Use of the Compatibility Factor to Select Materials for Efficient Segmented and Cascaded Thermoelectric Generators

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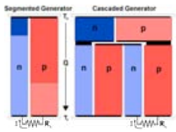
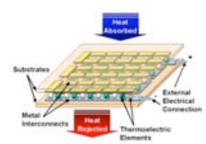
DARPA, ONR



THERMOELECTRICS



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Segmented Design

$$\eta \approx \frac{\Delta T}{T_h}\,\frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+1}$$

Use Largest Temperature Difference

- Maximize Carnot $\Delta T/T_h$
- 1200K to 300K for RTG

Interface Temperature Design

- Where zT cross
  - z is only *materials* parameter considered
- Adjusted with relative lengths l
  - $\Delta T \propto l/\kappa$

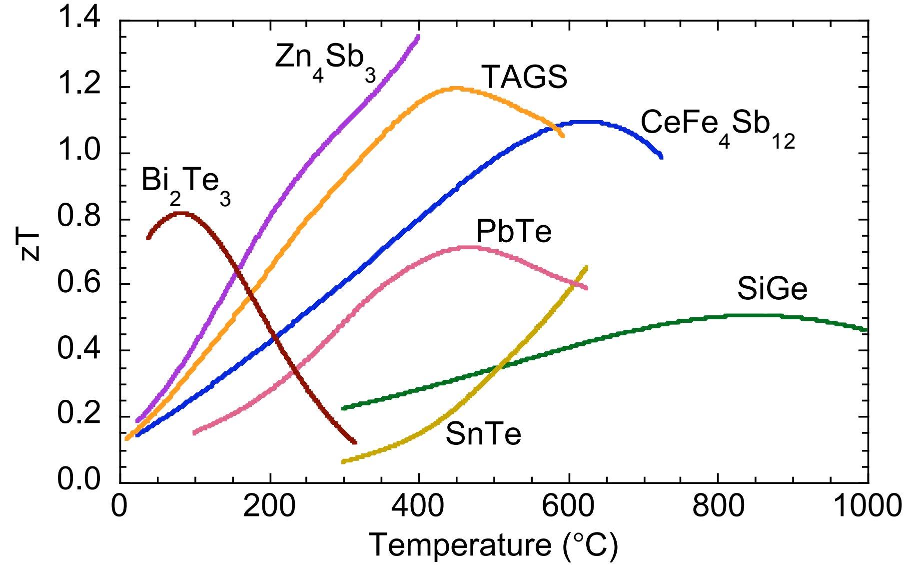
High Temperature Region

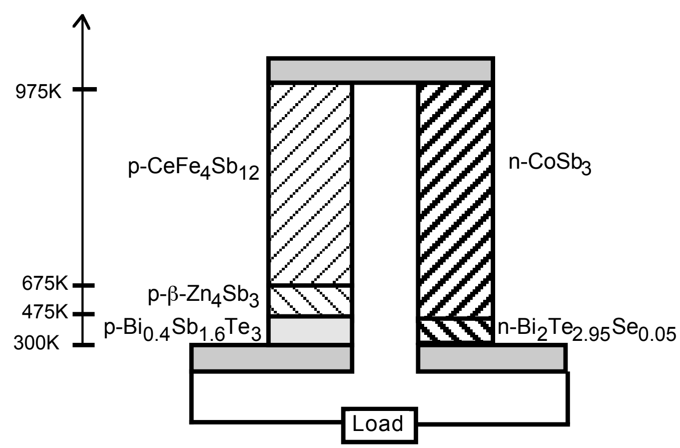
> 700°C Skutterudites

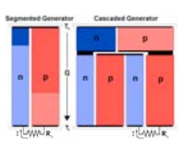
> 525°C TAGS

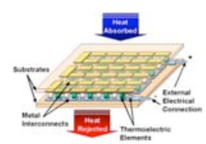
SiGe alloys have highest zT

Should be included in segmentation ?









Compatibility

Efficiency depends on reduced current, u

Just like the Power curve

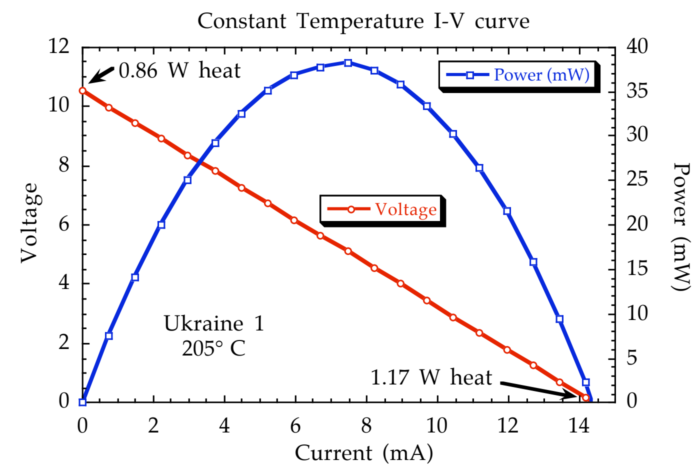
- Current draw gives IR drop
- $\eta = P/Q_{in}$

η maximum at specific reduced current (u)

$u = I/Q_c$

Best u at compatibility factor s

$$s = \frac{\sqrt{1 + zT} - 1}{\alpha T}$$

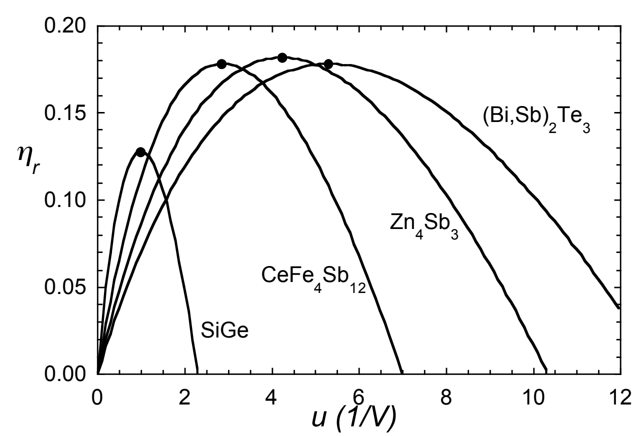


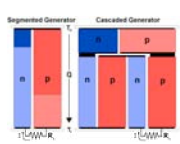
SiGe Requires different u compared with other TE materials

- Different s => not compatible

Goal

- High zT
  - Determines efficiency at $u = s$
- Compatible s
  - Within about a factor of 2





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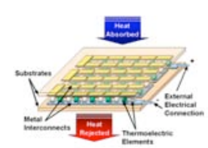

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Improved Segmented TAGS

TAGS has high zT - stable to 525°C

10.45% efficiency

n-PbTe stable to 600°C

525°C to 600°C p-type segment needed

p-PbTe has highest zT (before skutterudites)

But not compatible ($s_{PbTe} < 2\ s_{TAGS}$)

10.33% efficiency ***decrease***

p-SnTe has low zT, and some compatibility

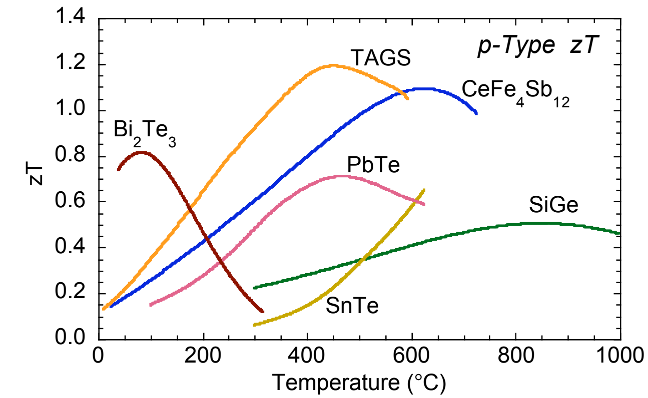
$s_{SnTe} \geq 2\ s_{TAGS}$

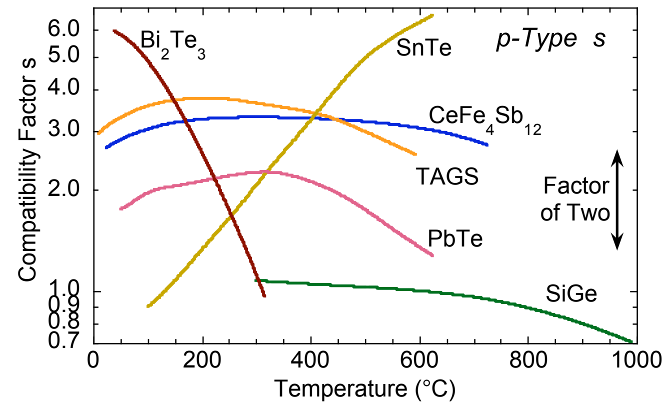
11.09% small efficiency increase

p-Skutterudite has high zT, *and compatibility*

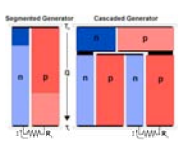
11.87% large efficiency increase

13.56% for 700°C hot side





Material	*Efficiency (%)*	*T_c (C)*	*$T_{Interface}$ (C)*	*T_h (C)*	*$u(T_c)$ (V^{-1})*
p-TAGS	10.45	100		525	2.97
p-TAGS/PbTe	10.33	100	525	600	2.33
p-TAGS/SnTe	11.09	100	525	600	2.84
p-TAGS/$CeFe_4Sb_{12}$	11.87	100	525	600	2.94
p-TAGS/$CeFe_4Sb_{12}$	13.56	100	525	700	2.88



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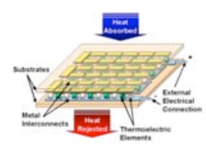


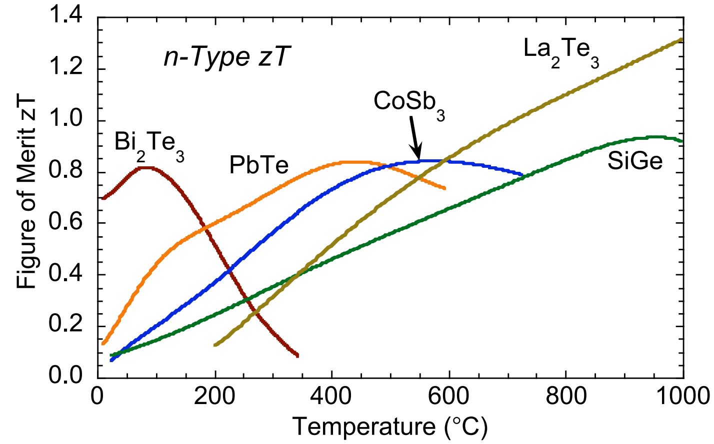
High Temperature High Efficiency

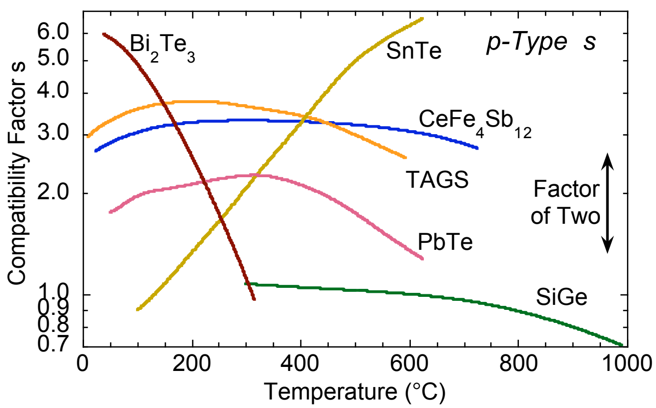
Segmented n-type can go to 1000°C

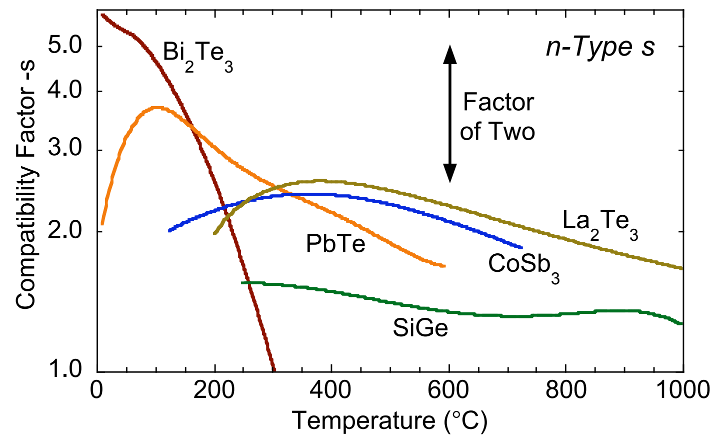
- 13.76% Efficiency with n-SiGe
  - Some compatibility
- 15.56% Efficiency with La_2Te_3
  - Good compatibility, high *zT*

Problem: no compatible p-type

- p-SiGe *lowers* efficiency







Material	*Efficiency (%)*	T_c *(C)*	T_{Int} *(C)*	T_h *(C)*	$u(T_c)$ *(V^{-1})*
n-PbTe	**9.87**	**100**		**600**	**-2.00**
n-PbTe/SiGe	**13.76**	**100**	**600**	**1000**	**-1.46**
n-PbTe/La_2Te_3	**15.56**	**100**	**600**	**1000**	**-1.80**
n-SiGe	**5.44**	**600**		**1000**	**-1.29**

p-Type Material Needed

Must have high temperature p-Type

To utilize high n-type efficiency

Must have high *s*

Otherwise will decrease efficiency

$s \approx z/2\alpha$

Must have appreciable zT (0.5)

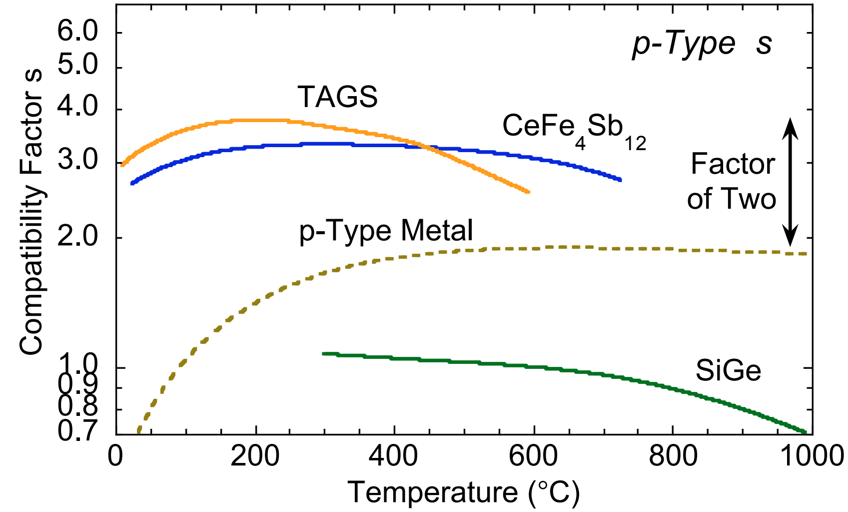
But *not* particularly high α

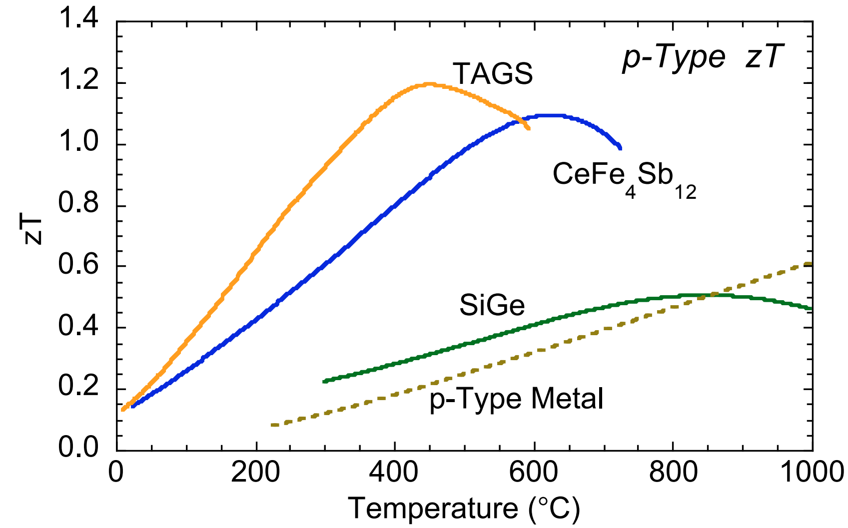
No large band gap semiconductors

SiGe

No small polaron conductors

Boron Carbides



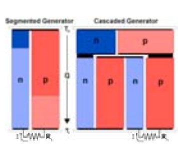


Require p-type Metal

$\kappa \approx \kappa_e = LT/\rho$ (Wiedemann Franz)

With good thermopower

$\alpha > 100\mu V/K$ at 1000K



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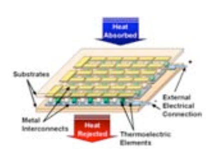

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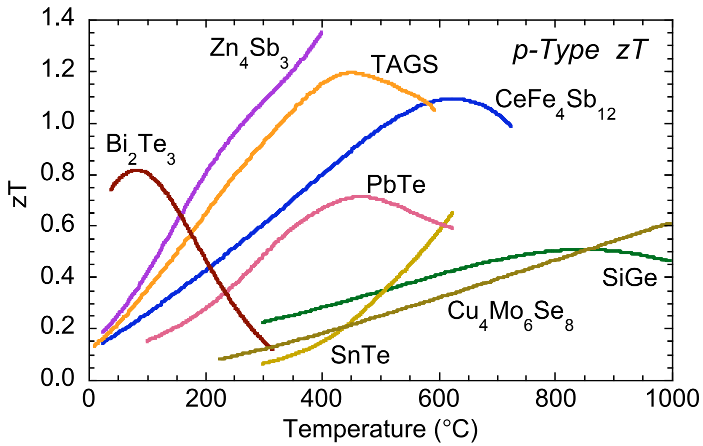
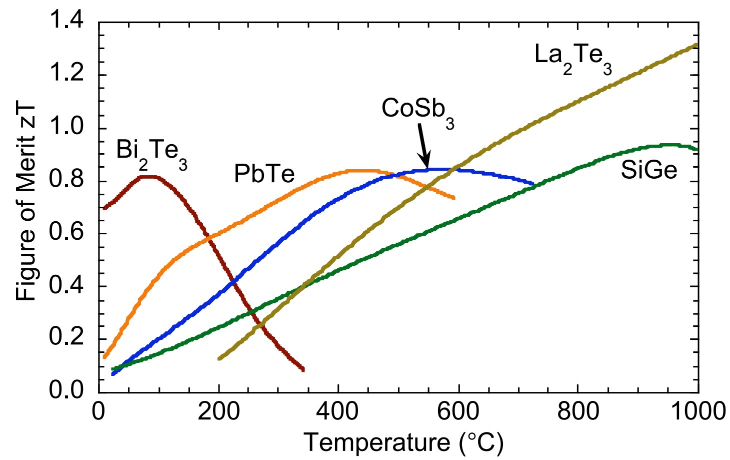
Fully Segmented Generator





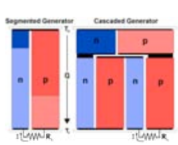
P-Element

$Cu_4Mo_6Se_8$	(to 1000° C)
$CeFe_4Sb_{12}$	(to 700° C)
TAGS	(to 525° C)
Zn_4Sb_3	(to 400° C)
$(Bi,Sb)_2Te_3$	(25° C to 170° C)

N-Element

La_2Te_3	(to 1000° C)
$CoSb_3$	(to 600° C)
PbTe	(to 480° C)
Bi_2Te_3	(25° C to 190° C)

18.1 % Generator Efficiency (25°C to 1000° C)



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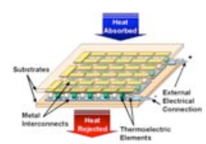

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Progress Status of Skutterudite-Based Segmented Thermoelectric Technology Development

2004 DOE High Efficiency Thermoelectric Workshop

T. Caillat, J. Sakamoto, L. Lara, A. Jewell, A.Kisor

Jet Propulsion Laboratory/California Institute of Technology

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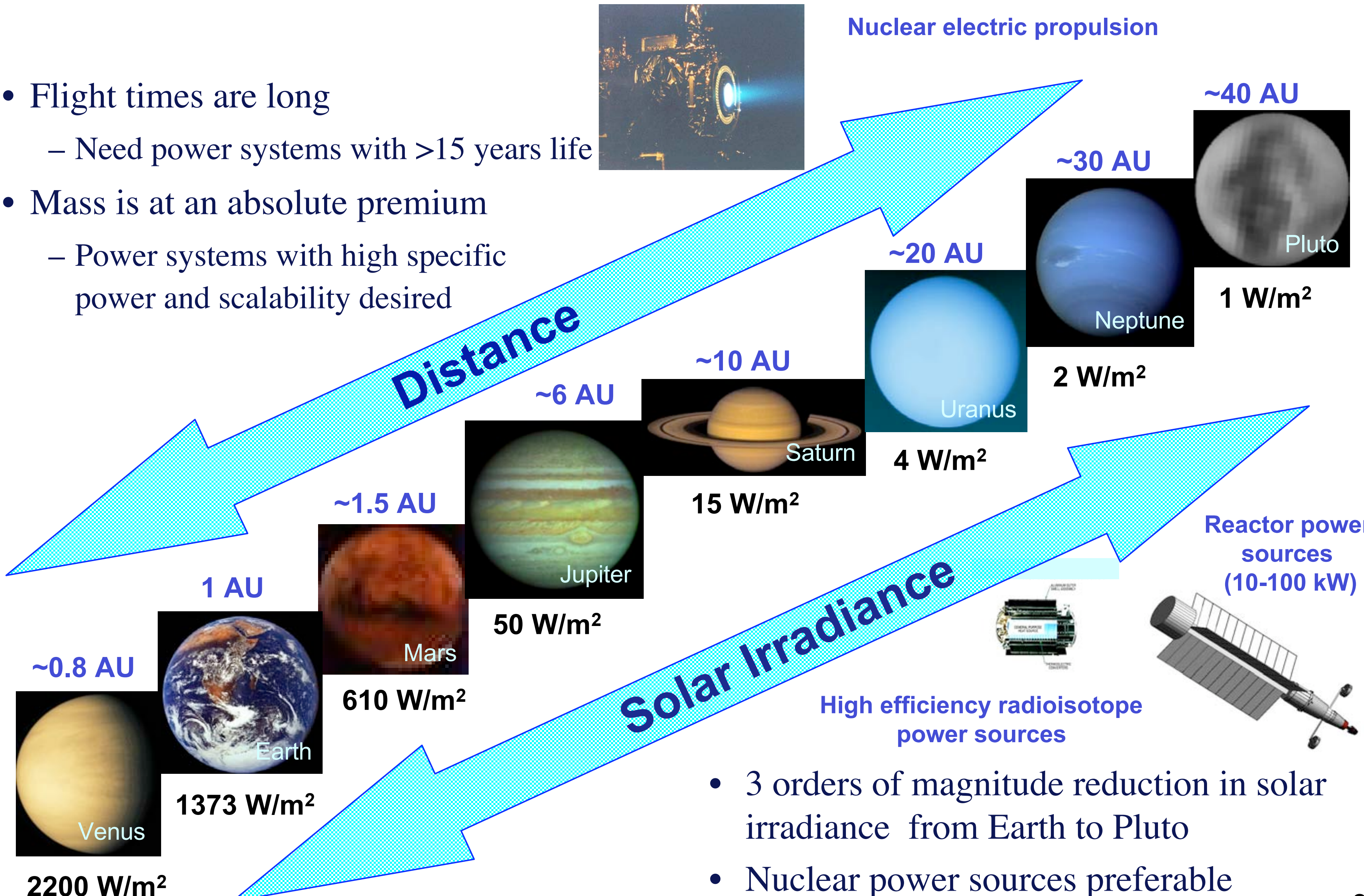
Power Technology

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



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

Advanced Radioisotope Power Systems (APRS) for NASA missions

- **Overall objective:**

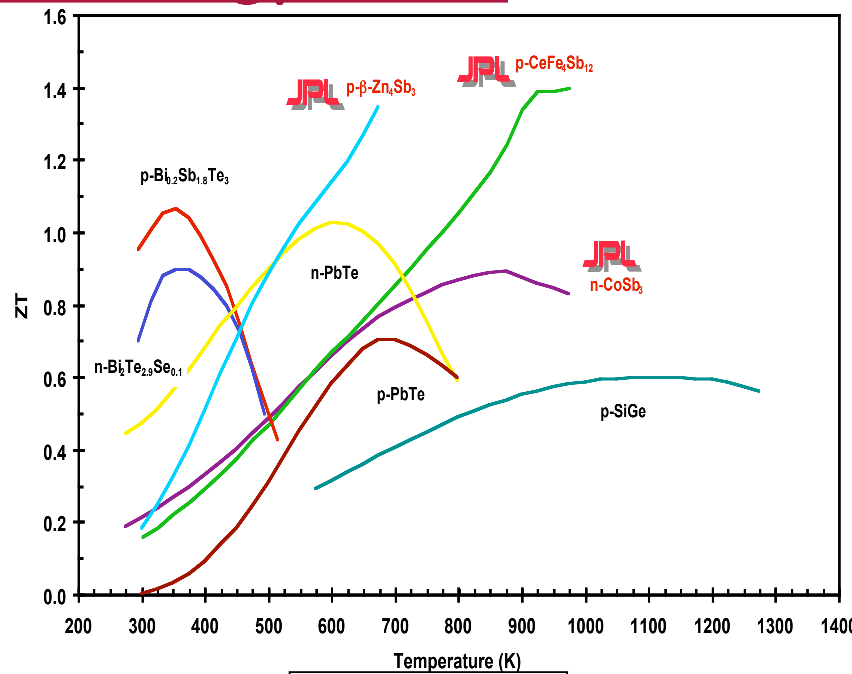
  Develop low mass, high efficiency, low-cost Advanced Radioisotope Power System with double the Specific Power and Efficiency over state-of-the-art radioisotope thermoelectric generators (RTGs)

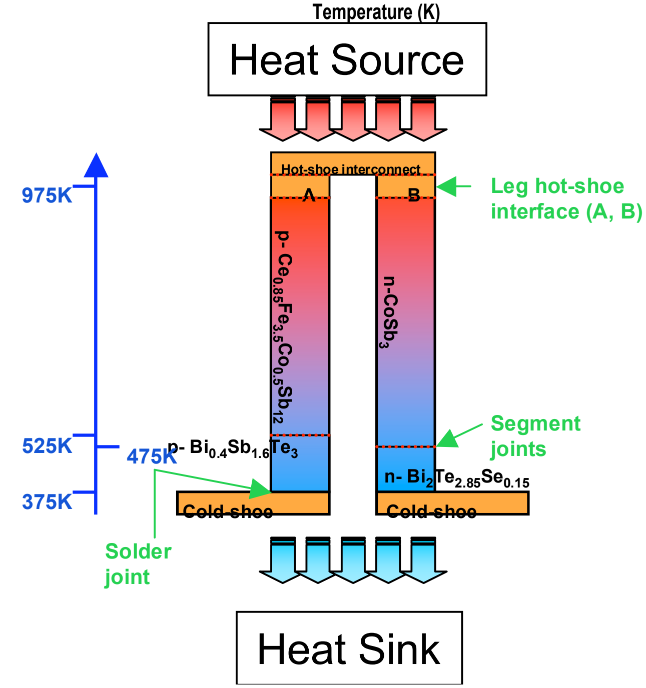
Segmented Thermoelectric Technology (STE)

- **New high ZT materials**
  - Development initiated in 1991 and supported by ONR and DARPA (Skutterudites and Zn_4Sb_3)
  - Substantial increase in efficiency over state-of-the-art
- **Segmented unicouples**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials (Bi_2Te_3-based materials) and new, high ZT materials developed at JPL
    - Skutterudites : $CeFe_4Sb_{12}$ and $CoSb_3$
    - Zn_4Sb_3
  - Current new materials operation limited to ~ 975K
  - Higher average ZT values
  - ➔ Higher material conversion efficiency
    - ➔ Up to 15 % for a 300-975K temperature gradient

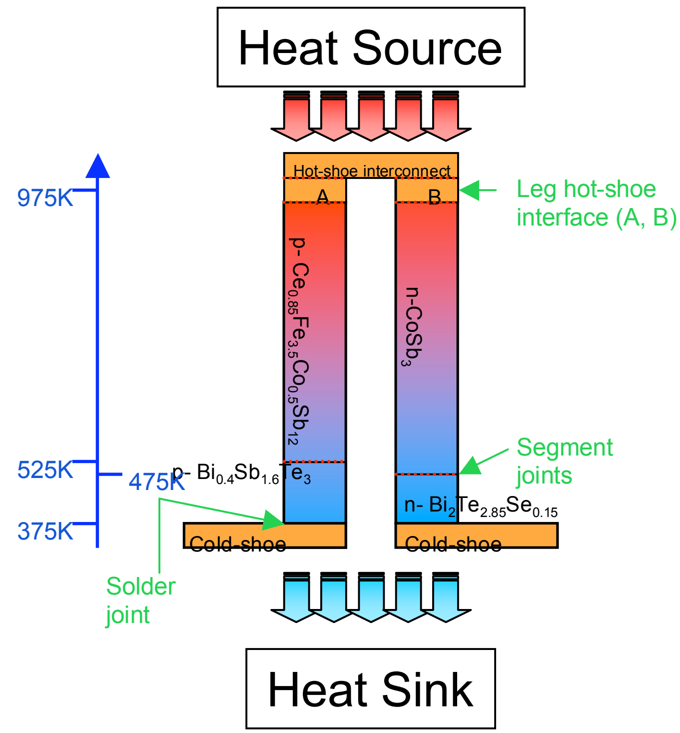
Efficiency

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





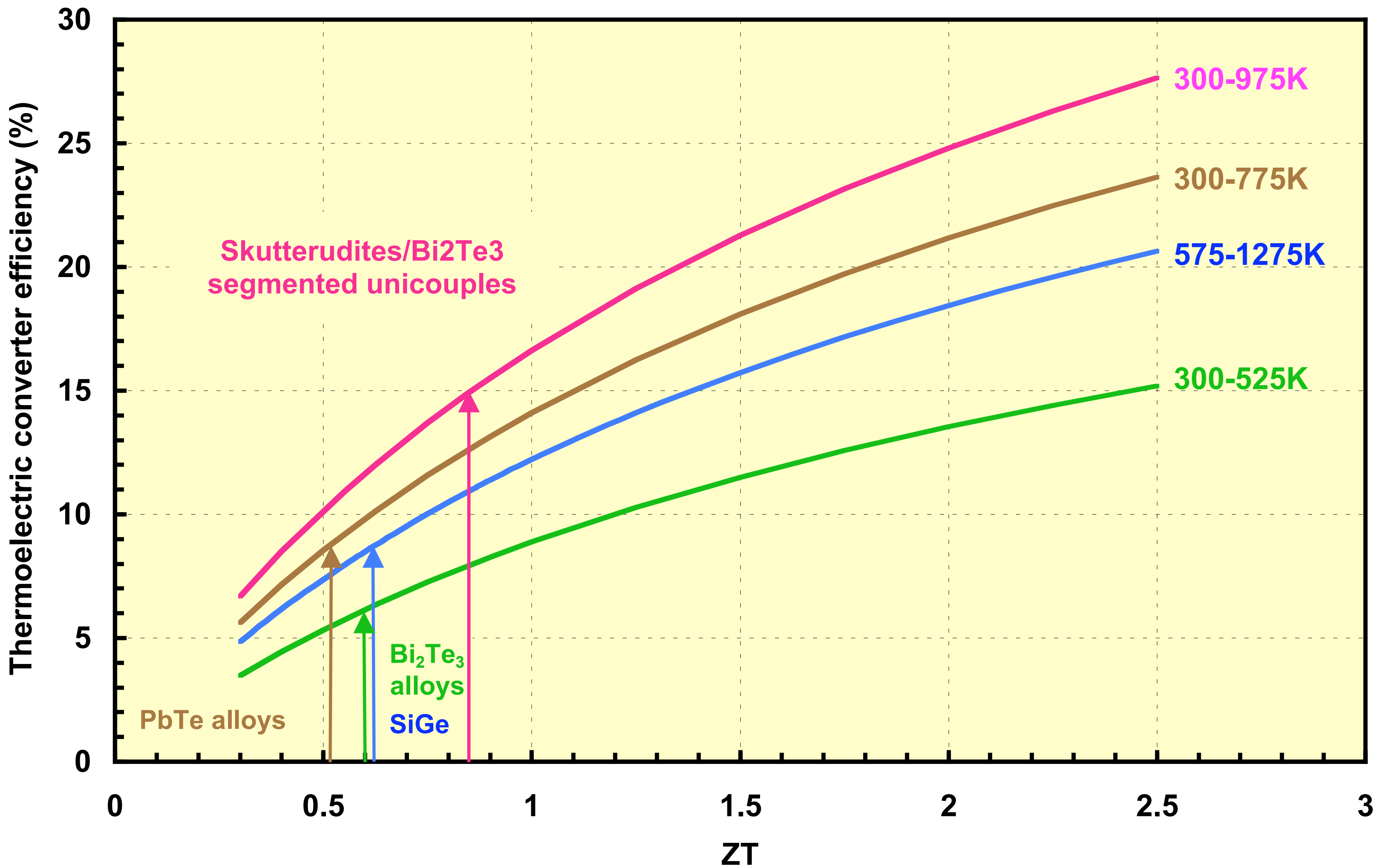
Key Technology Challenges



Key technology challenges

- **TE materials processing and segmented leg fabrication**
- **Low electrical contact resistance between segments and between segments and cold- and hot-shoes**
- **Unicouple mechanical integrity**
- **Lifetime**
  - **Sublimation control**
  - **Stable thermoelectric properties**
  - **Life time prediction model**
- **Demonstrate unicouple performance**
  - **Testing and modeling**

Converter efficiency : state-of-the-art vs. segmented thermoelectric technology

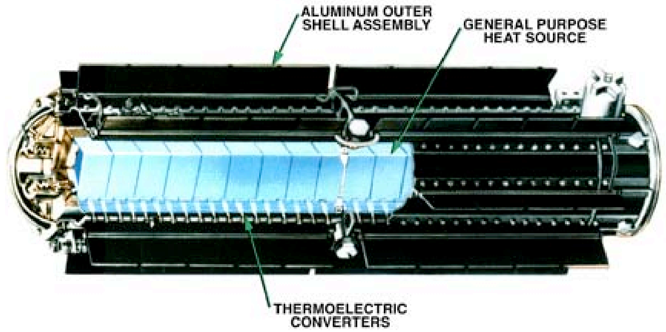


A 2x increase in efficiency over SOA thermoelectrics has been demonstrated for the STE technology

General Purpose Heat Source RTG

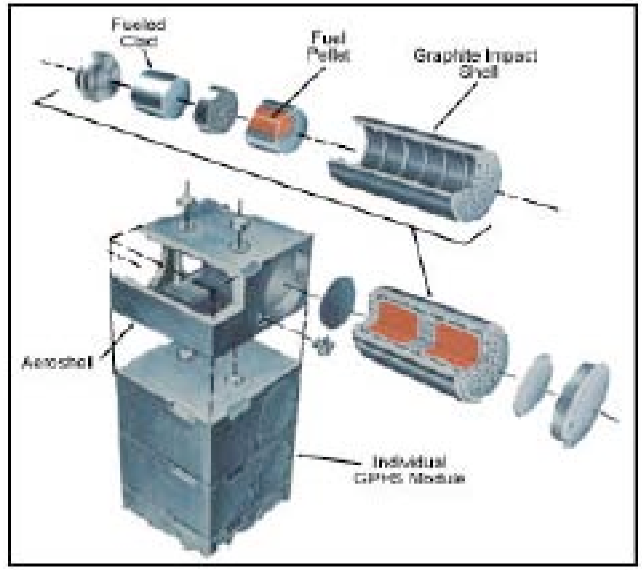
General Purpose Heat Source (GPHS)

Radioisotope Thermoelectric Generator (RTG)

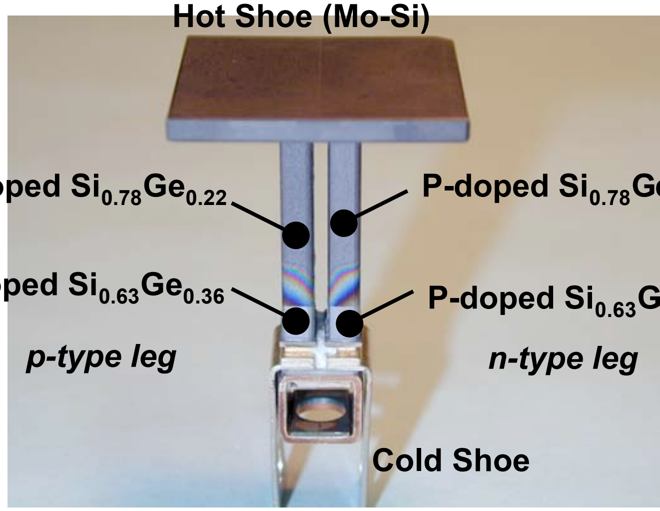


- POWER OUTPUT – 285 W(e)
- FUEL LOADING – 4400 W(t); 132,500 Ci
- WEIGHT – 124 lbs
- SIZE – 16.6 in x 44.5 in

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.



General Purpose Heat Source Module



GPHS SiGe unicouple

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_2**
Thermoelectric material	**SiGe**
Numbers of unicouples	**572**
Mass of Pu-238-g	**7,561**

STE-ARPS

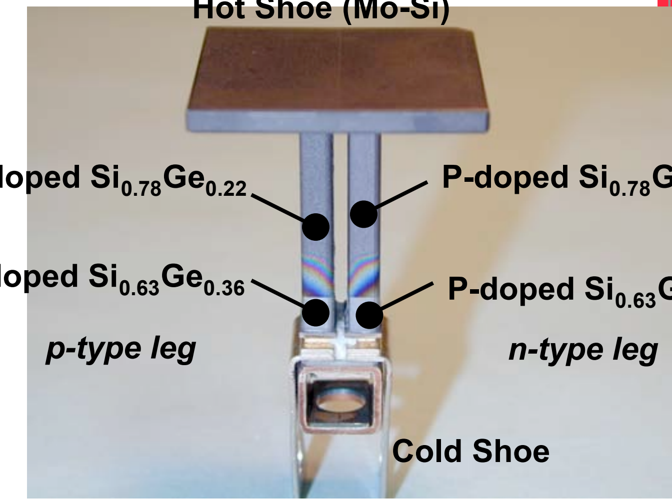
• STE-ARPS

- Would use advanced materials segmented legs
- 700 to 100°C operation
- Current GPHS-RTG unicouple design would be mostly conserved
- Modifications required to radiator fins to accommodate for lower rejection temperature
- Shorter housing

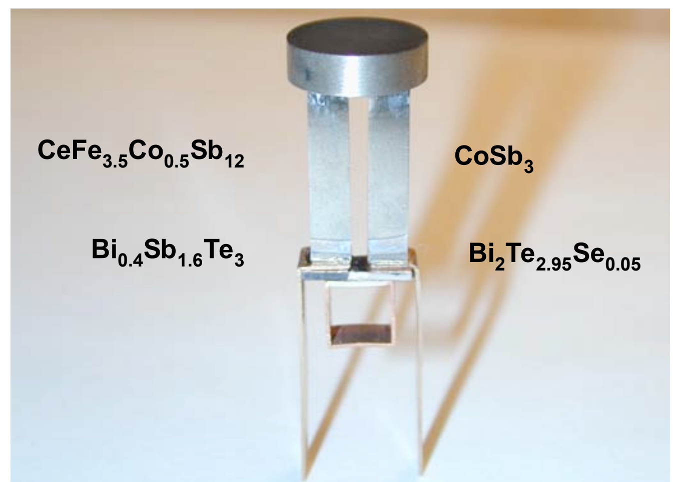
➢New segmented unicouples could “replace” unicouples almost “one for one”

• Advantages of thermoelectrics

- Flight proven, long life demonstrated
- Solid state energy conversion -> reliability, no vibration, no moving parts
- Scalable
- No single point failure
- Significant system heritage

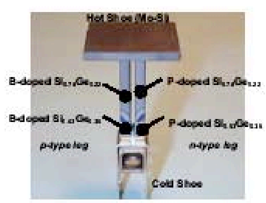
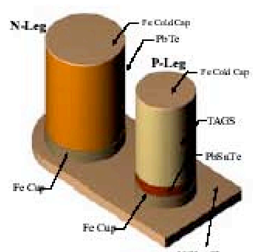
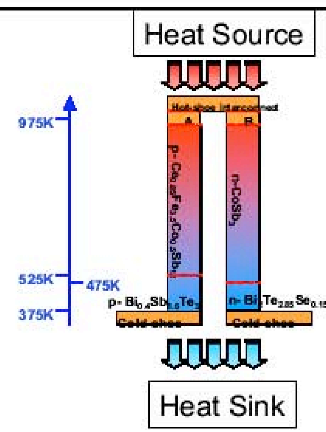
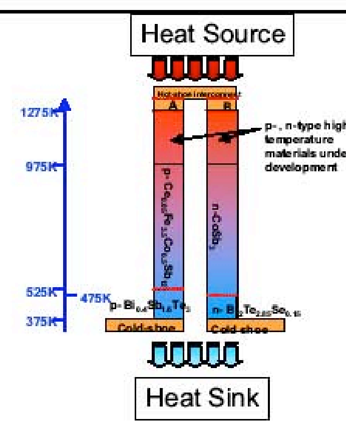


GPHS SiGe unicouple



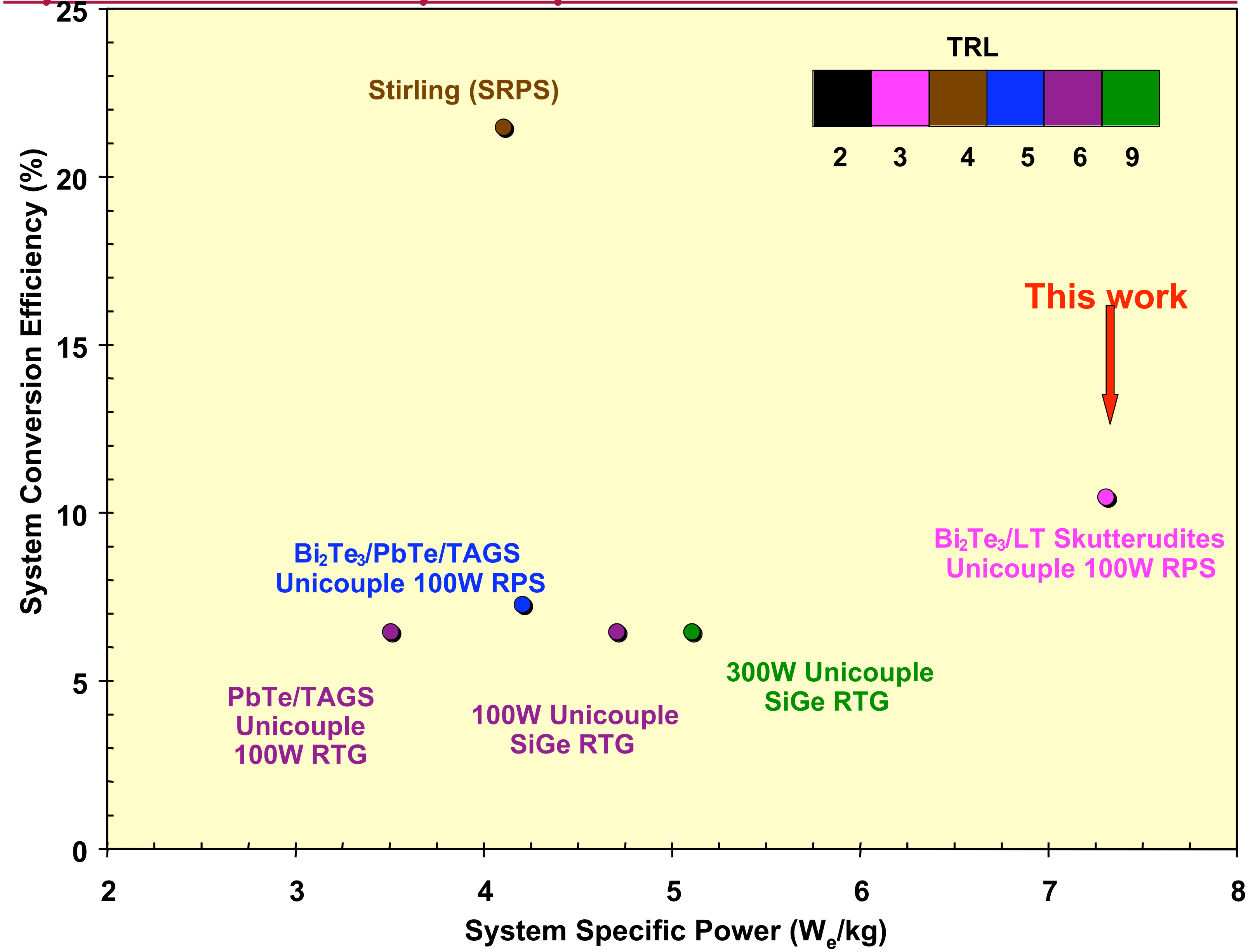
Skutterudite/Bi_2Te_3 segmented unicouples

Projected STE 100W class ARPS specifications vs. SOA

Item/Converter	SiGe-RTG	PbTe/TAGS MMRTG	Low T STE (LSTE)	High Temperature TE (HSTE)
Hot side temperature (K)	**1273**	**823**	**975**	**1200**
Cold side temperature (K)	**573**	**453**	**375**	**375**
Converter efficiency (%)	**7.2**	**7.6**	**12.5**	**14.7**
System efficiency (%)*	**6.5**	**6.4**	**11.18**	**13.3**
Thermal power (BOM)(W_{th})	2000	2000	1250	1000
Thermal efficiency (%)	85		85	85
Electrical power (BOM) (W_e)	107	110	118.8	113.0
Number of modules	**8**	**8**	**5**	**4**
Total PuO_2 mass (kg)	**5.02**	**5.02**	**3.138**	**2.51**
Total system mass estimate (kg)	**23.24**	**38.1**	**16.3**	**13.1**
- GPHs mass (kg)	11.54	12.83	7.215	5.77
- Housing (Kg)	3.1	4.2	1.90	1.55
- Radiator fins (kg)	0.45	3.32	1.7	1.36
- Converter (kg)	5.65	10	3.9	3.12
- Other structure (kg)	2.5	5.5	1.6	1.28
Specific power estimate (W_e/kg)	**4.6**	**2.88**	**7.28**	**8.64**
Unicouples				

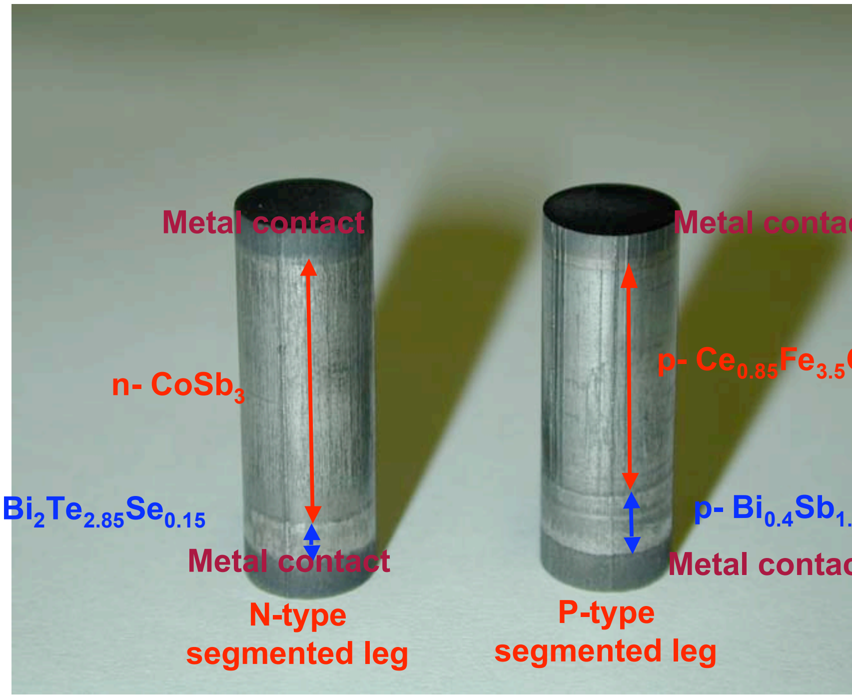
* 90% of converter efficiency

System Efficiency & Specific Power: STE vs. SOA



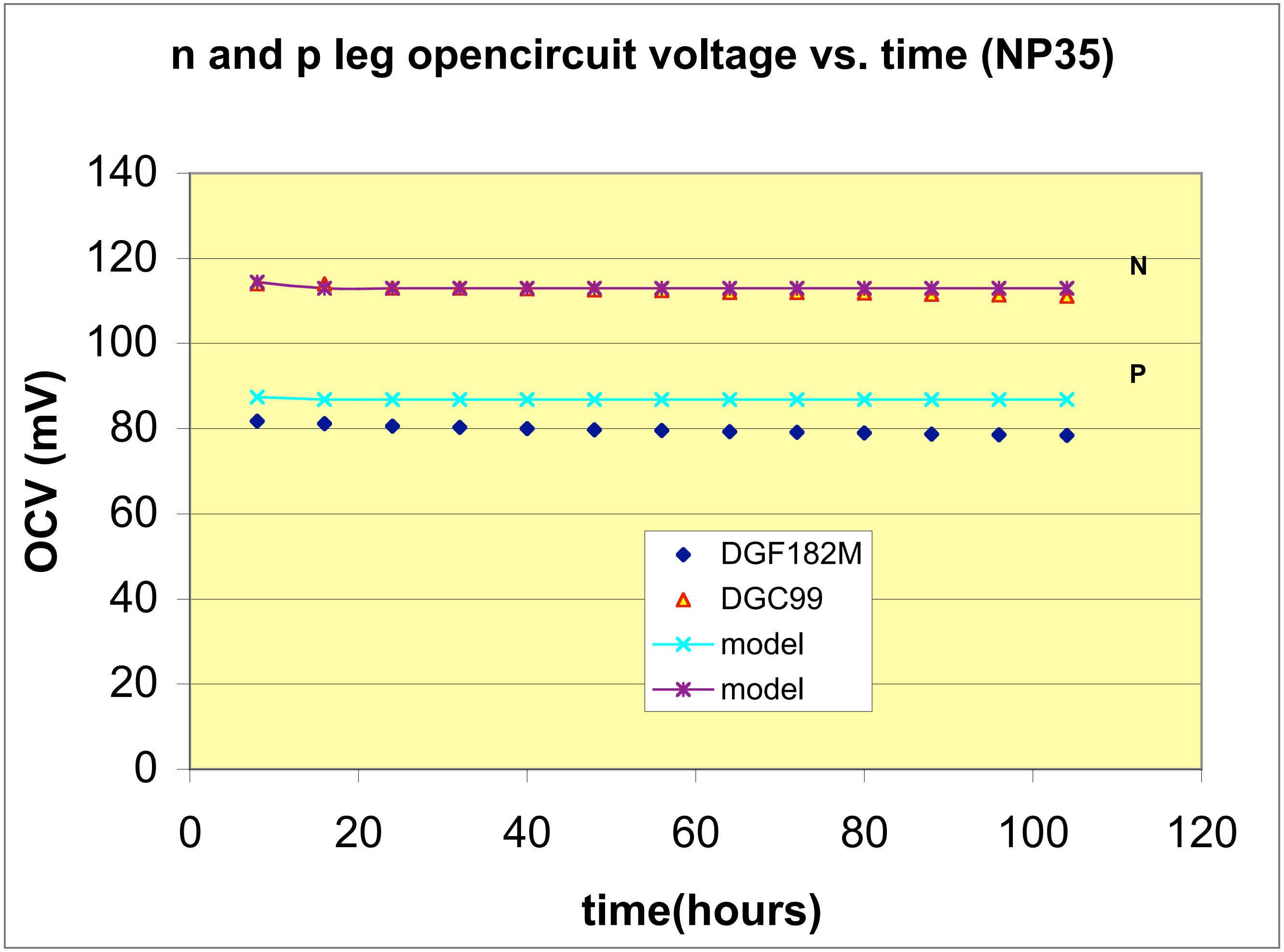
Unicouples legs

- **Developed uniaxial hot-pressing technique for legs fabrication**
  - Powdered materials stacked on the top of each other
  - Temperature optimized → density close to theoretical value
  - In graphite dies and under argon atmosphere
  - With metallic diffusion barriers between the TE materials
  - Metallic contacts at hot- and cold-side
  - Low electrical resistance bonds (<5μΩcm²) achieved ➔ negligible impact on overall unicouple performance



Unicouple legs - In-gradient testing

– **N- and p-type in gradient (975K-350K) testing of n- and p-skutterudite legs confirm model performance prediction and show little voltage decrease after ~ 100 hours of testing**

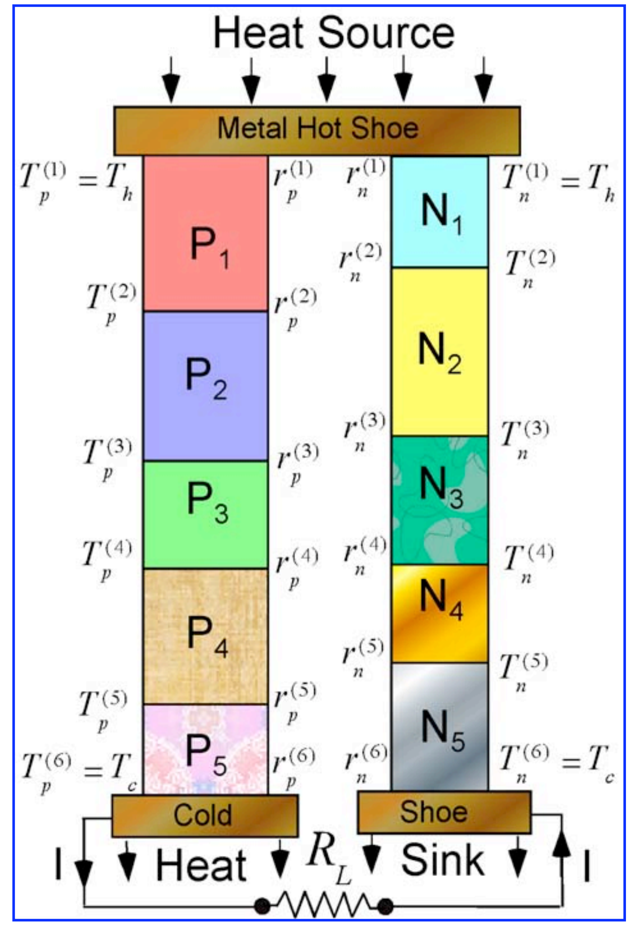


1-D Analytical Model of Segmented Thermoelectric Unicouples

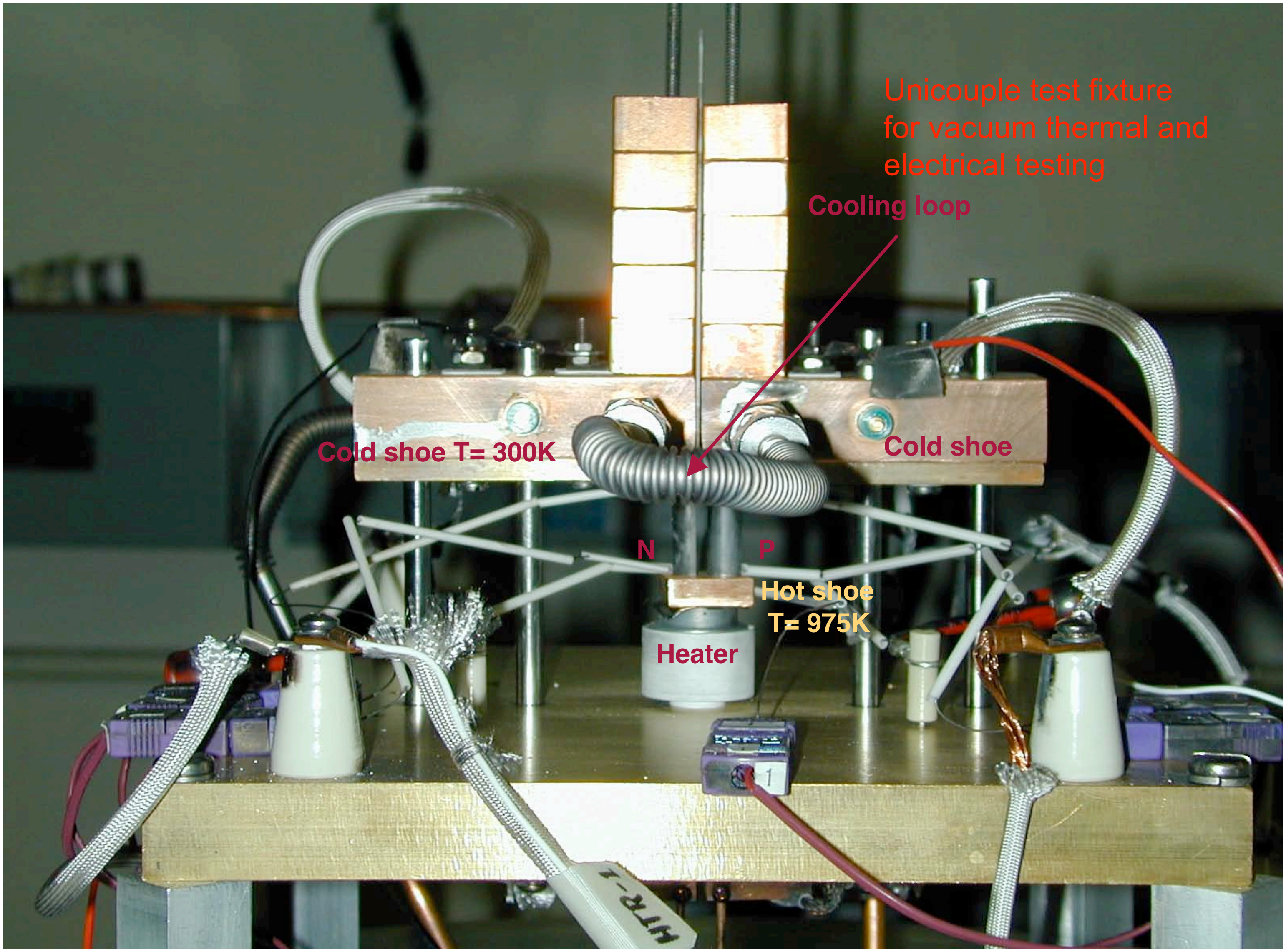
– One-dimensional analytical model of STEs, with up to 5 segments per leg, is coupled to a *genetic algorithm* for maximizing either electrical power of efficiency

– **Input:**
  - TE materials properties
  - Total length and composition of n- and p-legs
  - Cross sectional area of the p-leg (or the n-leg)
  - Hot and cold shoe temperatures
  - Total contact resistance per leg

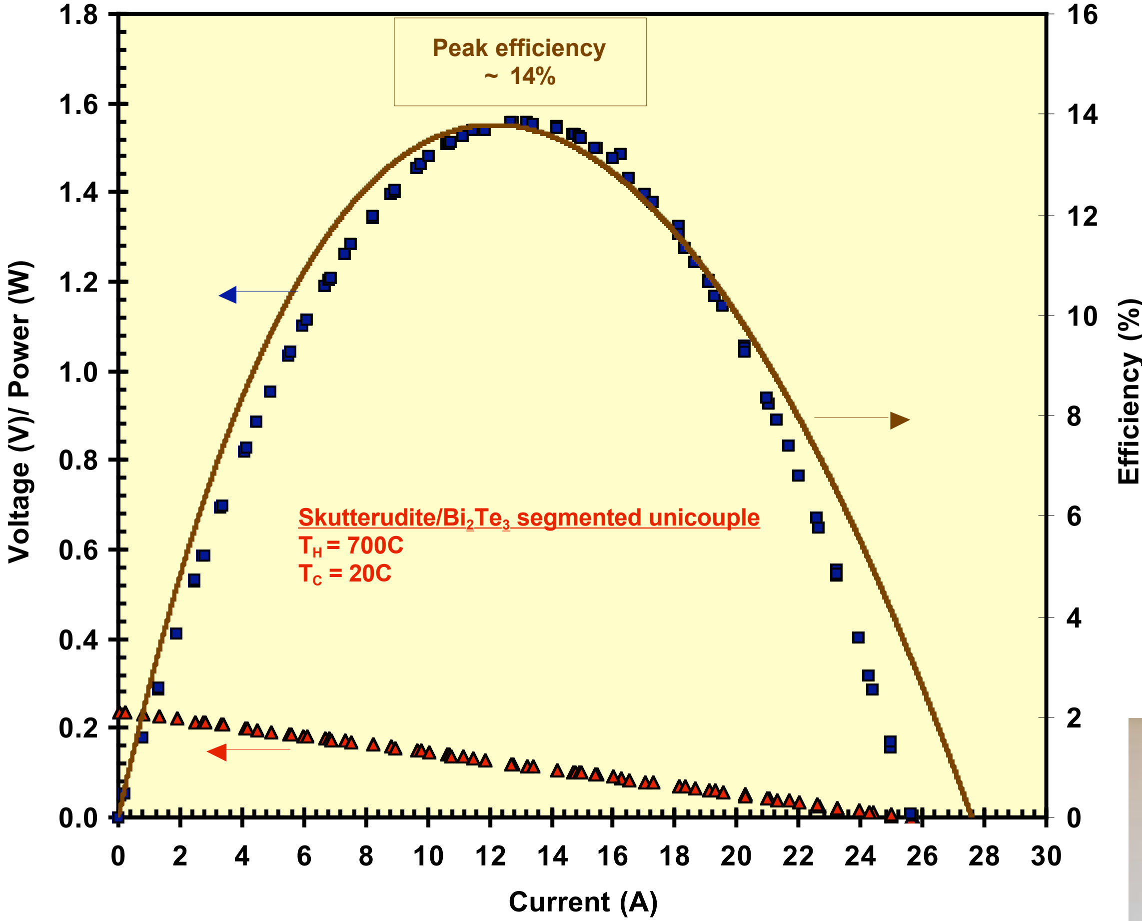
– **Output**
  - Number of needed segments in n- and p-legs
  - Interface temperatures between various segments
  - Lengths of various segments in n- and p-legs
  - Cross sectional area of n-leg and p-legs
  - Electrical power and conversion efficiency curves
  - Operation I-V characteristics

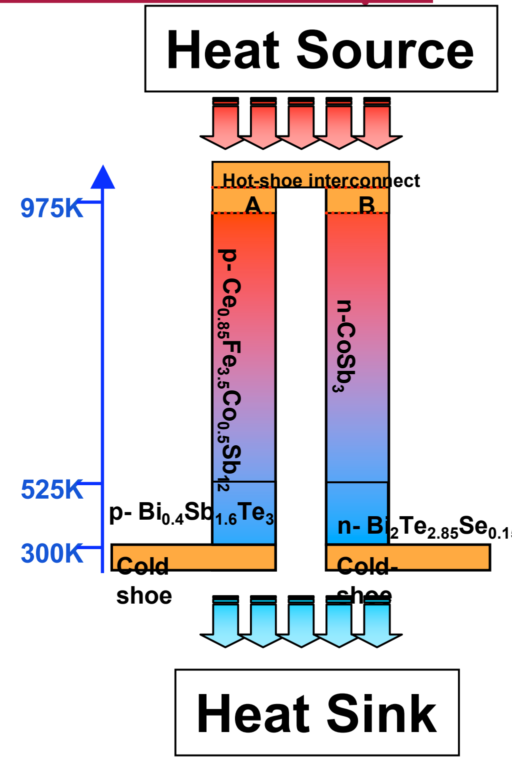


Unicouple thermal and electrical testing



Thermal and electrical testing - Segmented unicouple

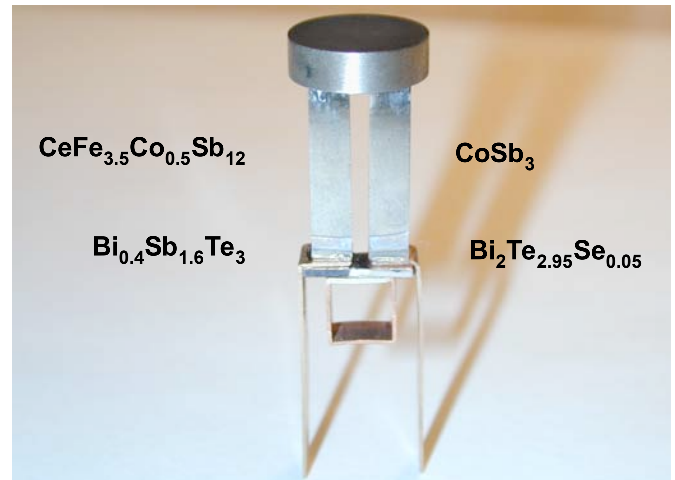




- **Achieved ~14 % efficiency for 975K-300K ΔT**
  - **For fully segmented unicouple**

➔ **Translate into 12.5% efficiency for 975K-375K ΔT**

- **Fully validate projected efficiency performance**



Skutterudite/Bi_2Te_3 segmented unicouples

Lifetime performance testing and modeling development

THERMOELECTRIC PROPERTIES (FY04)

Examples :
- SiGe: dopant precipitation
- Fine grained SiGe: grain growth
- TAGS : compositional change

Testing:
- Coupons

Impact:
- Change in efficiency, P output

Solution:
- Composition, doping control

MATERIALS SUBLIMATION (FY04)

Examples :
- SiGe: Si & Ge
- TAGS, PbTe: Te, Se, Ag, Sb
- Skutterudites : Sb

Testing:
- Coupons

Impact:
- A/I, porosity, contact resistance, mechanical failure

Solution:
- Encapsulation, coatings
- More refractory materials

THERMAL INSULATION (FY05-06)

Examples :
- Si in MFI

Testing:
- Unicouple

Impact:
- Shorting
- Contamination

Solution:
- Processing and engineering control

THERMO-MECHANICAL INTEGRITY (FY05-06)

Testing:
- Unicouple

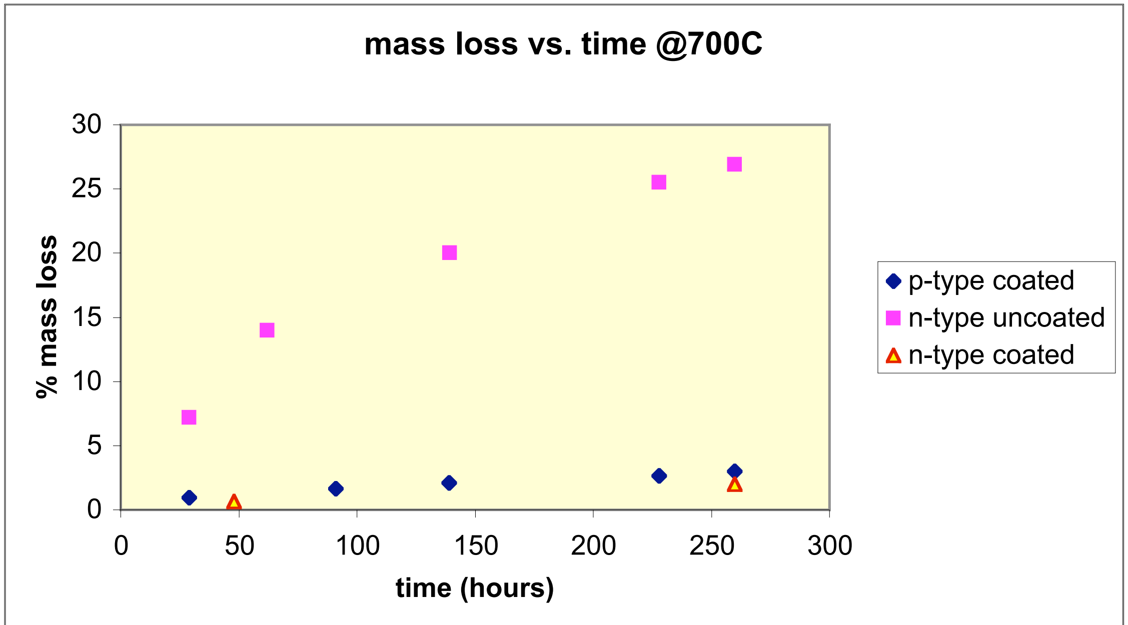
Impact:
- Contact resistance
- Mechanical failure

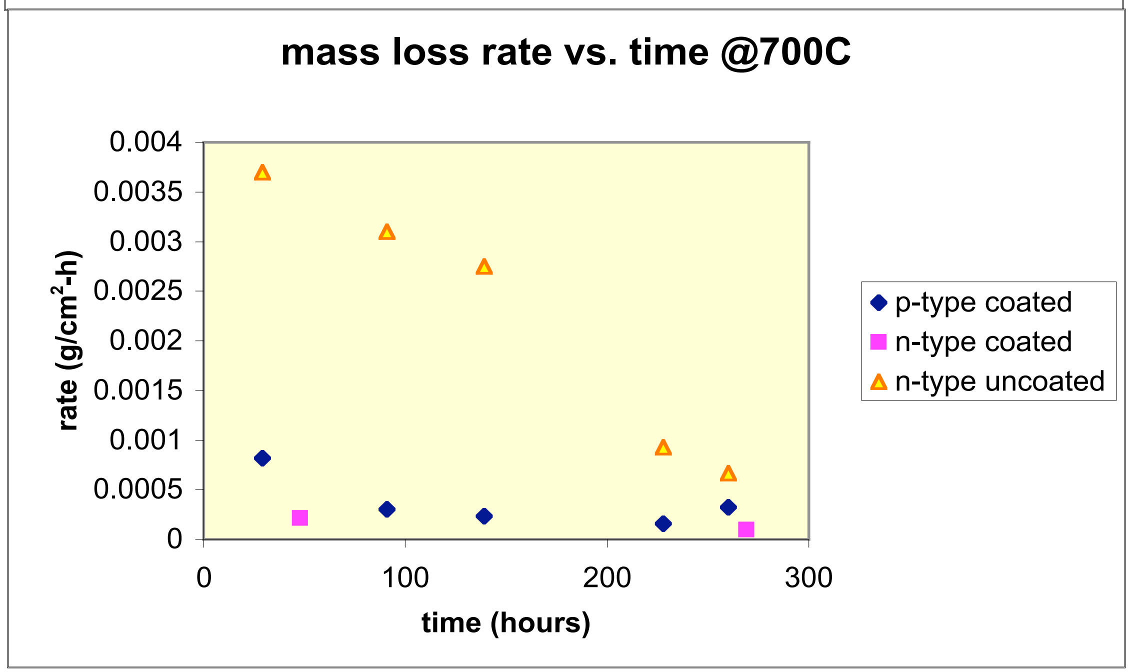
Solution:
- Device engineering/modeling

FUEL DECAY

LIFETIME MODEL

Mass loss experiments results

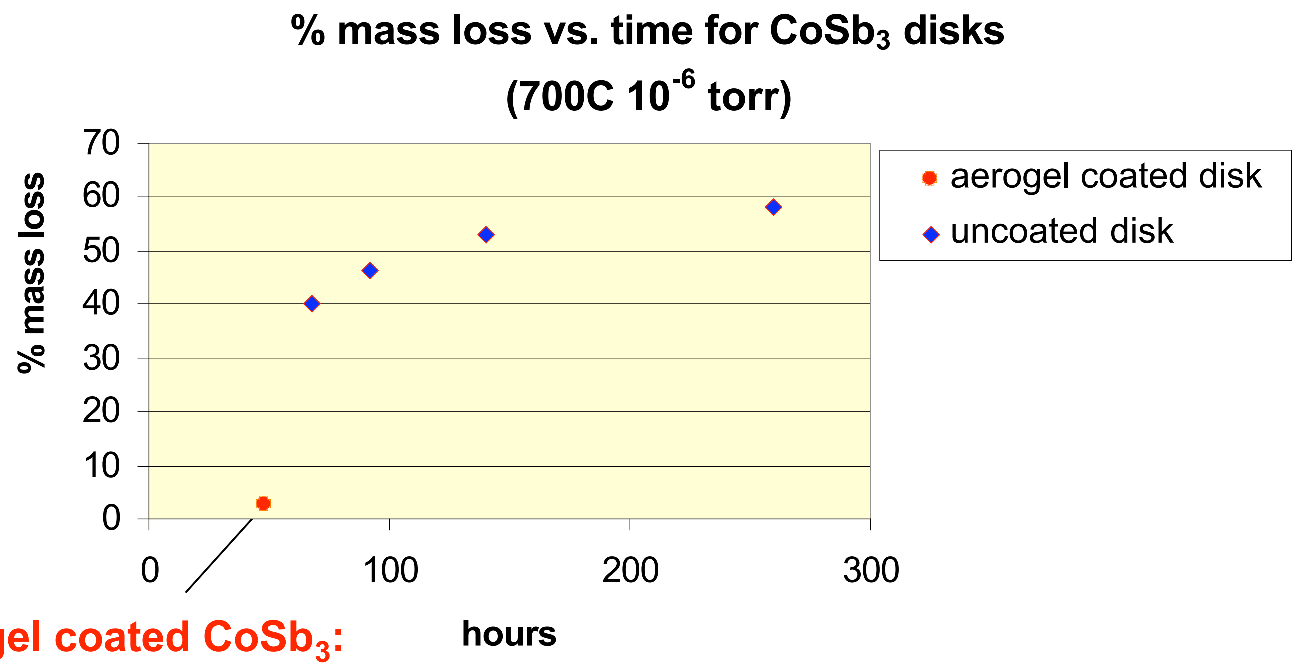




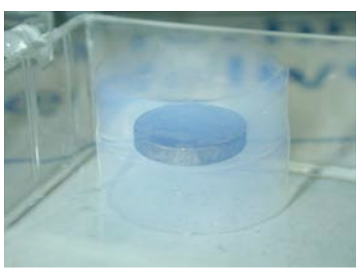
N-type Ti coated skutterudite leg

- Ti coating results in a significant mass loss reduction over uncoated

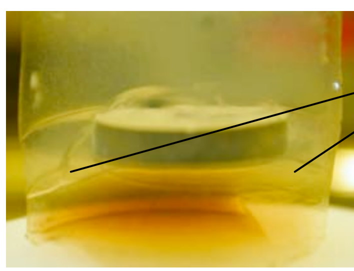
Aerogel encapsulated samples weight loss experiments



Aerogel coated $CoSb_3$: despite some cracks in aerogel, no depletion layer after 48h at 700C



before heating



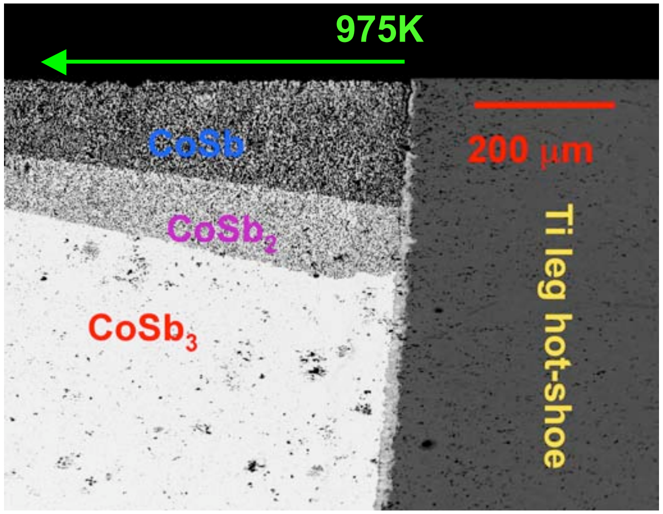
after 48h at 700C

Cracks most likely result from aerogel shrinkage around disk: need to improve thermal stability and/or strength of aerogel

Back-up charts

Sublimation control experiments

- **Isothermal anneal studies**
  - **Confirmed that n- and p-type skutterudites are phase stable at 700°C**
- **Uncoated samples**
  - **Weight loss and temperature stability showed Sb sublimation in dynamic vacuum for T from ~ 875 to 975K for N-and p-type skutterudites**
  - **Decomposition into lower antimonide compounds**
  - **Appears to be diffusion limited**

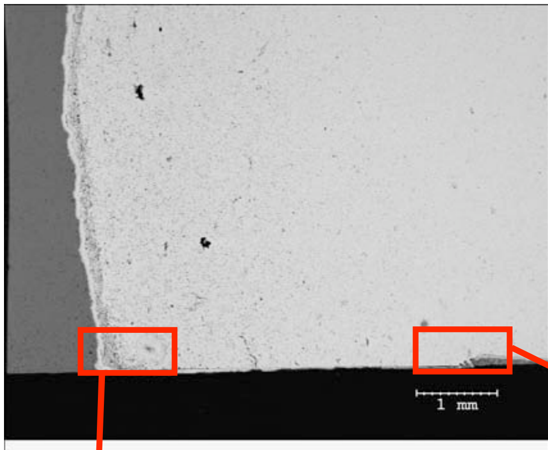


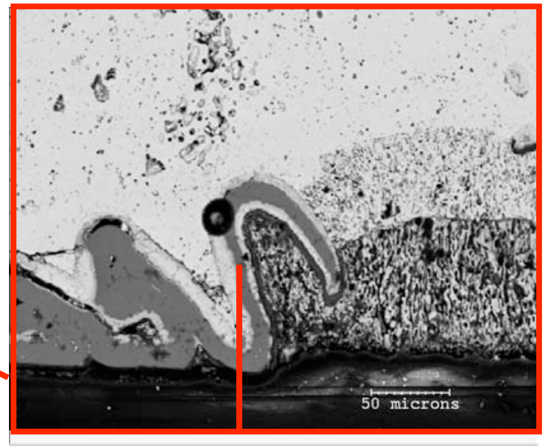
Photograph showing the decomposition of a $CoSb_3$ sample annealed in gradient for 3 months

- **Initial Sb sublimation control studies**
  - **Use of cover gas significantly suppresses Sb sublimation**
  - **Thin metallic film applied during hot-pressing to the sample also significantly suppresses sublimation**
- **Thermal/mechanical modeling performed to evaluate impact on unicouple performance**

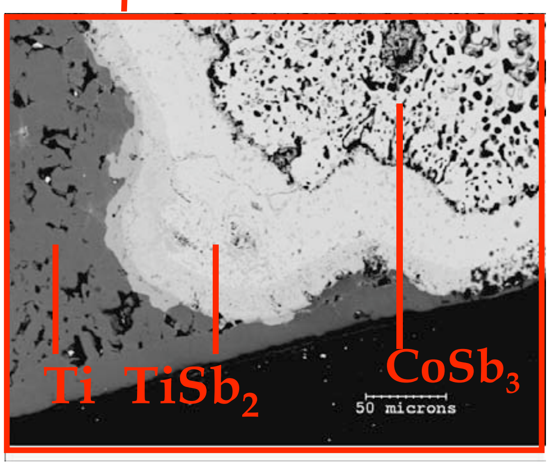
Coated n-type tested in-gradient for 20 days

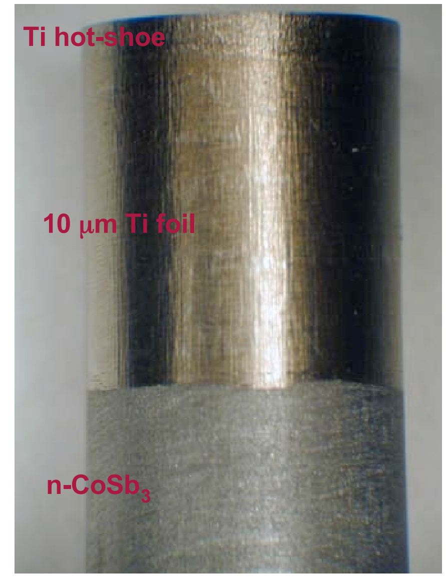
975K





Coating stops

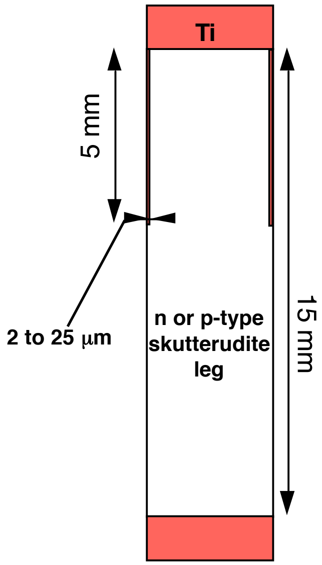


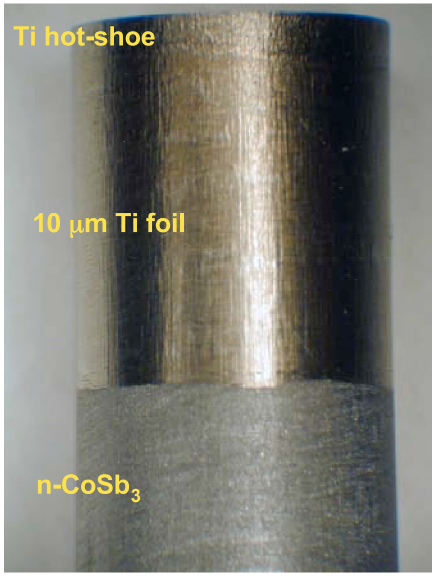


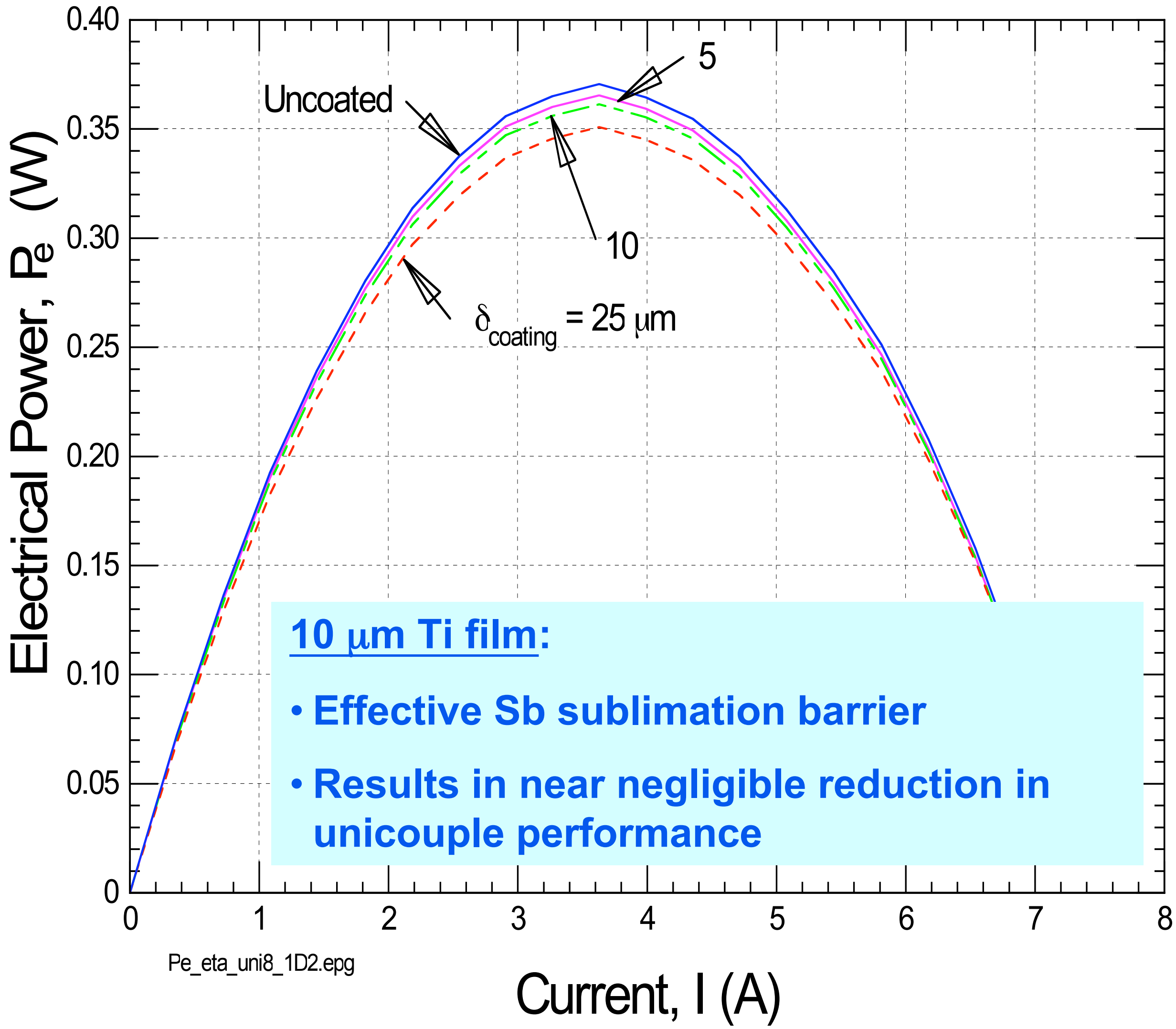
N-type Ti coated skutterudite leg

- No apparent degradation after 20 days
- Metal junction still intact
- Significant improvement over uncoated

975K-375K Segmented TE Unicouple performance modeling (UNM)





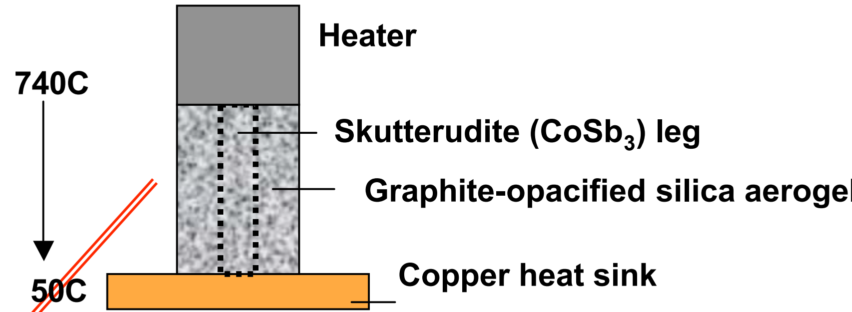


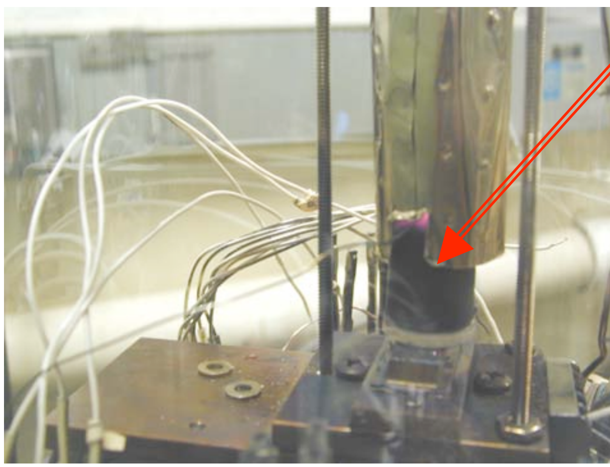
10 μm Ti film:

- Effective Sb sublimation barrier
- Results in near negligible reduction in unicouple performance

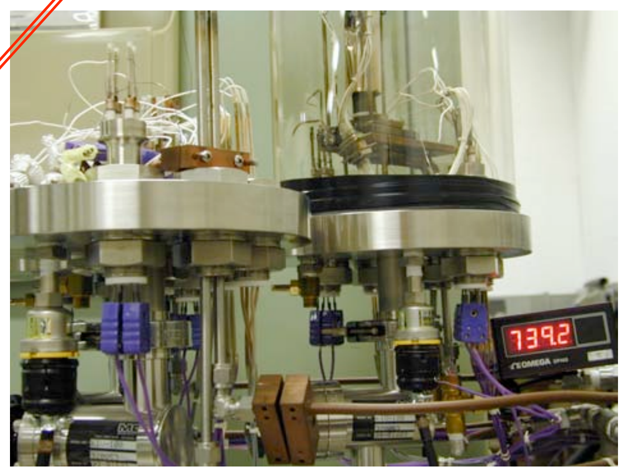
Coating Material: Ti (length 5 mm and thickness = 0-25 μm)

Aerogel encapsulated skutterudite sublimation test

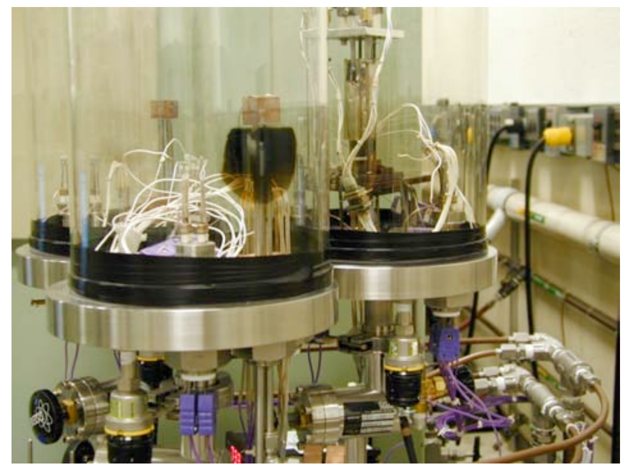




Skutterudite leg coated with graphite-opacified, silica aerogel. At 10^{-6} torr for 6 days. The absence of condensate on the inner-wall of the bell jar indicates that sublimation is completely suppressed.



Vacuum test station used to test sublimation coatings.



Condensation pattern of previous non-encapsulated sample sublimation test provides evidence of antimony sublimation.

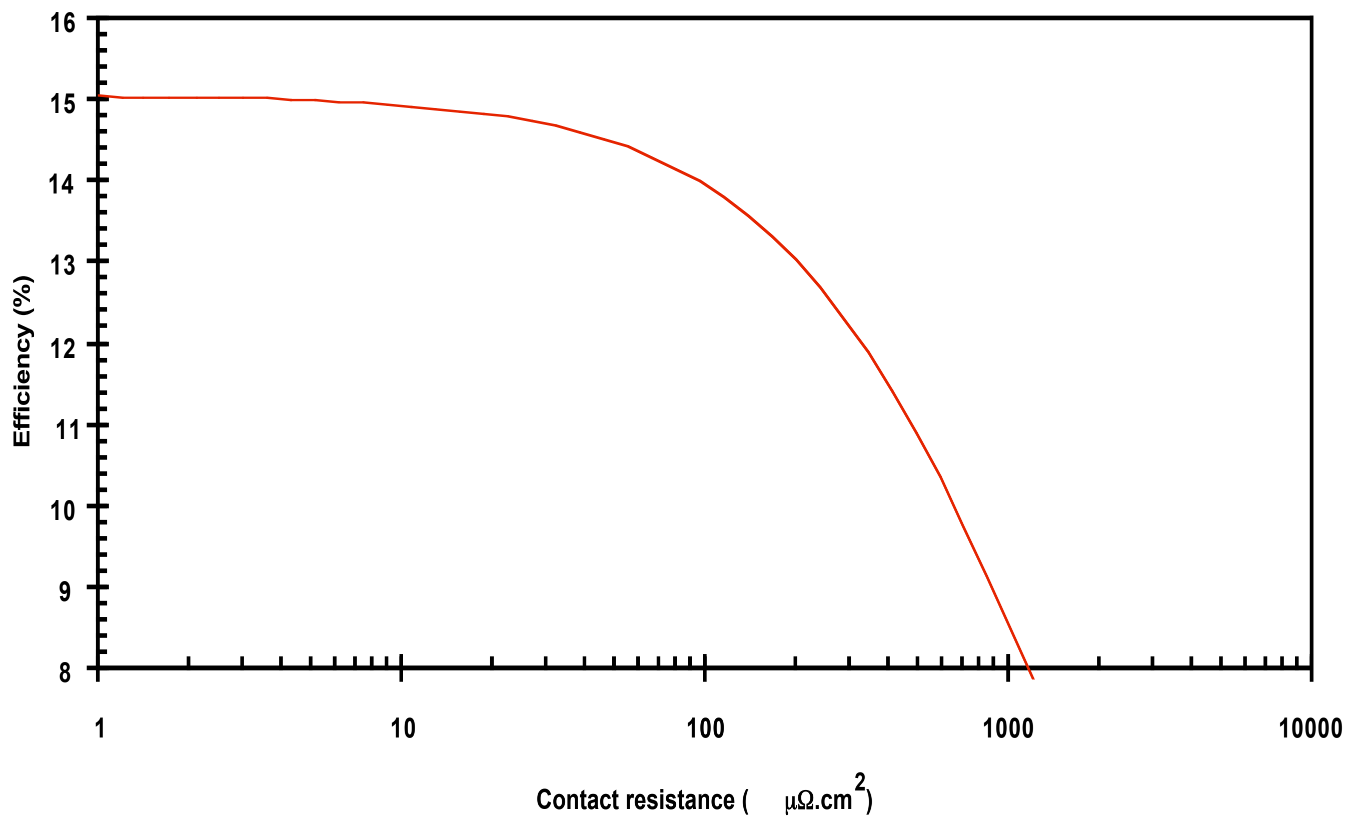
Summary

- Demonstrated ~ 14% efficiency for STE unicouples for 975K-300K ΔT
- Initiated life time studies

FY04-06 Major Focus Areas

- Optimize unicouple fabrication technique ; develop unicouple thermo-mechanical model
- Perform life testing of STE materials, coupons, components and unicouples
- Further develop sublimation control techniques/materials
- Develop lifetime model

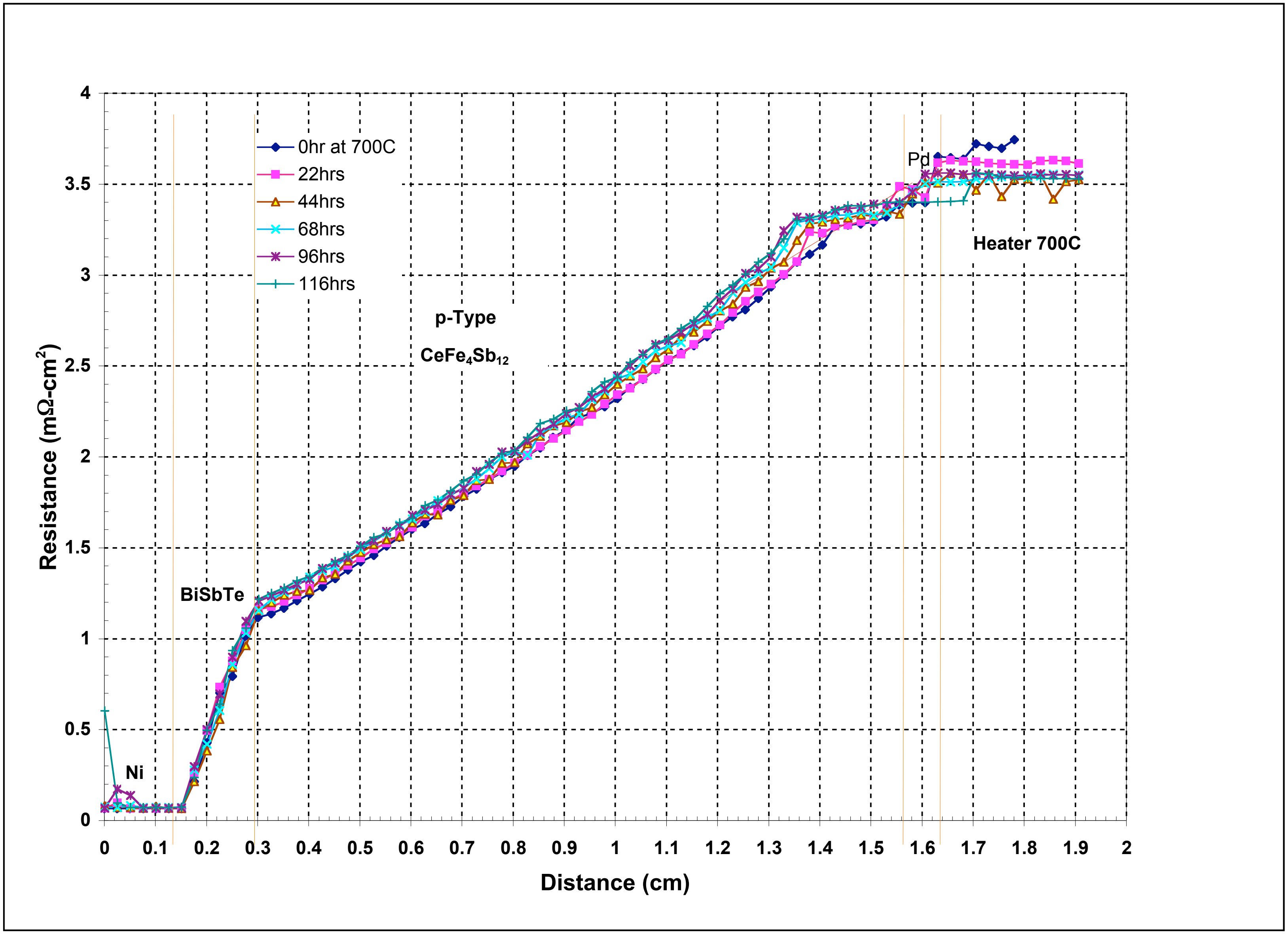
Impact of electrical contact resistance on unicouple efficiency



- **Electrical contact resistance needs to be < 5 μΩcm² to prevent impact on converter efficiency**

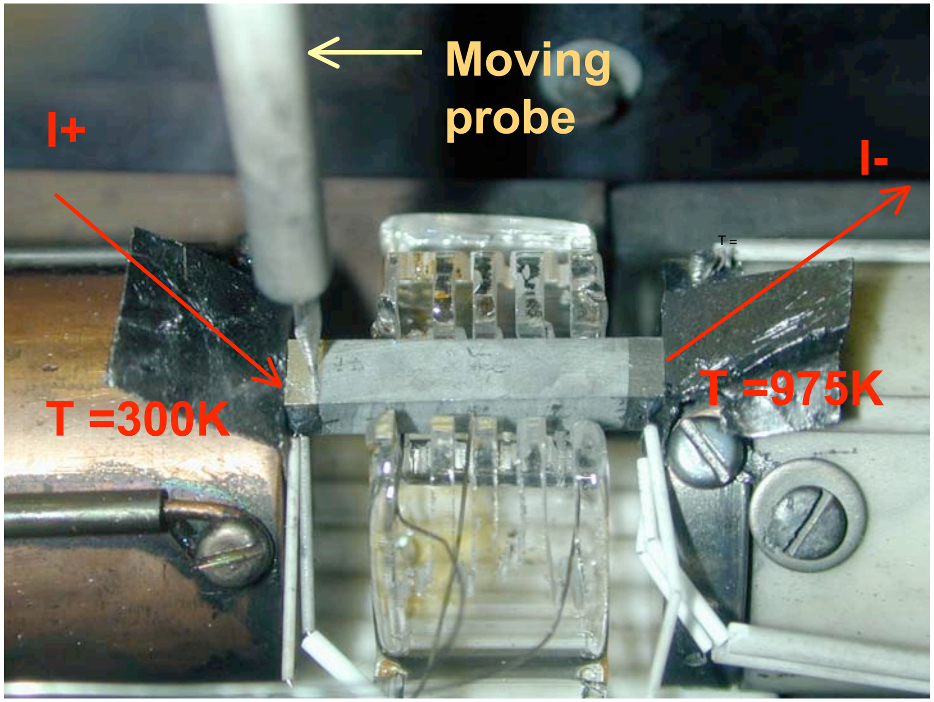
Electrical contact resistance measurements

– **Achieved electrical contact resistance < 5 μΩcm² at the segmented legs interfaces**



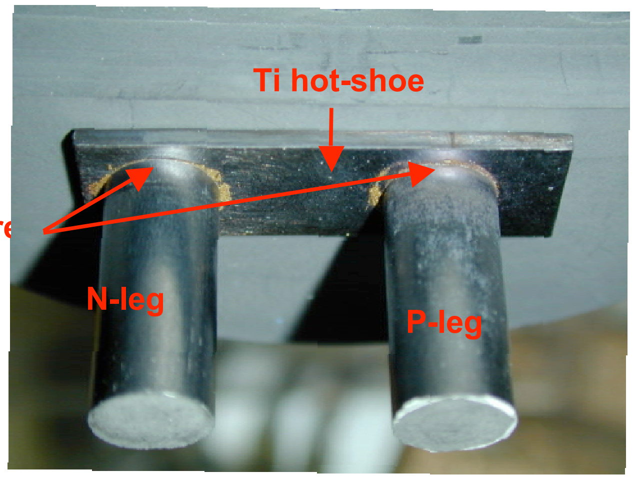
Segmented legs electrical contact resistance measurements

- Bond quality
  - Electrical contact resistance measurement
  - Microprobe analysis
    - Diffusion
    - Chemical reaction and interface layer analysis



Electrical contact resistance measurements set-up

Unicouple fabrication process developed



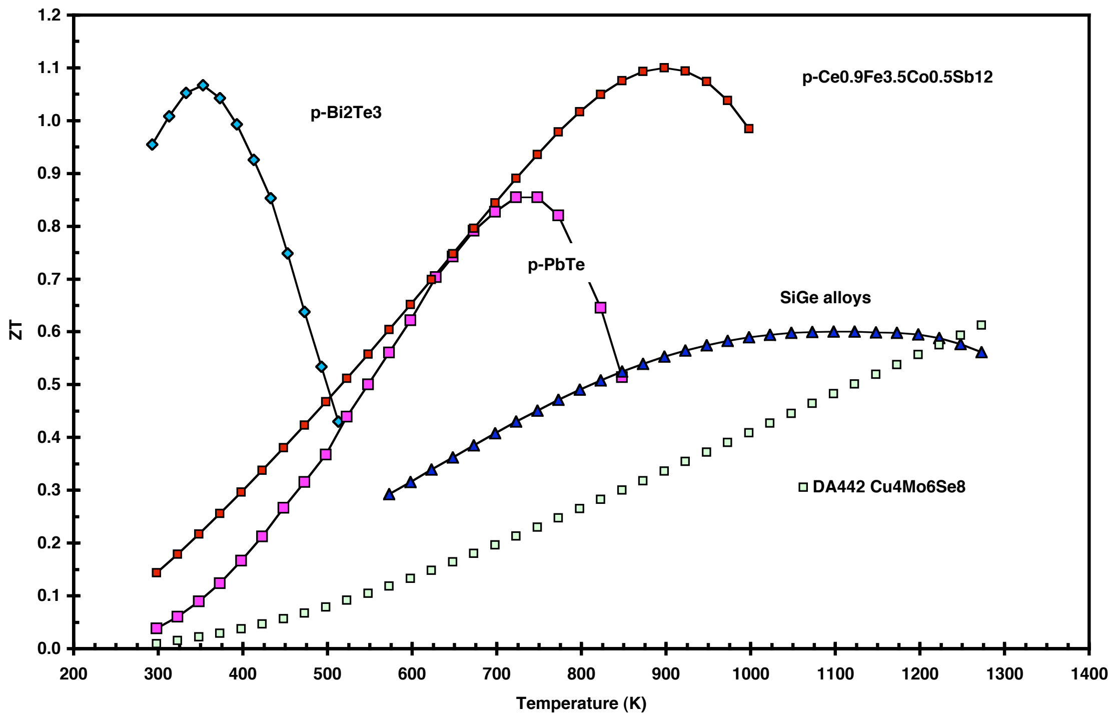
Unicouple fabricated by hot-pressing

Graphite die used for unicouple fabrication

- Developed a process to fabricate unicouple by hot-pressing
  - P- and n-leg alternatively hot-pressed onto a Ti hot-shoe
  - No measurable electrical contact resistance between TE legs and Ti hot-shoe
  - Requires further optimization but very promising
- Process compatible with batch manufacturing

High Temperature Materials

- **Chevrel chalcogenides (Mo_6Se_8-based)**
  - Synthesized several additional Cu and Fe filled Mo_6Se_8 compositions using a powder metallurgy technique
  - Measured Seebeck coefficient, electrical resistivity, and thermal conductivity from 300K to 1275K
  - Achieved ZT ~0.6 a 1275K for $Cu_4Mo_6Se_8$ composition, comparable to SiGe
  - Tested $Cu_4Mo_6Se_8$ sample under electrical load (potential Cu electromigration)
    - Sample shows no indication of electromigration after 6 days at 900°C under 5A load current



CuMo$_6$Se$_8$ sample tested for 6 days at 900C under 5A load