Waste Heat Recovery Opportunities for Thermoelectric Generators

presented at the

2009 Thermoelectric Applications Workshop

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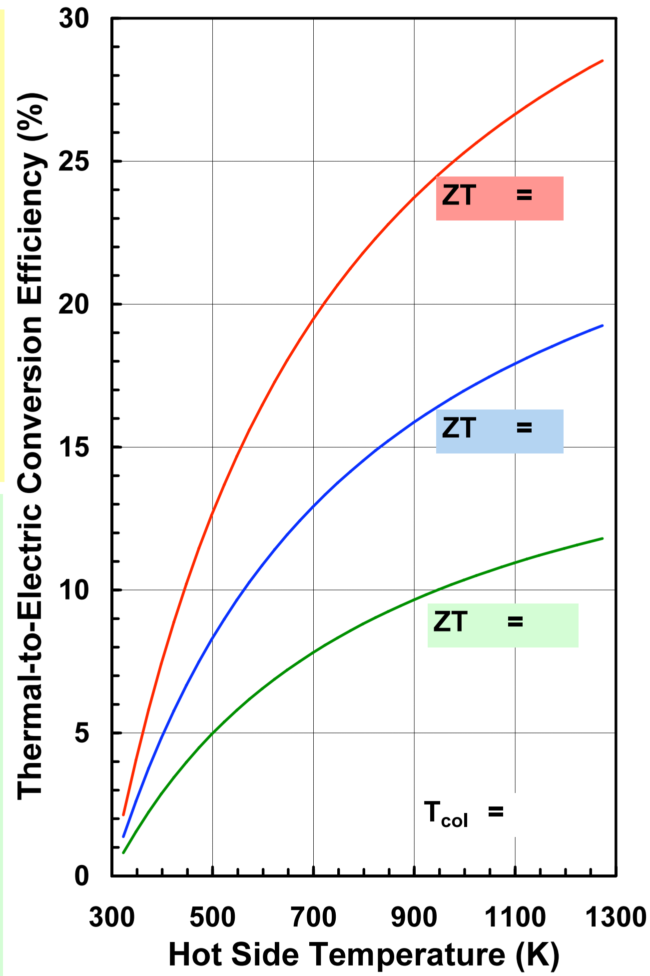
The Case For Thermoelectrics (TE)

- Current TE conversion efficiency usually too low to compete with dynamic technologies for stand-alone systems
  - Current TE materials:
    - Power: 8 to 15% against 25 to 45%
    - Cooling: COP is 3x lower than typical compressor
  - Advanced TE materials goals in the next 3-5 years:
    - Power: 20-30% efficiency (*average ZT of 2.0*)
    - Cooling: 2x to 5x increase in COP, 100x power density

- But TE technology has highly valuable attributes
  - Solid-state, highly scalable and modular
    - No moving parts, no vibrations, silent operation
    - Can outperform competition for small scale applications
  - High level of reliability and redundancy
    - Proven record of long life space and terrestrial applications

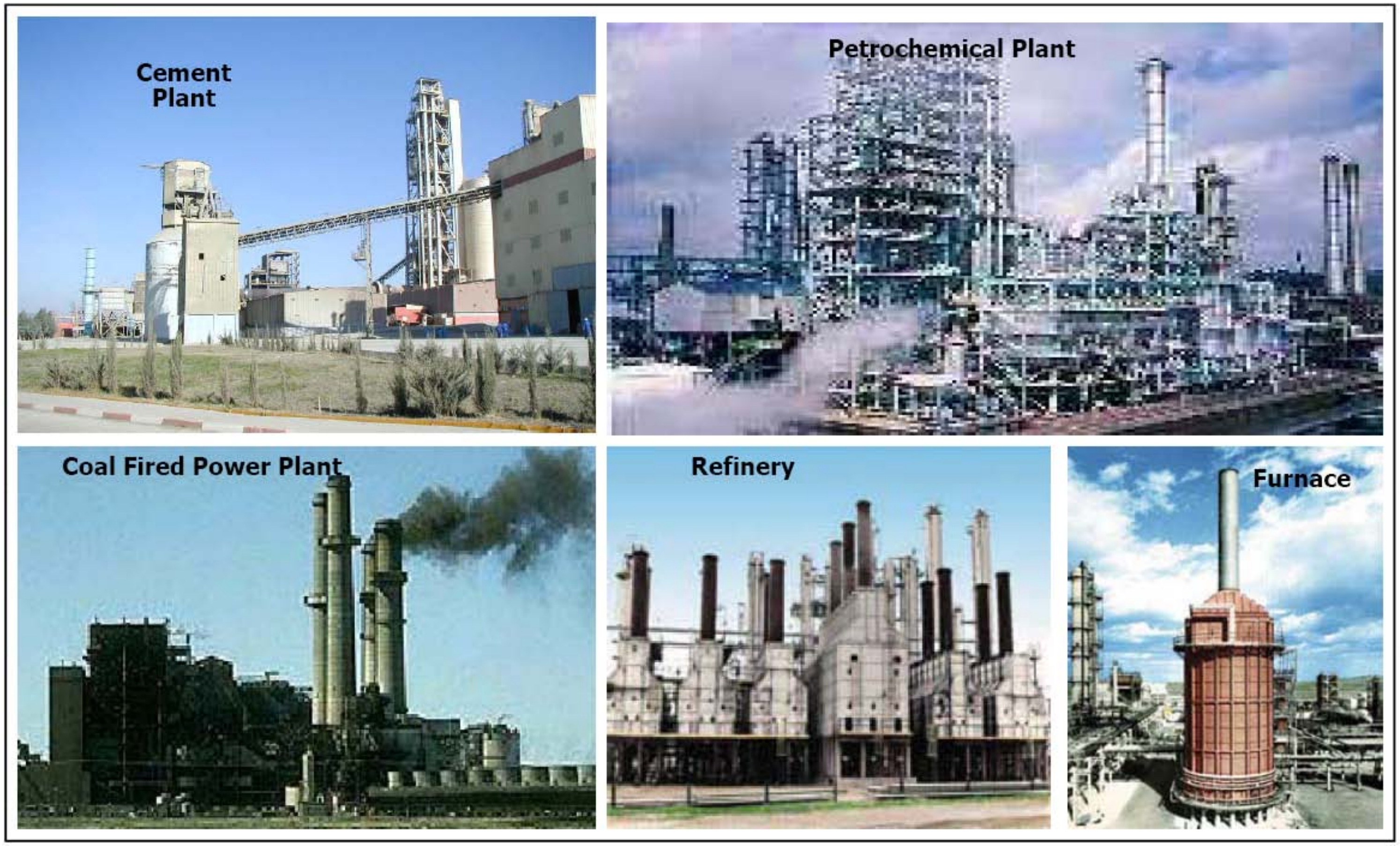
- Waste Heat Recovery is attractive application for TE
  - Thermal energy source is "free"
  - TE generator as a "bottoming/topping cycle retrofit"
  - Scalability and mass production lead to low cost $/kWh



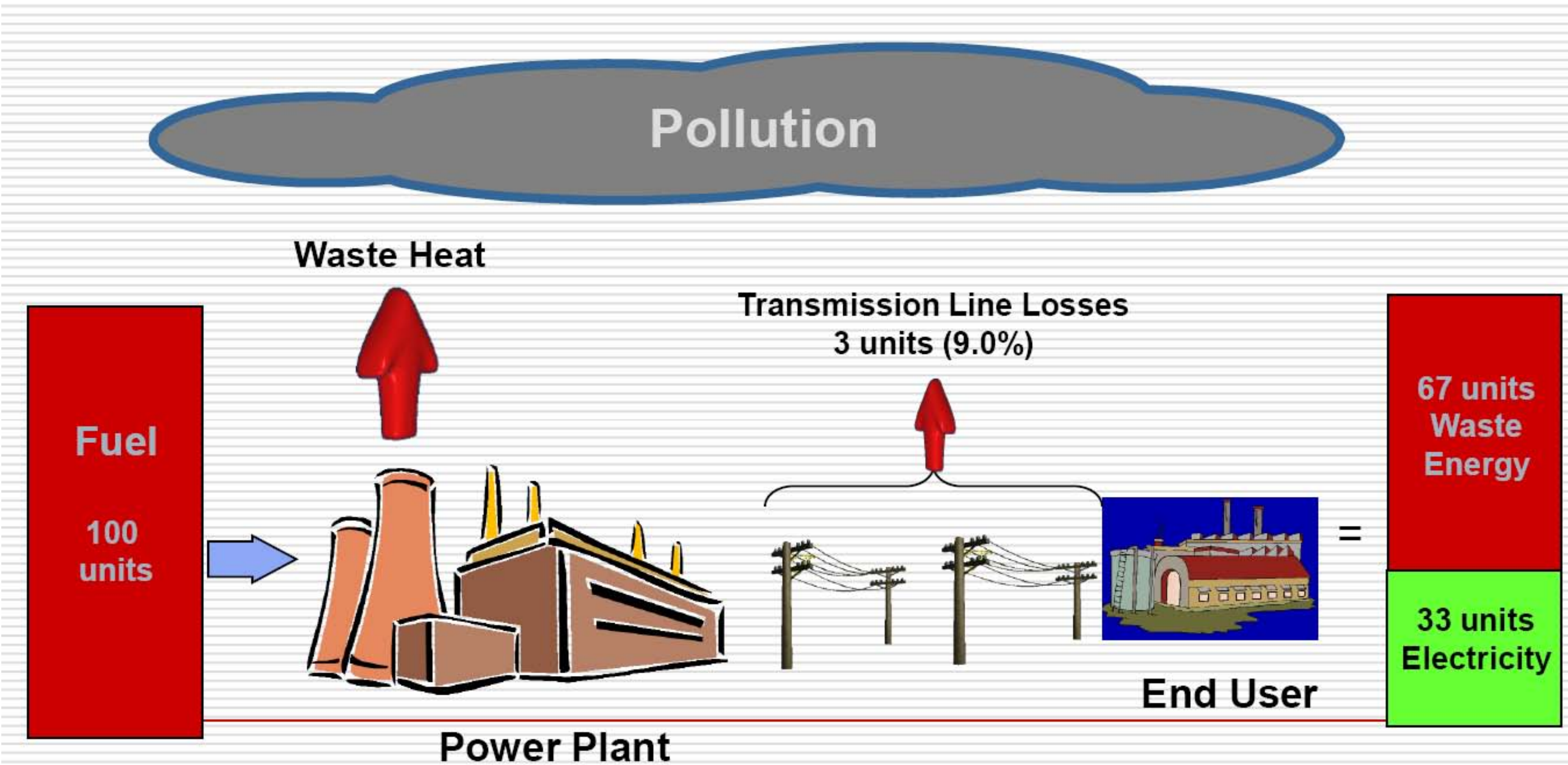
Power generation

State-Of-Practice materials: $ZT_{average}$ ~ 0.5
State-Of-the-Art materials: $ZT_{average}$ ~ 0.9
Best SOA materials: ZT_{peak} ~ 1.5 to 2.0

Waste Heat Sources



Average Power Plant Generation Efficiency

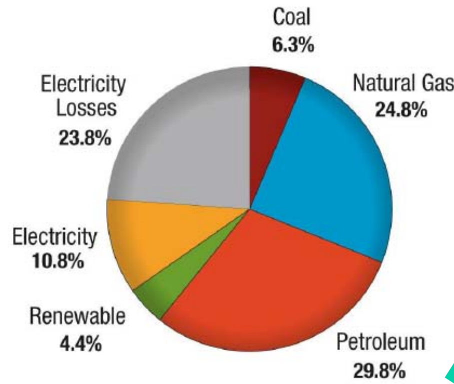


- Efficiency has not improved significantly in last 40 years for large scale power plants

Opportunities for Power Generation by Recovering Waste Heat

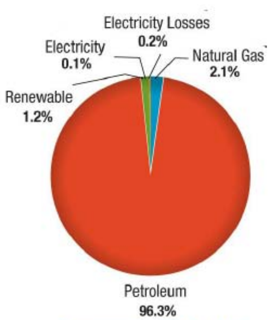
Industrial Sector

- >200,000 sites
- 14.3 million jobs
- $5,900 billion in shipments
- $980 billion in exports

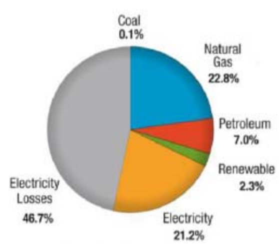


Industrial Sector
Energy Consumption
32.0

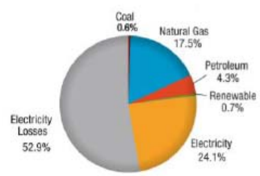
Wide range of heat source types and temperatures from energy intensive industrial processes



Transportation Sector
Energy Consumption
28.1

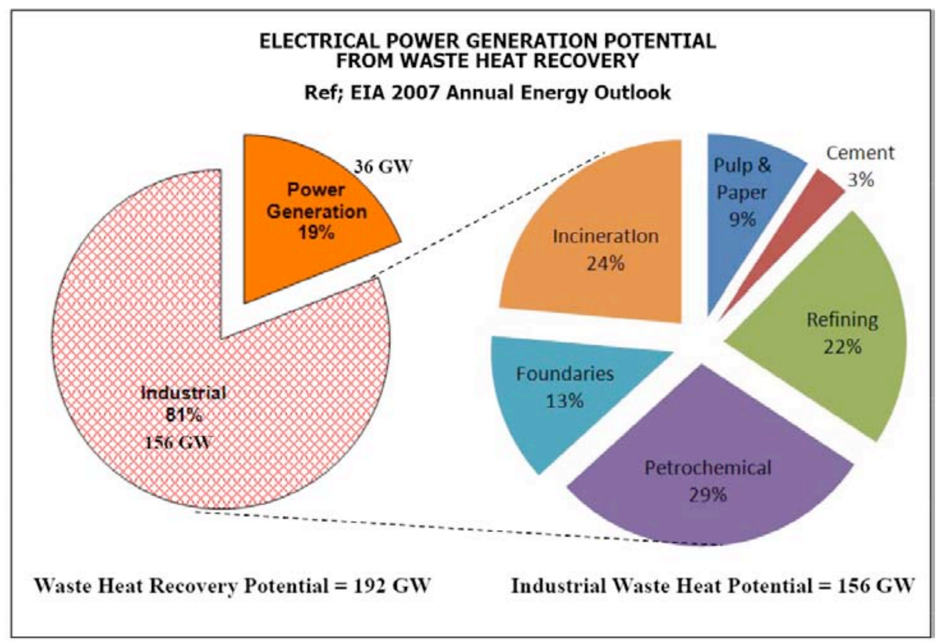


Residential Sector
Energy Consumption
21.9



Commercial Sector
Energy Consumption
18.0

** USA data*



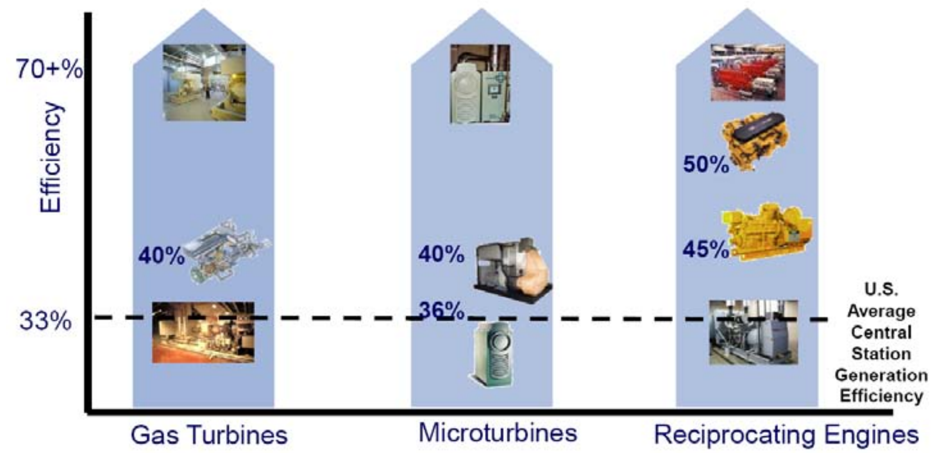
Technologies for Waste Heat Recovery Power Generation

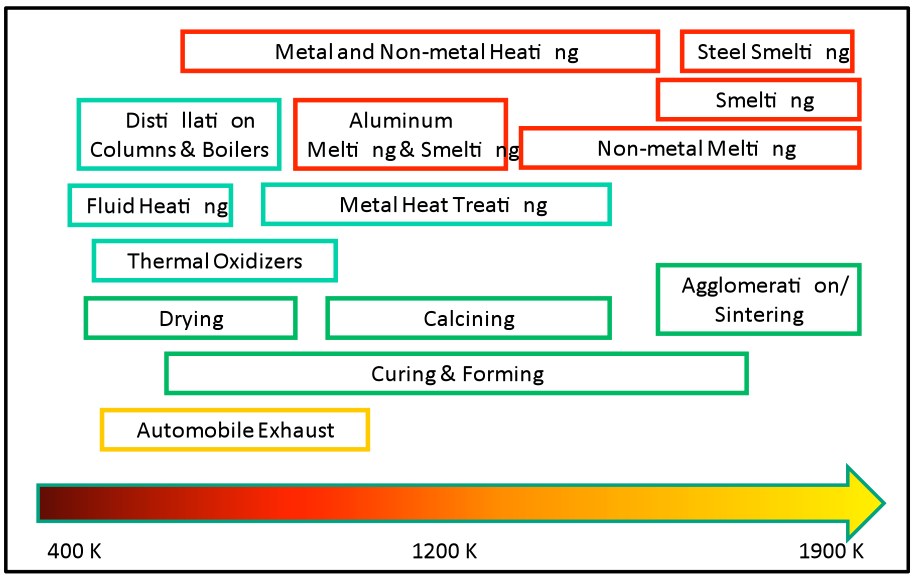
- Commercial Technologies
  - Single Fluid Rankine Cycle
    - Steam cycle
    - Hydrocarbons
    - Ammonia
  - Binary/Mixed Fluid Cycle
    - Ammonia/water absorption cycle
    - Mixed-hydrocarbon cycle
- Emerging Technologies
  - Supercritical CO_2 Brayton Cycle
  - Thermoelectric energy conversion
- Combined Cycles

- Technology Merits
  - Conversion efficiency and effective utilization of waste heat
  - Heat transfer equipment
  - System integration and interfacing with industrial processes
  - System reliability
  - Economic values
  - Ability to integrate into combined cycles

Dynamic Power Systems Are Efficient

- Thermoelectrics cannot compete "head-on" with dynamic technologies





- 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

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).

Major Opportunities in Manufacturing & Energy Industries

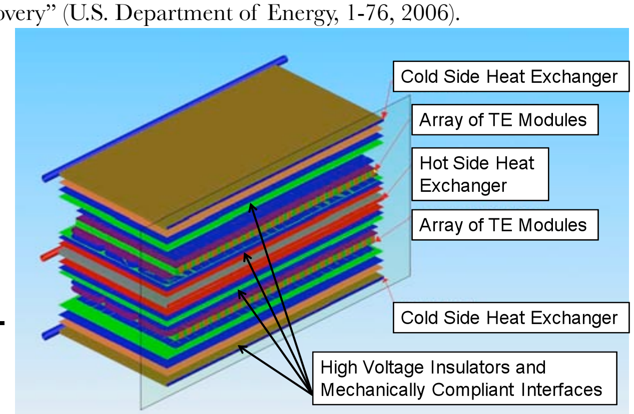
- Large scale waste heat recovery of industrial and power generation processes
  - Benefit from higher energy costs and reduction of fossil fuel pollution to retrofit existing facilities
  - High grade waste heat sources from a variety of industrial manufacturing processes
    - For near term applications 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 modules are required
    - Also need to focus on economical, low toxicity materials

		T_{source} (K)	Available Waste Heat GWh/year	TEG Recoverable Waste Heat 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 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 temperature, mixed flue gas quality						
	Cement Kiln (no pre-heater)	1000	2,460	117	381	615
	Glass Oxy-fuel Furnace	1700	1,406	59	205	351
	Glass Regenerative	750	3,456	176	527	879
	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).

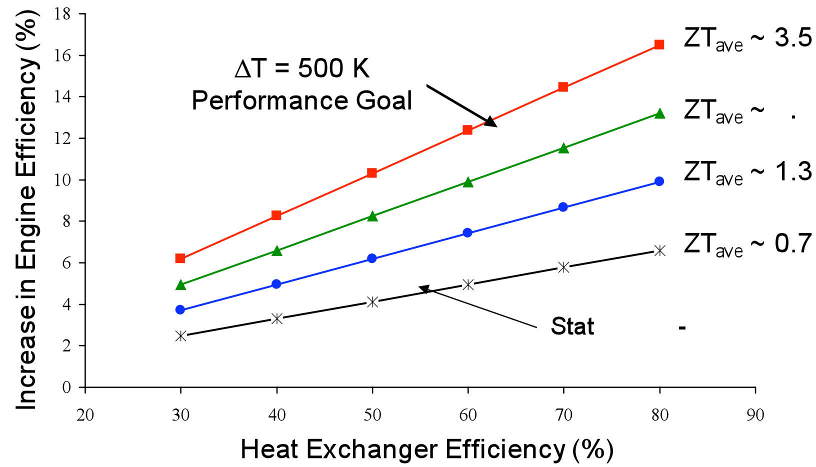
Potential High Temperature Thermoelectric Waste Heat Recovery System

(concept developed for 100 kW-class thermoelectric generators operating up to 1275 K)

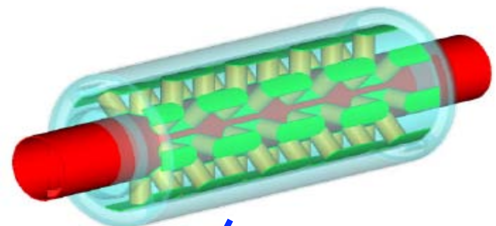


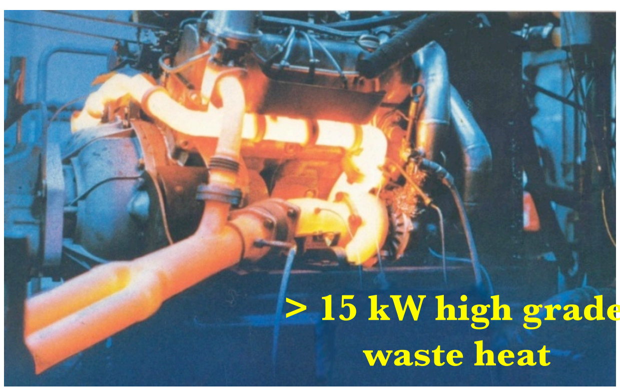
TE for Vehicle Waste Heat Recovery

- Thermoelectrics in Vehicles
  - TE has unique advantages for integration
- What has been done?
  - Low efficiency Bi_2Te_3-based TE generators (TEG) demonstrations
- What is needed?
  - Increase TEG operating temperatures, ΔT
  - Integrate higher ZT materials (ZT_{ave} ~ 1.5 to 2)
  - Develop and scale up HT TE module technology
  - Integrate with efficient heat exchangers

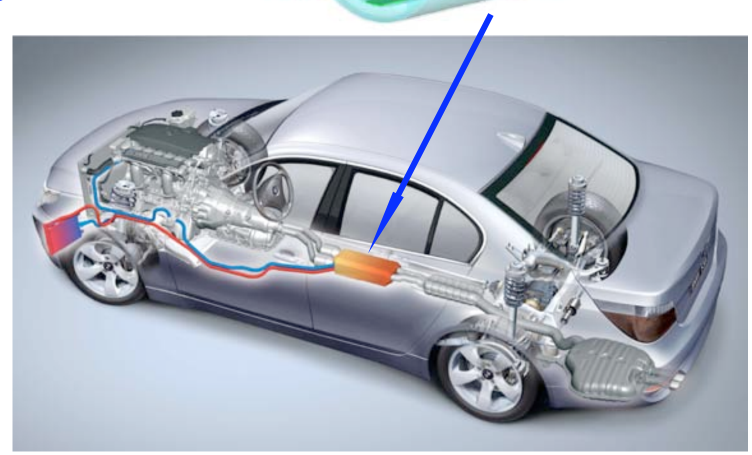


Exhaust Pipe TE Electrical power generator





> 10% Fuel Efficiency improvement with exhaust waste heat recovery



TE Materials Considerations for Large Scale Waste Heat Recovery Applications

- Cost of pure elements (see table for preliminary assessment)
  - Must take into account volume of material required for practical, efficient device design
- Future availability of pure elements
  - Te, Ge…
- Toxicity of elements
  - PbTe….
- Materials and device processing costs
  - Also, how energy intensive these processes are ("energy payback time") is important

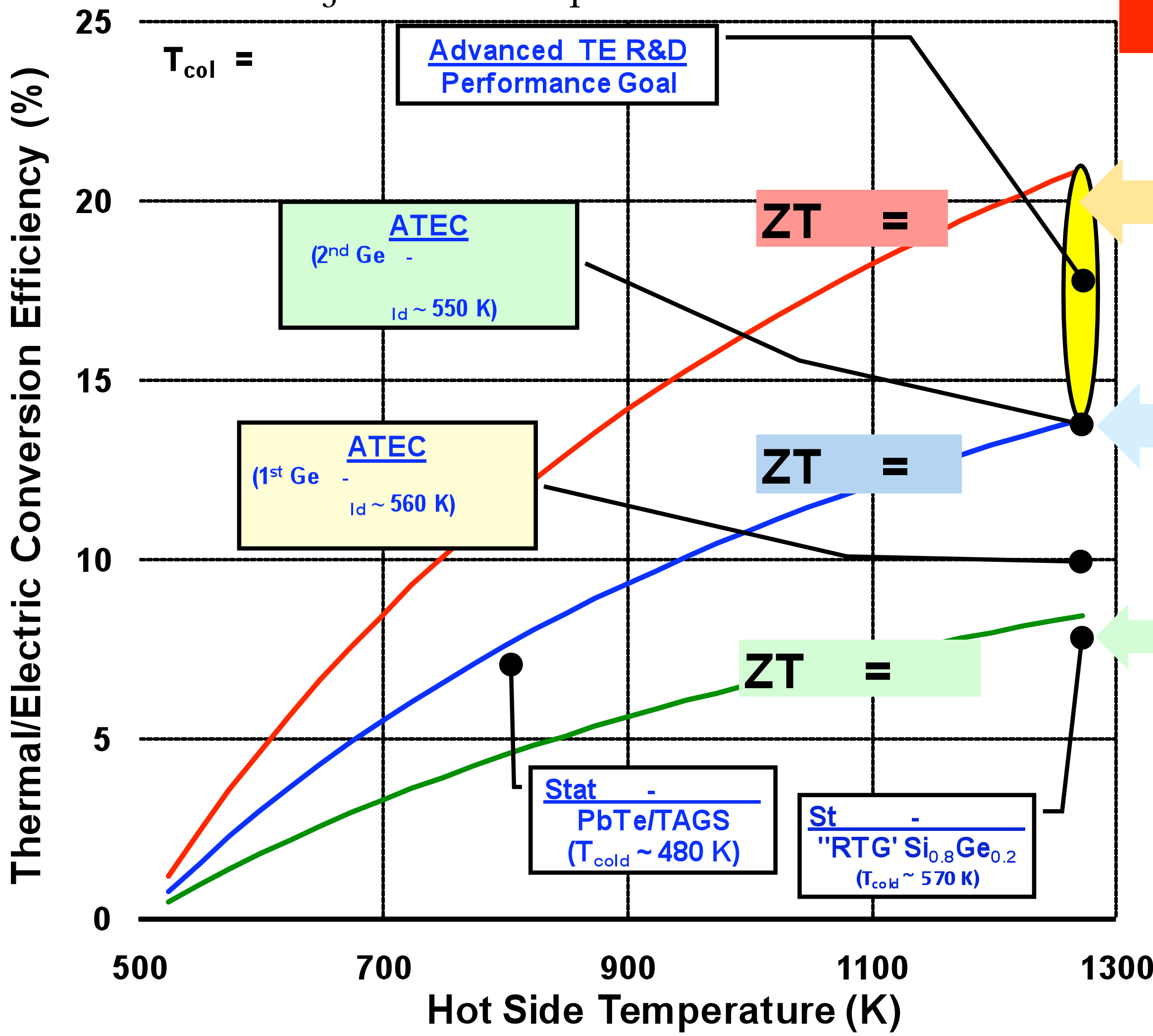
Material	\$ per kg[1]	Max T_{hot} (K)[2]	Temperature Gradient (K/cm)[3]	Materials Efficiency	W/kg[4]	\$/W
$Si_{80}Ge_{20}$	630	1275	183	9.8	60	10.4
$Si_{98}Ge_2$	83	1275	162	7.1	47	1.8
$Yb_{14}MnSb_{11}$/ $La_{3-x}Te_4$	163	1275	744	11.6	104	1.6
$Mg_2Si_{0.6}Sn_{0.4}$ (n)	11	750	133		56	0.2
Skutterudites	12	875	239	10.2	58	0.2
TAGS (p)	631	673			153	4.1
PbTe	83	825	421	8.8	77	1.1
Bi_2Te_3	170	525	592	7.1	221	0.8
Segmented[5]	117	1275	519	19.5	114	1.0

[1]Used 2008 USGS data (mostly)
[2]For long term operation
[3]Based on 300 K cold side temperature, (except for TAGS)
[4]Assumed 10 W/cm^2 heat flux to size up amount of TE material required
[5]Used Zintl/SKD/$(Bi,Sb)_2Te_3$ and $La_{3-x}Te_4$/ SKD/$Bi_2(Te,Se)_3$; similar efficiency results can be achieved with PbTe-based materials

NASA's Advanced TE Research &Technology Program

TE Materials Performance Objective

TE conversion efficiency as a function of hot junction temperature and ZT



Best experimentally demonstrated maximum ZT values ~ 1.5 to 2.0 for Bulk Materials

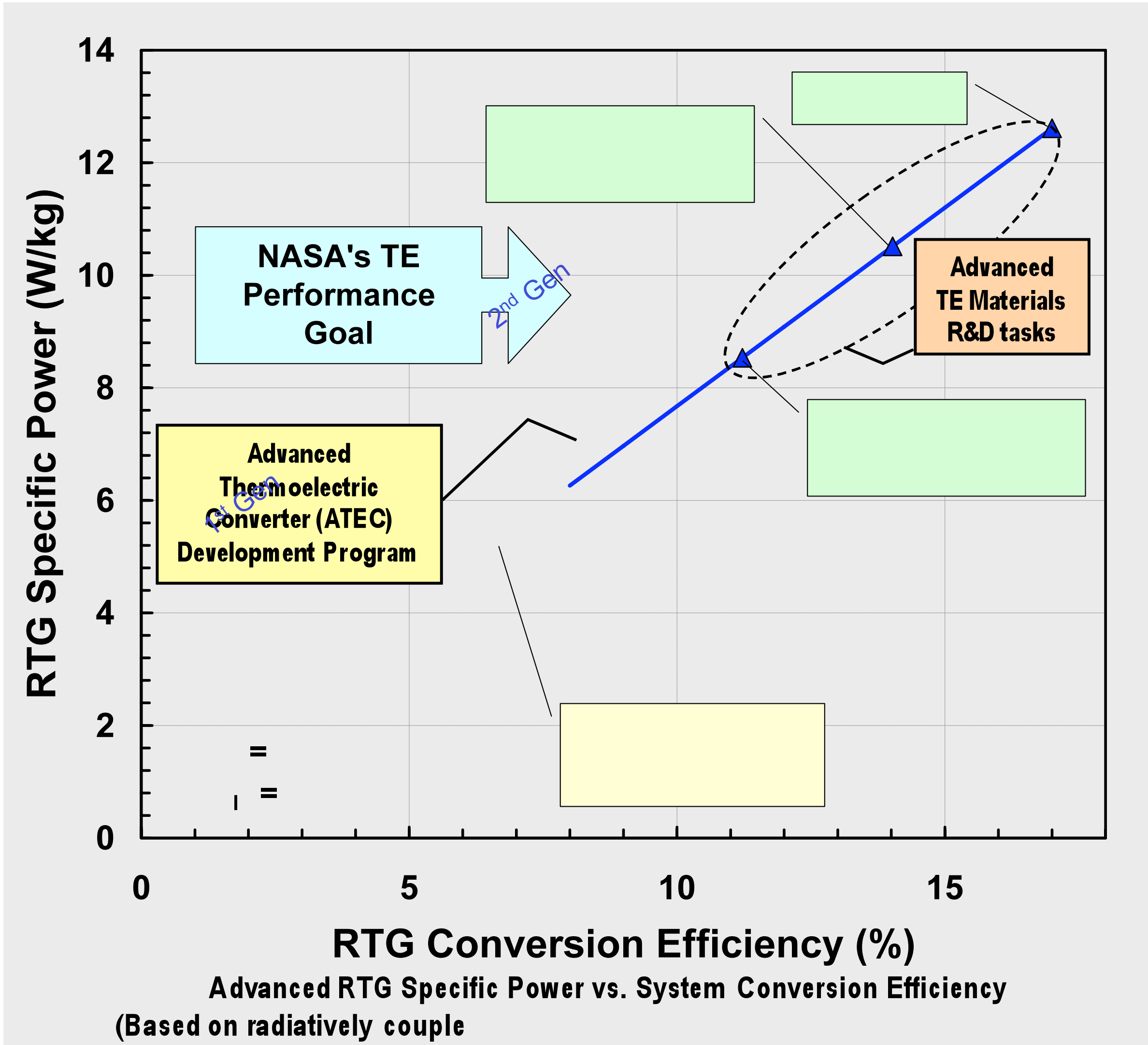
Goal for Advanced TE Materials Integrated in Segmented Configuration for maximizing ZT over Wide ΔT

Current Best TE Materials Integrated in Segmented Configuration for maximizing ZT over Wide ΔT

TE Materials for RTGs Flown on NASA Missions

New materials could also be used in high grade waste terrestrial applications

Impact of Advanced high temperature materials on RTG Performance

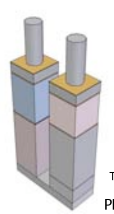


Ultimate goal: > 15% efficient, 10 W_e/kg Advanced RTGs

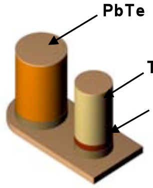
TE Converter Configurations

P-leg	N-leg	Configuration	Program
Bi_2Te_3/TAGS/PbSnTe	Bi_2Te_3/PbTe	Segmented Unicouple	Terrestrial RTG
TAGS/PbSnTe	PbTe	Segmented Unicouple	SNAP-19, MMRTG
$Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$	$Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$	Segmented Unicouple	MHW-, GPHS-RTG
Bi_2Te_3/Filled Skutterudite	Bi_2Te_3/Skutterudite	Segmented Unicouple	Segmented TE Unicouple
Zintl	Nano $Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$	Segmented Unicouple	ATEC-1
Filled Skutterudite/Zintl	Nanocomposite Filled Skutterudite/$La_{3-x}Te_4$	Segmented Unicouple	ATEC-2
Filled Skutterudite	Skutterudite	Multicouple	STMC (2005)
$Si_{0.8}Ge_{0.2}$	$Si_{0.8}Ge_{0.2}$	Multicouple	SP-100, MOD-RTG

Terrestrial RTG

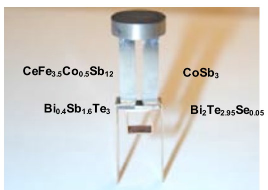


MM-RTG



PbSnTe/TAGS+ PbTe couples

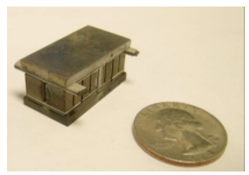
STE



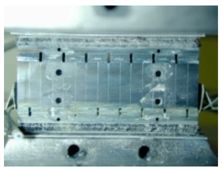
Skutterudite/Bi_2Te_3 segmented unicouple

MHW-RTG

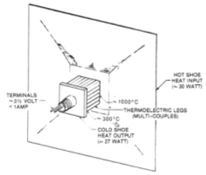
STMC



SP-100



MOD-RTG



- **Multicouples best suited to higher power systems**
- **Unicouples are simpler, lower risk devices suitable for lower power systems**
- **Segmenting has been preferred method to maximize ZT across large ΔT due to simpler system integration**

Candidate TE Materials for HT Power Applications

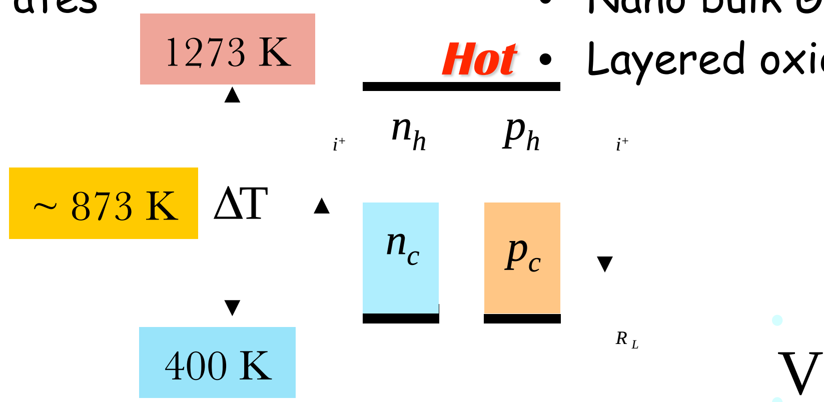
Complex Low λ_L Materials and Nanostructured High PF Compounds

High Temperature *n*-type

- Si-based Clathrates
- oxides

High Temperature *p*-type

- Nano bulk GaAs
- Layered oxides



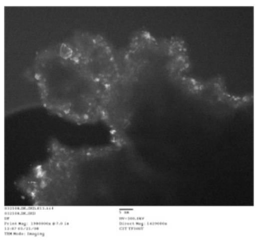
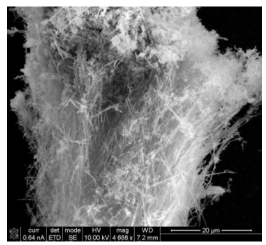
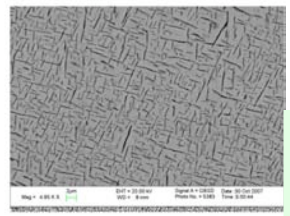
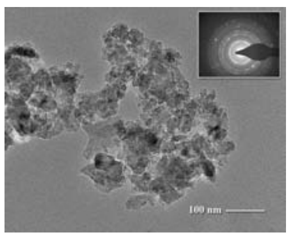
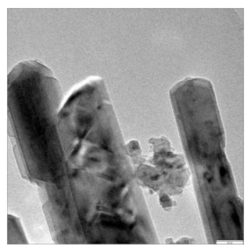
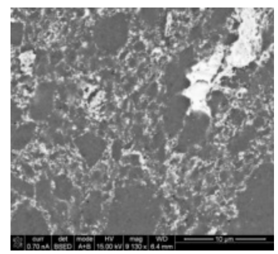
low Temperature *n*-type

- Nano bulk III-V compounds

low Temperature *p*-type

- Nano bulk III-V compounds
- Self-assembling nanostructured Chalcogenides

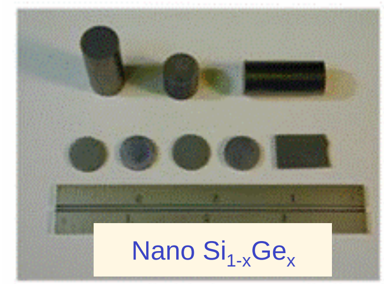
Developing Efficient High Temperature TE Materials

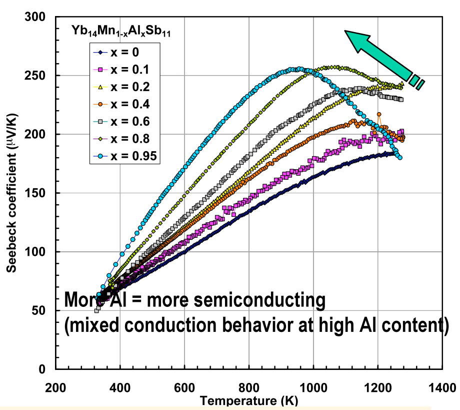







Nanoscale features produced using high energy ball milling and self-assembling synthesis techniques

Bulk Nanostructured and Bulk Nanocomposite Materials

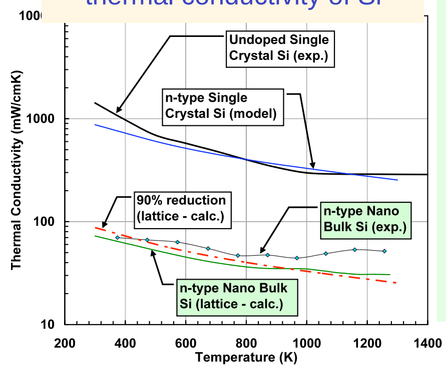
Materials Synthesis Scale-up and Reproducibility of TE properties



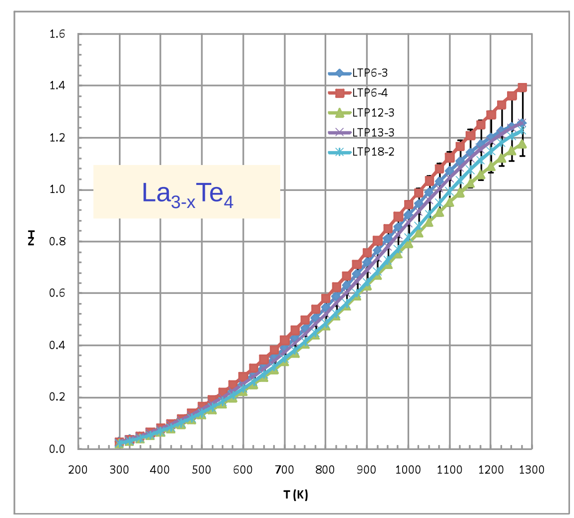


Tuning electrical transport in complex rare earth compounds

x30 reduction in lattice thermal conductivity of Si



Basic Transport Property Modeling/Analysis and Guidance to Experimental Materials Research



Maturity of Advanced Materials for High Temperature Converter Development

Initial Selection for 1st generation ATEC RTG

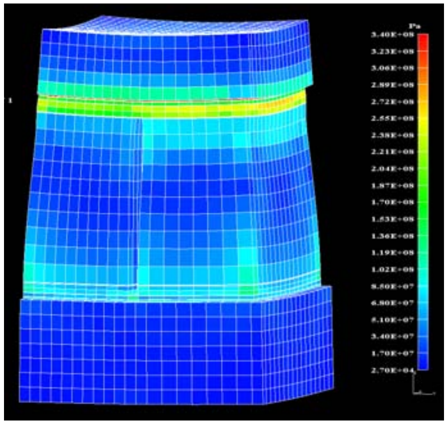
Alternate for 1st generation ATEC RTG

	Nano Bulk Si-Ge (p&n)	14-1-11 Zintl (p)	$La_{3-x}Te_4$ (n)	Skutterudites (p&n)	Other Materials (Clathrates, Tl-doped PbTe)
Reproducible TE properties	☑	☑	☑	☑	☑
Scale-up of synthesis	☑	☑	☑	☑	☐
Thermally stable TE properties	☑	☑	☑ (up to 1500h)	☑	☐
Sublimation suppression possible	☑	☑	☑	☑	☐
Stable low resistance metallizations	☑	☑	☑ (up to 1000h)	☑ (up to 1500h)	☐
Temperature dependence of basic mechanical properties	☑	☑	☑ (partial set of data)	☑	☐

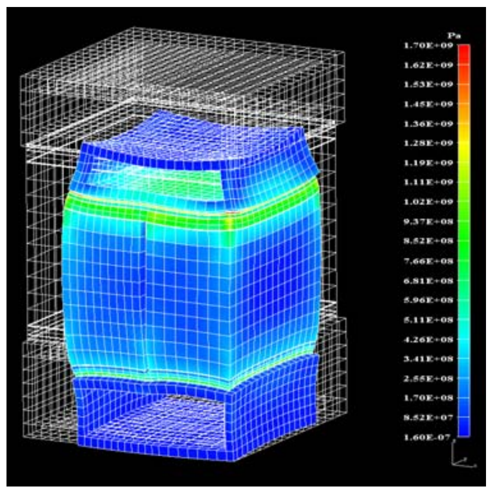
Initial Selection of 2nd generation ATEC RTG

Thermal/Mechanical Considerations for Development of High Temperature TE Converters

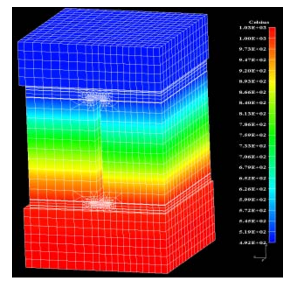
- **Critical Structural Integrity Issues**
  - Coefficient of thermal expansion mismatches within TE device stack, and between stack and large heat exchangers
  - "Bowing" of TE legs due to large DT
  - Surviving fabrication and assembly steps – and operation

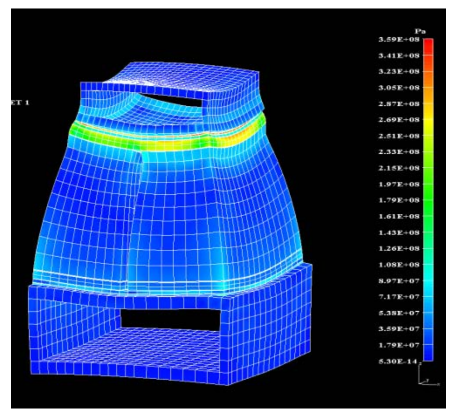


Stresses during high temperature fabrication steps



Stresses back at room temperature after fabrication

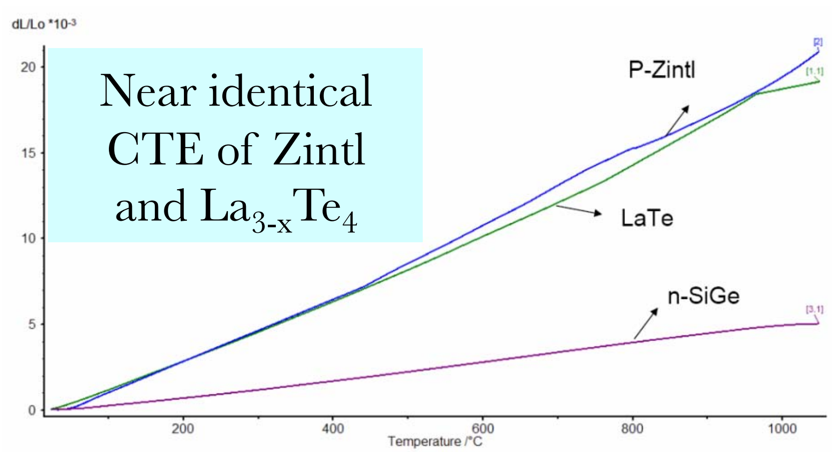




Stresses when operating across large ΔT Bonded to hot and cold side heat exchangers

TE Materials Selection for Segmented Device

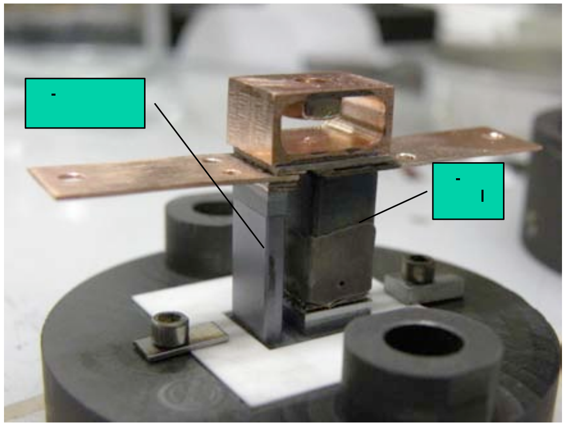
- Si-Ge alloys have much lower coefficient of thermal expansion (CTE) and their TE properties are not compatible with those of other candidate materials
  - Would require cascading, not practical for RTG applications
- Zintl and $La_{3-x}Te_4$ best high temperature materials for segmented devices
  - Excellent CTE match for both refractory rare earth compounds
  - Good TE compatibility with skutterudites, PbTe, TAGS
  - Characterization of basic high temperature mechanical properties conducted in FY09
    - With U. Mississipi collaboration
- Segmentation with skutterudites
  - Would result in couple efficiency increase from ~ 10% to more than 13%



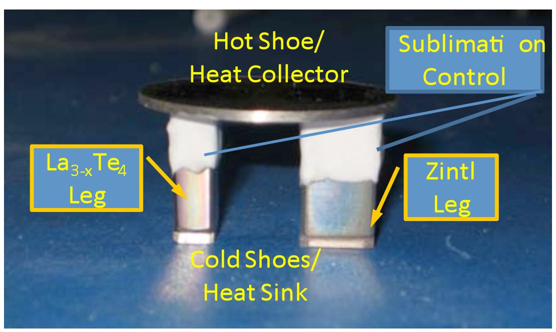
Material	Mass Density (g/cm^3)	CTE (10^{-6} K^{-1})	Maximum T_{hot} (K)	ZT_{peak}
	N-type materials			
Nanostructured $Si_{80}Ge_{20}$	2.9	4.1*	1275	1.05
$La_{3-x}Te_4$	6.7	18.0	1275	1.25
$CoSb_3$	7.6	12.2*	875	1.1
PbTe	8.3	~ 20	815	0.85
	P-type materials			
* Nanostructured $Si_{80}Ge_{20}$	2.9	4.4*	1275	0.8
$Yb_{14}MnSb_{11}$	8.4	17.5*	1275	1.45
$CeFe_4Sb_{12}$	7.9	14.5*	875	0.85
PbTe	8.3	~ 20	815	0.9
TAGS	6.5	~ 16	675	1.2

** Ravi et al., J. Electronic Materials, published online 28 March 2009*

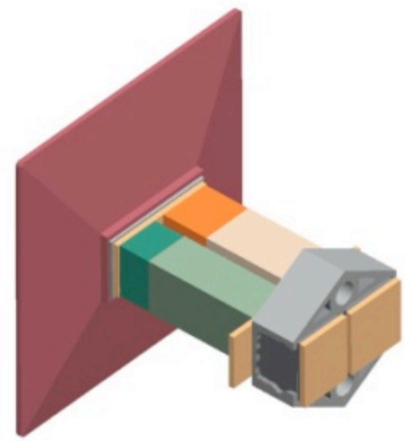
Couple Configurations in Development



Zintl / NanoSiGe Couple

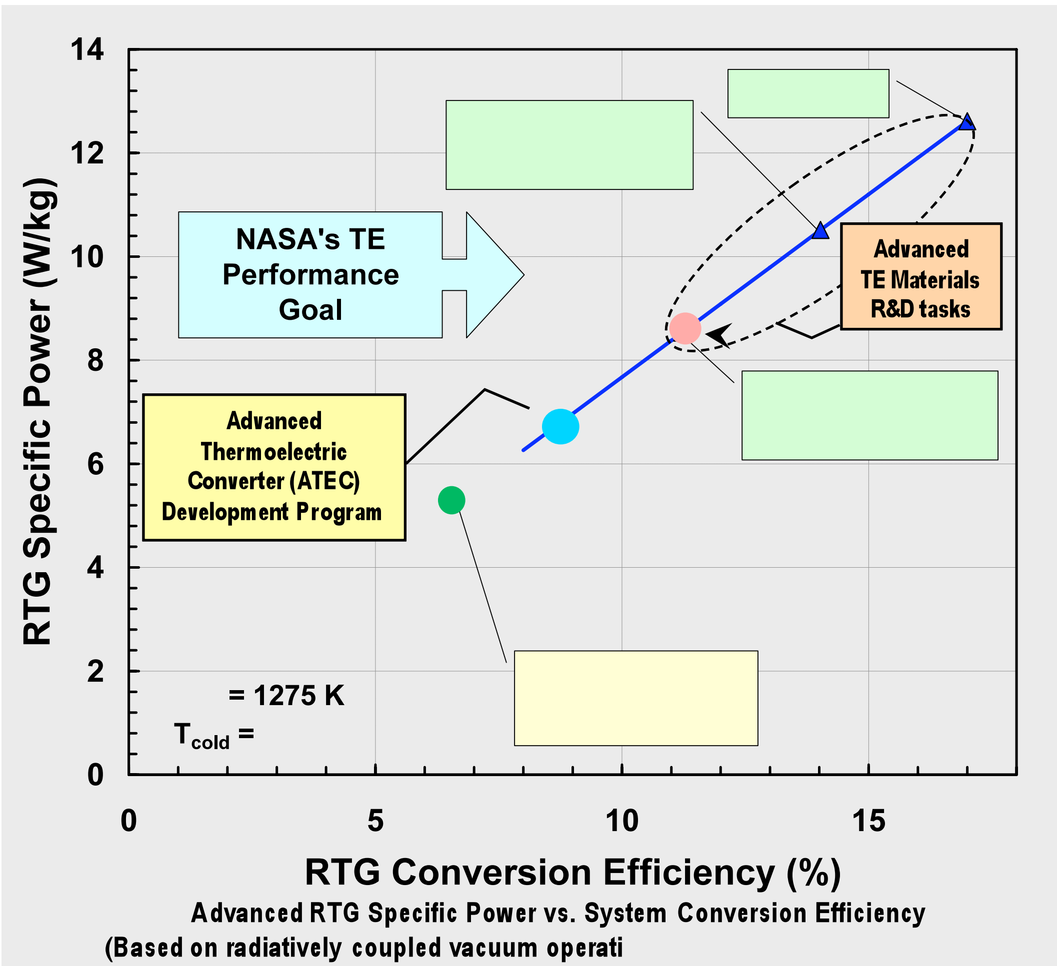


Zintl / $La_{3-x}Te_4$ Couple



Zintl/SKD // $La_{3-x}Te_4$/SKD
Segmented Couple

Advanced TE Research &Technology Program
How far are we?



(Based on radiatively coupled vacuum operation unicouple based RTG concept)

Current (FY09) System Performance Projection when using best TE materials in segmented couple configuration:
n-type $La_{3-x}Te_4$/double filled SKD with p-type $Yb_{14}MnSb_{11}$/nanoPbTe
ZT_{ave} ~ 1.15
(~ 15% couple efficiency)
~ 12.5% System efficiency

ZT_{ave} ~ 1.5 needed between 1273 K and 500 K to achieve 15% RTG system efficiency

Computational models based on experimental data on bulk nanostructured materials predict ZT_{ave} > 2

Summary and Conclusions

- Thermoelectrics have unique advantages for integration into selected waste heat recovery applications
  - Long, proven track record of high temperature TEGs
  - Well understood technology development roadmap
- Significant opportunities available in waste heat recovery
  - Vehicle exhaust heat recovery could provide “proving grounds” as best combination of small scale TEG system with large scale application
- TE materials efficiency is critical to TEG performance:
  - x 2 to 3 increase in ZT_{ave} needed, especially for low to medium grade waste heat
  - But cost, environmental friendliness and availability are also key parameters (potential issues with elements such as Ge, Te, Pb, Tl)
- Most of the technology risk lies in TE couple/module development and is a must to enable new applications
- Converter & heat exchanger designs are critical to efficient system implementation
- Demonstrated new high temperature couple based on new materials
  - Now focusing on development of segmented devices

Acknowlegments

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  - University of California at Los Angeles
  - University of California at Davis
  - Boston College
  - Massachusetts Institute of Technology

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