Novel, High Efficiency Segmented Thermoelectric Unicouples for Space and Terrestrial Applications

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presented by
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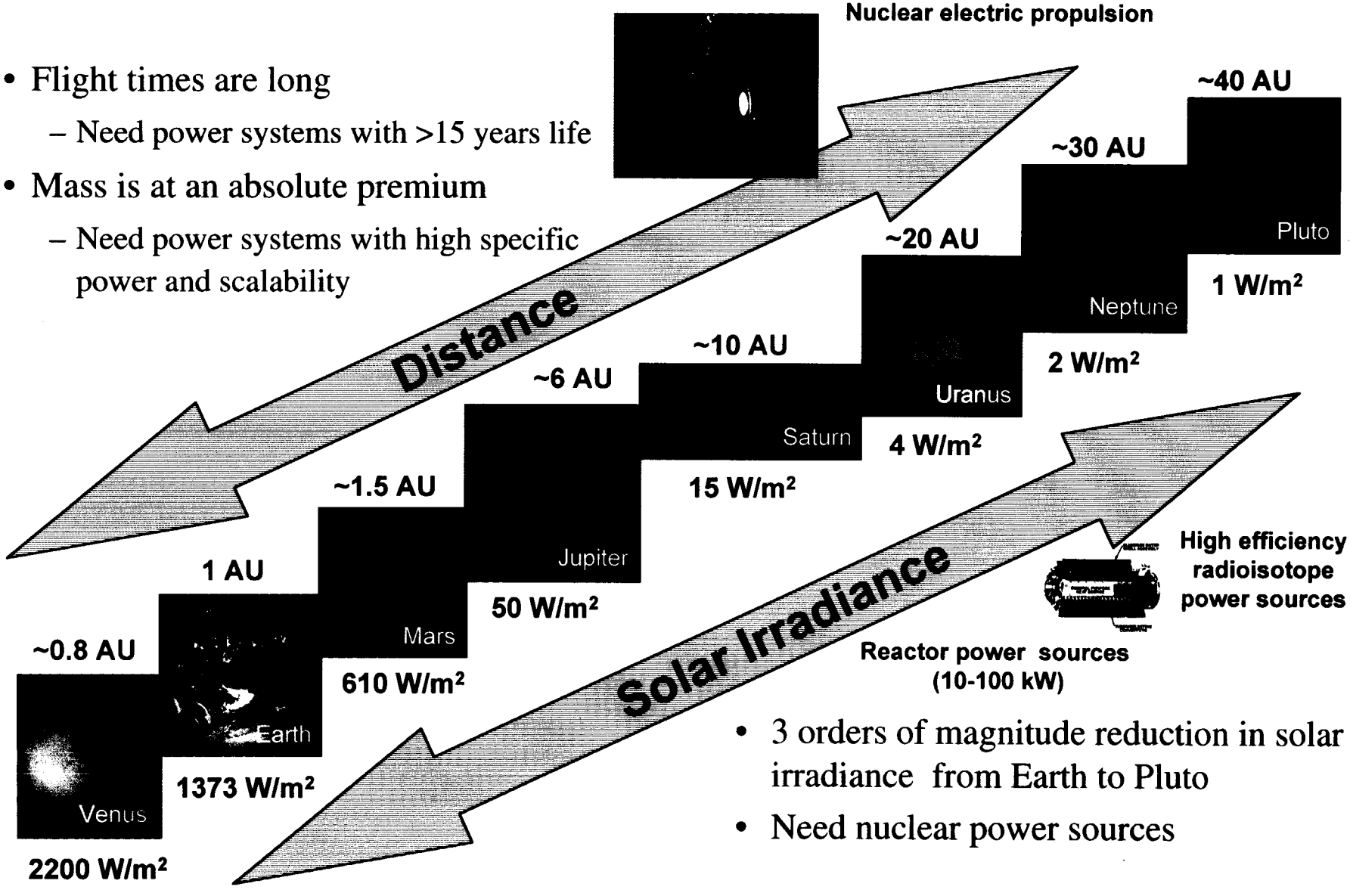
Deep Space Exploration

Power Technology

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

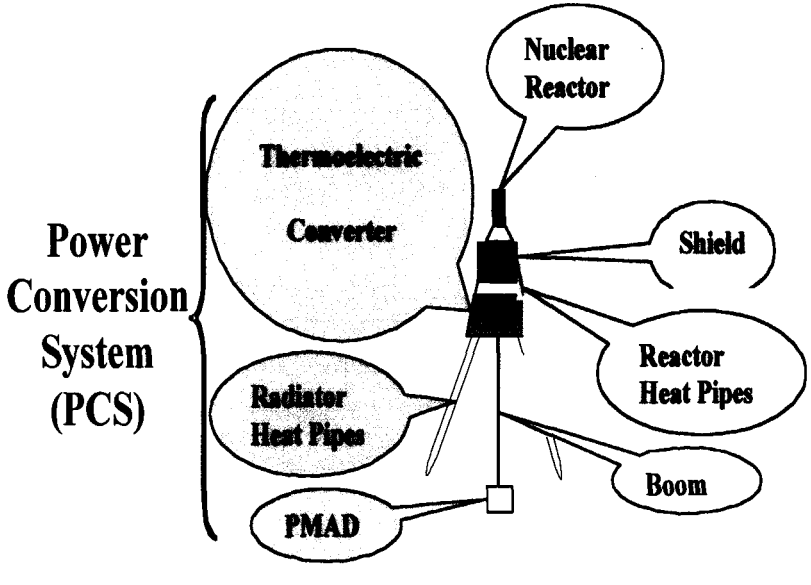


- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Need nuclear power sources

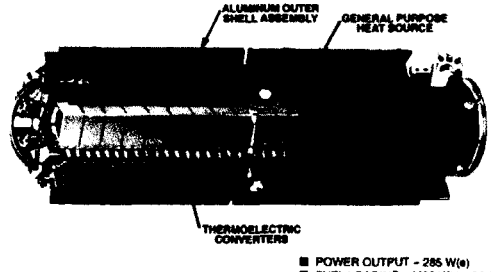
Space Nuclear Power Sources

- **Radioisotope Thermoelectric Generators (RTGs)**
  - Use heat generated by radioactive decay of a radioisotope
  - Used on a number of deep space probe missions
  - Over 20 years of continuous operation for Voyager 1 and 2!
  - Using PbTe and SiGe thermoelectric materials based technology
  - Power output 25 to a few 100 Ws
- **Nuclear Reactor Power Sources**
  - Use heat generated by nuclear fission
  - 10 to 1000 kWe power levels

The Cassini spacecraft on its way to the ringed planet Saturn



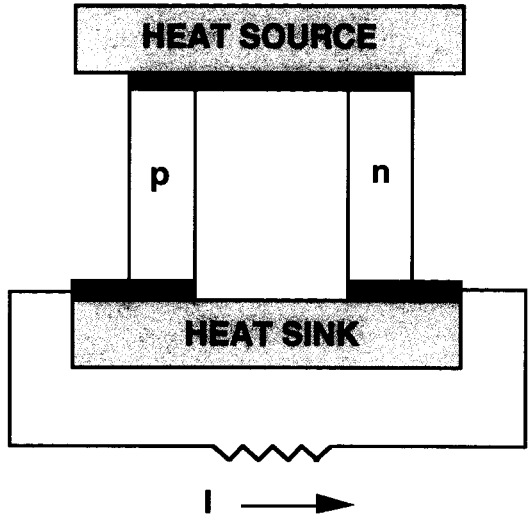
General Purpose Heat Source (GPHS)
Radioisotope Thermoelectric Generator (RTG)



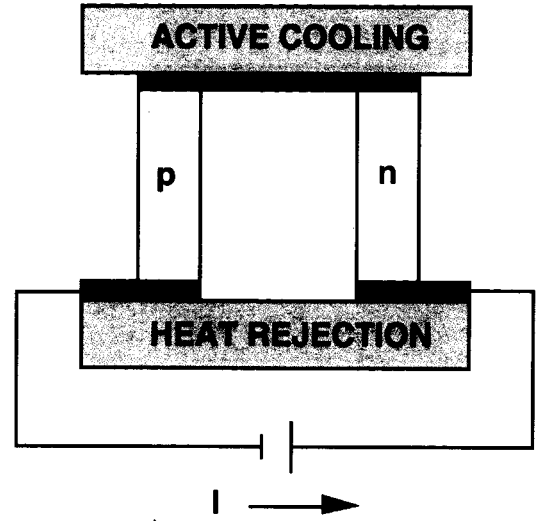
- POWER OUTPUT - 285 W(e)
- FUEL LOADING - 4400 W(t); 132,500 Ci
- WEIGHT - 124 lbs
- SIZE - 16.6 in x 44.5 in

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.

Thermoelectrics basics



Power generation



Refrigeration

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

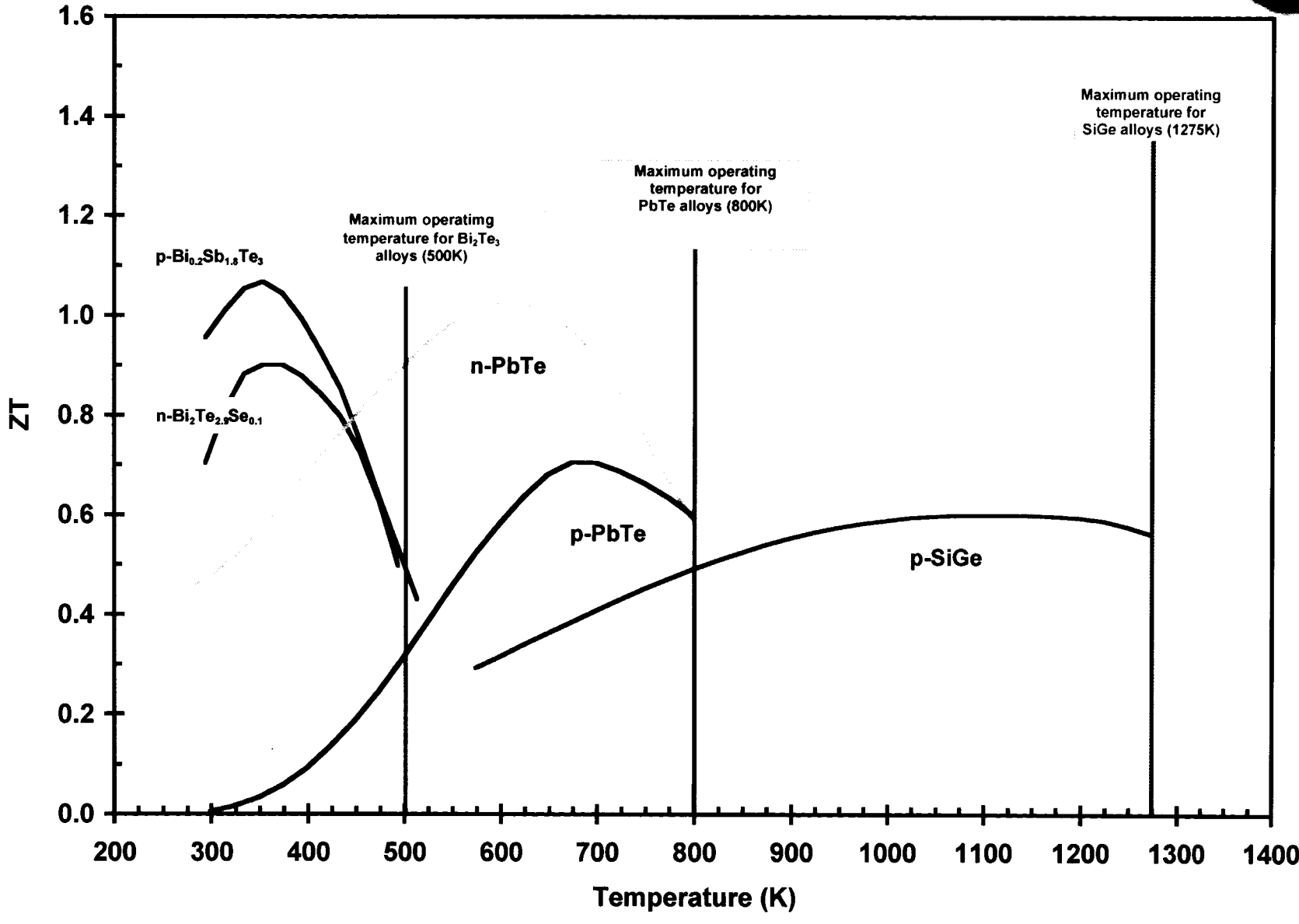
$$\text{C.O.P.} = \frac{(\gamma T_C - T_H)}{[(T_H - T_C + (1+\gamma)]}$$

With: $\gamma = (1+ZT)^{1/2}$ $\quad Z = \frac{\alpha^2}{\rho\lambda}$

α: Seebeck coefficient
ρ: electrical resistivity
λ: thermal conductivity

→ **Large ZT values are needed to achieve high conversion efficiency**

ZT values for SOA TE materials

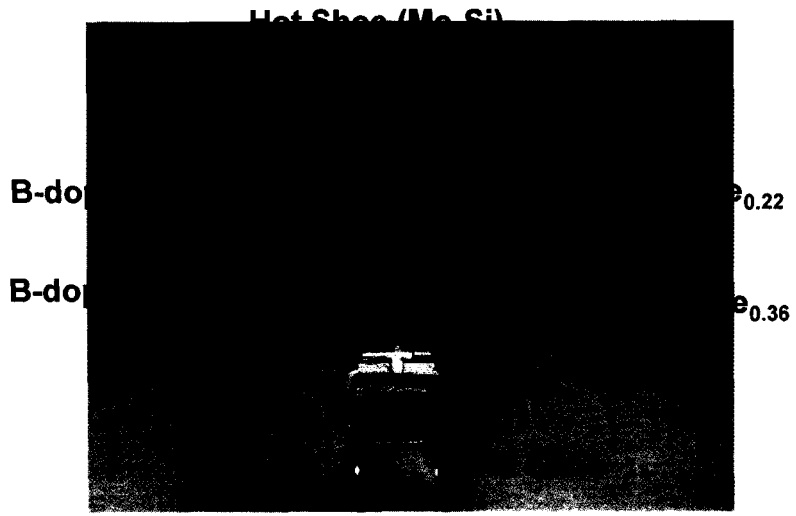


Performance of 100 We SiGe Thermoelectric Power System

SOA RTG Power System
8 GPHS Modules

Item/Converter	SiGe-RTG
Hot junction temperature (K)	**1273**
Cold junction temperature (K)	**573**
System efficiency (%)*	**6.5**
Total thermal power (BOM) (W_{th})	2000
System thermal efficiency (%)	**85**
Total electrical power (BOM) (W_e)	107
Number of modules	**8**
Total PuO_2 mass (kg)	**5.02**
Total system mass estimate (kg)	**23.24**
- GPHs mass (kg)	11.54
- Housing (Kg)	3.1
- Radiator fins (kg)	0.45
- Converter (kg)	5.65
- Other structure (kg)	2.5
Specific power estimate (W_e/kg)	**4.6**

MHW/GPHS SiGe unicouple



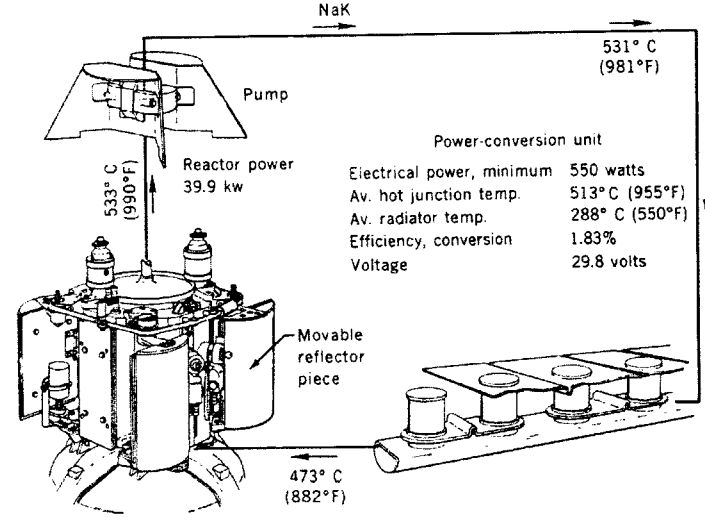
Space Reactors

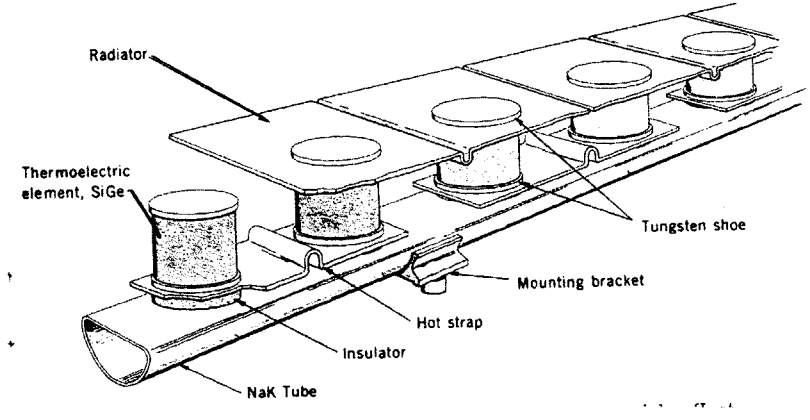
- **United States**
  - SNAP 10-A
    - Completed ; in orbit April 1965
    - Used SiGe thermoelectric elements
  - SP100 - project
    - Started in 1983
    - Assess potential and feasibility of a nuclear reactor power reactor power system
      - 100 kW_e
      - 4000 kg
      - 7 years operational lifetime
    - Technology considered : Thermionics, Brayton, Stirling, and thermoelectrics
    - Thermoelectric selected later on for further development based on
      - Lifetime issues, slightly higher mass and lack of technology maturity for dynamic and thermionic technologies
    - Significant technology development during SP-100 program
      - Reactor
      - Heat transport
      - Heat rejection
- **Former Soviet Union**
  - 35 known Soviet reactors
  - All used static conversion systems
  - 33 used SiGe thermoelectric elements
  - 2 used thermionic conversion

SNAP 10A Space Power Reactor

- <u>Completed ; in orbit April 1965</u>

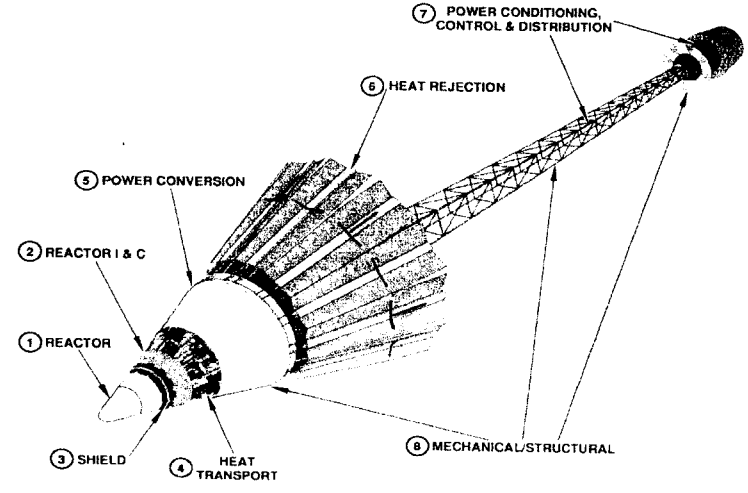
- Energy conversion : Thermoelectric (SiGe materials)
- SiGe couples mounted between the hot NaK pipes and the radiator
- Reactor power : 39.9 kW
- Mass : 427kg
- Power level : 500W
- Specific mass : 908 kg/kW
- Av. hot junction temperature : 786K
- Av. Cold junction temperature: 561K
- Conversion efficiency : 1.83%
- Overall efficiency : 1.6%
- Voltage : 29.8 Volts



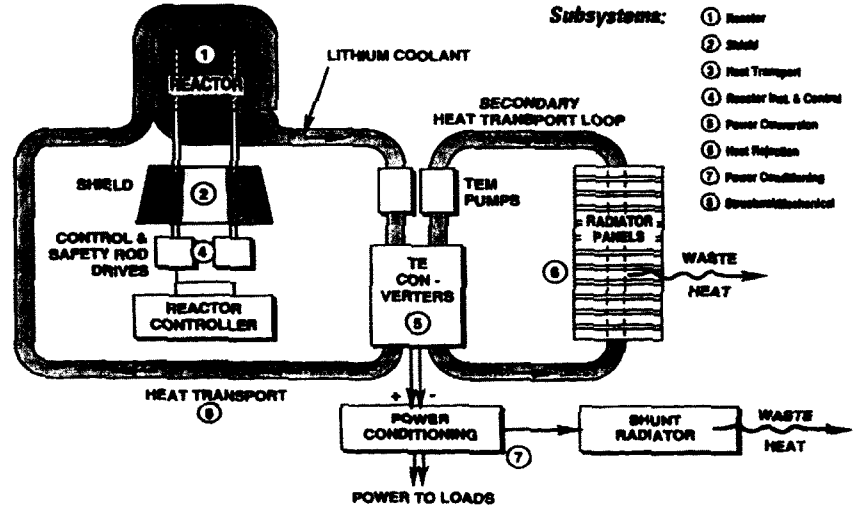


SP-100 SiGe based Design Characteristics

System Performance	SP-100
Electrical Power Output (kW_e)	100
Nuclear Reactor Outlet Temperature (K)	1375
Reactor Thermal Power (kW_t)	2500
Power Converter Operational Temperature range (K)	1275K to 875K
Efficiency (%) Power System Multicouple	 4.0 4.5
Average Radiator Temperature (K)	790
Subsystem Mass (kg)	
Nuclear Reactor	700
Shield	930
Instrumentation and Control for Reactor	320
Primary Heat Transport	520
Power Converter	530
Heat Rejection	960
PMAD	390
Mechanical/Structural	250
Total System Mass	4600



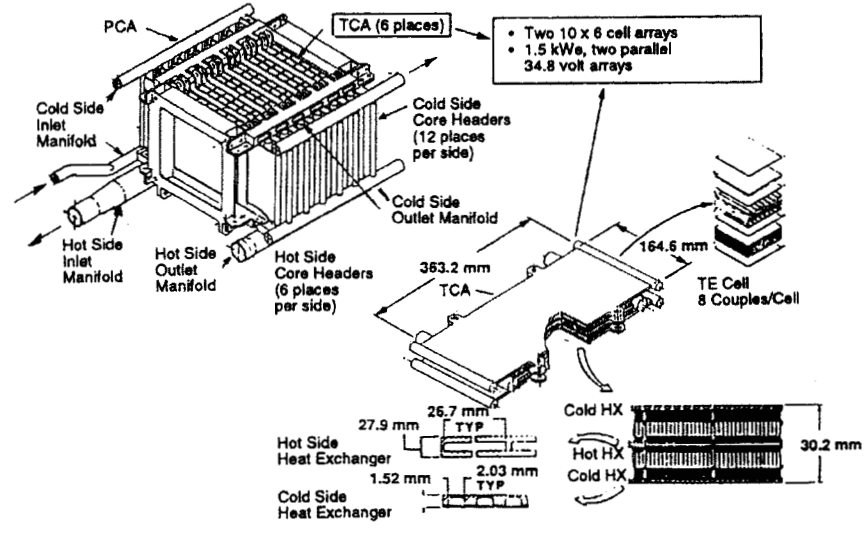
Simplified System Diagram



SP-100 Thermoelectric power conversion assembly

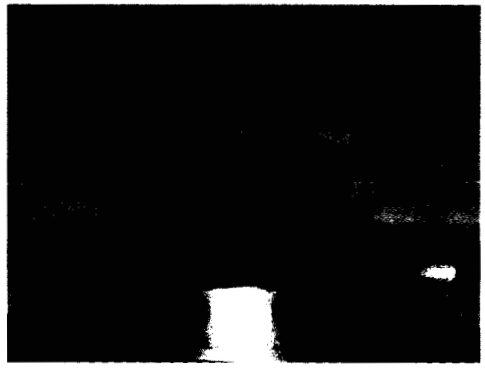
Power conversion assembly

- Made of building blocks
  - Thermoelectric cells
  - Thermoelectric converter assembly (6 x10 cell arrays)
- 8,640 cells required for a 100 kW_e system
- 5,5 m^2 for a 100 kW_e system
- TE cells conductively coupled to hot-side and cold side heat exchangers heated and cooled by Li heat pipes

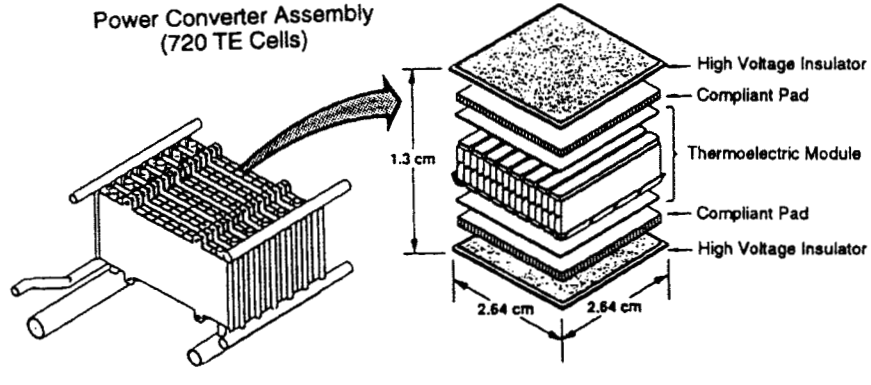


Scalability

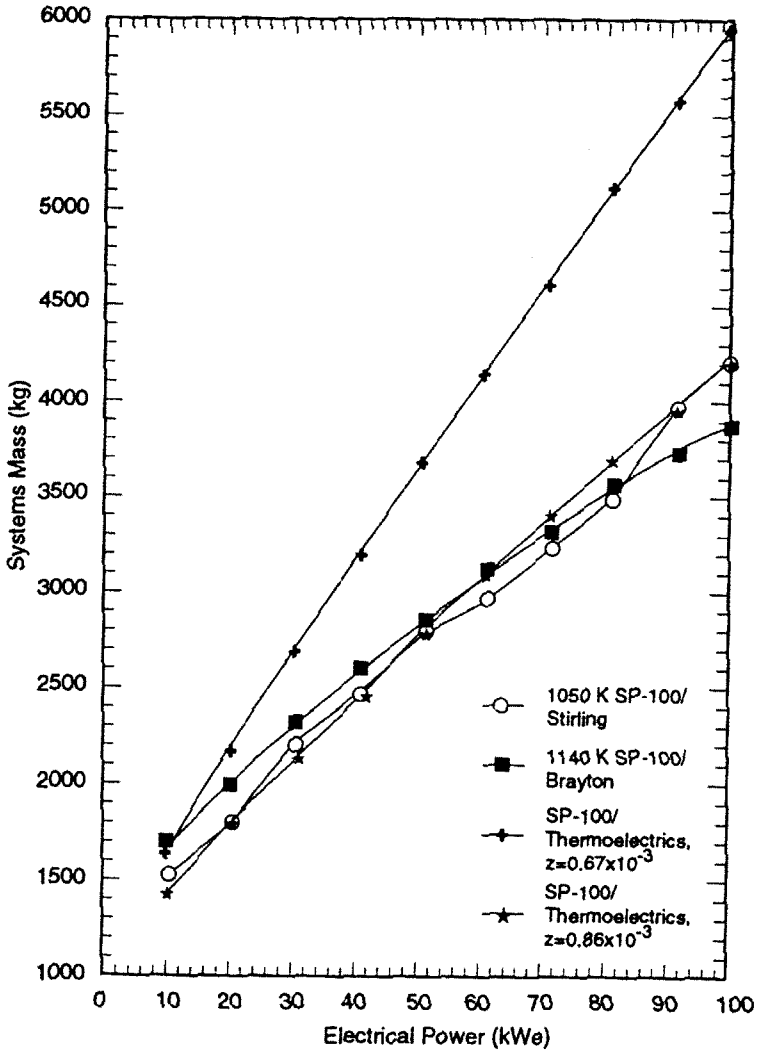
- Power levels can be adjusted
- Concepts from 8 to 200 kW_e have been configured



SP-100 Power Converter Components



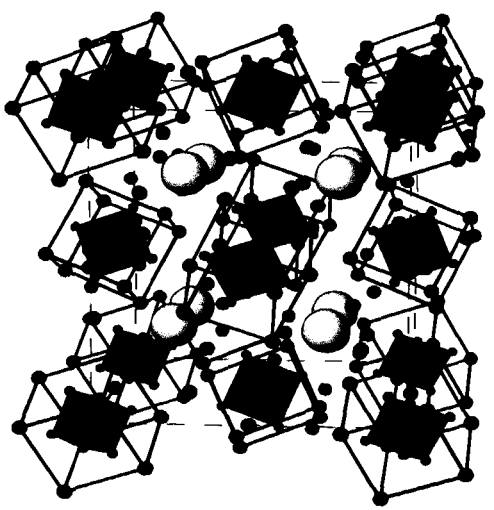
SP-100 Thermoelectric power conversion assembly

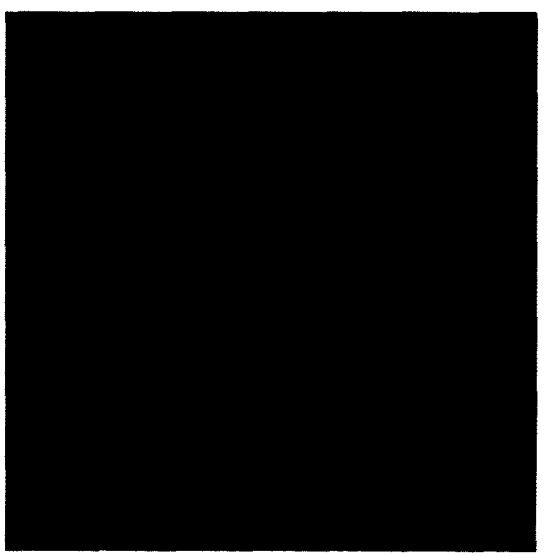


Advanced Thermoelectrics DARPA & ONR effort at JPL

- **DARPA "Advanced Thermoelectrics" and ONR "Skutterudites"**
  - Focus on TE materials for cooling and power generation up to 600-700°C
  - Identification, characterization and optimization of some new, promising materials
- Preparation, characterization, and optimization of several families of compounds with low thermal conductivities, metal-to-semiconductor transition (collaboration with NRL, RPI, U. Michigan)

- **Advanced bulk thermoelectric materials**
  - Zn_4Sb_3 alloys
  - Skutterudites (antimonides, arsenides, phosphides)
  - Chevrel phases
  - Spinel chalcogenides and related AB_2X_4 compounds
  - Layered chalcogenides

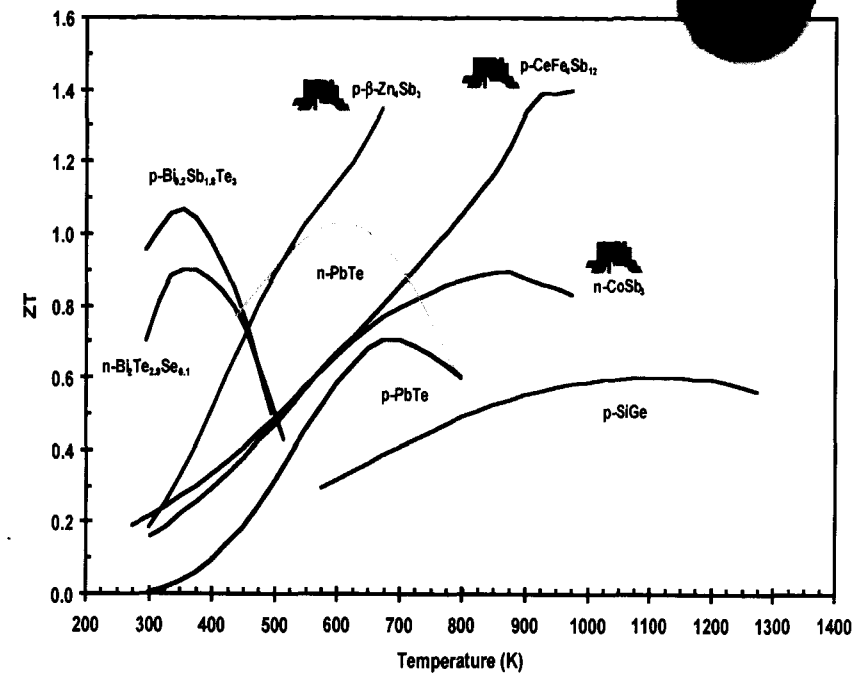


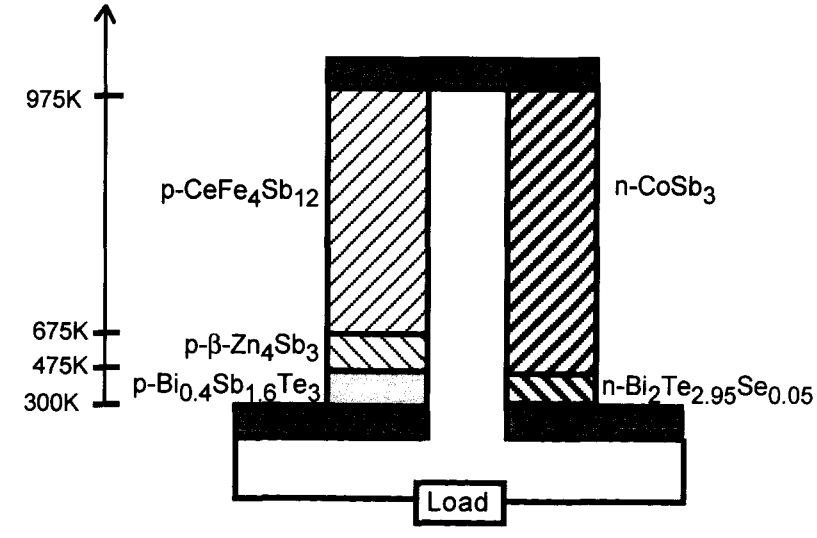


New developments

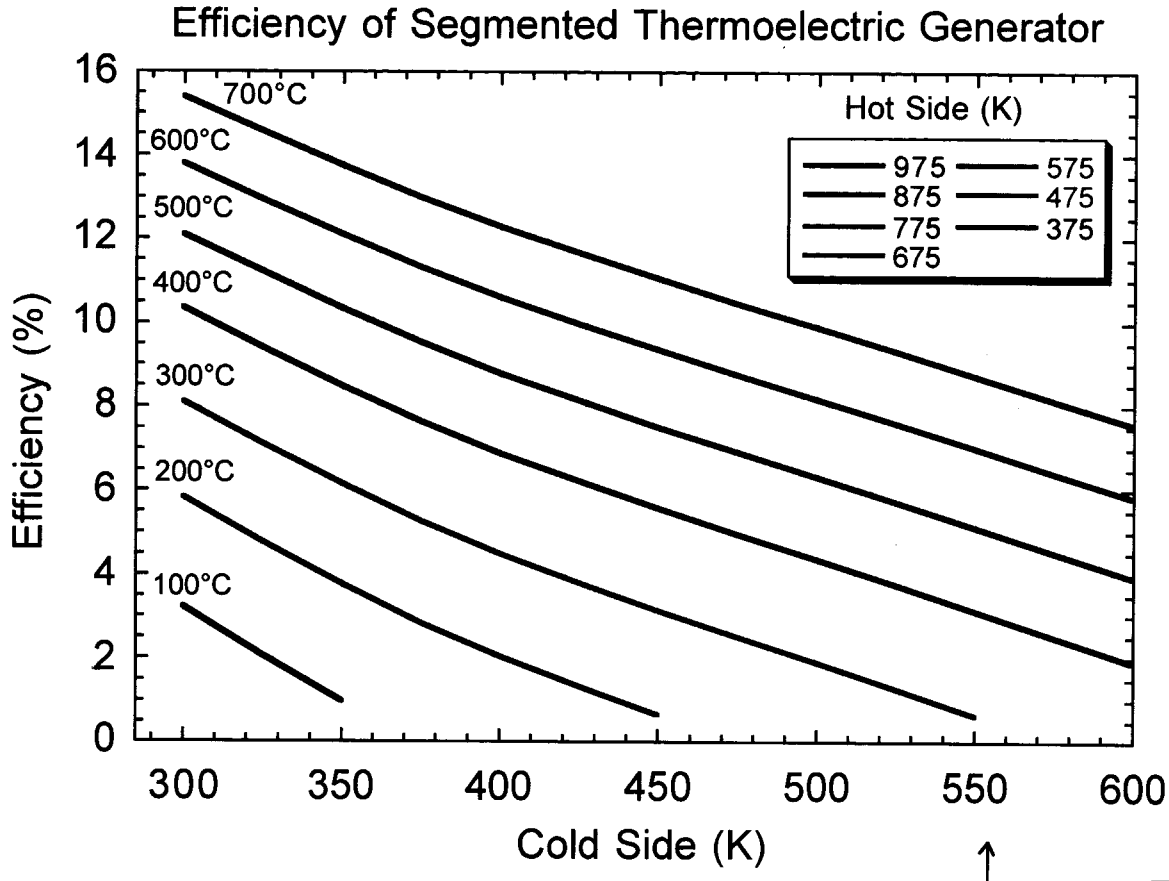
- **Improvement in ZT possible !**
  - Higher efficiency values
- **Segmented unicouples**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials (Bi_2Te_3-based materials) and new, high ZT materials developed at JPL
    - Skutterudites : $CeFe_4Sb_{12}$ and $CoSb_3$
    - 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

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

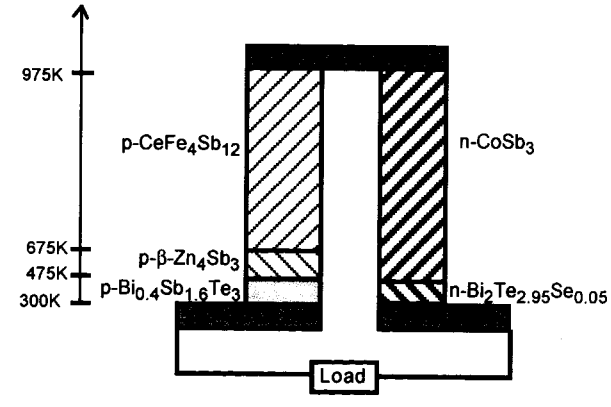




Calculated thermal to electrical efficiency values



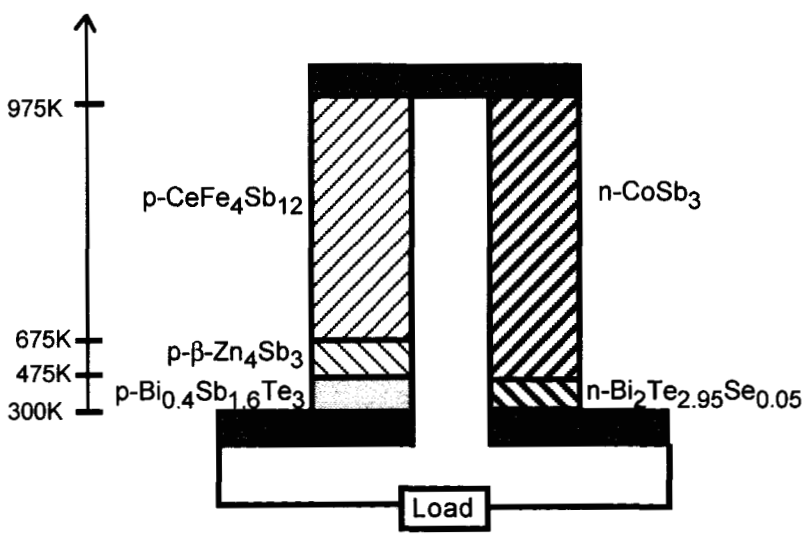
- **Using 1st generation of advanced materials developed at JPL**
- **System efficiency depends on amount of heat going through TE**

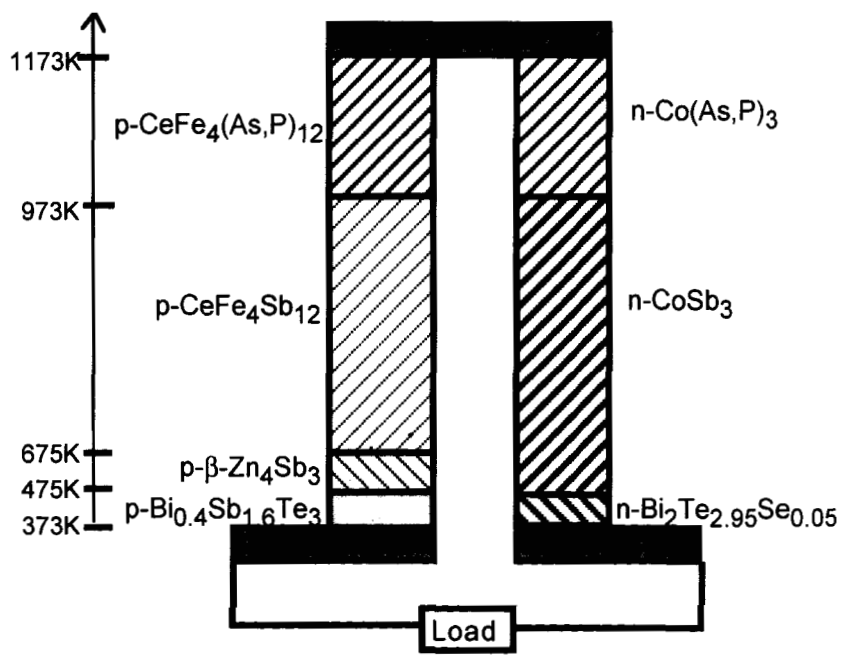


Segmented Thermoelectric Technology

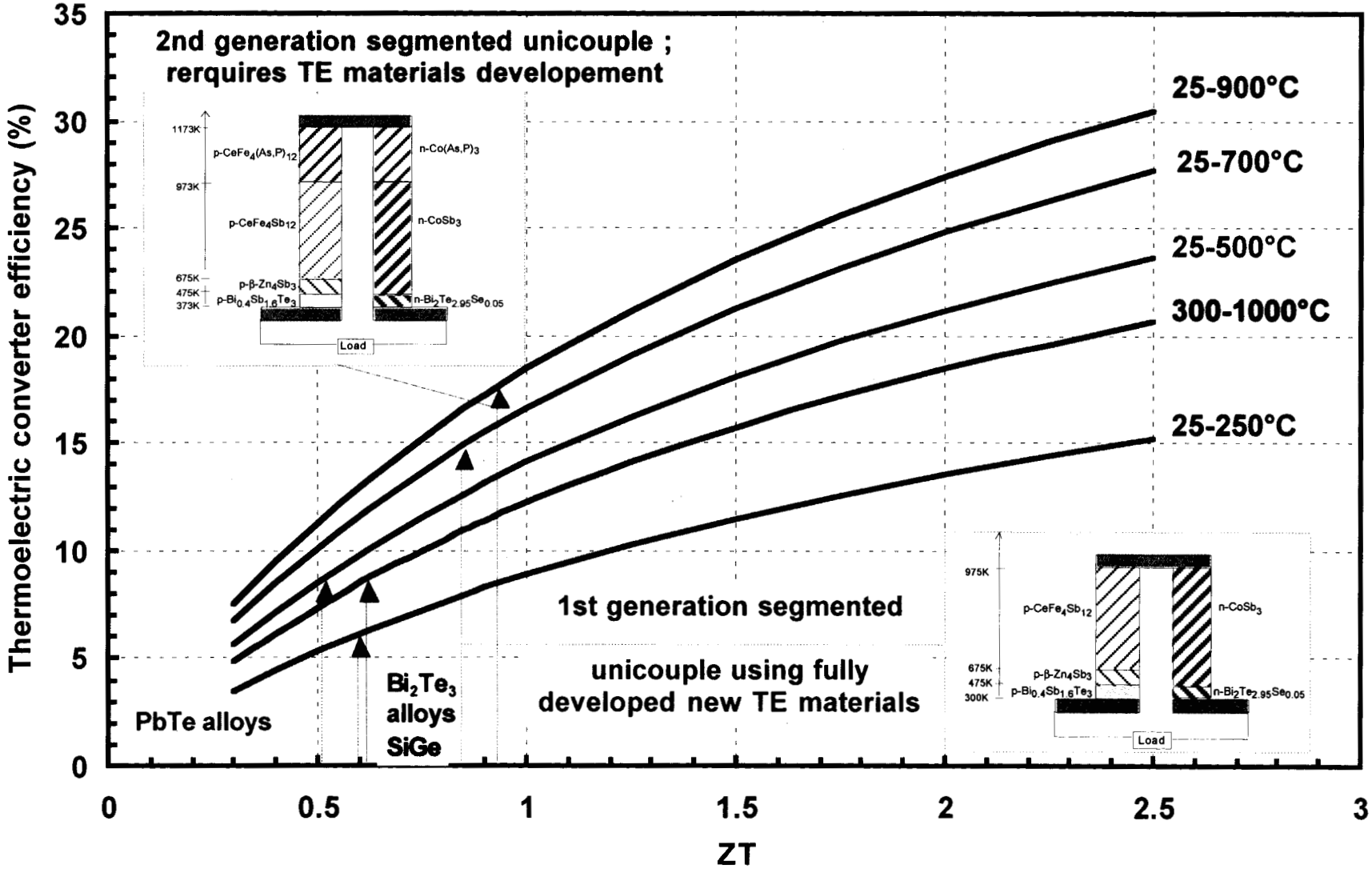
- **1st generation segmented technology**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials (Bi_2Te_3-based materials) and new, high ZT materials developed at JPL
    - Skutterudites : $CeFe_4Sb_{12}$ and $CoSb_3$
    - Zn_4Sb_3
    - JPL/Caltech patents issued and pending
  - Maximum hot-side operating temperature ~ 700°C
  - Maximum thermal to electrical conversion efficiency ~ 15%

- **2nd generation segmented technology**
  - Maximum hot-side operating temperature ~ 900°C
  - Maximum thermal to electrical conversion efficiency ~ 17%
    - Will depend on high temperature materials ZT in 700-900°C range

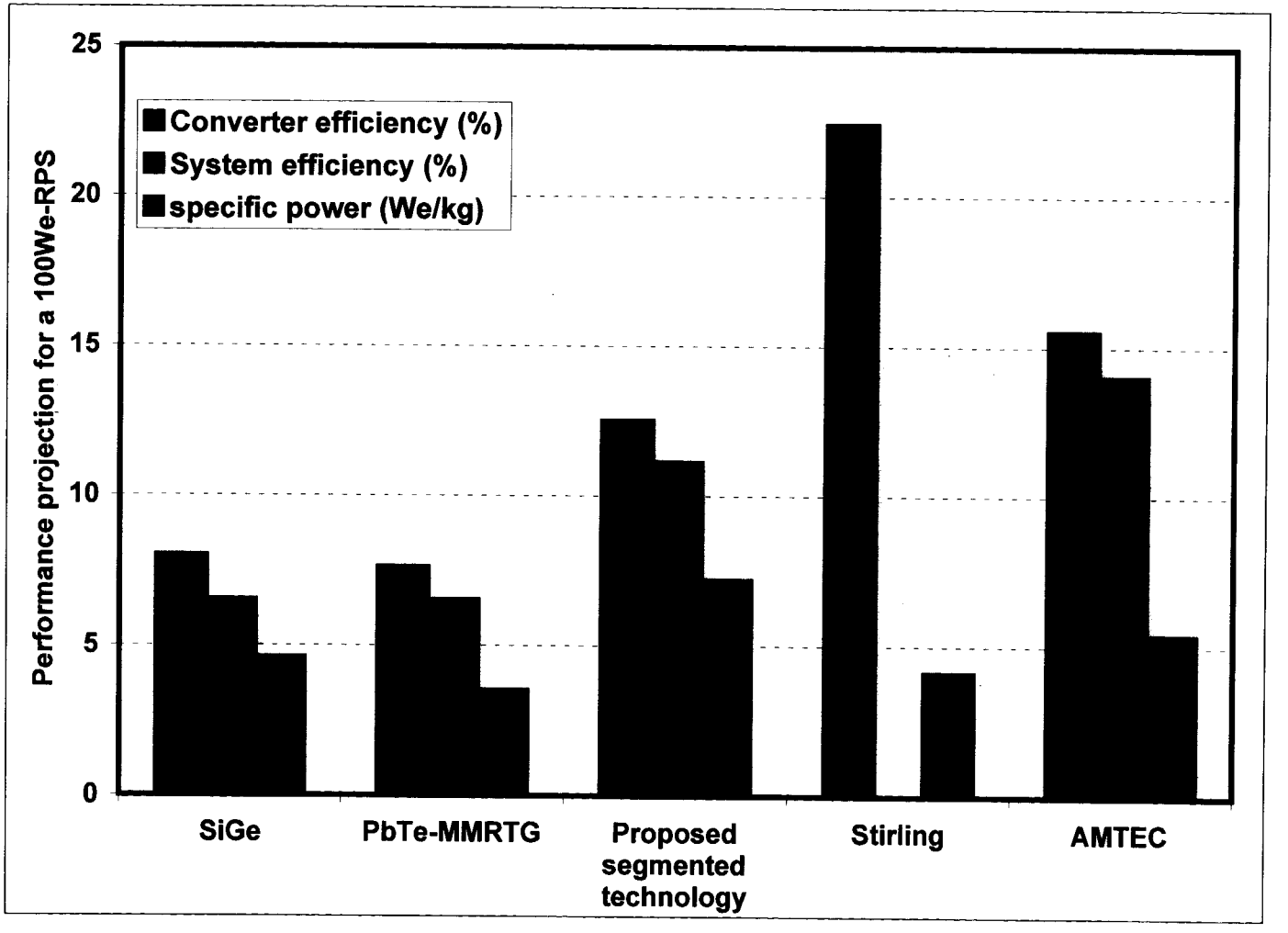




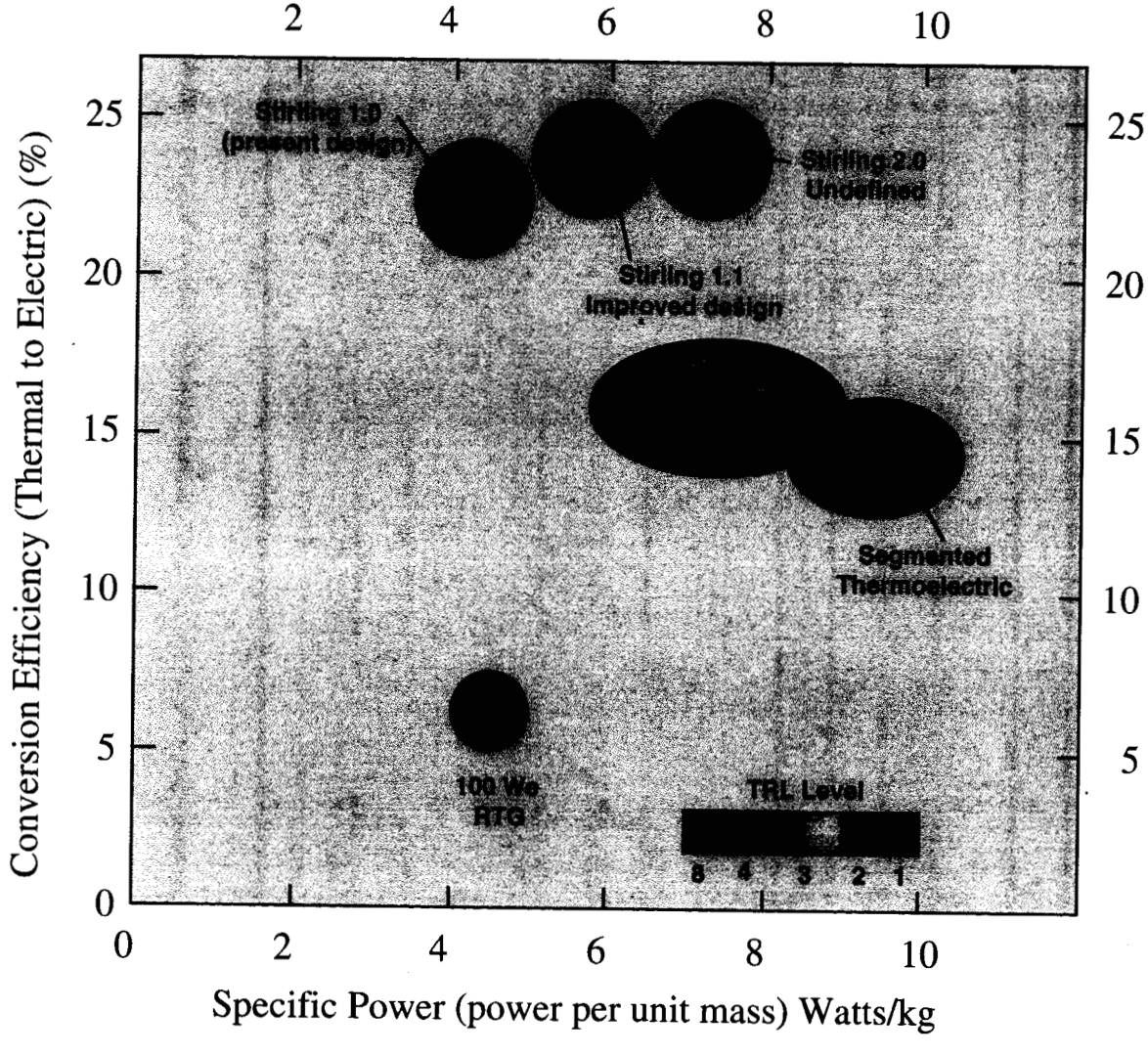
State-of-the-art vs. advanced thermoelectric technology

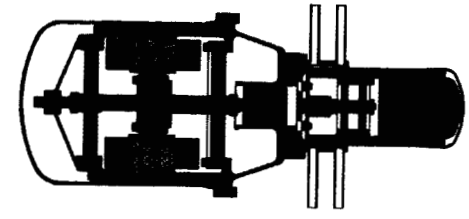


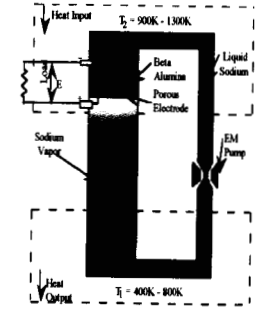
Projected performance for a 100We RPS

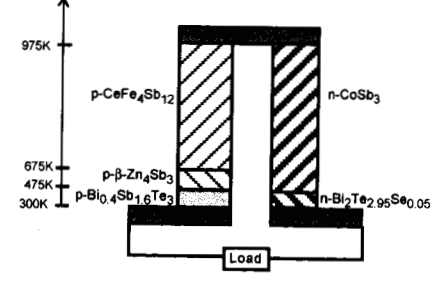


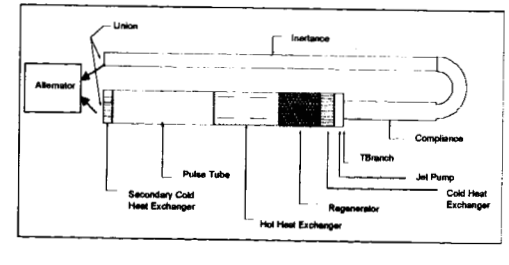
Comparison of Radioisotope Power System Technologies





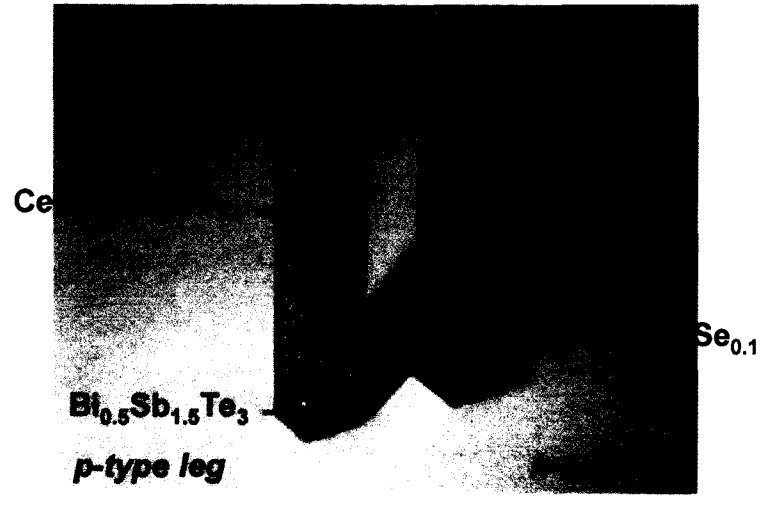






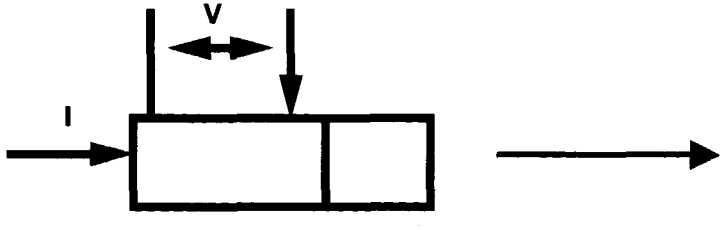
Segmented legs fabrication and testing

- **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

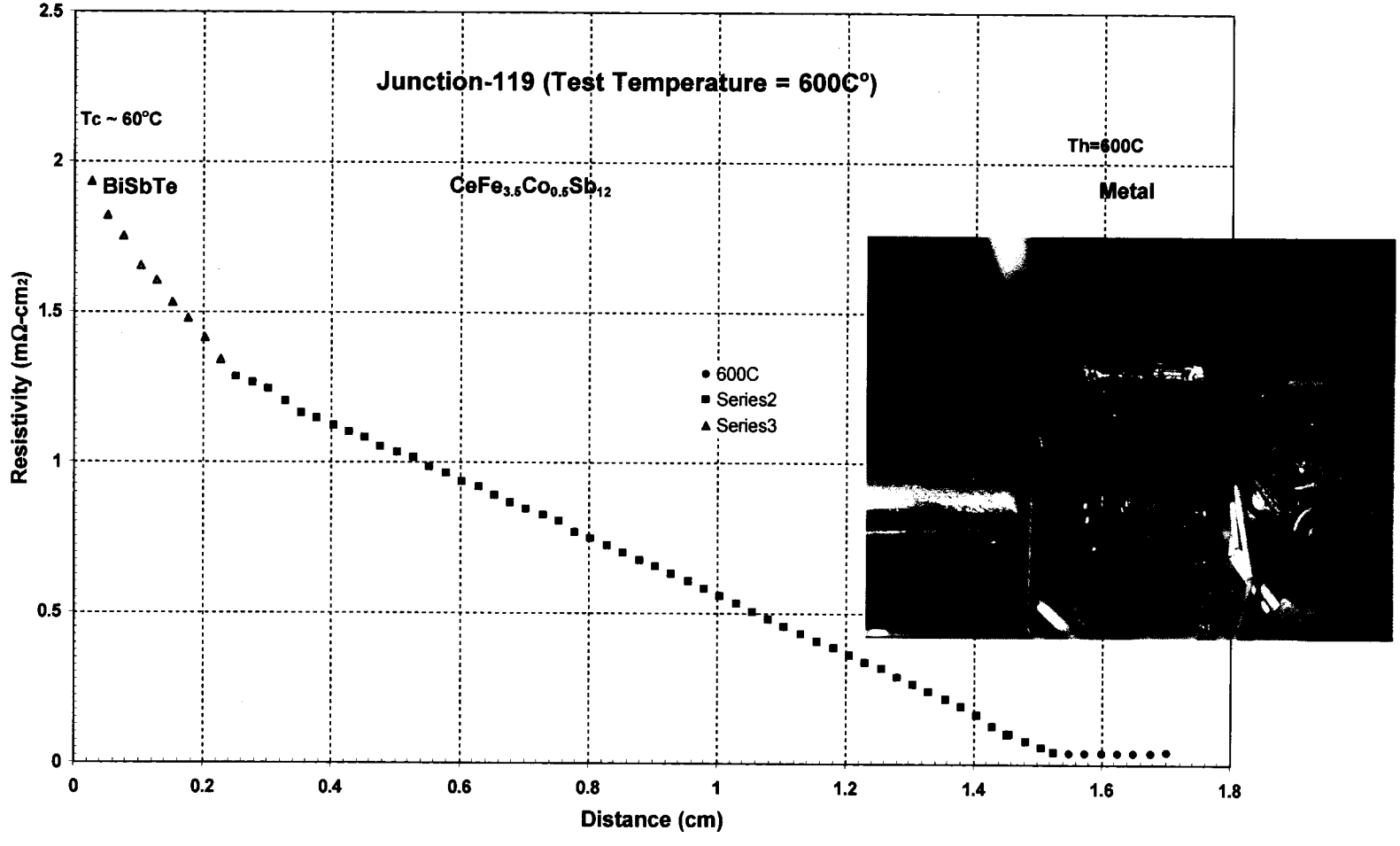


Segmented legs fabricated by uniaxial hot-pressing

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

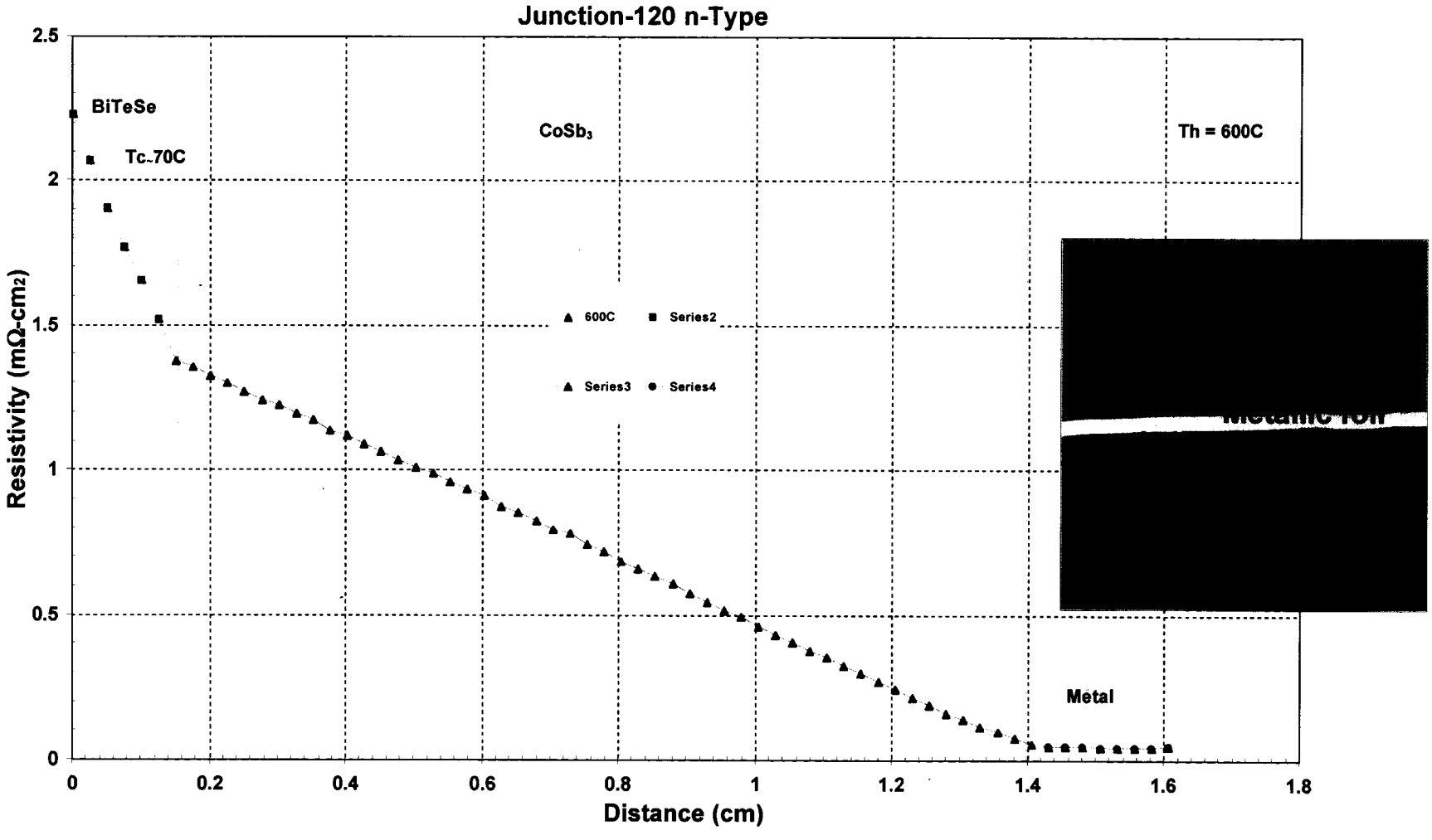


Electrical contact resistance measurements for p-type segmented leg



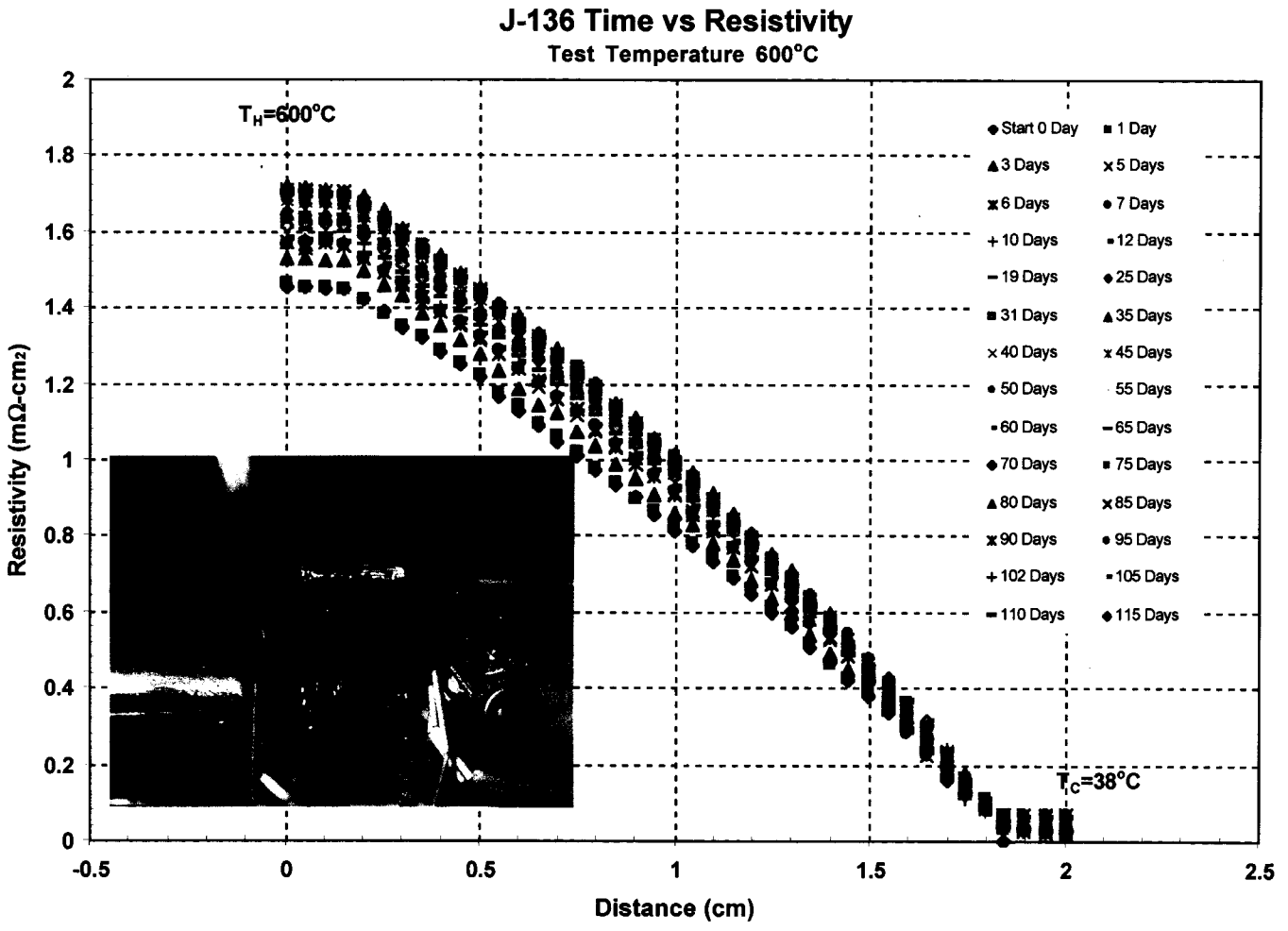
- Low electrical contact resistance achieved (< 5 $\mu\Omega cm^2$)

Electrical contact resistance measurements for n-type segmented leg



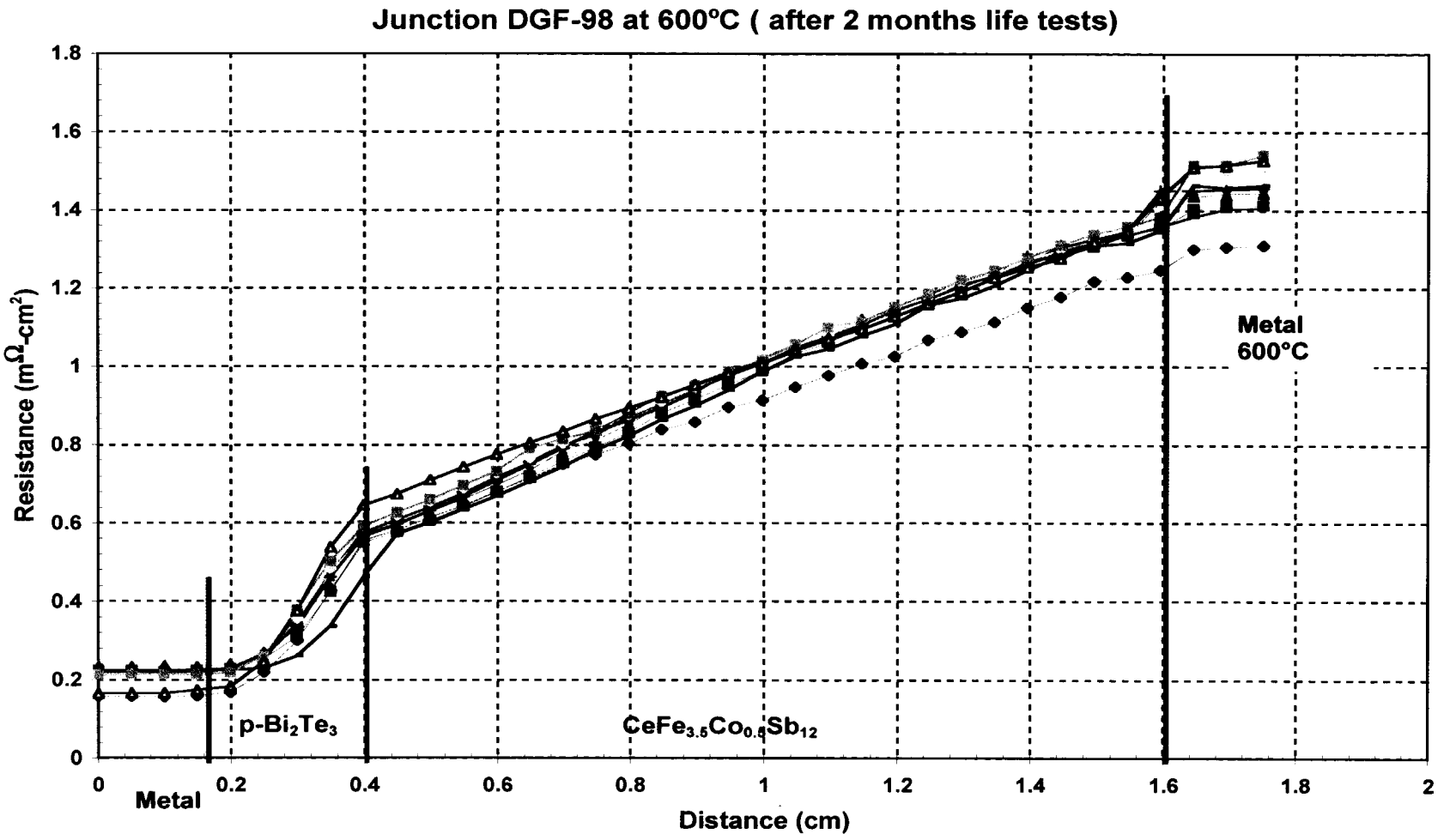
- Low electrical contact resistance achieved (< 5 $\mu\Omega cm^2$)

Contact resistance result for metal/$CoSb_3$/metal leg

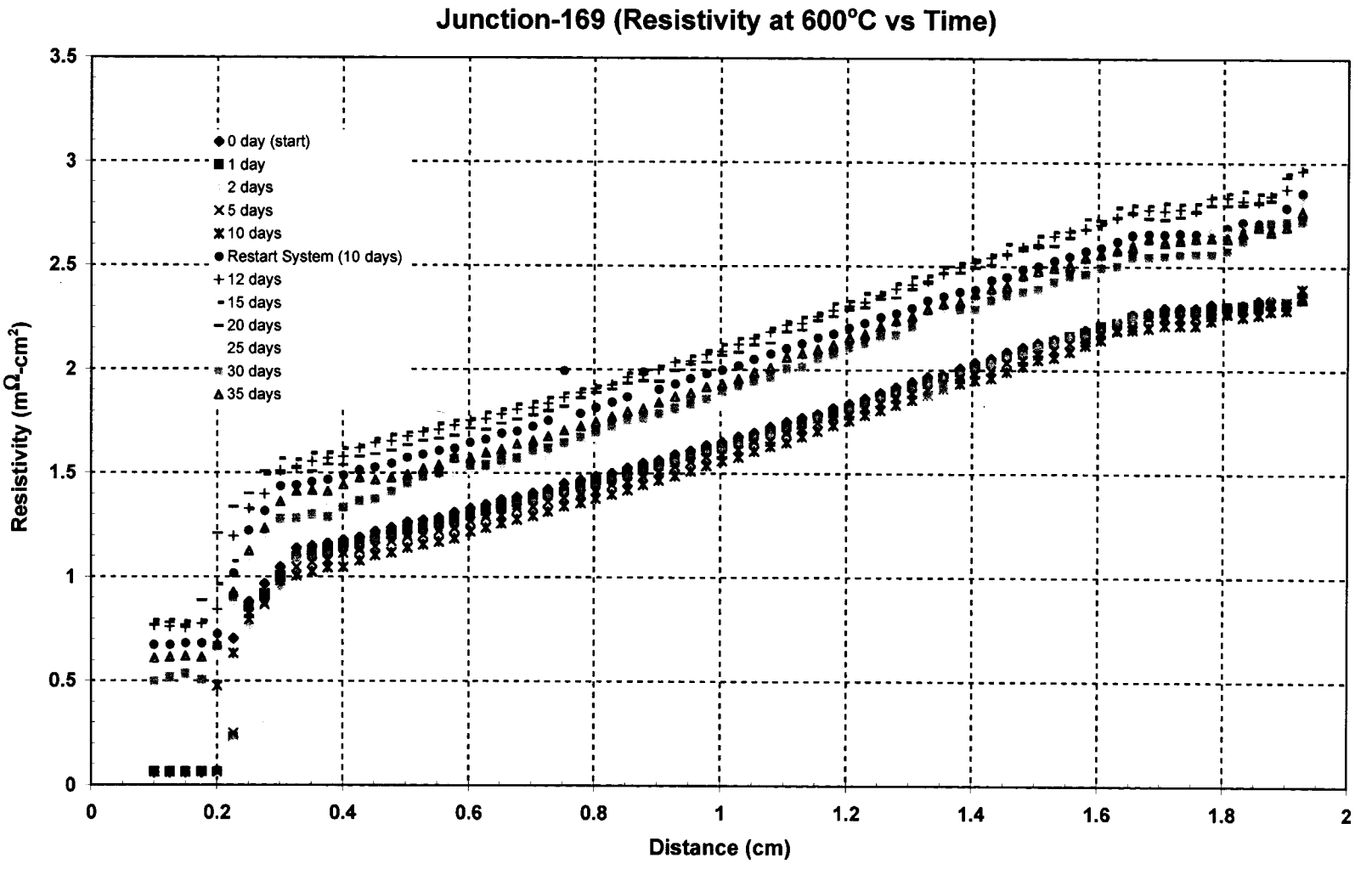


- Demonstrated low electrical resistance contacts between metallic ends and $CoSb_3$ for up to 4 months at operating temperatures

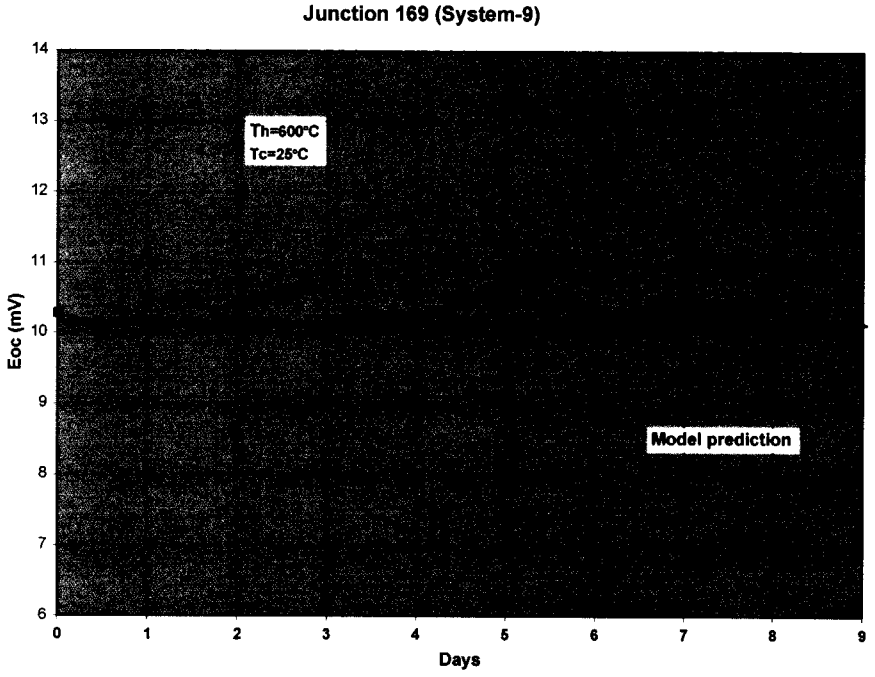
In gradient electrical contact resistance life tests on a metal/p-Bi_2Te_3/$CeFe_{3.5}Co_{0.5}Sb_{12}$/metal segmented leg

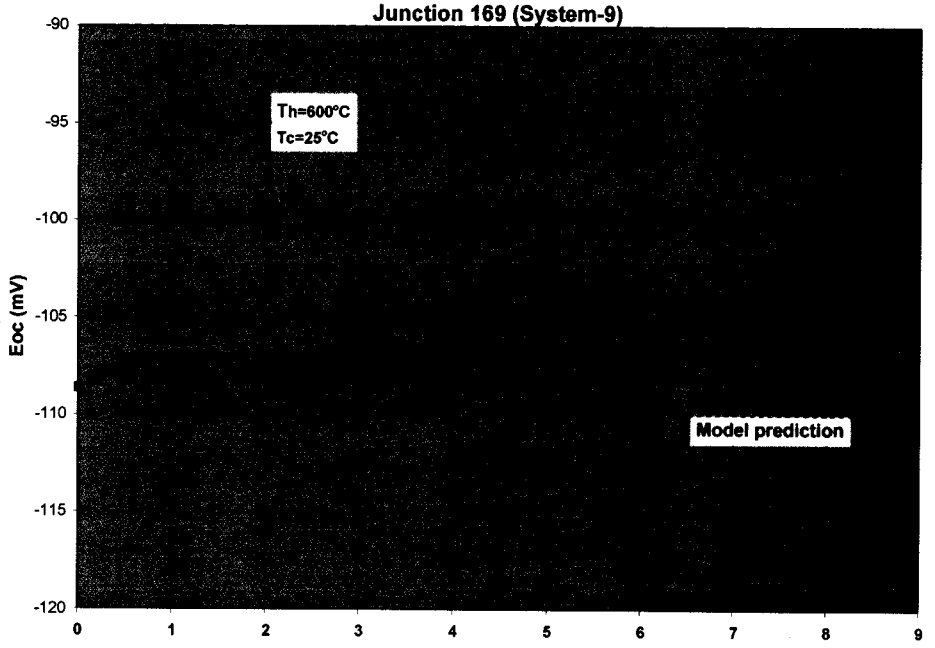


In gradient electrical contact resistance life tests on metal/$Bi_2Te_{2.85}Se_{0.15}CoSb_3$/metal segmented leg

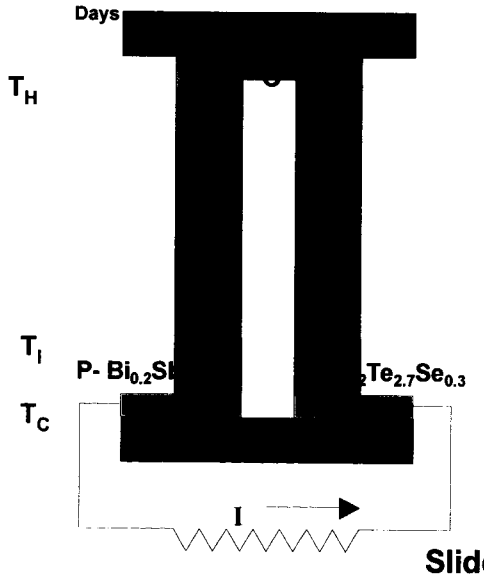


In gradient voltage output and resistance measurement result metal/$Bi_2Te_{2.85}Se_{0.15}$/$CoSb_3$/metal segmented leg

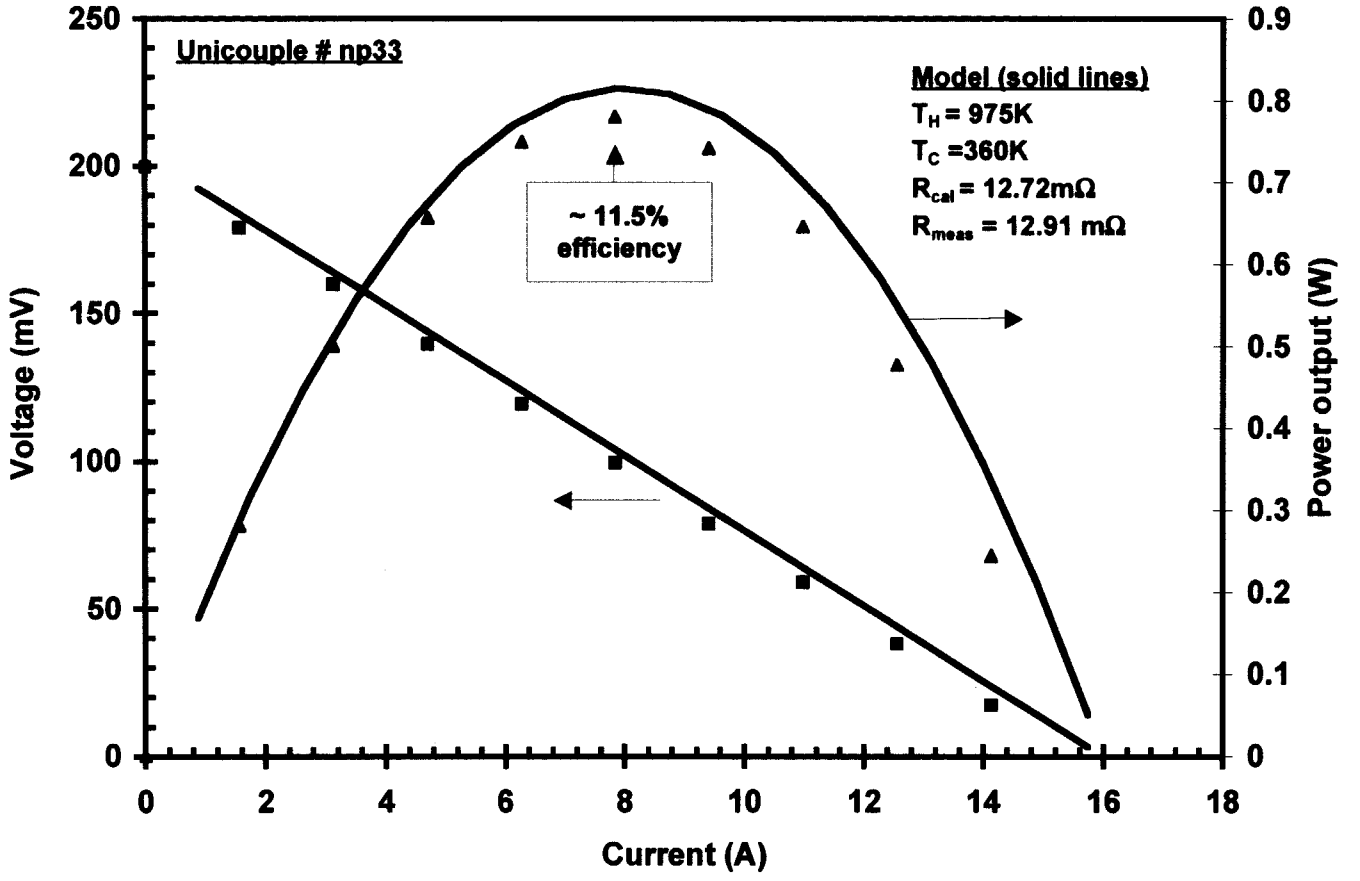


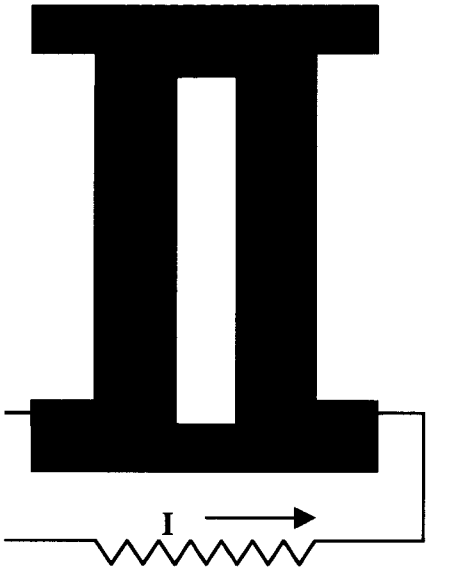


- Results validate thermoelectric properties of n-type $CoSb_3$ metal/$Bi_2Te_{2.85}Se_{0.15}$/$CoSb_3$/metal segmented leg
- Confirms low electrical contact resistance between segments



Thermal and electrical testing - All skutterudite unicouple

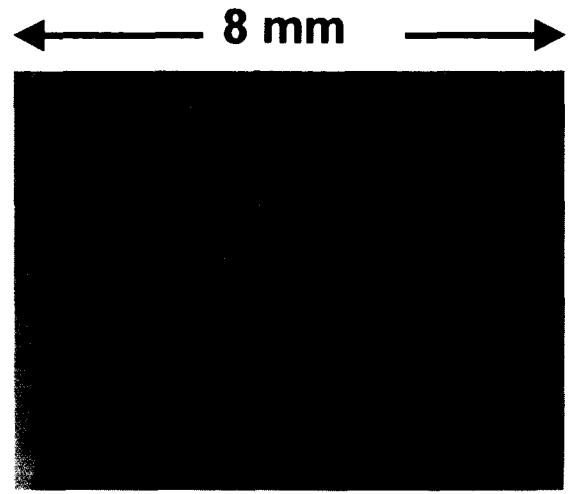




- Further optimized thermal and electrical testing set-up (insulation, temperature measurements, determination of contact resistance at interfaces)
- Demonstrated ~ 11.5% efficiency on a a second unicouple for 975K-360K ΔT (in agreement with model prediction)

Sublimation studies

- **Uncoated samples**
  - Additional weight loss and temperature stability confirmed Sb sublimation in dynamic vacuum for T from ~ 875 to 975K for N-$CoSb_3$
  - Decomposition into lower antimonide compounds
  - Appears to be diffusion limited
  - Weight loss experiments in progress for p-type



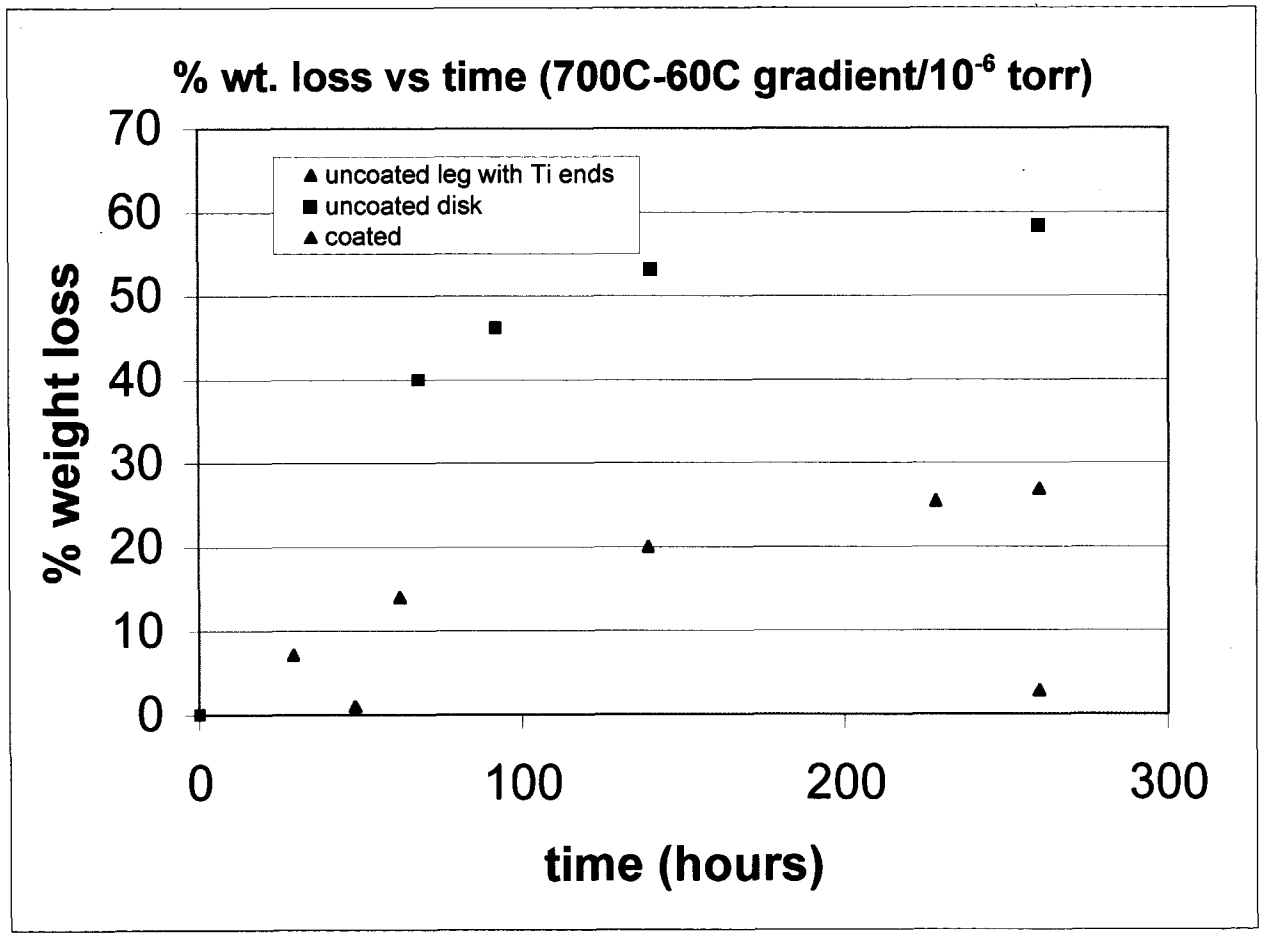
Photograph showing the decomposition of an uncoated $CoSb_3$ sample annealed at 975K for 10 days in dynamic vacuum

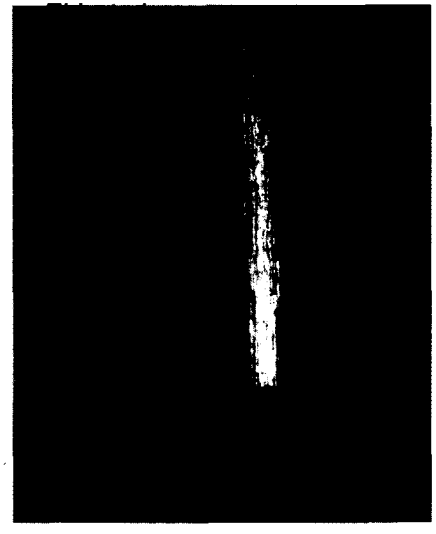
N-type Ti coated skutterudite leg

Coating studies

- Ti coated (~10μm) p- and n-leg fabricated
- Experimented with Mo coating
  - Mo potentially less reactive with Sb and more refractory than Ti
  - Weight loss experiments in progress
- Initiated research for alternate coating techniques
  - More compatible with batch process for unicouple leg fabrication

Weight loss experiments



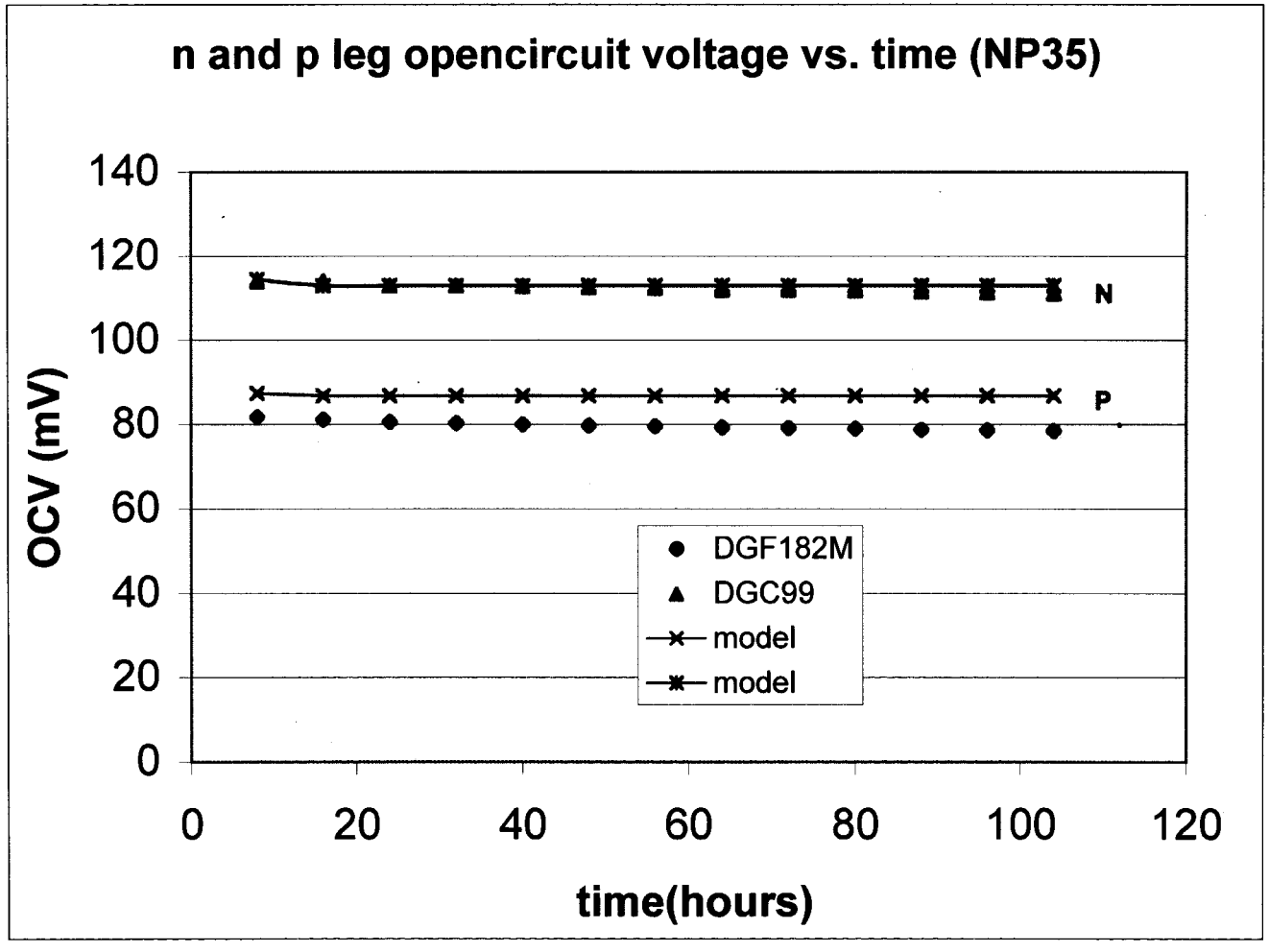


N-type Ti coated skutterudite leg

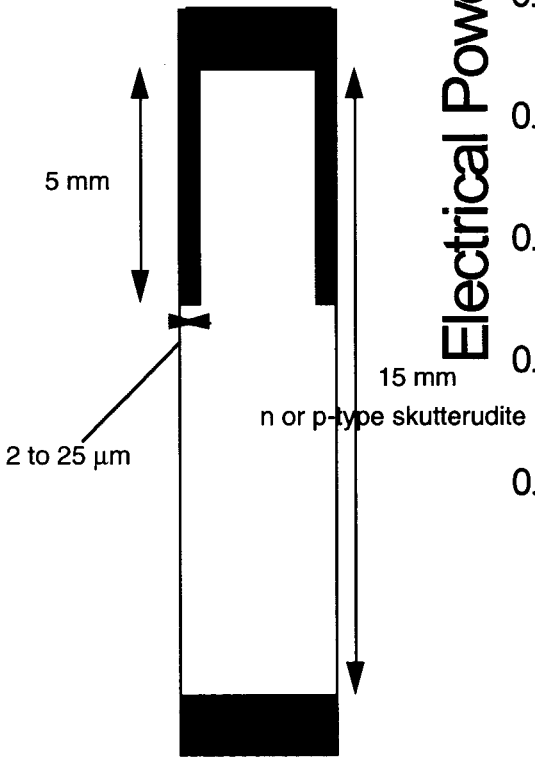
	Uncoated $CoSb_3$	Ti coated $CoSb_3$
Weight loss After 10 days in dynamic vacuum	27%	2.5%

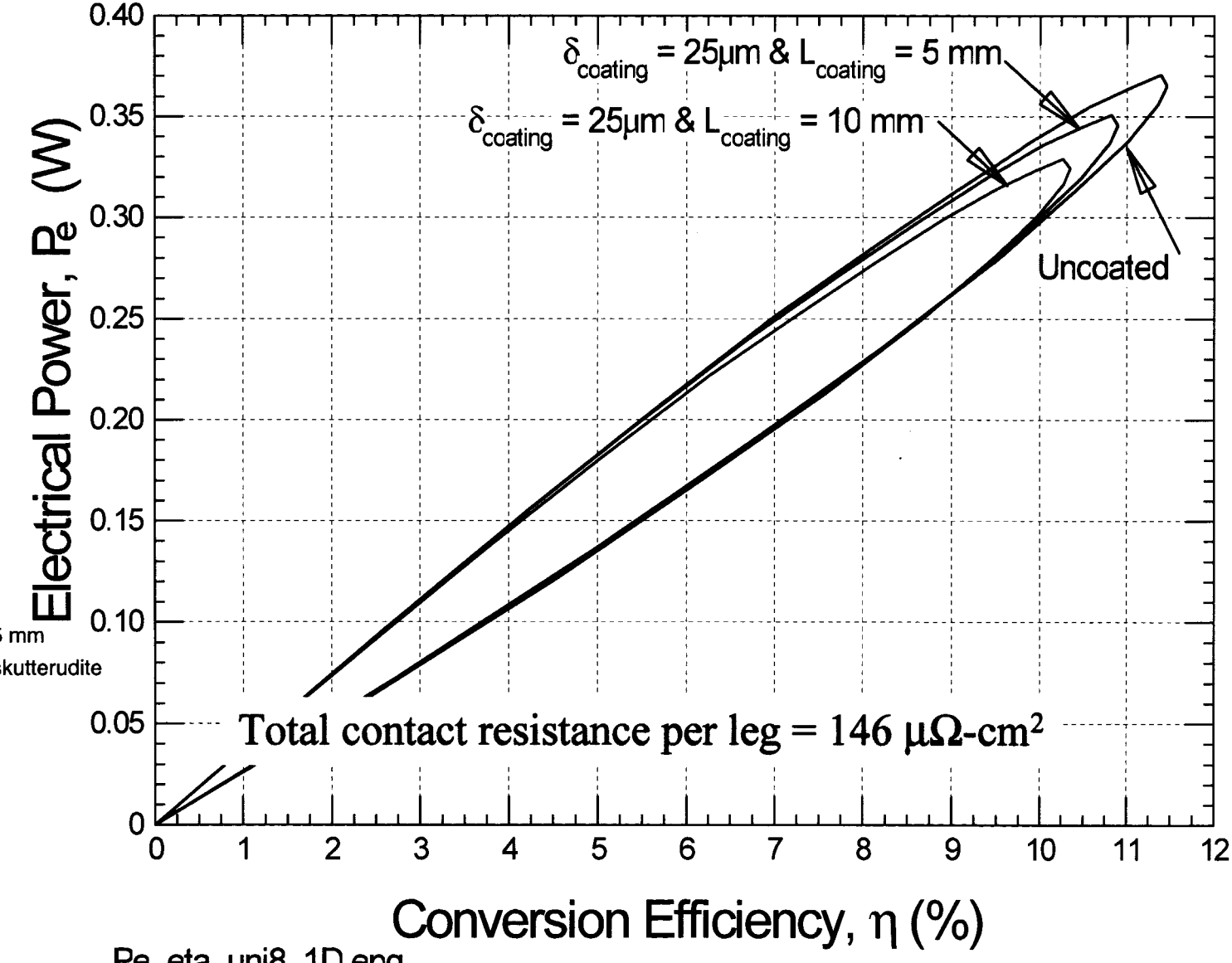
Accomplishments - Unicouple Development

- 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



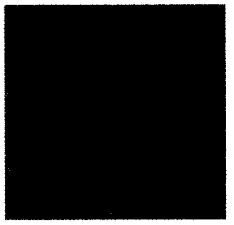
Thermal/mechanical modeling
(University of New Mexico)





Pe_eta_uni8_1D.epg

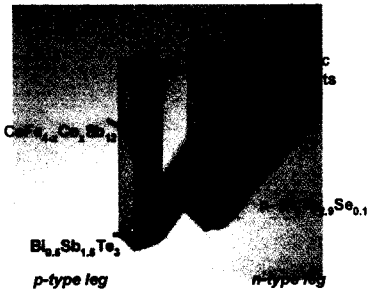
Thermoelectric technology development path



Skutterudite crystal structure

Advanced TE materials
Higher ZT values

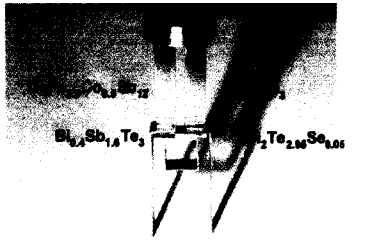
$$ZT = \alpha^2 / \rho \lambda$$



Segmented legs

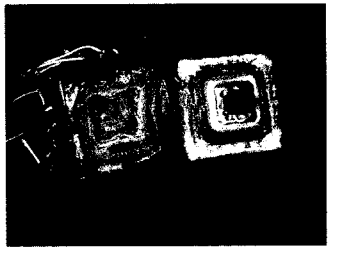
Materials selection for maximizing conversion efficiency

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



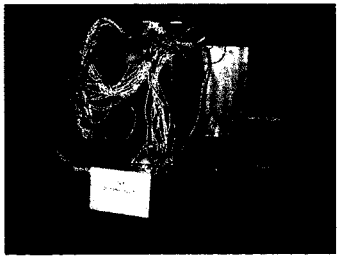
Skutterudite/Bi_2Te_3 segmented unicouple

Advanced segmented unicouples
Higher efficiency
& mechanical integrity
Preliminary life tests



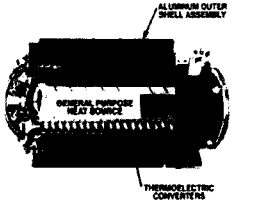
4 unicouple module

Life tests
Performance



18 unicouple module

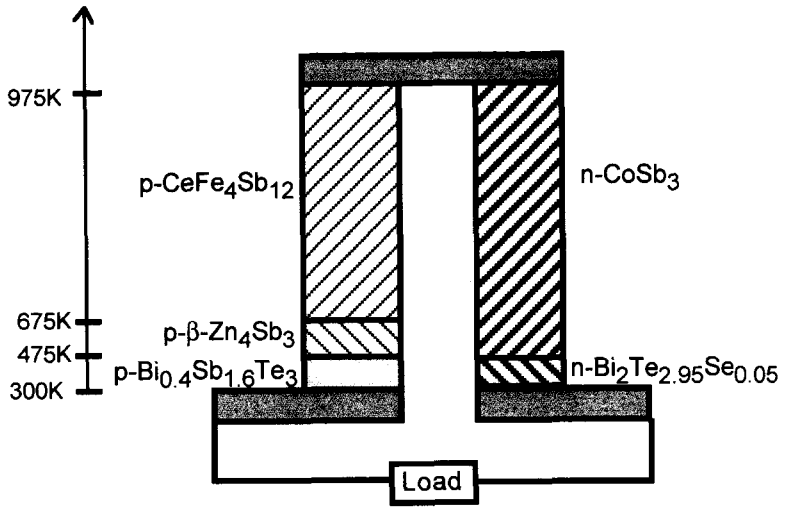
Life tests
System engineering
module efficiency



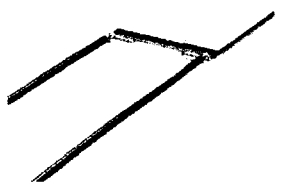
200W STERPS generator
System efficiency
Specific power

Potential applications

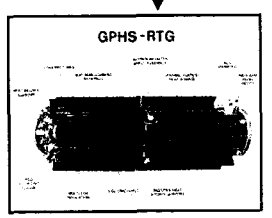
- Thermal to Electric Power Generation
  - Integration with any heat source
    - Combustors
    - Catalytic reactors
    - Radioisotope heat source
- Waste heat recovery
  - Automobile exhaust
    - Supplement or replace electrical power generator with electrical power generated from engine waste heat
    - T ~ 400 to 600°C downstream of the catalytic converter
    - ~1 kW power generator
    - Cost is critical (~$100/kW)
  - Power plants
  - Geothermal energy
- Solid State Advantage
  - No moving parts
  - No maintenance
  - Long life
- Scalability



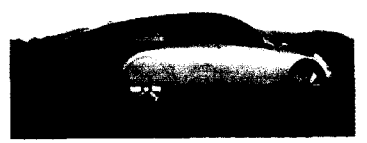
Advanced TE Segmented Unicouples



Advanced Power Generation TE Modules



Radioisotope Thermoelectric Generators



Waste heat Automobile