# PROGRESS IN THE DEVELOPMENT OF HIGH EFFICIENCY SEGMENTED THERMOELECTRIC U[redacted]

**20th Symposium on Space Nuclear Power**

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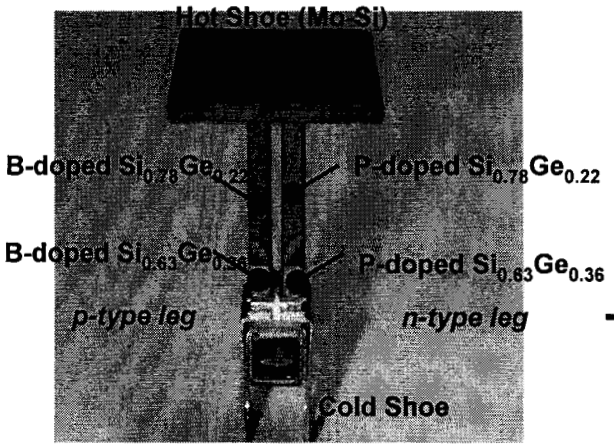
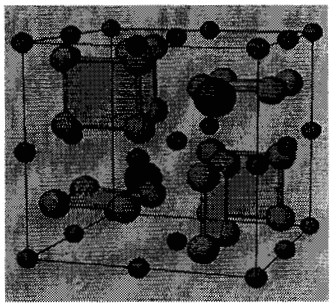
**Pasadena, CA**

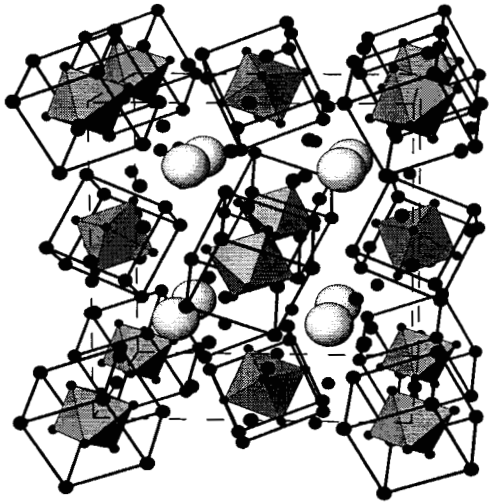
***Acknowledgement***

*DARPA, ONR & NASA for funding*

# Thermoelectric materials development funded by DARPA and C





1992

2004

PbTe ($T_{max}$ ~ 800K)
SiGe materials ($T_{max}$ ~ 1275K)
(TRL9)

New materials
- Skutterudites
- Chevrels
- Others

(TRL 2-3)

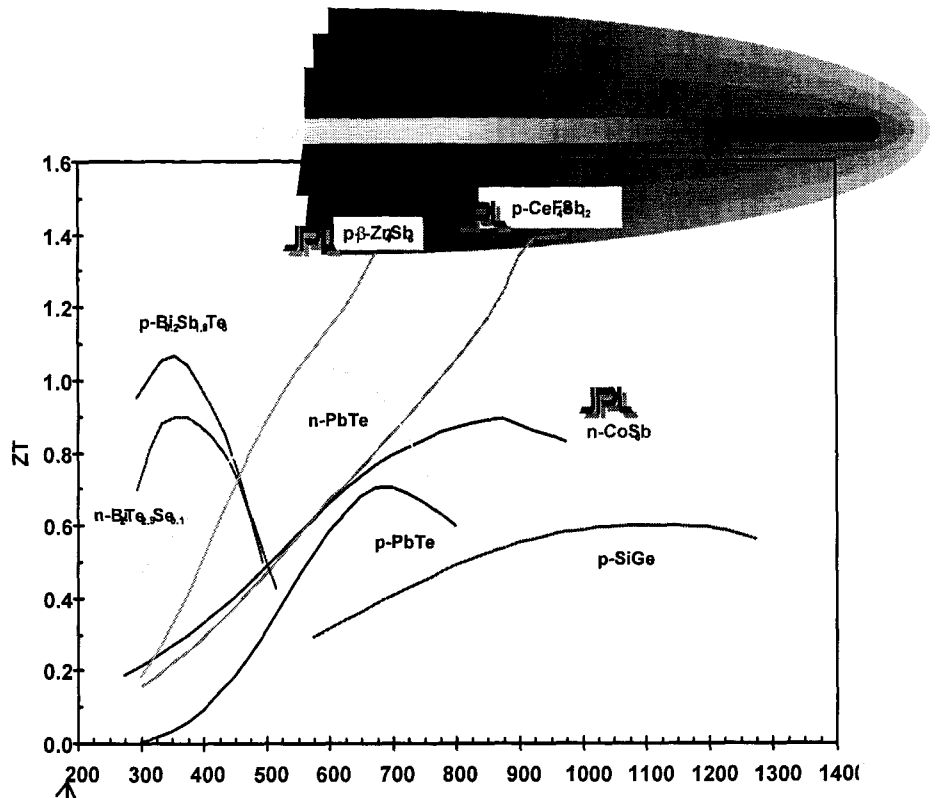
2nd generation advanced materials
(TRL 1-2)

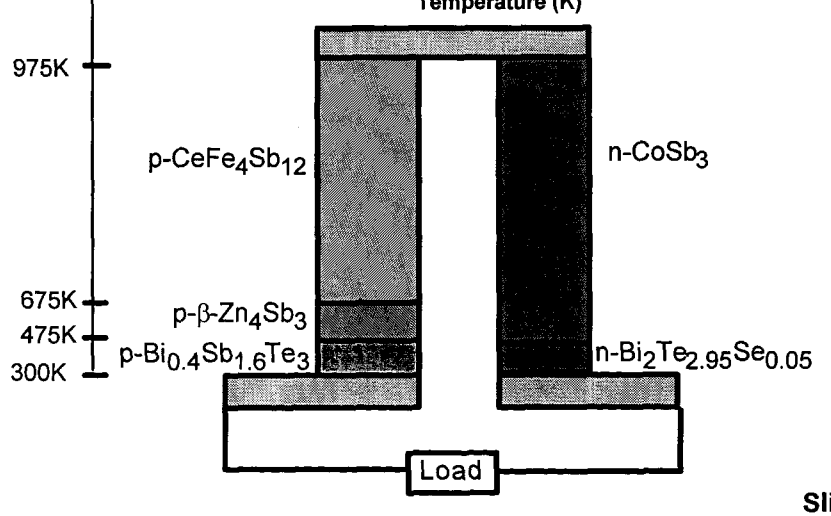
ZT

# New developments

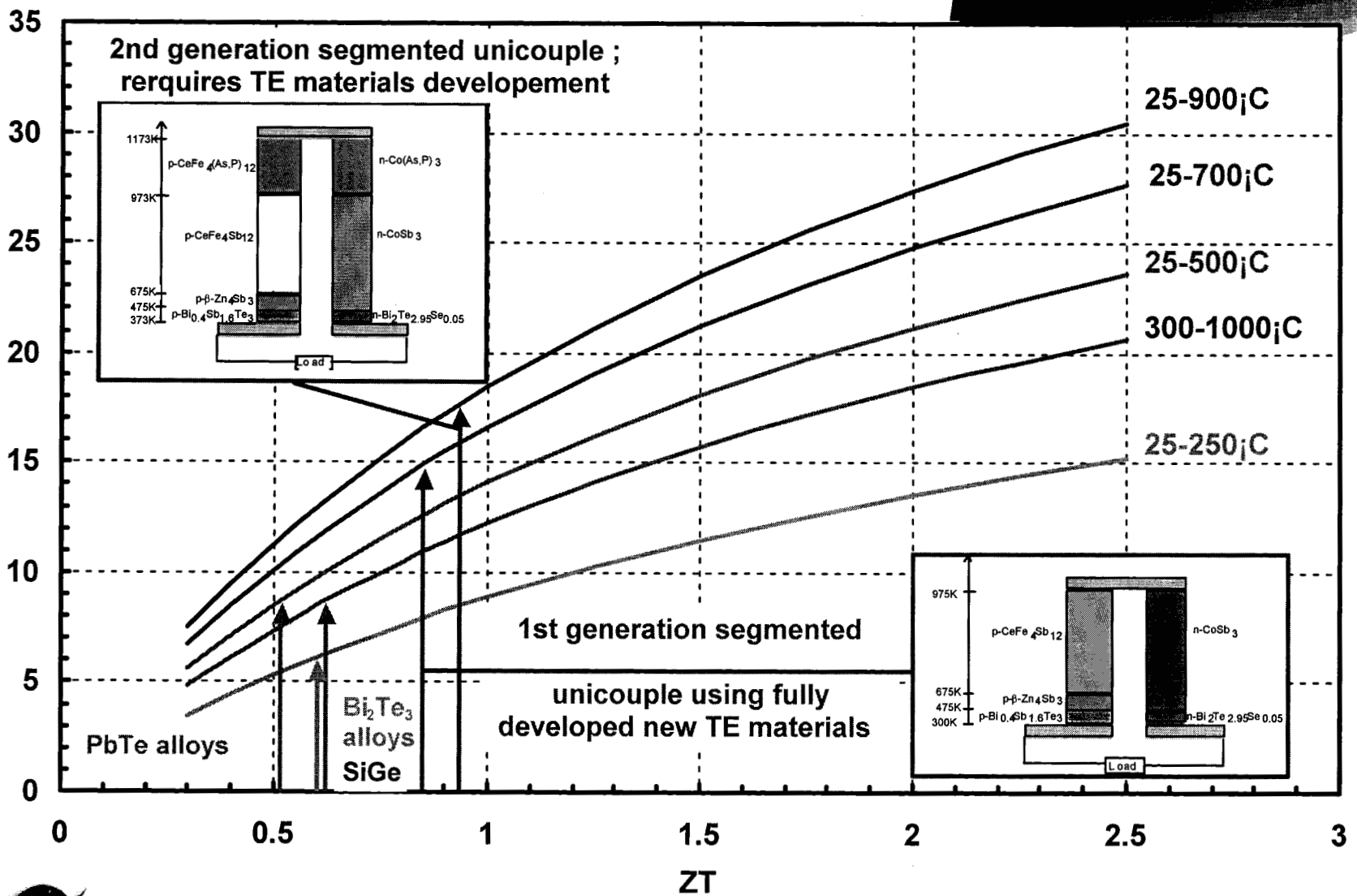
- **Improvement in ZT possible !**
  - Higher efficiency values
- **Segmented unicouples**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials ($Bi_2Te_3$-based materials) and new, high ZT materials developed at JPL
    - Skutterudites : $CeFe_4Sb_{12}$ and $CoSb_3$
    - $Zn_4Sb_3$
    - JPL/Caltech patents issued and pending
  - Higher average ZT values
  - → Higher material conversion efficiency
    - → Up to 15 % for a 300-975K temperature gradient
  - Less than 975K operation

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

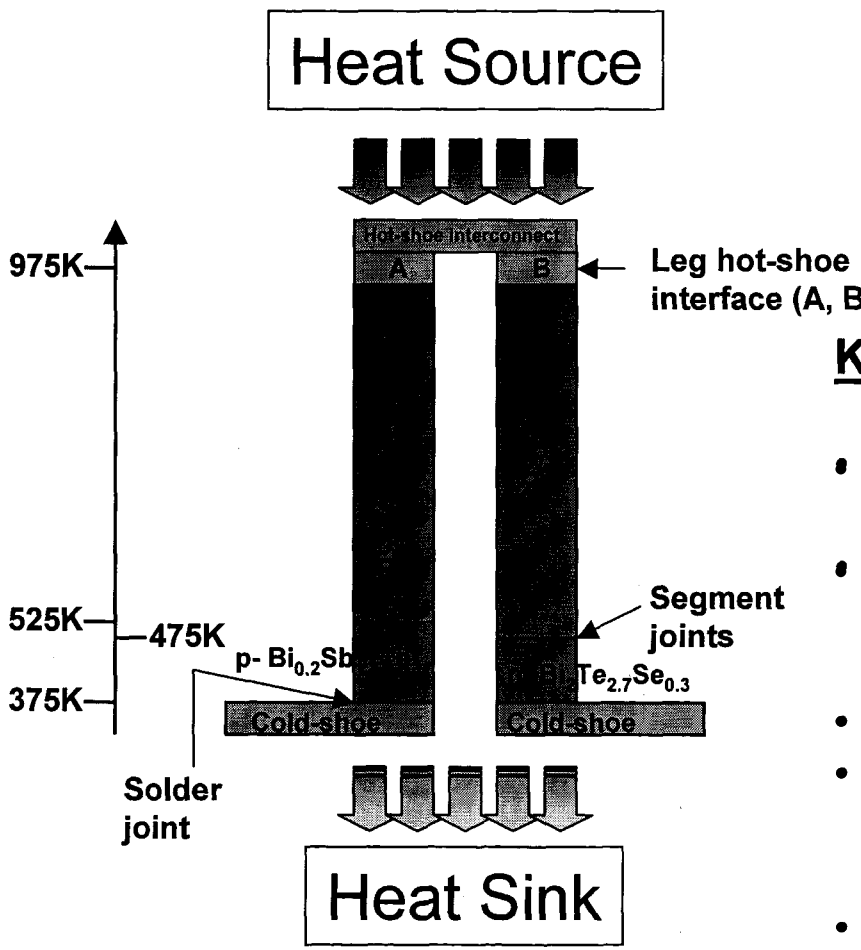


# State-of-the-art vs. advanced thermoelectri[redacted]



# 975K-375K Segmented Unicouple Technology Development




## Projected 97[redacted]formance

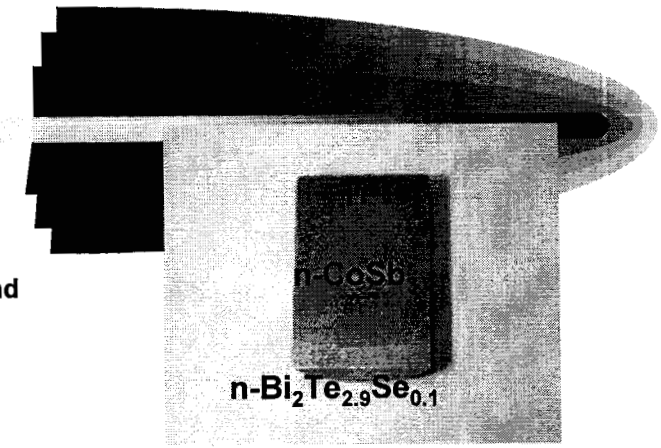
| RPS (multi-hundred Watts) | GPHS-RTG | LT STE-RPS |
|---|---|---|
| $T_{hot}$ (K) | 1275 | 975 |
| $T_{cold}$ (K) | 575 | 375 |
| Converter Efficiency (%) | 8 | 12.5 |
| System Efficiency (%) | 6.5 | 10.1 |
| Specific Power ($W_e$/kg) | 5.2 | 8.0 |

## Key technology challenges

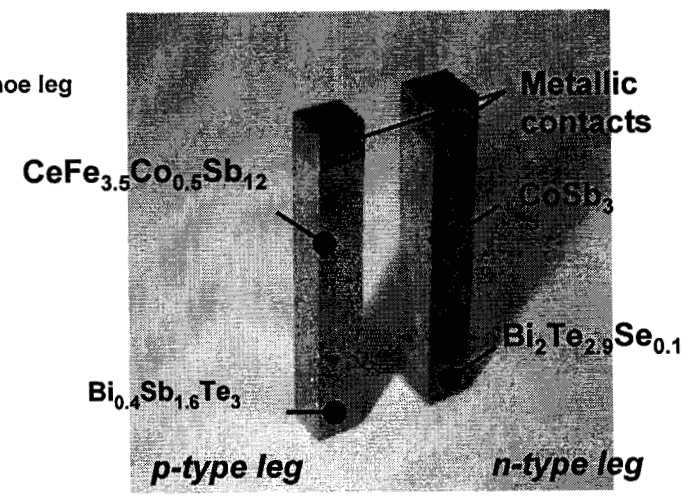
- TE materials processing and segmented leg fabrication
- Low electrical contact resistance between segments and between segments and cold- and hot-shoes
- Unicouple mechanical integrity
- Demonstrate TE materials stability
  - Sublimation control
  - Stable thermoelectric properties
- Demonstrate unicouple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

# 975K-375K Segmented TE Unicouple
# TE materials processing & legs fabrication

- **Thermoelectric materials processing**
  - Developed ~100 g batch powder metallurgy process for n- and p-type skutterudites and $Bi_2Te_3$ alloys
  - Optimized milling process to achieve uniform grain size
  - Completed optimization of p-type skutterudite for leg fabrication
- **Developed fabrication process for p- and n-segmented legs**
  - Single hot-pressing processing parameters optimized
    - Includes segment joints (diffusion barrier and mechanical bond) and metallic hot-shoe leg interfaces
  - Performed in-gradient electrical contact resistance measurements
- **n- and p-legs performance**
  - Achieved performance goals for n-type legs
    - Consistent with 12.5% unicouple conversion efficiency goal
  - p-leg evaluation in progress
- **Initiated in-gradient life tests on segmented legs**



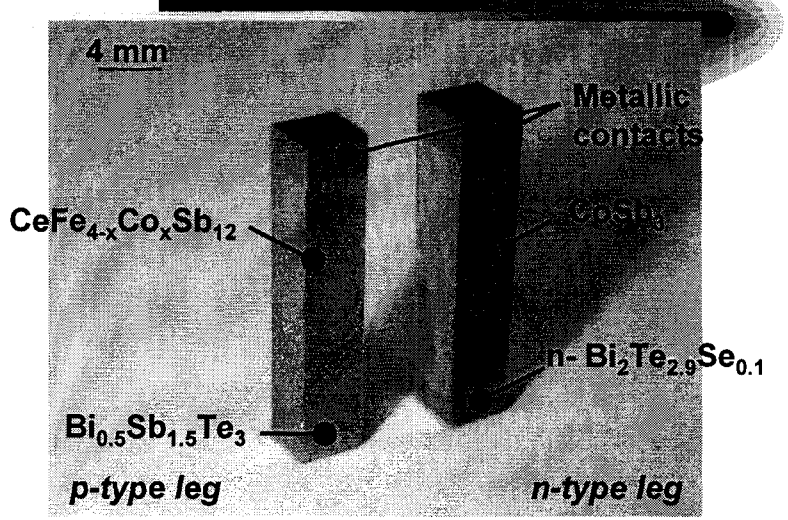

N-type segmented leg




Segmented legs fabricated by uniaxial hot-pressing

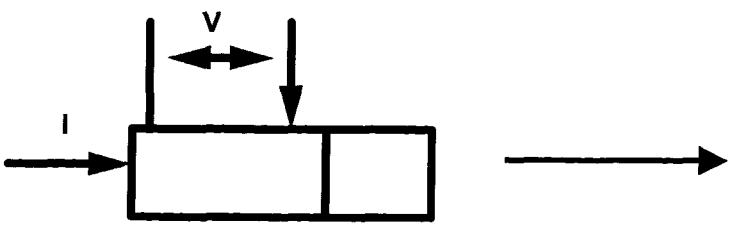
# Segmented legs fabrication and tes[redacted]

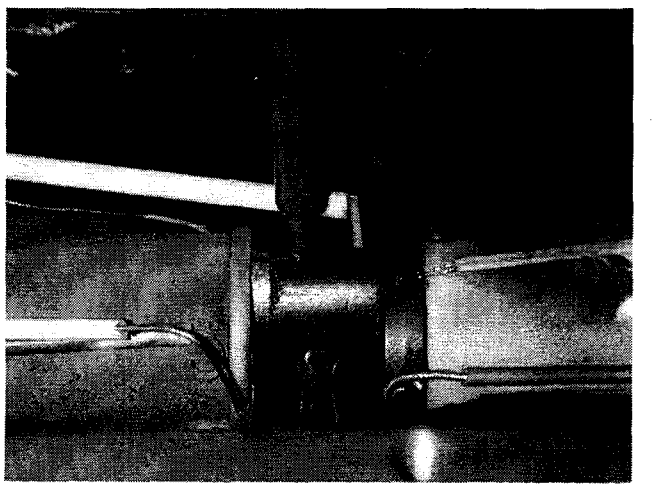
- **Segmented legs fabrication**
  - Unixaxial hot-pressing of powdered materials stacked on the top of each other
    - Temperature optimized
      → density close to theoretical value
    - In graphite dies and argon atmosphere
  - With metallic foils between the different segments of the legs
    - Selected to compensate for coefficient of thermal expansion mismatch
    - Diffusion barrier
    - Should react chemically with both materials to be bonded
    - Low electrical resistance bond (<10$\mu\Omega cm^2$)
  - Metallic contacts at hot-side



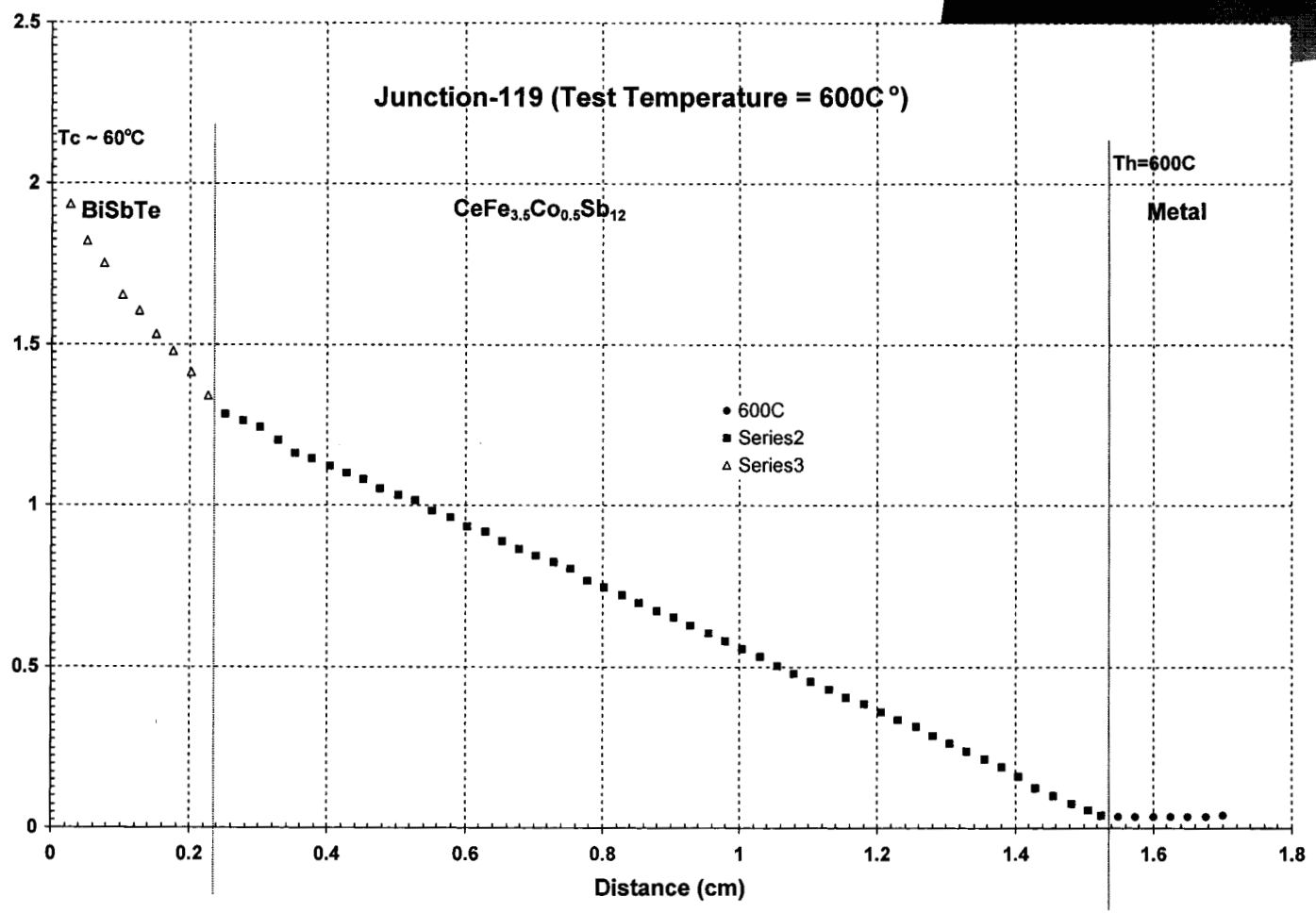

**Segmented legs fabricated by uniaxial hot-pressing**

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



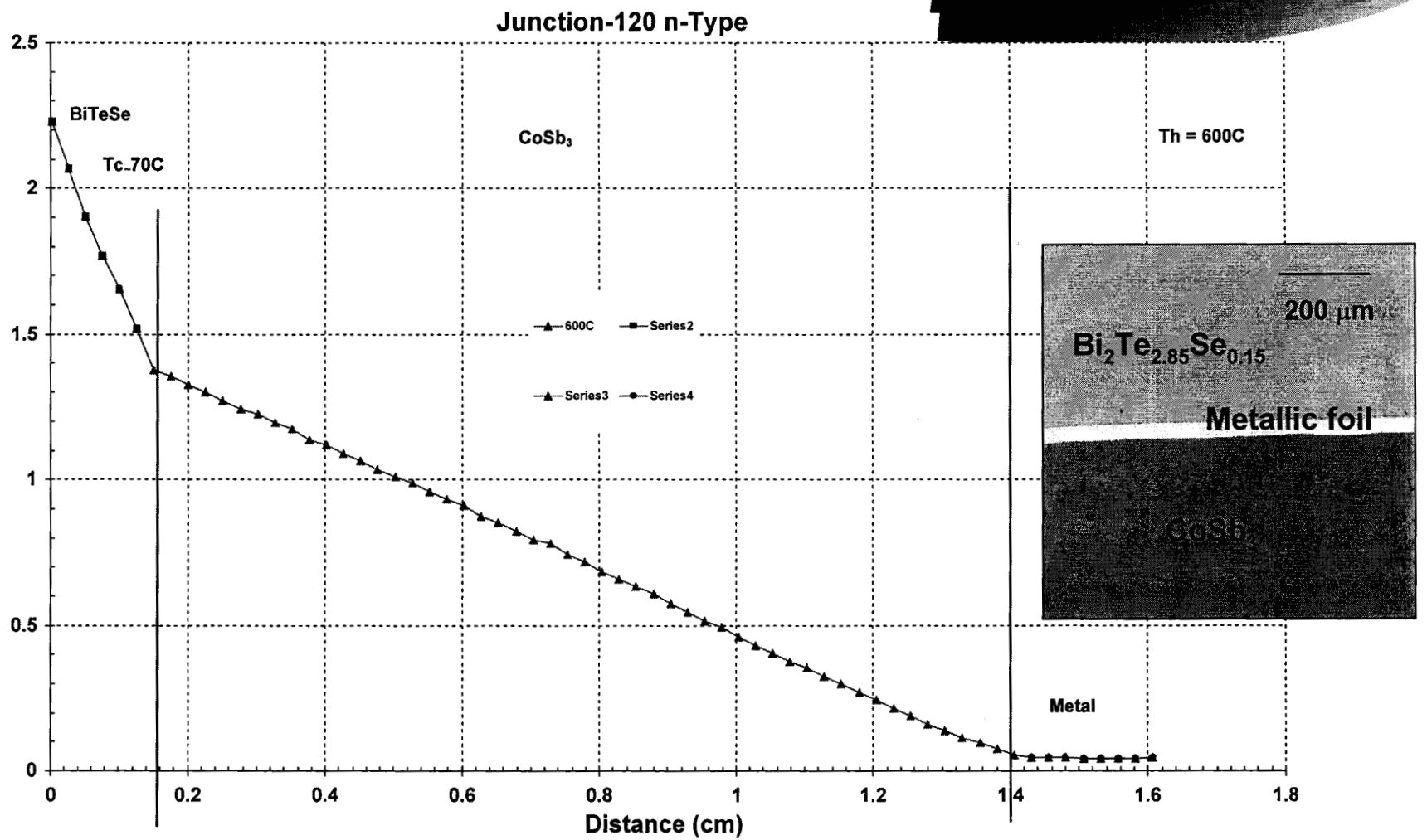



# Electrical contact resistance measurements for p-type segmented leg




- Low electrical contact resistance achieved (< 5 $\mu\Omega cm^2$)

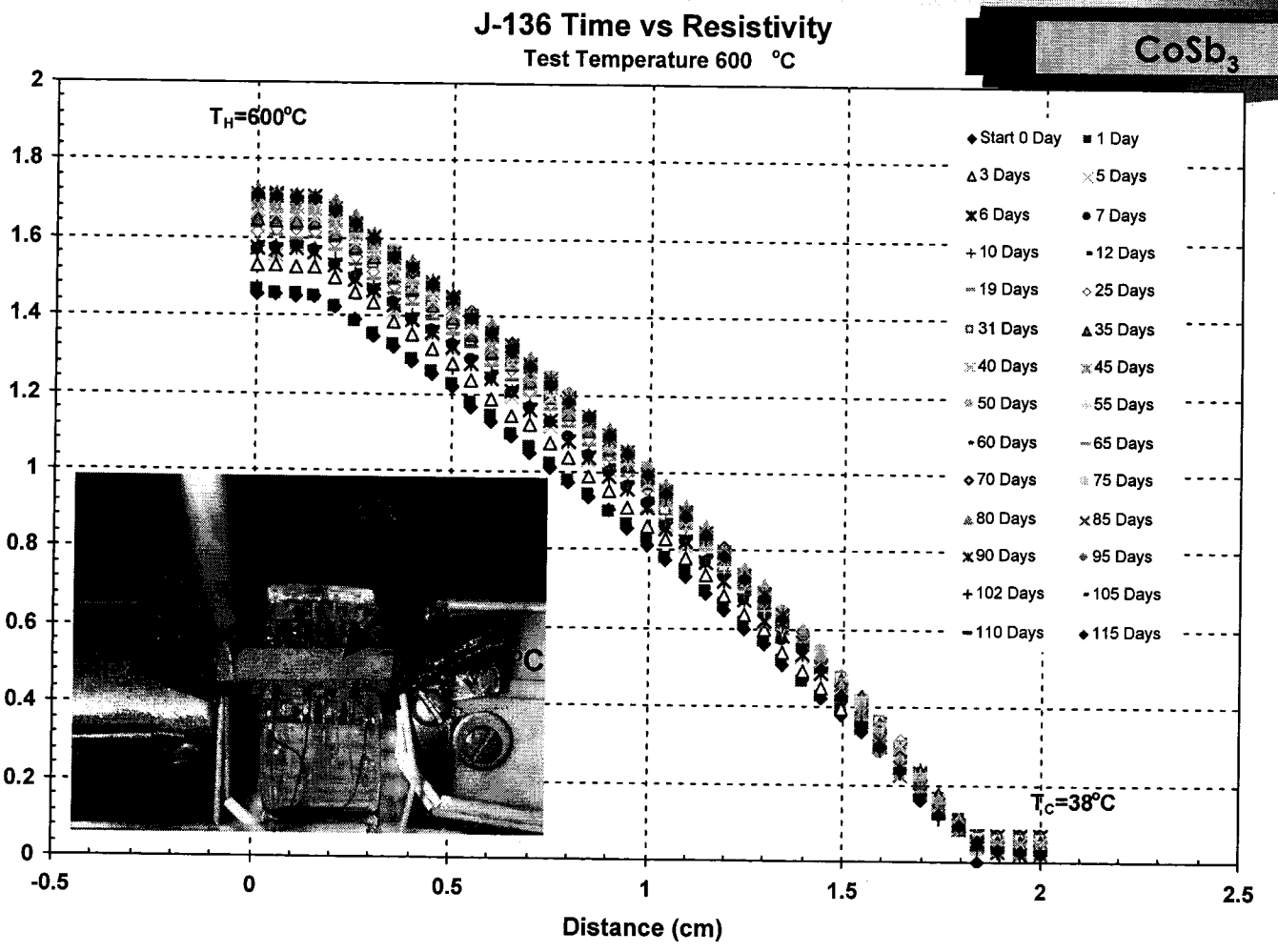
# Electrical contact resistance measurements for n-type segmented leg




- Low electrical contact resistance achieved (< 5 $\mu\Omega cm^2$)

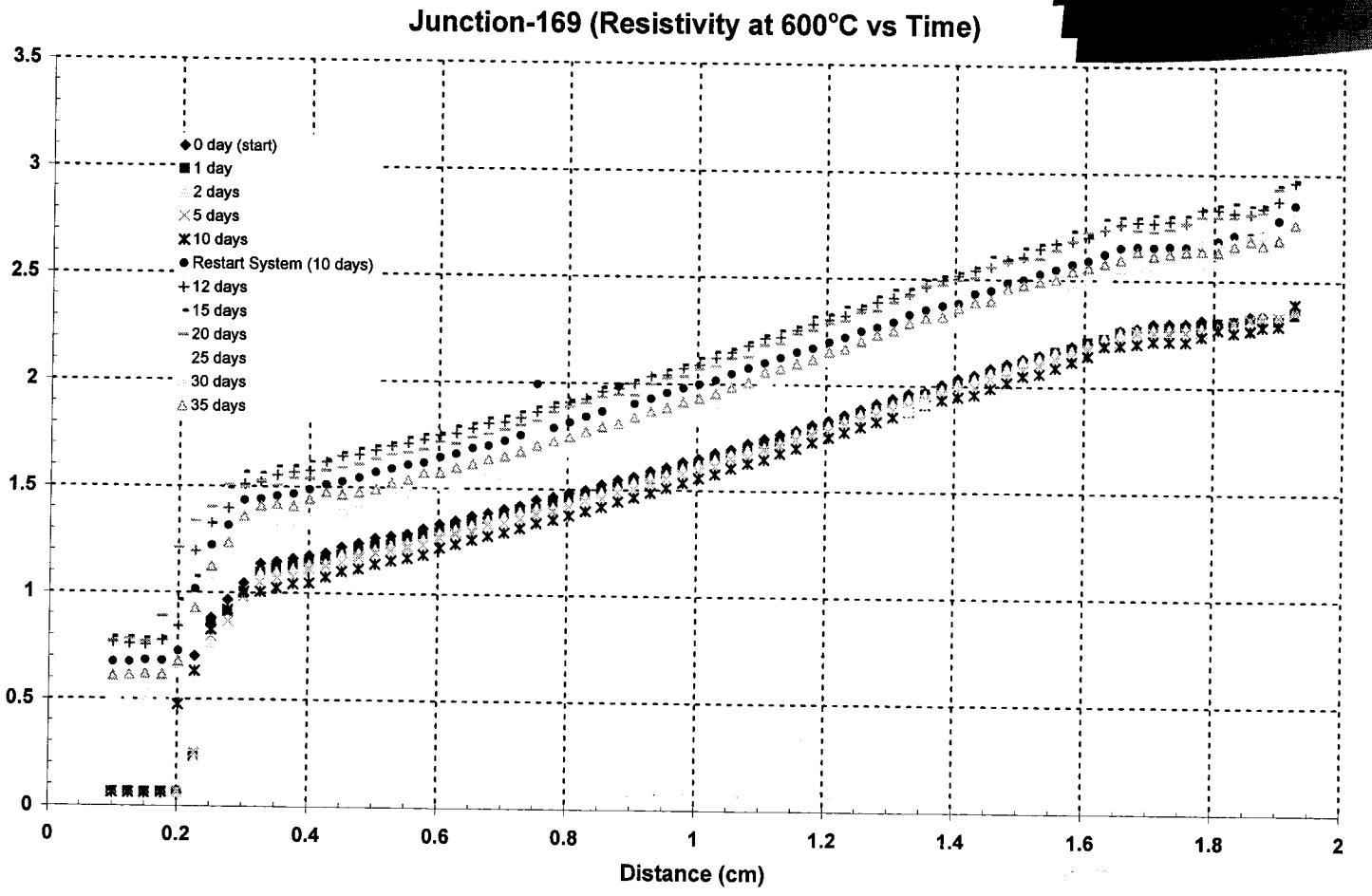
# 975K-375K Segmented TE Unicouple n-type leg: low contact resistances ac

$CoSb_3$




- Demonstrated n-type leg low electrical resistance contacts between Ti and $CoSb_3$ for up to 4 months at operating temperatures

# In gradient electrical contact resistance life tests on $Bi_2Te_{2.85}Se_{0.15}$/Ti/$CoSb_3$/Ti segmented le[redacted]

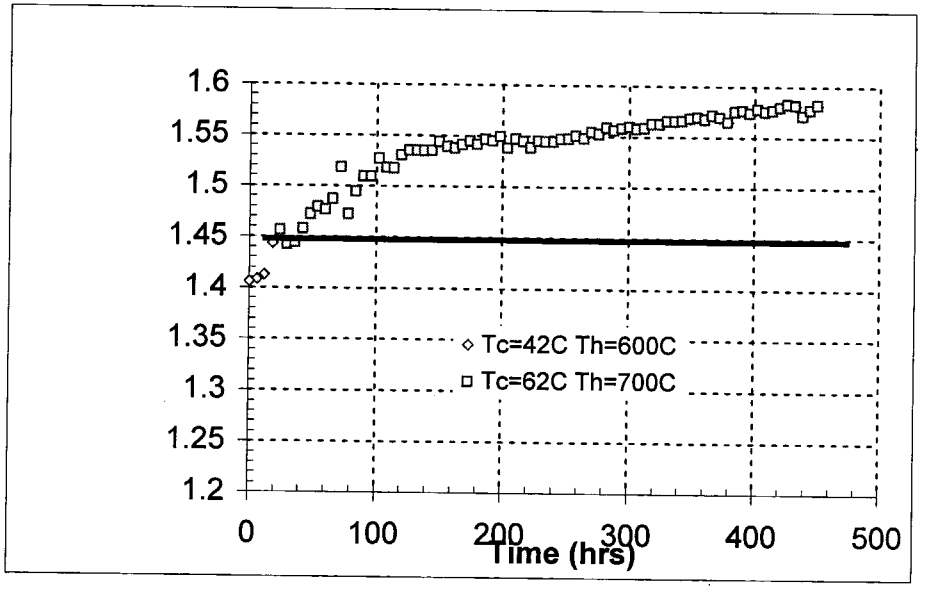


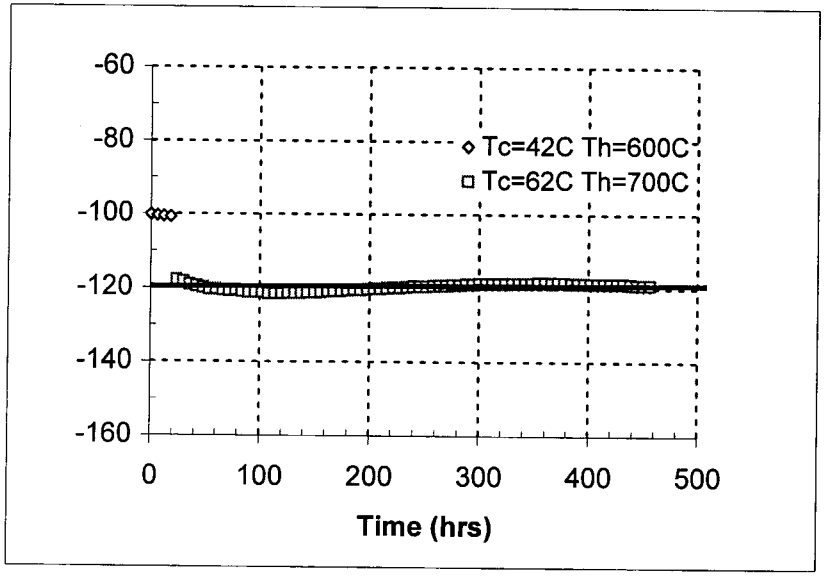

- Demonstrated low electrical resistance contacts between for $Bi_2Te_{2.85}Se_{0.15}$ and Ti/$CoSb_3$/Ti segmented leg

# 975K-375K Segmented TE Unicoup[redacted]

- Achieved performance goals for n-type segmented and non-seg[redacted]

  → Validation of n-type $CoSb_3$ properties and performance

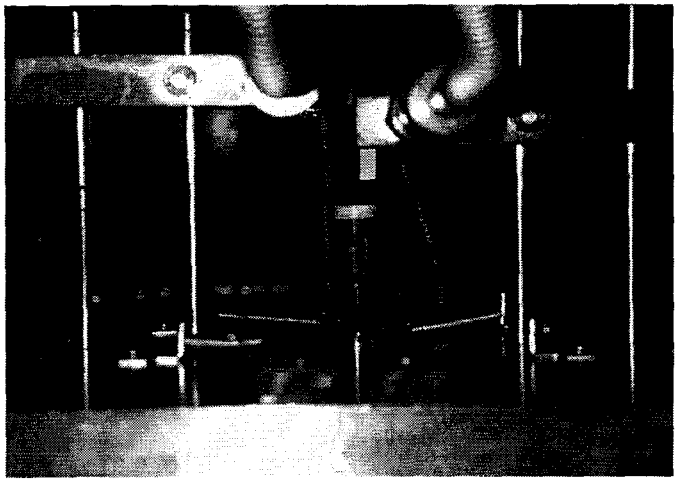



Model prediction ———

# 975K-375K Segmented TE Unicouple Unicouple fabrication and testing

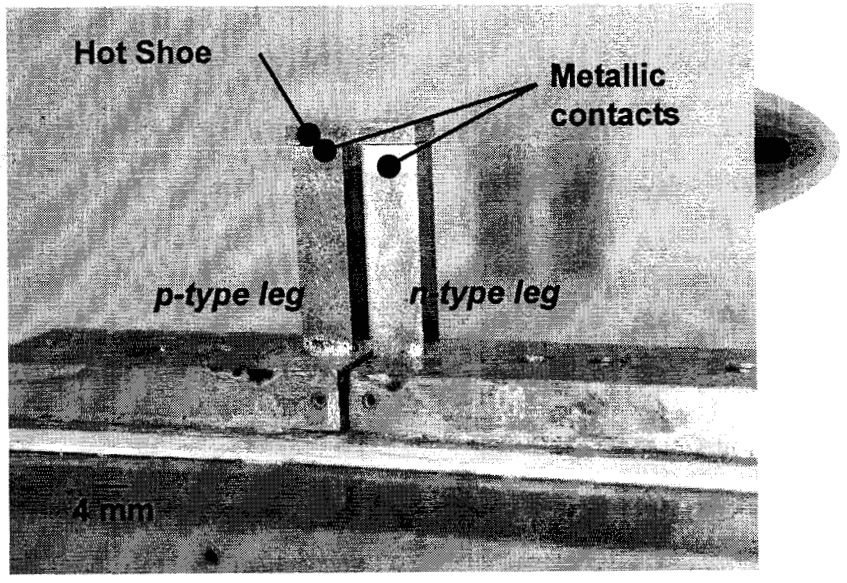
- Unicouple fabrication for $T_{H\,max}$ = 975K
  - Over 20 segmented and non-segmented unicouples fabricated and tested for thermal and electrical performance
  - Used various techniques and materials for joining n- and p- legs to a hot-shoe
  - Attempted to co-press n- and p-legs simultaneously
- Unicouple thermal and electrical testing
  - Developed testing procedure and hardware for unicouples; low-stress test set-up built
  - Measured I-V curves for selected unicouples
  - Main technical issue :
    - Electrical contact resistance at the hot-shoe resulting in a 10% increase of the unicouple expected resistance
    - Developing better brazing materials and techniques
- Best results to date
  - ~ 11.5% thermal to electrical efficiency at $T_C$ ~ 360K and $T_H$ = 975K
  - 10% for 4 different unicouples at $T_C$ ~ 360K and $T_H$ = 875K

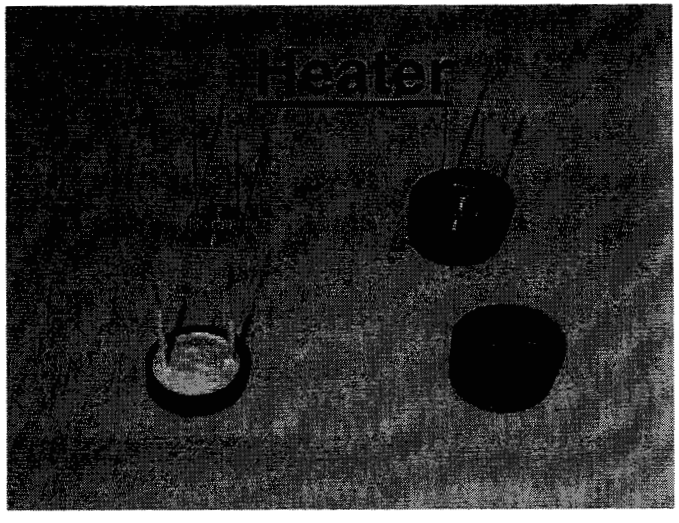


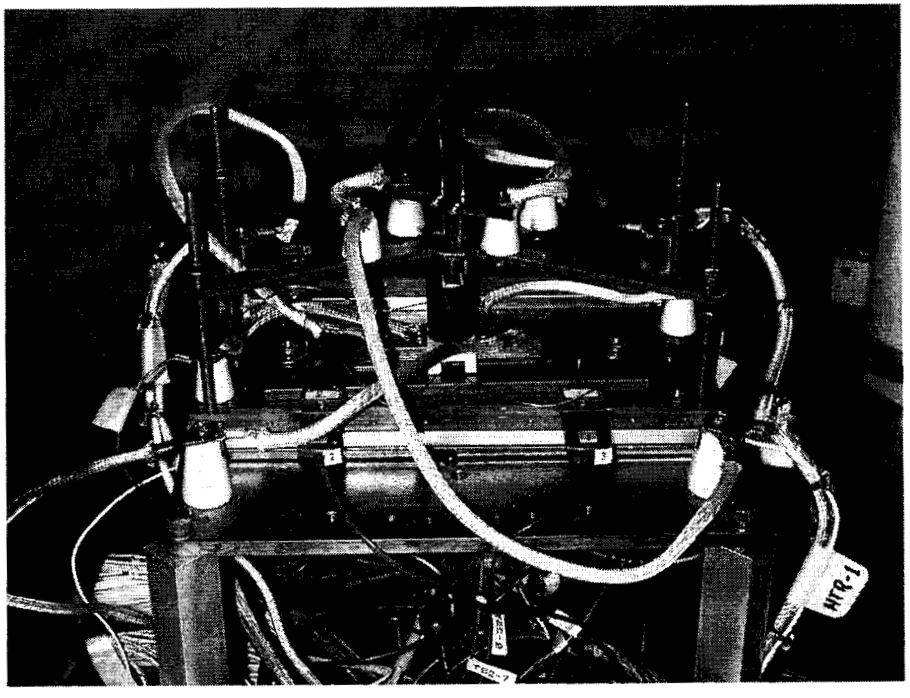
Low-stress test set-up for unicouples ; the cold shoes can independently move

# *Unicouple fabrication and testing*

- **Brazing to metallic hot-shoe**
  - **Top metallic contacts brazed to hot-shoe**
- **Cold-shoe**
  - **Lower $Bi_2Te_3$-based segments soldered to Cu blocks using Bi-Sn solder & Ni as diffusion barrier**
  - **Cu blocks soldered to a Cu plated $Al_2O_3$ plate**

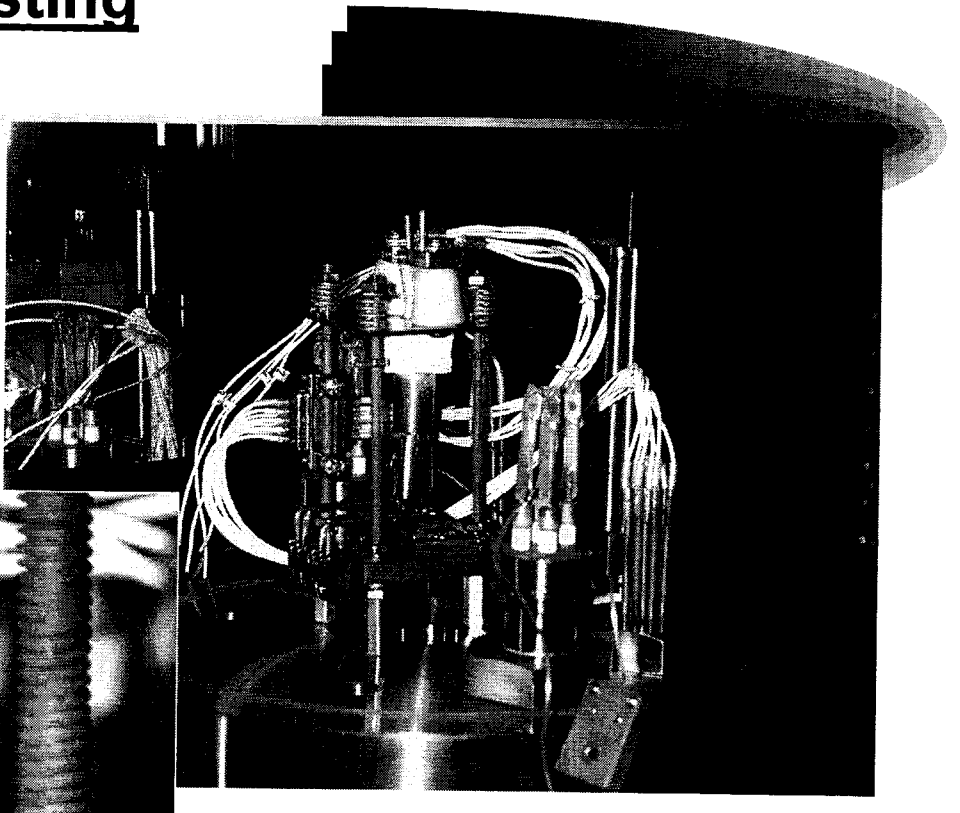


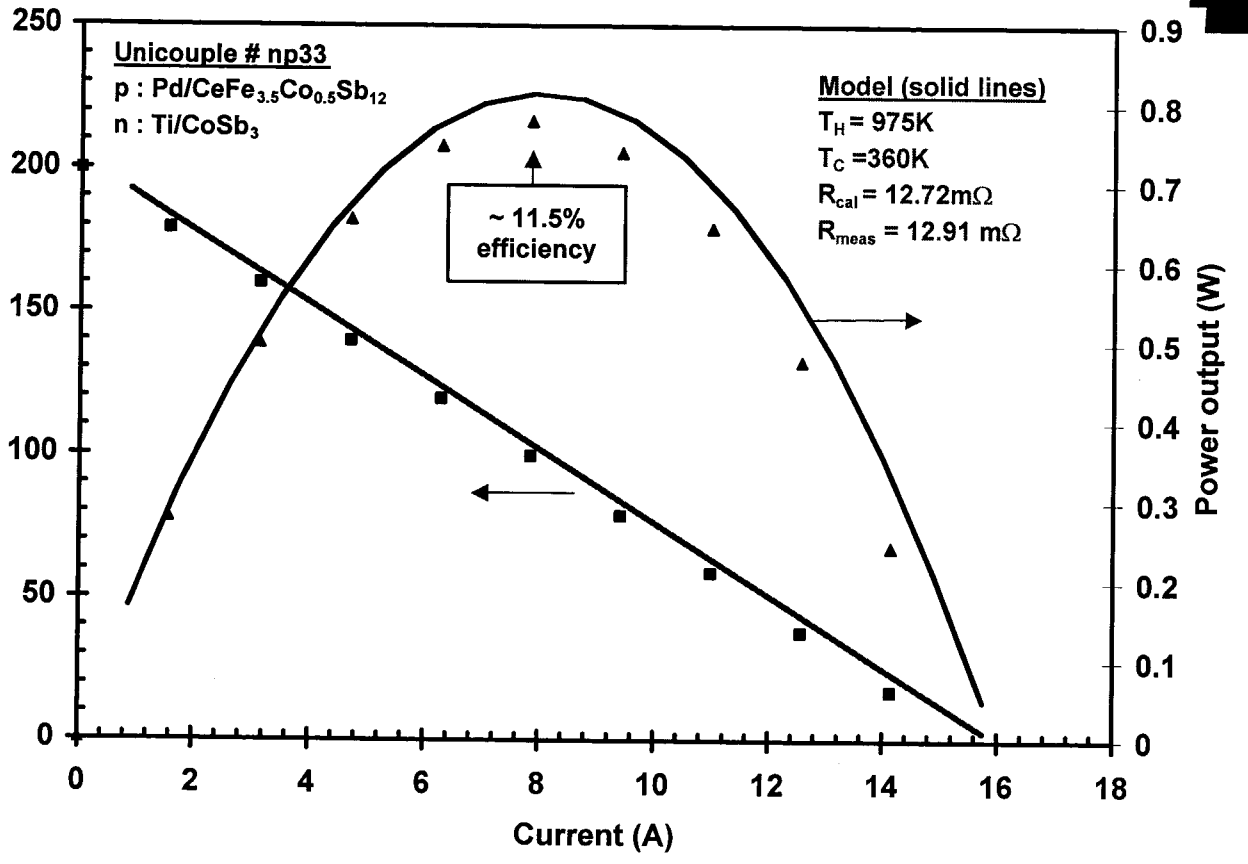
# Thermal and electrical testing

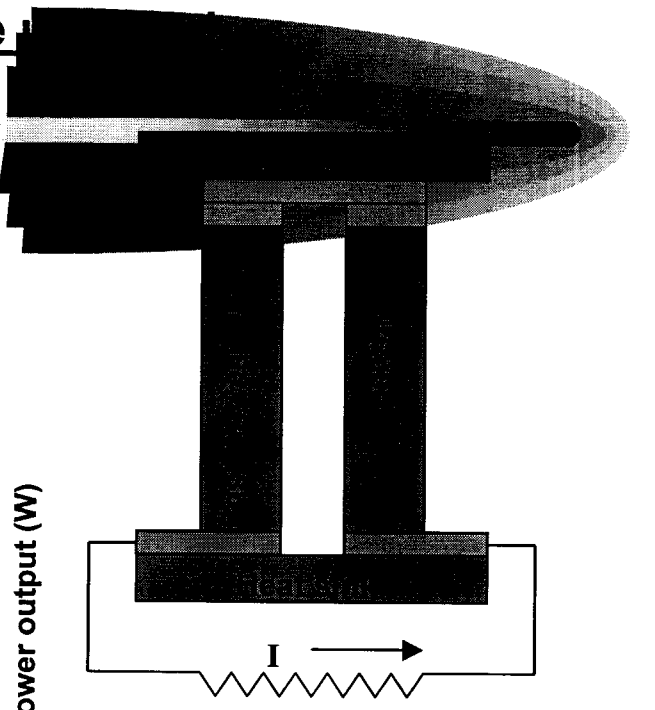
- **Testing Set-up**
  - Vacuum ($10^{-5}$ Torr)
  - Cu plated $Al_2O_3$ attached to a water cooled heat sink
  - Heat shield around the unicouple to minimize heat losses by radiation

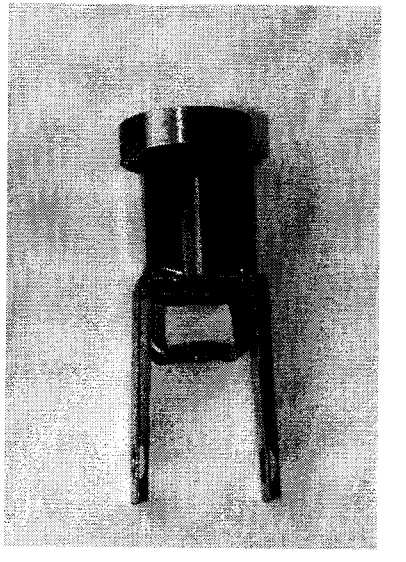


- Thermocouples recording temperature inside top metallic contacts of the legs
- Temperature measured under each leg
- Automated system
  - Control hot-side temperature
  - I-V curves

# 1st generation segmented unicouple
# Thermal and electrical testing - All skutterudite



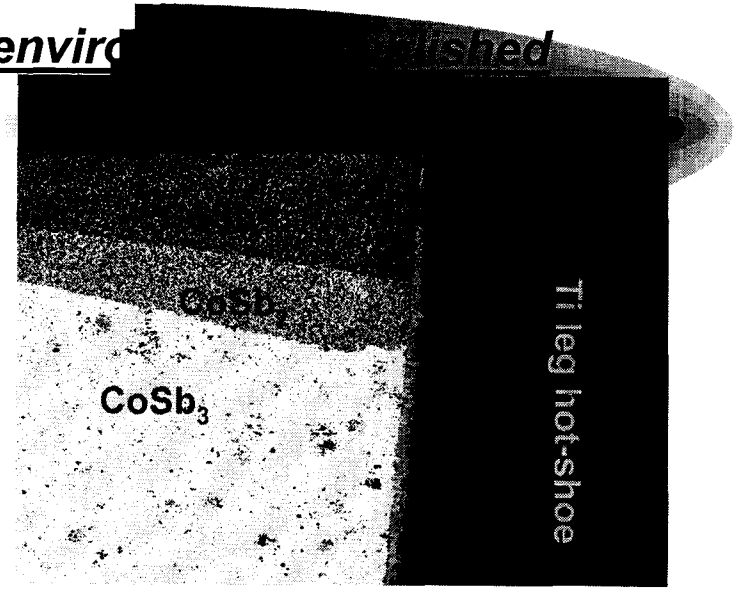



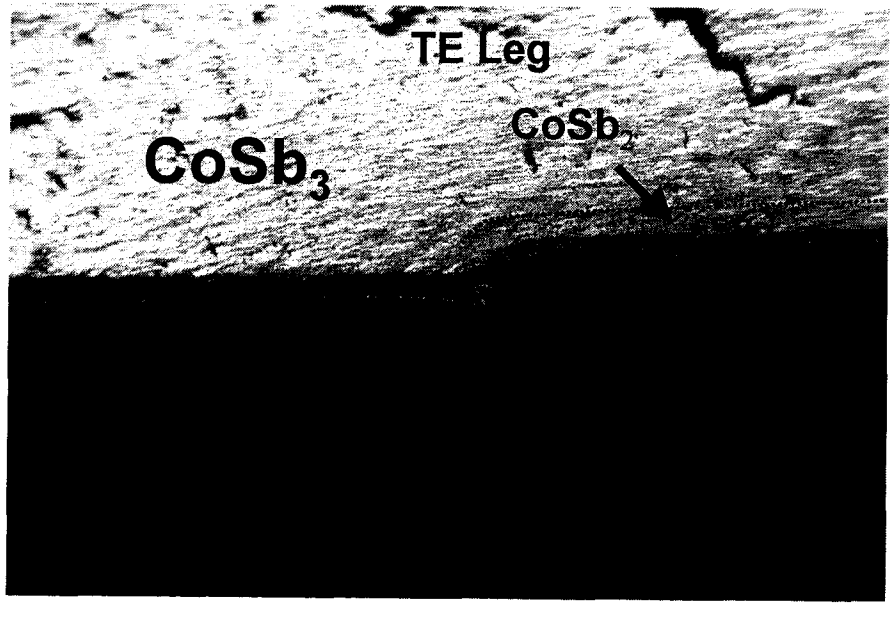
- 11.5% efficiency demonstrated to date

# 975K-375K Segmented TE Unicouple
## Approach to long life in vacuum operating envir[illegible]lished

- **Sublimation studies**
  - Confirmed Sb sublimation as the predominant materials degradation mechanism
  - Evaluated Sb sublimation rates at 975K and 875K
  - Cover gas suppresses Sb sublimation




Photograph showing the decomposition of a $CoSb_3$ sample annealed at 875K for 3 months

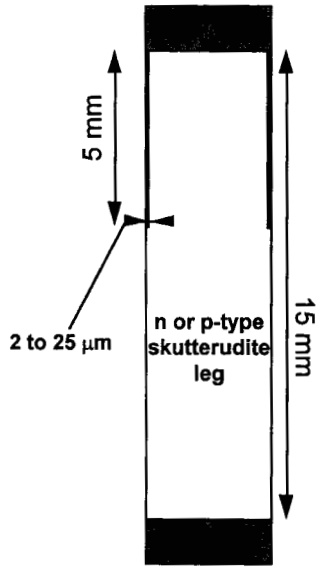


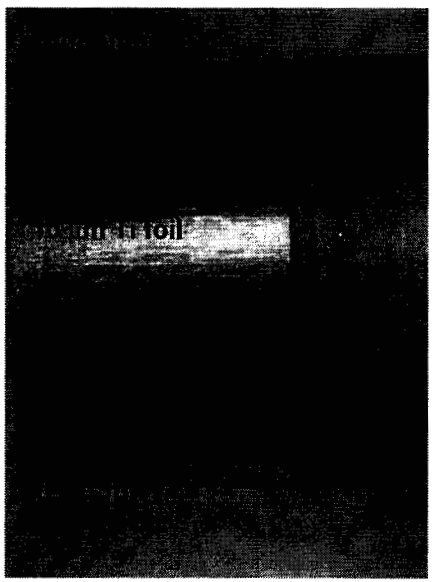

Photograph of $CoSb_3$ sample annealed at 975K for 5 days

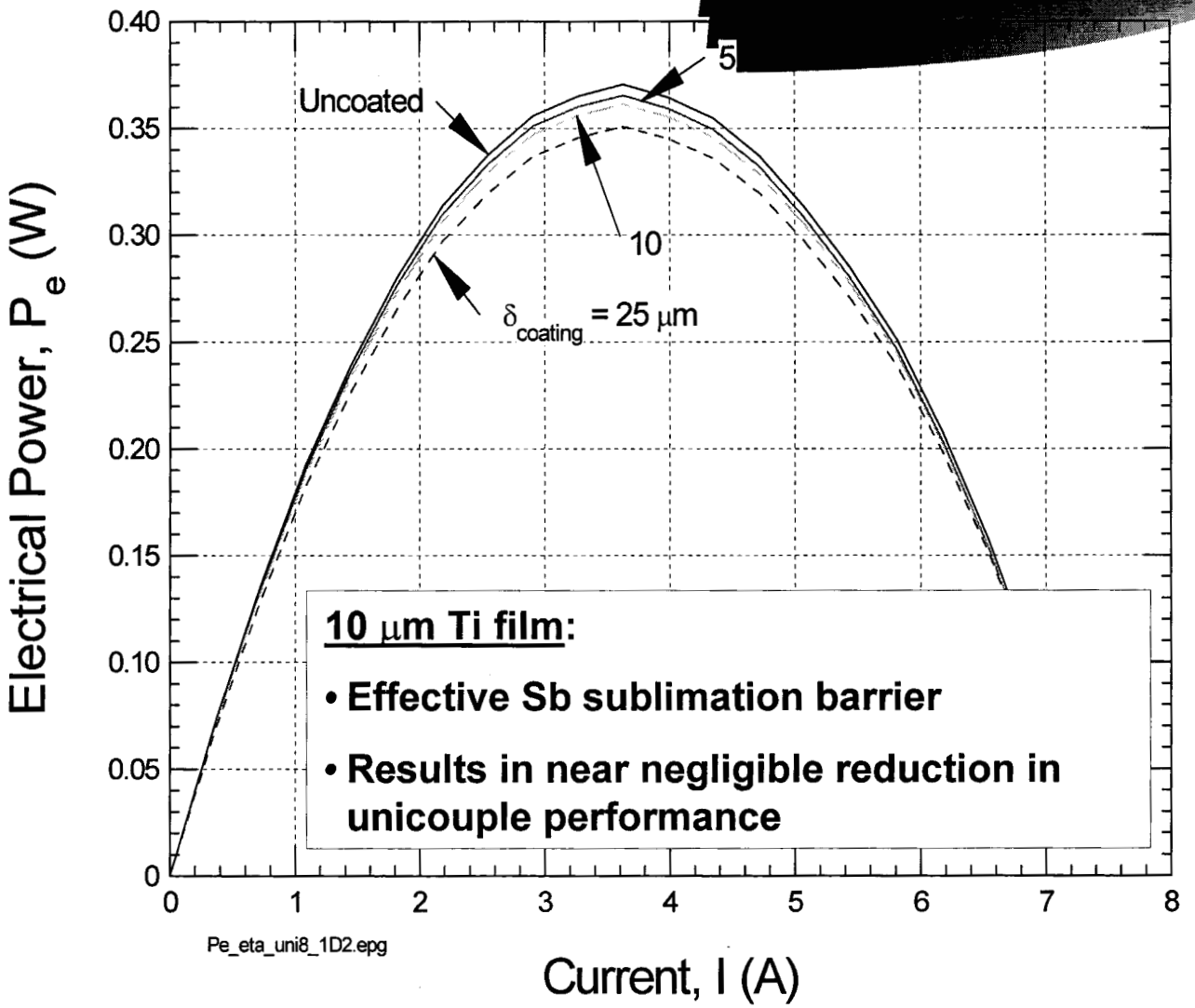
- **Coatings studies**
- Experimented with $Si_3N_4$ , $SiO_2$ and Ti as sublimation barriers
- Ti coatings very promising
  - Initial results show Ti film suppresses Sb sublimation
  - Ti film applied during hot-pressing
  - Ti film-coated leg life tests initiated
  - Thermal/mechanical modeling performed to evaluate impact on unicouple performance

# 975K-375K Segmented TE Unicouple

## Thermal/mechanical performance modeling



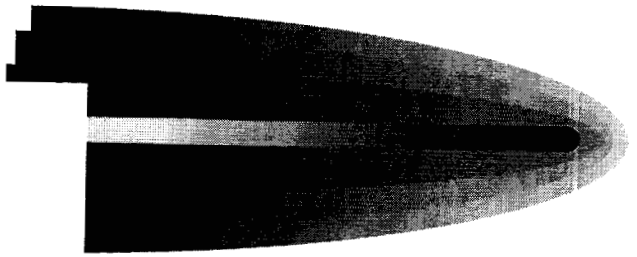



**10 μm Ti film:**

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

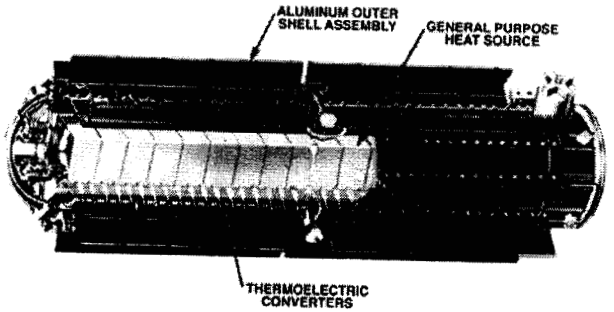
*Coating Material: Ti (length 5 mm and thickness = 0-25 μm)*

# Advanced RTG (ARPS-TE)



## General Purpose Heat Source (GPHS)

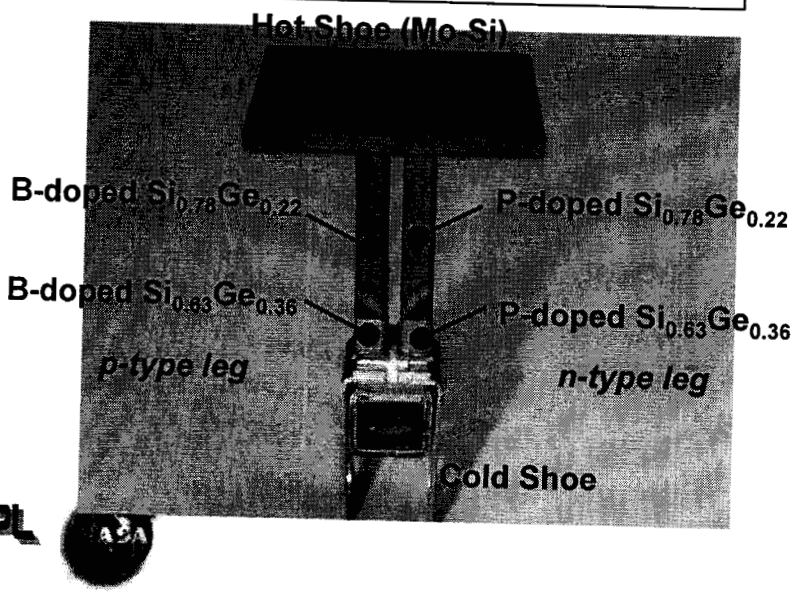
**Radioisotope Thermoelectric Generator (RTG)**



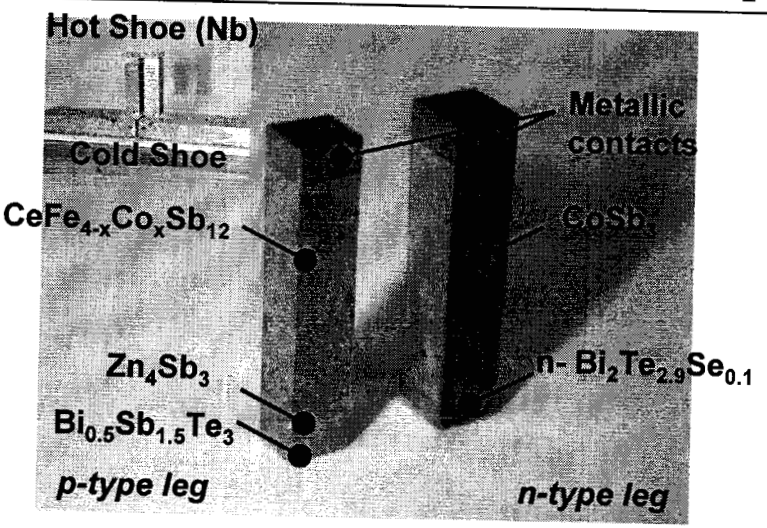

- POWER OUTPUT – 285 W(e)
- FUEL LOADING – 4400 W(t); 132,500 Ci
- WEIGHT – 124 lbs
- SIZE – 16.6 in x 44.5 in

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.

## MHW/GPHS SiGe unicouple

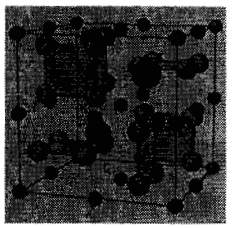



## Segmented New Materials Unicouple



# 975K-375K Segmented Unicouple Development Path

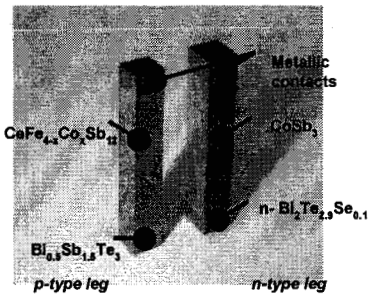
## TRL 1-2



Skutterudite crystal structure

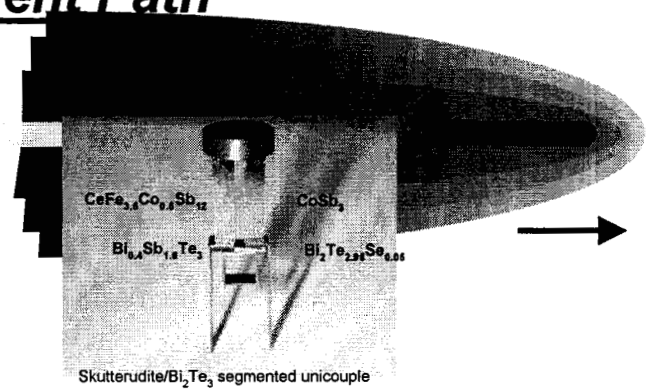
**Advanced TE materials**
**Higher ZT values**

## TRL 2-3




Segmented legs

**Materials selection for maximizing conversion efficiency (FY02)**

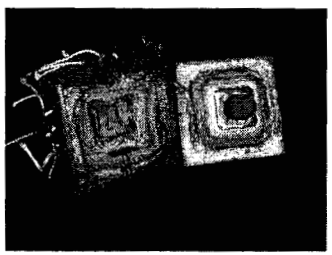



Skutterudite/$Bi_2Te_3$ segmented unicouple

**Advanced segmented unicouples**
**Higher efficiency**
**& mechanical integrity**
**Initial life tests (FY02-03)**

$$ZT = \frac{S^2 T}{\rho \lambda} \qquad \eta_{\max} = \frac{P_{\max}}{Q_{hot}} = \frac{T_{hot} - T_{cold}}{T_{hot}} \; \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_{cold}}{T_{hot}}}$$

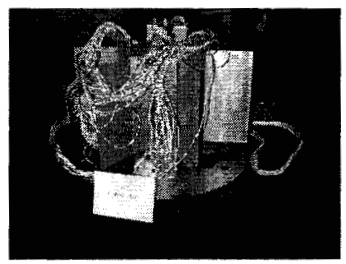
## TRL 4



4 unicouple module

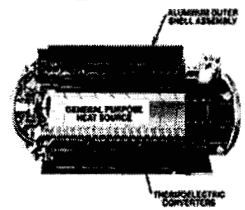
**Life tests**
**Performance**

## TRL 5



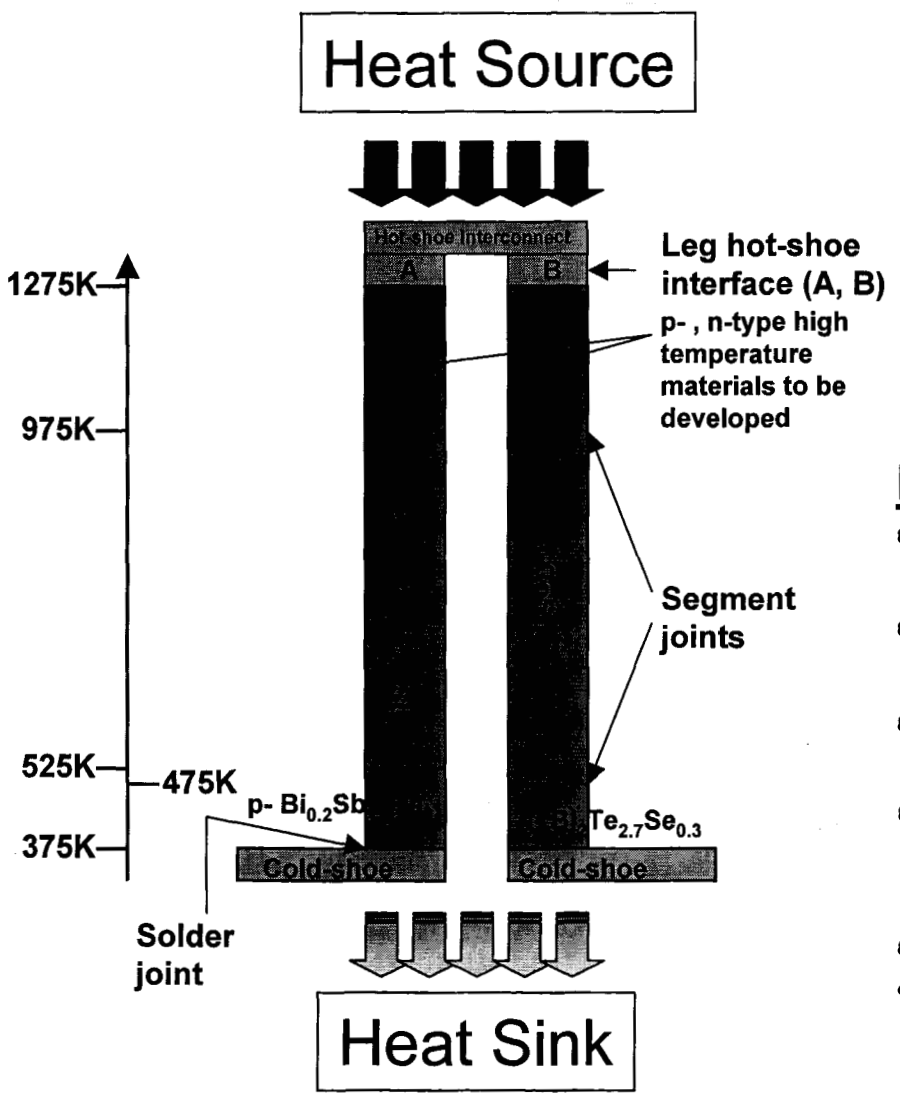
18 unicouple module

**Life tests**
**System engineering**
**module efficiency**



**300W STERPS generator**
**System efficiency**
**Specific power**

# 1275K-375K Segmented Unicouple Technology [redacted]




## Projected 12[redacted]mance

| RPS (multi-hundred Watts) | GPHS-RTG | HT-STE-RPS* |
|---|---|---|
| $T_{hot}$ (K) | 1275 | 1275 |
| $T_{cold}$ (K) | 575 | 375 |
| Converter Efficiency (%) | 8 | 17 |
| System Efficiency (%) | 6.5 | 13.6 |
| Specific Power ($W_e$/kg) | 5.2 | 10.1 |

* *Assumes $ZT_{average}$=1 for advanced materials in 1275K-975K range*

## Key technology challenges

- Select, synthesize and optimize 1275K-975K thermoelectric materials
- Demonstrate $ZT_{average}$~1 for both p-, n-type thermoelectric materials in 1275K-975K
- TE materials processing and segmented leg fabrication
- Low electrical contact resistance between segments and between segments and cold- and hot-shoes
- Demonstrate performance of n-,p-type legs
- Evaluate thermoelectric materials stability
  - Sublimation
  - Changes in thermoelectric properties