radioisotope Thermoelectric Generator

- Voyager, Galileo, Cassini, New Horizons (right)
- ~55 kg
- ~7% efficiency
- $T_{\text{hot}} = 1300 \text{ K}$, $T_{\text{cold}} = 600 \text{ K}$
- 240 W_e
- > 1,000,000,000,000 device hours
- The capability of building new SiGe unicouples has been lost
- Leading group: [Fleuriel/Caillat, JPL-Caltech]



- NASA uses thermoelectrics
 - Not because they are efficient
 - they are reliable & lightweight
 - No alternatives (yet)

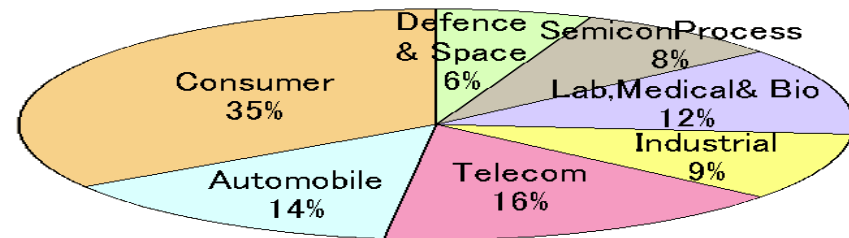


TE Business Status

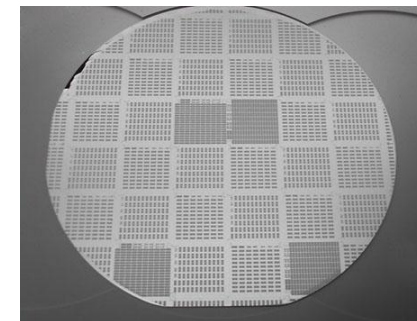
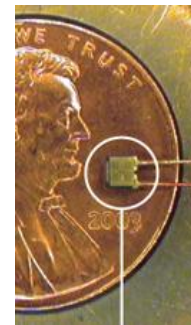
- Tiny world market for TE power generation
 - US\$25-50M/yr (full systems)
 - [Global Thermoelectric]
- World market for cooling modules
 - US\$200-250M/yr (modules)
- New engineering beginning to appear in marketplace
 - Amerigon (car seat cooler/heater)
 - Micropelt (miniature devices)
- Recent materials R&D (ZT) has yet to reach the marketplace
 - A few are close, for cooling
 - Nextreme (thin film, based on high ZT)
 - GMZ Energy (2008, nano/bulk materials)



500 W TEG, natural gas pipeline, Peru
[LeSage, Global Thermoelectric]



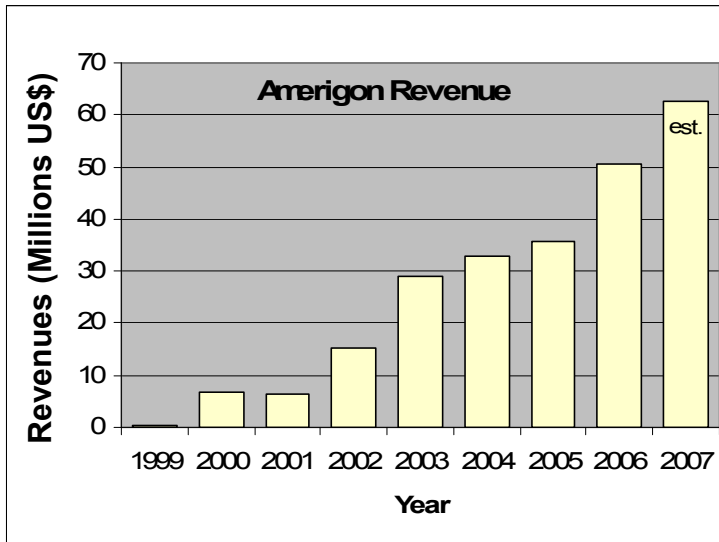
Market Distribution for TE Cooling Modules.
[Komatsu-2007]



Nextreme (left) thin-film TE cooler and MicroPelt (right) 4" Bi₂Te₃ thin-film TE wafer.

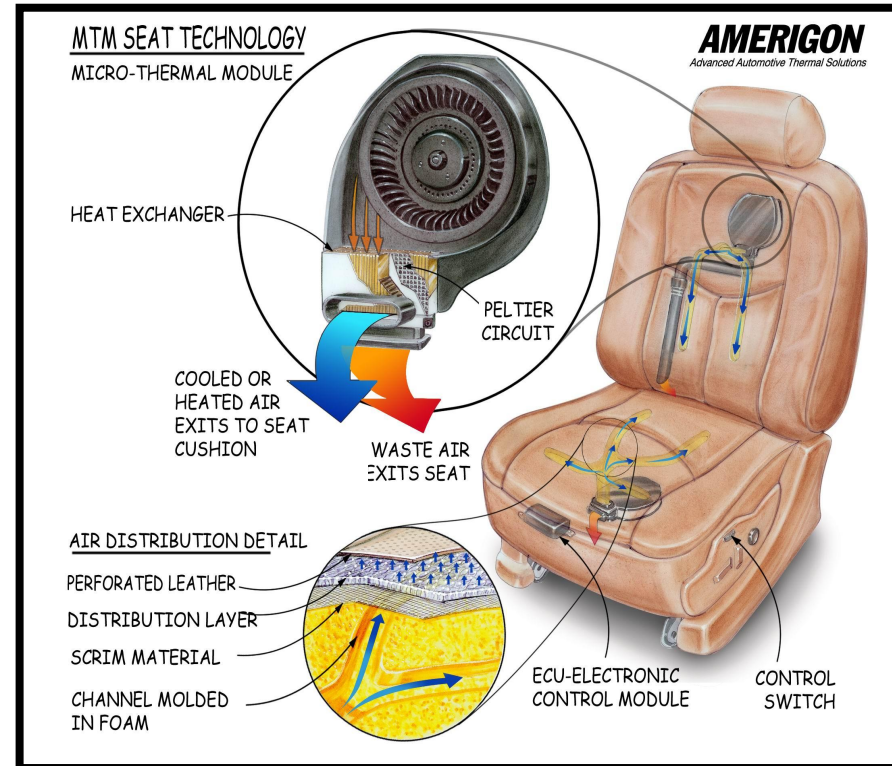
TE business today is mainly cooling

Business Developments



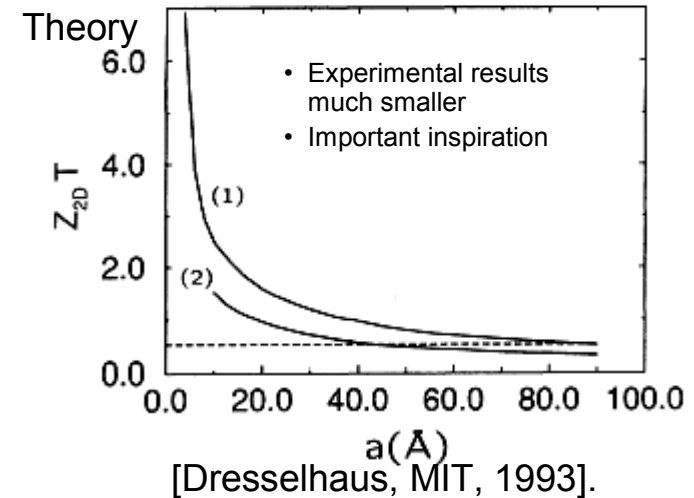
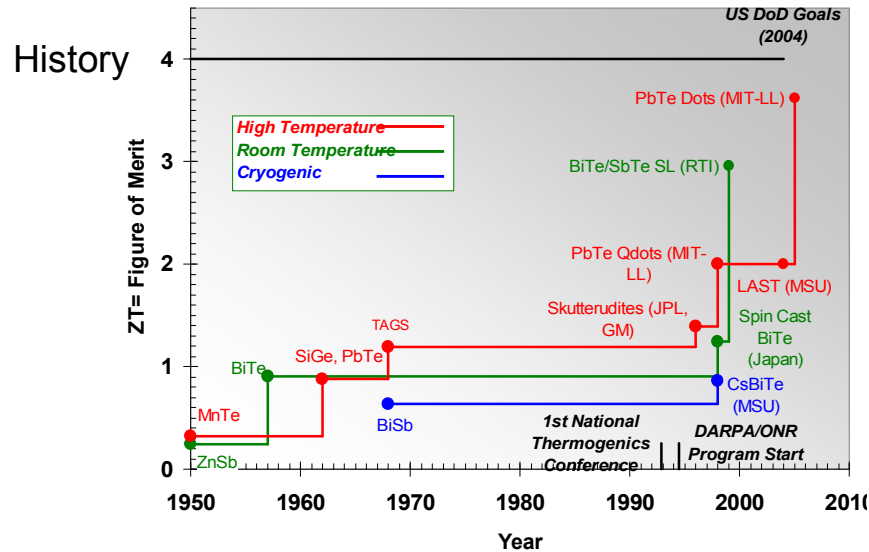
Amerigon revenue 1999-2007

- 'Old' ZT
- innovative engineering
- reduced costs
- can be used in other new products
- possible 2% fuel savings



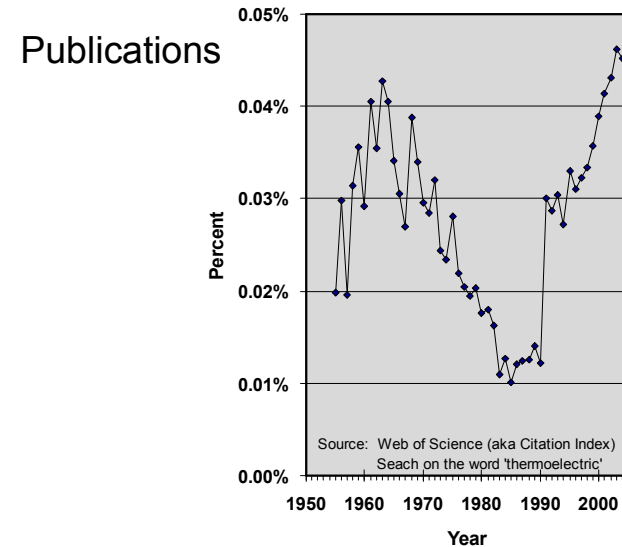
Amerigon: Climate Control Seat™ (CCS™)
[Bell, Amerigon/BSST]

1992-3: R&D Resurgence

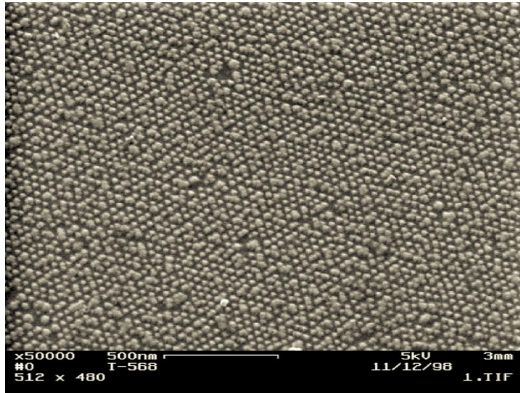


- Army Night Vision Lab provided key stimulus & inspiration (1992)
- DARPA & ONR initiate support for basic R&D (~1993)

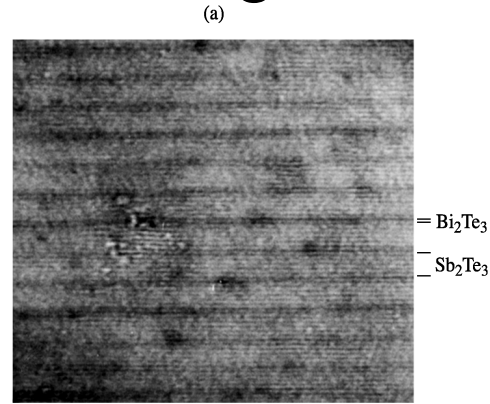
New ideas + funding = progress



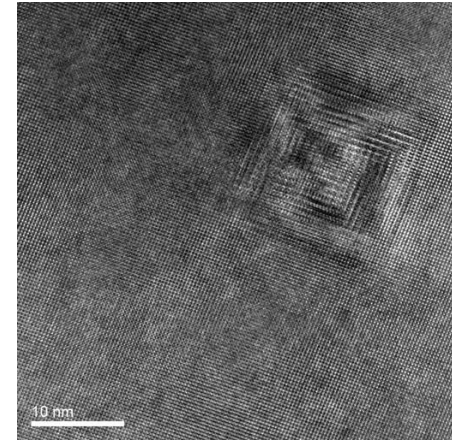
Nano-scale Engineering in Thermoelectrics



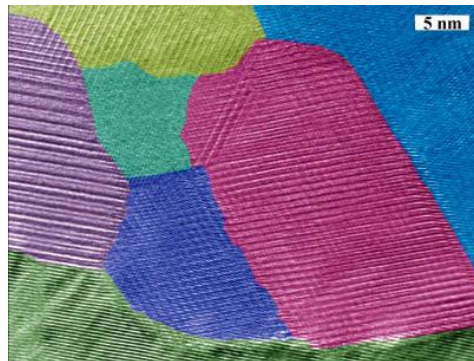
ZT~3.5 @ 575 K
quantum dot superlattice (MBE)
n-type, PbSeTe/PbTe
 [Harman, MIT-LL, J. Elec.Mat. 2000].



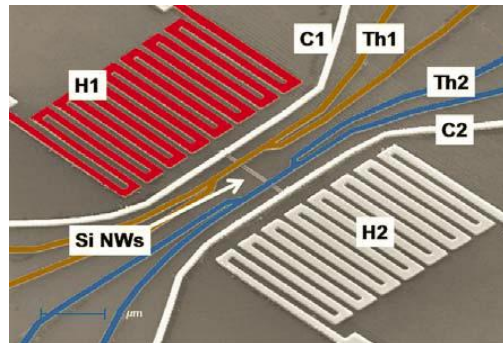
ZT~2.4 @ 300 K
superlattice (CVD)
p-type, Bi₂Te₃/Sb₂Te₃
 [Venkatasubramanian, RTI/Nextreme, 2001].



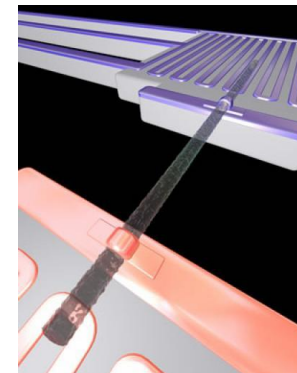
ZT~2.2 @ 800 K
bulk – ‘natural’ nanodots
n-type, AgSbTe₂-PbTe (aka ‘LAST’)
 [Kanatzidis, Northwestern, 2004]



ZT~1.4 @ 373 K
bulk – fine grain
p-type, (Bi,Sb)₂Te₃
 [15 authors, BC/MIT/GMZ
 Energy/Nanjing University, 2008].



ZT~1.2 @ 350 K
nanowire
p-type, Si
 [Heath, Caltech, 2008]



ZT~0.6 @ 300 K
nanowire
p-type, Si
 [Yang/Majumdar, Berkeley, 2008]

TE Applications w.r.t. Climate Crisis

Vehicle heat recovery:

- FreedomCAR
- Program Managers: John Fairbanks, Aaron Yocum
- Goals
 - Target cars and trucks
 - Improve fuel efficiency by 10%
 - In production 2011-2014

Other Possibilities:

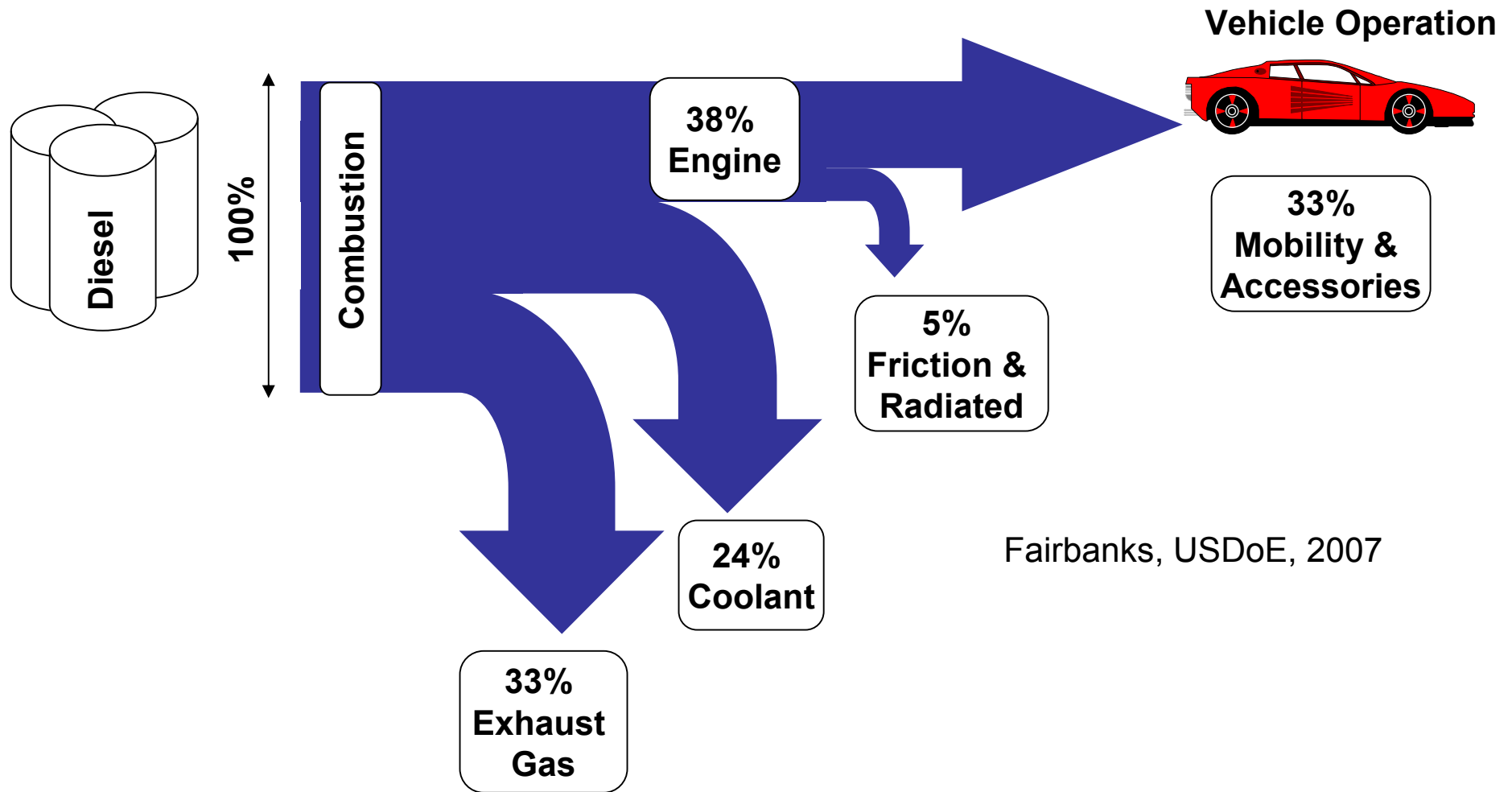
- Car seat cooling/heating
 - No refrigerants
 - Estimated 2% fuel savings
 - Passengers turn down A/C
 - More efficient heating
- Home Cogeneration of Electricity
 - (Water heater/furnace) + TE = electricity
- R134a Replacement Needed?
 - R134a has $GWP_{20} = 3830 \times CO_2$

Unlikely Candidates:

- TE too inefficient, even with better ZT
- Solar Thermoelectrics
 - TE + concentrated solar heat [Lewis and Crabtree, 2007]
 - Some DoE funding for higher ZT
- Industrial waste heat
 - NEDO (Japan) invested in TE waste heat since 1997
 - Goal: 15% efficiency
 - Goal: reduce CO₂ emissions
 - 5 year project invested US\$24M
 - National project concluded 2007
 - Possible new project in 2009

The most promising TE greentech application: vehicle waste heat

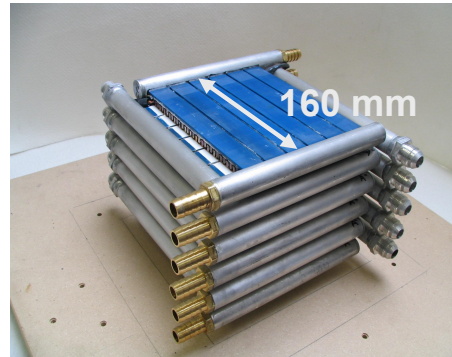
Heat Distribution in Vehicles



Exhaust is the most promising source.
In some cases, coolant too.

DoE FreedomCar Thermoelectric/Vehicle Programs

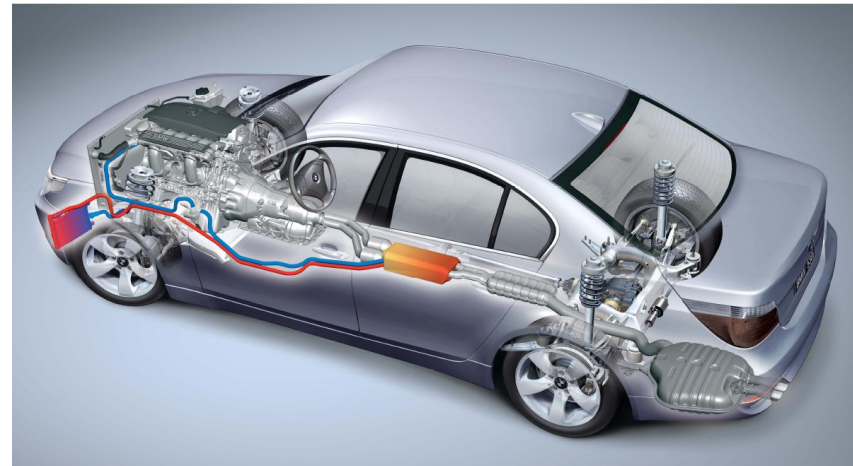
- Thermoelectric Generator Teams
 - **BSST** with BMW, Visteon, **Marlow**, Virginia Tech, Purdue, UC-Santa Cruz
 - **GM** with GE, U of Michigan, U of South Florida, ORNL, RTI
 - **Michigan State** with Cummins, **Tellurex**, NASA-JPL, Iowa State
 - **United Technologies** with Pratt & Whitney, **Hi-Z**, Pacific Northwest National Lab., and Caterpillar
- Nano/high ZT materials not yet available
- Barriers to entry
 - Cost
 - Heat transfer to/from TEG
 - Weight
 - Acceptance of change
 - Competition
 - Honda / Rankine (+3.8%)
 - BMW / Turbosteamer (15%)



500 Watt BiTe TEG [BSST]



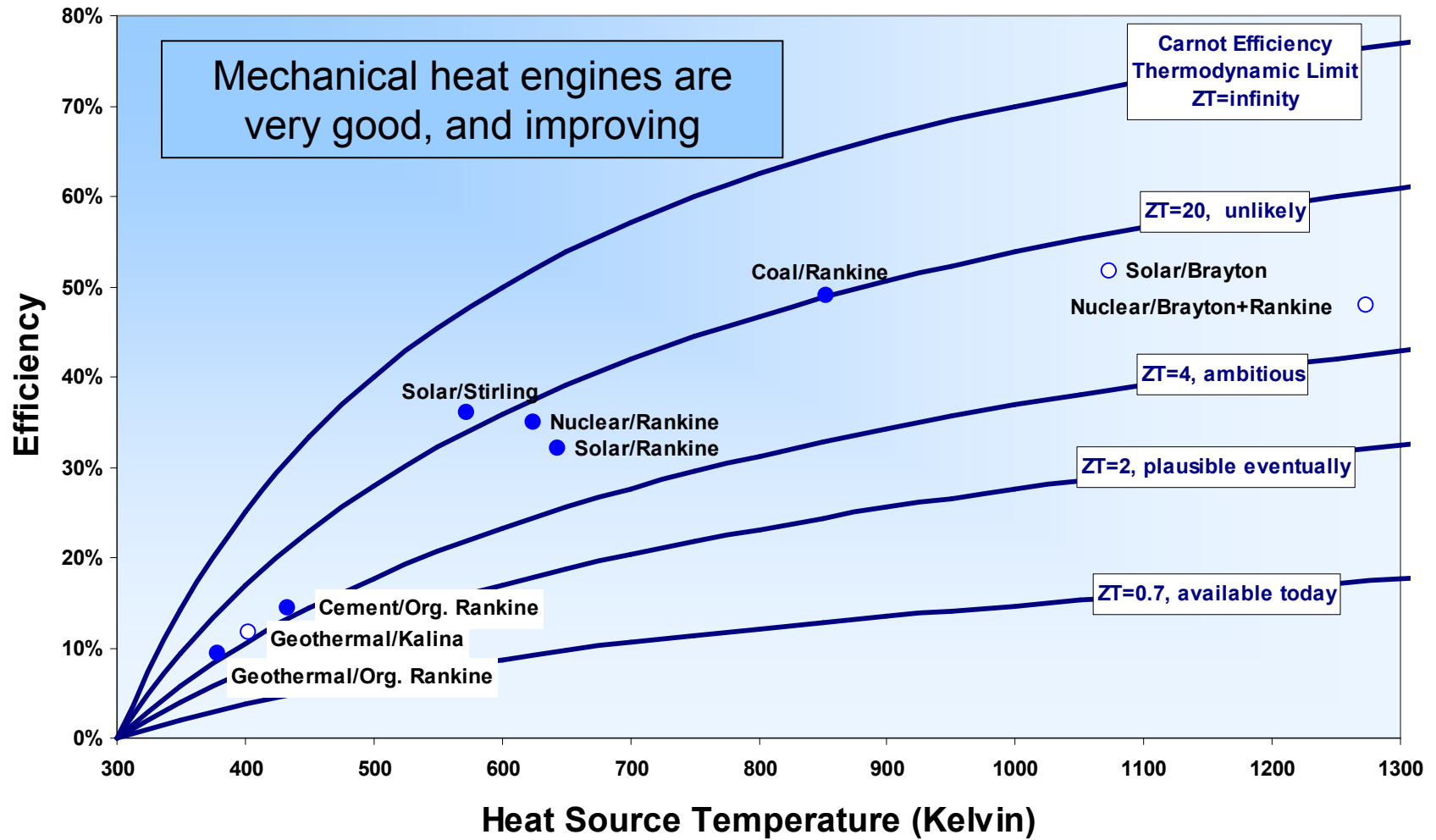
1 kW TEG on a Kenworth Truck [Hi-Z]



BMW 530i Concept with TE Generator (yellow) [BMW]

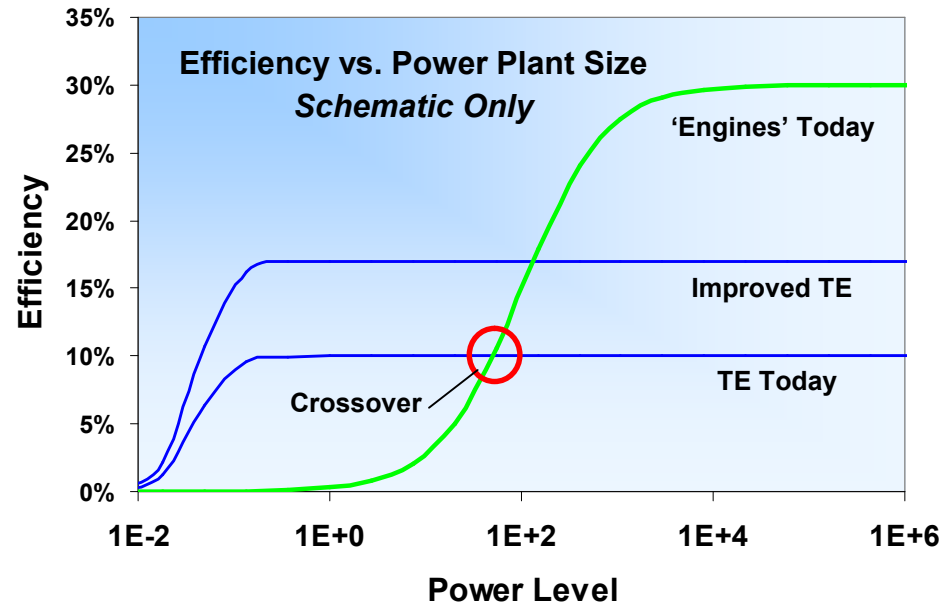
The most promising TE greentech application: vehicle waste heat

'Best Practice' vs. Thermoelectric Efficiency



Heat Source, Size & Converter Choice

- Below some 'crossover' power level, thermoelectric technology is favored
- 'crossover' point depends on current status of each conversion technology
- One answer for cars, another for geothermal, etc.



Higher ZT enhances TE technology

ROM (i.e. WAG): Potential TE Impact on CC

Application Type	Power Scale (kW_e)	Examples	Required Device ZT	Impact on CC
I	> 1000s	Solar Thermal Steam Turbine Replacement	> 8-20	Highly Unlikely
II	> 10s	Industrial Waste Heat Geothermal Bottoming Cycles	> 4	Unlikely
III	0.5 – several	Car Waste Heat Car Seat Coolers/Heaters Home Co-generation (?)	> 1.5-2	TBD
IV	< 0.5	Remote Power 'Personal' Micropower All Existing Applications	> 0.5-1	(almost) None

Thermoelectrics *may* be able to contribute to Type III applications

Woodstove – Third World

Philips Research – Woodstove

- Paul van der Sluis
 - Philips Research Eindhoven, The Netherlands
- 400 million stoves world wide market
- Pilot of 1000 pieces in India
- TEG powers fan
 - Recharges ignition battery
 - Powers fan – improved combustion



ILLUSTRATION: BRYAN CHRISTIE

Efficiency unimportant

Summary

- Admirable progress in 15 years
 - *Laboratory* ZT values increased several fold
 - Startups introducing next-generation TE
 - TE 'business as usual' future is strong
- Basic (ZT) R&D has hardly affected products
 - Nano/high(er) ZT materials not yet available for engineering work
- R&D Challenge: transfer new TE materials to products
- Even higher ZT won't have major impact on Climate Crisis
 - Medium and large scale TE systems are not competitive
 - TE may be competitive for smaller, decentralized applications
- Auto/truck exhaust heat recovery is the most promising candidate

Nano + thermoelectrics + vehicle waste heat
may help and it's worth finding out

Acknowledgments

- The author wishes to thank
 - L. Bell, Amerigon/BSST
 - J. Snyder, Caltech/JPL
 - J. Stockholm, Marvel Thermoelectics
 - C. Uher, U. Michigan
 - B. LeSage, Global Thermoelectric
 - B. Nickerson, Marlow
 - R. Venkatasubramanian RTI/Nextreme
 - D. Rowe, U. Wales
 - T. Kajikawa, Shonan U.
 - J-P Fleurial, JPL/CalTech
 - T. Caillat, JPL/CalTech
 - J. Heath, CalTech
 - L. Whitlow, poet
 - H. Böttner, Fraunhofer/Micropelt
 - E. P. Vining, SWMBO
- And many others throughout the thermoelectric community for supportive discussions and input.
- The opinions, errors and omissions, however, are solely the author's.

Supplementary Material

Questions Addressed In This Presentation

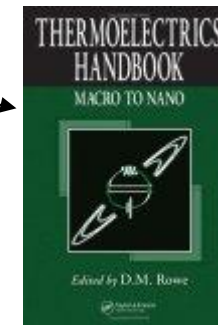
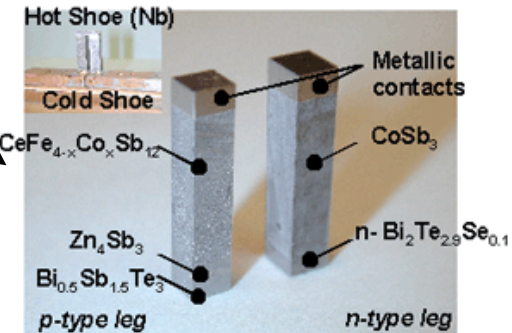
1. Please provide a brief overview of what thermoelectrics are.
2. Do you they have a role to play in greentech and if so, what are the possible applications?
3. What are the difficulties in applying thermoelectrics to greentech?
4. Are there any thermoelectric applications that are close to the market?
5. What are the main factors that determine thermoelectric performance and cost, and how could nanotechnology play a role in improving these attributes?
6. What will be required for thermoelectrics to be applied in mainstream heat-to electricity conversion applications (e.g. exhaust of power plants or heat engines)?
7. Will thermoelectrics ever achieve higher ZT than 2?
8. Who are the leading researchers in thermoelectrics and how do their approaches differ?
9. What, if any, are the potential long-term thermoelectric technologies or processes coming down the pipeline?
10. Which approaches seem the most promising?

Further Leading TE Groups

In addition to those discussed in main text (alpha. order)

- Fleurial, Caillat, NASA/Jet Propulsion Laboratory-Caltech
 - Space power, materials, measurements
 - Involved in nearly all aspects of TE
- Hendricks, Pacific Northwest National Lab
- Rowe, Univ. Cardiff, Wales
 - Systems studies, waste heat
- Tritt, Clemson Univ.
 - DoE Center of Excellence in Thermoelectric Materials Research
 - Materials, measurements

Segmented New Materials Unicouple

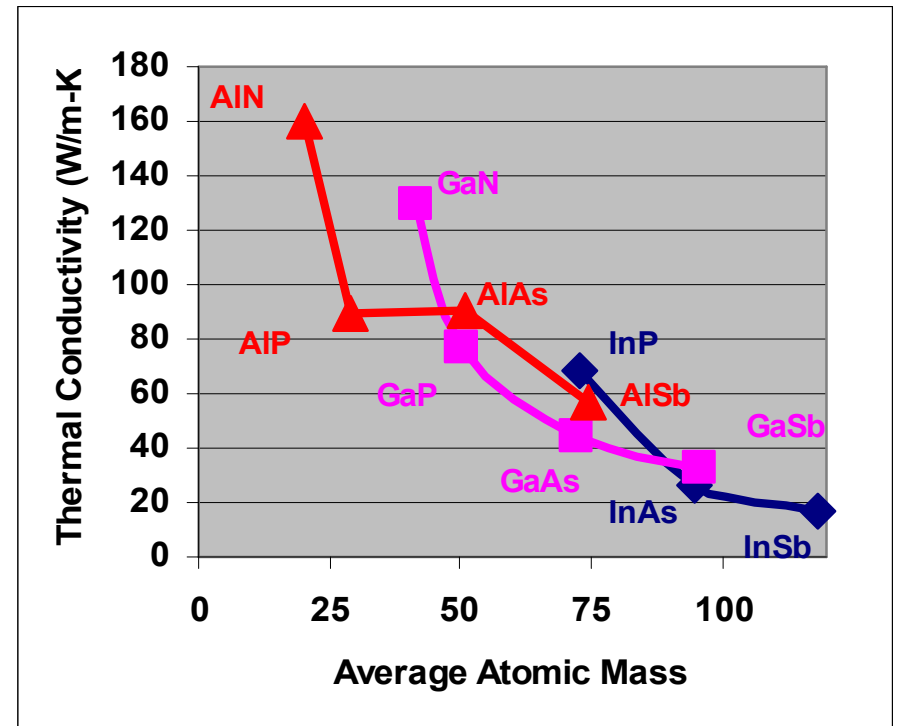


- Many more groups in US and abroad doing good science.
- Progress requires a community, not just 'leaders'
- Not everyone has 'hit' a large ZT, not everyone is doing 'nano'

Physics of Thermoelectric Materials

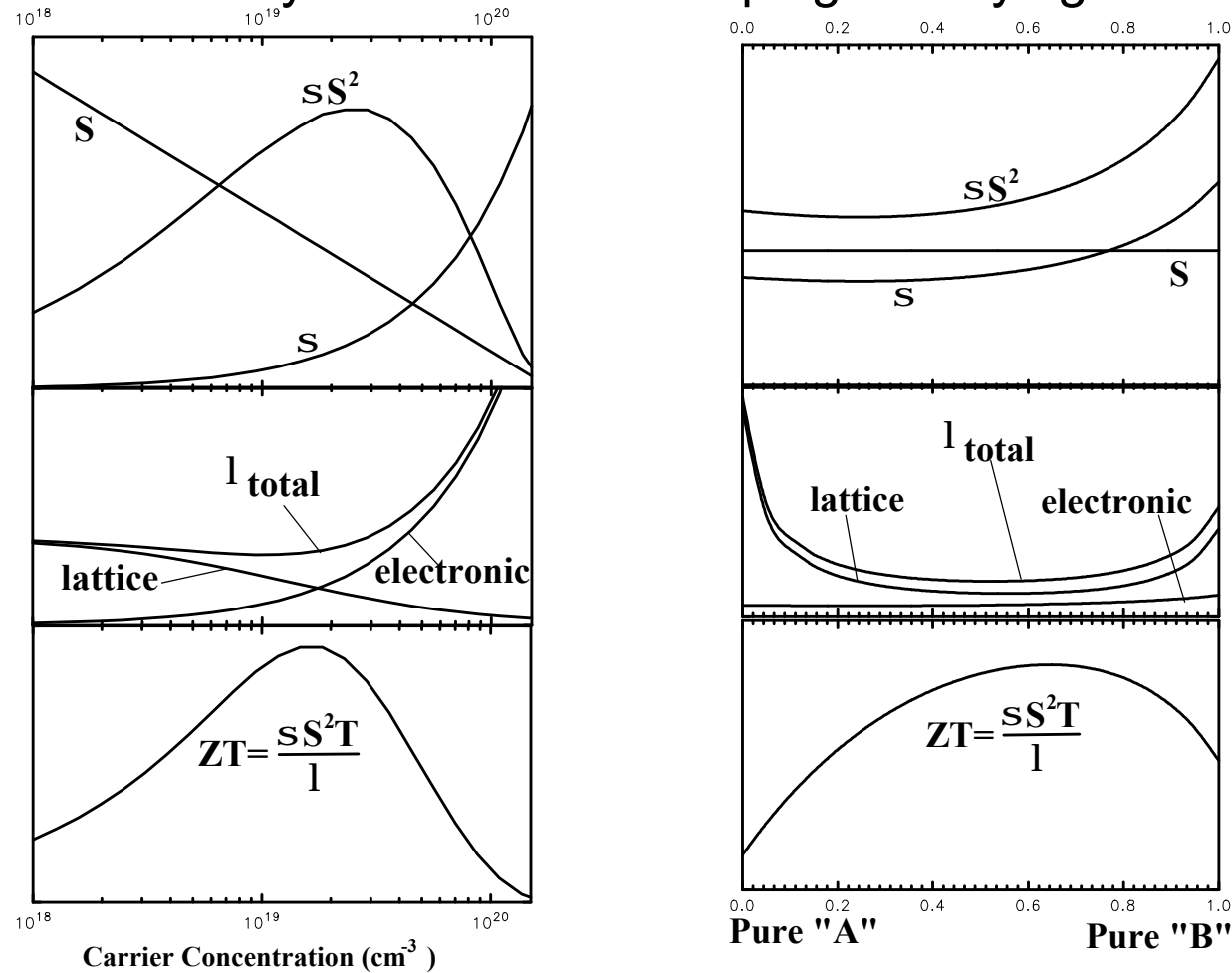
Effect of Atomic Mass on Thermal Conductivity

- Other factors enter, but the mass of the atoms is a huge effect
 - Heavy mass = atoms vibrate slowly
- This is why you see a lot of Sb, Bi, Pb, & Te
 - They are all heavy
- Large unit cell size is also a plus
 - Some vibration modes don't carry heat well
 - Ex: Skutterudites, Clathrates, Chevrel Phase & others



Still today, usually want heavy atoms'

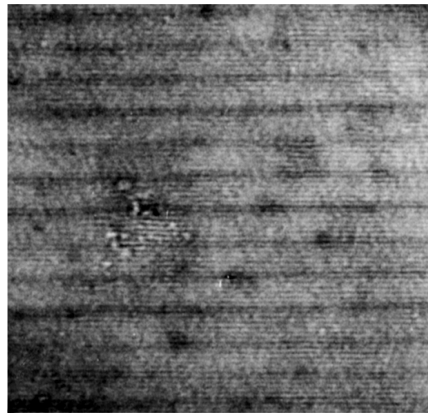
Old rules for thermoelectric materials: Heavy Mass Atoms + Doping + Alloying



- Classical method for optimizing thermoelectrics
- Still apply today, plus new nano effects

Effect of 'Nano' on Thermal Conductivity

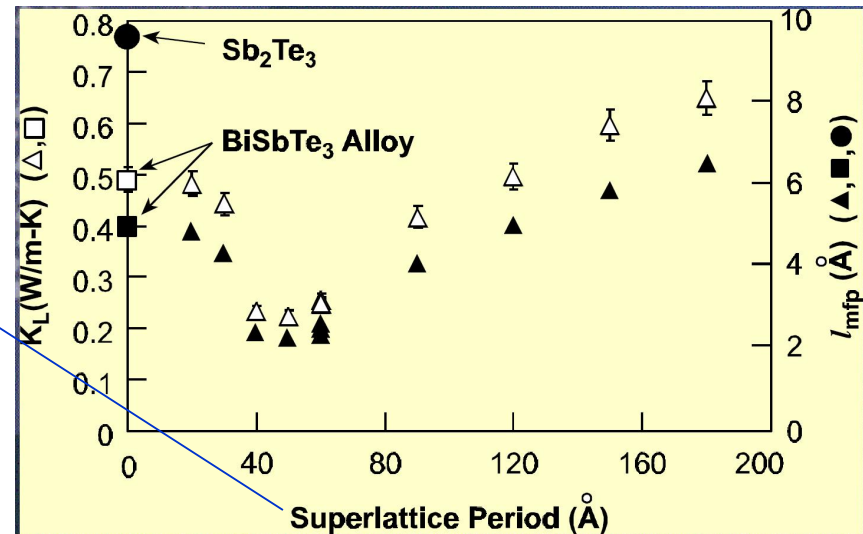
(a)



= Bi₂Te₃
= Sb₂Te₃

12 nm
ZT~2.4 @ 300 K
superlattice (CVD)
p-type, Bi₂Te₃/Sb₂Te₃

[Venkatasubramanian, RTI/Nextreme, 2001].

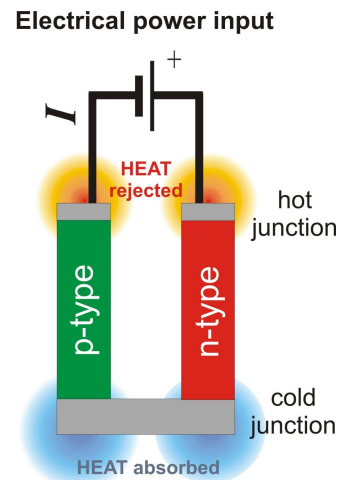


Venkatasubramanian, RTI/Nextreme, 2000

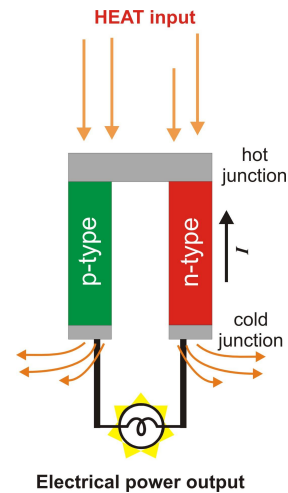
Smaller thermal conductivity (k), bigger ZT, more efficient

Other Points of Interest

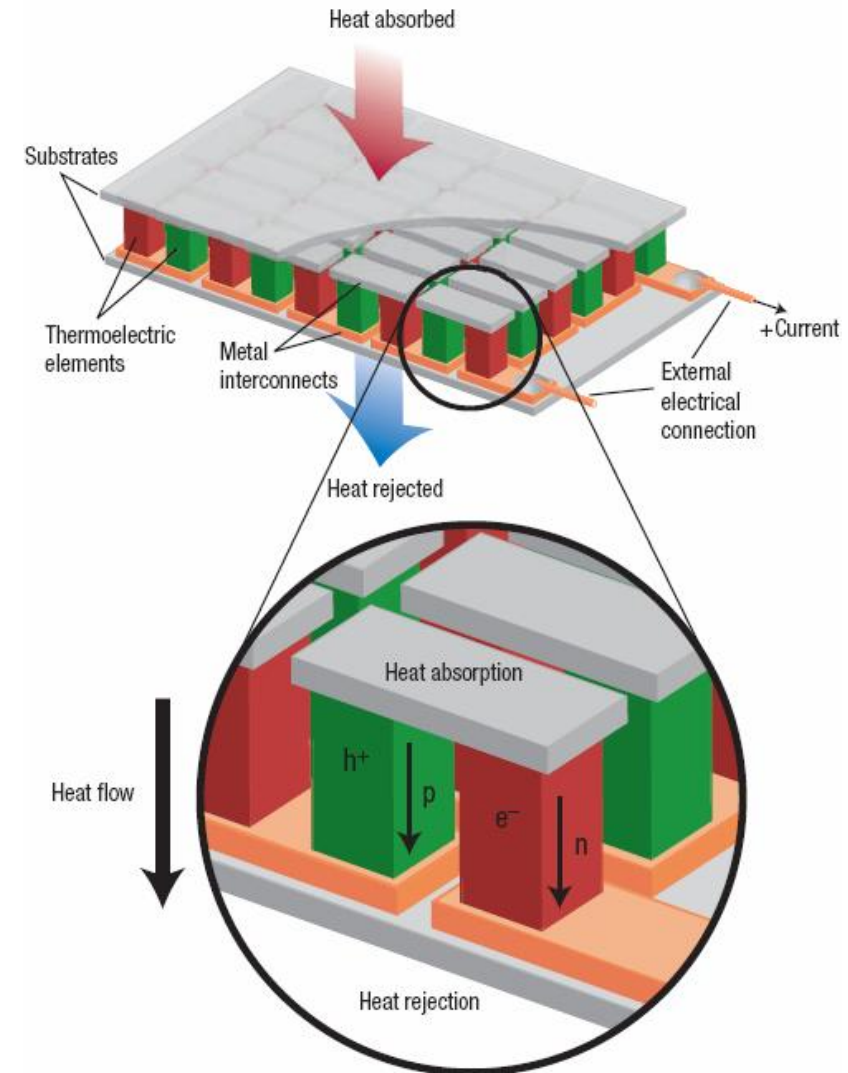
Simple Thermoelectric Devices



Cooler Mode Thermocouple



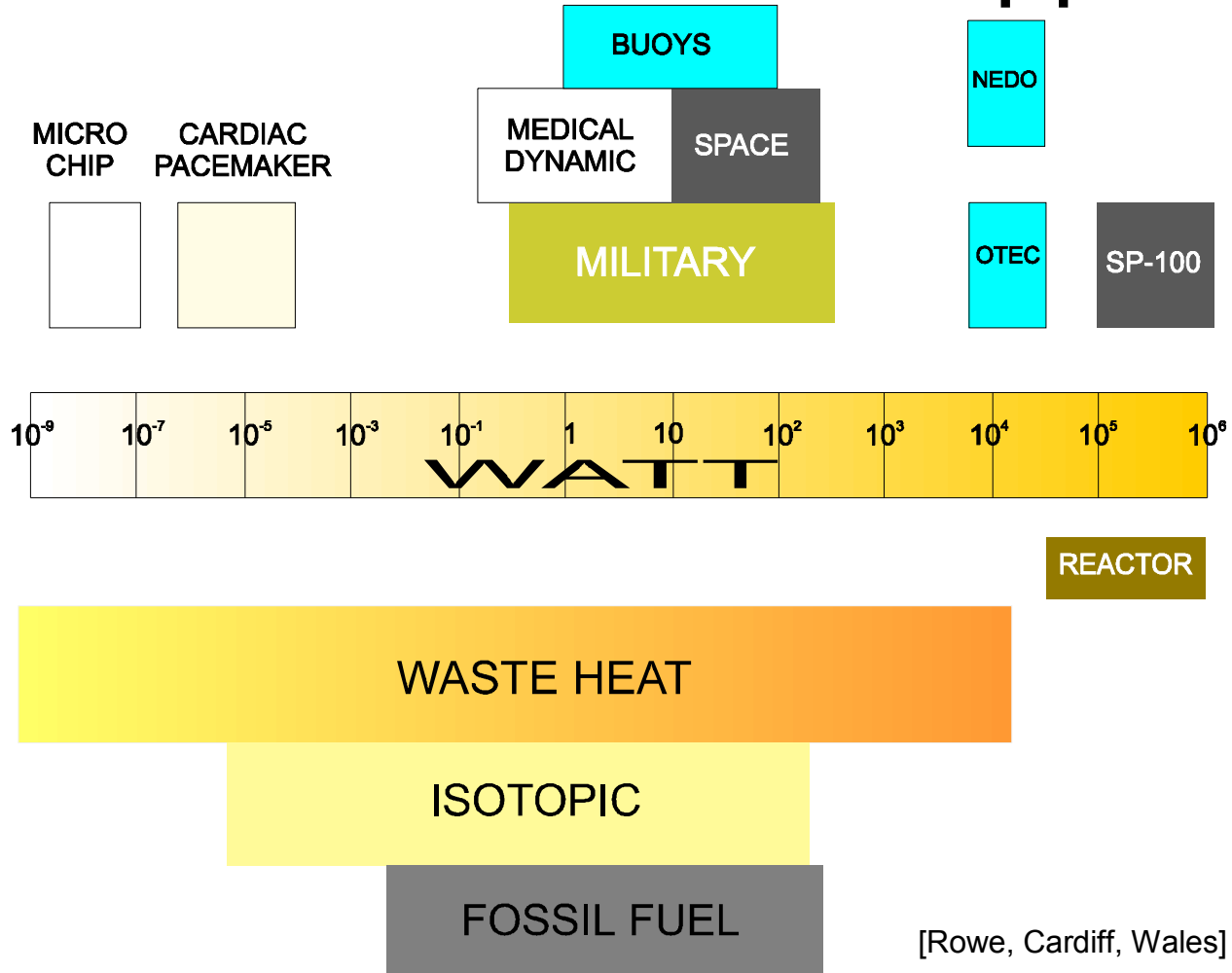
Power Generation Thermocouple



'Close Packed' modules easier to handle, lower losses than individual thermocouples

[Snyder, Caltech, <http://thermoelectrics.caltech.edu/>]

TE Power Generation Applications



[Rowe, Cardiff, Wales]

TE power generation (actual + studies) cover > 12 orders of magnitude

USS DOLPHIN AGSS 555

Uses Thermoelectric Air Conditioning - Test for Silent Running



There are few examples of large-scale thermoelectric applications due to efficiency & cost

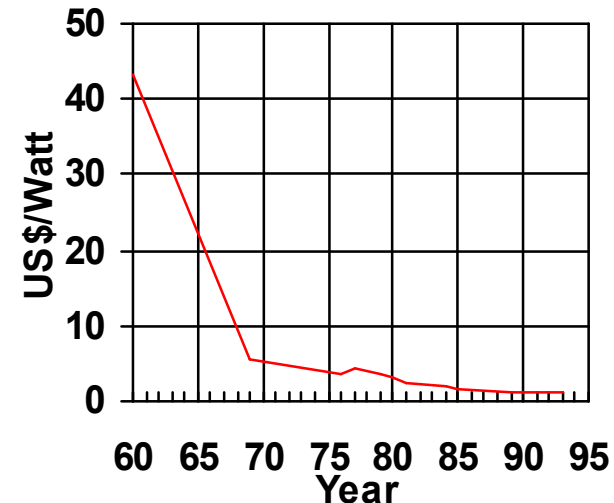
Business Developments

Investments In Thermoelectric Companies

Year	Company	Investor	Investment
2008	GMZ Energy	Kleiner-Perkins	N/A
2006	Micropelt	Fraunhofer/Infion	N/A
2005	Nord	FerroTec	N/A
2005	Melcor	Laird	\$20M
2005	Nextreme	RTI/Startup	\$8M
2004	Marlow	II-VI Inc.	\$31M
2003	Nanocoolers	Startup (folded 2008)	\$8.5M
2003	Teledyne (Telan)	FerroTec	N/A
1998	Amerigon	Internal	N/A
1992	Melcor	Fedders	\$14.9M

*N/A = Not Available, Blue = New, higher ZT technologies

High(er) ZT materials not yet commercial



Price per Watt of cooling in 1993 US\$
[Buist-1993]

- Manufacturers in China and Former Soviet Union have emerged as low cost suppliers
 - China: Fuxin Electronics, Hui Mao, HiCool, Hangzhou Jianhua Semiconductor Cooler, Hebei IT Shanghai, Taicang TE Cooler, and Taihuaxing Trading/Thermonamic Electronics.
 - Fuxin reported sales US\$50M.
 - Former Soviet Union: Thermion (our host), Altec, Kryotherm, Nord, Osterm, RIF Corp., RMT, Thermix, and ADV-Engineering.

TEs for Telecom Cooling

- Melcor, Marlow and many other TE manufacturers provide coolers specifically designed for Telecom laser-cooling applications



From Melcor, <http://www.melcor.com>

Higher ZT = better, cheaper

A large advertisement for Melcor Thermoelectrics. The main image shows a TEC mounted in a metal housing with a black cable. The text reads "MELCOR Thermoelectrics for Telecom Cooling" and "ISO 9001 CERTIFIED". At the bottom, it says "The Standard in Thermoelectrics" and provides contact information: "1040 Spruce Street • Trenton, NJ 08648 USA (800) 383-4178 • FAX (609) 383-9461 WEB: www.melcor.com". There is also a small inset image showing two TECs with wires.

MELCOR
Thermoelectrics
for Telecom Cooling

ISO 9001
CERTIFIED

The Standard in Thermoelectrics
1040 Spruce Street • Trenton, NJ 08648 USA
(800) 383-4178 • FAX (609) 383-9461
WEB: www.melcor.com

A PEDIERER ENGINEERED PRODUCTS COMPANY

Herman Miller C2

Climate Control for the Cubicle
Based on Amerigon CSS Car Seat cooler/heater

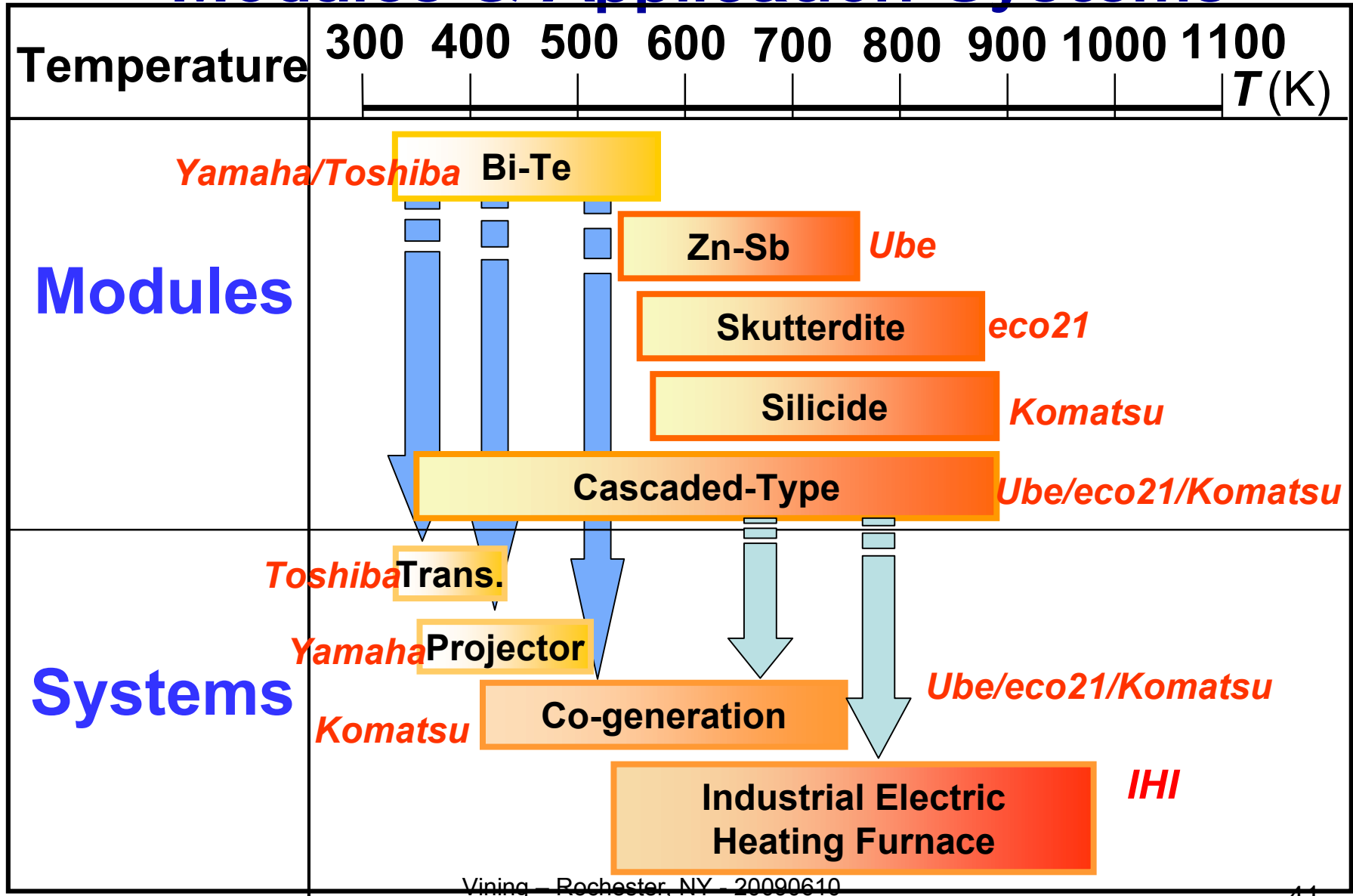


Device has won several awards including Popular Mechanics Magazine's Best of Green Design 2008

Thermoelectric Programs in Japan: NEDO

Prof. Kajikawa, Shonan University

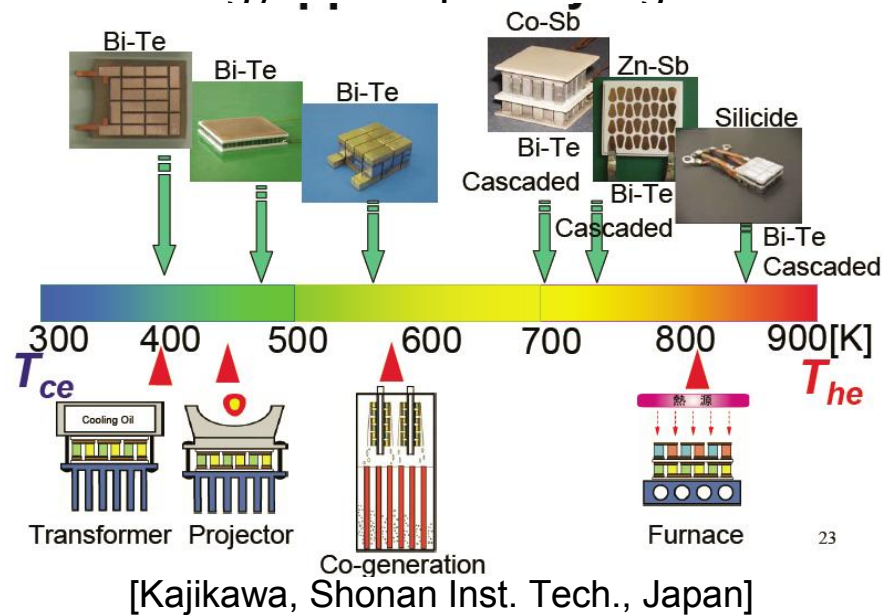
Temperature Range of Modules & Application Systems



Japanese Programs

NEDO – New Energy and Industrial Technology Development Organization

- US\$24M over 5 years
 - Transportation
 - Co-Generation
 - Industrial waste heat
- Goal:
 - Near term: practical demo
 - Advanced: 15%
- Completed March, 2007
 - Possible follow-on 2009
 - Partners may pursue commercialization

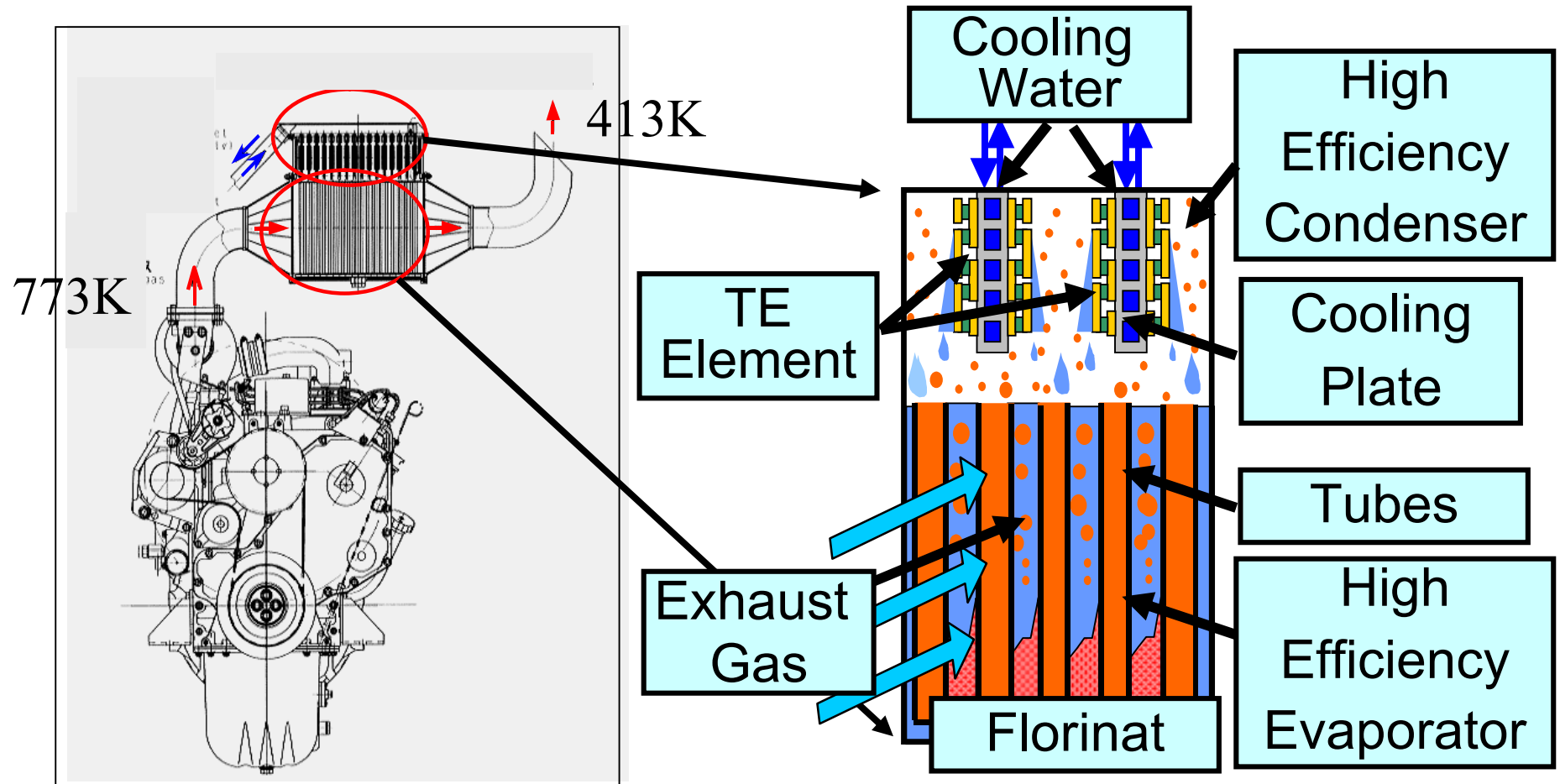


OTEC – Ocean Thermal Energy Conversion (1980-2)

Test Plant – 500 TEG modules [Uemura, ITTJ]

Vining – Rochester, NY - 20090610

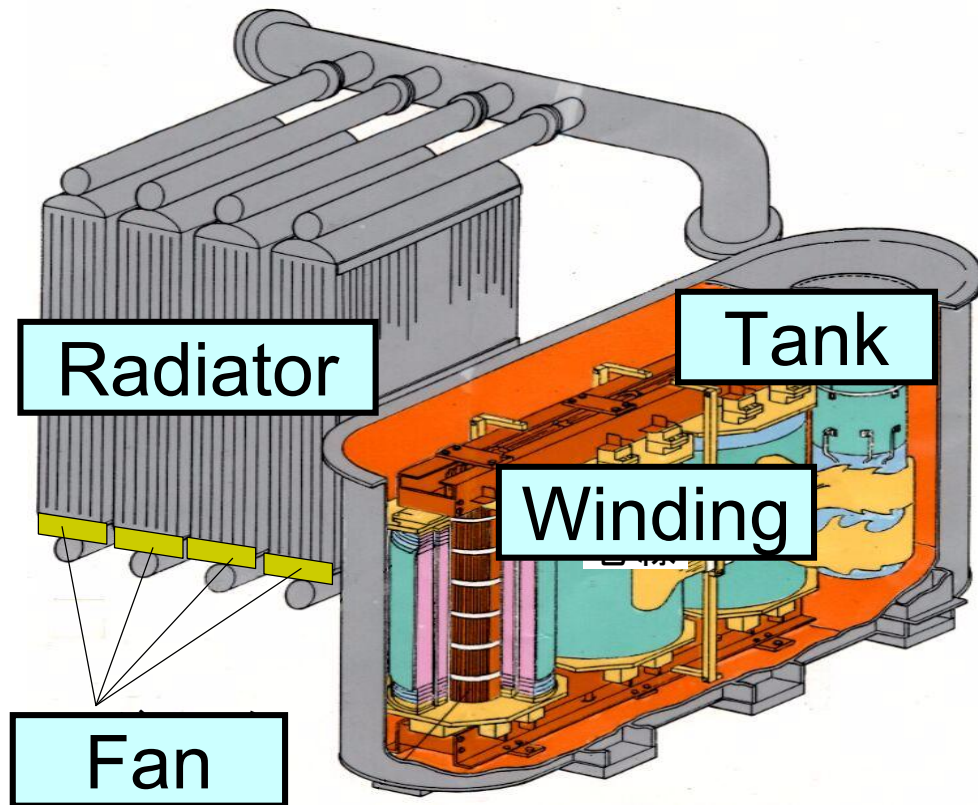
Thermoelectric Power Generation System for Diesel Engine Co-Generation System



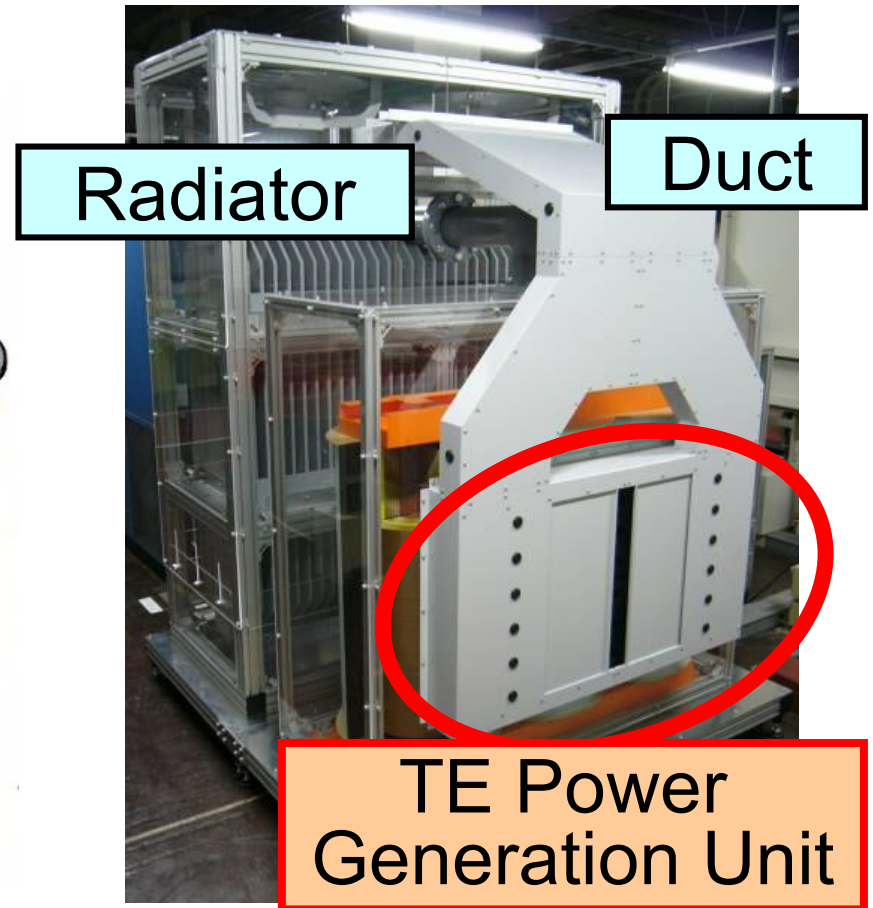
Diesel Engine

Schematic of Thermo-Siphon Type Heat Recovery TE System

Thermoelectric Power Generation System using rejected heat from Electric Transformer



Schematic of Electric Transformer

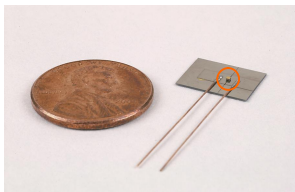


Demonstrated system

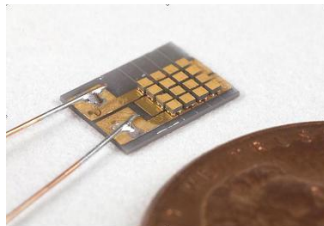
Research Triangle Institute
Spinoff: Nextreme
Rama Venkatasubramanian

Large Scale Superlattice Thin-film Modules using thin-films of $\sim 10 \mu\text{m}$ for both p and n legs

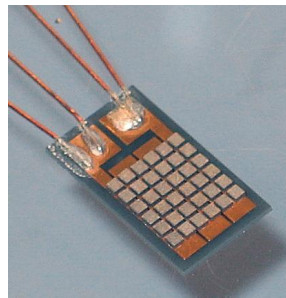
1 p-n couple
P ~ 0.055 W



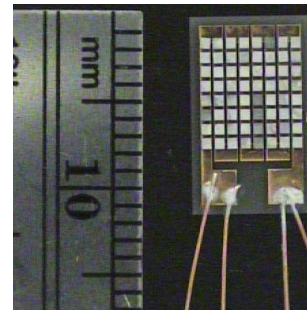
4x4 module
P ~ 1 W



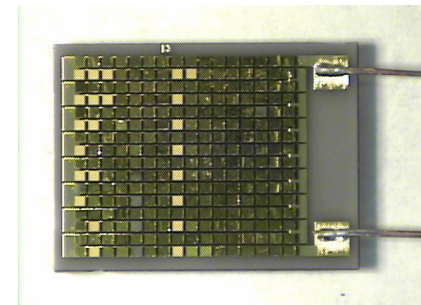
6x6 module
P ~ 2.1 W



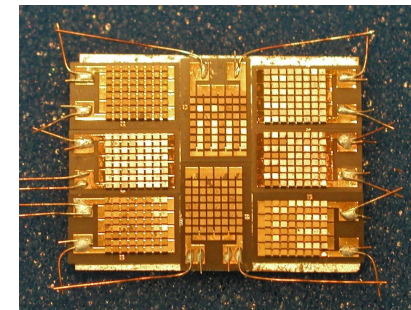
8x8 module
P ~ 3.4 W



16x16 module
P ~ 10W



Multi-Module-Array
P ~ 14.6 W



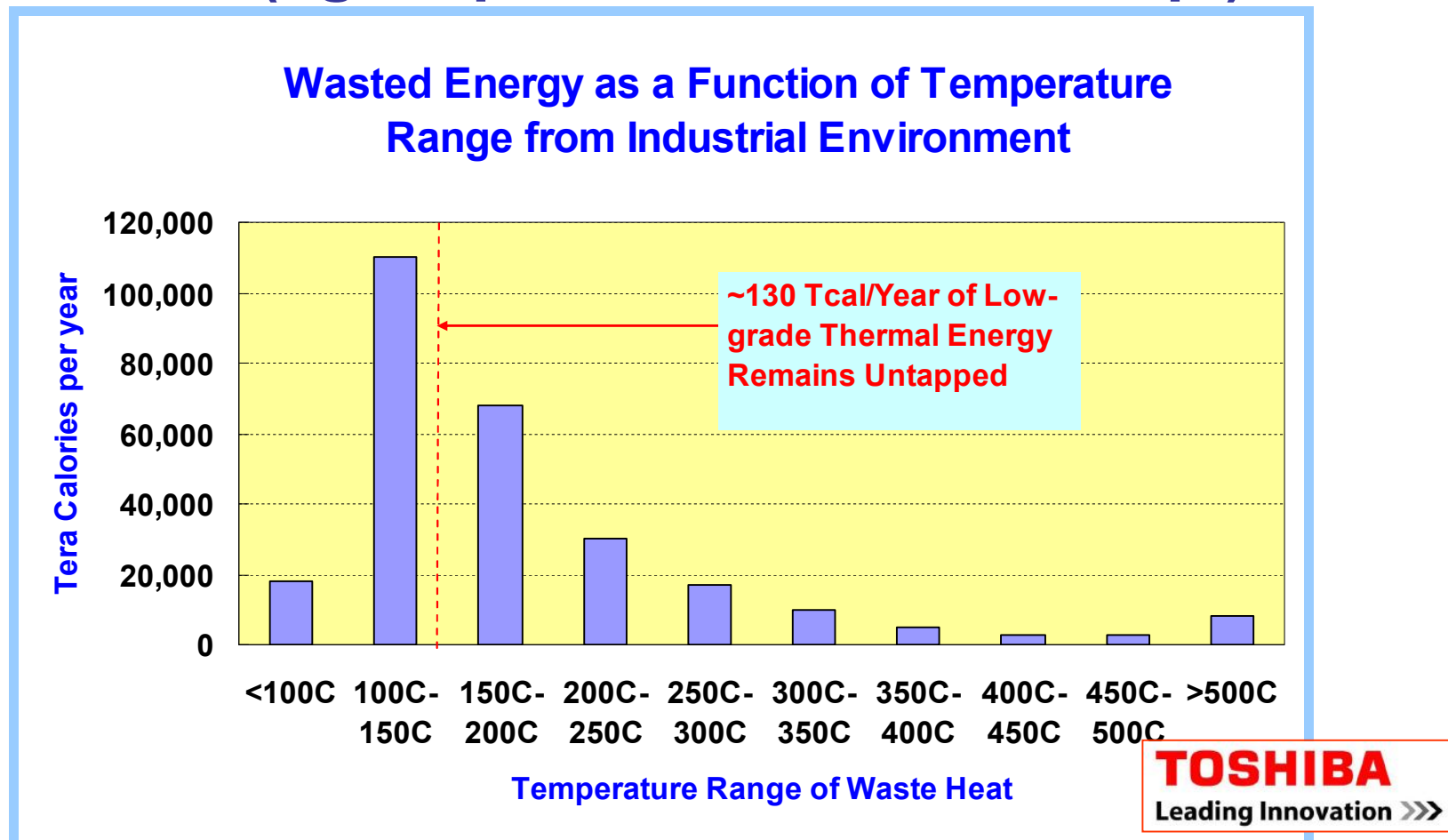
Comparison with Commercial off-the-shelf (COTS)

	Units	RTI Bi ₂ Te ₃ -SL Module	Toshiba Giga Topaz™ module	Modules currently on the market		
		State-of-the-art	Giga Topaz™	Compact type	Midsize type	Large type
Temperature on high-temperature side	[°C]	157	500	230	230	230
Temperature on low-temperature side	[°C]	57	20	30	30	30
Voltage	[V]	11.2	3.6	3.3	1.7	[3.8]
Current	[A]	1.3	4.2	0.8	8	5
Output	[W]	14.6	15.0	2.5	14.0	19.0
Width × height	[cm]	2.3 × 2.0	3.7 × 3.9	2.9 × 2.9	6.3 × 6.3	7.5 × 7.5
Weight	[gm]	2.5*	40	14	82	115
Output per unit of surface area	[W / cm ²]	3.2	1.04	0.30	0.36	0.34
Output per unit of weight	[W / g]	5.8	0.38	0.18	0.17	0.17

Ref: <http://kagakukan.toshiba.co.jp/en/06energy/newtech141.html>

* Includes heat-sink carrier and all wire harness

Abundance of Thermal Energy in Industrial Waste Heat (eg: Japan; Ref: Toshiba Corp.)



- Low grade heat in one sector - 130 Tcal/yr – equivalent to 250 Million Pounds of CO₂
- Capturing low-grade waste heat into useful power is intrinsically a difficult thermodynamic problem
 - Ø Carnot Efficiency $\sim (DT/T_{hot})$