# *Thermoelectric Generator Energy Harvesting Research at NASA-JPL – Where We Are Now & Where Can We Go*

***Thermoelectric Materials & Systems – From Basic Science to Applications***

*presented at*

McMaster Institute of Energy Studies
McMaster University
Hamilton, Ontario, Canada


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**Pasadena, California, USA**


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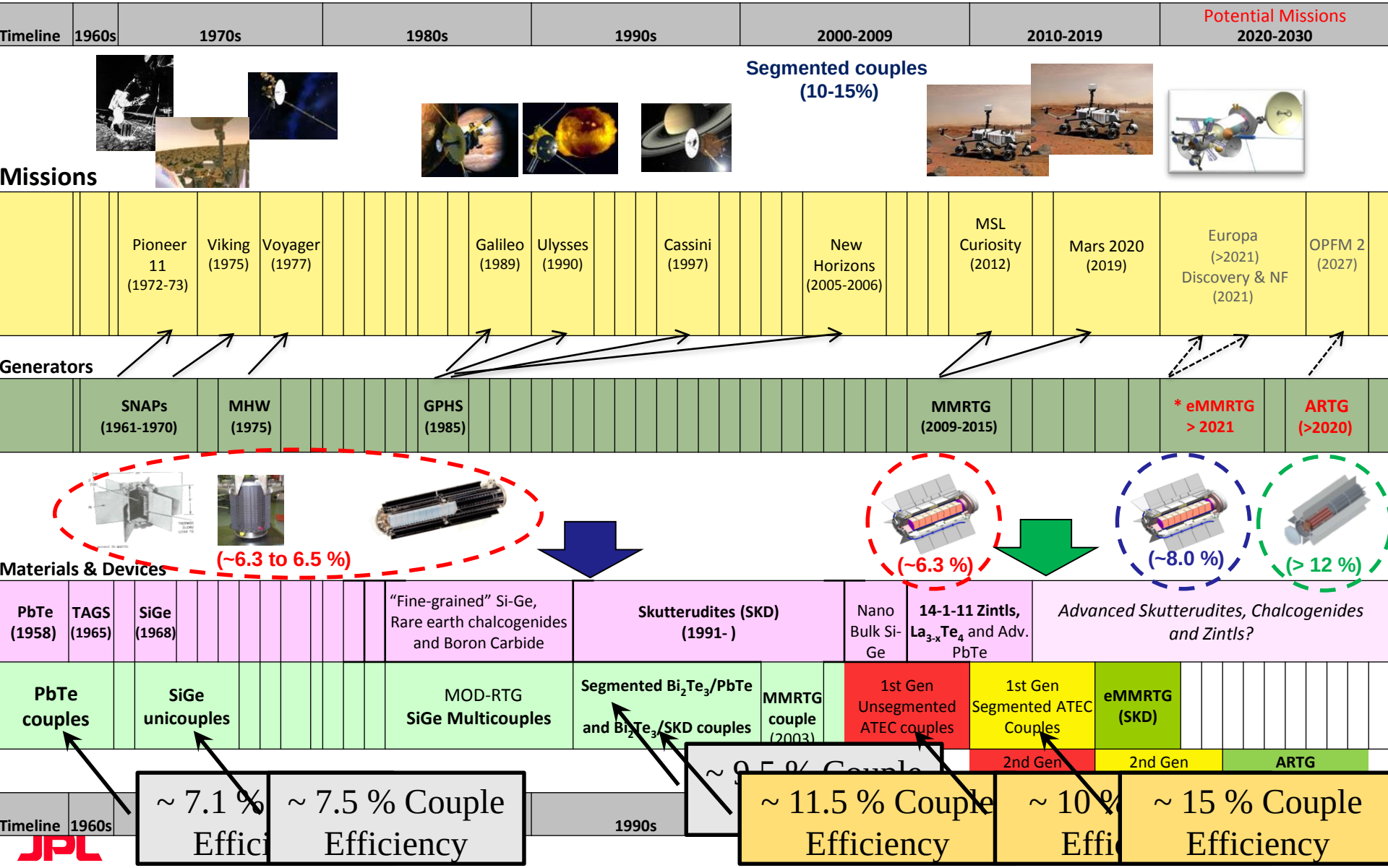
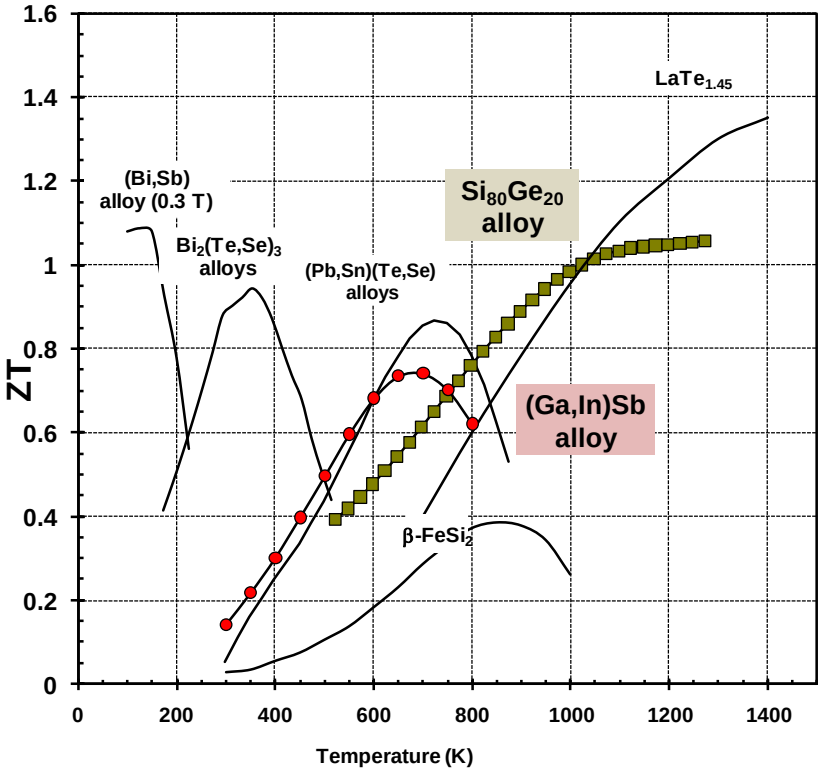
# High Temperature TE Materials
# TE Generator Technology Development Timeline



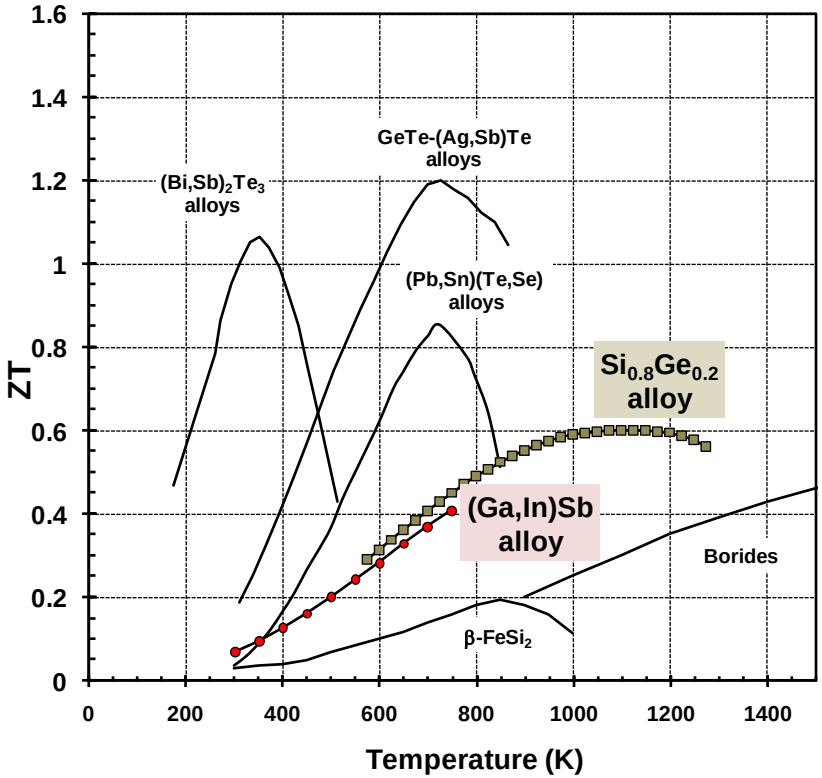
# Advances in Bulk Materials

# State-of-the-Art Thermoelectric Materials:
## Best ZT values circa 1990

n-type materials



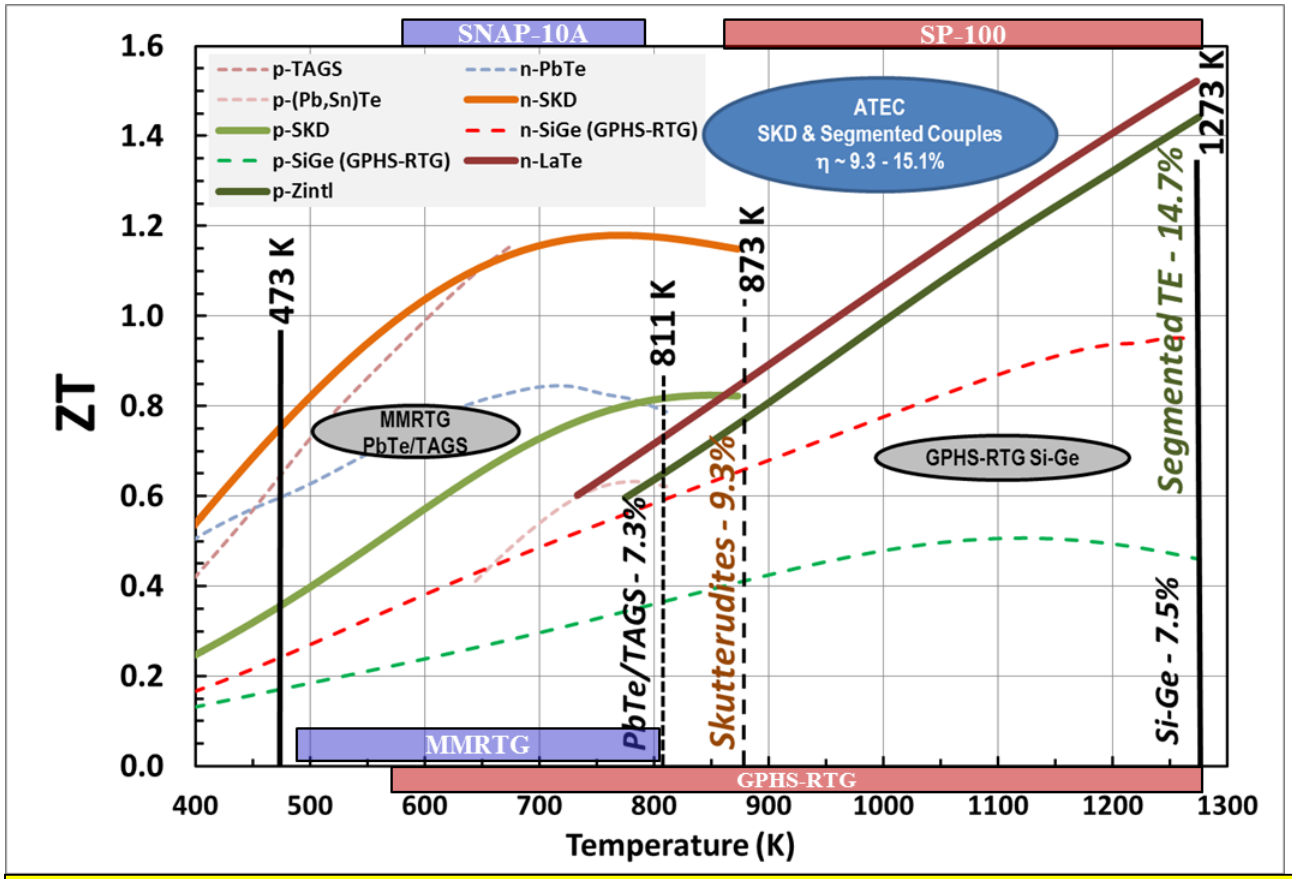

p-type materials




- Conventional III-V alloys had reasonable ZT values in intermediate temperature range
- Si-Ge alloys have until recently been the best practical high temperature materials (used in space power systems)
- Both III-Vs and Si-Ge have fairly large lattice thermal conductivity values

# Basis for TE RPS and FPS:
# x2 Increase in TE Materials Performance

- Thermoelectric energy conversion efficiency increases with larger ΔT (Carnot) and higher ZT (TE materials Figure of Merit)
- Significant breakthroughs in ZT values achieved in last 10-20 years




FPS Temperature Range

RPS Temperature Range

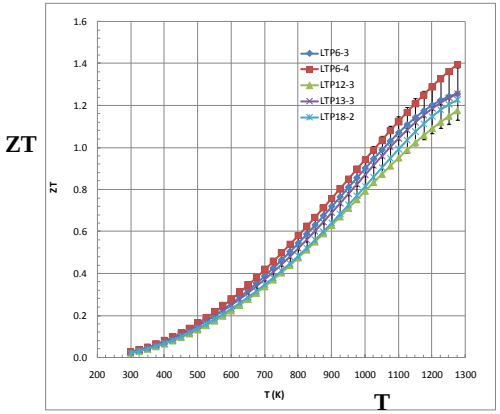
**x 2 increase in $ZT_{ave}$ over SOA Si-Ge alloys *(1275 to 475 K ΔT)* when combined through segmentation**

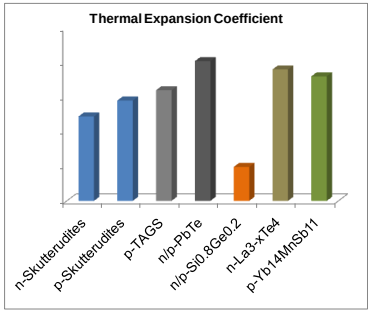
# TE Technology Development using Advanced Materials: Materials, Components & Device Roadmap

## Materials

TE materials

- Batch Synthesis Scale-up
- Reproducibility and stability of TE Properties
- Mechanical property characterization

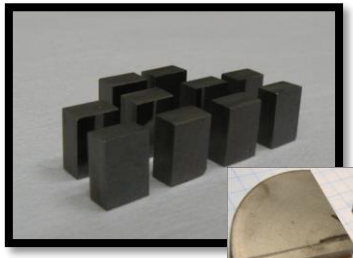


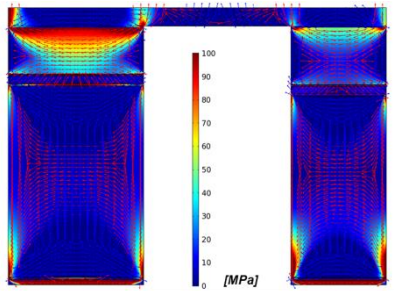




## Components

Leg segments

- Processing/Machining
- Metallizations
- Diffusion barriers
- Sublimation control



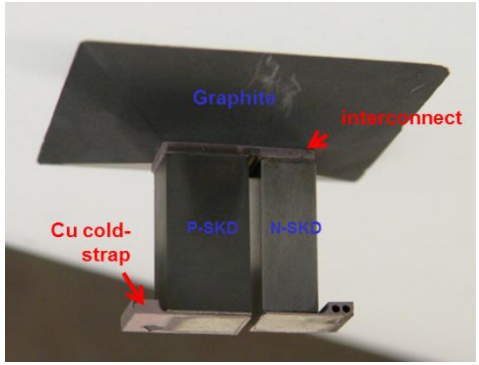


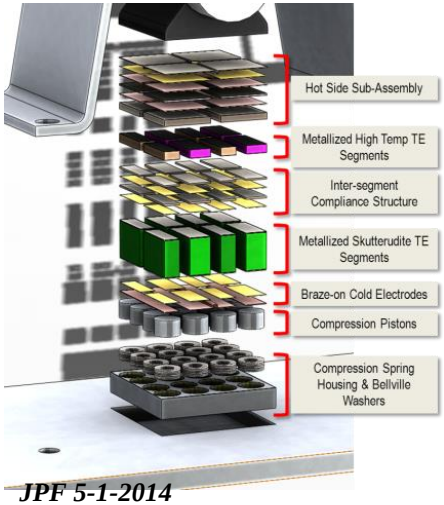

FEA for thermal, mechanical and electrical

## Couples & Modules

Design, Fabrication Assembly & Testing

- Robust, mechanically compliant design
- Stable, low electrical contact resistance interfaces
- Couple/Module Assembly
- Thermal Insulation
- Life demonstration



# Current Snapshot of Segmented TE Technology Advancement for Potential Infusion into future RTGs

Basis for eMMRTG Tech Maturation

| | 14-1-11 Zintl (p) | $La_{3-x}Te_4$ (n) | Filled SKD (p&n) |
|---|---|---|---|
| Materials Readiness date | 2006 | 2009 | 2004 |
| Reproducible TE properties on large batches | ☑ | ☑ | ☑ |
| Long term testing of TE properties | ☑ | ☑ | ☑ |
| | > 24 months up to 1325 K | > 24 months up to 1325 K | > 12 months up to 875 K |
| Long term sublimation suppression demonstrated | ☑ coating | ☑ (ongoing for > 1200 K) | ☑ aerogel |
| Stable low resistance metallizations (≤ 20 $\mu\Omega.cm^2$) | ☑ | ☑ | ☑ |
| Sufficient long term stability of Interfaces to interconnects | ☐ (ongoing ATEC R&D for hot side) | ☐ (ongoing ATEC R&D for hot side) | ☑ > 12 months up to 875 K |
| Temperature dependence of basic mechanical properties | ☑ | ☑ | ☑ |

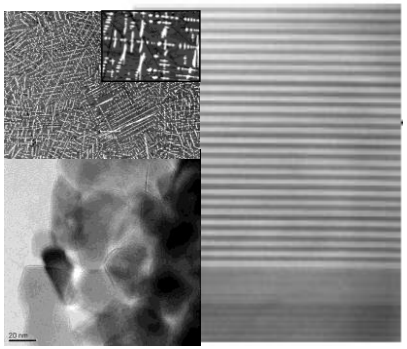
Current focus of ATEC efforts

Basis for SMRTG Tech Maturation

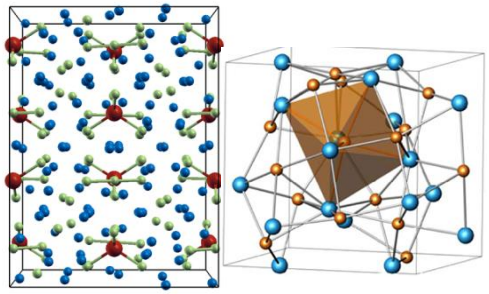
# Next Generation Bulk TE Materials

# General Approach to Achieving > 20% Conversion Efficiency in TE Devices for Space Power Systems

- **Develop thermally stable nanostructured TE materials**
  - "Designer materials", synthesized through "force engineering" and "self-assembling" techniques, allowing for independent manipulation of electrical and thermal transport properties
- **Develop new high temperature complex compounds**
  - Ultra-low thermal conductivity compounds with complex crystal structures and tunable electric properties
  - Electronic band engineering in good thermoelectric materials



**Engineered Nanostructured Bulk Materials**

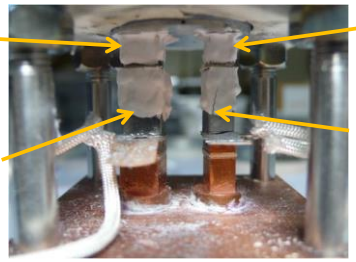


**Complex Structure Materials**

Combine "Complex Bulk" and "Low Dimensional" Approaches!

- Achieve High ZT in Practical Bulk Materials
- Segment for Operation Across large ΔT

- **Validate high materials conversion efficiency**
  - Using segmented TE couple demonstration that achieves highest ZT across large ΔT (**<u>1273 – 473 K</u>**)

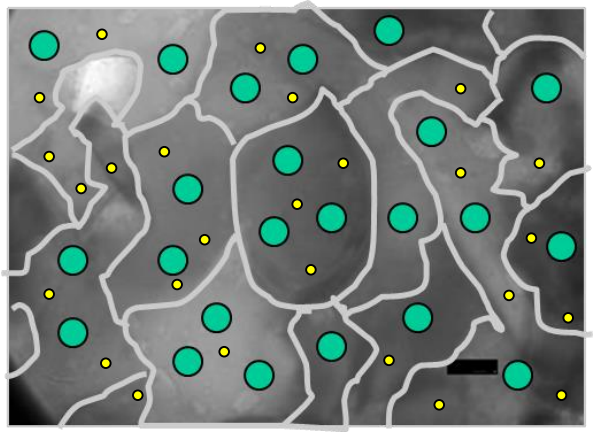


# Strategies for Nanostructuring Good Electronic Semiconductors

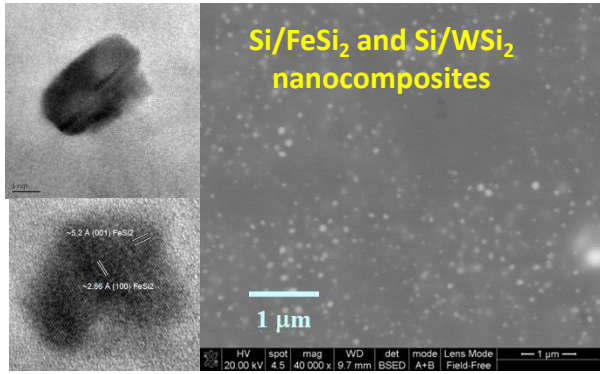
- "Controlled" nanostructuring offer additional tools for enhancing ZT:
  - Enhanced density of states due to quantum confinement or band structure engineering
  - Screening of "cold" charge carriers (energy filtering)

  → Increase S without reducing $\sigma$
  - Tunable structural features controlled at the nanoscale level to effectively scatter phonons across a wide range of frequencies
  - Grain boundaries, periodical lattice defects

  → Reduce $\lambda_L$ much more than $\sigma$
- Nanostructing and compositing also has potential for tuning and/or improving key mechanical properties
  - High temperature TE materials mostly behave as brittle ceramics with low fracture toughness



**An "Ideal" High ZT Bulk Nanocomposite**




**Only partial decoupling of electrical and thermal transport properties achieved to date**

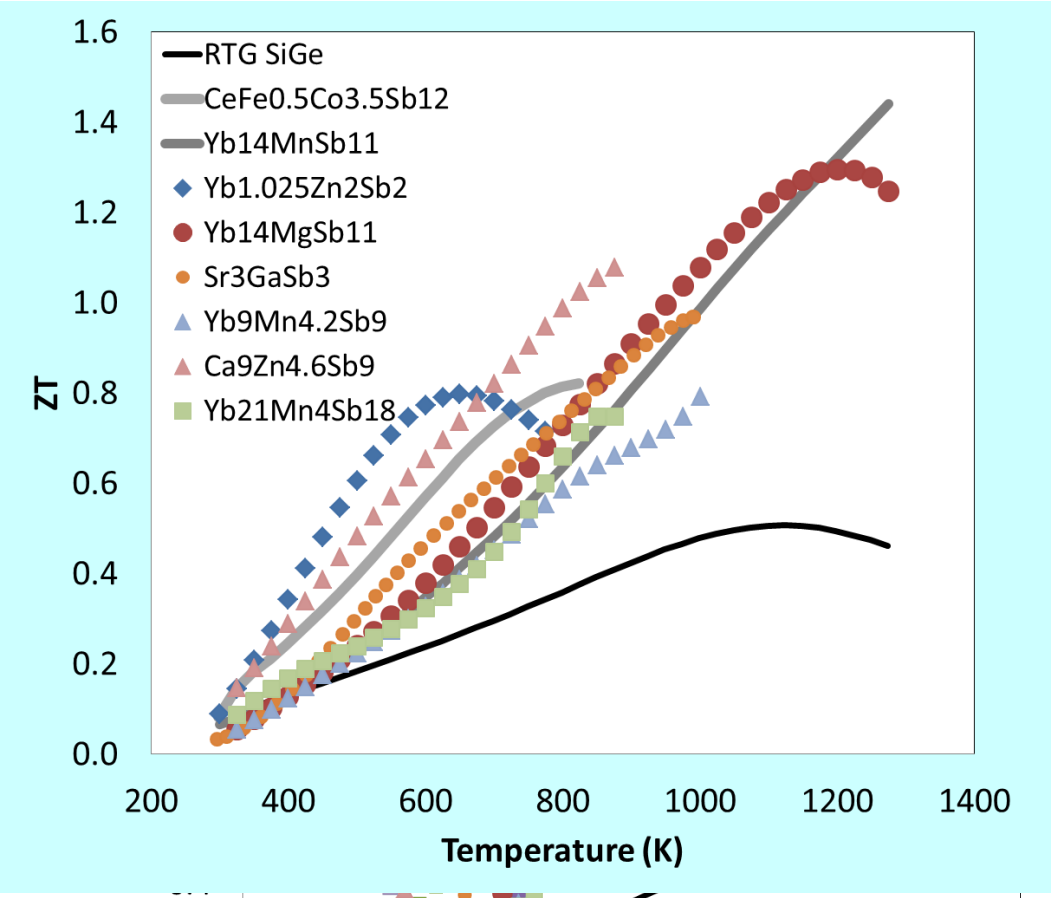
**Challenge: Design optimum morphology, demonstrate control on the micro- and nano-scale, and verify thermal stability of "engineered" features**

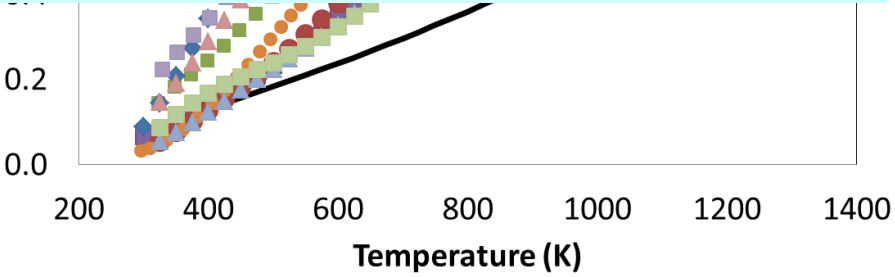
# Current Strategies for Complex Structure Materials

- Focus on manipulating electronic structures
  - Lattice thermal conductivity of complex structures already very low!
- Close coupling between theoretical simulations and systematic experimental research
  - Computational work to guide experimental
  - Semi-emperical modeling to optimize materials systems
- Use of innovative synthesis techniques to control materials on the nanoscale/microscale level

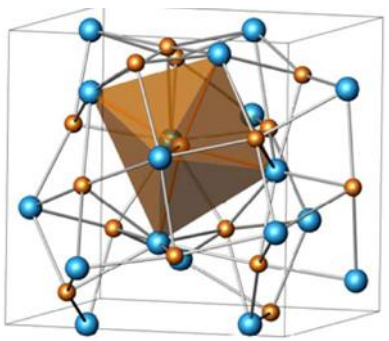
# Rich Literature on Zintl Phases for TE

- Web of Science: 225 articles from 2006-Present with terms "Zintl and Thermoelectrics"
- Many Zintl Phases have significantly higher ZTs than heritage SiGe (some 3x better)
- Some Zintl phases are even better than skutterudite phases and slightly better than $Yb_{14}MnSb_{11}$…

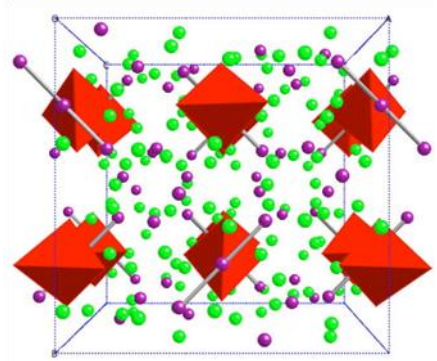


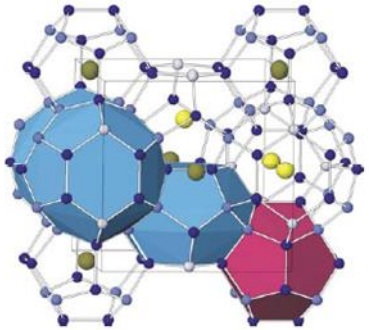
# Motivation: *Complex Zintl thermoelectrics*



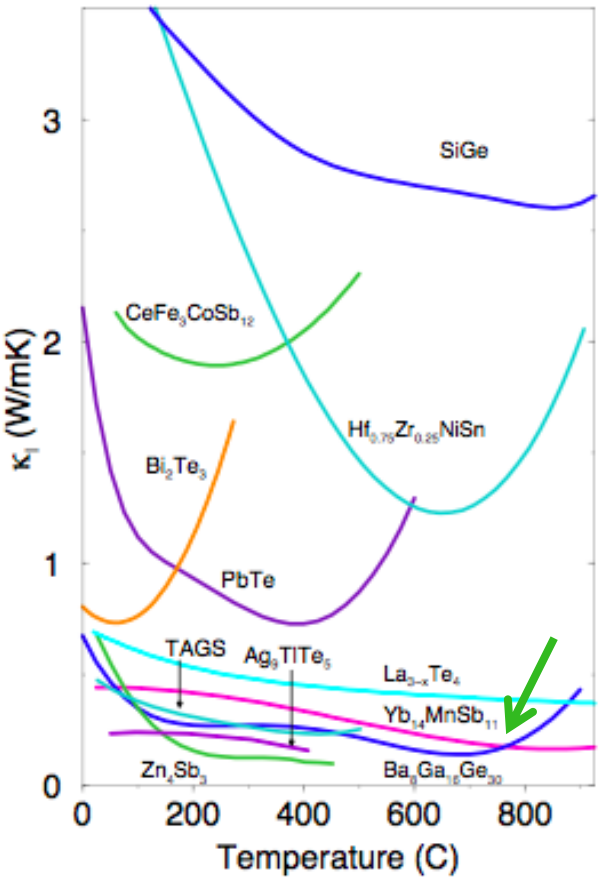
$La_3Te_4$



$Yb_{14}MnSb_{11}$



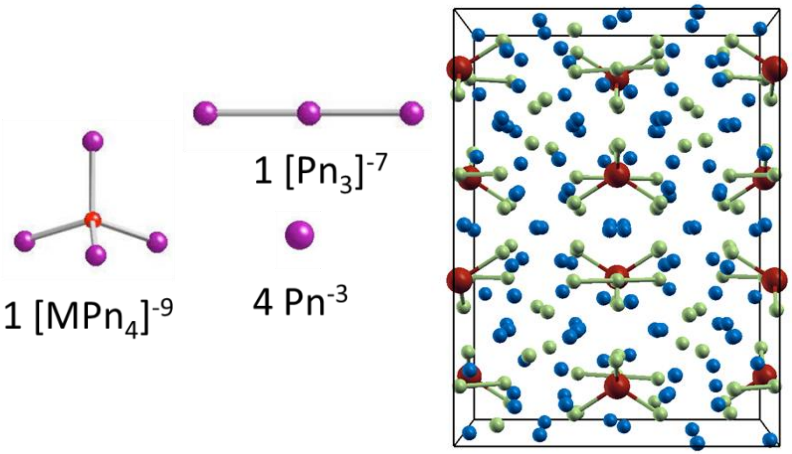
$Ba_6Ga_{16}Ge_{30}$

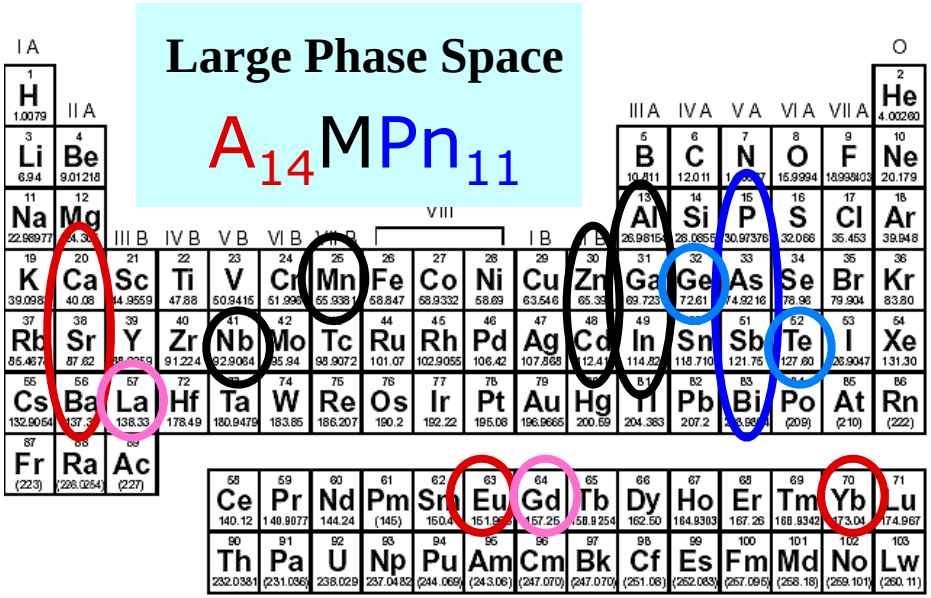



*Snyder, Nature Materials 7, 105 (2008)*
*Brown, Kauzlarich, Gascoin, Snyder, Chem. Mat. 18, 873 (2006)*
*Toberer, May, Snyder Chem. Mat., (DOI 10.1021, cm901956r*

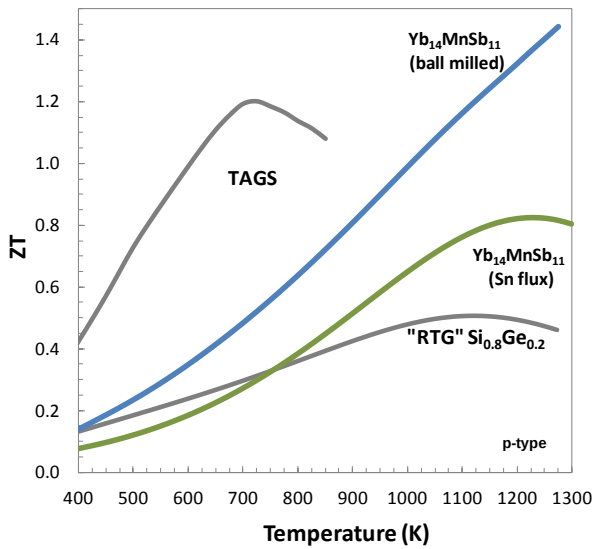
- **These materials have similar features:**
- Structurally complex
  - Good for low lattice thermal conductivity
- Related to intrinsic semiconductor
  - Possible chemical substitution and structural modifications to improve transport properties
- High ZT values experimentally demonstrated
- Other complex Zintl structures also of interest
  - (2-1-2, 3-1-3,11-1-9, 21-4-18,…)

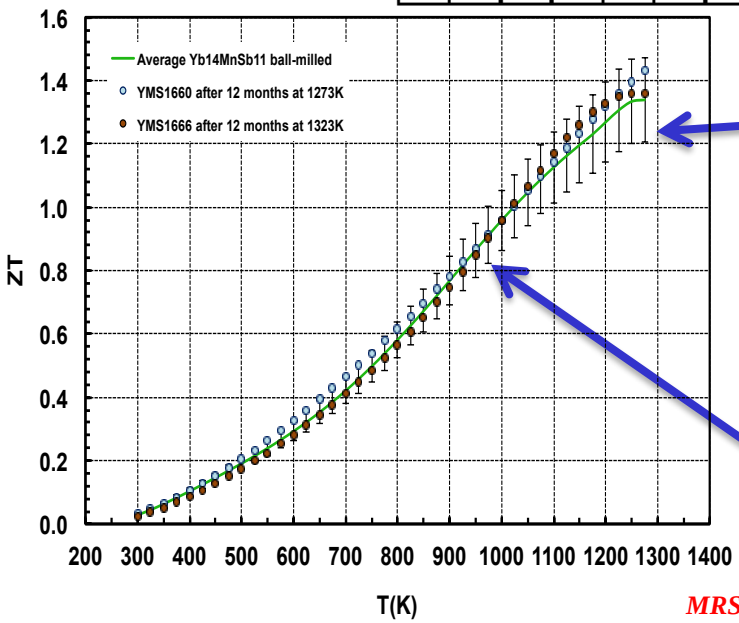
# 14-1-11 Zintls – x2 ZT improvement over Si-Ge




Body centered tetragonal $I4_1/acd$ space group
Unit cell: total of 104 atoms
Block (4X): $[MPn_4]^{9-}$, $[Pn_3]^{7-}$, $4Pn^{3-}$, $14A^{2+}$




**Ball milled $Yb_{14}MnSb_{11}$ shows a highly reproducible peak zT ~1.3 @1273K**

**18-month stability demonstration of $Yb_{14}MnSb_{11}$ at 1323 K**

# Evaluation of Novel Complex Zintls

- Investigating thermoelectric properties of other Zintl phases
  - Screening methods: Literature search of complex crystal structures, small band gaps
    - Also using modeling to predict properties

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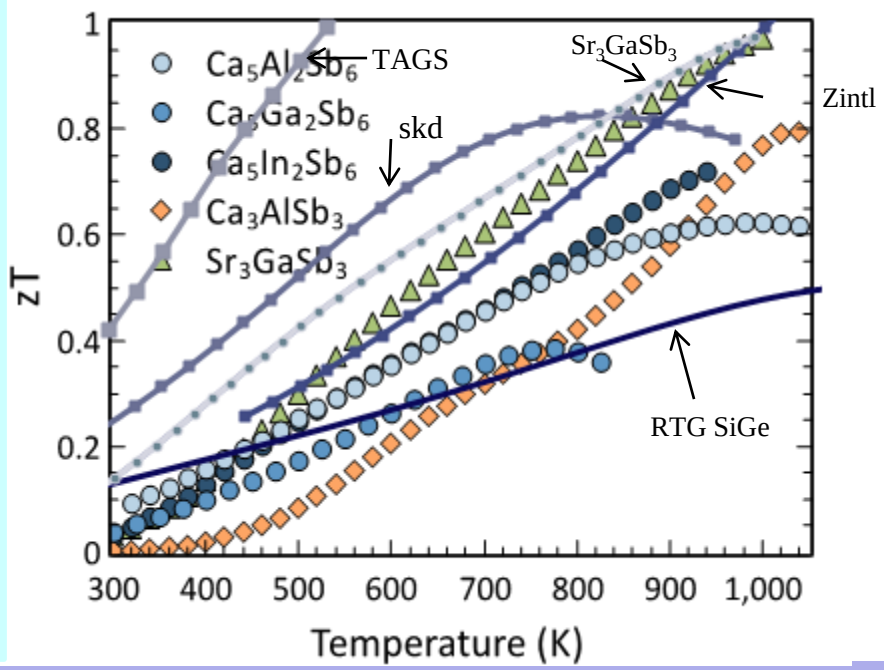
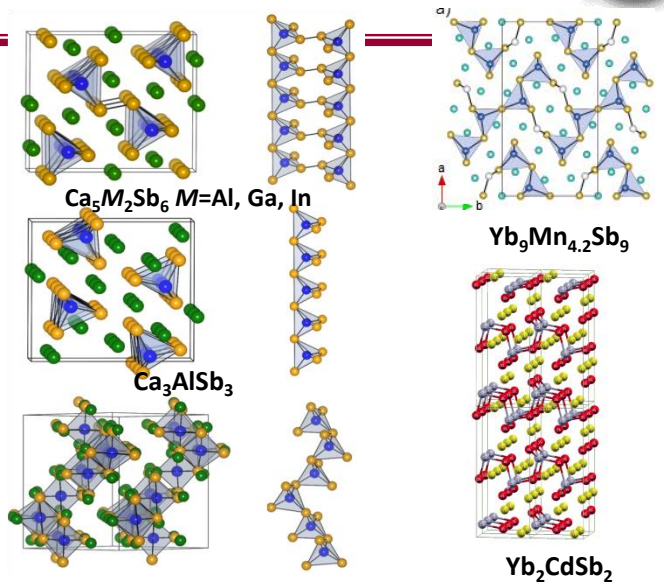
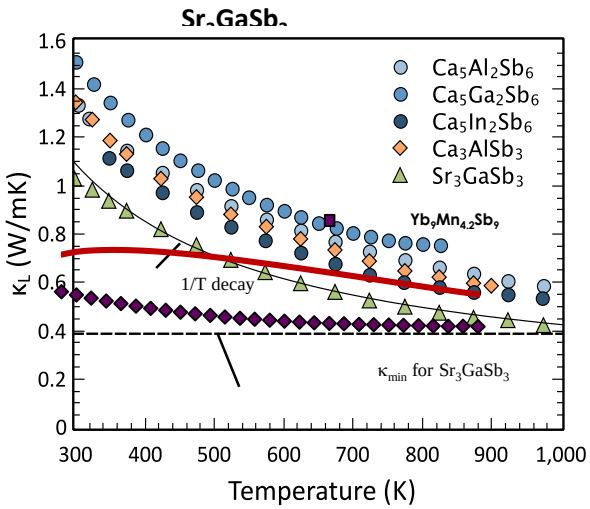


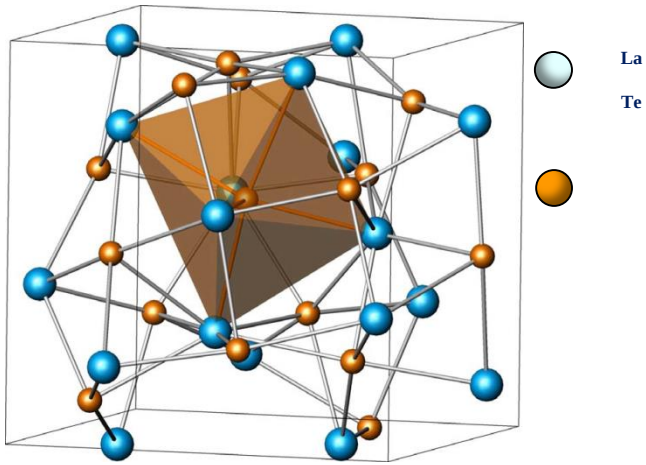




Very low glass like thermal conductivity

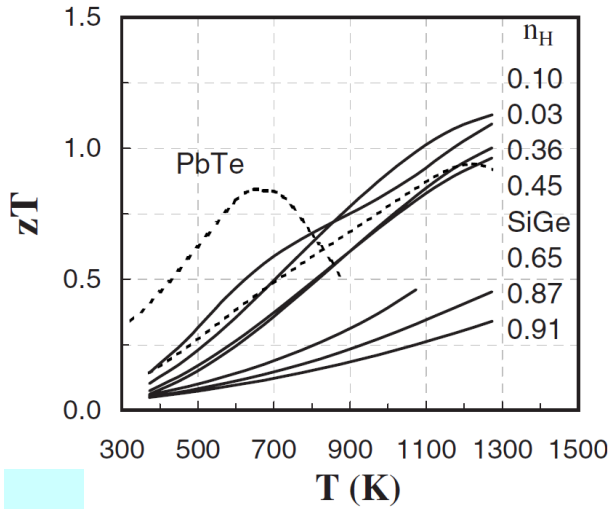
- ***First report of the thermoelectric properties of all the materials presented***
- ***Many Zintl phases are promising high ZT thermoelectric materials, potential for segmentation***

# n-type $La_{3-x}Te_4$

- Complex crystal structure
  - Defect structure
    - Up to 1/9 of La positions can be vacant
  - Low thermal conductivity
  - Decent electrical properties
    - Can be controlled by vacancies
- Investigated in the late 1980s but was difficult to synthesize and optimize electronic properties
- In 2008 May et. al. developed mechanochemical synthesis
  - Easily control La vacancies
- 20% improvement over n-type SiGe




Fully filled crystal structure of $La_3Te_4$. Up to 1/9 of the La positions can be vacant.




Previous work done on $La_{3-x}Te_4$

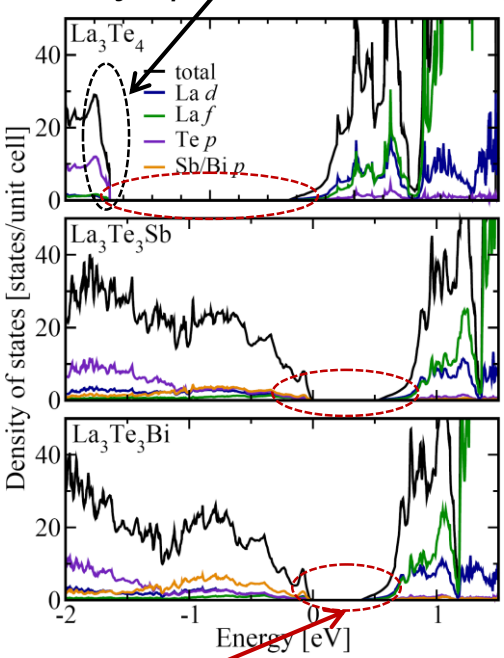
May et. al. *Phys. Rev.* 2008, 78, 125205

# Improved $La_{3-x}Te_4$ Performance Through DOS Tuning

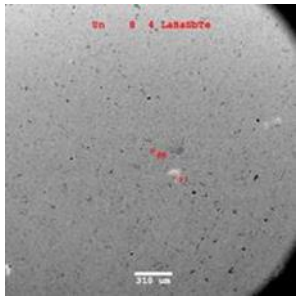
- Optimization guided by first principle electronic band structure calculations
  - Suggest substitutions on La site needed to impact Seebeck coefficient

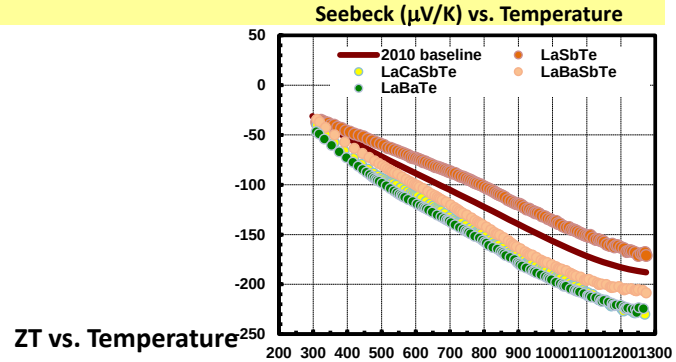
- **Substitutions on La site lead to improved Seebeck coefficient and 20% increase in ZT values across relevant ΔT**
  - Single Phase samples
  - Increased Seebeck observed for same carrier concentration

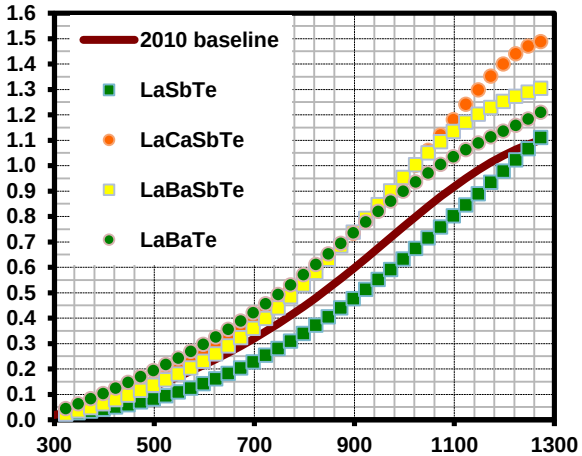
*Density of states controlled by La d states*




*Band gap controlled by Te site substitutions*

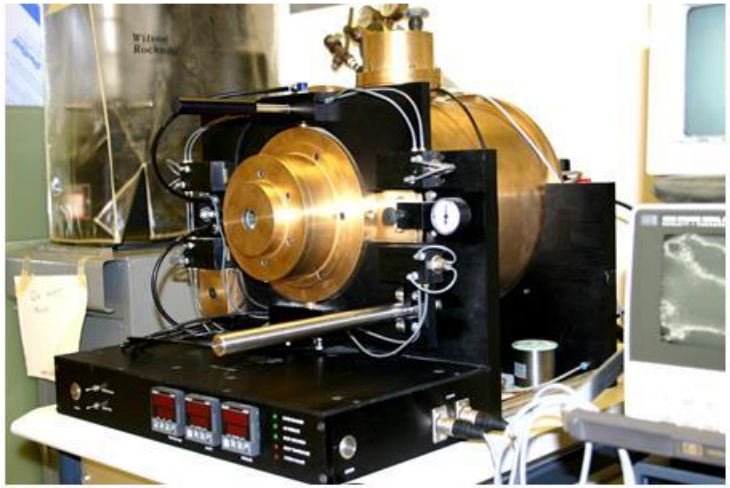


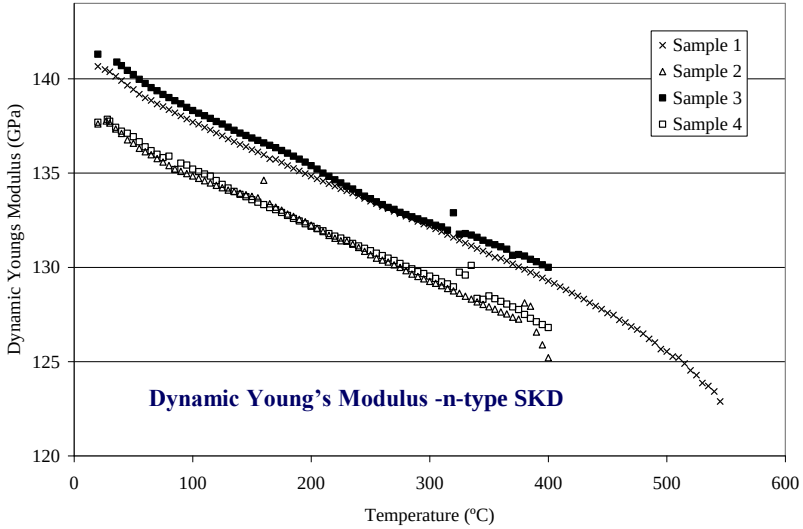



$La_{3-x}Te_4$ Baseline

# Characterization of Temperature Dependent Mechanical Properties






- Young's modulus at 20 C ~ 137 - 141 GPa
- E decreases as T increases, reaching 127 GPa at 400 ° C

- Determination of key mechanical properties required for prediction of short and long-term performance of thermoelectric devices: Strength, Stiffness, Toughness
- Internal capabilities and external collaborations
- Types of measurements: flexural (4-pt, biaxial), dynamic moduli, RUS, compression, etc.
- TE materials tested to date include:
- Skutterudites, nano - structured Silicon – Germanium, $Yb_{14}MnSb_{11}$ (Zintl) and lanthanum telluride

# RT Flexural properties of selected TE materials

| | N-SKD | P-SKD | $LaTe_{1.43}$ | Zintl ($Yb_{14}MnSb_{11}$) | N-$Si_{0.8}Ge_{0.2}$ |
|---|---|---|---|---|---|
| Characteristic strength (MPa) | 100 | 99 | 35 | 40 | 192 |
| Weibull Modulus | 8 | 4.4 | 4 | 4.3 | 7.4 |
| Number of test samples | 8 | 8 | 30 | 8 | 21 |
| Test type | ROR | ROR | ROR | ROR | 4-pt |

- **SKD materials are mechanically robust and compare well with heritage SiGe technology**
- **LaTe and Zintl are comparable to lead telluride and TAGS**

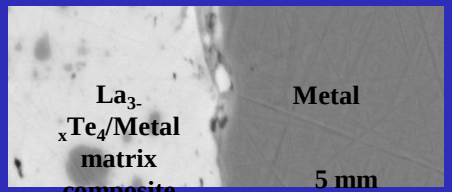
# ATOM→ATEC Transfers/Accomplishments

## Materials

- p-type $Yb_{14}MnSb_{11}$, n-type $LaTe_{1.46}$
- Improved $Yb_{14}MnSb_{11}$ processing via Mn excess
- n-type $IrSb_3$
- p-type $Yb_{14}MgSb_{11}$
- Metal/inclusion composite screening study
- Ni/Co-$LaTe_{1.46}$ CAFÉ composites
- W-skutterudite composites
  - Used in tech mat alternate metallization study

## Processing/Fabrication

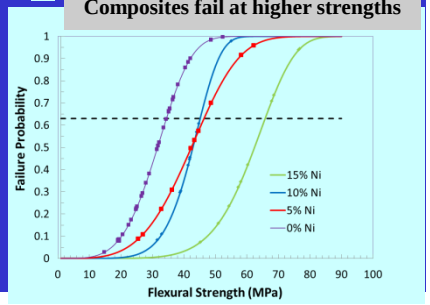
- End milling of La/Ce
- Cryomilling of La/Yb
- In situ metallization/compaction of Ni/Ni-$LaTe_{1.46}$ composites via SPS




## Thermomechanical

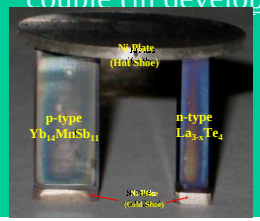
- Mechanically robust TE materials via metal compositing
- *Increased thermal stability via early rare earth doping in $Yb_{14-x}RE_xMnSb_{11}$ (RE = La, Ce, Pr)
- *Lower sublimation in $Yb_{14}MgSb_{11}$

**Trend is that higher vol % Ni Composites fail at higher strengths**




## Devices

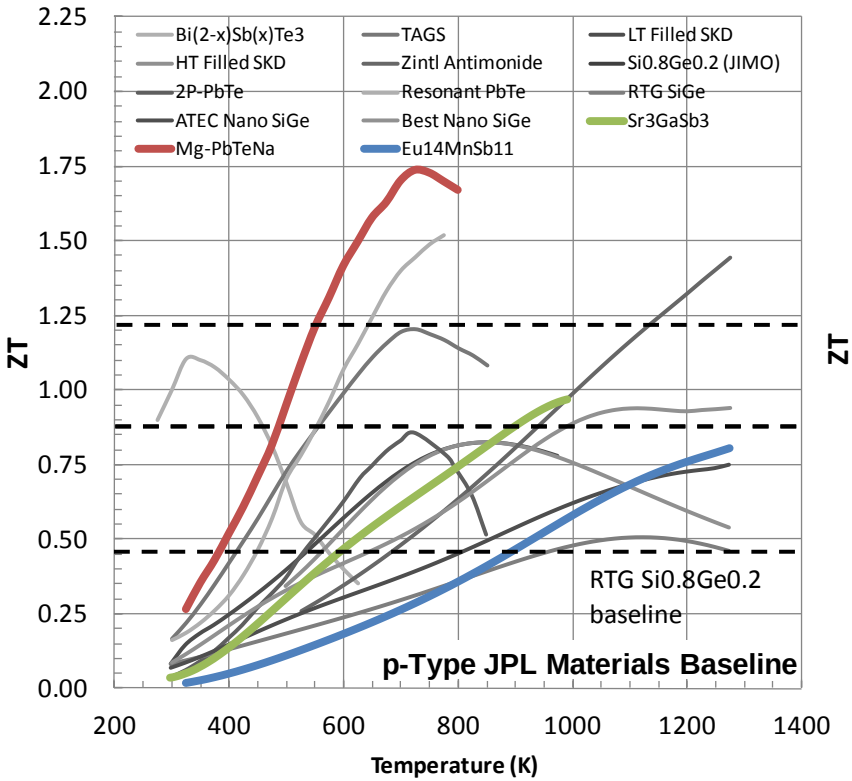
- Rare earth couple: $Yb_{14}MnSb_{11}/LaTe_{1.46}$ Couple (1275-473 K)
- Segmented couple: $Yb_{14}MnSb_{11}$/p-skd-$LaTe_{1.46}$/n-skd couple (1275-473 K)
- Segmented Skutterudite couple: $CeRuSb_3$/p-skd-$IrSb_3$/n-skd couple (1075-473 K)
- *All p-type Zintl couple: $Yb_{14}MgSb_{11}/YbZn_2Sb_2$-Ni-$LaTe_{1.46}$ couple (in development)

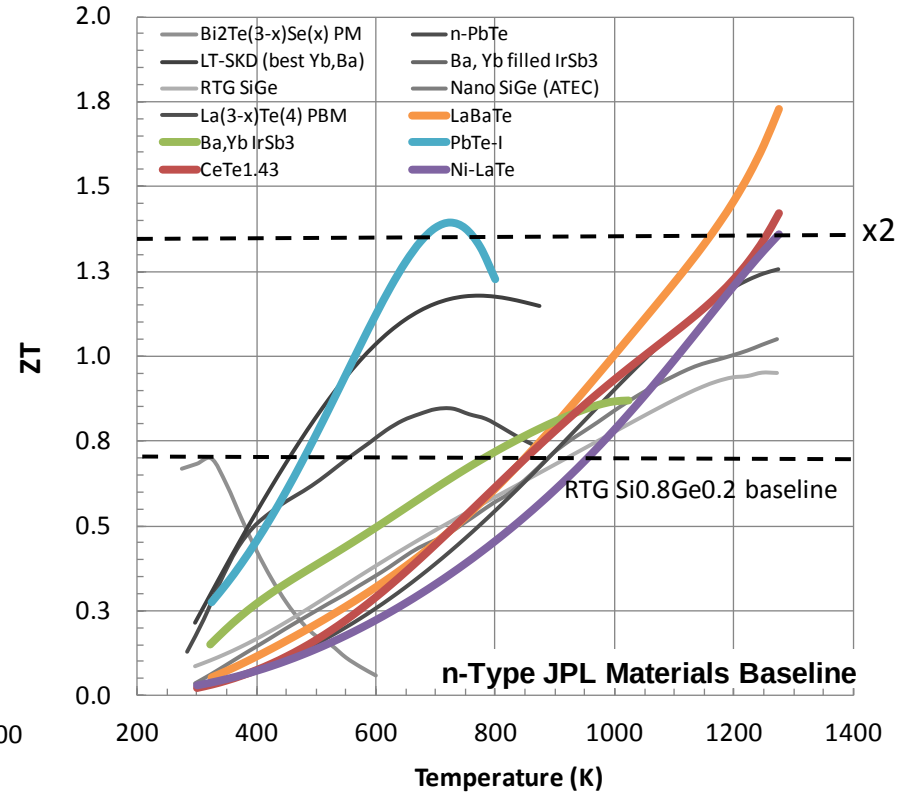


*High Temperature Segmented Zintl/ $La_{3-x}Te_4$/ SKD Couple Spring-loaded Performance Test Configuration*

*new in FY16

# Advanced High Temperature TE Materials Status




- **Best <u>demonstrated</u> couple efficiency of 15% for 1273 K- 473 K using "mature" bulk TE materials; still work to do for demonstrating long life of device/generator technology**
- **Best segmented couple combination of TE materials <u>predicted</u> to result in ~ 17% couple-level efficiency for Tcold ~ 473 K (space) and ~ 20% for Tcold of 300 K (terrestrial, water cooled)**

*All materials made either in house or leveraged through collaborations*

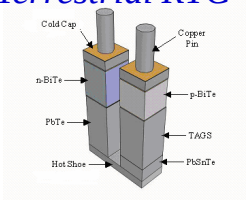
# Advanced Devices

# High Temperature TE Couple Technologies

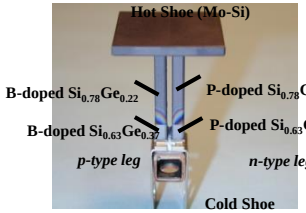
| Couple Configuration | P-leg | N-leg | Heat Source Coupling | Program |
|---|---|---|---|---|
| Segmented | $Bi_2Te_3$/TAGS/PbSnTe | $Bi_2Te_3$/PbTe | Conductive | Terrestrial RTGs |
| Segmented | TAGS/PbSnTe | PbTe | Conductive | SNAP-19, MMRTG |
| Segmented | $Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$ | $Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$ | Radiative | MHW-, GPHS-RTG |
| Segmented | $Bi_2Te_3$/SKD* | $Bi_2Te_3$/SKD | Conductive | Segmented TE Couple (2002) |
| Unsegmented | Zintl | Nano $Si_{0.8}Ge_{0.2}$ | Radiative | 2008 |
| Unsegmented | Zintl | $La_{3-x}Te_4$ | Conductive or radiative | 2009 ATEC |
| Segmented | SKD/Zintl | SKD/$La_{3-x}Te_4$ | Conductive or radiative | 2011 |
| Segmented | Adv. PbTe/Zintl | Adv. PbTe/$La_{3-x}Te_4$ | Conductive | 2012 |
| Unsegmented | Filled SKD | Filled SKD | Con | MMRTG |

~ 9.3 to 15 % efficiency with $T_{cold}$ ~ 473 K

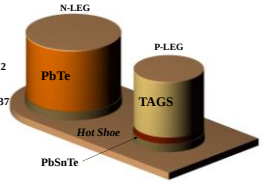
*Terrestrial RTG*



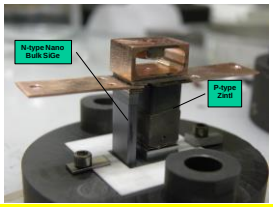

*MHW-RTG*



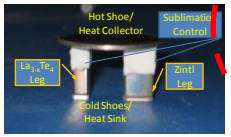

*MMRTG*



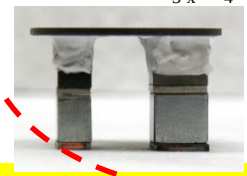

*ATEC*



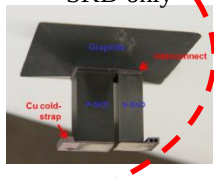

*ATEC*
Zintl/$La_{3-x}Te_4$




*ATEC*
SKD/Zintl/$La_{3-x}Te_4$



*ATEC*
SKD only



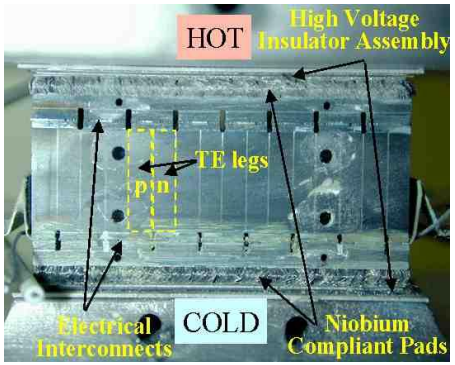

Arrays of discrete couples typically used for RTGs

**Filled skutterudites currently being considered for use in enhanced MMRTG**

# Mechanically Compliant High Temperature TE Module Technologies at NASA & DOE

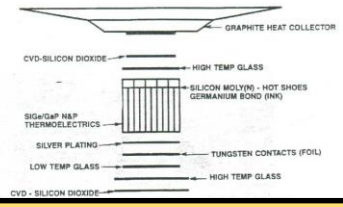
## SP-100 SiGe Multicouple (1990s)

- Conductively coupled on hot side with built in compliant pads
- Tested for up to 25,000 hours




**Designed for integration with flat plate HXs, 873 K - 1273 K Steady State Hot Side operation**

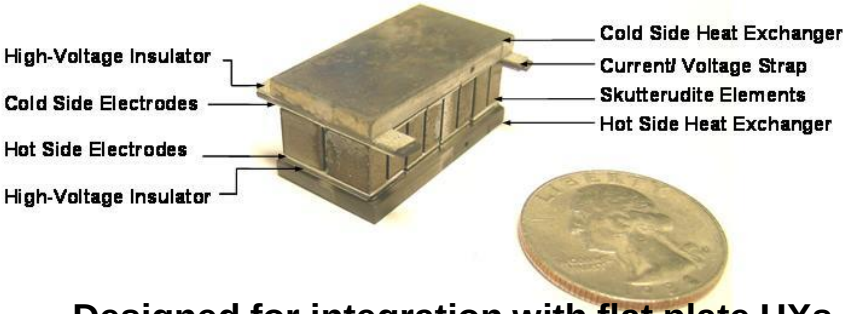
## MOD-RTG SiGe Multicouple Technology (1980s)

- Graphite heat collector, bolted on radiator side
- 


**Designed for radiative coupling in RTG, 573 K - 1273 K Steady State operation**

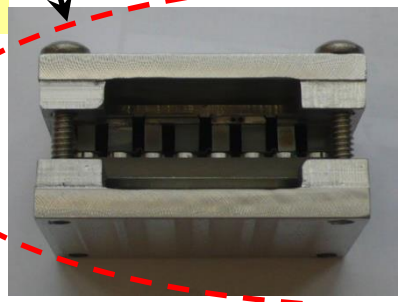
~ 11 to 17 % efficiency with $T_{cold}$ ~ 300 K

## Skutterudite Module Developed at JPL under NASA/SMD In-Space Propulsion Program (2004-2005)

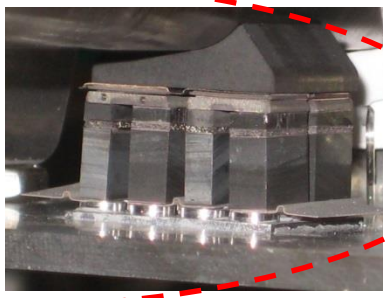



**Designed for integration with flat plate HXs, 473 K - 873 K Steady State operation**

## HT Modules under development for kW-class power systems (Since 2011)



Skutterudite-only module



SKD/$La_{3-x}Te_4$/Zintl module

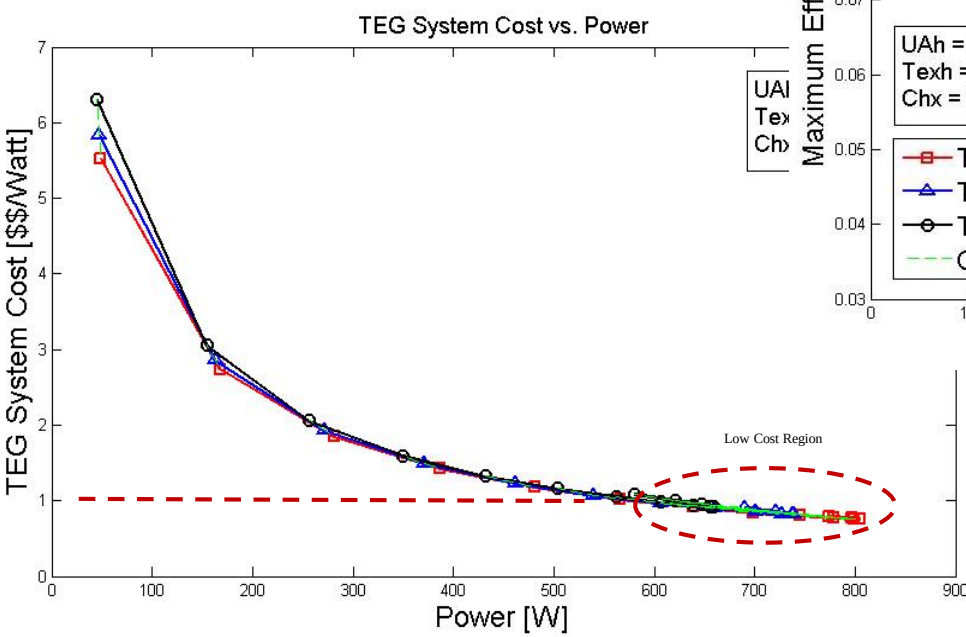
**Designed for integration with various heat sources, up to 1273 K operation with multiple thermal cycles in vacuum or atmospheric environments**

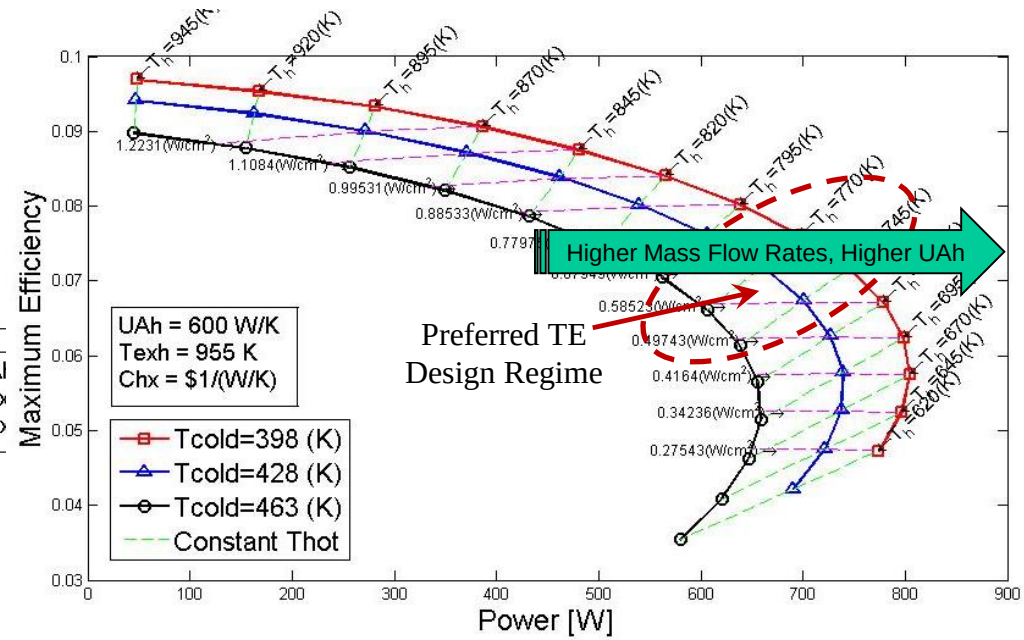
# TE System Level Analyses

# Results – $T_{exh}$ = 955 K, Heat Exchanger Costs $1/(W/K)

Waste Energy Recovery Analyses

- Preferred TE Design Regime Identified
  - Cost Dependence on Power, $T_{cold}$ , $T_{hot}$ Shown Below



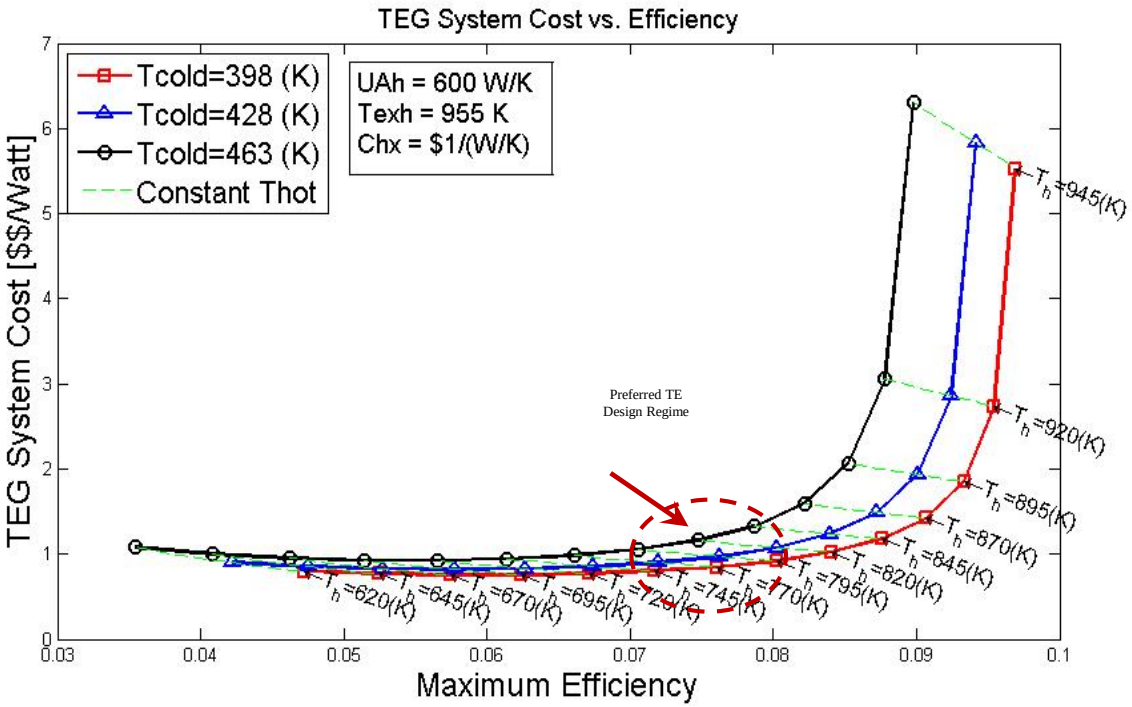

- Cost-per-Watt Asymptotically Approaches Low Cost Regions (Basically ∝1/P When Heat Exchangers Dominate)
- Approaches Point of Diminishing Returns

Hendricks, T.J., Yee, S., LeBlanc, S., "Cost Scaling of a Real-World Exhaust Waste Heat Recovery Thermoelectric Generator: A Deeper Dive," *Journal of Electronic Materials*, **45**, Issue 3, DOI 10.1007/s11664-015-4201-y, Springer, New York, 2015.

# Results – $T_{exh}$ = 955 K, Heat Exchanger Costs $1/(W/K)

- TE Designs Can Approach $1/W Only When Heat Exchanger Costs Approach $1/(W/K) and One is in Preferred TE Design Regime
- Preferred TE Design Regimes Allow us to Move into Higher Efficiency, Higher Power Densities and Fluxes With Very Little Cost and Power Penalties – "PRETE (Pretty)" Design Regime
  - We Can Win
  - If and only if Heat Exchanger Costs Are Low Enough
- Point of Diminishing Returns Evident Here Also

Heat Exchangers Dominate The Costs, Even at Low Cost Levels and It is Extremely Difficult to Escape this Regime






Hendricks, T.J., Yee, S., LeBlanc, S., "Cost Scaling of a Real-World Exhaust Waste Heat Recovery Thermoelectric Generator: A Deeper Dive," *Journal of Electronic Materials*, **45**, Issue 3, DOI 10.1007/s11664-015-4201-y, Springer, New York, 2015.

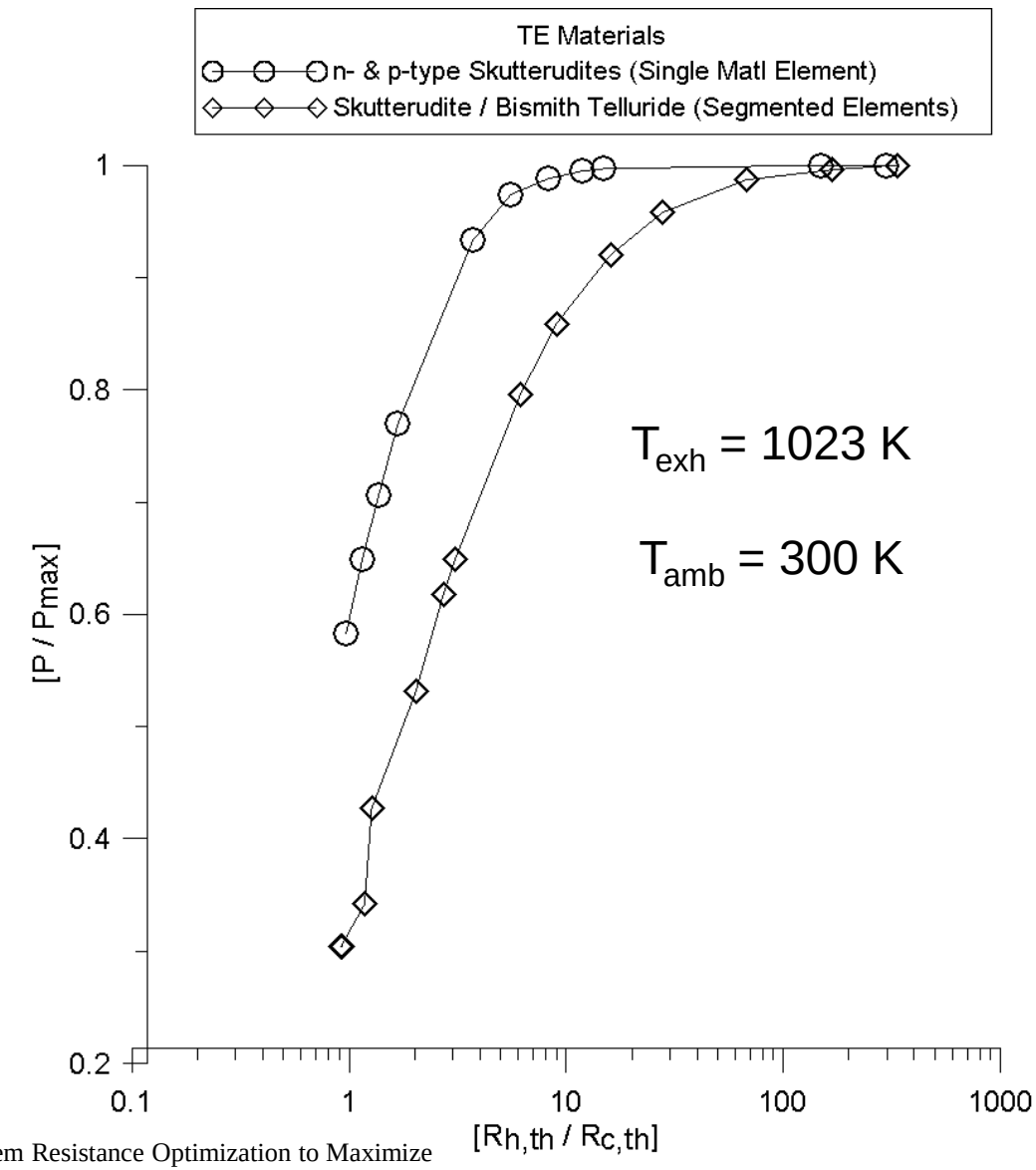
# Optimizing TE Energy Recovery Systems

- Thermoelectric Energy Recovery Useful in Hybrid Systems
- Maximzing Power is Key
- Thermoelectric Criteria <u>and</u> Newly Quantified Thermal Criteria Required

$$\left(\frac{P}{P_{\max}}\right) = f\left[\left(\frac{R_{h,th}}{R_{c,th}}\right), TE \cdot Material \cdot \Pr operties\right]$$

$$\left(\frac{T_h - T_c}{T_{exh} - T_{amb}}\right) = f\left[\left(\frac{R_{h,th}}{R_{c,th}}\right), TE \cdot Material \cdot \Pr operties\right]$$

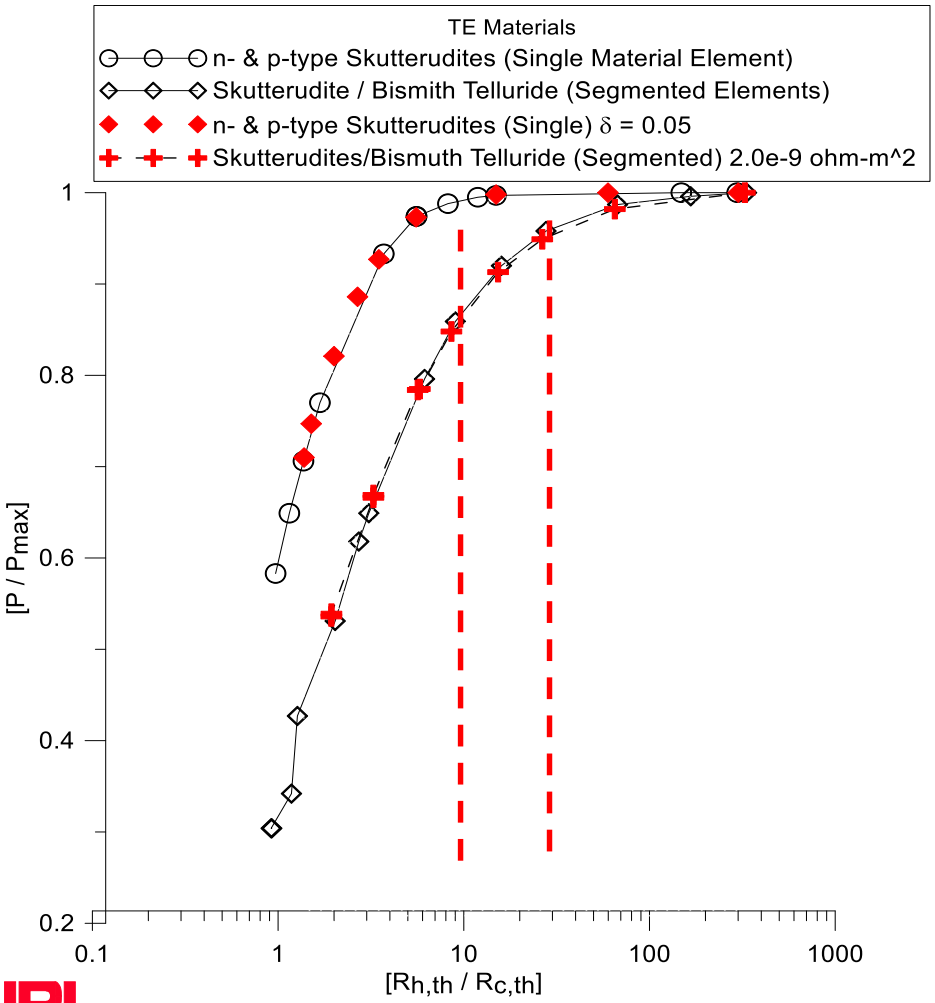
- Unique, Wide-Ranging ($P/P_{max}$) Relationship Holds for Given TE Materials

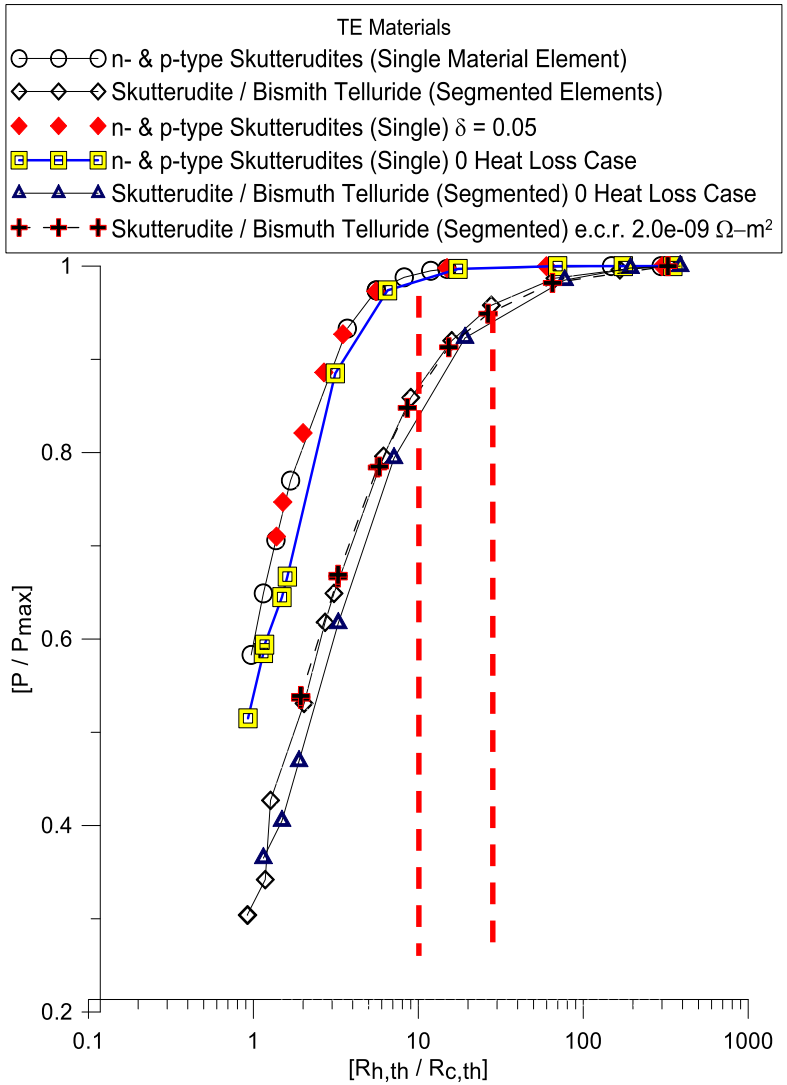



T. J. Hendricks, "Integrated Thermoelectric–Thermal System Resistance Optimization to Maximize Power Output in Thermoelectric Energy Recovery Systems, Mater. Res. Soc. Symp. Proceedings, **1642**, Materials Research Society, mrsf13-1642-bb02-04 doi:10.1557/opl.2014.443, 2014.

# Contact Resistance & Heat Loss Effects

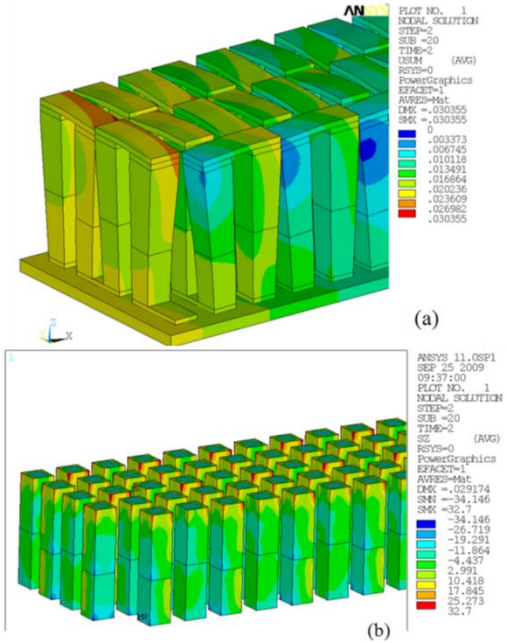
- Relationship Universal for Different Contact Resistances & Heat Loss
- Maximum Power Requires $(R_{h,th} / R_{c,th})_{opt} \geq 10\text{-}30$

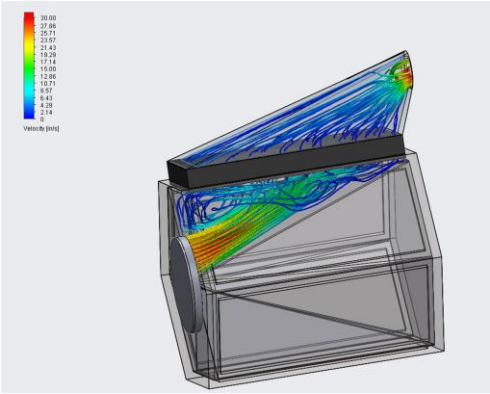


# TEG System-Level Analyses

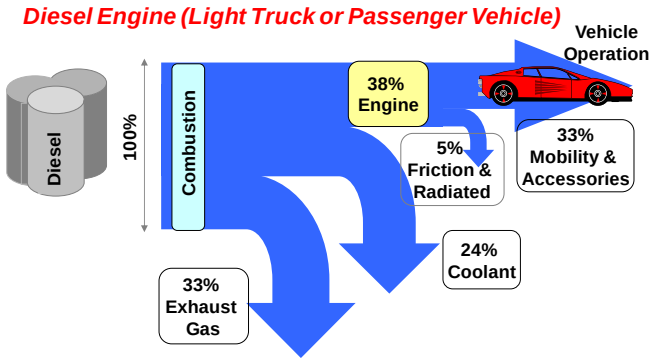
- System Analysis Capability Allows Us to Successfully Deal With System Design Complexities
  - Mechanical Strength (COMSOL, ANSYS)
  - Differential Thermal Expansion (COMSOL)
  - Thermomechanical Analysis (COMSOL, ANSYS)
  - Fluid Dynamics in Energy Recovery (COMSOL, ANSYS)

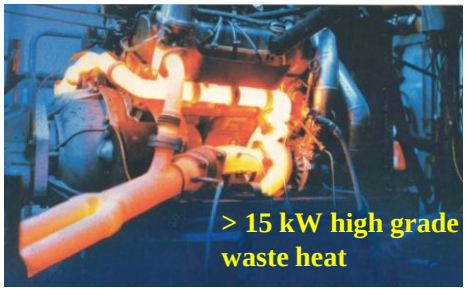


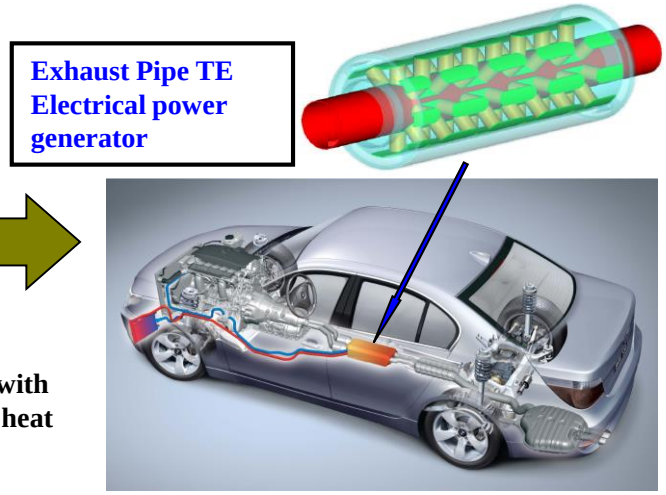
# TE for Vehicle Energy Harvesting & Utilization

- Thermoelectrics in Vehicles
  - TE has unique advantages for integration
  - Reliability, Modularity, Compactness
- What has been done?
  - U.S. DOE & U.S. DoD Projects
  - Low efficiency $Bi_2Te_3$-based TE generators (TEG) demonstrations
  - Higher efficiency Skutterudite & LAST/LASTT module demonstrations
  - ~650 W Systems Demonstrated
- What is needed?
  - Increase TEG operating temperatures, $\Delta T$
  - Integrate higher ZT materials ($ZT_{ave}$ ~ 1.5 to 2)
  - Develop and scale up HT TE module technology
  - Integrate with efficient heat exchangers




**~2-3% Fuel Efficiency improvement with exhaust waste heat recovery**



# Terrestrial Industrial Process Waste Heat Recovery

- System Solutions Needed to Recover Energy Throughout the Industrial Processing Complex
  - Produce Power
  - Residential & Commercial Space Heating
  - Radiant Collectors, Rankine cycles, Stirling cycles, & Thermoelectric Conversion
  - High-Temperature TE & Structural Materials and Systems; High Temperature Thermal Energy Storage
- Steel Industry
  - Electric Arc & Blast Furnaces, Steel Slabs, Slag By-Products
  - 10's of Megawatts of Thermal Energy Available in Each Potential Location in Steel Processing
  - Process Temperatures Available: 200-1000°C
  - 13 GW Total Potential Power Production in U.S. Alone
- Various Other Industrial Processes
  - Glass Furnaces, Aluminum Processes, Petro-chemical All Have Common Requirements
  - Process Temperatures Available: 760 – 1400°C
  - Another >39 GW Potential Power Production in These Industries in U.S.
  - Large International Interest in WHR Systems
    - Latest International Conference on Thermoelectrics 2015, Dresden, Germany
    - Energy Harvesting - 2014 U.S. Emerging Technology Conference & Exhibition, Santa Clara, CA

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# Conclusions

- Infusion of new high temperature materials $Yb_{14}MnSb_{11}$ and $La_{3-x}Te_4$ for space power systems applications.
  - High ZT validated by couple demonstrations ~ 10% efficiency (vs 7% SOA)
    - Currently being considered for "upgrading" multi-mission RTG
- Segmenting improves the average ZT and enables 15% efficiency
- Currently could achieve 20% efficiency in TE devices by lowering cold side to 300 K and adding $Bi_2Te_3$
  - Not practical for most space applications
- Discussed strategies to achieve 20% conversion efficiency at higher $T_{cold}$
  - Strategies for nanostructuring of good electronic semiconductors (Si) are well understood but very experimentally challenging to realize in the bulk material
  - Efforts at JPL are focused on complex crystal structures with inherently low lattice thermal conductivities
- Also developing advanced component preparation techniques and robust materials, couples and modules
- TE system-level analyses required in formulating and refining TEG designs

# Acknowlegments


- This work was performed at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration
- This work is conducted under the NASA Radioisotope Power Systems' Technology Advancement Project
- The work presented here benefited from contributions from several university collaborators
  - University of California at Los Angeles (Profs. Rick Kaner and Bruce Dunn)
  - University of California at Davis (Prof. Susan Kauzlarich)
  - California Institute of Technology (Dr. Jeff Snyder)