New Materials and Devices for Thermoelectric Applications

presented at the

Electronics Division Meeting
Of the American Ceramic Society

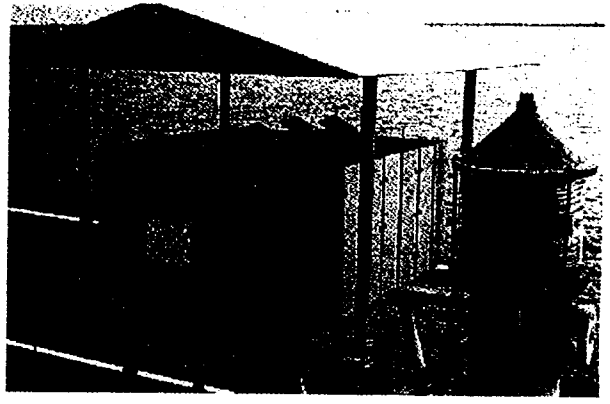
by

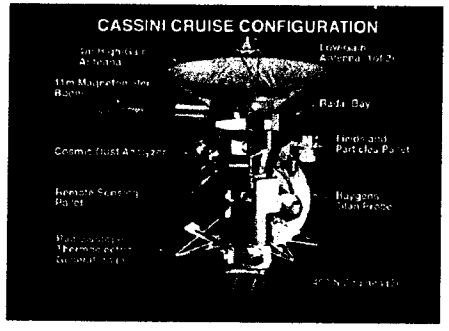
T. Caillat

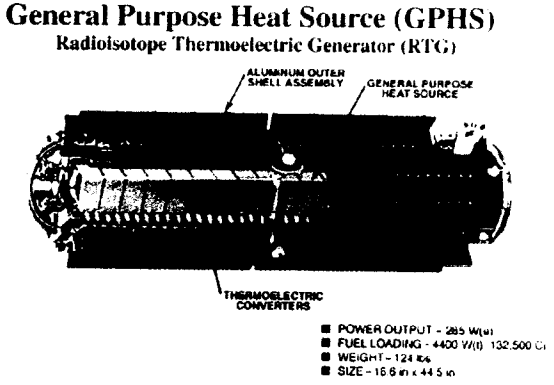
Jet Propulsion Laboratory/California Institute of Technology
Pasadena, CA, USA

Thermoelectrics: Some Successes...

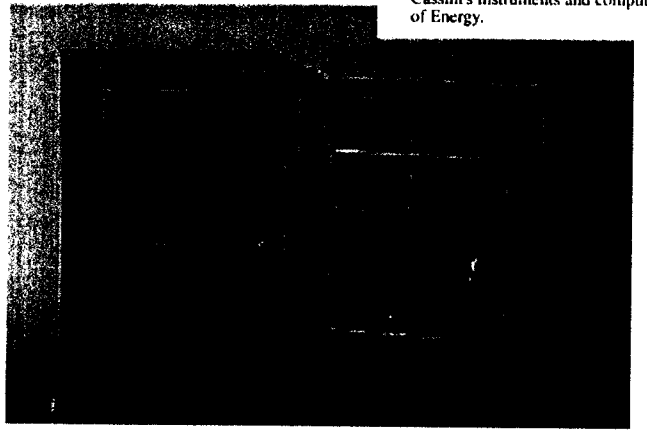
- **Thermoelectric power generation:**
  - Remote, unattended terrestrial power sources for harsh environments
    - Operating on hydrocarbon fuel
    - Small commercial market
  - Radioisotope thermoelectric generator (RTG)
    - Used on a number of deep space probe missions
    - Over 20 years of continuous operation for Voyager 1 and 2!
- **Thermoelectric cooling:**
  - Small scale cooling applications
    - Picnic boxes, small domestic refrigerators and air conditioning
  - Specialized application
    - Thermal management of optoelectronic devices
    - Detectors, microprocessors...



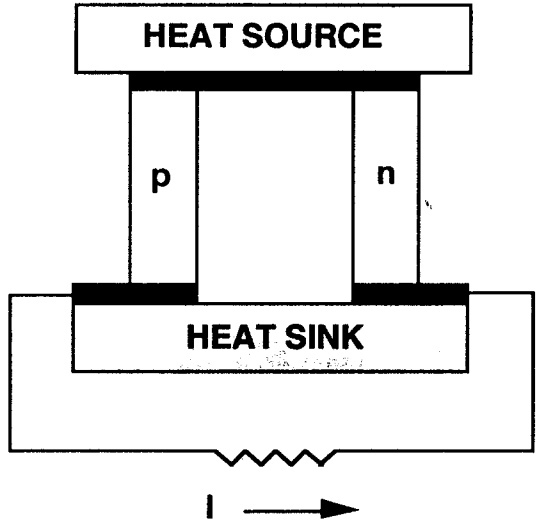




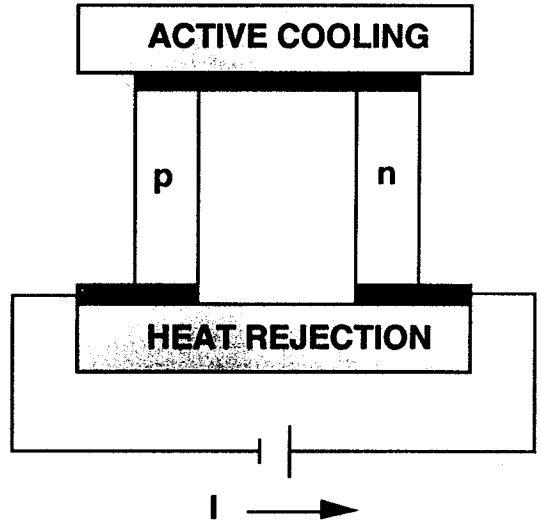
The three Radioisotope Thermoelectric Generators (RTGs) provide electrical power for Cassini's instruments and computers. They are being provided by the U.S. Department of Energy.



Thermoelectrics basics



Power generation



Refrigeration

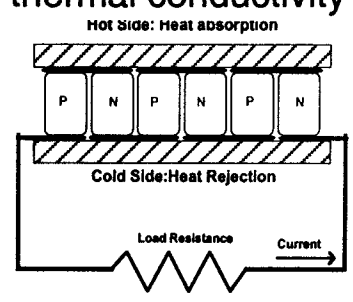
Efficiency:

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

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

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

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



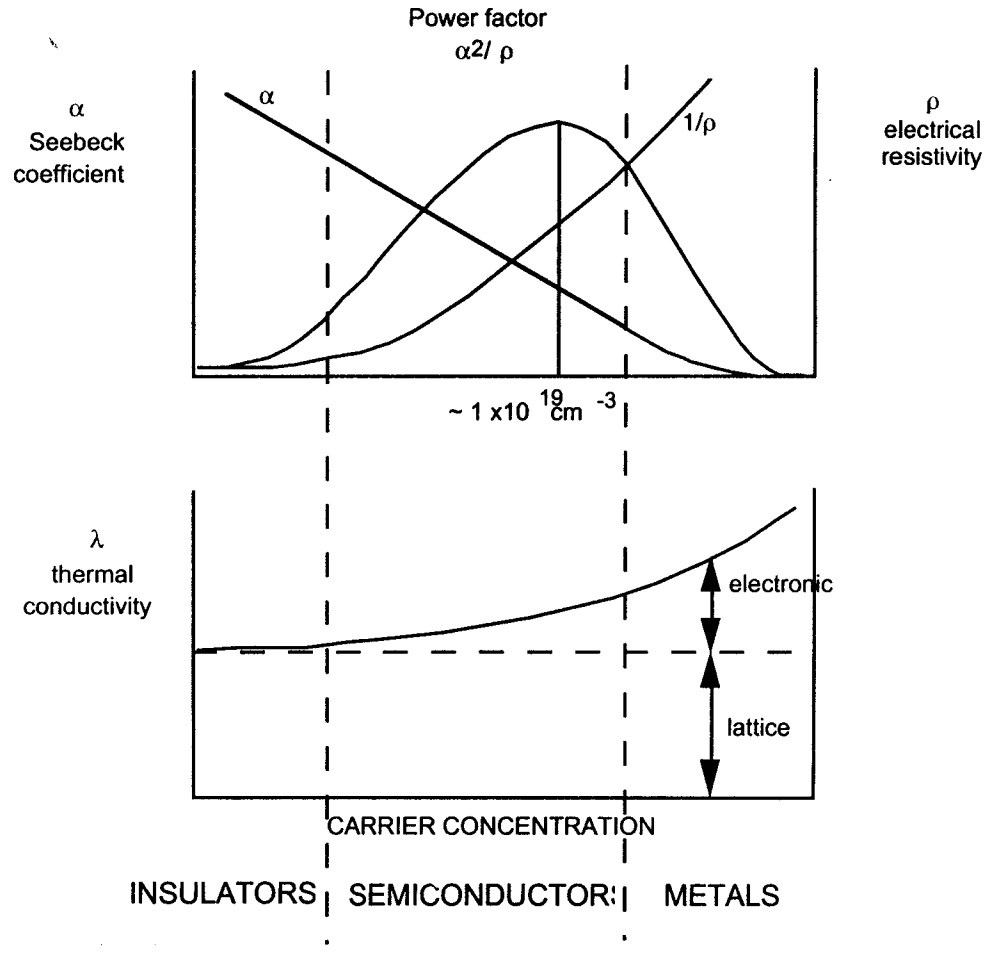
TE Module

→ **Large ZT values are needed**

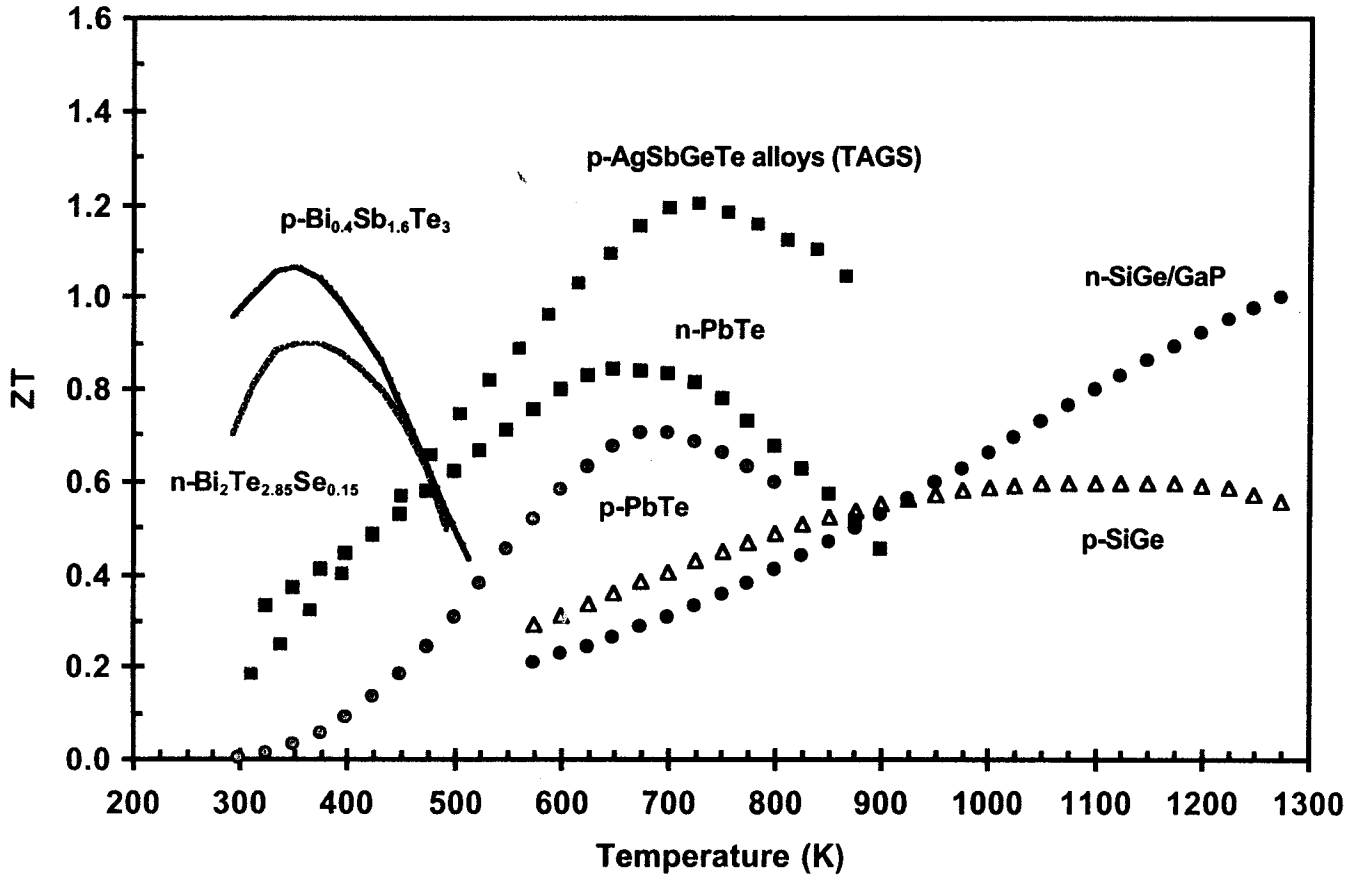
Thermoelectric figure of merit

$$Z = \frac{\alpha^2}{\rho\lambda}$$

- α, ρ, and λ depend on the carrier concentration
- Best compromise usually found for heavily doped semiconductors



State-of-the-art thermoelectric materials

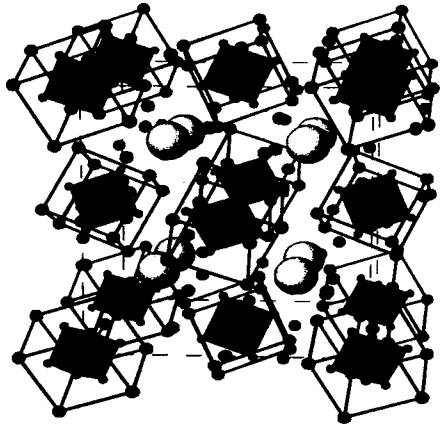


- **Conversion efficiency (η) of thermoelectric devices**
  - Large ΔT, high ZT -> high efficiency
  - Conversion efficiency has been limited up to now by low ZT values
  - **Need for new, high ZT materials !**

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

Advanced Thermoelectrics

- **Bulk materials**
  - Focus on TE materials for cooling and power generation up to 600-700°C only
  - Identification, characterization and optimization of some new, promising materials
    - Zn_4Sb_3 alloys
    - Skutterudites (in collaboration with Stanford University)
  - Preparation and characterization of several families of compounds with low thermal conductivities, metal-to-semiconductor transition (collaboration with NRL, RPI, U. Michigan)
    - Chevrel phases
    - Spinel chalcogenides and related AB_2X_4 compounds
    - Layered chalcogenides



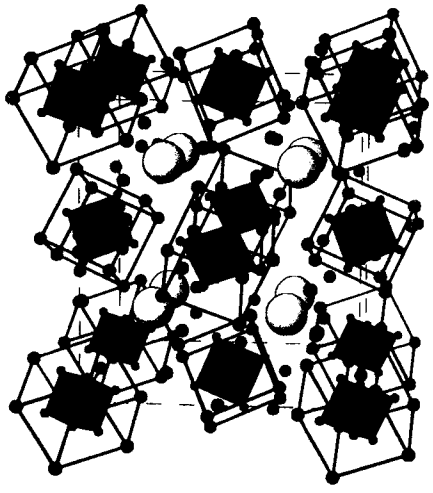
High Performance Thermoelectric Materials

The search for thermoelectric materials with high ZT values is guided by a certain number of criteria, including:

- Semiconducting properties
  - **Both n-type and p-type conduction types, band gap E_g of at least 4kT to minimize minority conduction effects**
  - **High doping levels, semimetallic behavior**
- Large Seebeck coefficient
  - **Wide band gap, high density of states near Fermi level, heavy effective masses m*, transition bands, ionized impurity carrier scattering**
- High carrier mobility, high electrical conductivity
  - **Highly covalent atomic bonds, low effective mass, high doping levels, acoustic phonon scattering of the carriers**

High Performance Thermoelectric Materials

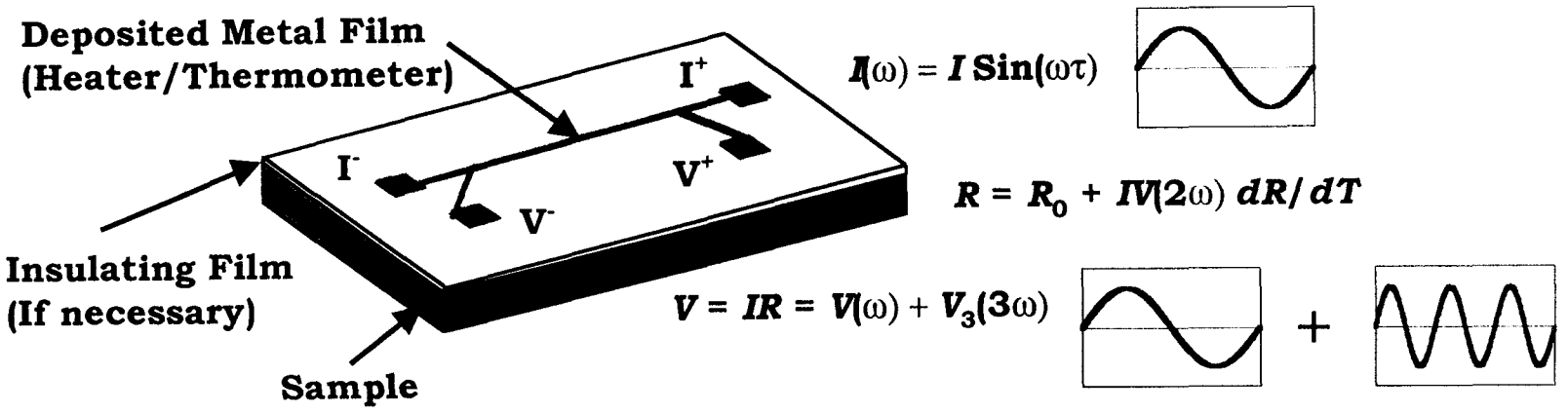
- Low lattice thermal conductivity
  - **High mean atomic weight, high electronegativity difference ΔX**
  - **Formation of solid solutions with isostructural compounds**
  - **"Open" complex crystal structure**
  - **High melting point and low vapor pressure**
  - **Relatively to its temperature range of interest**
  - **Considerably restricted list of compounds for high temperature applications**



- Selection of high performance thermoelectric materials necessitates striking a balance between conflicting requirements for the optimization of the various transport properties
  - **Slack's Phonon-Glass-Electron-Crystal ideal compound!**
    - **"Glassy" thermal conductivity**
    - **"Electronic" single crystal**

Measurement Capabilities

- A variety of custom-configured automated systems
- High Temperature Measurements 300K - 1300K
  - **Seebeck – large or small gradient**
  - **Resistivity – low or high impedance**
  - **Contact Resistance**
  - **Hall Effect**
    - **Electrical Conductivity, Mobility, Carrier Concentration**
  - **Thermal Diffusivity**
    - **Thermal Conductivity, Heat Capacity**
- Low Temperature Measurements 4K - 300K
  - **Seebeck**
  - **Resistivity and Hall Effect**
  - **Thermal Conductivity – comparative, 3-omega**



Filled Skutterudites

- JPL identified skutterudite family as good candidates for thermoelectric materials (1993)
  - Prototype $CoAs_3$; named after the first mineral found in Skutterud (Norway)
  - Very large family of compounds : antimonides, arsenides, and phosphides
- Binary Compounds (Ex: $CoSb_3$)
  - Nine semiconducting and two metallic compounds
- Solid solutions (Ex: $CoAs_{3-x}Sb_3$)
  - Found solid solutions exist between most binary skutterudites as well as in many other systems
- New phases are derived from binary compounds (Ex : $Ru_{0.5}Pd_{0.5}Sb_3$)
  - By replacing the transition metal or the pnicogen or both elements
  - By conserving the number of valence electrons
  - Numerous related skutterudite phases exist
- Filled skutterudites (Ex: $CeFe_4Sb_{12}$)
  - Filled skutterudites can be formed by filling the two empty octants present in the 32 atoms unit cell
  - The number of valence electrons needs to remain constant to conserve a semiconducting behavior
  - Studies mostly focused on antimonides up to now
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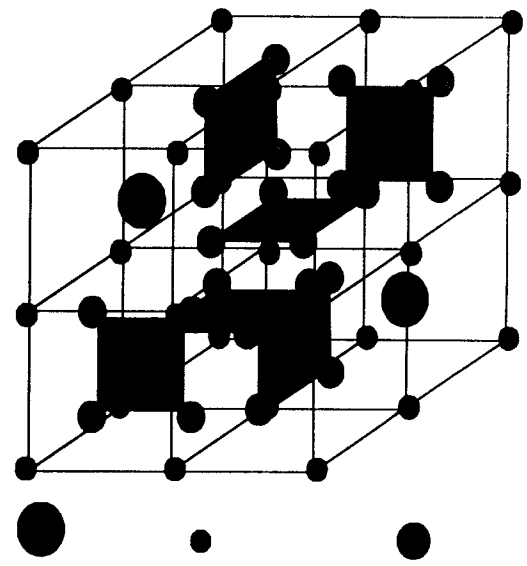
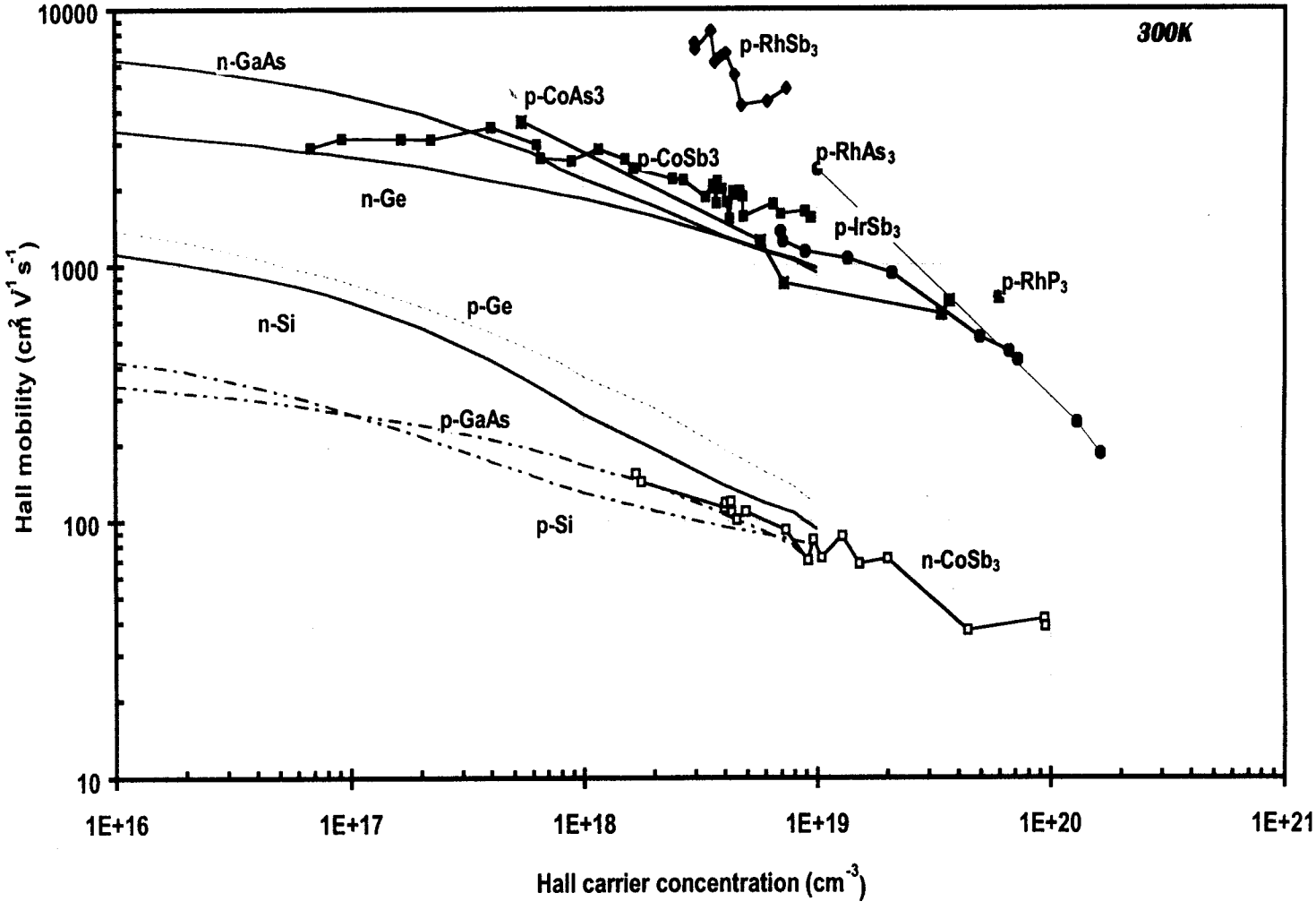
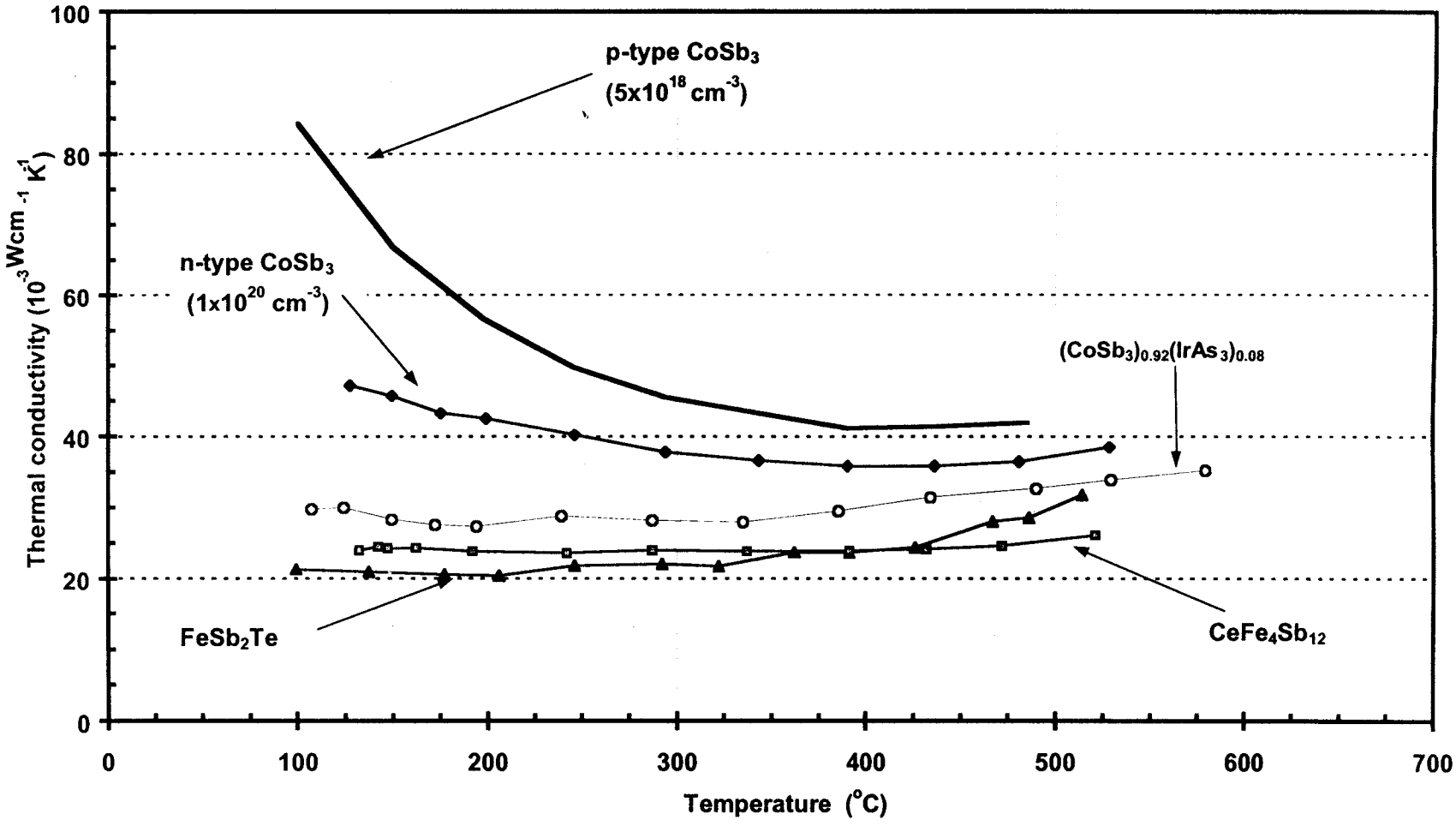


- Cubic, 34 atoms/unit cell
- 8 transition metal atoms
- 24 pnicogen atoms
- 2 rare earth atoms in empty octants
- Space group *Im3* (T^5_h)

Carrier Mobility of Skutterudites

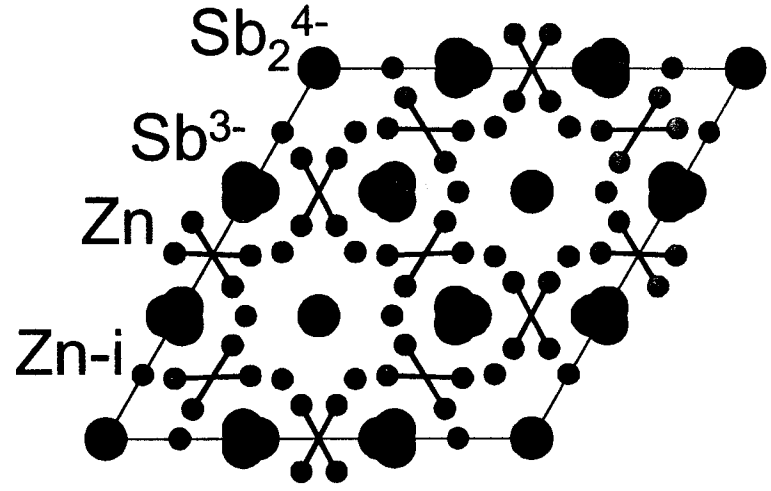


Reducing the Thermal Conductivity in Skutterudites



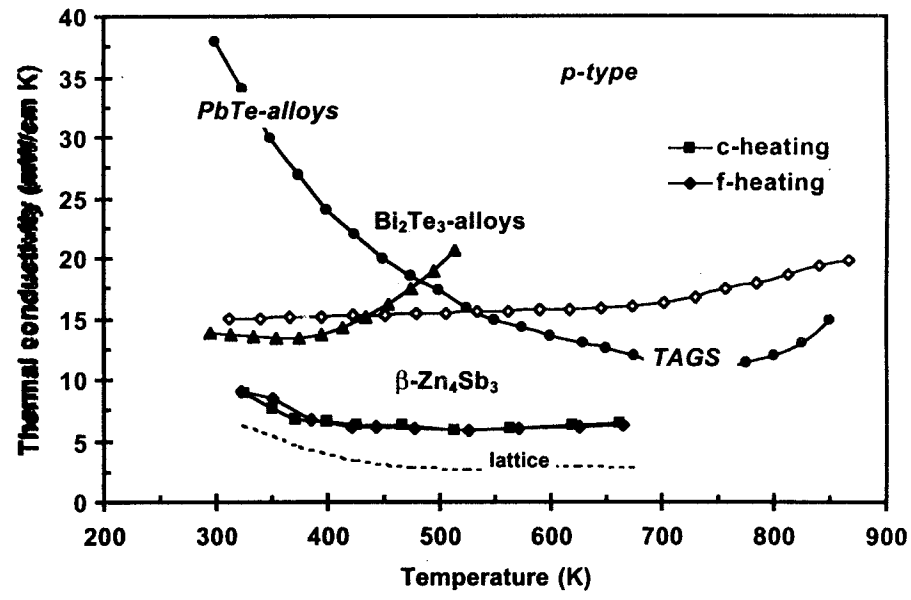
Zn_4Sb_3 and its alloys

- Crystal structure
  - Highly disordered structure
  - Large unit cell
  - Localized deviations form the stoichiometry revealed by Auger spectroscopy: vacancies
  - Potential for low thermal conductivity
- Form solid solutions with Cd_4Sb_3

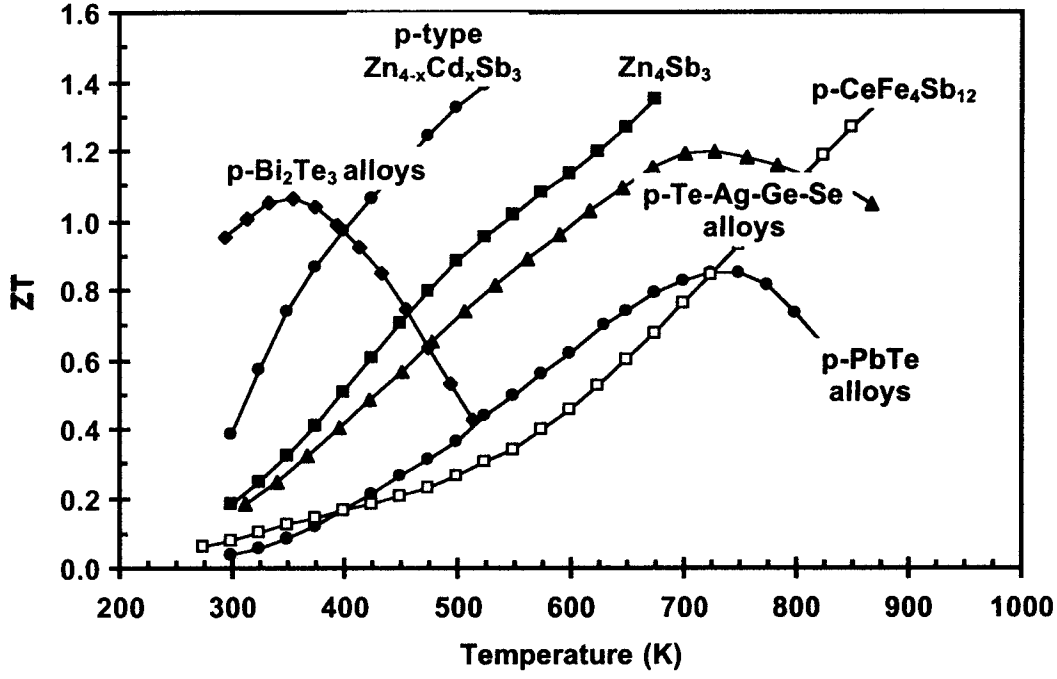


Property	β-Zn_4Sb_3
Melting point (C)	566 *
Type of formation	peritectoid*
Structure type	hexagonal rhombohedric *
Number of atoms/unit cell	66 *
Lattice parameter	a=12.231, c=12.428Å *
X-ray density (g cm^{-3})	6.077
Thermal expansion coefficient (C^{-1})	1.93×10^{-5}
Energy band gap (eV)	1.2 *
Conductivity type	p
Electrical resistivity (mΩ cm)	2
Hall mobility ($cm^2 V^{-1} s^{-1}$)	30
Hall carrier concentration (cm^{-3})	9×10^{19}
Seebeck coefficient (μVK^{-1})	120
Thermal conductivity (mW $cm^{-1} K^{-1}$)	9

* Literature results

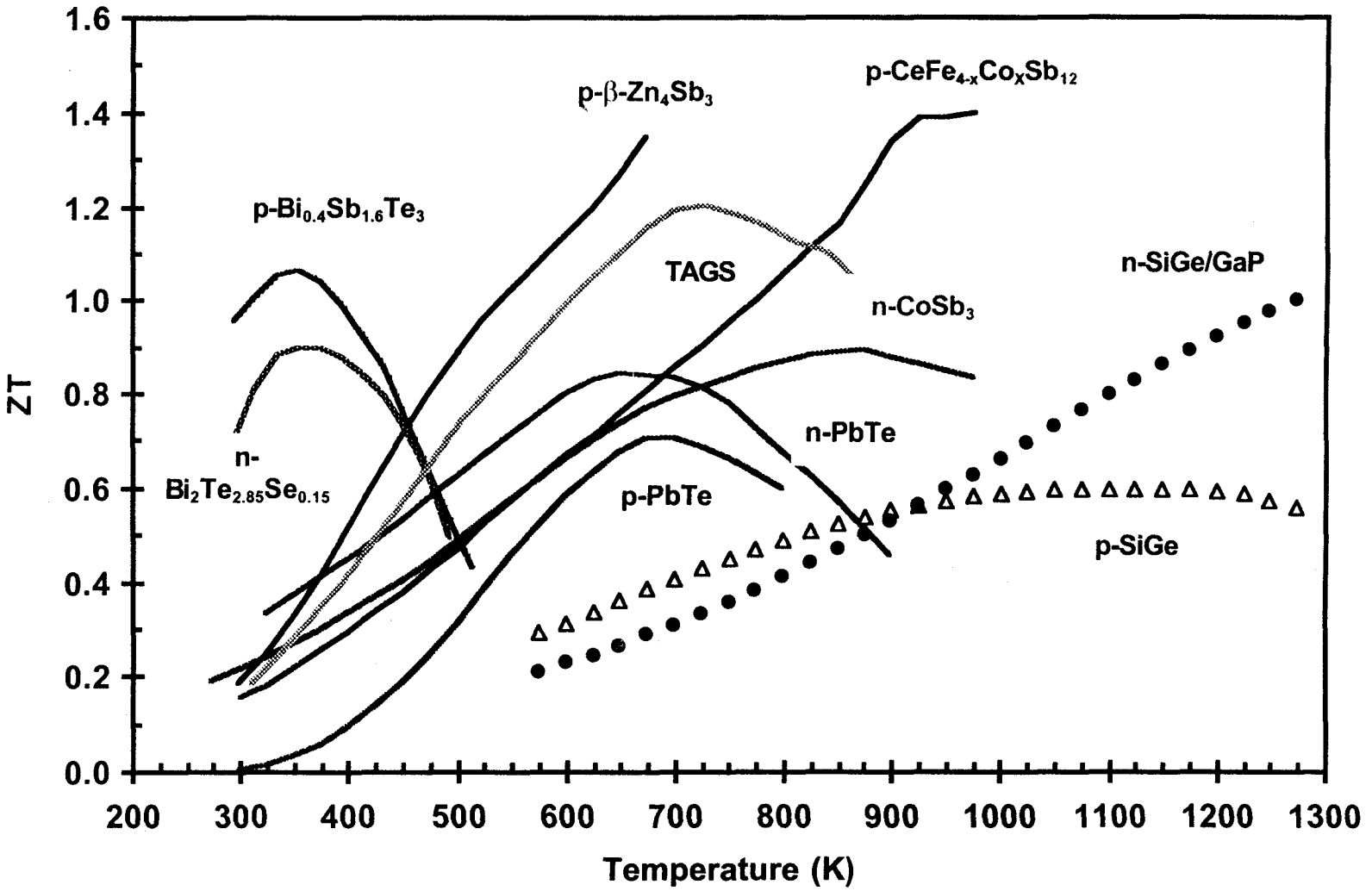


Best ZT to date on Zn_4Sb_3 based materials



- Zn_4Sb_3
  - ZT~1.4 at 675K
  - Phase transformation above this temperature
- $Zn_{4-x}Cd_xSb_3$
  - ZT~ 1.4 at 525K
  - Less stable above 525K for high Cd content than Zn_4Sb_3

Best ZT to date on new materials developed at JPL



Best ZT to date on new materials developed at JPL

- High ZTs achieved for skutterudites and Zn_4Sb_3 materials
  - Results reproducibly confirmed by other labs in US and Japan
- Maximum temperature of operation
  - Antimonide skutterudites : n-$CoSb_3$ & p-type $CeFe_{3.5}Co_{0.5}Sb_{12}$
    - Limited to about 975K
    - Sublimation possible for higher temperatures
  - Zn_4Sb_3
    - Limited to about 675K
    - Solid state phase transformation above this temperature
- High ZT possible for other materials
  - Arsenide and phosphide skutterudites
  - Chevrel phases

Arsenide and phosphide skutterudites

- Peritectic decomposition temperature
  - $CoSb_3$ (1132K) → $CoAs_3$ (>1200) → CoP_3 (>1300K)
  - $CeFe_4Sb_{12}$ (~1100K) → $CeFe_4As_{12}$ (>1200) → $CeFe_4P_{12}$ (>1300K)

- Band gap
  - Band gap increases from Sb → As → P compounds ($CoSb_3$: 0.56eV → $CoAs_3$: 0.87 eV)
  - Arsenide and phosphide compounds have better potential for performance optimization at temperatures higher than 900K than antimonides

- Some studies conducted under ONR and DARPA program
  - Several filled and unfilled arsenide and phosphide compounds synthesized and characterized
  - n- and p-type $CoAs_3$ and $RhAs_3$
  - $CeRu_4Sb_{11.4}As_{0.6}$ and $CeRu_4Sb_{10.8}As_{1.2}$
    - Reduction in carrier concentration compared to $CeRu_4Sb_{12}$
    - Illustrate influence of point defect, void filling and charge carrier scattering on phonons
  - CoP_3, $CeFe_4P_{12}$, $CeRu_4P_{12}$, $PrFe_4P_{12}$, $LaCo_4P_{12}$, $CeCo_4Si_3P_9$, $Ce_{0.2}Co_4Ge_{0.6}P_{11.4}$
    (Synthesized at Stanford University)

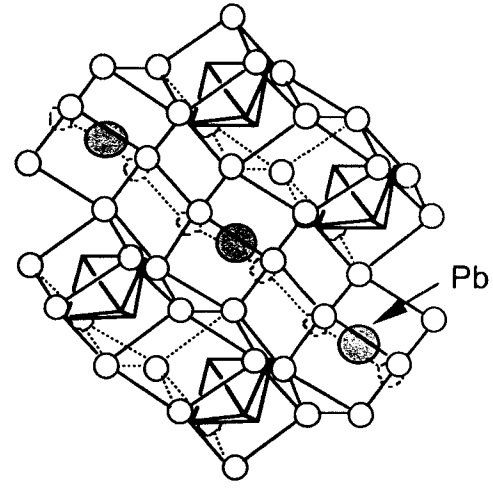
Arsenide and phosphide skutterudites

- Initial results
  - Characterization limited to up to about 1000K maximum
  - Thermoelectric property measurements results
    - Similar trends in the thermoelectric properties than for antimonide compounds
    - More semiconducting
    - Could potentially be doped n- and p-type
    - Larger band gaps

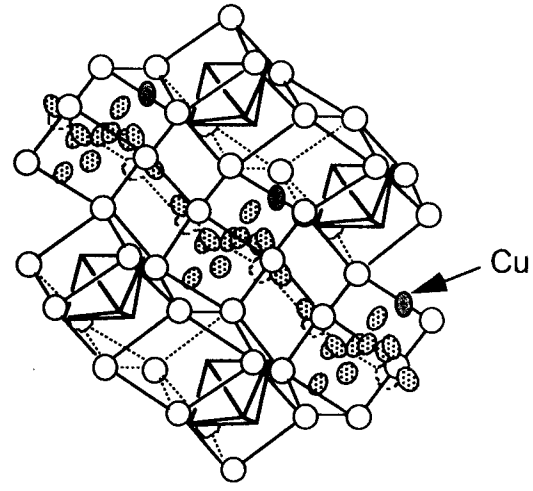
- Potential for optimization in the 900 to 1250K temperature range

$M_xMo_6Se_8$ Filled Ternary Chevrel Compounds

- Structure contain channels where additional atoms can be inserted
  - Cavities can be filled with a variety of atoms of different size and mass
  - Sizes and shapes of the cavities depend on the composition and degree of filling
- M = large atoms such as Pb or La
  - Can occupied only the largest of the voids
  - Big atoms can occupy the center of a cube shaped cavity at the origin of the unit cell
  - Octahedral coordination
  - Experimental limit: $x_{max}=1$
- M = small atoms such as Cu, Ni or Co
  - Can occupied 12 different smaller holes
  - Holes interconnected and form infinite channels in form of zigzag chains
  - Experimental filling limit: $x_{max} \sim 4$
  - Tetrahedral coordination
- Cluster VEC
  - Number of electrons per $[Mo_6]$ cluster
  - Counting electrons assuming that non metal p states are completely filled by charge transfer from the metal atom states
  - Band structure calculations results show an energy gap in the electronic band structure for Chevrel phases with a VEC of 24



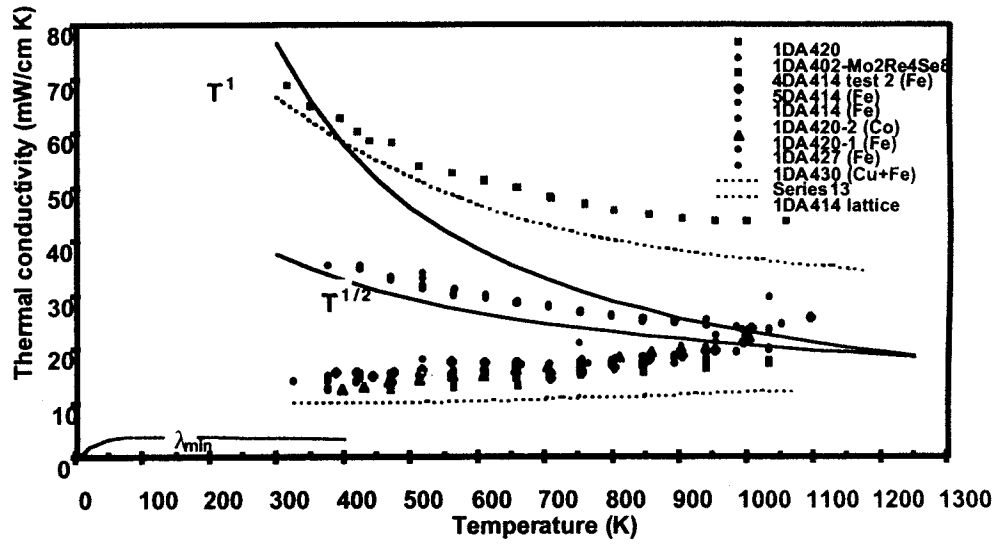
$PbMo_6Se_8$

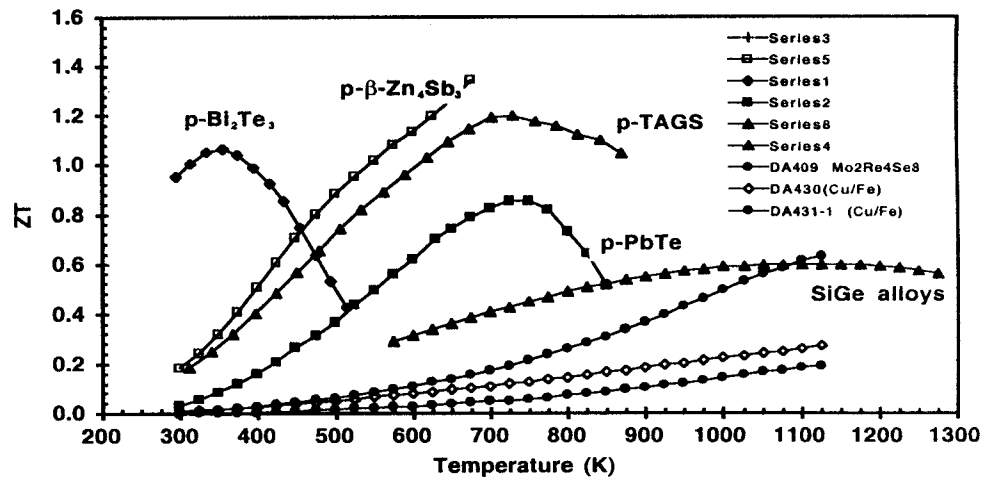


$Cu_xMo_6Se_8$

Summary of Chevrel compositions investigated and results

- Binary samples
  - Mo_6Se_8
  - Mo_6Te_8
  - $T_{decomposition}$ > 1300K
- Pseudobinary samples
  - $Mo_2Re_4Se_8$ VEC of 24 → semiconducting
- Filled compositions $M_xMo_6Se_8$
  - $Fe_xMo_6Se_8$
  - $Co_xMo_6Se_8$
  - $Ni_xMo_6Se_8$
  - $Zn_xMo_6Se_8$
  - $(CuFe)_xMo_6Se_8$
  - $(Li)_xMo_6Se_8$
  - $Ti_xMo_6Se_8$ → semiconducting
- Further work needed
  - Achieve full filling
  - Optimization of electronic properties

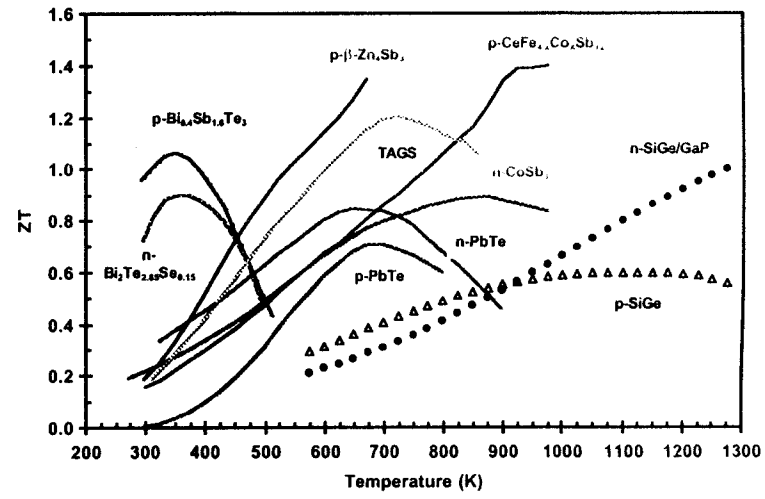


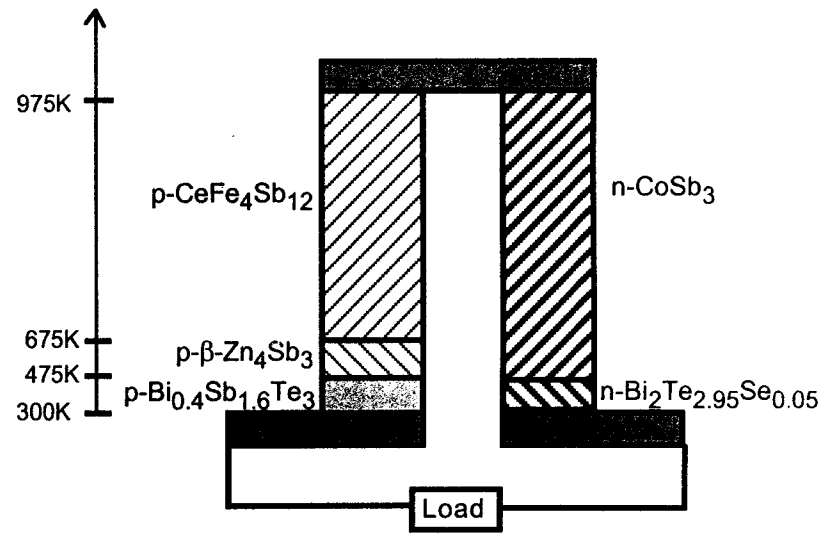


Segmented Unicouples

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

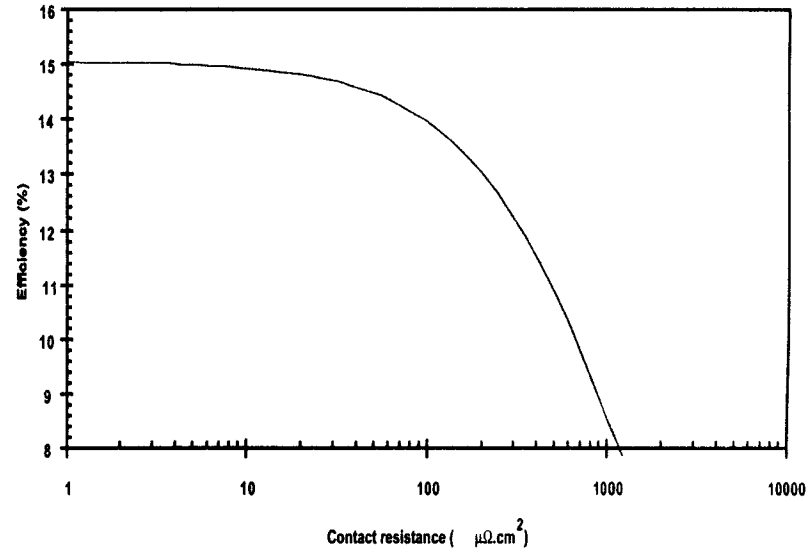
- **Segmented unicouples**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials(Bi_2Te_3-based materials)and new, high ZT materials developed at JPL
    - Skutterudites : $CeFe_4Sb_{12}$ and $CoSb_3$
    - Zn_4Sb_3
    - Patents issued and pending
  - Higher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





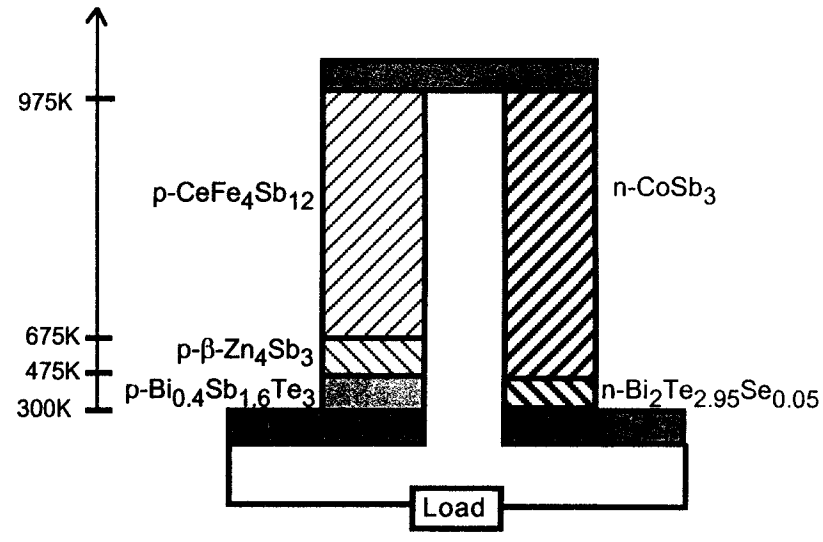
Optimization of the unicouple geometry

- **Model**
  - **Select temperature for interfaces based on ZT values**
  - **Balance heat at the interfaces**
  - **Includes contact resistance at the interfaces**
- **Results**
  - **Relative lengths of segments**
  - **Relative areas of p/n legs**
  - **Optimum load resistance**
  - **Power, current, and resistance of the device**
  - **Efficiency**



Optimum design parameters for segmented generator

Overall length (mm)	15
Area of p-leg (cross section) (mm^2)	5.7
Area of n-leg (cross section) (mm^2)	3.9
Device resistance (mΩ)	8.7
Load resistance (mΩ)	13.06
Current (A)	10.4
Power (W)	1.43



Calculated thermal-to-electrical efficiency

Thermal to electrical efficiency (%)

Cold side temperature (K)

Hot side temperature

975K

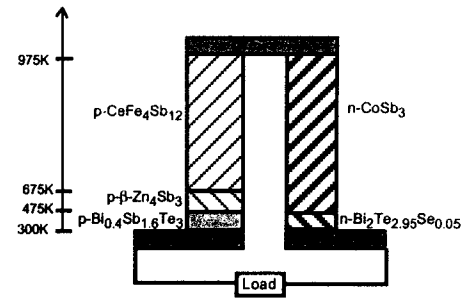
875K

775K

675K

575K

- Using 1st generation of advanced materials developed at JPL

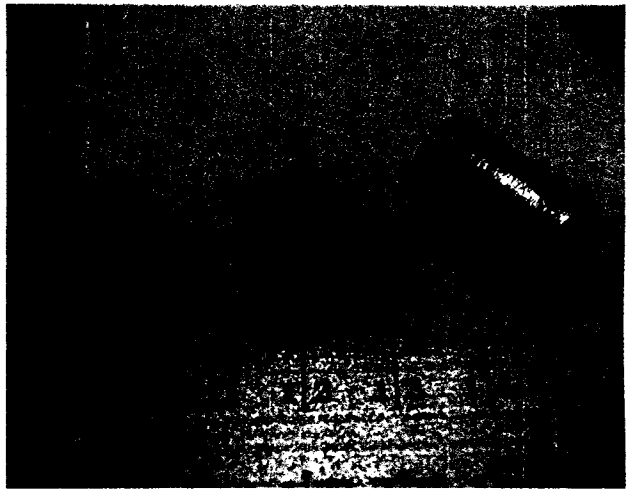


Temperature stability of new thermoelectric materials (summary)

- Zn_4Sb_3
  - Samples annealed for up to 5 months in vacuum at a temperature of 400°C (maximum temperature of operation in the unicouple) did not show any dissociation or significant changes in their properties and composition
- Stability of Zn_4Sb_3 in a temperature gradient (vacuum)
  - Several samples tested in a 150-400°C temperature gradient
  - No change in appearance, properties or composition of the samples observed after up to 2 weeks of testing with a hot side temperature between 350 and 400°C
- $CeFe_{4-x}Co_xSb_{12}$ and $CoSb_3$
  - Samples annealed for up to 2 weeks in vacuum at a temperature of 700°C did not show any dissociation or significant changes in their properties or composition

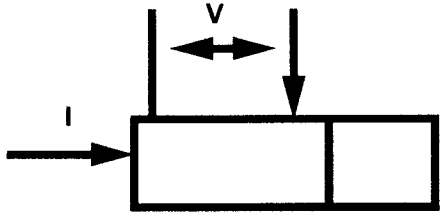
Segmented legs fabrication and testing

- Bonding of thermoelectric materials
  - 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
    - Pd, Pd-Ag, Ni, Ta, Ti, etc ...
    - 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$\mu\Omega cm^2$)

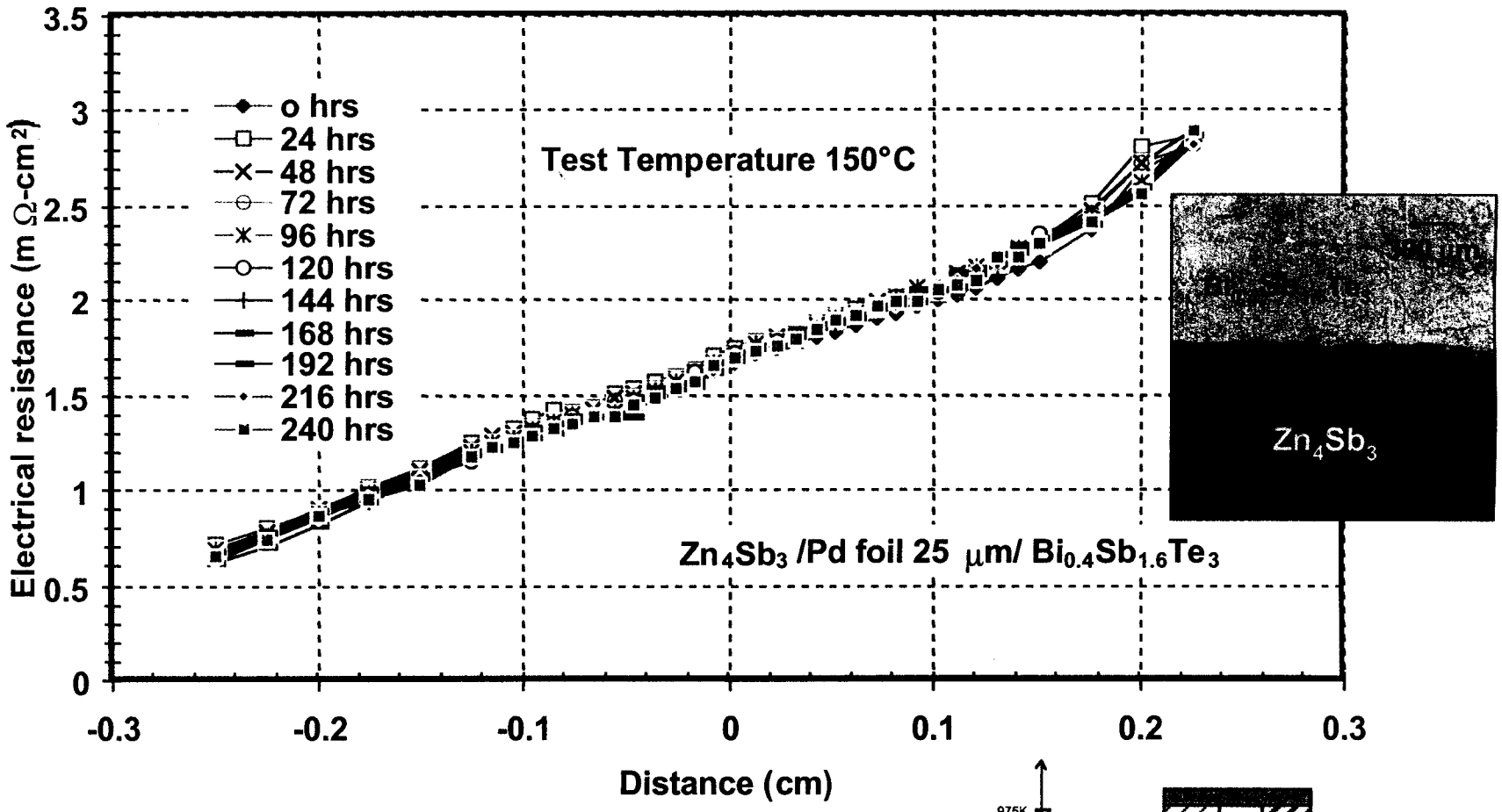


Segmented legs fabricated by uniaxial hot-pressing

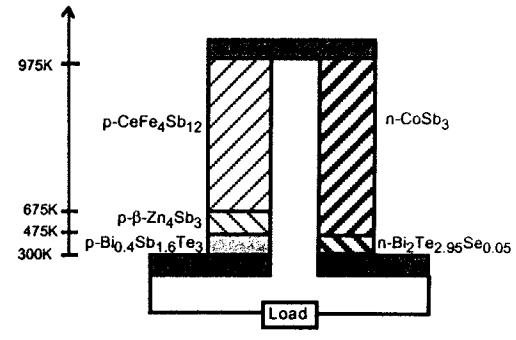
- Bond quality
  - Electrical contact resistance measurement
  - Microprobe analysis
    - Diffusion
    - Chemical reaction and interface layer analysis



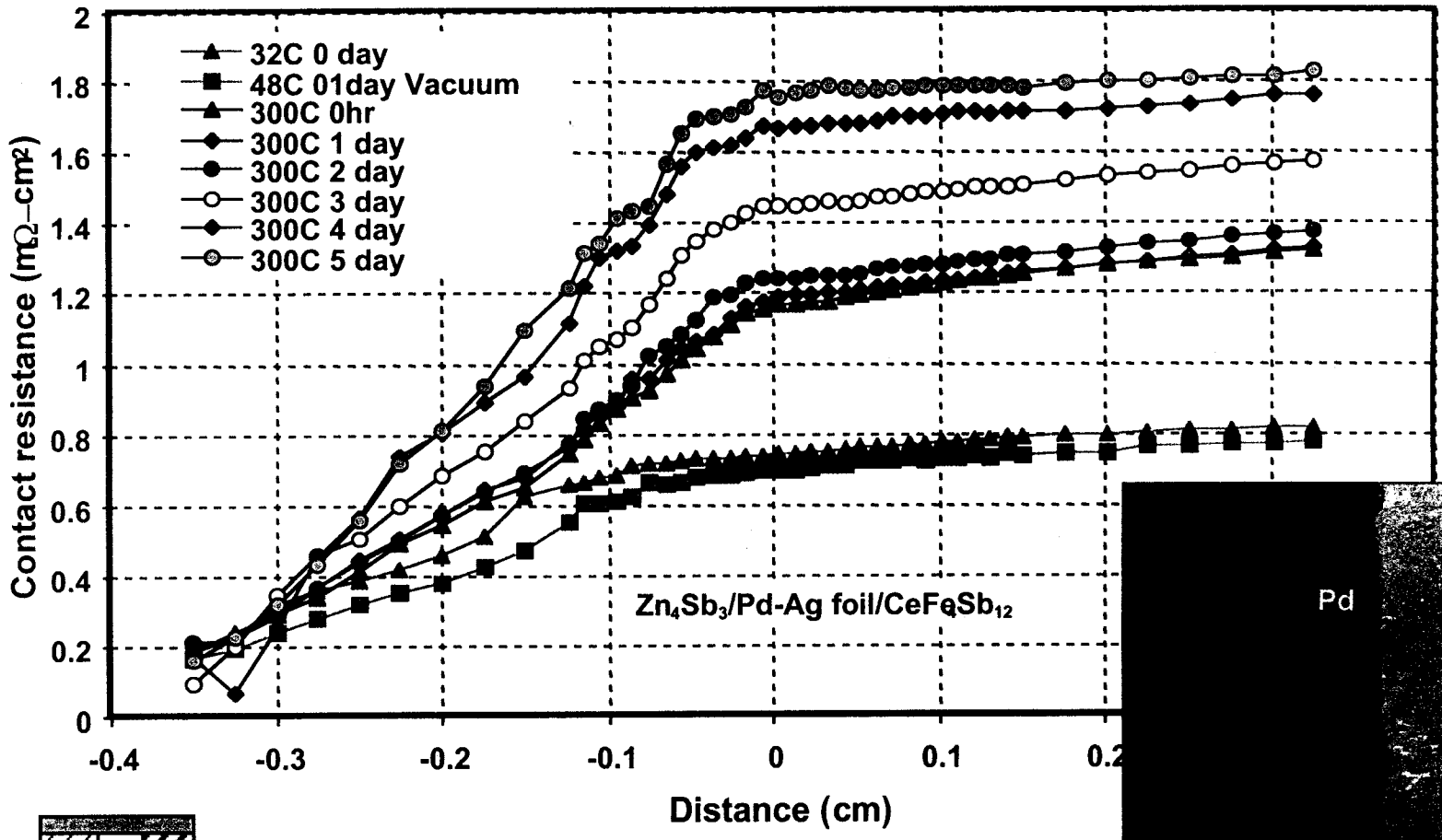
Zn_4Sb_3/Pd/$Bi_{0.4}Sb_{1.6}Te_3$ bonding

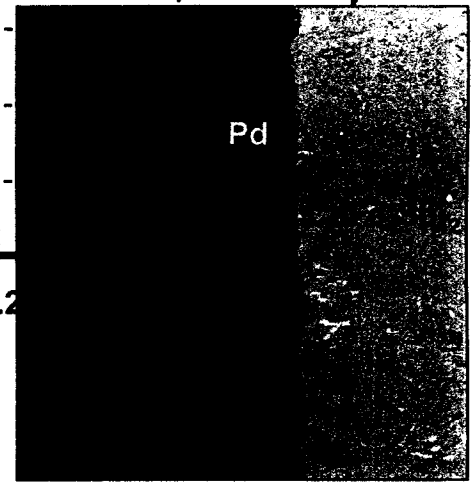


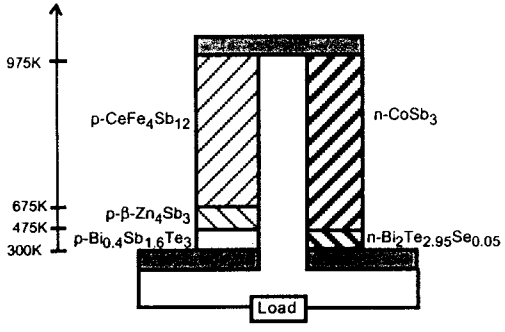
- Zn_4Sb_3 to $Bi_{0.4}Sb_{1.6}Te_3$
  - using a 25 μm Pd foil interface
  - junction tested for up to 2 weeks at 150°C
  - no interdiffusion and low contact resistance (<5 μΩ.cm²)



Zn_4Sb_3/Pd/$CeFe_4Sb_{12}$ bonding studies

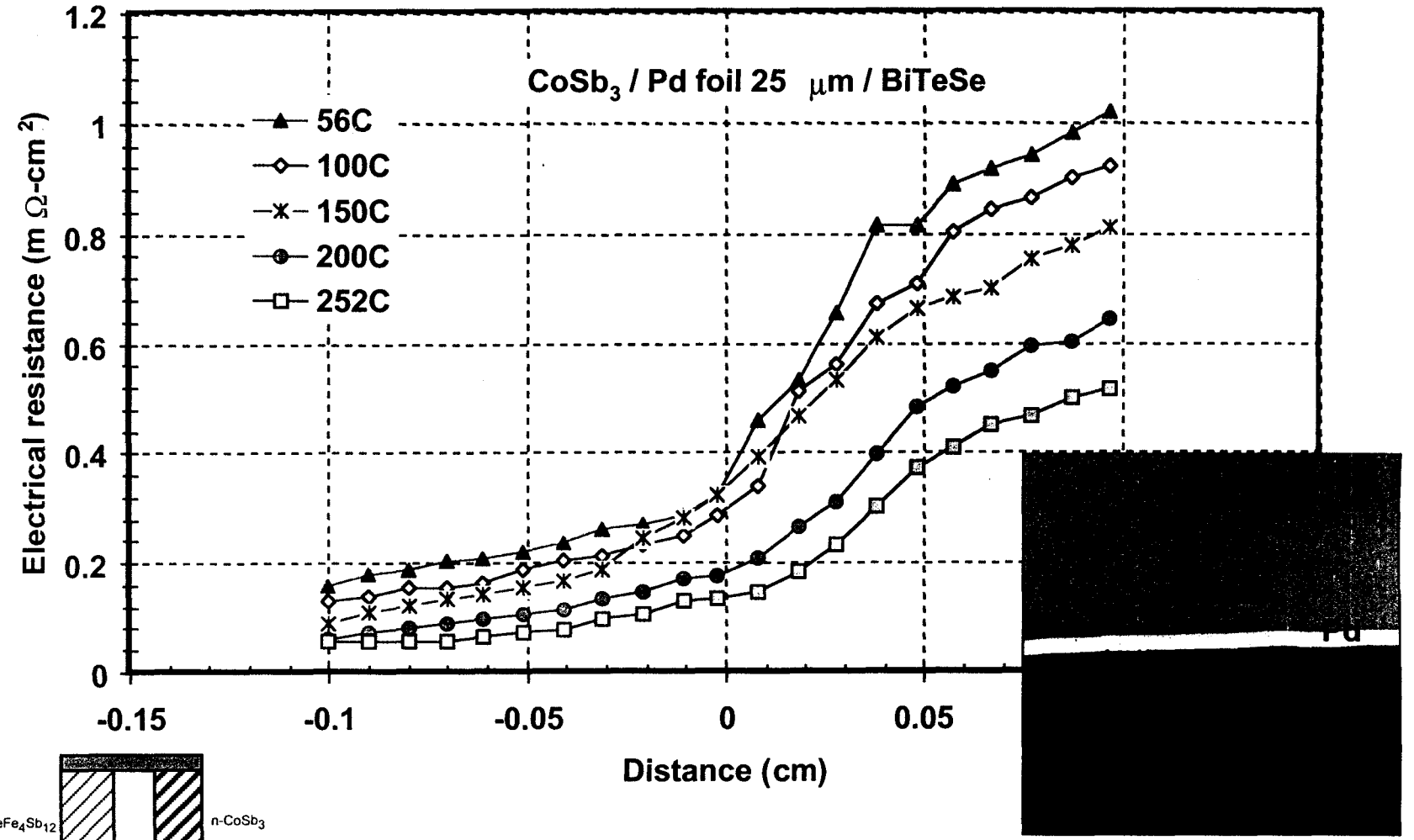


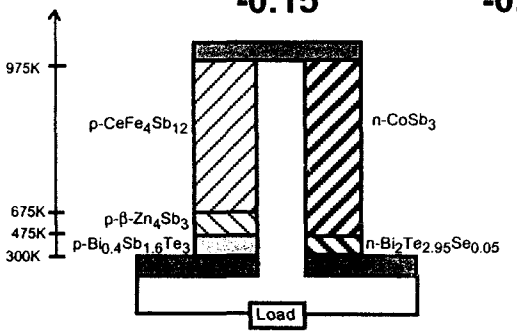




- Zn_4Sb_3 to $CeFe_4Sb_{12}$
  - using a 25 μm Pd foil interface
  - junction tested up to 400°C
  - no interdiffusion ; low contact resistance (<5 μΩ.cm²)

$CoSb_3$/Pd/$Bi_2Te_{2.85}Se_{0.15}$ bonding studies

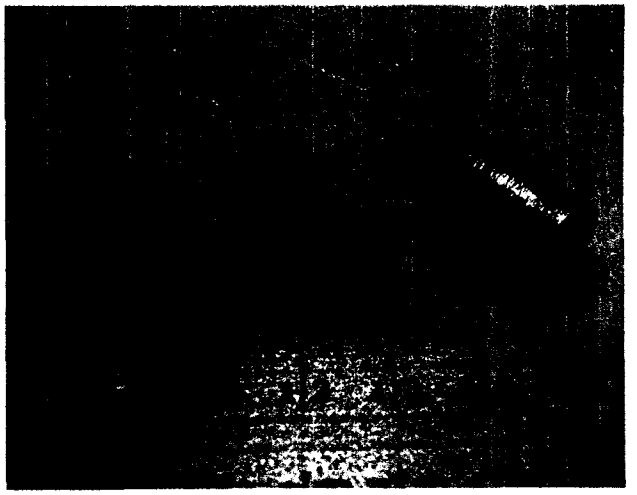




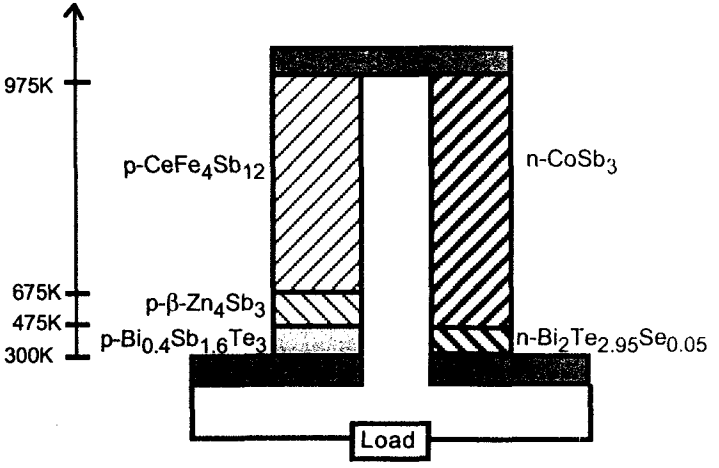
- $CoSb_3$ to $Bi_2Te_{2.85}Se_{0.15}$
  - using a 25 μm Pd foil
  - no interdiffusion and low contact resistance (<5 μΩ.cm²) up to 250°C

Thermoelectric Materials Bonding Studies - Summary

- Zn_4Sb_3 to $Bi_{0.4}Sb_{1.6}Te_3$
  - using a 25 μm Pd foil interface
  - junction tested for up to 2 weeks at 150°C
  - no interdiffusion and low contact resistance (<5 $\mu\Omega.cm^2$)
- Zn_4Sb_3 to $CeFe_4Sb_{12}$
  - using a 25 μm Pd foil interface
  - junction tested up to 400°C for up to 4 days
  - no interdiffusion ; low contact resistance (<5 $\mu\Omega.cm^2$)
- $CoSb_3$ to $Bi_2Te_{2.85}Se_{0.15}$
  - using a 25 μm Pd foil ;
  - no interdiffusion and low contact resistance (<5 $\mu\Omega.cm^2$) up to 250°C for up to 4 days
- Full n- and p-segmented legs fabricated



Segmented legs fabricated by uniaxial hot-pressing

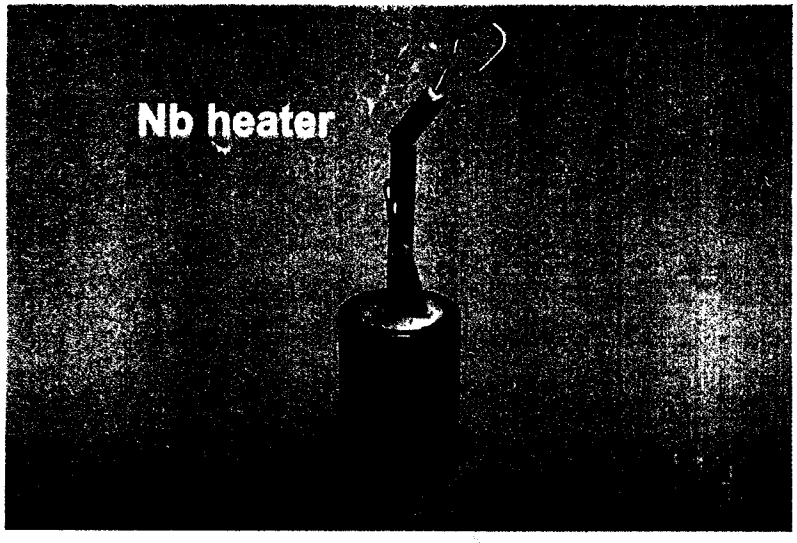


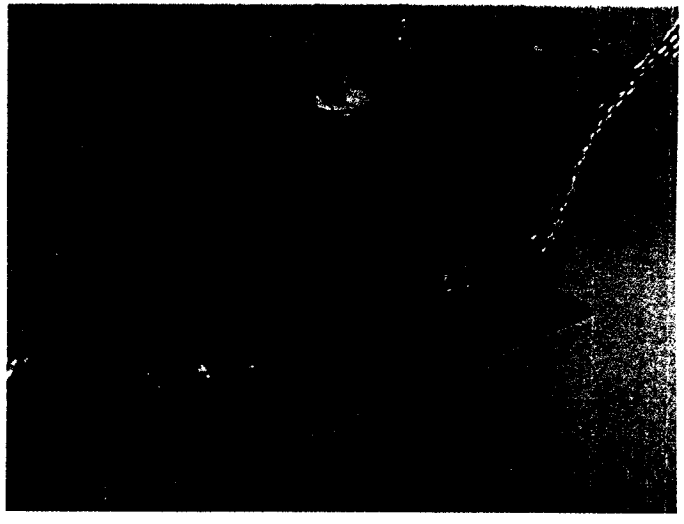
Interconnects

- 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 using PbSn solder
- Hot-shoe
  - $CeFe_4Sb_{12}$ and $CoSb_3$ brazed to Nb
    - Using Cu-Ag brazing alloy
    - Low contact resistance (<5 $\mu\Omega.cm^2$)
    - No interdiffusion up to 700°C
  - Issues
    - High temperature required for brazing (up to 700°C)
    - Some pressure required
    - Increased electrical contact resistance at the junctions and caused ruptures in some cases
  - → Alternative techniques being considered

Interconnects for hot side of the unicouple

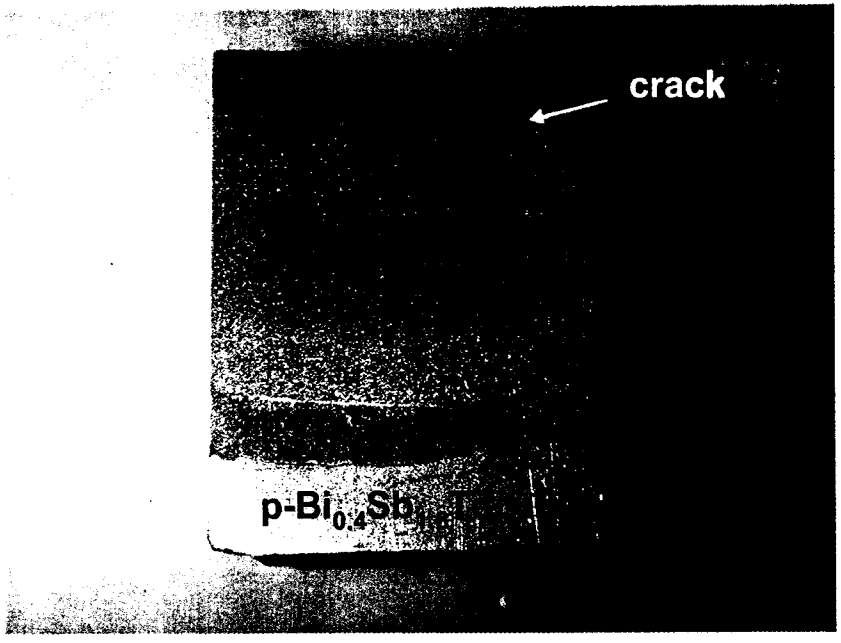
- Fabricate segmented legs with top metallic segments
  - Add metallic powder on top of segmented legs during hot pressing
  - No brazing required
  - Two type of metallic powders investigated to date : Ni and Nb
- Connecting n- and p-legs
  - Cut full cylindrical legs in half
  - Connect them to a metallic interconnect by brazing
  - Interconnect can be a heater for thermal and electrical testing



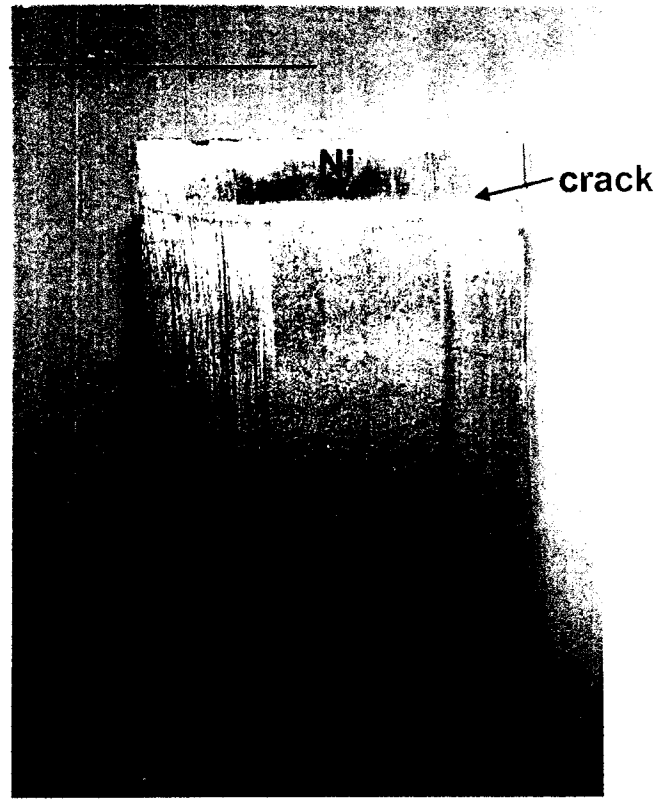


Results for Ni

- Good bond between Ni and top skutterudite segments
- Ni density about 91 % of the theoretical density
- But cracks within skutterudite materials near Ni/skutterudite interfaces
- Presumably due to thermal expansion coefficient mismatch
  - 13.3 x 10^{-6}/K for Ni
  - 7.5 x x 10^{-6}/K for p-$CeFe_{3.75}Co_{0.25}Sb_{12}$ and 6.36 x 10^{-6}/K for n- $CoSb_3$



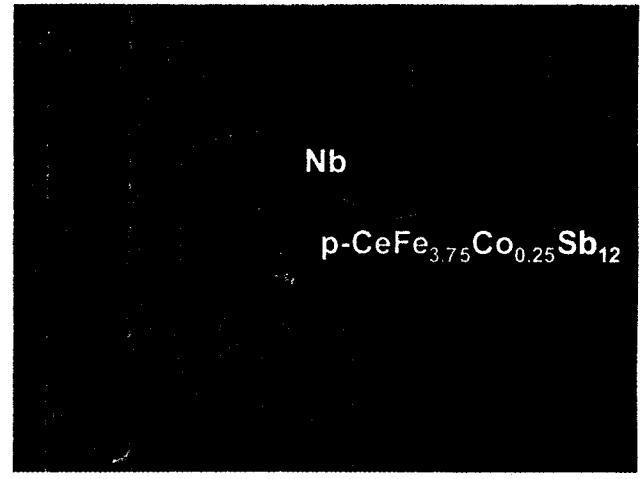
P-leg



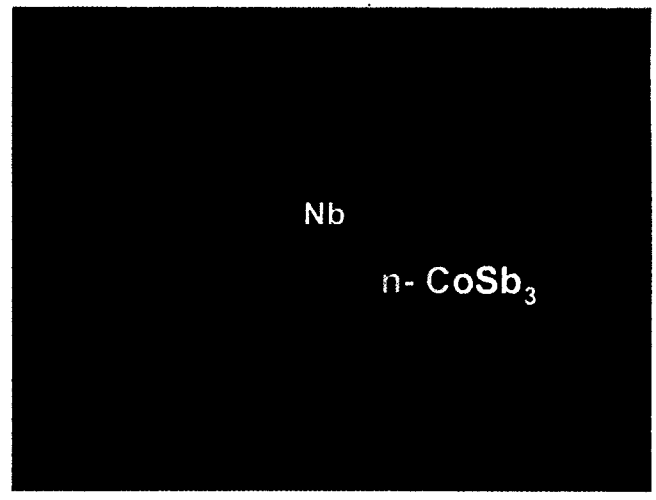
N-leg

Results for Nb

- Nb/skutterudite junctions
  - Good bond between Nb and top skutterudite segments
  - Nb density about 80 % of the theoretical density
  - No visible cracks
  - Presumably due to a better thermal expansion coefficient match
    - 7.1 x 10^{-6}/K for Nb
    - 7.5 x x 10^{-6}/K for p-$CeFe_{3.75}Co_{0.25}Sb_{12}$ and 6.36 x 10^{-6}/K for n- $CoSb_3$



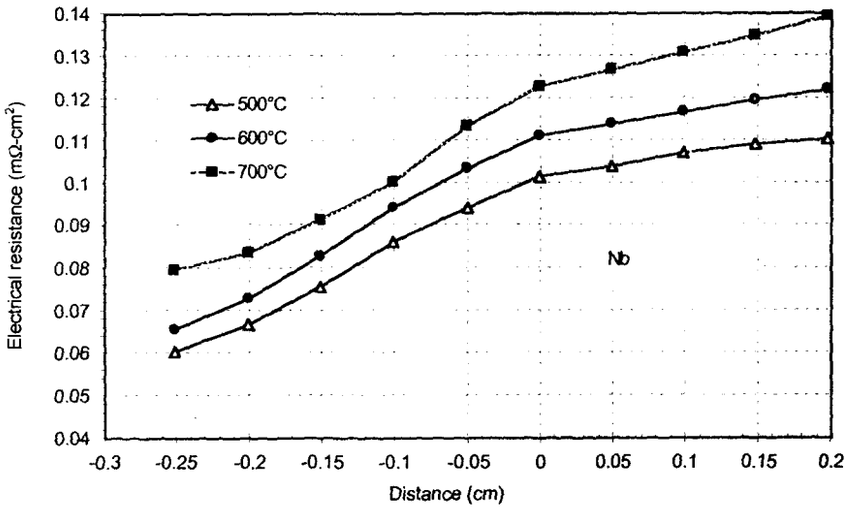
P-leg



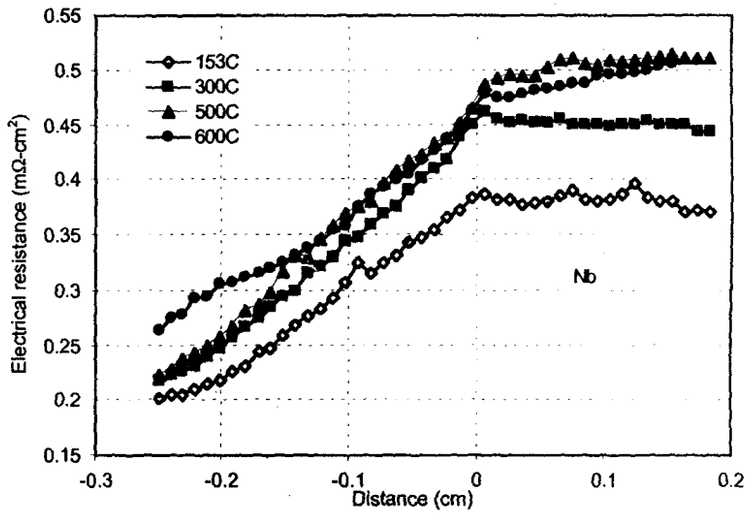
N-leg

Electrical contact resistance measurements for Nb/skutterudite junctions

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



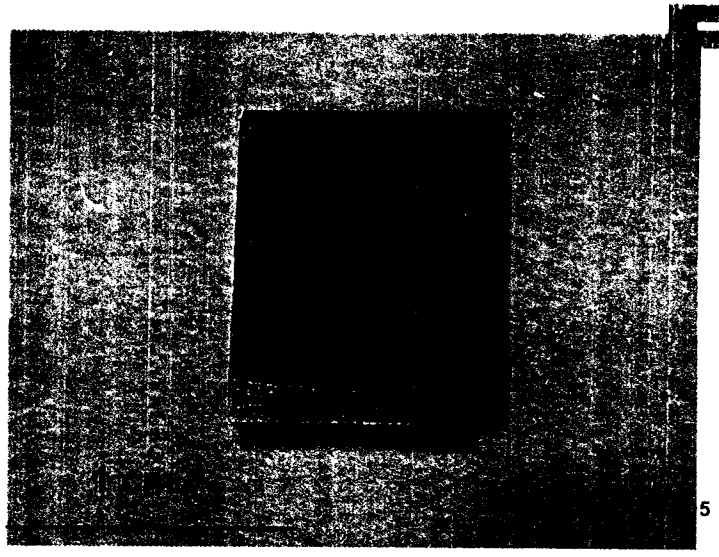
N-type

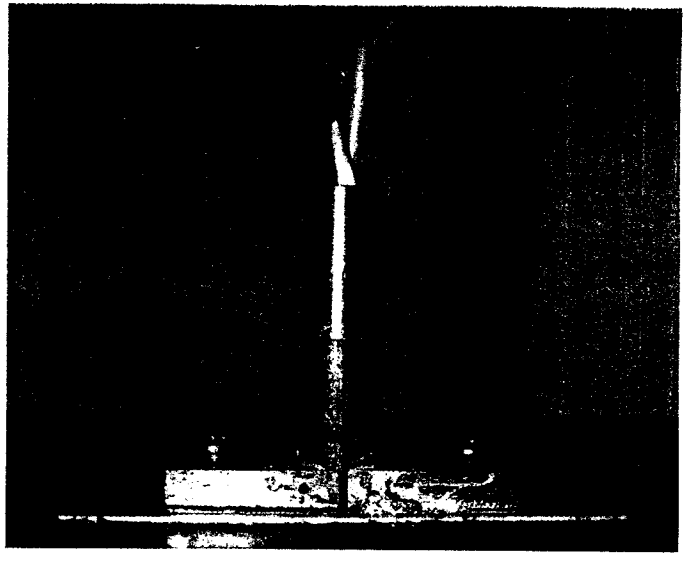


P-type

Interconnects

- Hot-shoe
  - N-and p-type legs pressed with a Nb layer on the top of the skutterudite segments
    - Low electrical contact resistance bonds (<5 $\mu\Omega.cm^2$)
  - Nb density about 80 % of the theoretical density
    - Added resistance negligible
    - ~0.4% of the total resistance for 1.5 cm long segmented legs
  - Good thermal expansion coefficient match
    - 7.1×10^{-6}/K for Nb
    - $7.5 \times \times 10^{-6}$/K for p-$CeFe_{3.75}Co_{0.25}Sb_{12}$ and 6.36×10^{-6}/K for n- $CoSb_3$
- Brazing to Nb heating element
  - Using a CuAgZnSn brazing alloy
  - Good mechanical and low electrical contact resistance bonds obtained at temperatures as low as 600°C
  - Minimal pressure contact required
- 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 using PbSn solder

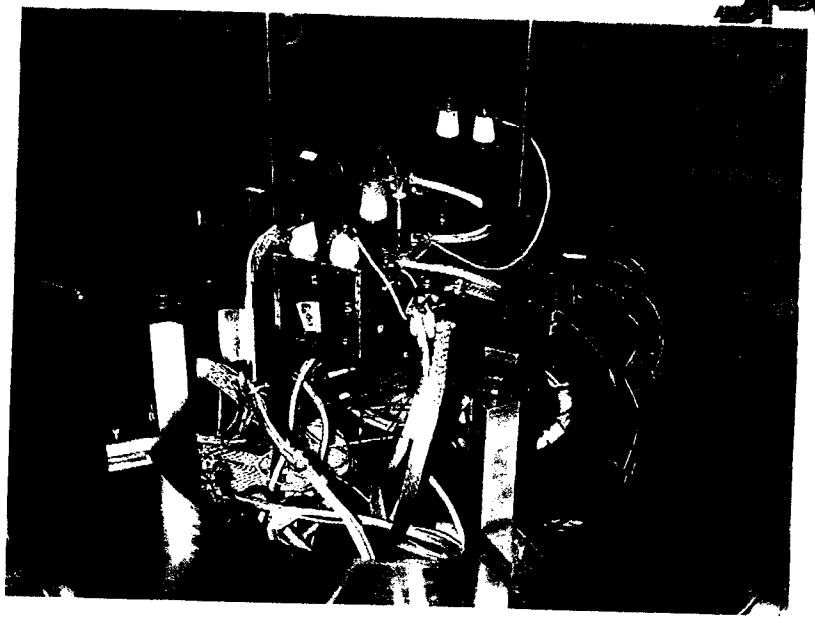


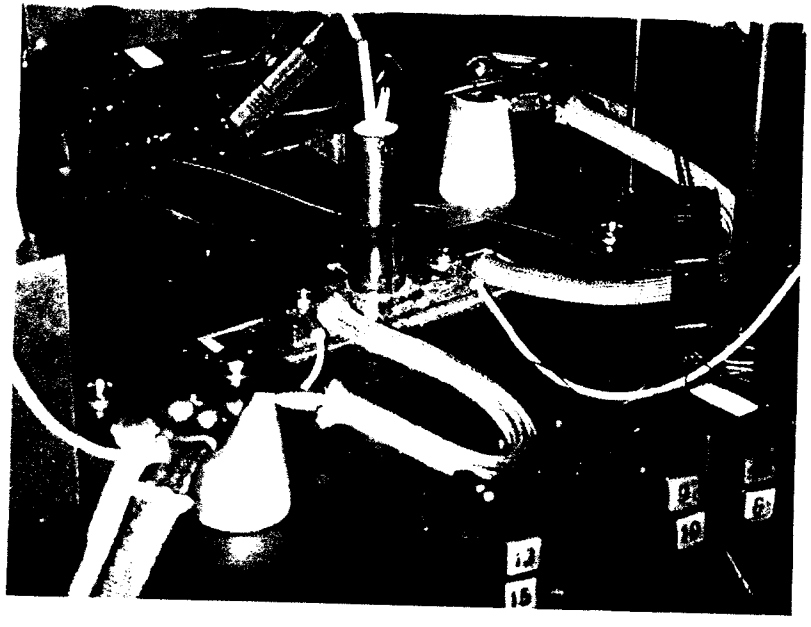


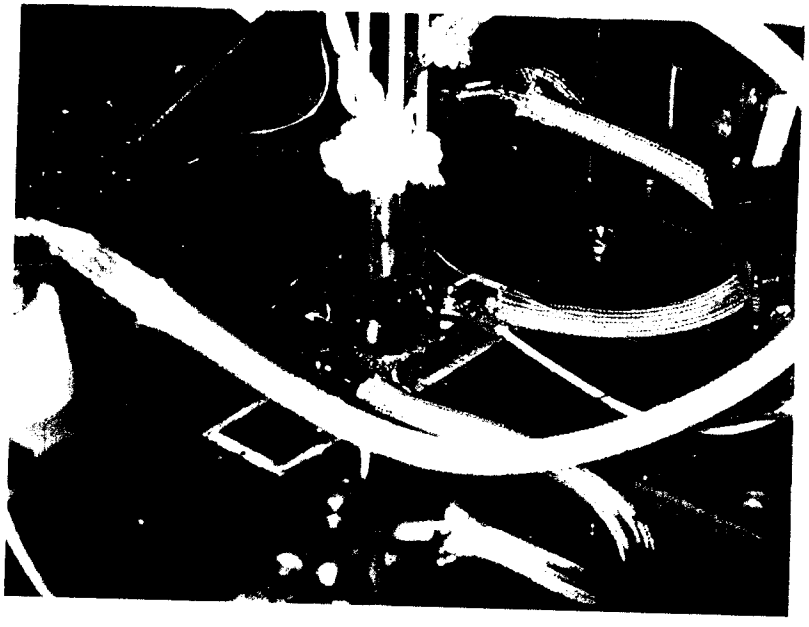
First unicouple fabricated for thermal and electrical testing

Thermal and electrical testing

- Testing Set-up
  - Vacuum (10^{-5} Torr)
  - Cu plated Al_2O_3 attached to a water cooled heat sink
  - Heat shields around the unicouple to minimize heat losses by radiation
  - Thermocouples cemented inside lower portion of the heater
    - Monitor hot-side temperature
    - Measure heat flux and estimate power input
  - Temperature measured under each leg

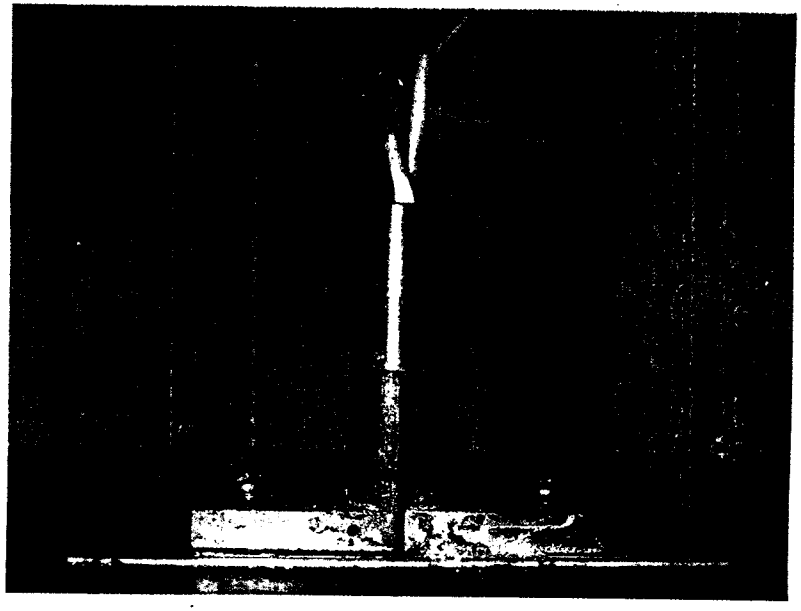






Thermal and electrical testing (continued)

- Unicouple tested for about 24 hrs
- Unicouple resistance
  - 20 mΩ vs. ~ 9 mΩ calculated & expected from experimental electrical resistivity of fabricated legs
  - Mostly due to contact resistance at the hot-side junction between the legs and the Nb heater
  - Can be improved
- Power out put
  - ~ 500 mW peak vs. 1.4 W calculated
  - Due to resistance increase at the heater/Nb interfaces
- Voltage
  - 210 mV open circuit voltage vs. 260 mV predicted
  - Slight variations in thermoelectric segment length can impact temperature profile and voltage output
  - Heat radiation losses on top of p- and n-legs can impact temperature profile in the legs

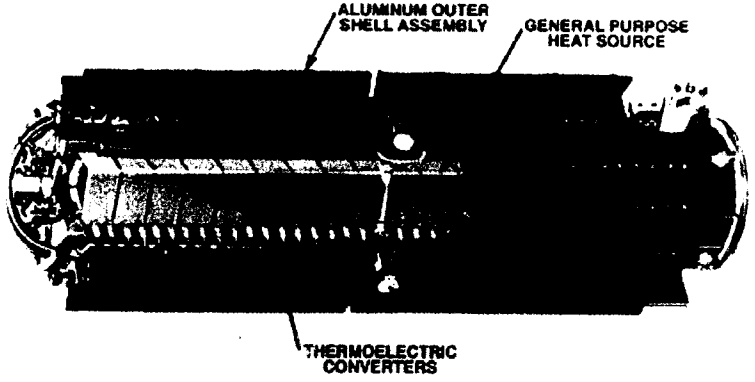


Advanced RTG (ARPS-TE)

- Incorporate advanced unicouples or multi-couples into RTGs
  - Substituting advanced unicouples or multi-couples for Si-Ge currently used
- Performance
  - Superior efficiency for TE materials
  - → Less PuO_2 required
  - → Increased specific power
- Design
  - Current GPHS-RTG unicouple design would be mostly conserved
  - MOD-RTG multi-couple design could also be considered
  - Modifications required to radiator fins to accommodate for lower rejection temperature
  - Shorter housing

General Purpose Heat Source (GPHS)

Radioisotope Thermoelectric Generator (RTG)

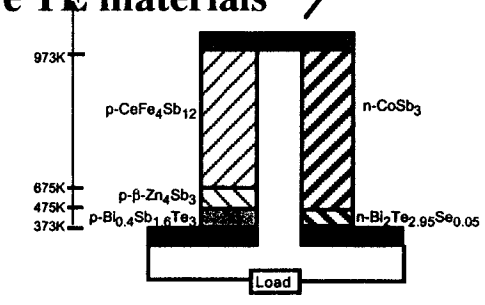
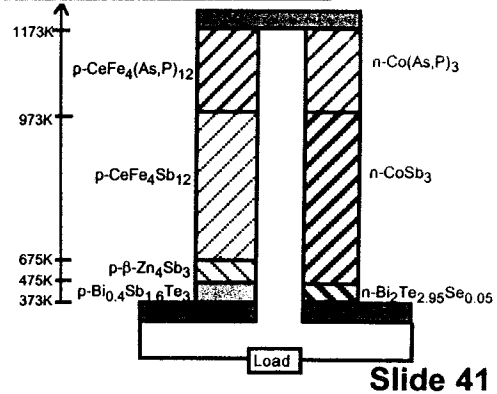


- POWER OUTPUT - 285 W(e)
- FUEL LOADING - 4400 W(t); 132,500 Ci
- WEIGHT - 124 lbs
- SIZE - 16.6 in x 44.5 in

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.

Comparison of Different Thermoelectric Conversion Technologies for 100 We RPS

Item/Converter	SiGe-RTG	Mod*-RTG	Seg.TEs	Advanced Seg. TEs*
• Hot Junction Temperature (K)	1273	1273	973	1173
• Cold Junction Temperature (K)	573	573	373	373
• Converter Efficiency (%)	6.4	7.5	11	13.3
• Total Thermal Power (BOM)(W_{th})	1750	1500	1000	750
• Total Electrical Power (BOM)(W_e)	112	112	110	100
• Number of Modules	7	6	4	3
• Total PuO_2 Fuel Mass (kg)	4.2	3.6	2.4	1.8
• Total System Mass Estimate (kg)	20.44	14.98	14.88 (11.85*)	11.16 (8.89*)
- GPHS Mass (kg)	10	8.55	5.72	4.29
- Housing (kg)	2.64	2.04	1.95 (1.46*)	1.46 (1.10*)
- Radiator fins (kg)	0.38	0.3	1.2	0.90
- Converter (kg)	5.44	2.8	3.66 (1.95*)	2.75 (1.46*)
- Other structure (kg)	1.98	1.3	2.34 (1.52*)	1.76 (1.14*)
• Specific Power Estimate (We/kg)	5.46	7.48	7.39 (9.28*)	8.96 (11.25*)

* Using advanced modular TE multi-couples technology.

* Incorporating advanced, higher temperature TE materials