Progress Status of Skutterudite-Based Segmented Thermoelectric Technology Development

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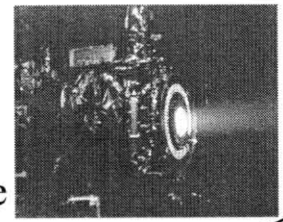
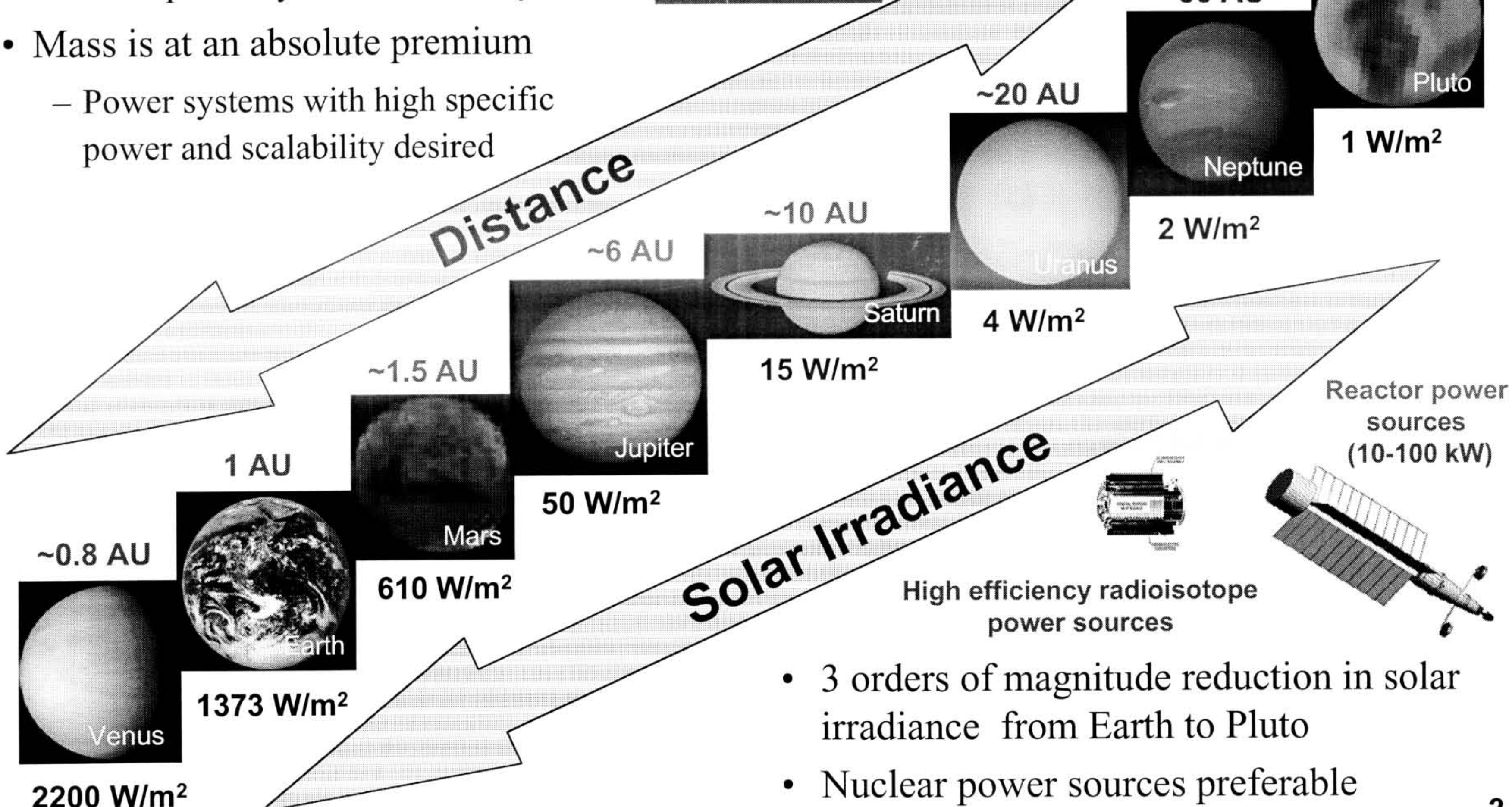
NASA (Project Prometheus), ONR & DARPA

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

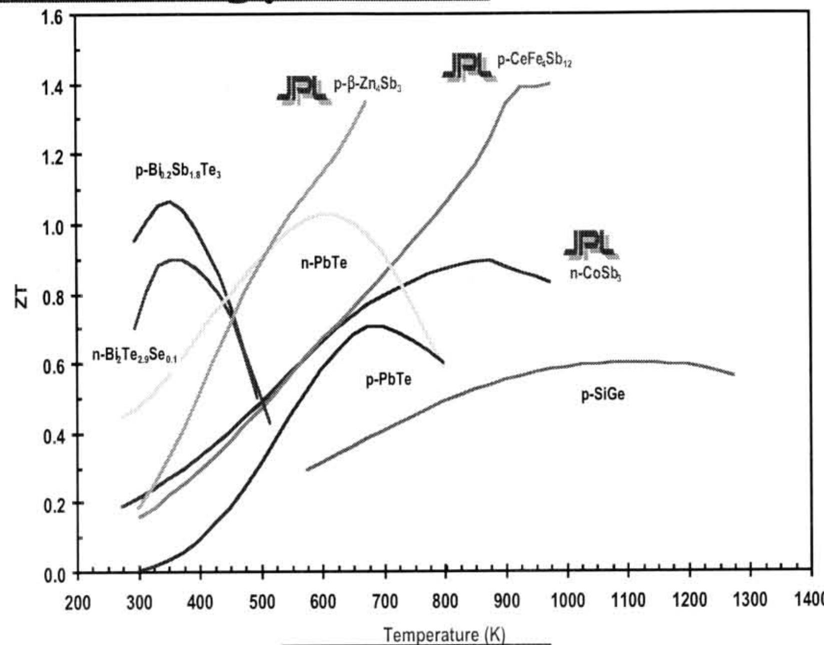
- Overall objective

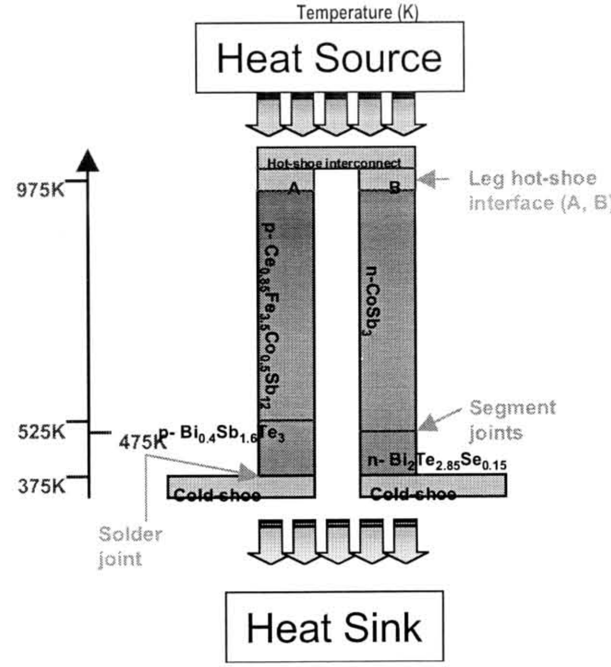
  Develop low mass, high efficiency, low-cost Advanced Radioisotope Power System with double the Specific Power and Efficiency over state-of-the-art radioisotope thermoelectric generators (RTGs)

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





JPL Segmented Thermoelectrics (STE) Task overview

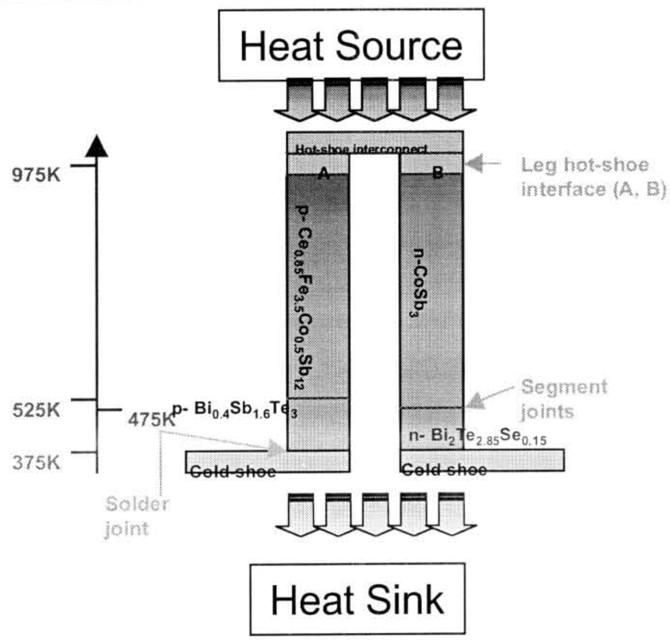


Illustration of 12.5% efficiency

975K-375K segmented unicouple

Overall objectives

- Develop Segmented Thermoelectric technology to from TRL 3 to TRL4 by end of FY06
- Transfer technology to industry/DOE for integration into a radioisotope power system that can provide ~7-8 W_e/kg specific power and ~10% system efficiency

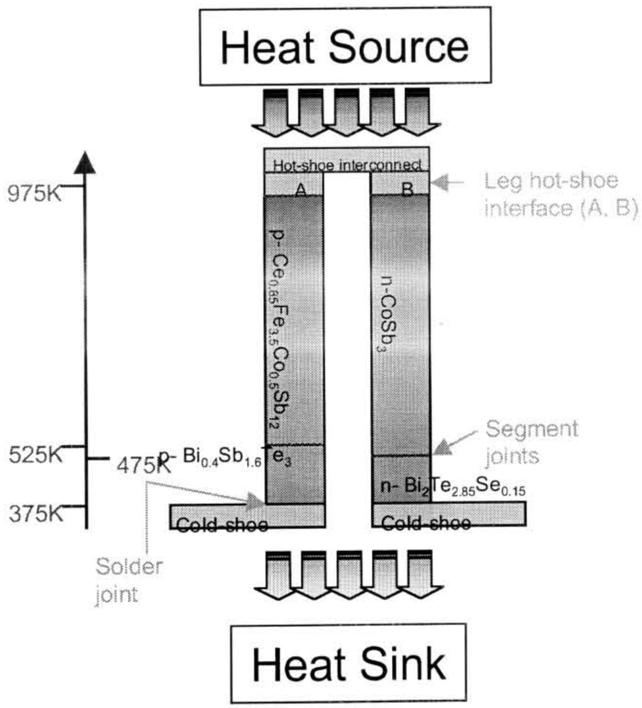
FY04-06 Major Goals

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

Schedule

Top-level Tasks	FY04	FY05	FY06
Unicouple development	——◆		
Baseline TE materials/coupons life testing and modeling	———	———	——◆
Unicouple/components life testing		———	——◆
Unicouple/TE materials optimization	———	———	——◆
Manage and report	———	———	——◆

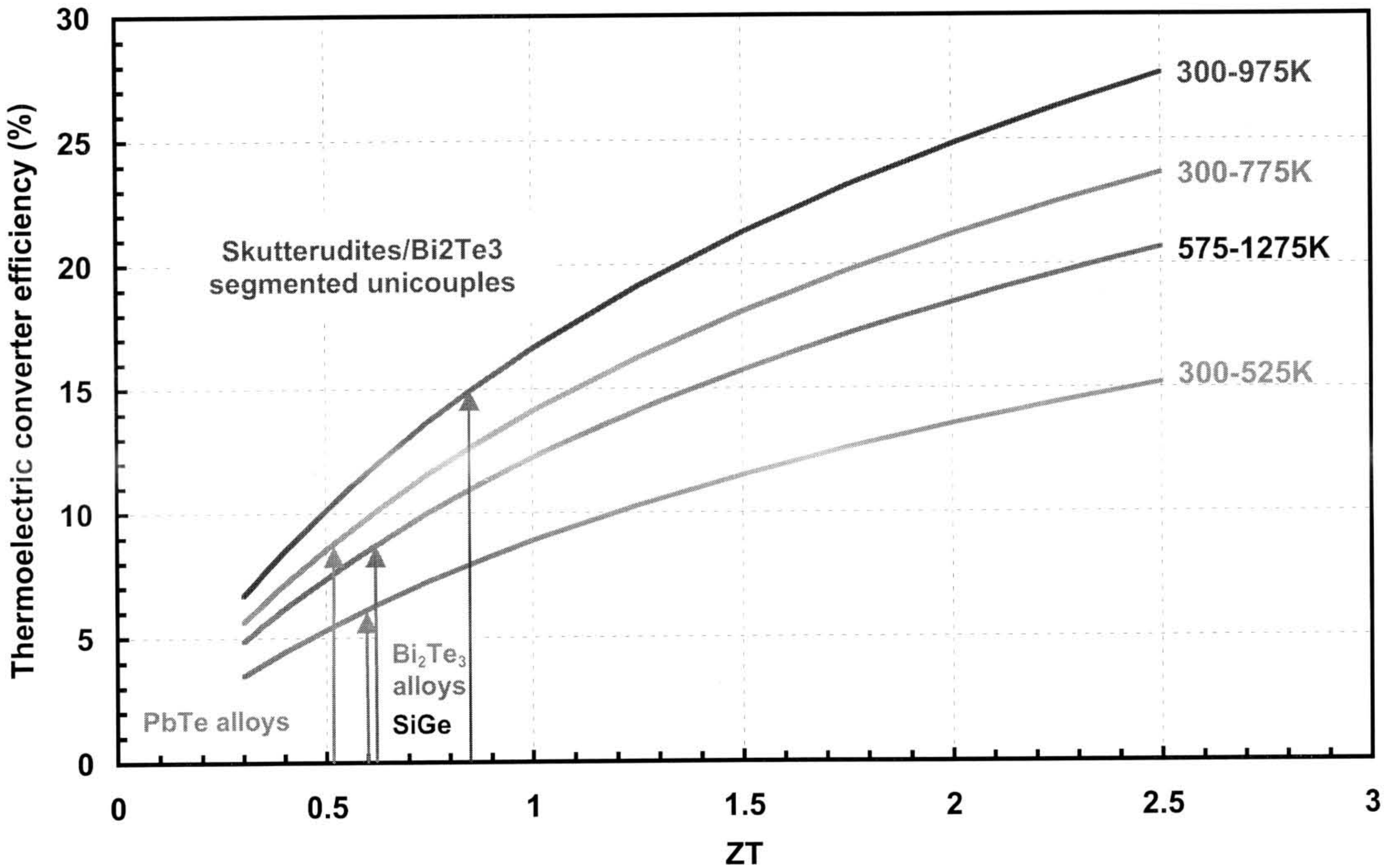
Key Technology Challenges



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

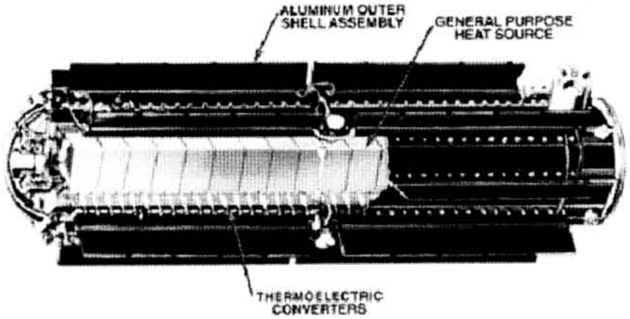


A 2x increase in efficiency over SOA thermoelectrics has been demonstrated for the STE technology

General Purpose Heat Source RTG

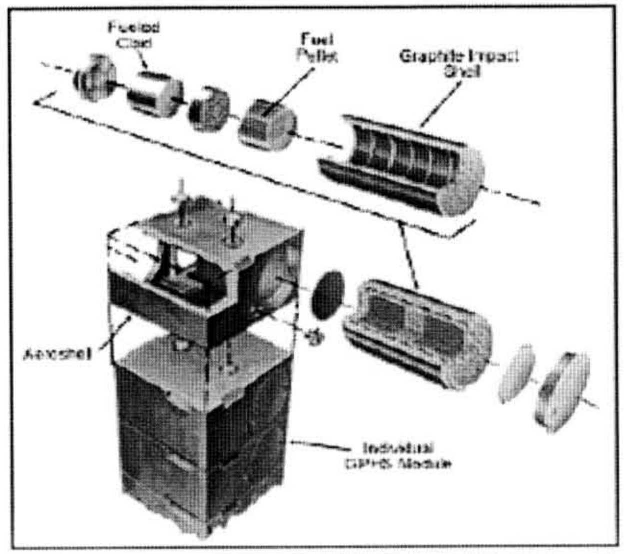
General Purpose Heat Source (GPHS)

Radioisotope Thermoelectric Generator (RTG)

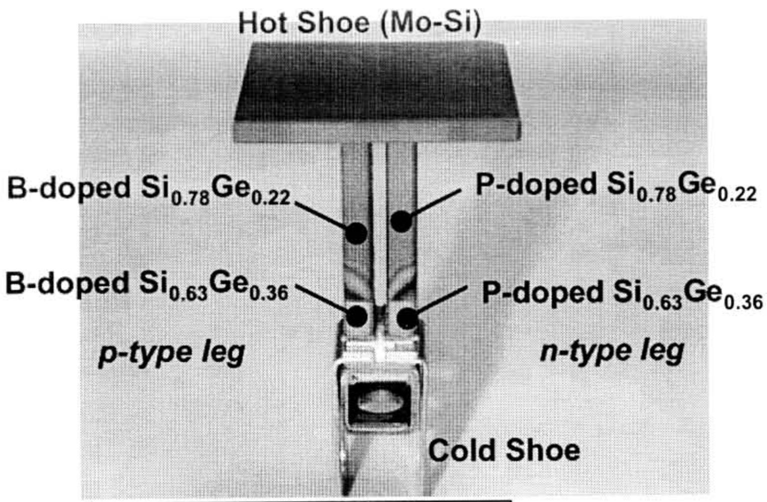


- POWER OUTPUT – 285 W(e)
- FUEL LOADING – 4400 W(t); 132,500 Ci
- WEIGHT – 124 lbs
- SIZE – 16.6 in x 44.5 in

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

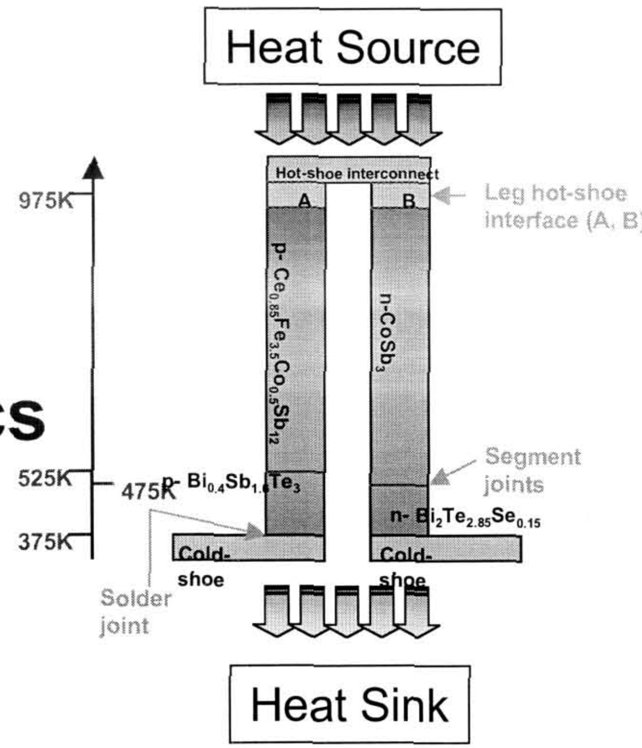
Power output-We	290 beginning of life 250 end of life
Operational life - hrs	40,000 after launch
Weight-kg	55.5
Output voltage	28
Dimensions	42.2 diameter 114 long
Hot junction temperature-K	1270
Cold junction temperature-K	566
Fuel	PuO_2
Thermoelectric material	SiGe
Numbers of unicouples	572
Mass of 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"



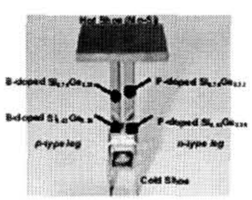
•Advantages of thermoelectrics

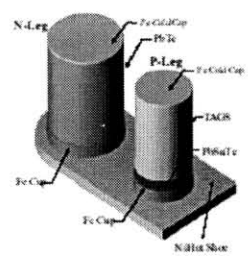
- Flight proven, long life demonstrated
- Solid state energy conversion -> reliability, no vibration, no moving parts
- *Scalable*
- No single point failure
- Significant system heritage

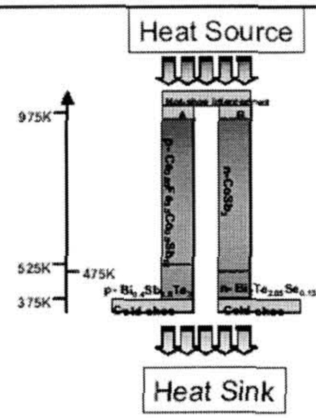
Projected STE 100W class ARPS specifications vs. SOA

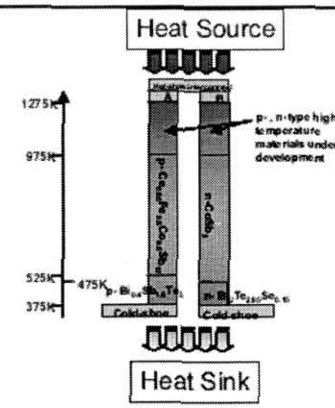
Item/Converter	SiGe-RTG	PbTe/TAGS MMRTG	Low T STE (LSTE)	High Temperature TE (HSTE)
Hot side temperature (K)	**1273**	**823**	**975**	**1200**
Cold side temperature (K)	**573**	**453**	**375**	**375**
Converter efficiency (%)	7.2	7.6	12.5	14.7
System efficiency (%)*	6.5	6.4	11.18	13.3
Thermal power (BOM)(W_{th})	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



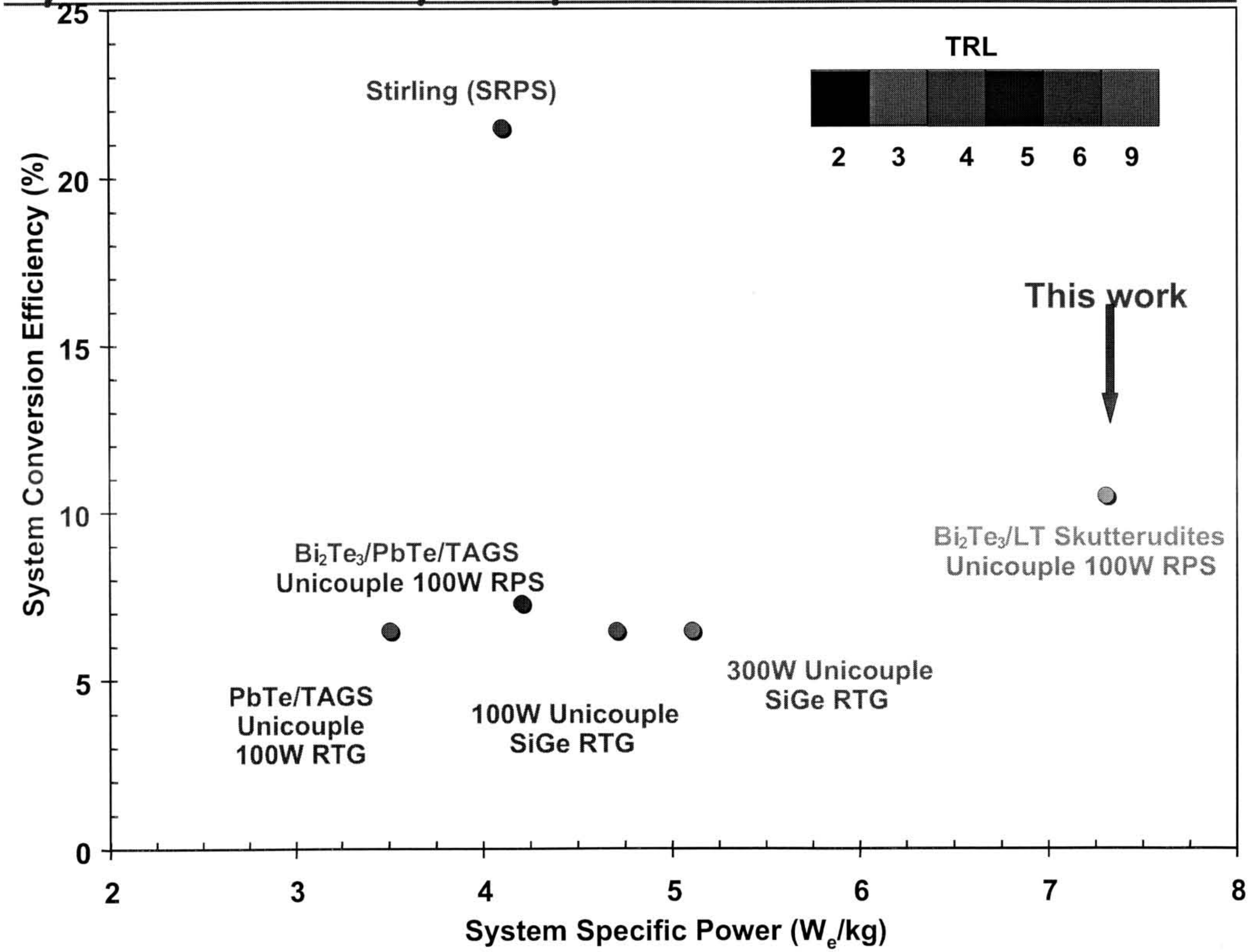






* 90% of converter efficiency

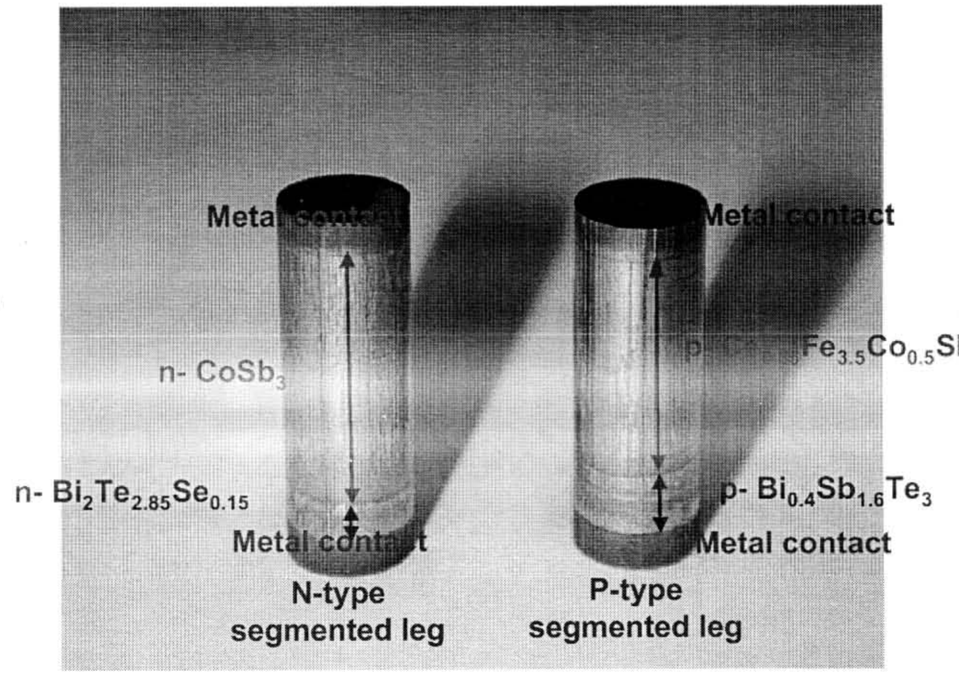
System Efficiency & Specific Power: STE vs. SOA



Segmented legs fabrication and characterization

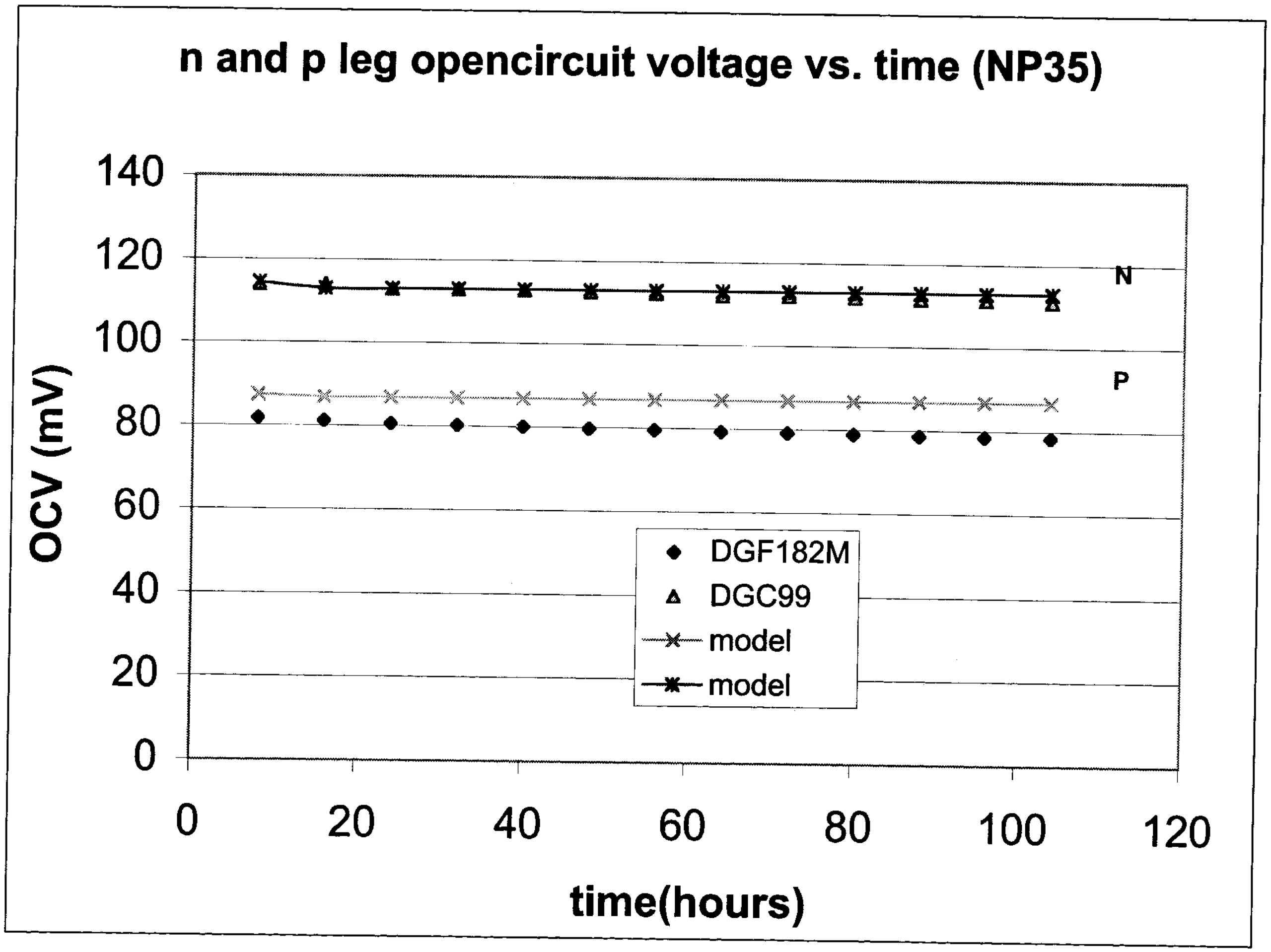
Unicouples legs

- **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 ($<5\mu\Omega cm^2$) achieved ➔ negligible impact on overall unicouple performance



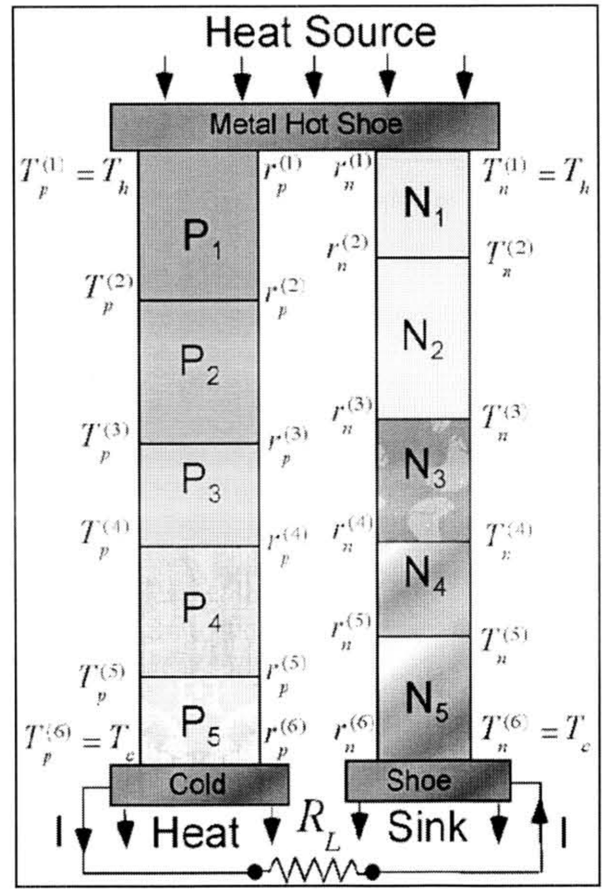
Unicouple legs - In-gradient testing

- 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

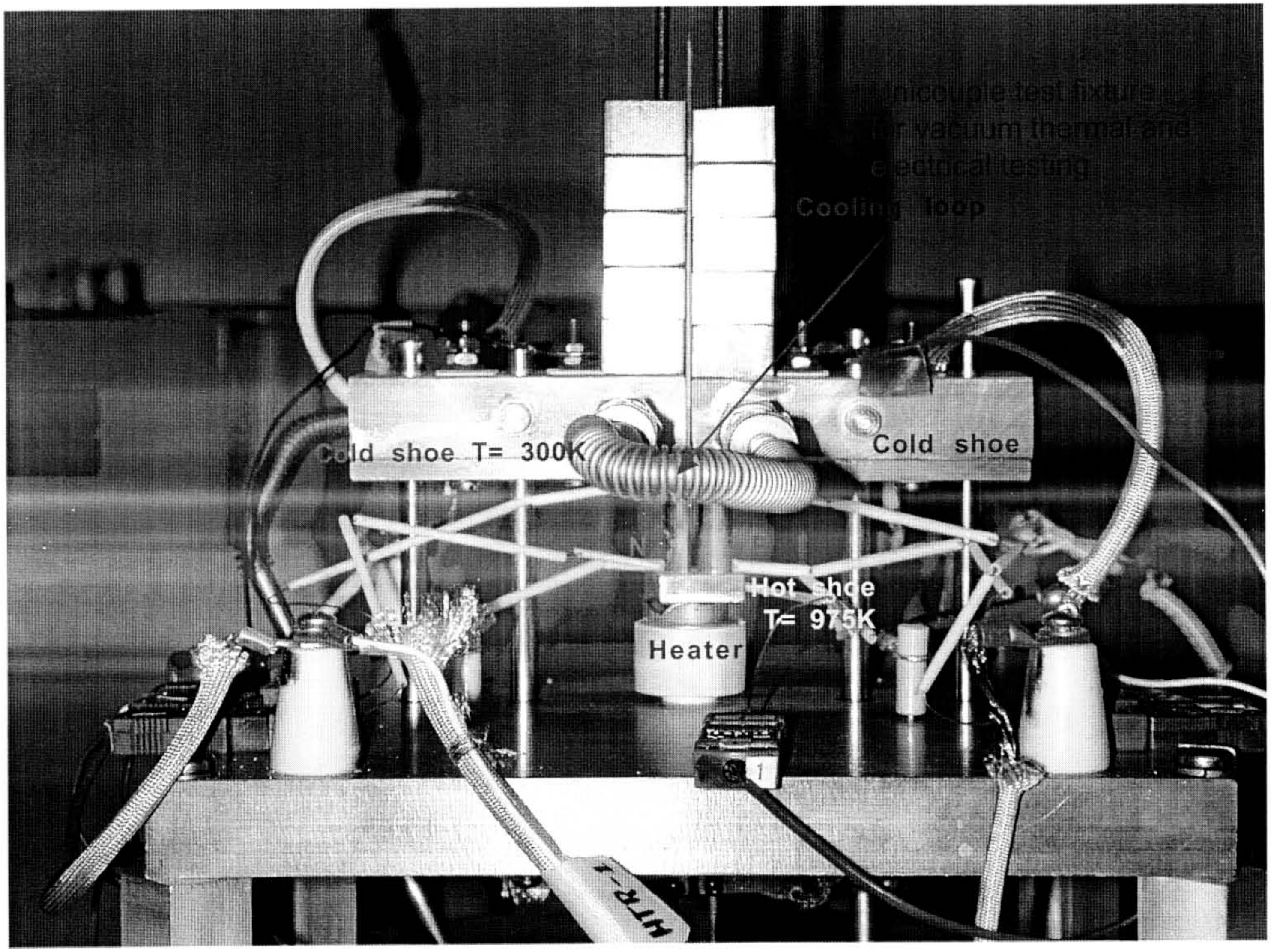


1-D Analytical Model of Segmented Thermoelectric Unicouples

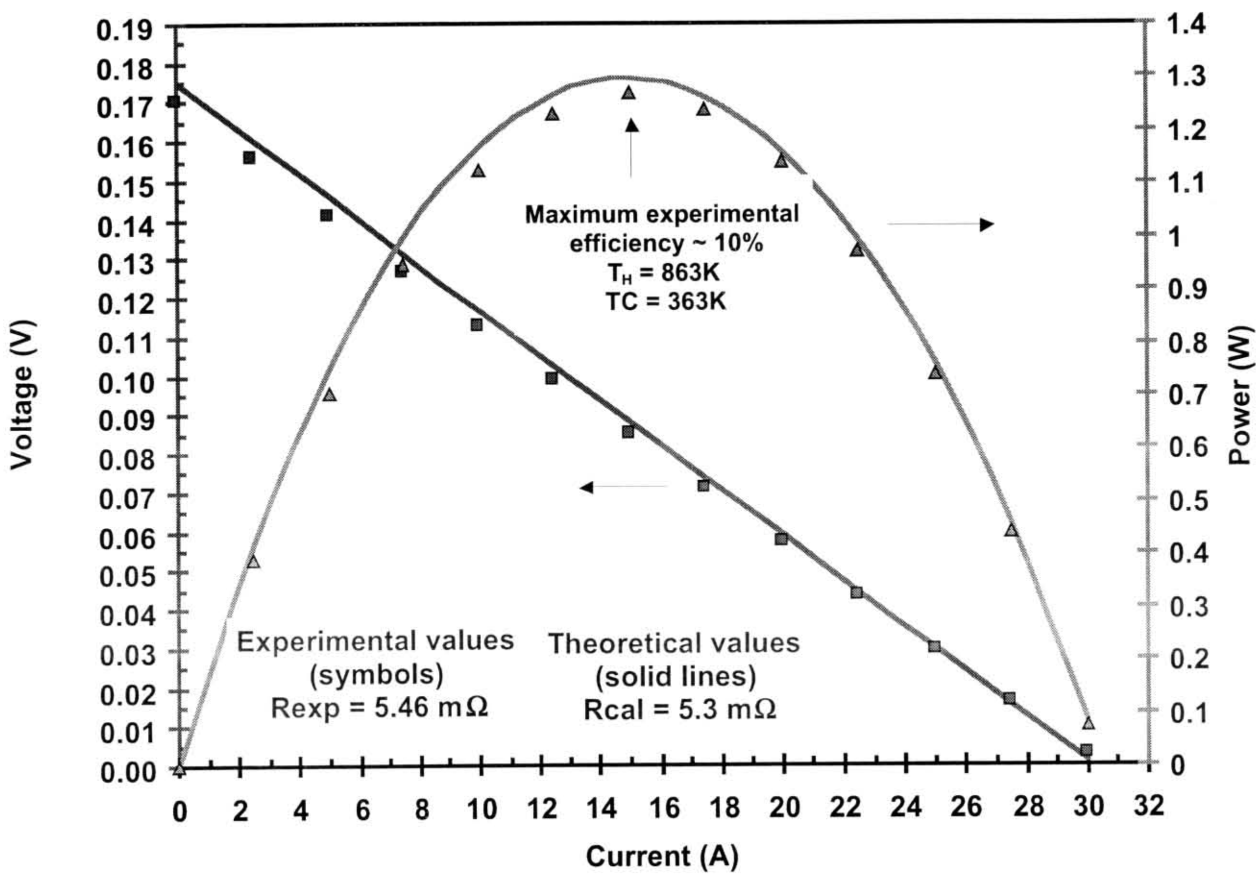
- One-dimensional analytical model of STEs, with up to 5 segments per leg, is coupled to a *genetic algorithm* for maximizing either electrical power of efficiency
- **Input:**
  - TE materials properties
  - Total length and composition of n- and p-legs
  - Cross sectional area of the p-leg (or the 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

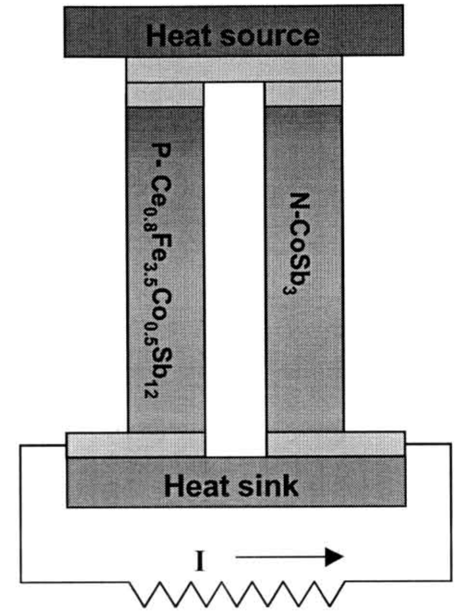


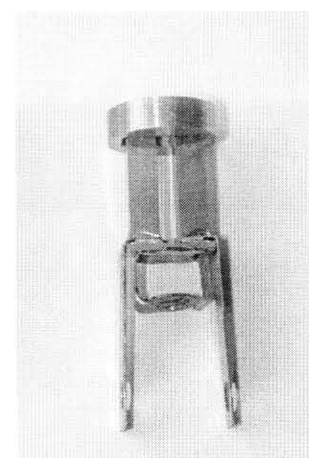
Unicouple thermal and electrical testing



Thermal and electrical Testing : Skutterudite only unicouple

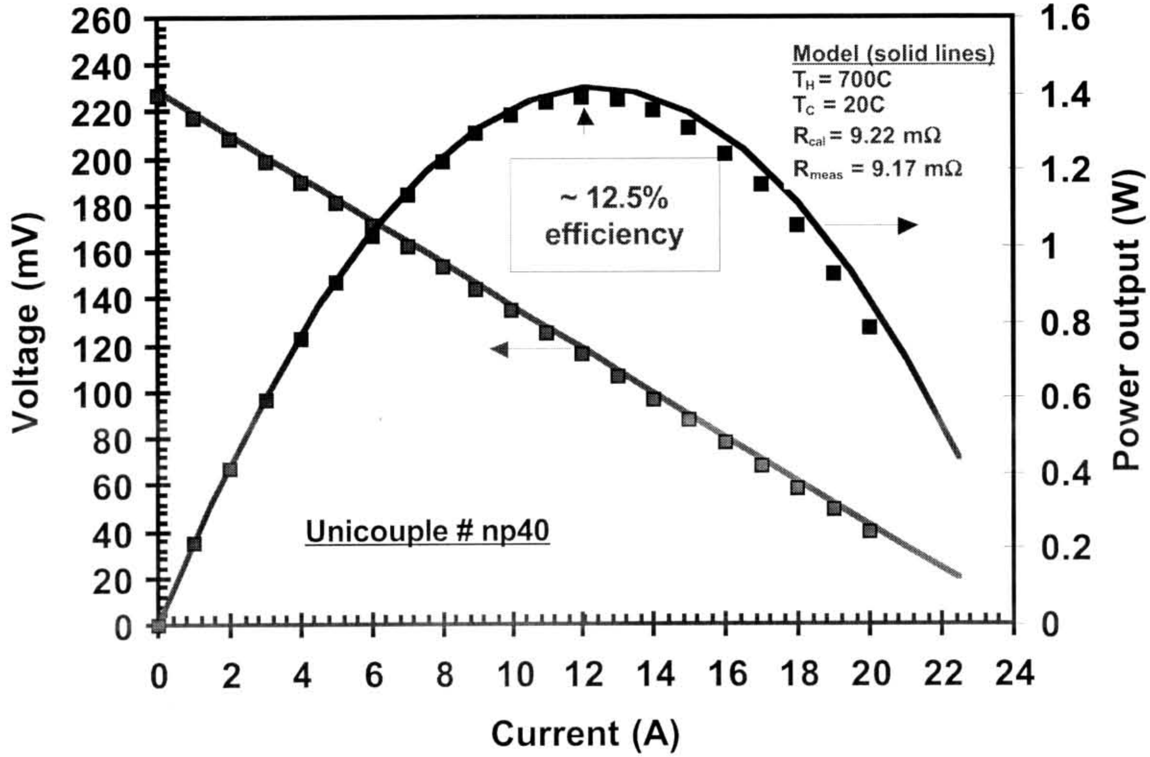


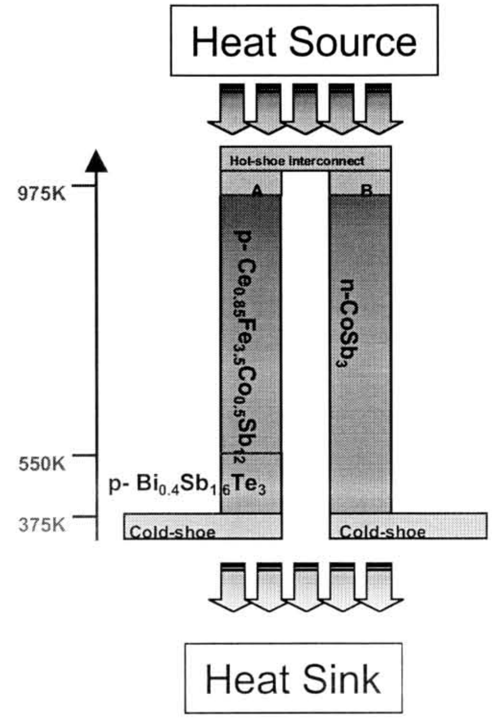




- **Unicouple performance**
  - Low electrical contact resistance
  - Thermal to electrical efficiency : calculated ≈ experimental (~ 10%)
  - Open circuit voltage = 170 mV
  - Maximum power output ~ 1.3W

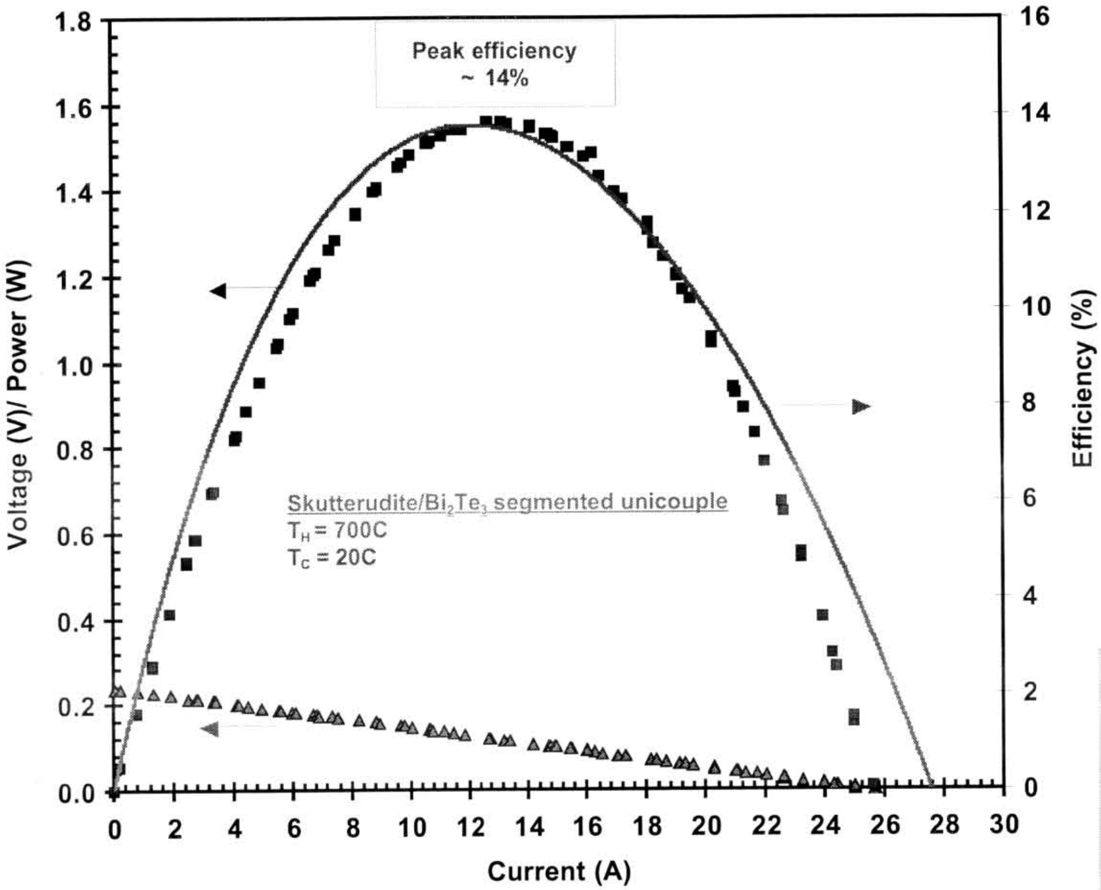
Thermal and electrical testing - Segmented unicouple

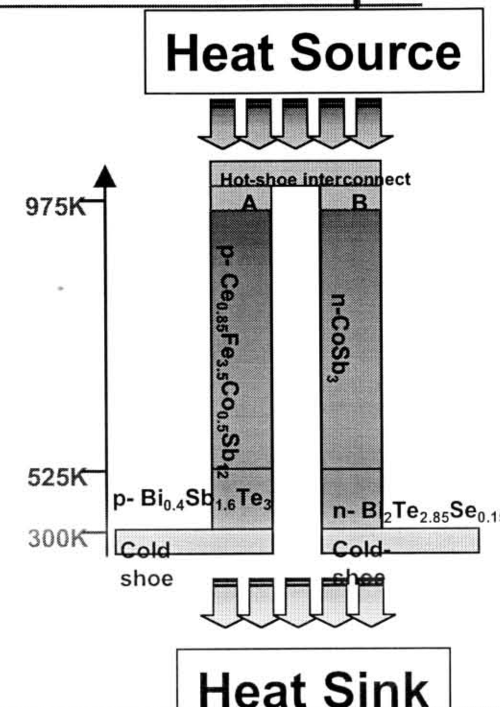


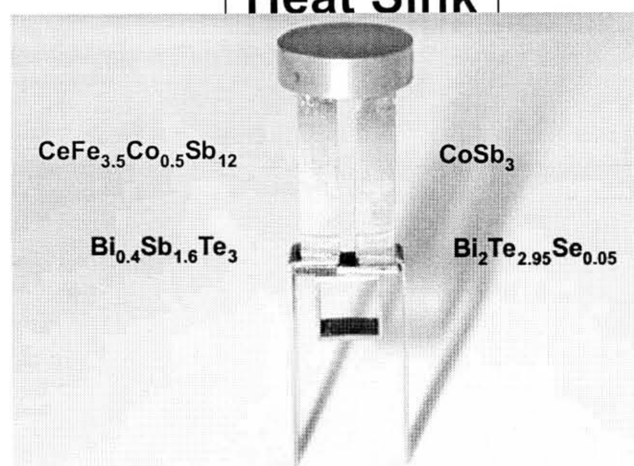


- **Achieved 12.5% efficiency for 975K-300K ΔT**
  - With p-segmented leg and n-skutterudite leg
  - Consistent with model prediction

Thermal and electrical testing - Segmented unicouple







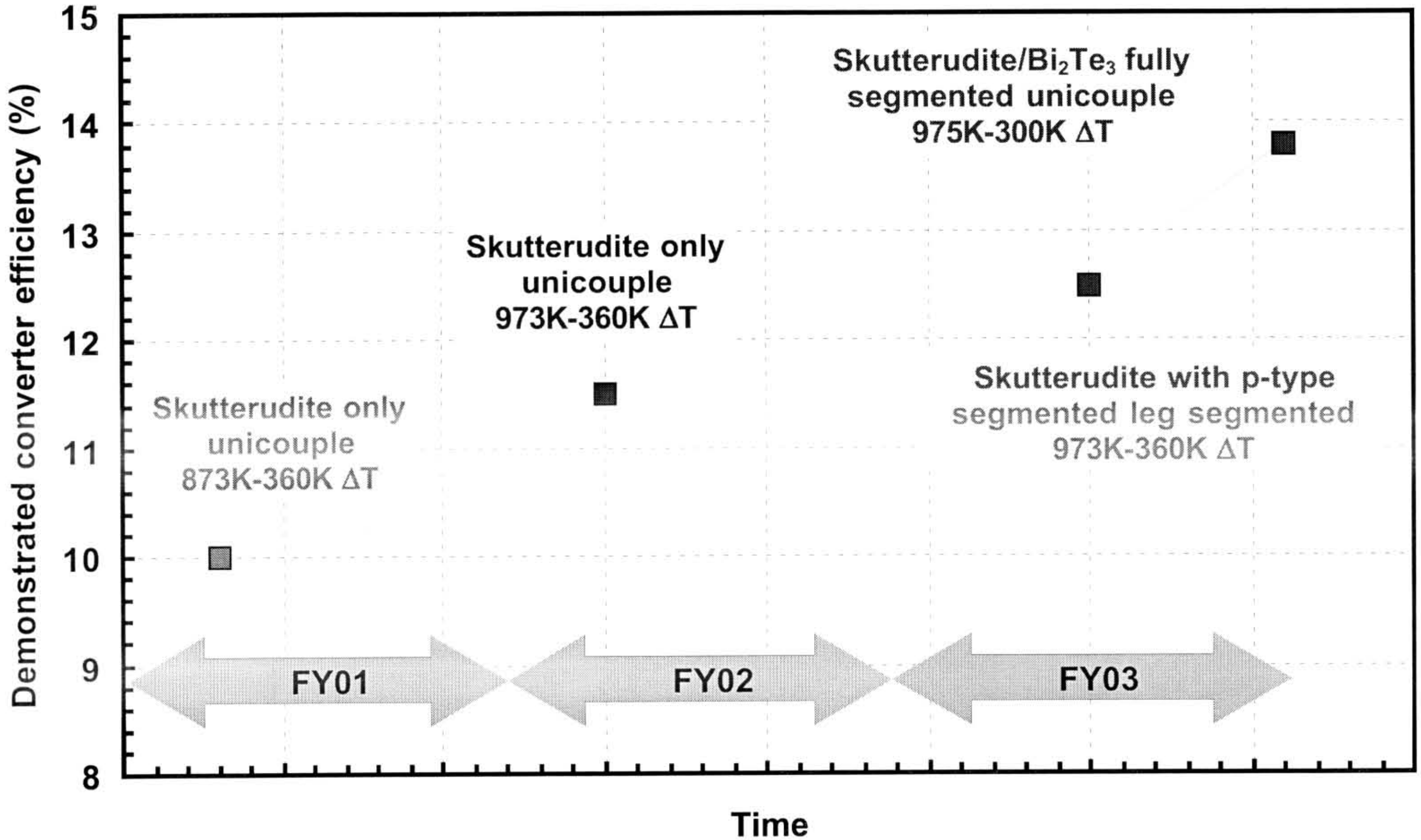
Skutterudite/Bi_2Te_3 segmented unicouples

- **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**

FY01-03 efficiency demonstration



- Latest results fully validate projected performance

Preliminary lifetime & Sublimation studies

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

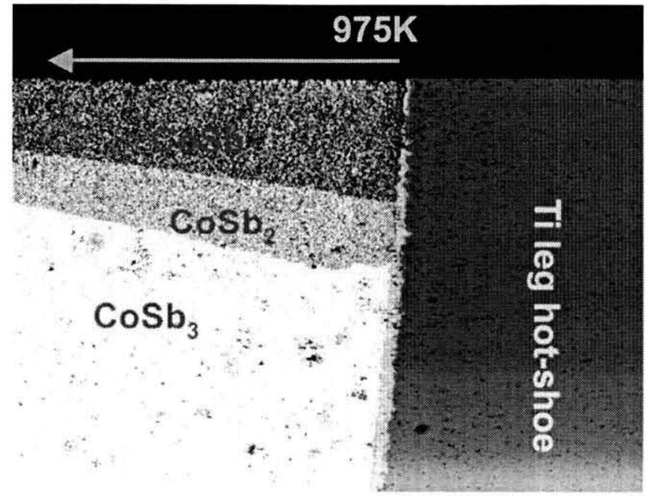
Impact:
- Contact resistance
- Mechanical failure

Solution:
- Device engineering/modeling

LIFETIME MODEL

FUEL DECAY

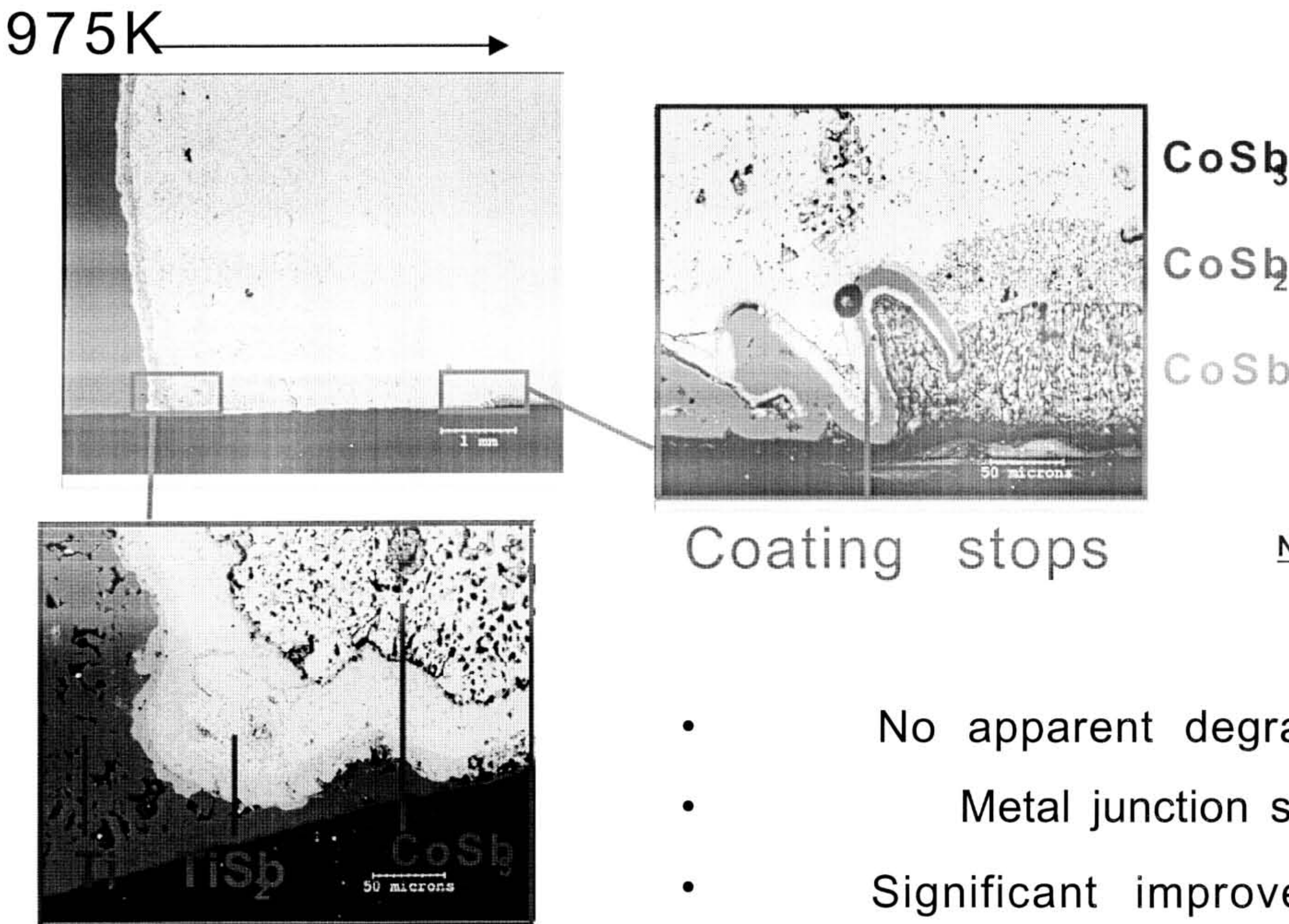
Sublimation control experiments

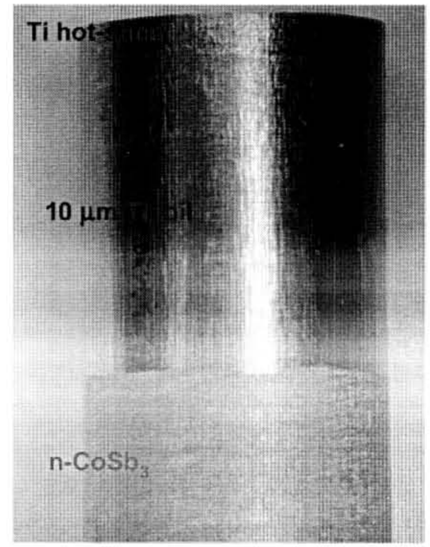


Photograph showing the decomposition of a $CoSb_3$ sample annealed in gradient for 3 months

- 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
- 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

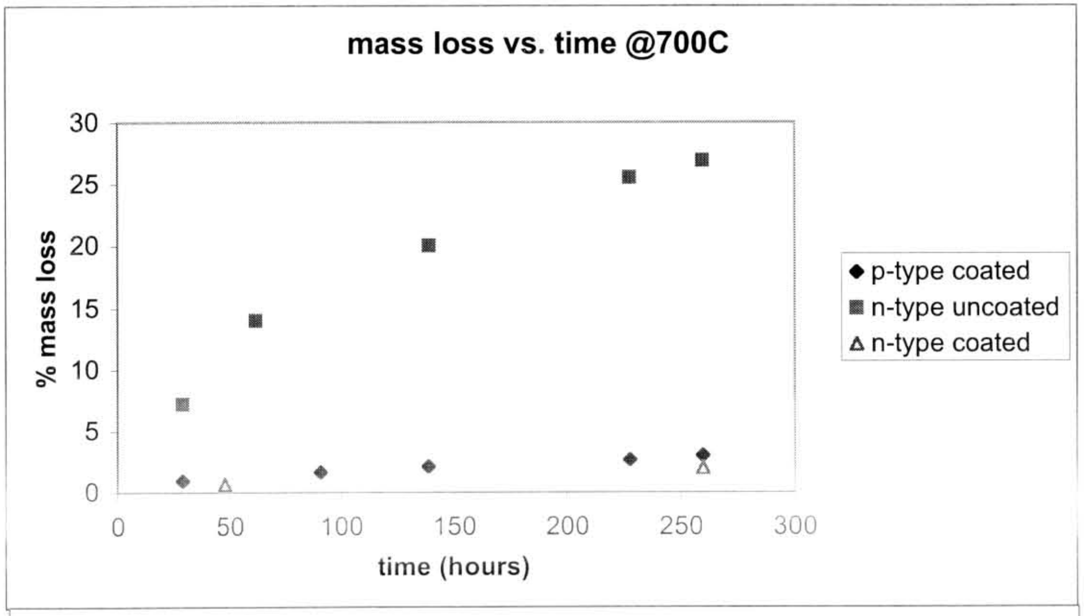


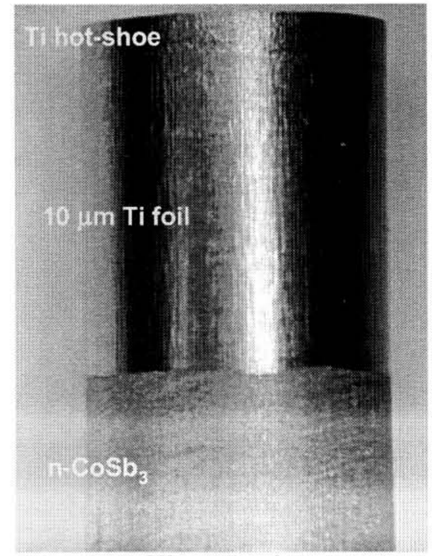


N-type Ti coated skutterudite leg

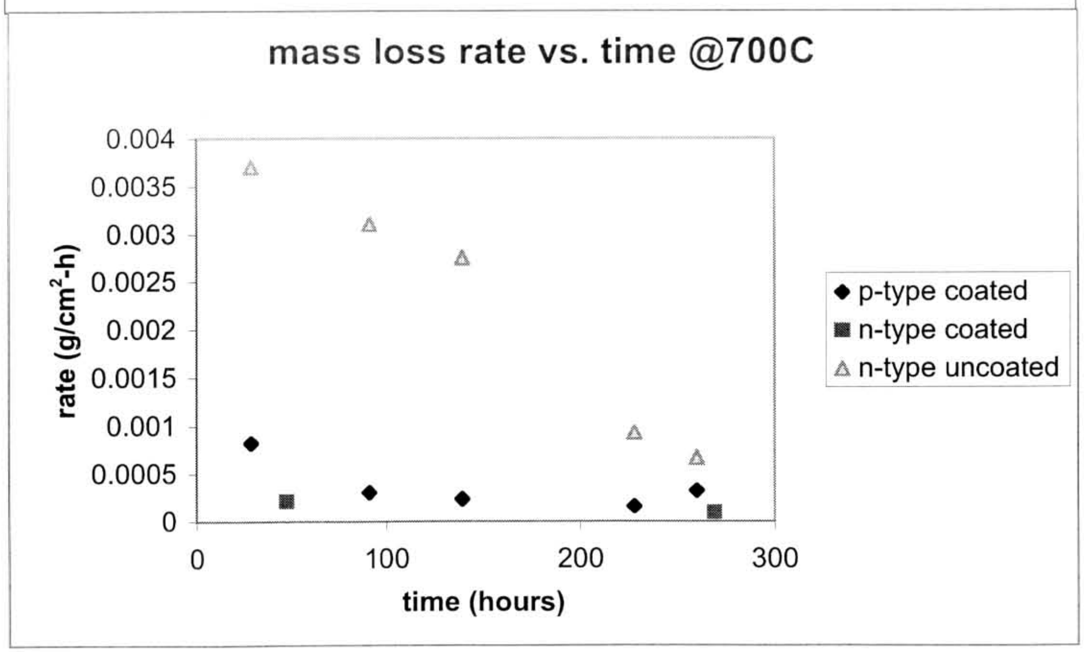
- No apparent degradation after 20 days
- Metal junction still intact
- Significant improvement over uncoated

Mass loss experiments results



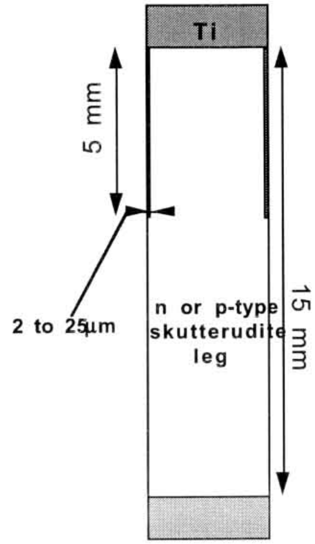


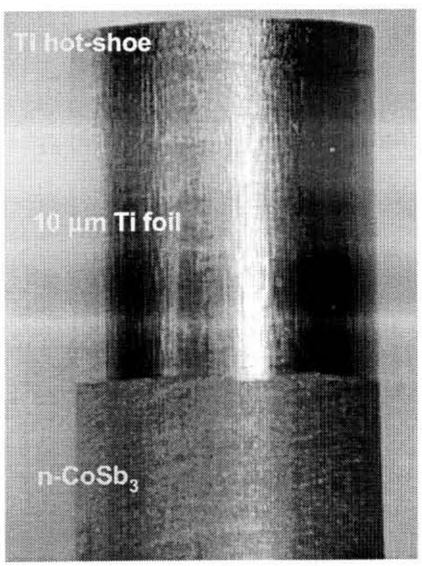
N-type Ti coated skutterudite leg

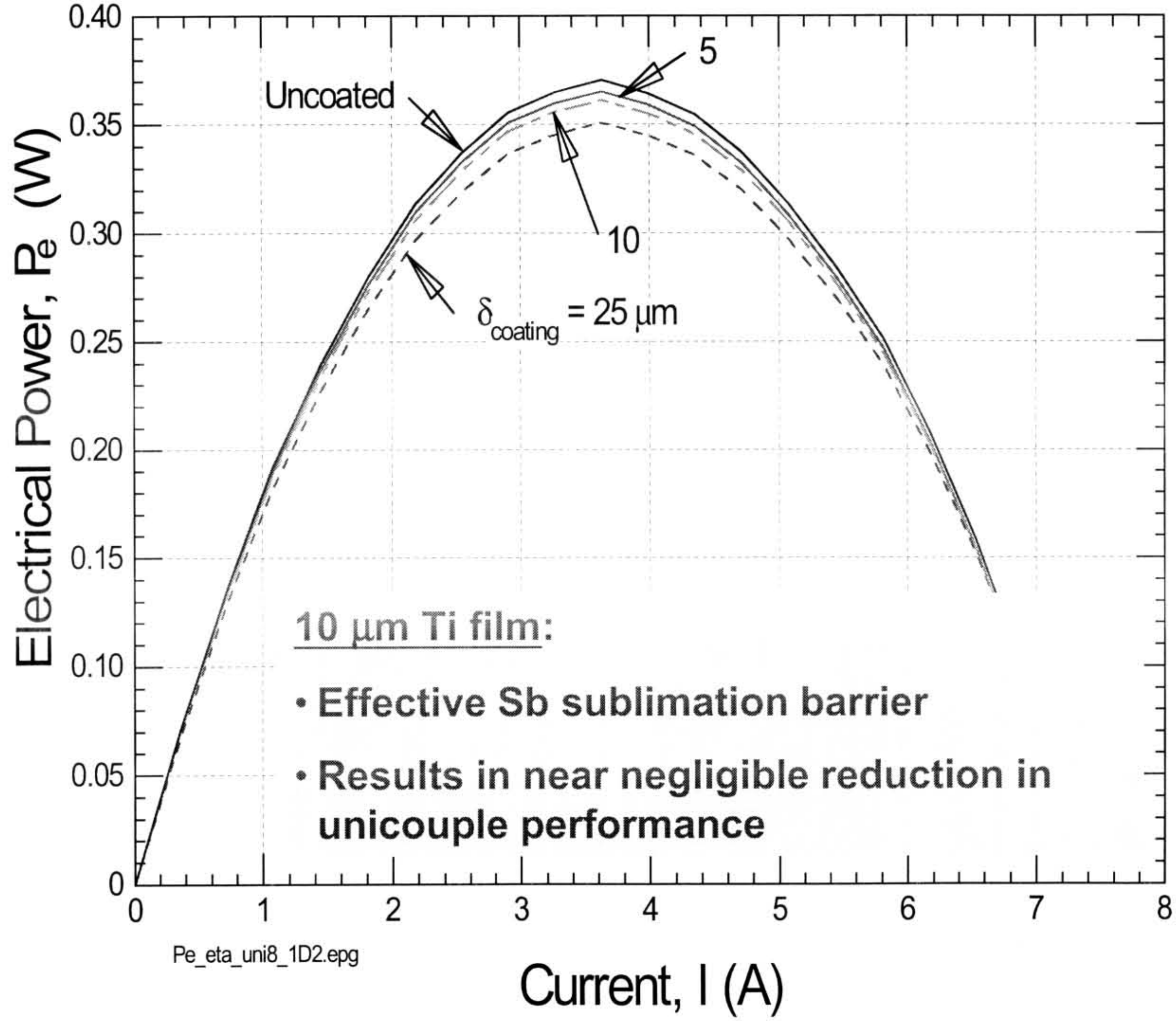


- Ti coating results in a significant mass loss reduction over uncoated

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

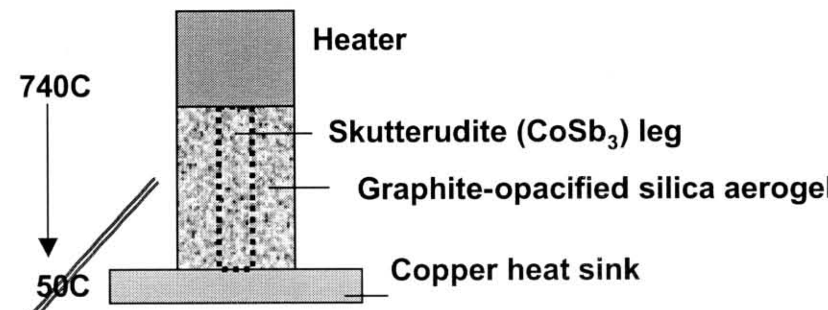


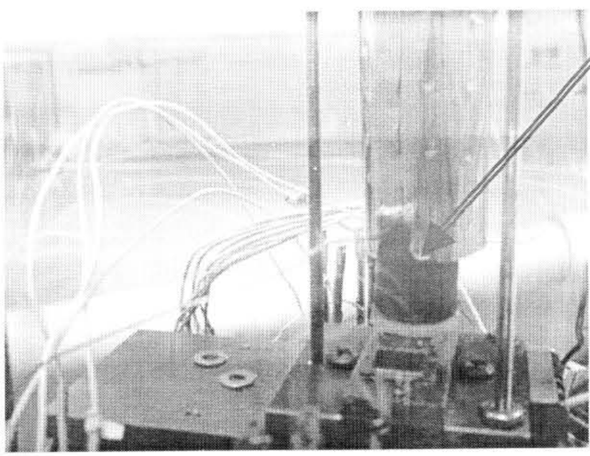




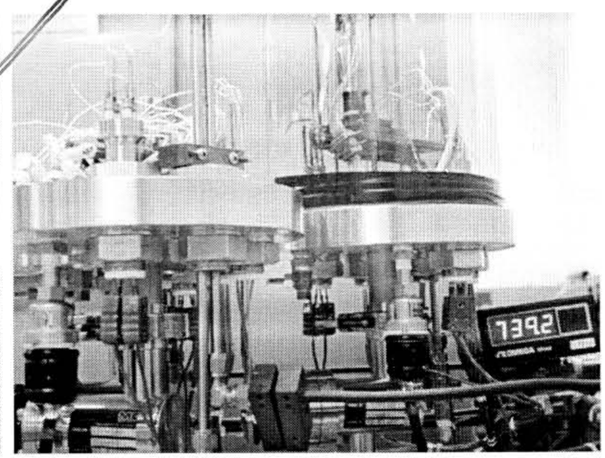
Coating Material: Ti (length 5 mm and thickness = 0-25 μm)

Aerogel encapsulated skutterudite sublimation test

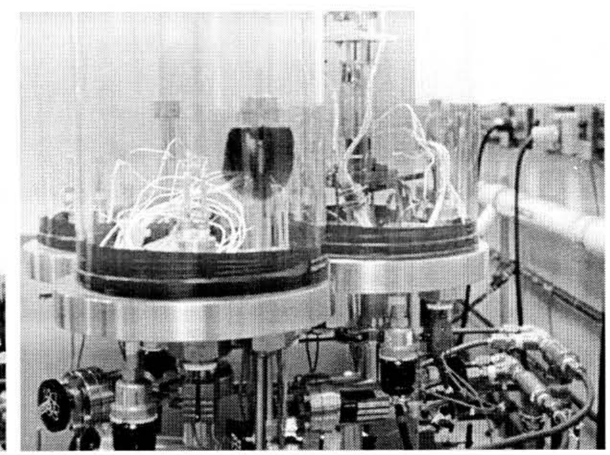




Skutterudite leg coated with graphite-opacified, silica aerogel. At 10^{-6} torr for 6 days. The absence of condensate on the inner-wall of the bell jar indicates that sublimation is completely suppressed.



Vacuum test station used to test sublimation coatings.

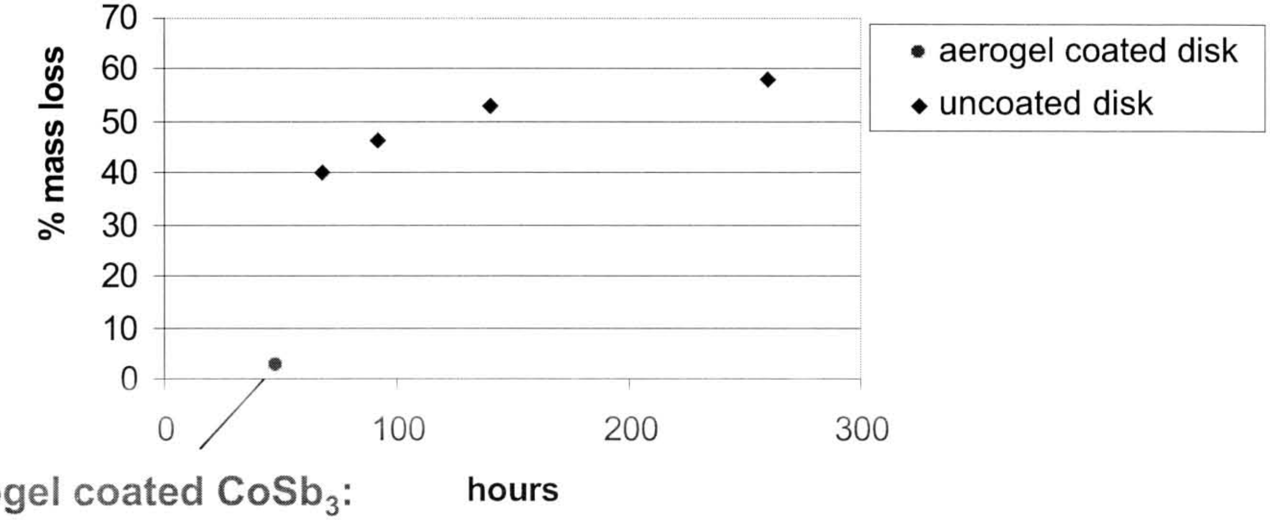


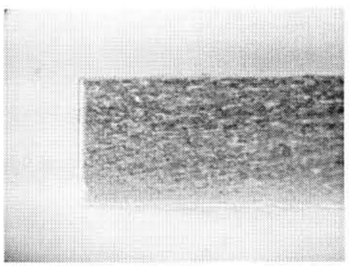
Condensation pattern of previous non-encapsulated sample sublimation test provides evidence of antimony sublimation.

Aerogel encapsulated samples weight loss experiments

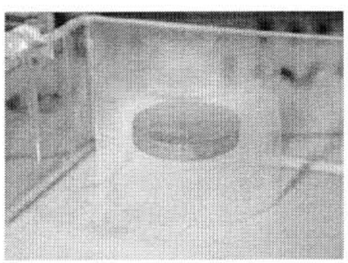
% mass loss vs. time for $CoSb_3$ disks

(700C 10^{-6} torr)

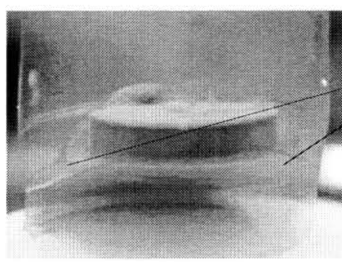




Aerogel coated $CoSb_3$: despite some cracks in aerogel, no depletion layer after 48h at 700C



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

Summary

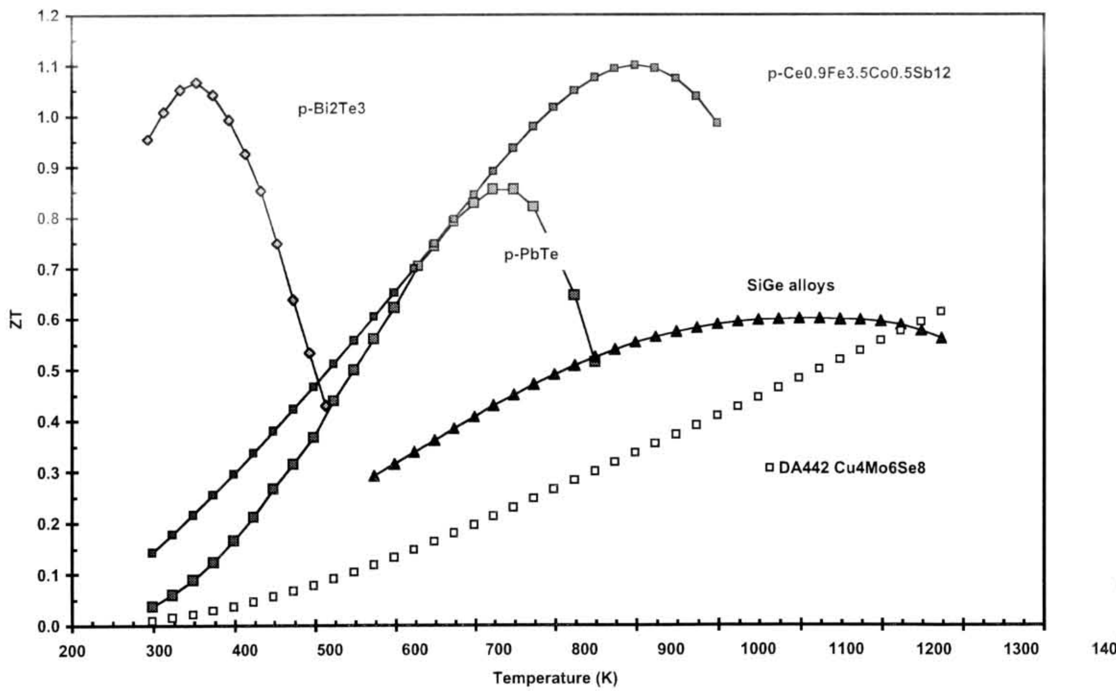
- Demonstrated ~ 14% efficiency for STE unicouples for 975K-300K ΔT
- Initiated life time studies

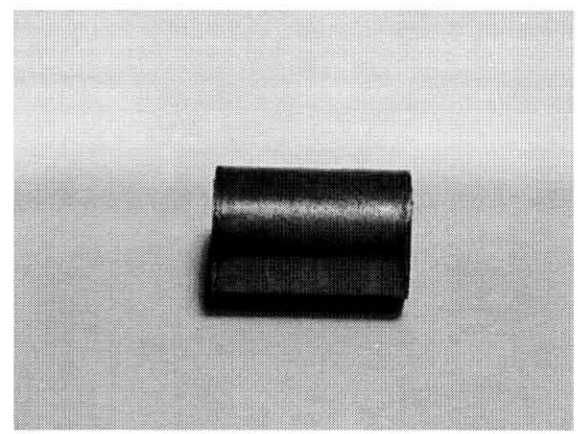
FY04-06 Major Focus Areas

- 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

High Temperature Materials

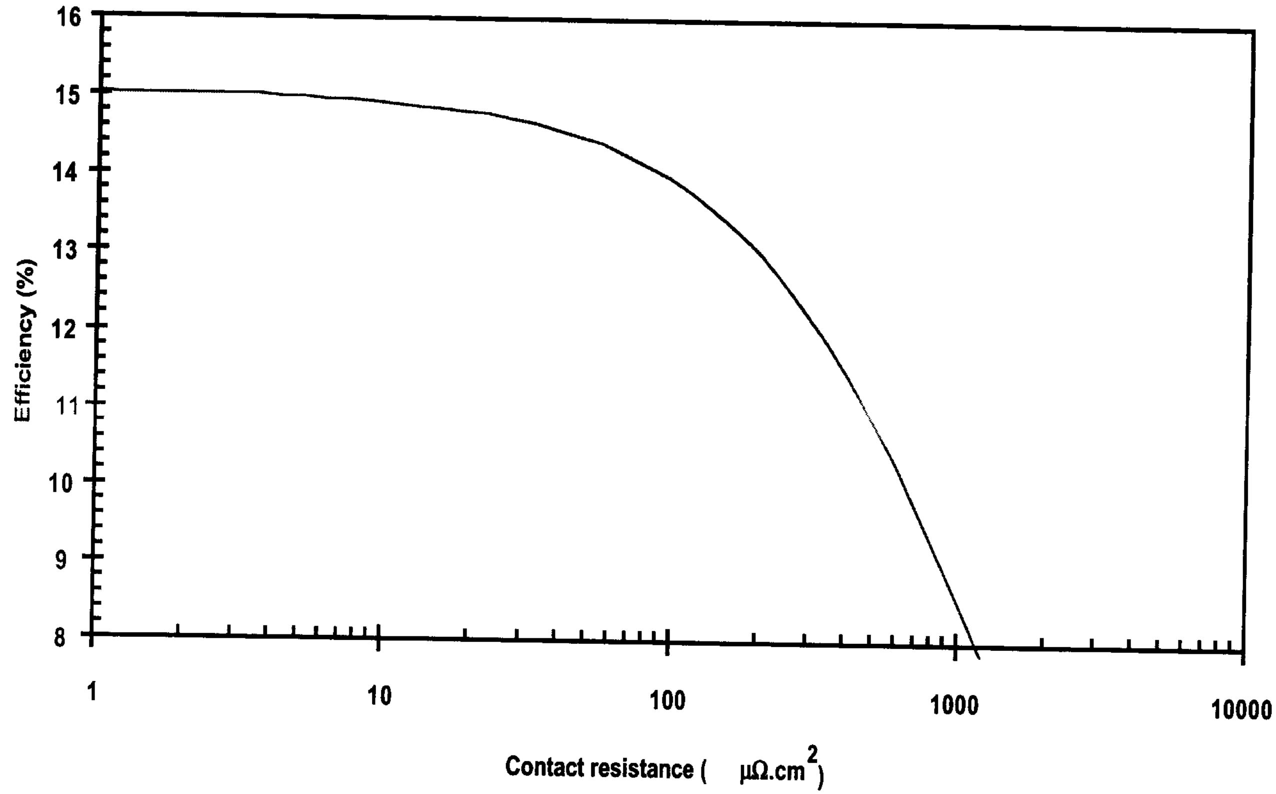
- Chevrel chalcogenides (Mo_6Se_8-based)
  - Synthesized several additional Cu and Fe filled Mo_6Se_8 compositions using a powder metallurgy technique
  - Measured Seebeck coefficient, electrical resistivity, and thermal conductivity from 300K to 1275K
  - Achieved ZT ~0.6 a 1275K for $Cu_4Mo_6Se_8$ 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





$CuMo_6Se_8$ sample tested for 6 days at 900C under 5A load

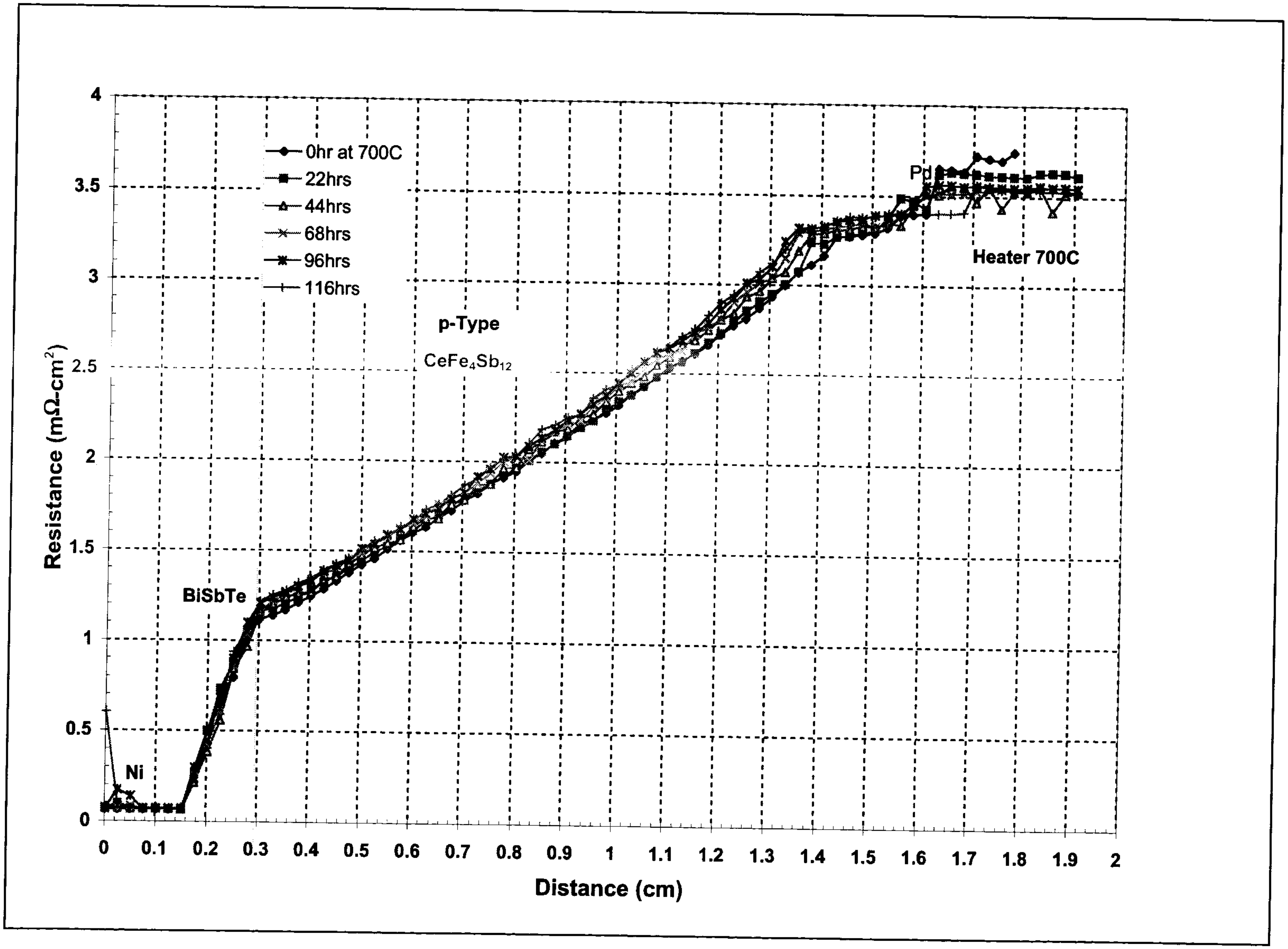
Impact of electrical contact resistance on unicouple efficiency



- Electrical contact resistance needs to be < 5 $\mu\Omega cm^2$ to prevent impact on converter efficiency

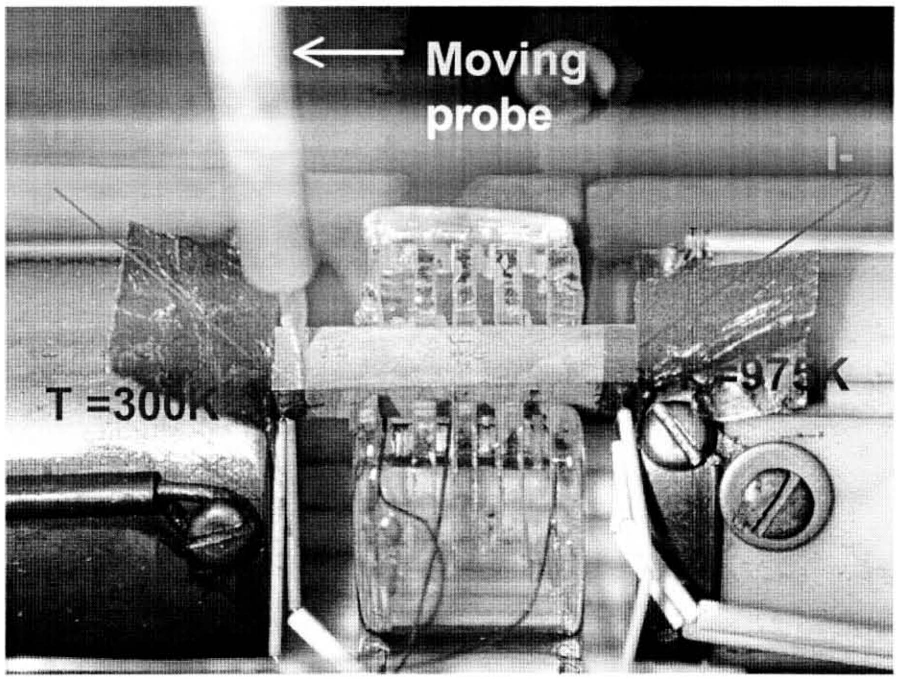
Electrical contact resistance measurements

- **Achieved electrical contact resistance < 5 $\mu\Omega cm^2$ at the segmented legs interfaces**



Segmented legs electrical contact resistance measurements

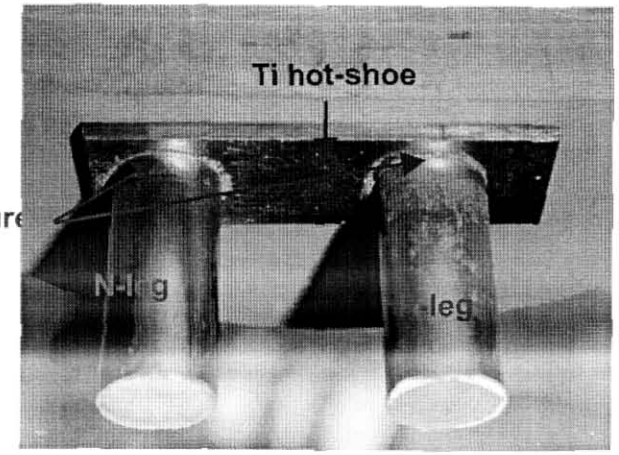
- Bond quality
  - Electrical contact resistance measurement
  - Microprobe analysis
    - Diffusion
    - Chemical reaction and interface layer analysis



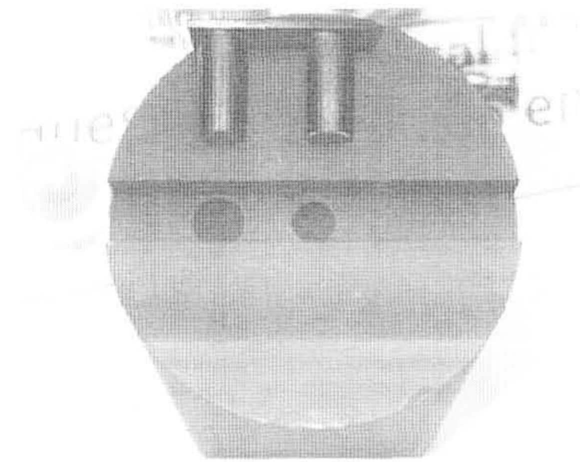
Electrical contact resistance measurements set-up

Unicouple fabrication process developed

Ti to Ti pressure bonds



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**