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# Advanced Thermoelectric Power Generation Technology Development at JPL

**3rd European Conference on Thermoelectrics**  
**September 2005**  
**Nancy, France**

presented by

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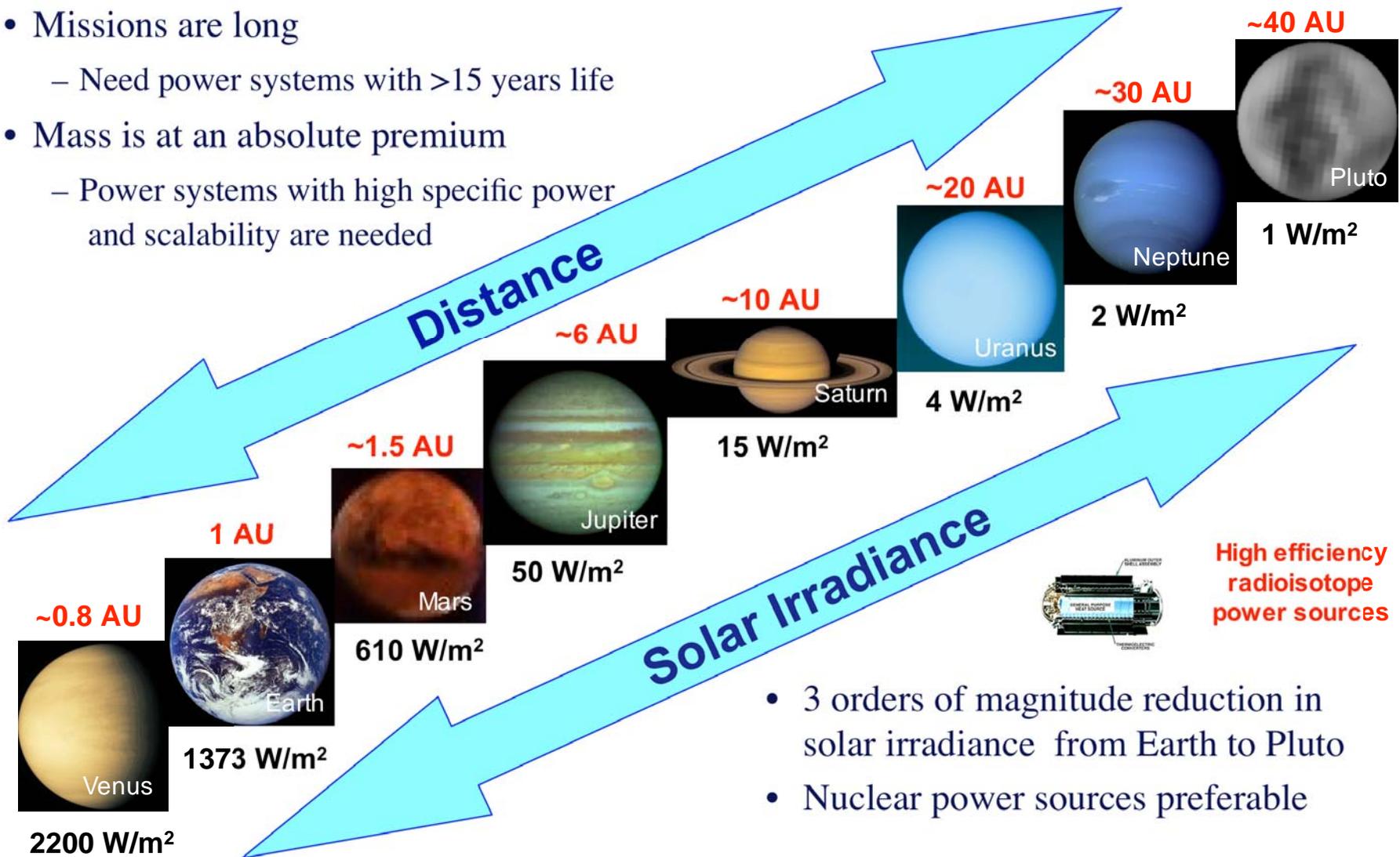
- **State-of-practice Radioisotope Thermoelectric Generators**
- **975K-300K skutterudite unicouples and multicouples development**
- **High-temperature materials and devices for operation up to 1275K**
- **Future work and conclusions**



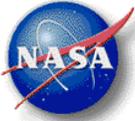
# Power Technology



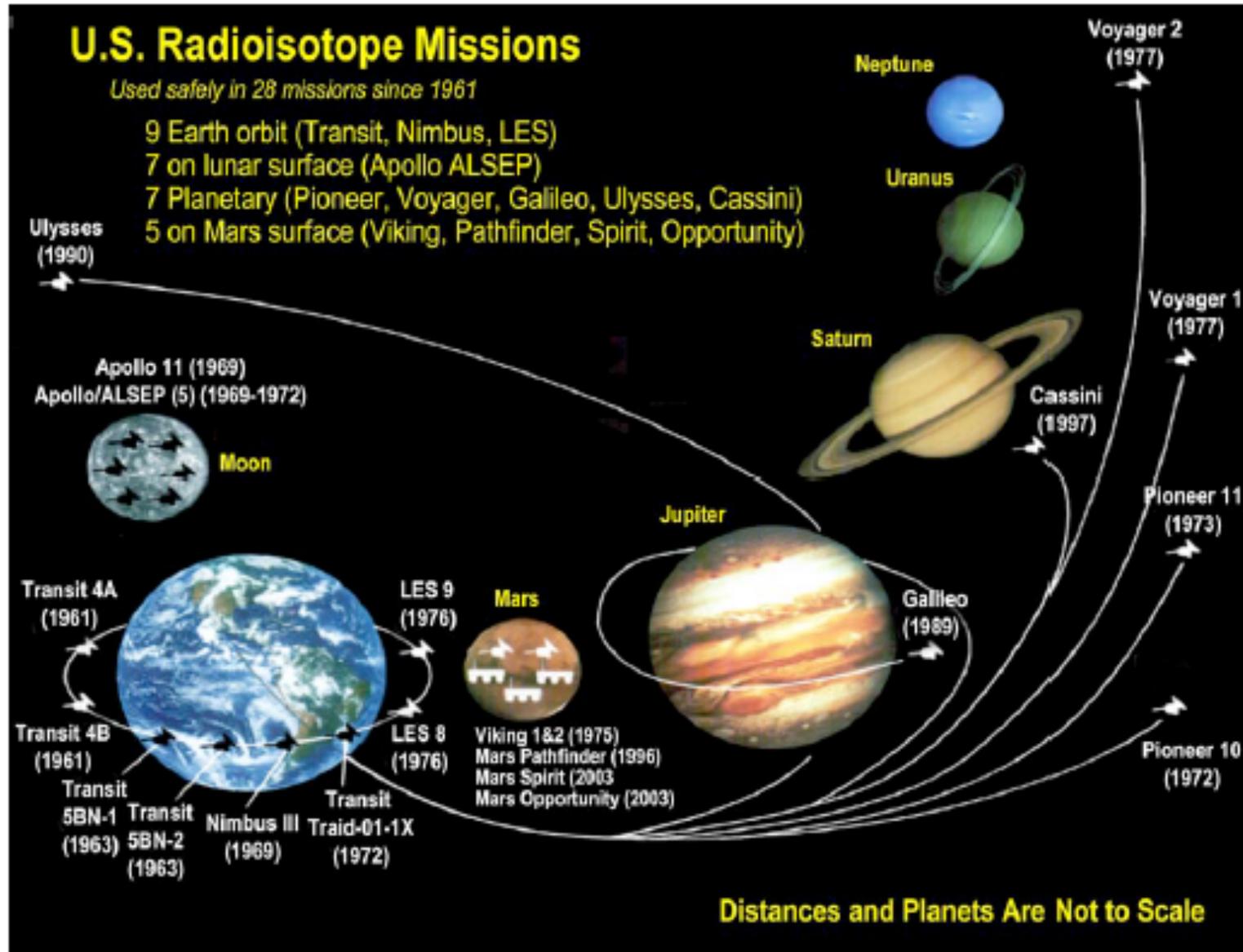
- Missions are long
  - Need power systems with >15 years life
- Mass is at an absolute premium
  - Power systems with high specific power and scalability are needed



- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Nuclear power sources preferable

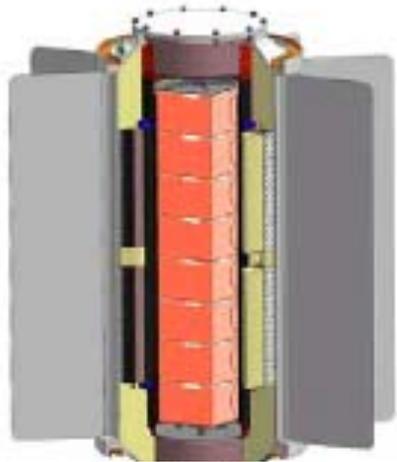


# U.S. missions using radioisotopes power and/or heating sources

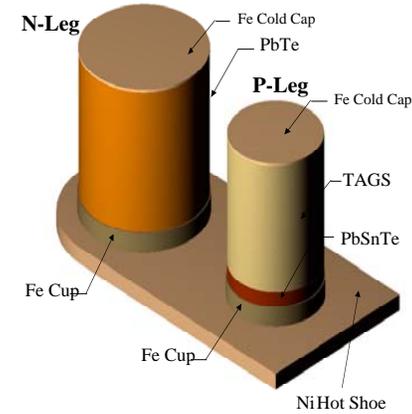




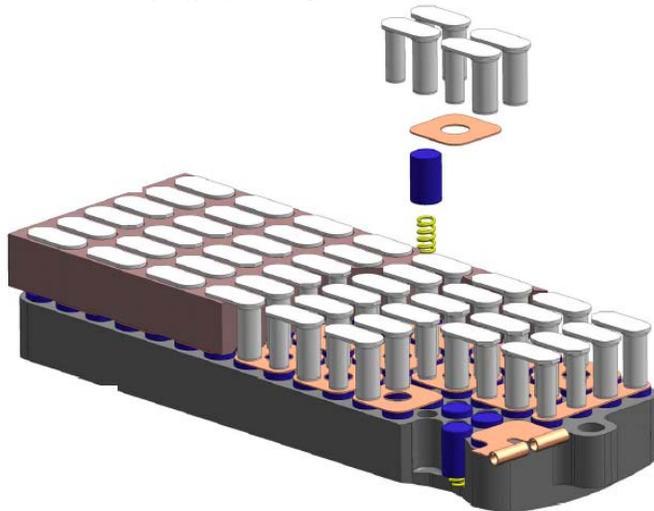
# Multi-Mission PbTe/TAGS conductively coupled RTG (MMRTG)



**MMRTG**



**MMRTG couple**



**Spring-loaded TE converter**

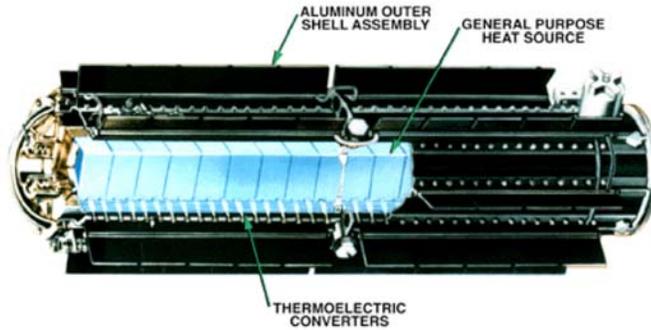
<i>Item/Converter</i>	<b>PbTe/TAGS MMRTG</b>
Hot side temperature (K)	<b>823</b>
Cold side temperature (K)	<b>483</b>
Converter efficiency (%)	<b>7.6</b>
System efficiency (%)*	<b>6.4</b>
Thermal power (BOM) ( $W_{th}$ )	2000
Thermal efficiency (%)	
Electrical power (BOM) ( $W_e$ )	125.3
Number of GPHS modules	<b>8</b>
Total $PuO_2$ mass (kg)	<b>5.02</b>
Total system mass estimate (kg)	<b>43.8</b>
Specific power estimate ( $W_e/kg$ )	<b>2.85</b>



# General Purpose Heat Source RTG

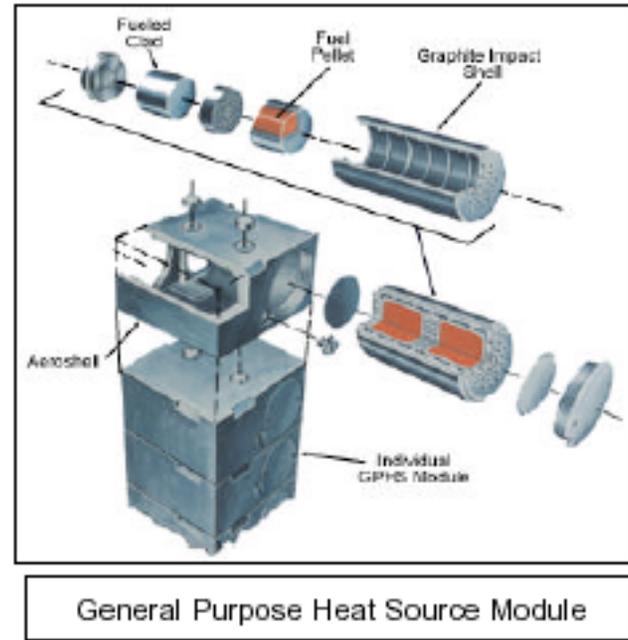


## General Purpose Heat Source (GPHS) Radioisotope Thermoelectric Generator (RTG)



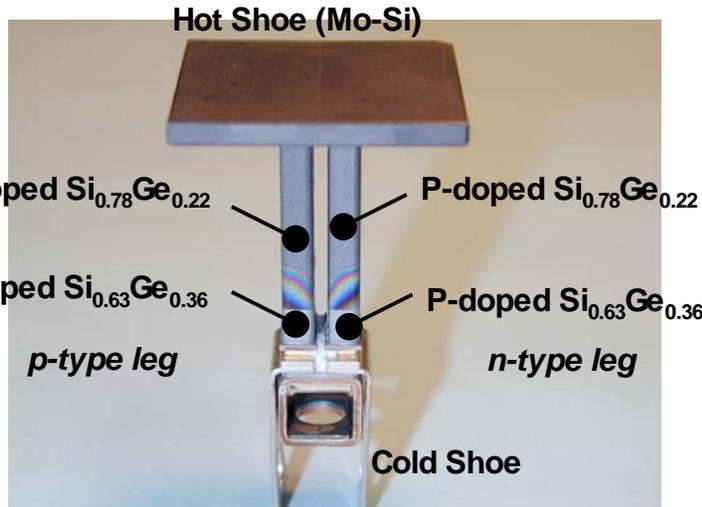
- POWER OUTPUT - 285 W(e)
- FUEL LOADING - 4400 W(t); 132,500 Ci
- WEIGHT - 124 lbs
- SIZE - 16.6 in x 44.5 in

The three Radioisotope Thermoelectric Generators (RTGs) provide electrical power for Cassini's instruments and computers. They are being provided by the U.S. Department of Energy.



### GPHS-RTG Performance Data

Power output-We	290 beginning of life 250 end of life
Operational life - hrs	40,000 after launch
Weight-kg	55.5
Output voltage	28
Dimensions	42.2 diameter 114 long
Hot junction temperature-K	1270
Cold junction temperature-K	566
Fuel	PuO <sub>2</sub>
Thermoelectric material	SiGe
Numbers of unicouples	572
Mass of Pu-238-g	7,561
<b>Specific power - We/kg</b>	<b>5.1</b>



**GPHS SiGe unicouple**



## Outline

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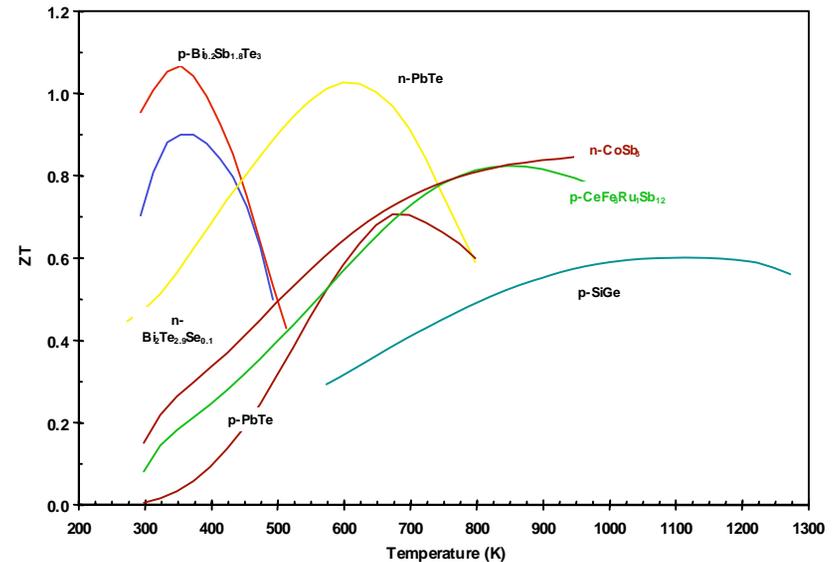
- **State-of-practice Radioisotope Thermoelectric Generators**
- **975K-300K skutterudite unicouples and multicouples development**
- **High-temperature materials and devices for operation up to 1275K**
- **Future work and conclusions**



# Segmented Thermoelectric Technology



- Uses improved high ZT materials
  - ◆ Development initiated in 1991 and supported by ONR and DARPA
  - ◆ Large  $\Delta T$ , high ZT  $\rightarrow$  high efficiency
  - ◆ Higher efficiency values compared to PbTe/TAGS
- Segmented unicouples development and integration into an advanced RTG
  - ◆ Using a combination of state-of-the-art TE materials ( $\text{Bi}_2\text{Te}_3$ -based materials) and new, high ZT materials developed at JPL
    - Skutterudites :  $\text{CeFe}_3\text{Ru}_4\text{Sb}_{12}$  and  $\text{CoSb}_3$
  - ◆ Current materials operation limited to  $\sim 1000\text{K}$
  - ◆ Higher average ZT values
  - Higher material conversion efficiency
    - **8.8 % for a 480-1000K temperature gradient**



**Skutterudite unicouples**

Efficiency  $\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$



## Skutterudite unicouple key technology gates

### Key technology gates

- Developed improved low temperature skutterudite materials ✓
- TE materials synthesis and scale up-processing ✓
- Low electrical contact resistance between TE segments and cold- and hot-shoes ✓
- Demonstrate unicouple performance through testing and modeling ✓
- Unicouple thermal-mechanical integrity
- Lifetime and performance validation
  - Sublimation control
  - Stable thermoelectric properties





## Current Focus

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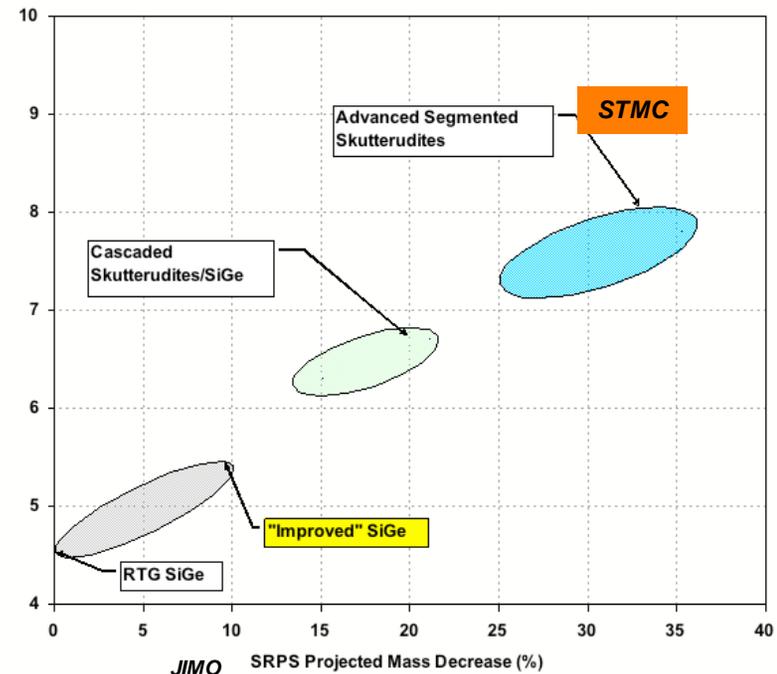
- Demonstrating skutterudite materials and bond stability and determining degradation mechanisms in order to validate lifetime operation up to 1000K
  - ◆ **Material property measurements as a function of time and temperature**
  - ◆ **Sublimation rates as a function of time, temperature, and environment**
    - **Sublimation control: thin metal foil, aerogel, pressurized environment**
  - ◆ **Interface diffusion studies**
  - ◆ **Couple screening tests and optimization of uncouple configuration in anticipation of lifetime testing**
  
- Design and fabrication of four couple modules to facilitate technology insertion into MMRTG



# High Power Thermoelectric Converter Technology Development for Future High Power Science Missions



- Segmented Thermoelectric Multicouple Converter (STMC) technology for 100 kWe class power systems
- Primary objective is technology development based on high performance advanced thermoelectric materials for future NASA missions
  - ◆ 2x increase in conversion efficiency
  - ◆ High rejection temperature (600-700K)
    - Limit size of heat rejection system
    - And minimize overall system mass
- Scope focused on:
  - ◆ Power Conversion System design and modeling
  - ◆ Advanced TE materials evaluation and optimization
  - ◆ Advanced TE Couple Array engineering development
  - ◆ Scale-up converter fabrication
  - ◆ Planning for technology insertion



## 100kW Thermoelectric Space Power System Goals

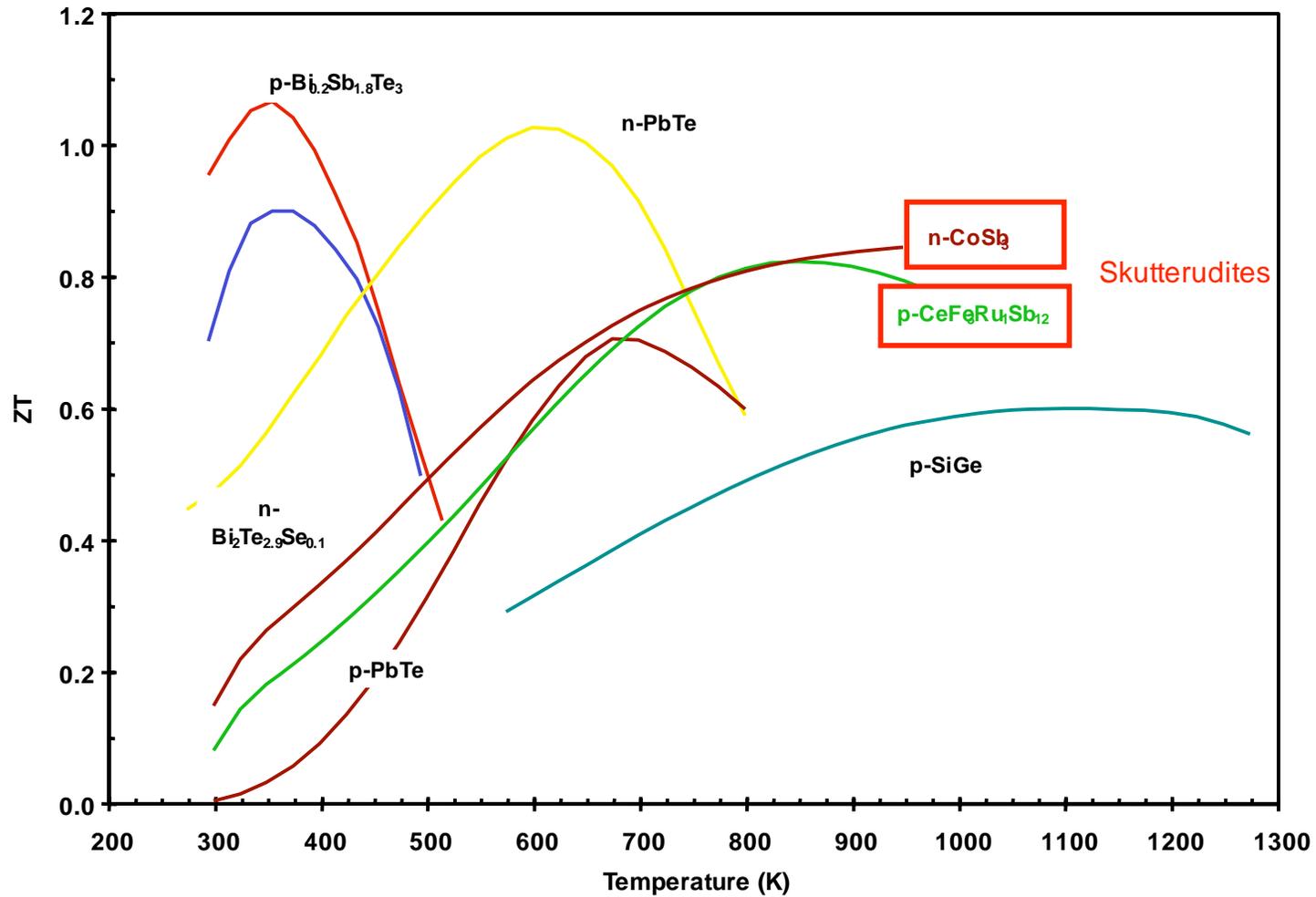
Projected Performance Improvements using Advanced TE Materials over SiGe Alloys used in RTGs

### STMC TE Technology Development Team

- Jet Propulsion Laboratory
- Boeing/Rocketdyne
- Teledyne Energy Systems
- University of Michigan
- Michigan State University
- University of South Florida
- University of California at Davis
- Clemson University
- Princeton University
- Cornell University
- University of Southern California
- University of New Mexico

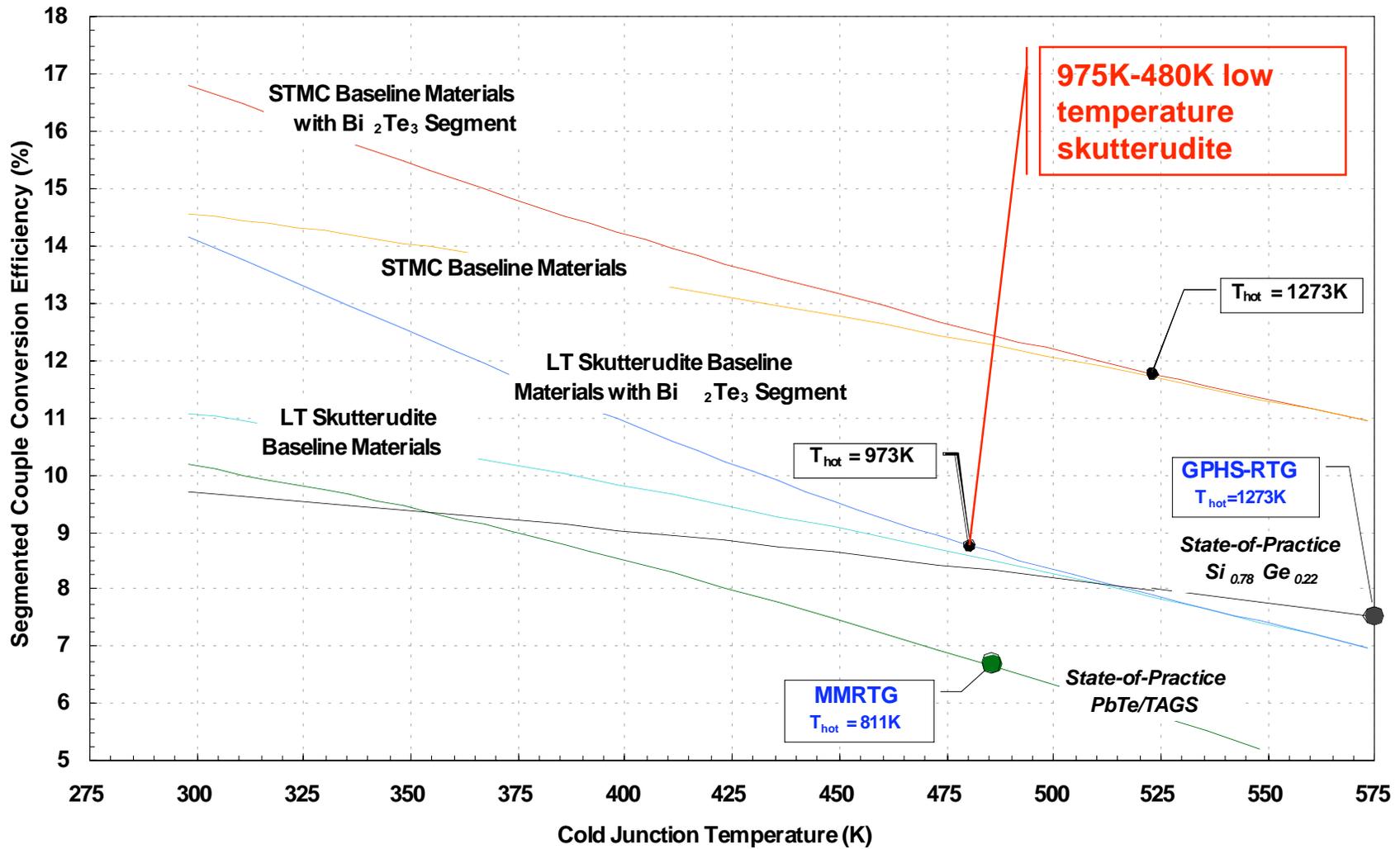


# ZT values for 1000K skutterudite baseline materials





# Advanced Materials Thermoelectric Conversion Efficiency





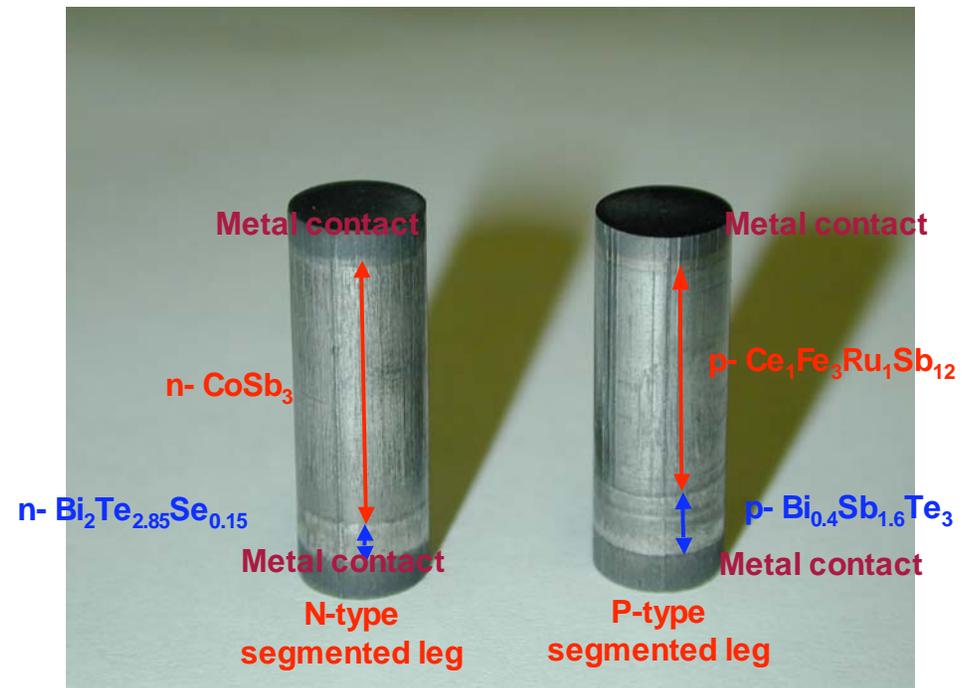
## Synthesis and some properties for n-CoSb<sub>3</sub> and Ce<sub>1</sub>Fe<sub>3</sub>Ru<sub>1</sub>Sb<sub>12</sub>

- Demonstrated materials synthesis scalability to large quantities
  - ◆ Melting (~1200C in glassy carbon crucibles) followed by ball milling in steel vials under Argon
  - ◆ Hot pressing at temperatures between 600 and 700C, graphite dies, 20,000 psi
  - ◆ Developed 100g batch process for n-type and p-type
  - ◆ Overall process similar to state-of-practice thermoelectrics; powder metallurgy process easily scalable to larger quantities
  
- Properties
  - ◆ N-type CoSb<sub>3</sub>
    - Uses Pd, Te (~ 1at% each) as dopants to optimize carrier concentration
    - CTE:  $9.1 \times 10^{-6}$ K
    - Decomposition temperature: 878C
  - ◆ Ce<sub>1</sub>Fe<sub>3</sub>Ru<sub>1</sub>Sb<sub>12</sub>
    - CTE:  $12.1 \times 10^{-6}$ K
    - Decomposition temperature: 830C



## Unicouples legs fabrication

- Developed uniaxial hot-pressing technique for segmented and un-segmented (skutterudite only) legs fabrication
  - ◆ Powdered materials stacked on the top of each other
  - ◆ Temperature optimized to achieve density close to theoretical value
  - ◆ In graphite dies and under argon atmosphere
  - ◆ With metallic diffusion barriers between the thermoelectric materials
  - ◆ Metallic contacts at hot- and cold-side
  - ◆ Low electrical resistance bonds ( $<5\mu\Omega\text{ cm}^2$ ) achieved → negligible impact on overall uncouple performance





## Unicouple fabrication techniques developed to date



Skutterudite unicouple with  
Mo-hot-shoe

### 1) Co-hot-pressing

- ◆ Hot-press first leg onto hot-shoe
- ◆ Hot-press second leg onto hot-shoe to complete unicouple fabrication



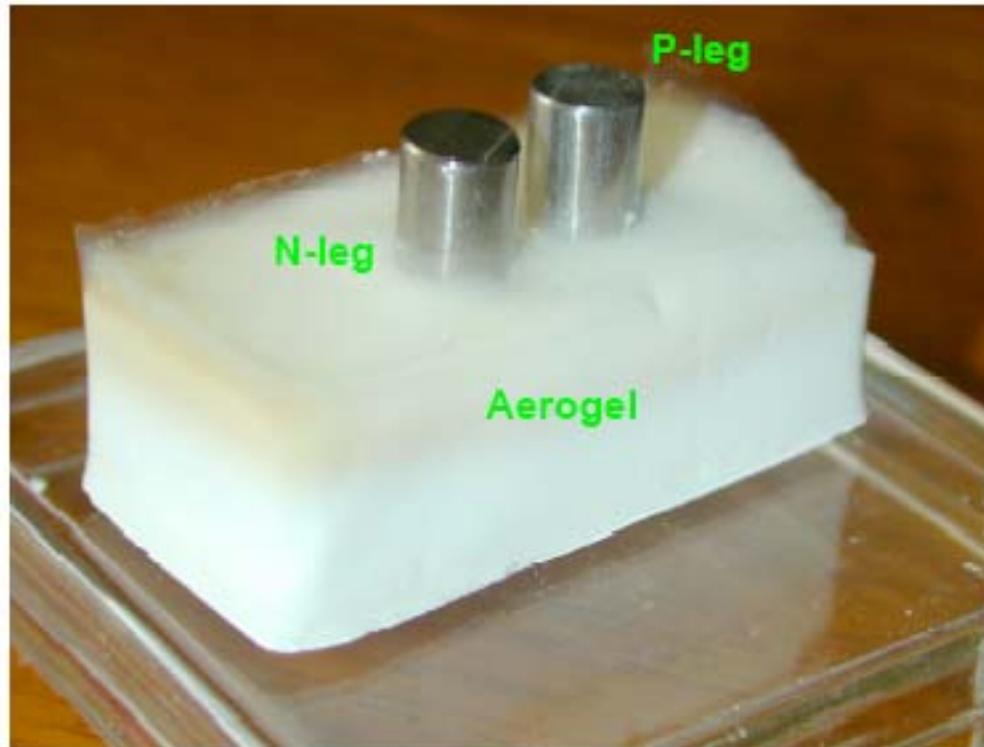
Skutterudite unicouples fabricated by  
diffusion bonding

### 2) Diffusion bonding technique

- ◆ Hot-press metallized legs first
- ◆ Diffusion bond legs to hot-shoe in a second step



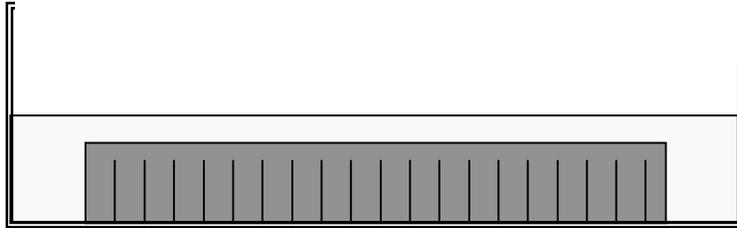
## Encapsulating Skutterudite Unicouples in Aerogel



**Close contact between aerogel and the unicouples legs can be achieved using the casting process**

## Thermoelectric module mock-up to test aerogel permeation

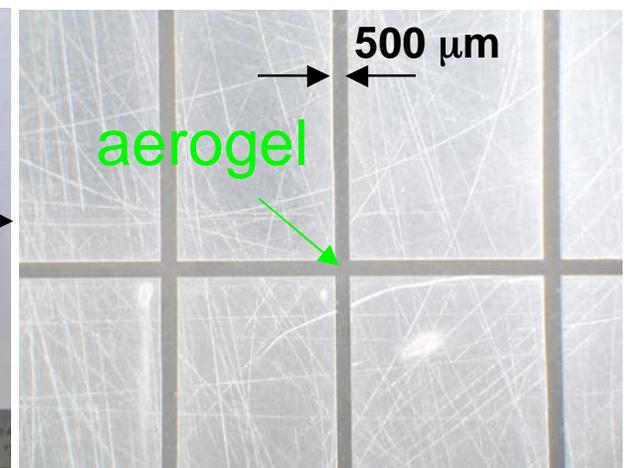
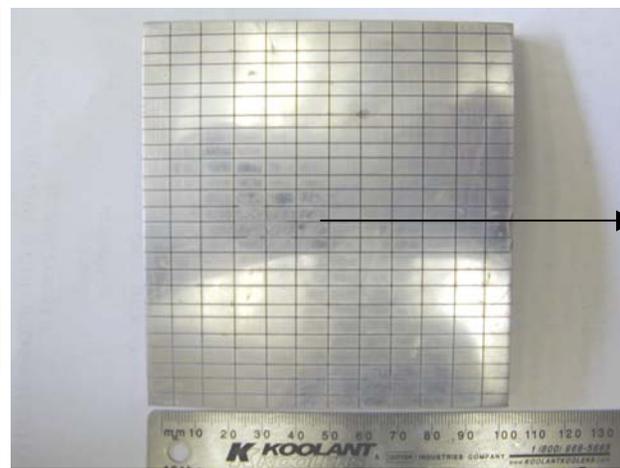
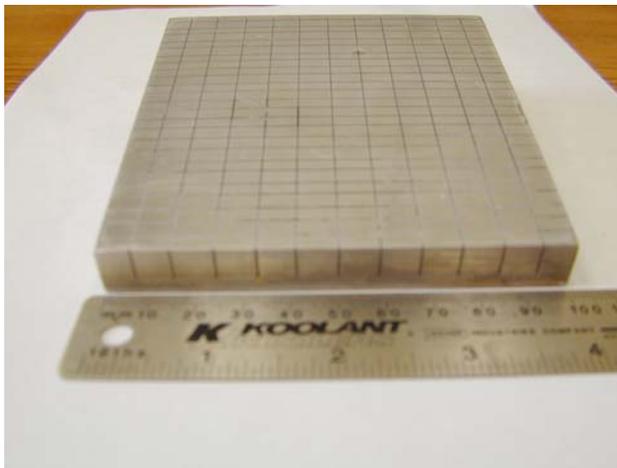
### How it was made



- Block placed upside down in mold so that notches were facing down.

- Liquid precursor (Sol) poured into mold. After several hours the liquid transformed into a free-standing gel

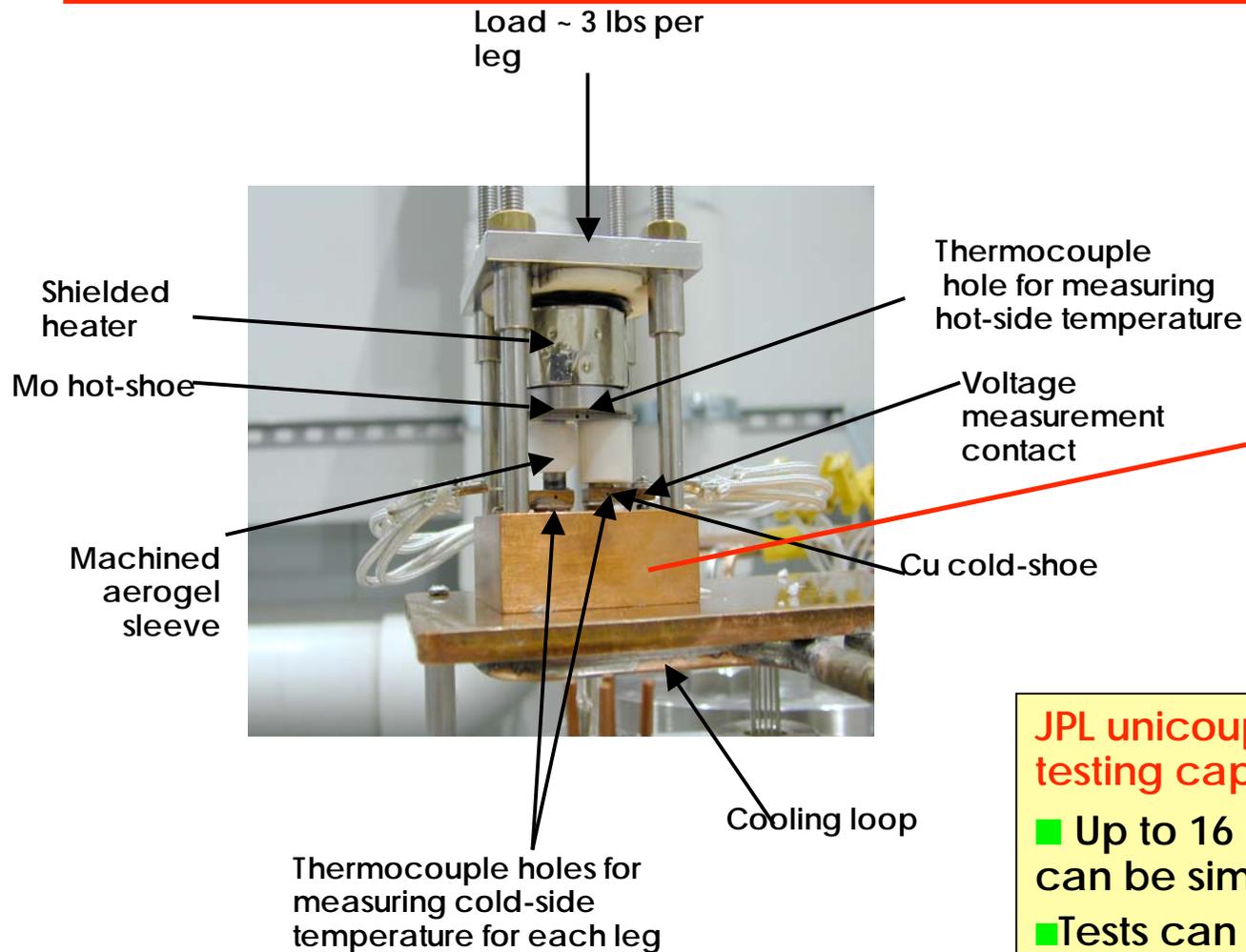
- The entire assembly including the mold was placed in the autoclave and supercritically dried



**Demonstrated aerogel permeation into narrow spacing down to ~ 10 μm**



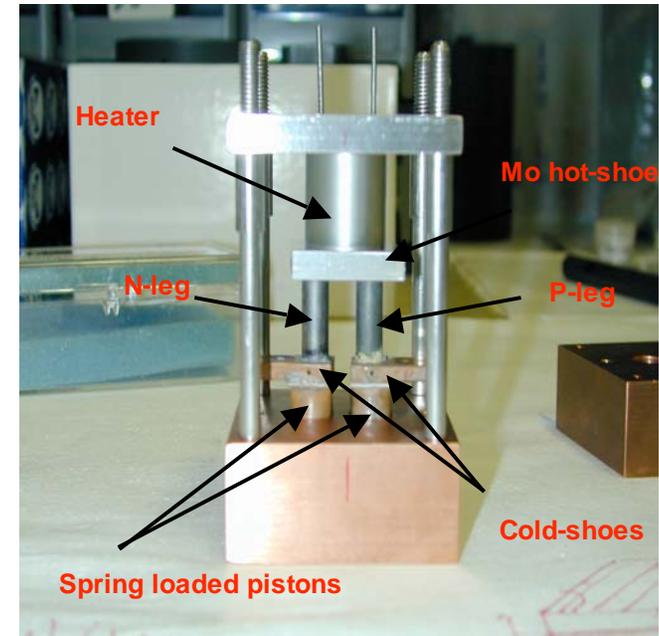
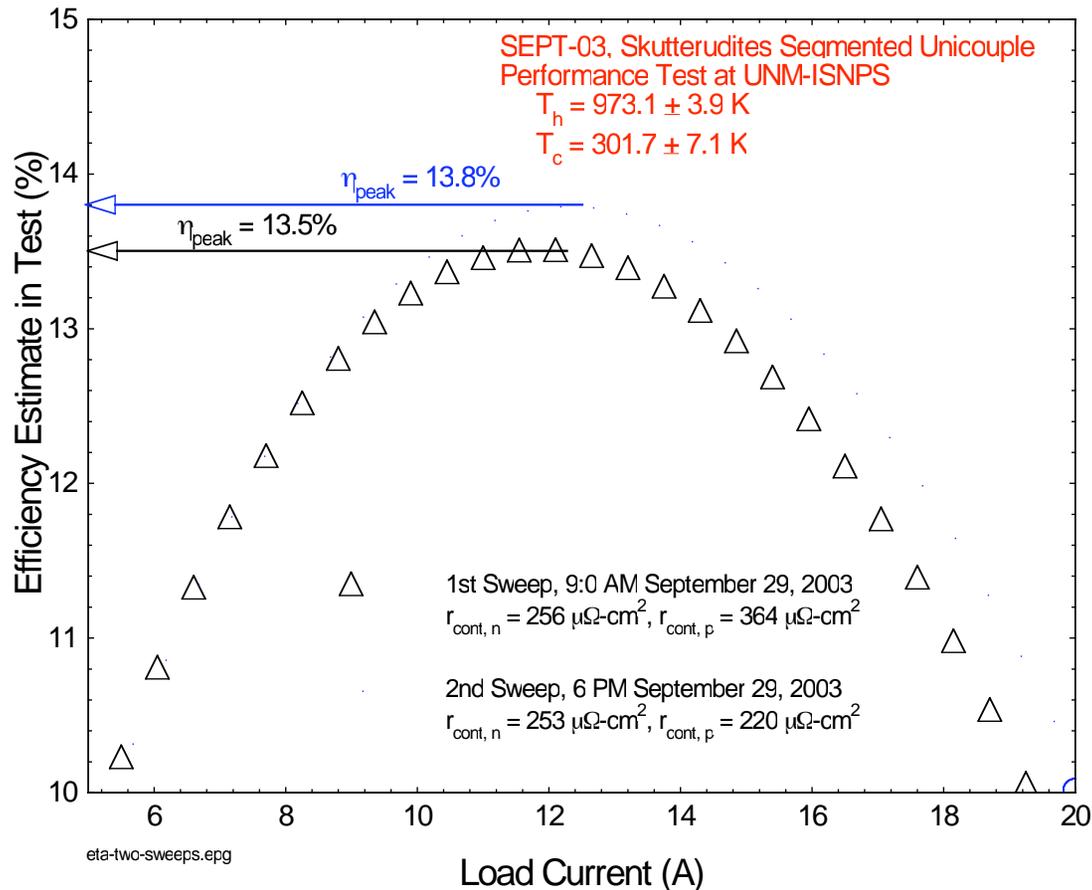
# Skutterudite unicouple performance testing



**Spring loaded unicouple test fixture for skutterudite unicouple performance testing**

## JPL unicouple and performance life testing capabilities

- Up to 16 unicouples/multicouples can be simultaneously tested
- Tests can be conducted in a vacuum or inert atmosphere
- Life tests designed to monitor power output performance over time



- Fully validated projected power performance on skutterudite and skutterudite/ $\text{Bi}_2\text{Te}_3$  unicouples (corresponds to ~ 14% efficiency for 975K-300K  $\Delta T$ )
- Independently confirmed at the University of New Mexico (for up to 1800 hrs of continuous testing)



# Thermoelectric Multicouple Enhancement Strategy

Planned improvements to fabrication and performance of conductively coupled Thermoelectric SiGe couple stack developed for SP-100

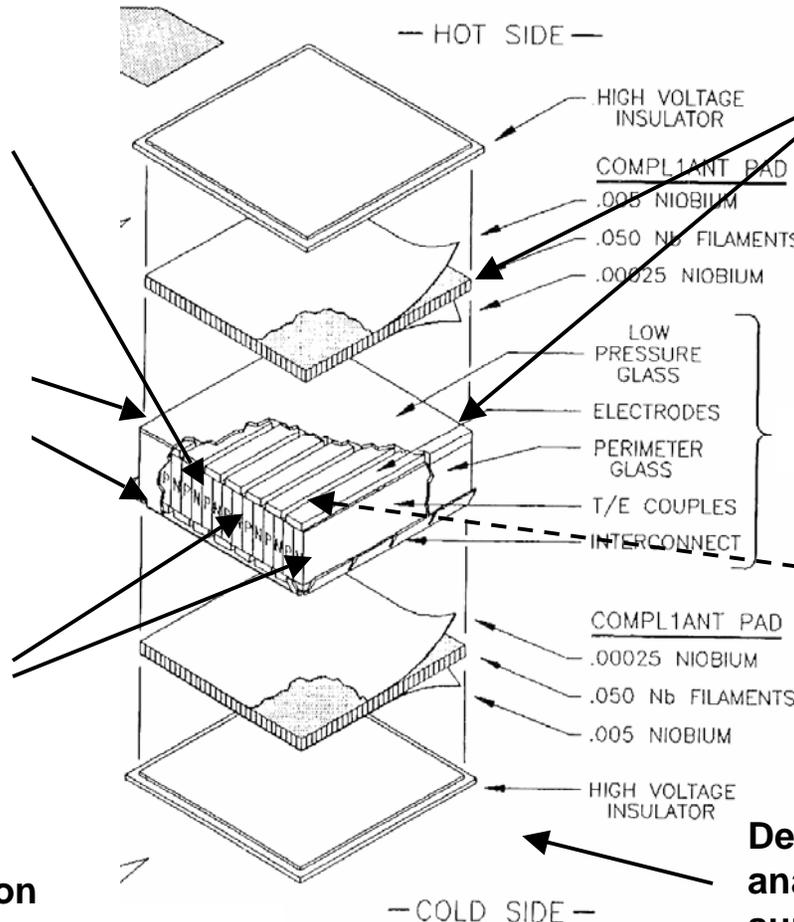
Improved TE Materials  
(increase conversion efficiency up to 10%)

Low contact resistance interconnects

(From 35-50 to less than 25  $\mu\Omega\cdot\text{cm}^2$  at 1275K)

Refractory Aerogel for superior thermal insulation and ease of module/TCA assembly (no glass between couple legs or around legs)

Module arrangement facilitates interconnection (all handled from exterior of TCA)



SP-100 Multicouple (8-couple series)

Thick compliant pads and graphite layers reduced/eliminated to reduce waste  $\Delta T$  from 30% to 5-10% (compliance achieved through structural engineering)

TE couples arranged in modules to facilitate fabrication, assembly and ensure lifetime

Detailed thermal/mechanical/fractural analysis for robust design that will survive fabrication, assembly and operation



## • Key Structural Integrity Challenges

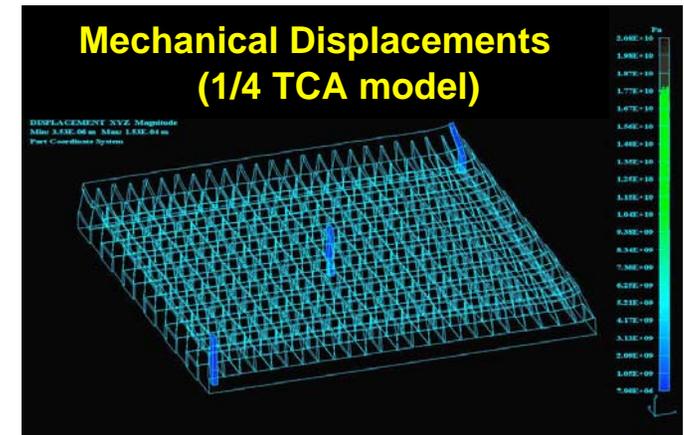
- Coefficient of thermal expansion mismatches within TE device stack, and between stack and large heat exchangers
- “Bowing” of thermoelectric legs due to large  $\Delta T$
- Surviving fabrication and assembly steps – and operation

## - Reviewed preliminary design of STMC and TCA

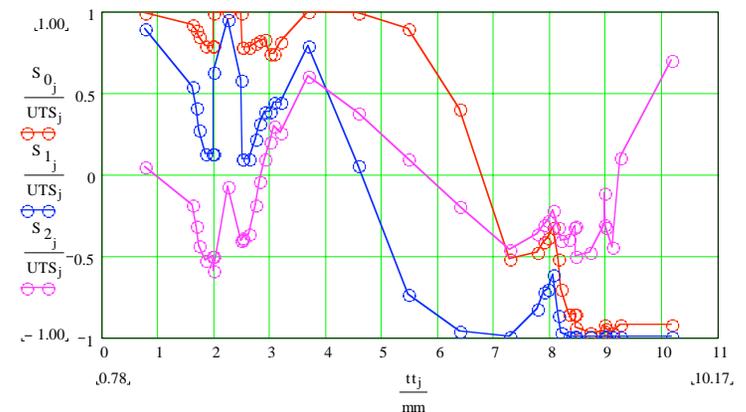
- Key goal is to redistribute thermally induced stresses by selecting optimal materials combinations, element geometries
- Secondary objective is to minimize parasitic losses ( $\Delta T$  across non-TE layers and fill factor thermal losses)

## • Mechanical tests of TE samples

- 4-point bend data obtained on skutterudites
- Testing and modeling of interface fracture toughness and development of fail-safe structures



**Elastic Stress Model of 1/2 STMC Stack**  
**Red Line** – Heat Exchanger Held Rigidly  
**Blue Line** – Free to Expand but no Bending  
**Purple Line** – Free to expand and bend



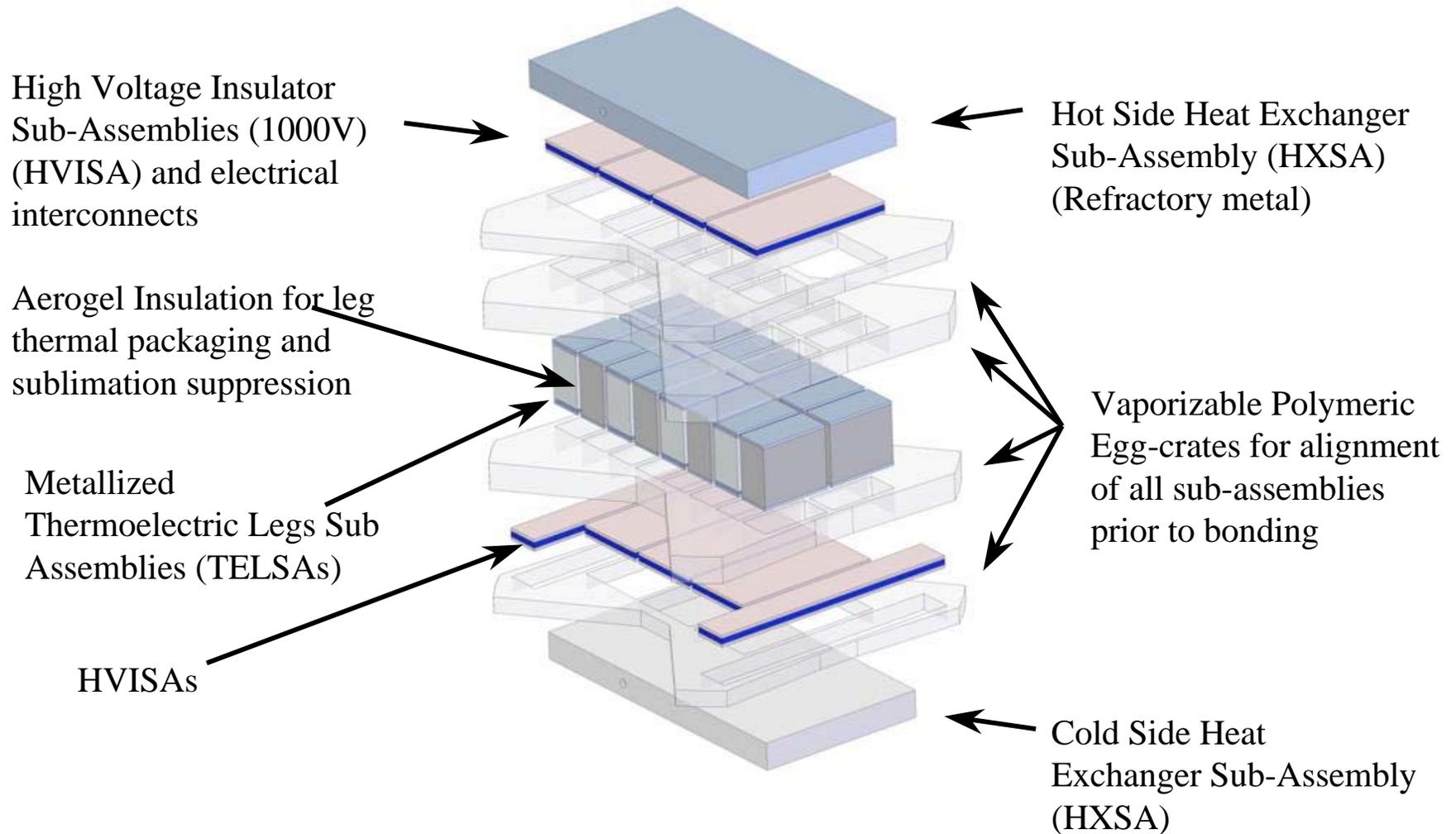
**Fraction of Ultimate Strain VS Distance in mm**



# STMC Module



STMC Module fabrication: fewer and simpler fabrication steps, scalable to mass production

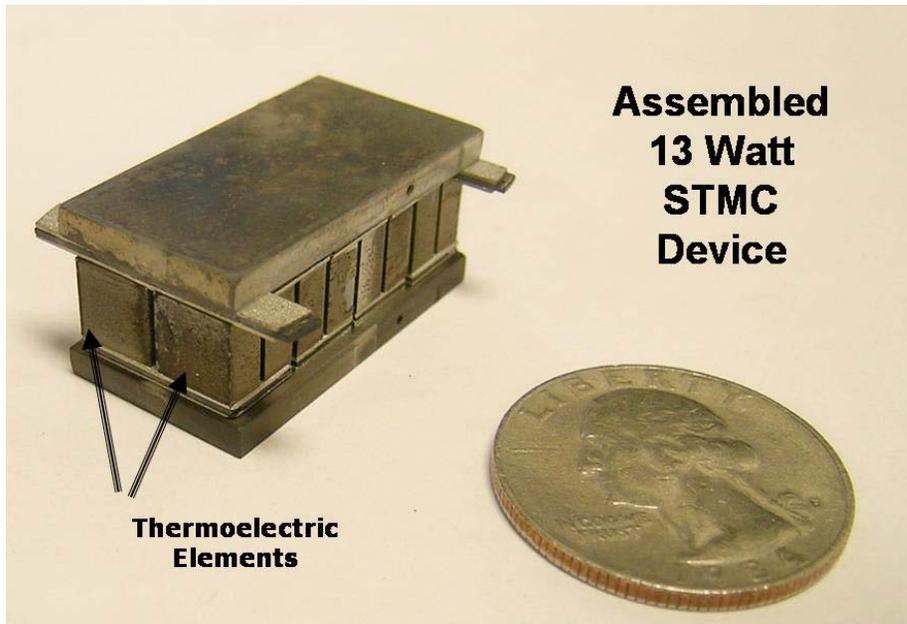




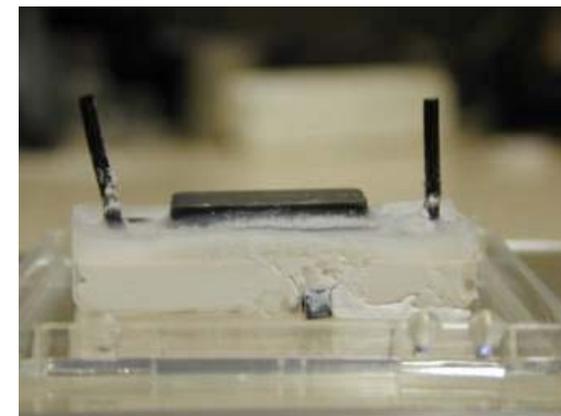
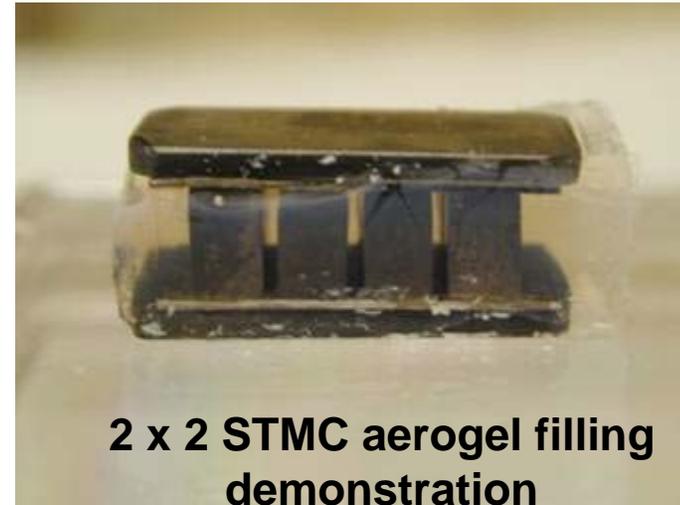
# Segmented Thermoelectric Multicouple Converter (STMC)

## 1000K STMC Technology Demonstration

- Fabrication of several modules completed in May 2005
- Performance testing to be started in late June 2005



**2 x 4 STMC Module**  
*1000K – 425K Operation, 13W*





## Outline

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- **State-of-practice Radioisotope Thermoelectric Generators**
- **975K-300K skutterudite unicouples and multicouples development**
- **High-temperature materials and devices for operation up to 1275K**
- **Future work and conclusions**

# TE Device Configuration: Segmenting vs Cascading

## Segmented Thermoelectric

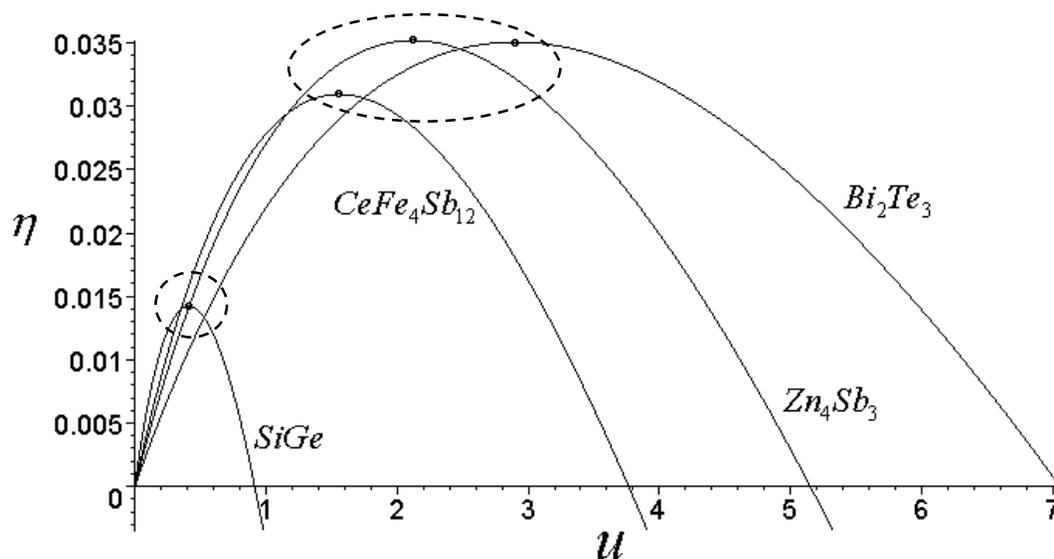
◆ constrained by constant current

- $u = I/Q_c$
- $u \approx \text{Constant}$

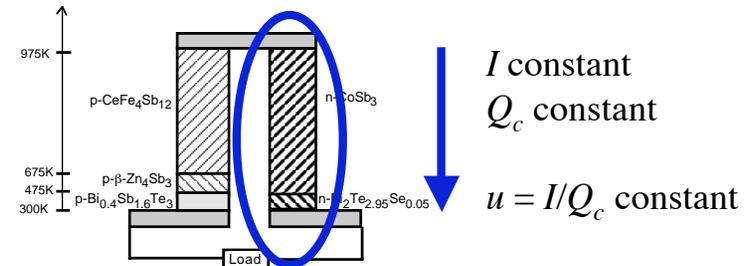
## Cascaded Thermoelectric

◆ independent circuits for each stage

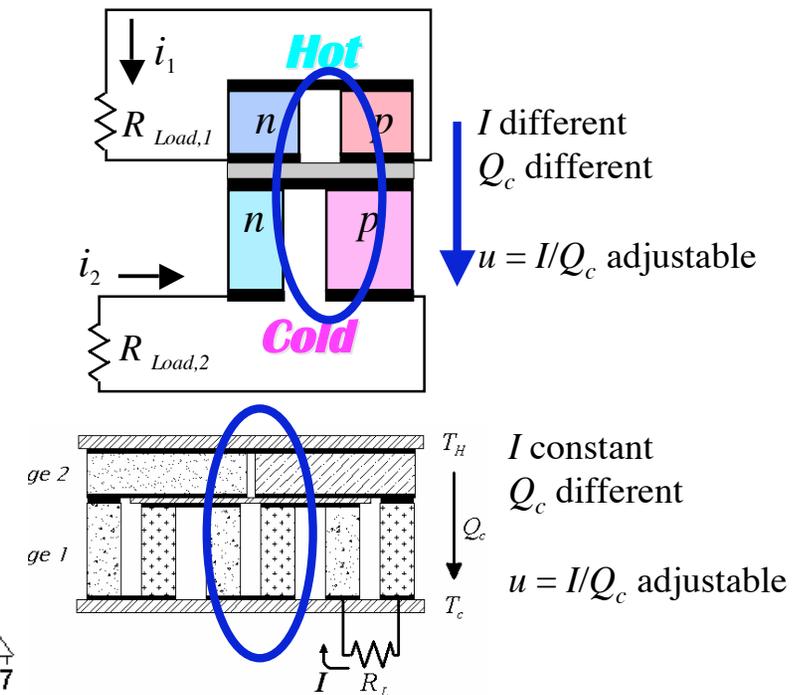
- Current different in each stage
- Heat different in each leg
- $u$  optimized for each stage



## Segmented TE Generator

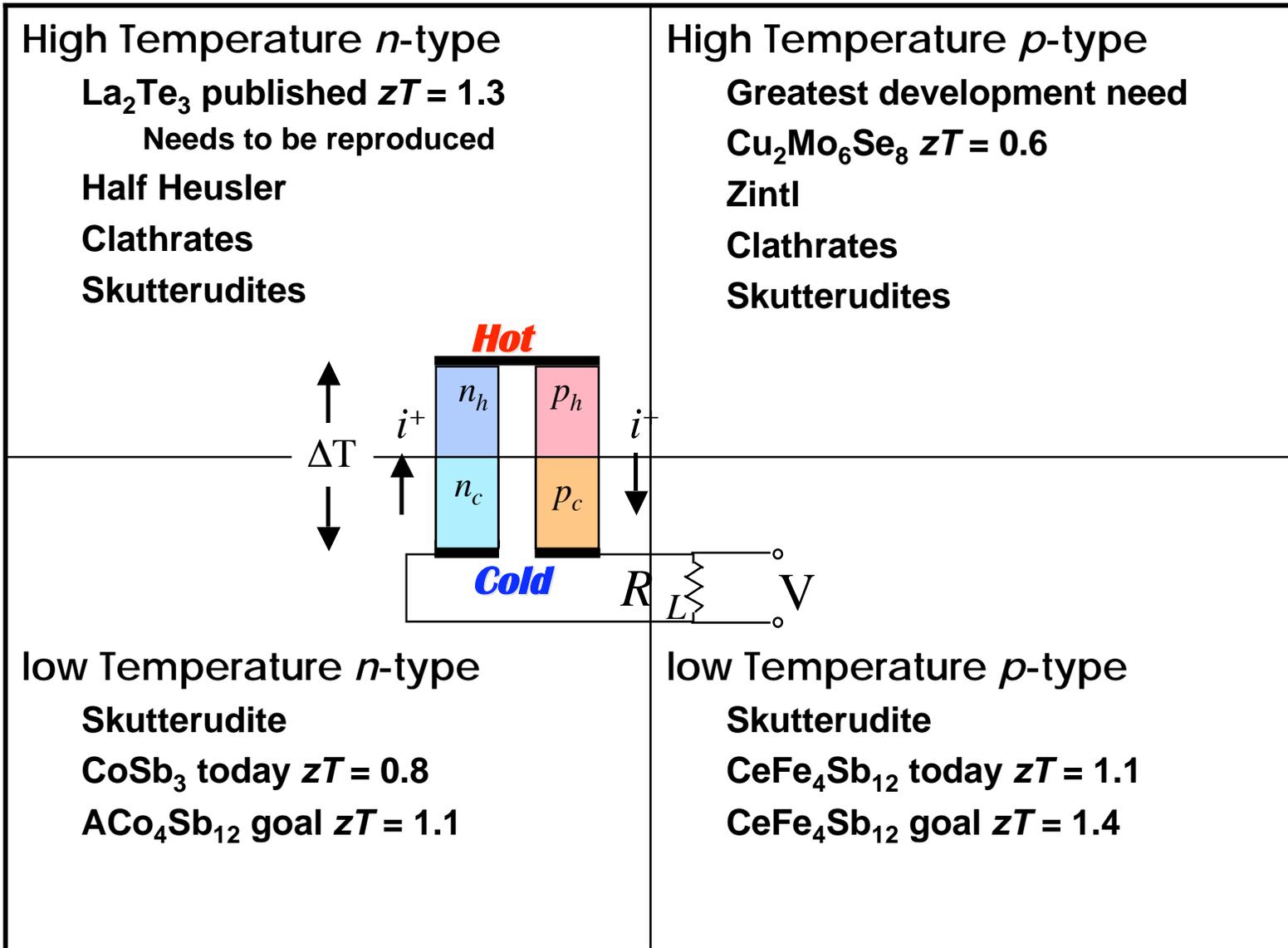


## Cascaded TE Generators



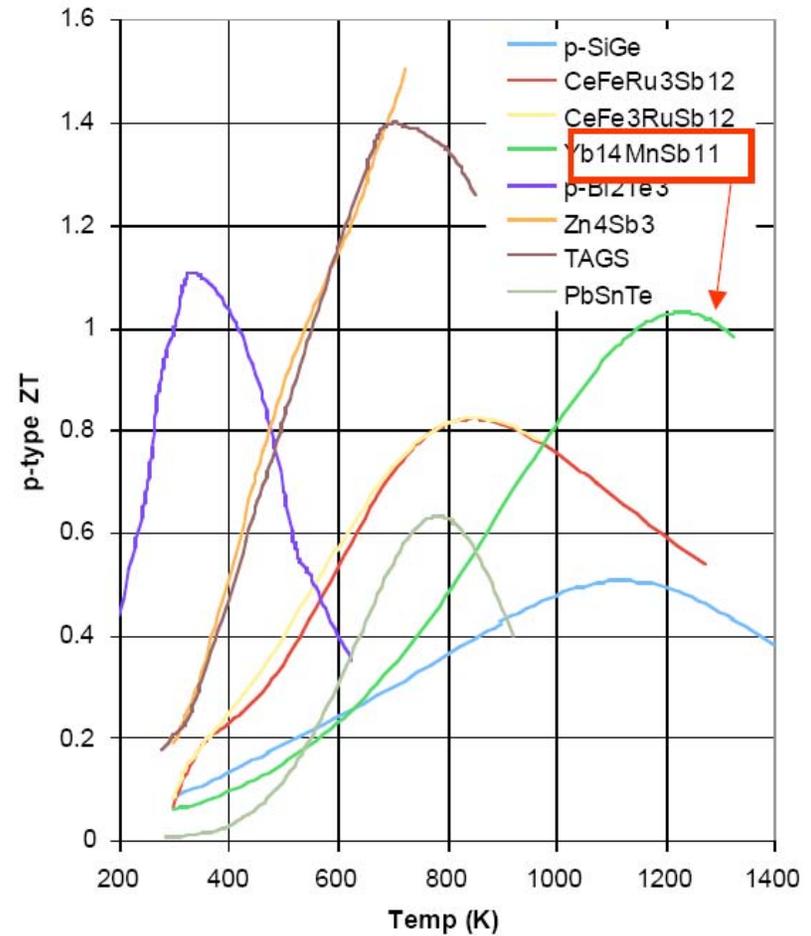
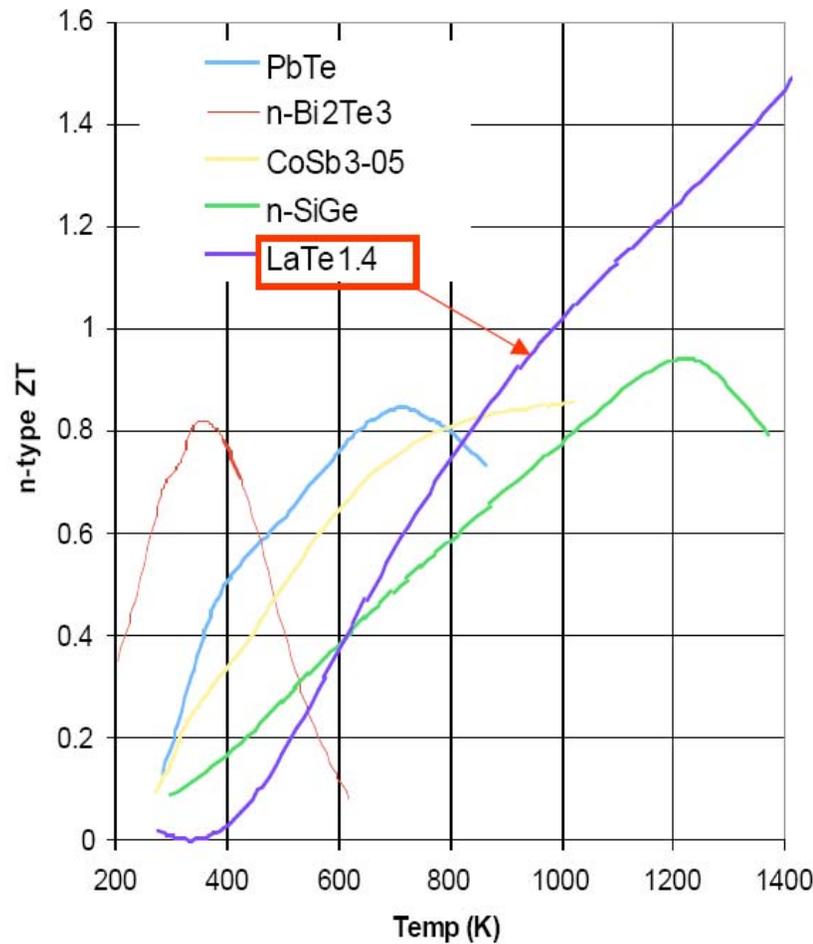


# STMC High Temperature TE Materials Effort





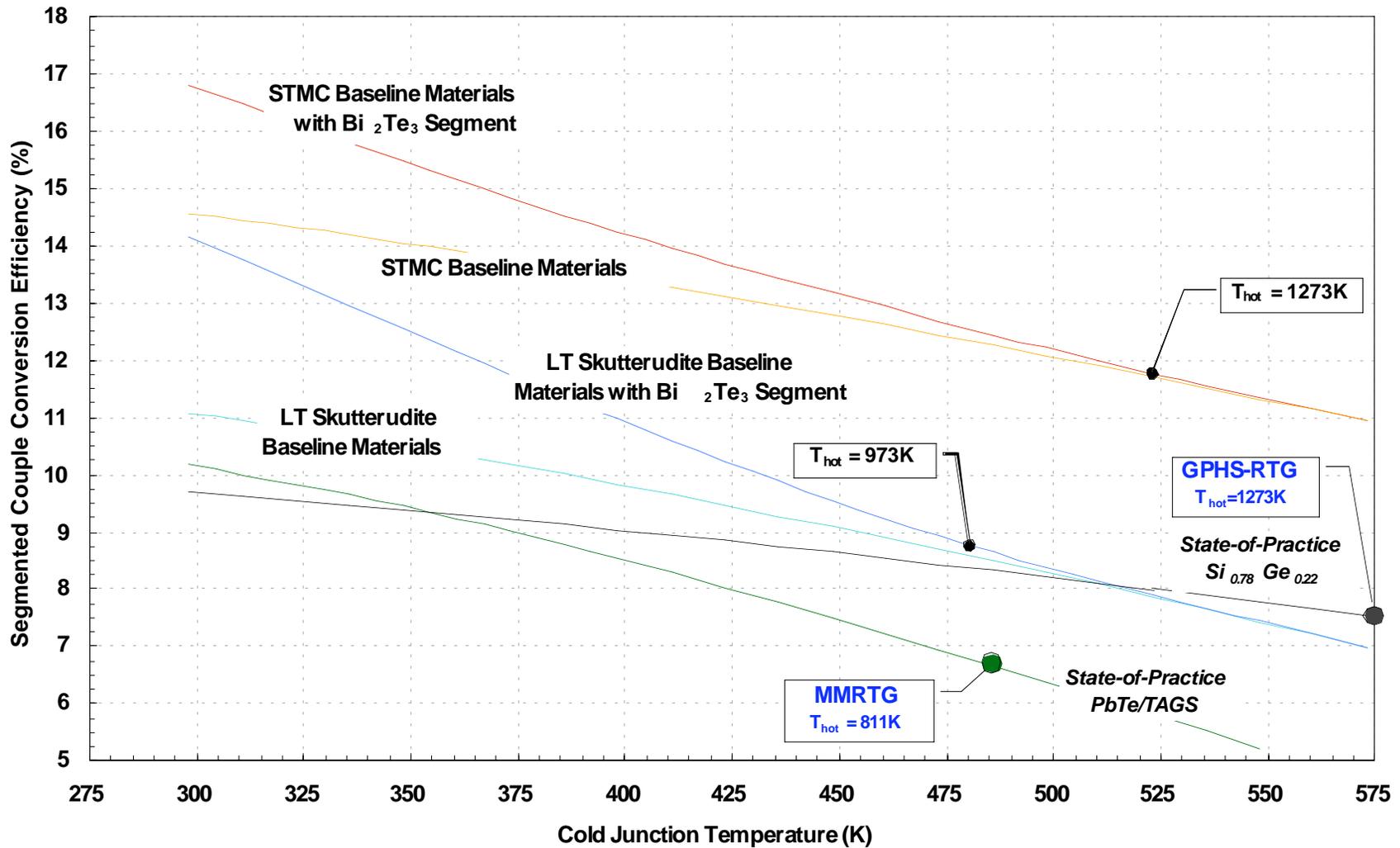
# Best TE Materials to Date



High-T materials are currently developed under STMC Task

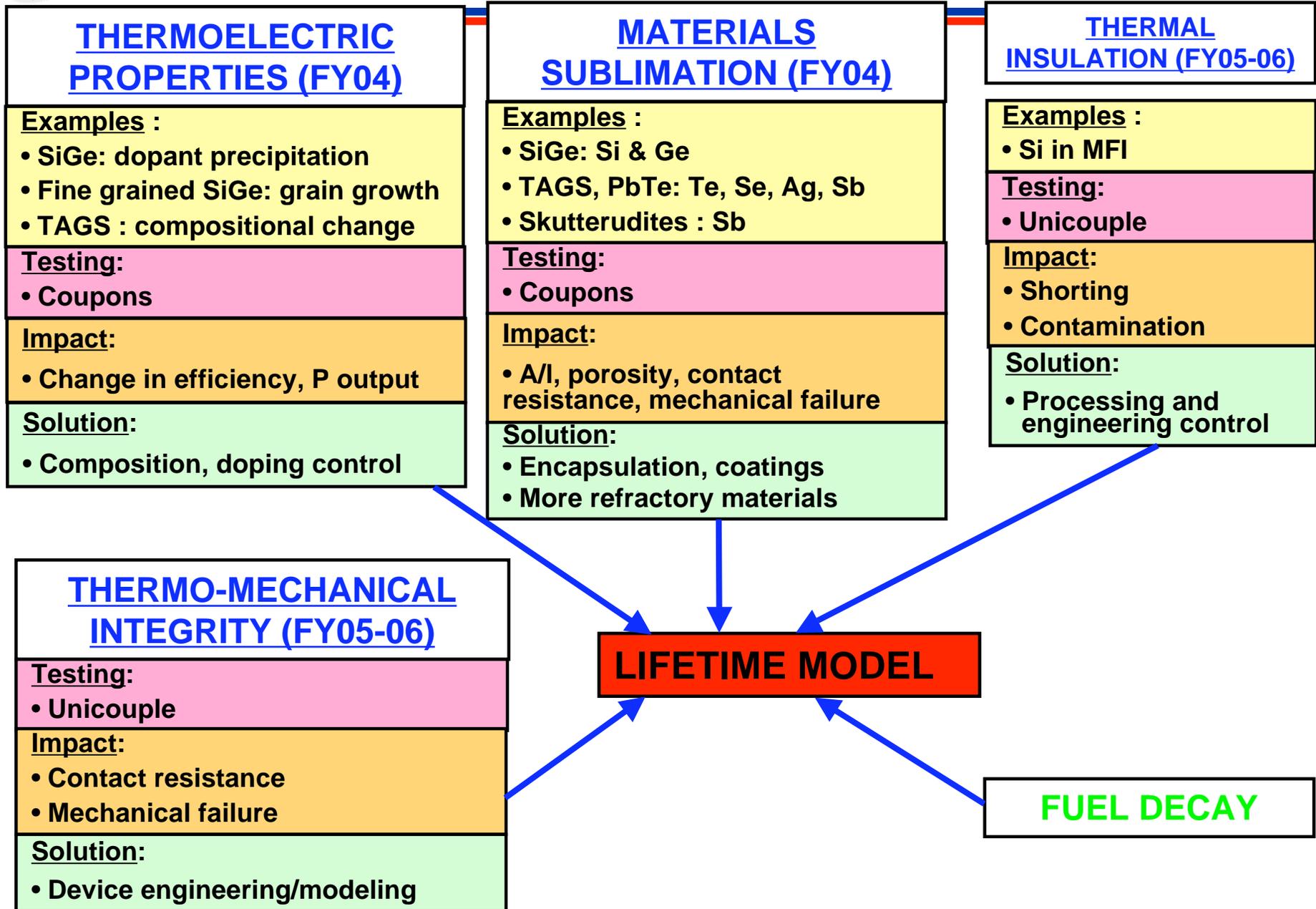


# Advanced Materials Thermoelectric Conversion Efficiency





# Lifetime performance demonstration elements





# Thermoelectric materials sublimation

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- Sublimation is the loss of volatile species in TE materials at or near hot-junctions of unicouples
- Rate is temperature and material dependent (different chemical bonding)
- Sublimation can result in life time issues:
  - ◆ **Electrical Resistance Increase**
    - Cross-sectional area reduction over time for congruent sublimation
  - ◆ **Change in uncouple performance**
    - Dissociation of TE materials into different compounds
    - Example  $\text{CoSb}_3 \rightarrow \text{CoSb}_2 \rightarrow \text{CoSb}$  as a result of Sb losses
  - ◆ **Electrical and Thermal shorting**
    - Sublimation products can condense on the cold-side of the unicouples and/or in the insulation between the legs, potentially forming electrical and thermal shorts



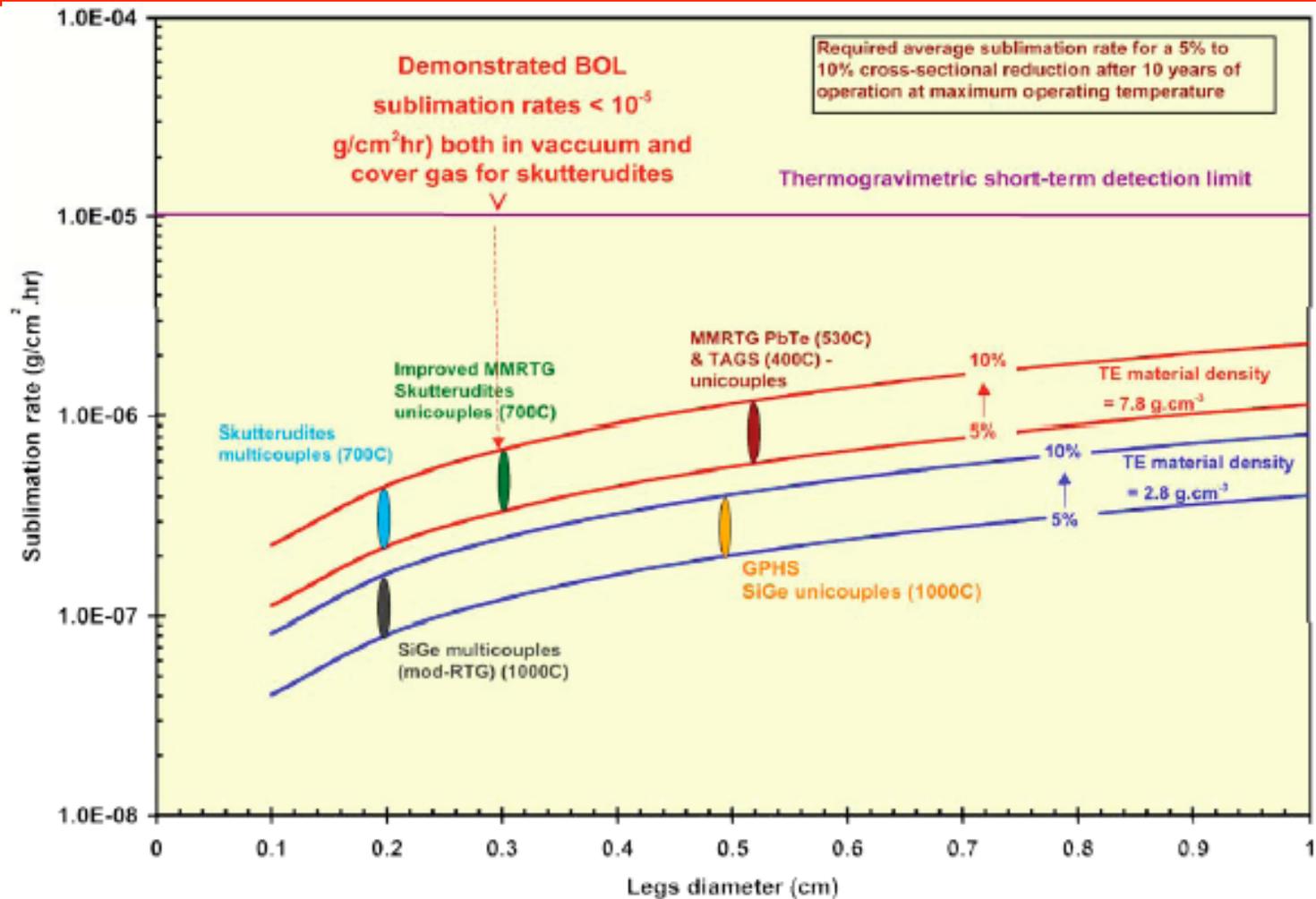
## High-temperature TE materials sublimation rates

Uncoated TE material: beginning of life sublimation rate at operating temperature (g/cm <sup>2</sup> hr)	
TAGS at 675K	~ 4.7 × 10 <sup>-2</sup>
PbTe at 800K	~ 1.1 × 10 <sup>-1</sup>
Low Temperature n-Skutterudites at 975K	~ 2.15 × 10 <sup>-2</sup>
Low Temperature p-Skutterudites at 975K	~ 1.40 × 10 <sup>-3</sup>
High-Temperature n-Skutterudites at 1175K	~ 1.62 × 10 <sup>-2</sup>
High-Temperature p-Skutterudites at 1175K	~ 1.05 × 10 <sup>-2</sup>
Chevrels (M <sub>x</sub> Mo <sub>6</sub> Se <sub>8</sub> ) at 1275K	~ 3.66 × 10 <sup>-3</sup>
P-type Zintl at 1275K	~ 4.04 × 10 <sup>-3</sup>
LaYbTe <sub>x</sub> at 1275K	~ 2.11 × 10 <sup>-4</sup>
SiGe at 1275K	~ 4.80 × 10 <sup>-5</sup>

- BOL sublimation rates in dynamic vacuum do not meet requirements for any of the bare TE materials
- Sublimation control techniques/materials are required and have been successfully developed for state of practice TE materials for over 20 years of operation



## Sublimation rates for skutterudites



- Demonstrated BOL sublimation rates  $< 10^{-5} \text{ g}/\text{cm}^2 \cdot \text{hr}$  both in vacuum (with metallic foil) and argon atmosphere (aerogel + 0.1 atm. Ar) ;comparable with other PbTe/TAGS at BOL
- Initiated life testing to determine rates over long period of time



## Conclusions and Future Work

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### ■ Conclusions

- ◆ Developed first generation 1000K-300K skutterudite-based unicouples and multicouples with 14% efficiency demonstrated; initiated life testing
- ◆ Identified 1275K-1000K high-temperature materials for integration into 2nd generation of segmented devices with the potential for achieving 17% conversion efficiency

### ■ Future work

- ◆ Continue life time studies for 1000K skutterudite materials, unicouples, and bond stability to validate lifetime operation up to 15 years
- ◆ Design and fabrication of four couple modules to facilitate technology insertion into advanced RTG
- ◆ Conduct performance testing of multicouple (Scheduled to start late June 2005)
- ◆ Further optimize 975K-375K skutterudite materials
- ◆ Continue development of high temperature materials (properties optimization, thermal stability and coatings development)
- ◆ Integration of high-temperature materials into high-T multicouples (up to 1300K)

### ■ Acknowledgements

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- ◆ Collaborators: Caltech, Boeing/Rocketdyne, Teledyne Energy Systems, University of Michigan, Michigan State University, University of South Florida, University of California at Davis, Clemson University, Princeton, University, Cornell University, University of Southern California, University of New Mexico