

Thermoelectrics: from Space to Terrestrial Applications – Successes, Challenges and Prospects

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Thermoelectric (TE) Applications Power, Cooling, Sensing



THERMOELECTRIC BASICS





Simple Thermoelectric Devices



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



Selection Criteria for TE Materials

Minimum κ_{ph}

$$\kappa_{ph} \approx \kappa_{\min} \approx 0.2 \frac{W}{m-K}$$

Maximum TEP

$$\widehat{\alpha_{SC}} \approx \frac{k_B}{e} \left(\frac{E_G}{2 k_B T} \right) > 200 \frac{\mu V}{K}$$

High Weighted mobility

$$U_M = \mu \left(\frac{m^*}{m_e}\right)^{3/2} \approx 750 \frac{cm^2}{V-s}$$

Other Critical Issues to consider:

- Materials Stability over time and temperatures
- Radiation tolerance
- Low Thermal and Electrical Contact Resistances
- Diffusion Barriers
- Thermal Expansion
- Heat Exchangers & Thermal Sinking
- Cost of TE materials



State-of-practice thermoelectric materials



TE materials used in commercial applications were discovered in the 1960's



 ZT_m vs. COP



- ZT ~ 3 would be needed for thermoelectrics to compete with vapor compression-based refrigeration systems
- Thermoelectrics prevails in niche applications where scalability and reliability are key and not efficiency



'Best Practice' vs. Thermoelectric Efficiency



- With current ZT values, thermoelectrics is not competitive with other current conversion technologies
- However, thermoelectrics prevails in niche applications where scalability and reliability are key



- 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)
 - Sheetak (low cost coolers)
 - 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 (nano/bulk materials)

TE business today is mainly cooling



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" Bi_2Te_3 thin-film TE wafer.

Courtesy of C. Vining



Cooling Applications



Applications



USS DOLPHIN AGSS 555 Uses Thermoelectric Air Conditioning - Test for Silent Running



- Solid-state, silent cooling is attractive for the Navy
- ZT values not high enough yet to be practical though



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



Business Developments



Amerigon revenue 1999-2007

- 'Old' Bi₂Te₃ TE materials
- Innovative engineering
- Reduced costs
- Can be used in other new products



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





Business Developments – Sheetak, Inc



- Low-cost coolers
- Innovative thermal management and lowcost TE materials processing



Heat circuits result in 3× reduction in energy consumption



 Low-cost thin-film TE materials processing





Recent development in thermoelectric materials R&D

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].

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C1 Th1 Th2 C2 Si NWS H2 H2 T~1.2 @ 350 K

nanowire p-type, Si [Heath, Caltech, 2008]



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

Recent materials R&D resulted in ZT >1 but advanced cooling materials not quite used for commercial applications yet



Power Generation Materials



Most new, bulk thermoelectric materials recently developed with ZT > 1 are power generation materials



Power Generation Applications



Thermoelectric Power Generation

Thermoelectric effects are defined by a coupling between the electrical and thermal currents induced by an electric field and a temperature gradient



Dimensionless Thermoelectric Figure of Merit, ZT $ZT = \frac{\sigma S^2 T}{\lambda} = \frac{S^2 T}{\rho \lambda}$

- Seebeck coefficient S
- Electrical resistivity ρ
- $\quad \text{Thermal conductivity } \lambda$



Thermoelectric Couple

Conversion efficiency is function of ZT and ΔT



Governing equations

 $I^2 R_L$ Efficiency (η) $\eta =$ $\overline{Q_K + (Q_P)_H - \frac{1}{2}Q_T - \frac{1}{2}Q_J}$ $Q_{\kappa} = K\Delta T$ Thermocouple conductance R₁ : load resistance $E_0 = \alpha \Delta T$ Total voltage R: thermocouple internal $I = \frac{\alpha \Delta T}{\Sigma}$ resistance **\pi** : Peltier coefficient Current $R + R_{I}$ $(Q_P)_H = I\pi$ Peltier cooling at the hot-side $Q_T = I\mu\Delta T$ Thomson heat $Q_I = I^2 R$ Joule heat

In an actual generator, there exist numerous electrical and thermal losses; the efficiency equation listed above therefore represents an upper limit



Converter Design & Operation





Device/system design considerations

- Efficiency vs. power output considerations
 - Fixed input temperatures power output and efficiency optimize for different values of R/R_L ; P max corresponds to $R = R_L$
 - Fixed heat input power output and efficiency optimize for the same value of R/R_L



- Cost
- Hot- and cold-side heat exchangers are key

Actual design requires to capture all system considerations and trades between engineering and economic factors



TE Power Generation Applications



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



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



Space Power Technology



Radioisotope Thermoelectric Generator Key Components





U.S. space missions that have used Radioisotope Thermoelectric Generators (RTGs)





Multi Mission-RTG Characteristics

- Electrical Power Output: ~ 123 W (BOL)
- Specific power: ~ 2.8 W_e/kg
- System Efficiency ~ 6.2%
- Voltage 28 VDC
- In-space & surface operational capability
- Qualified for 0.2 g²/Hz random vibrations
- Mission life design ~2 years





MMRTG

- Mass: ~ 44.1 kg
- 8 GPHS modules
- Thermal Power Input ~ 2000 W (BOL)
- 768 PbSnTe/TAGS +
 PbTe couples
 - T_{hot} ~ 811 K



Mars Science Laboratory (MSL)



RTG Technology Key Performance Characteristics

- Performance characteristics
 - Specific power (W/kg) -> Direct impact on science payload
 - T/E efficiency -> Reduce PuO_2 needs
 - Power output, voltage -> Mission needs



Couple Efficiency – State-of-Practice

	N-PbTe	P-TAGS/PbSnTe	N- GPHS RTG SiGe	P-GPHS RTG SiGe	
Average ZT	0.90	0.84	0.69	0.41	
Maximum Operating Temperature	800 K	675/800 K	1275 K	1275 K	
Couple Efficiency/ Design	7.0% [800 to 485K] PbTe TAGS PbSnTe Conductively coupled		7.5% [1275 to 575 K]		
System efficiency	6.2 %		6.3 %		
Application	Multi-Mi	ssion RTG 2.8 W/kg	GPHS	RTG 5.1 W/kg	



What Controls RTG Performance?

Most of RTG weight due to heat source and TE converter subsystems



High efficiency TE materials essential to achieve high specific power and reduce usage of PuO₂

Specific power, efficiency





Specific power vs. cold-junction temperature





- Highly reliable with a high level of redundancy
 - Hundreds of discrete converters in series/parallel configuration
- Proven long-life operation
 - Both Si-Ge and PbTe-based RTGs have demonstrated more than 30 years of operation
 - Well known converter aging mechanisms (all solid-state)
 - Failure mechanisms well understood
- Proven operation in extreme environments
 - Radiation resistant
- High grade waste heat available for spacecraft thermal management
- Friendly to science instruments
 - Produces no noise, vibration, or torque during operation
 - No electromagnetic interference
- Long life capability
 - Most outer planet missions > 10 years
 - Missions often get extended



Voyager MHW RTG Performance



MHRTG's provided power to Voyager I &II for over 30 years reliably



Cassini RTG Performance

CASSINI MISSION PREDICT





Advanced TE materials and components for next generation RTG





- 10 15% system efficiency (1.5 - 2.5 X over MMRTG)
- 6 10 We/kg
 (2 3 X improvement over MMRTG)
- $\cdot \ge 17$ year life





HT TE Materials – 14-1-11 Zintl Phases

• Yb₁₄MnSb₁₁ stable to >1300 K

- ZT > 1 in 1000 -1275K range
- Many opportunities for doping and disorder

p-type Zintl compositions derived from Yb₁₄MnSb₁₁

- Yb \rightarrow Ca, Sr, Eu, La, Ce, Y ...
- Mn \rightarrow Al, In, Ga, Zn ...
- Sb \rightarrow P, As, Bi
- Tetragonal; I41/acd Z = 8
- Lattice Parameters
 - -a = 16.615 Å
 - -c = 21.948 Å
- Primary unit cell
 - -1 MnSb₄ tetrahedron
 - -1 Sb₃ polyatomic anion
 - -4 Sb³⁻ anions
 - 14 Yb²⁺ cations





La_{3-x}Te₄ Structure and Stoichiometry

- $La_{3-x}Te_4$: defect Th₃P₄ structure-type (I-43d), up to 28 atoms per unit cell - 0 < x < 1/3
 - x = 0; Te/La = 1.33; metallic, electron concentration of ~ 4.49x10²¹ cm⁻³
 - -x = 1: Te/La = 1.50; highly resistive semiconductor (can be written as La₂Te₃)





- [V]_x : La vacancy concentration
- $[e^{-}]_{1-3x}$: electron concentration
- $La_{3-x}Yb_{v}Te_{4} \equiv [La^{3+}]_{3-x}[V]_{x}[Yb^{2+}]_{y}[Te^{2-}]_{4}[e^{-}]_{1-3x+2y}$ - Can independently vary vacancy and electron
 - concentrations







Filled skutterudites

- Many RT₄Pn₁₂ compounds exist such as LaFe₄As₁₂
- Derived from CoAs₃ skutterudite prototype:
 - By filling the empty octants present in the unit cell

Most have a metallic behavior

- Trivalent rare earth (La³⁺) and divalent transition metal (Fe²⁺)
- Valence electron count (1x3) + (4x8) + (12x3) = 71
- Count of 72 needed to conserve a semiconducting behavior
- Expected reduction in lattice thermal conductivity
 - "Rattlers"
 - Conduction in valence band dominated by Sb rings ; potentially, no significant impact on carrier mobility
 - ⇒ Phonon Glass Electron Crystal (PGEC) concept (G. Slack): decoupling of electrical and thermal transport i.e. conduct electricity like a perfect crystal with a glass-like thermal conductivity



Skutterudite crystal structure



CoAs₃ ores



ATEC advanced TE Materials



 $973K \le T \le 1273K$ **Neutron Irradiation of TE Materials** n-La_{3-x}Te₄ p-Yb₁₄MnSb₄ T~873K T~873K Observe the impact of neutron radiation on the • N-(Yb,Ba),CoSb3 thermoelectric properties of La_{3-x}Te₄, Yb₁₄MnSb₁₁, np- Ce_fFe_{3x}Co_xSb₁₂ and p-type skutterudites Neutron emitter Pu-240 is a contaminant in Pu-238 Cold-shoe Cold-shoe 3 samples of each were exposed to 17 years worth T~463K of neutron radiation in 35 minutes at the Ohio State Illustration of ATEC couple University Research Reactor (OSURR) (near room under development **RT Resistivity** temperature). 2.00 Absolute Value RT Seebeck Change E 1.50 1.00 50.0 Post-Irradiation 110.4 115.6 115.2 75.2 Pre-Irradiation 115.6 115.0 115.7 78.0 78.0 78.0 31.0 30.6 30.8 45.7

No significant change in room temperature electrical properties

• ATEC TE materials do not appear to be sensitive to exposure to neutrons

Sample ampoules for irradiation





• Skutterudite couple - (~ 9.3% efficiency – 873K-473K)



 Skutterudite couple encapsulated with aerogel



Zintl/LaTe/SKD ATEC couples



	14-1-11 Zintl	La _{3-x} Te ₄	Skutterudite
	(p)	(n)	(p & n)
Temperature dependent mechanical properties	CTE: 16-19 ppm	CTE: 17-20 ppm	CTE: 12-14 ppm



Demonstrated BOL efficiency





- Improve vehicle fuel efficiency
 - Customer driven requirement
 - Government driven requirements
- Requirements to lower CO₂ emissions
- Green image to help vehicle sales
- Support increased vehicle electrification
- Simpler than alternative systems:

- Rankine, Stirling, thermo-acoustic, etc.



Heat Distribution in Vehicles



Exhaust is the most promising waste heat source



TE for Vehicle Waste Heat Recovery

- Thermoelectrics in Vehicles
 - TE has unique advantages for integration
- What has been done?
 - Low efficiency Bi₂Te₃-based TE generators (TEG) demonstrations
- What is needed?
 - Increase TEG operating temperatures, ΔT
 - Integrate abundant, low-toxicity, higher ZT materials (ZT_{ave} ~ 1.5 to 2)
 - Develop and scale up HT TE module technology
 - Integrate with efficient heat exchangers



Exhaust Pipe TE Electrical power generator





> 10% Fuel Efficiency improvement with exhaust waste heat recovery





• TEG Unit

- Hot side heat exchanger & flow controls
- Cold side heat exchanger and flow controls
- Thermoelectric modules
- Enclosure
- Hoses, pipes, flow management
- Thermal management components (optional)
- Vehicle mechanical interface mounting
- DC to DC converter & electrical interface







- The real number to focus on is \$ per MPG (miles per gallon) improvement
 - May use \$ cost per Watt output for the complete TEG system
 - \sim \$1/W cost target
- The customer must perceive sufficient benefit to pay for the cost of a TEG
- Some of the benefit may be "Green Image" but most of the benefit has to translate into fuel savings
 - Eliminating the use of the conventional generator for a vehicle on a US Government fuel economy test (FTP) will save 1.5 to 3.0% fuel economy depending on the type of vehicle
 - Real world driving may provide additional fuel savings



Waste Heat Sources





Average Power Plant Generation Efficiency



Efficiency has not improved significantly in last 40 years for large scale power plants



Opportunities for Power Generation by Recovering Waste Heat





Dynamic Power Systems Are Efficient

 Thermoelectrics cannot compete "head-on" with dynamic technologies



Adapted from: Hendricks, T., Choate, W. T., Industrial Technologies Program, "Engineering Scoping Study of Thermoelectric Generator Systems for Industrial Waste Heat Recovery" (U.S. Department of Energy, 1-76, 2006).



- Some industrial processes are potentially attractive for TE systems
 - Medium to high grade heat Medium to high grade heat for aluminum, glass, metal casting, non-metal melting, ceramic sintering and steel manufacturing
 - Limited opportunity to reuse the waste heat
 - Difficulties in effectively transporting that heat to separate energy conversion systems



Major Opportunities in **Manufacturing & Energy Industries**

up to 1275 K)

Large scale waste heat recovery of industrial and power generation processes

- Benefit from higher energy costs and reduction of fossil fuel pollution to retrofit existing facilities
- High grade waste heat sources from a variety of industrial manufacturing processes
 - For near term applications in the US alone, between 0.9 and 2.8 TWh of electricity might be produced each year for materials with average ZT values ranging from 1 to 2
- Efficient heat exchangers, large scale production of TE materials and **Potential High Temperature** modules are required Thermoelectric Waste Heat **Recovery System**
 - Also need to focus on economical. low toxicity materials

		T _{source} (K)	Available Waste Heat	TEG Recoverable Waste Heat GWh/year		erable eat ar		
			GWh/year	ZT=1	ZT=2	ZT=4		
Applications Set A: low hot-side temperature, relatively clean flue gas								
Commercial	Water/Steam Boilers	425	164,010	n/a	n/a	n/a		
Industrial	Water/Steam Boilers	425	178,654	n/a	n/a	n/a		
	Ethylene Furnace	425	8,786	n/a	n/a	n/a		
Applications Set B: medium hot-side temperature, mixed flue gas quality								
	Aluminum Smelting	1230	1,230	59	176	293		
	Aluminum Melting	1025	8,376	410	1,259	2,109		
Metal Casting In Cupola	Metal Casting Iron Cupola	650						
	Steel Blast Furnace							
	Lime Kiln							
	Cement Kiln (with pre-heater)	475	2,050	88	293	498		
Applications	Set A: High hot-side	tempera	ture, mixed f	lue gas	quality			
	Cement Kiln (no pre- heater)	1000	2,460	117	381	615		
Glass Oxy-fuel Furnace	Glass Oxy-fuel Furnace	1700	1,406	59	205	351		
Glass Regenerative		750	3,456	176	527	879		
				\sim				
		Total	370,428	908	2,841	4,745		

Adapted from: Hendricks, T., Choate, W. T., Industrial Technologies Program, "Engineering Scoping Study of Thermoelectric Generator Systems for Industrial Waste Heat Recovery" (U.S. Department of Energy, 1-76, 2006).





Thermoelectric Power Generation System for Industrial Electric Heating Furnace





Thermoelectric Power Generation System using rejected heat from Electric Transformer



Schematic of Electric Transformer

Demonstrated system



Summary

- To date, thermoelectrics has been mostly applied for niche markets
 - Using TE materials developed in the 60's
- New development in TE materials may open up new markets
 - Automobile, industrial processes waste heat recovery
- Both low cost and smart system engineering are needed to make these applications viable
- ZT ~ 3 cooling materials would open larger markets