Advanced High-Temperature Thermoelectric Devices

DOE Thermoelectric Applications Workshop
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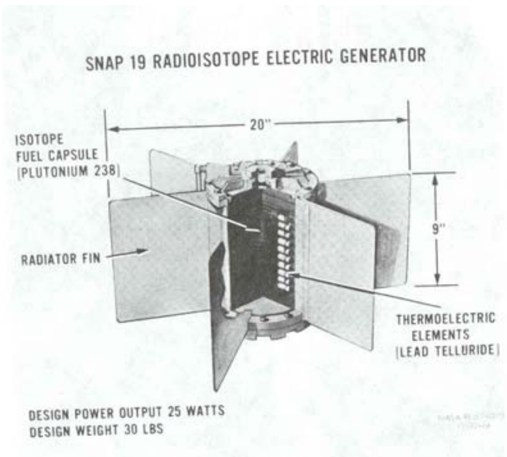
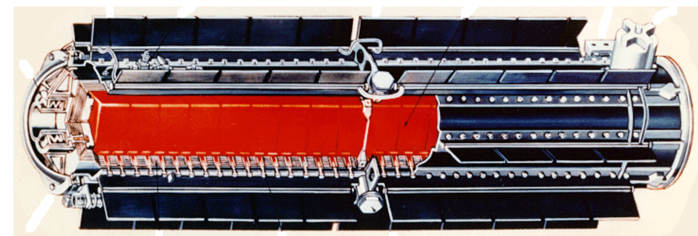
Flight Demonstrated Radioisotope Thermoelectric Generators
(3 Most Recently Flown Designs)

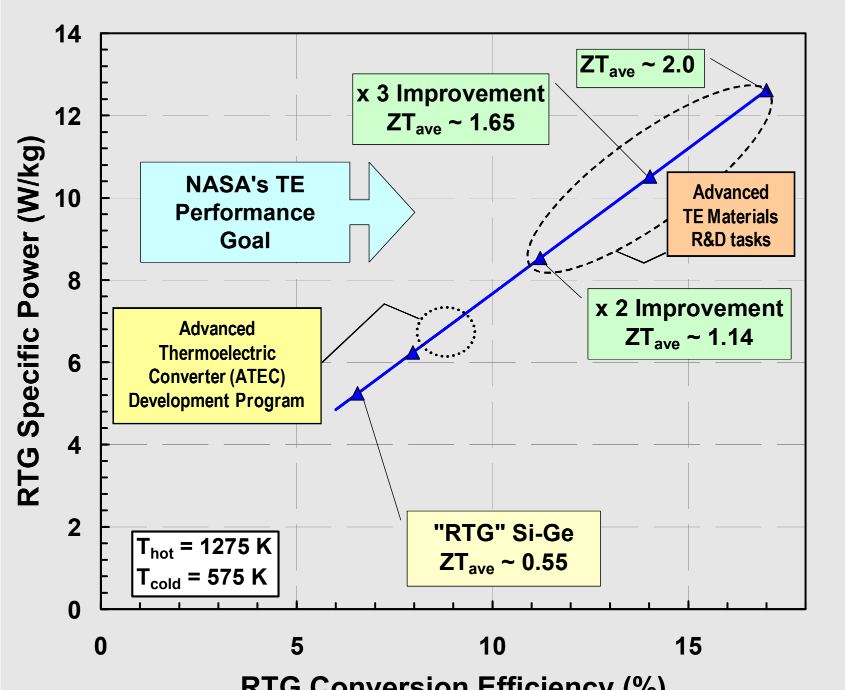




SNAP-19 (PbTe/TAGS RTG) (1960-70's)	SiGe MHW RTG (1970's)	SiGe GPHS RTG (1980-2006)
40.3 Watts (BOM)	158 We (BOM)	285 We (BOM)
6.2 % system efficiency	6.6 % system efficiency	6.8% system efficiency
3 We/kg	4.2 We/kg	5.1 We/kg
22.86 cm (9.0 in) long	58.4 cm (23 in) long	114 cm (44.9 in) long
50.8 cm (20 in) dia	39.7 cm (15.64 in) dia	42.7cm (16.8in) dia
~13 kg (28.6 lb)	38 kg (83.7lb)	56 kg (123 lb)
PbTe Thermoelectrics	SiGe Thermoelectrics	SiGe Thermoelectrics
T_H= 525C, T_C=210C	T_H= 1000C, T_C=300C	T_H= 1000C, T_C=300C
Nimbus B-1/III, Pioneer 10/11, Viking 1/2	LES 8/9, Voyager 1/2	Galileo, Ulysses, Cassini & New Horizons

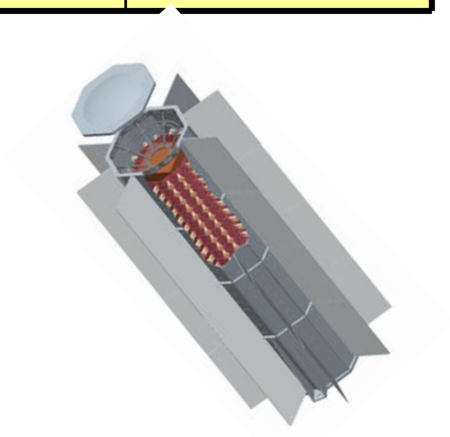
NASA Advanced RTG Needs

	Near Term	Long Term
Specific Power (W/kg)	6 - 8	> 10
Readiness	2015 - 2016	> 2020
Lifetime	> 14 years < 22% degradation	> 14 years < 22% degradation
Heat Source	Step 2 GPHS (8 to 12 units)	Step 2 GPHS (8 to 12 units)
System Efficiency (%)	8-10	13 - 15



Advanced RTG Specific Power vs. System Conversion Efficiency
(Based on radiatively coupled vacuum operation unicouple based RTG concept)

- **Advanced RTGs**
  - Require use of advanced TE materials to achieve higher efficiency
  - Advanced design to minimize electrical and thermal losses



ARTG Conceptual Design

For Planning and Discussion Purposes Only

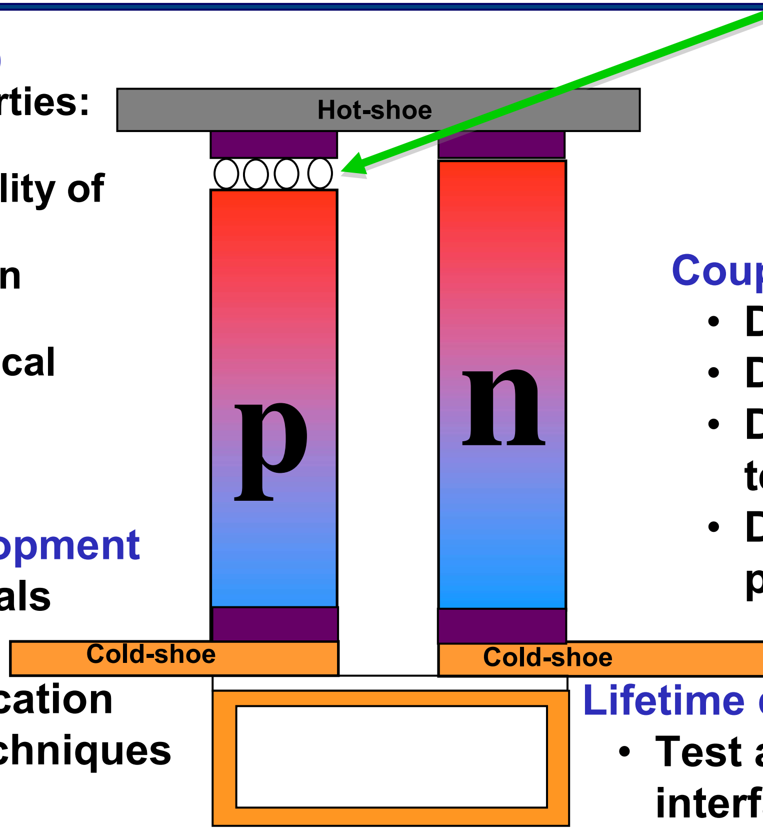
Advanced Couple Key Technology Development Elements

TE materials (n- and p-)

- Establish TE properties: ZT
- Establish repeatability of TE properties
- Develop sublimation control
- Determine mechanical properties

Bonds and legs development

- Develop TE materials metallization
- Develop legs fabrication and processing techniques
- Develop low electrical contact resistance bonds between the couple components
- Demonstrate mechanical and chemical stability at operating temperatures



Transition piece
(as required - to mitigate CTE mismatch between n- and p-legs)

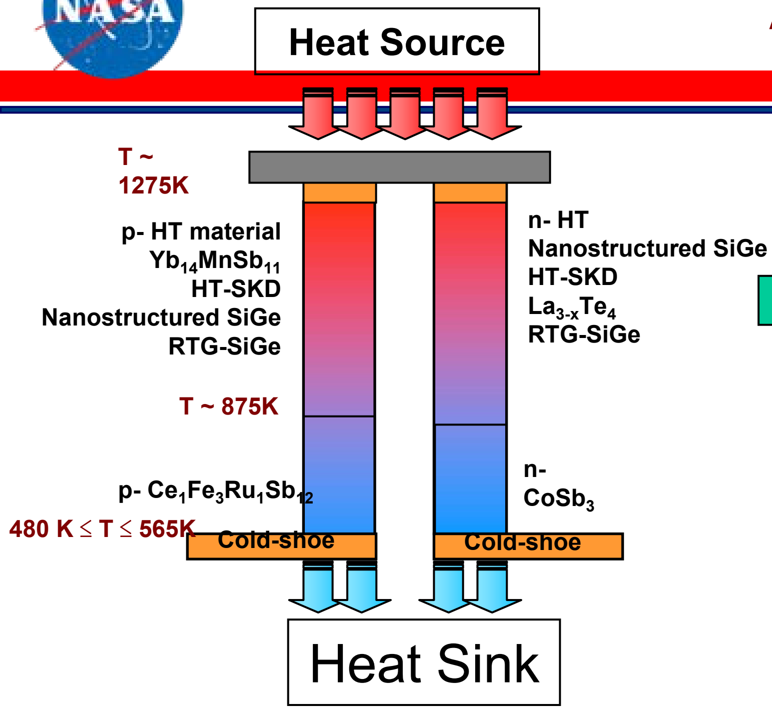
Couple assembly and testing

- Develop assembly procedure
- Develop tooling
- Develop couple performance test fixture
- Demonstrate BOL couple performance

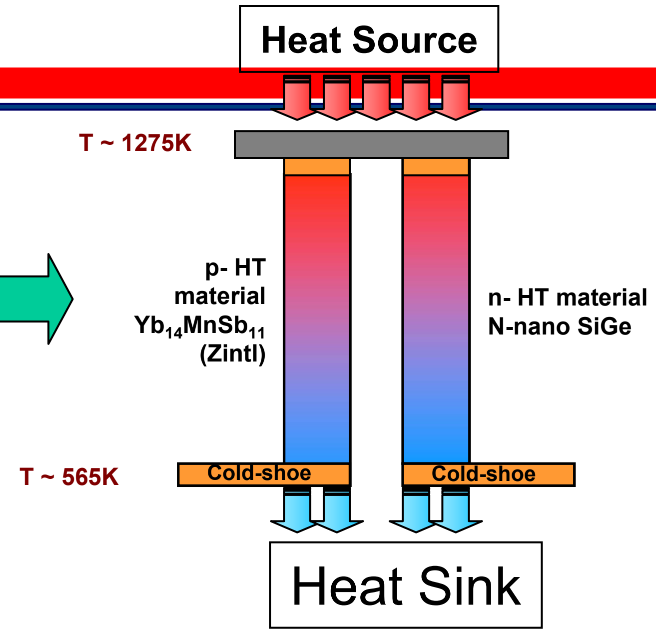
Lifetime demonstration

- Test and demonstrate couple interface mechanical and chemical stability
- Demonstrate sublimation control efficacy over time
- Establish TE properties change over time
- Establish couple performance change

TE Materials Selection for 1st Generation ATEC Couples



Selected p-type $Yb_{14}MnSb_{11}$(Zintl) and n-type nano SiGe as a baseline for couple development



- **Baseline**
  - **P-type $Yb_{14}MnSb_{11}$ (Zintl)**
  - **N-type nanostructured SiGe**

- **Alternate**
  - **P-Zintl**
  - **N-type $La_{3-x}Te_4$**

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TE materials synthesis

- Approach
  - Ball milling
    - Planetary ball mill
    - End product: powder
    - Scalable technique (100-250 g batches) (kilograms of TE materials can be synthesized per week)
  - Hot-pressing of powder into pucks

N-SiGe pucks

- Applied to Zintl, skutterudites and n- and p-type nanostructured SiGe

N-SiGe legs

Zintl leg

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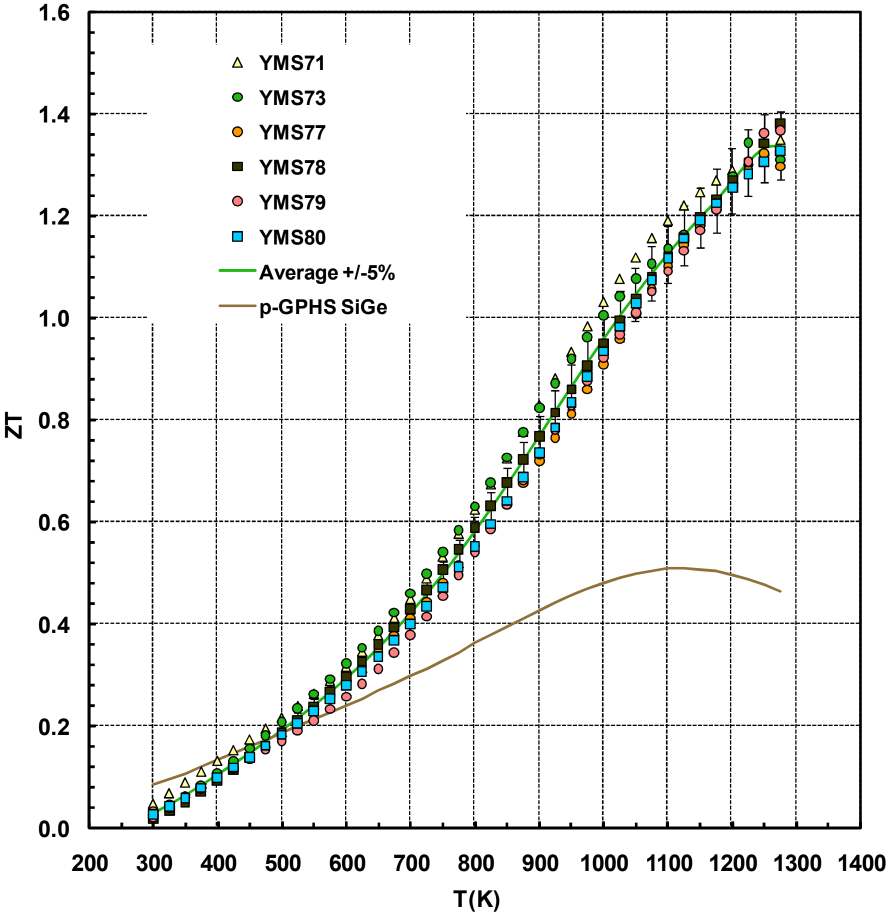
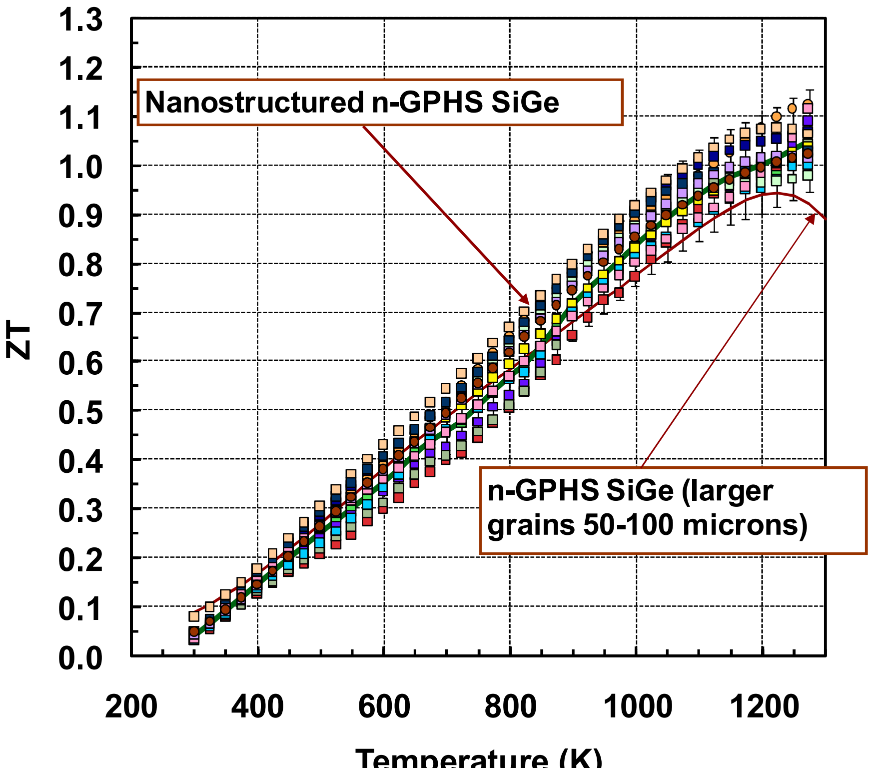
ZT



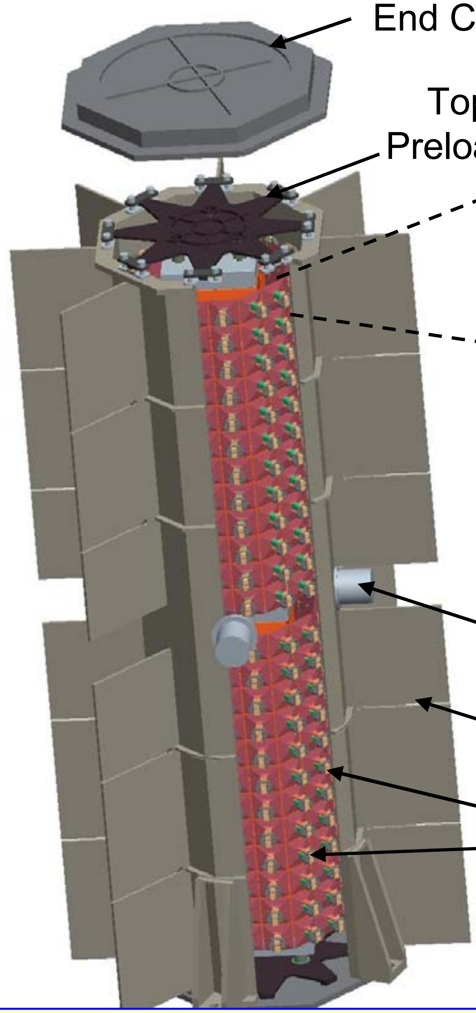
P-$Yb_{14}MnSb_{11}$



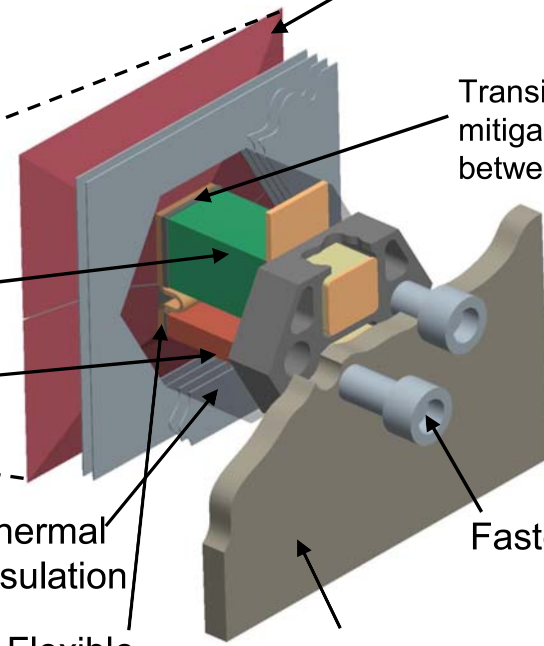
N-nanostructured SiGe

- Demonstrated batch-to-batch reproducibility

ARTG System Design - Overall Layout (Isometric View)



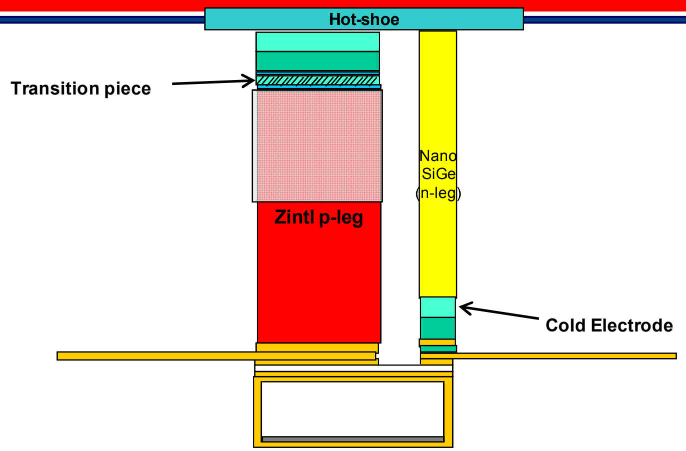
ARTG conceptual design



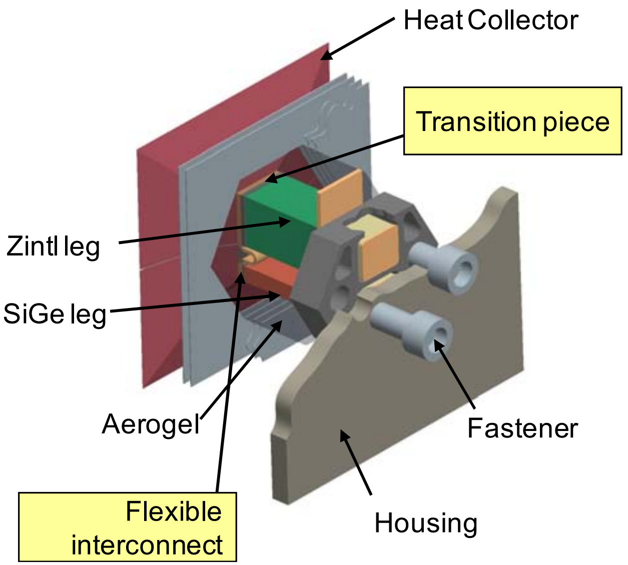
ATEC couple conceptual design

- **Developed ARTG design**
- **Evaluated several couple designs**
- **May use a transition piece and a flexible interconnect that allows for combining TE materials with different coefficient of thermal expansion**
  - **Zintl CTE ~ 18.0 ppm**
  - **SiGe CTE ~ 4.1 ppm**

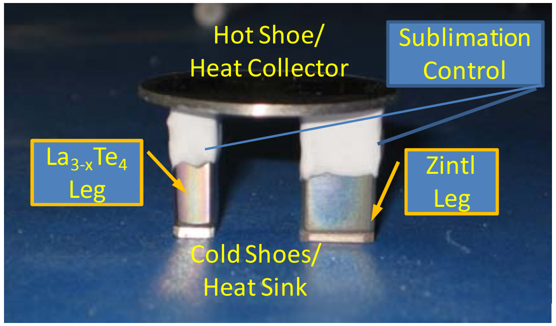
Couple Configurations in Development



Baseline ATEC Zintl/NanoSiGe Couple

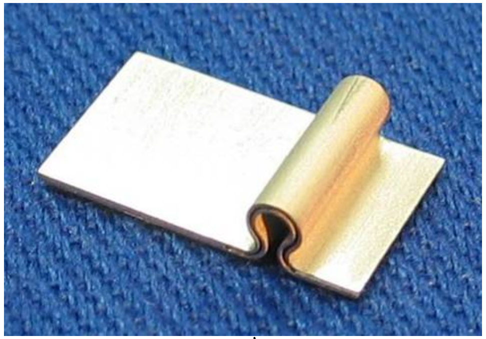


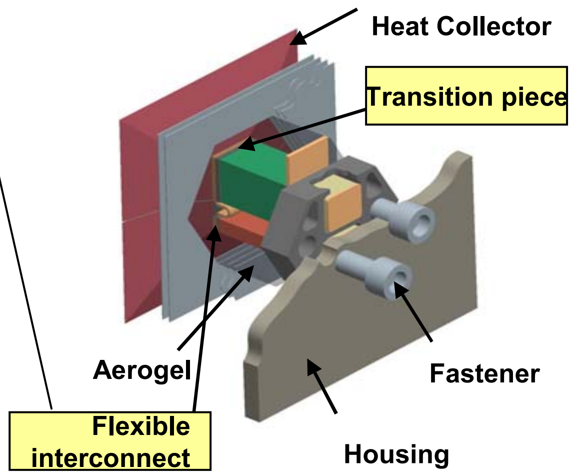
Alternate Baseline ATEC Zintl/NanoSiGe Couple

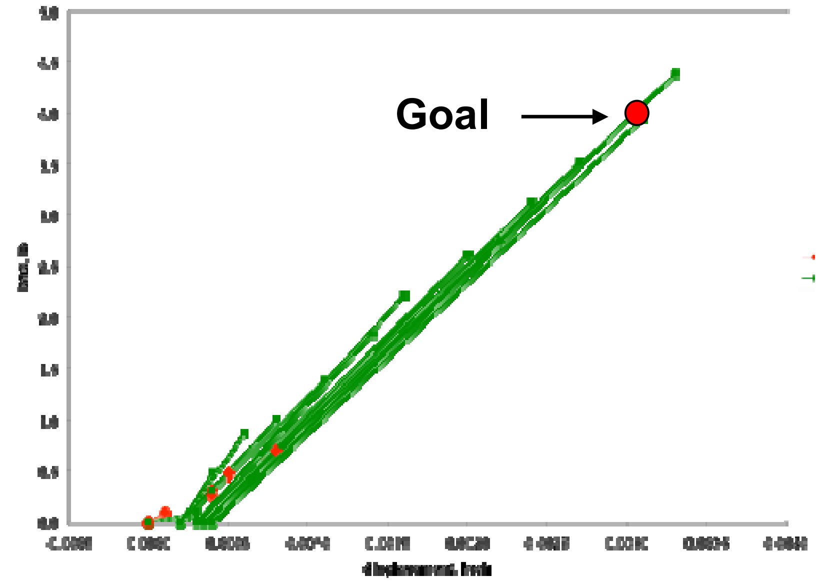


JPL Advanced Zintl/$La_{3-x}Te_4$ Couple

Couple Development - Components for Reliable Thermal/Mechanical Integration



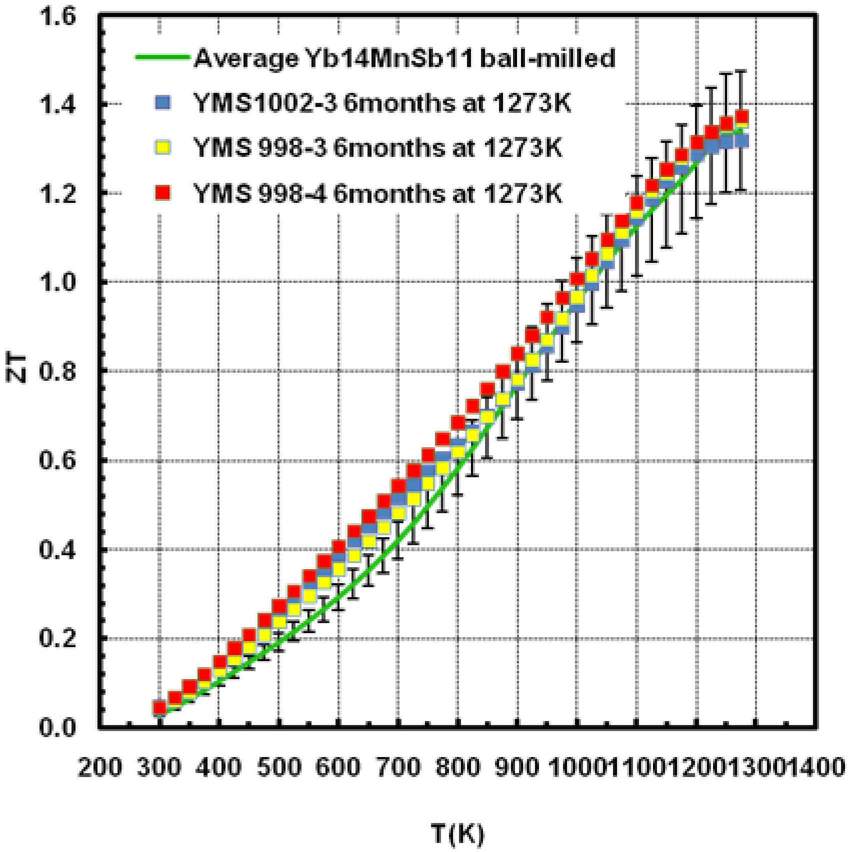


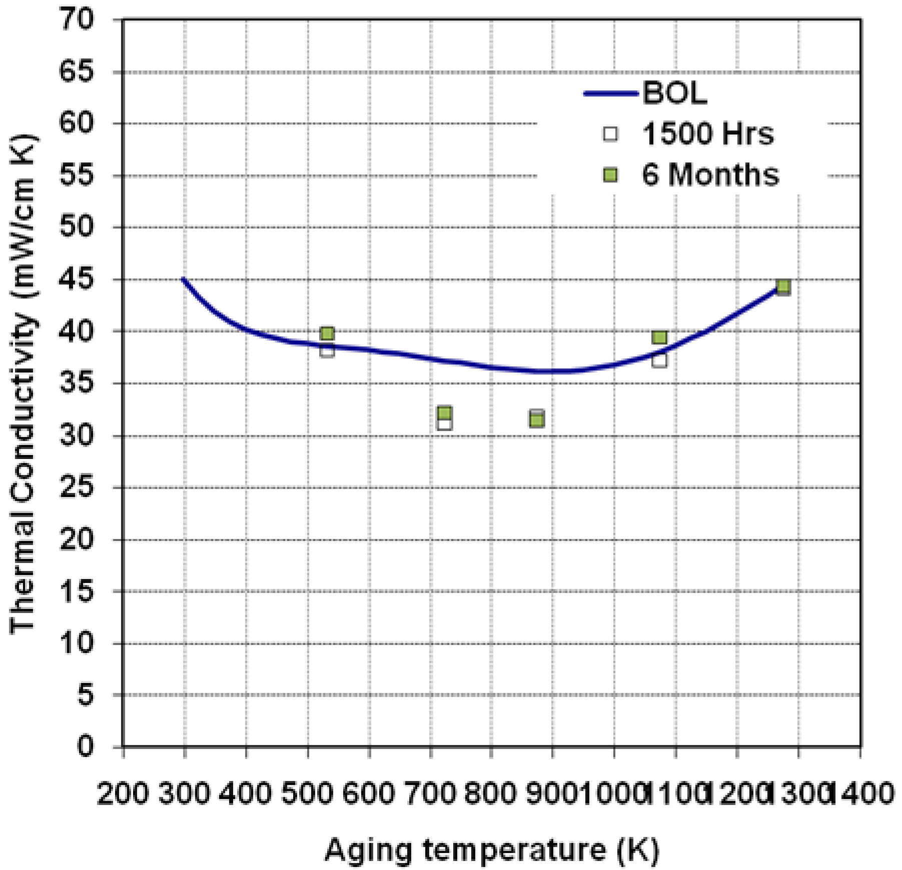


Load-displacement test data validating that the transition piece meets functionality requirements

Successfully developed flexible interconnect and transition piece that are key components for integrating TE materials with different coefficient of thermal expansion such as Zintl and nanostructured SiGe

Lifetime Validation - TE properties

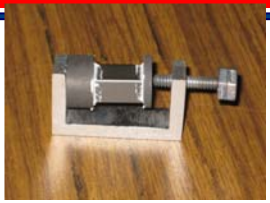




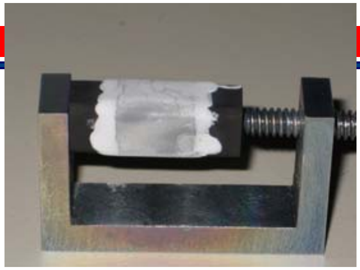
Demonstrated stability of TE properties for Zintl and nanostructured SiGe up to 1273K for ≥ 6 months

→ Enables couple-level lifetime demonstration

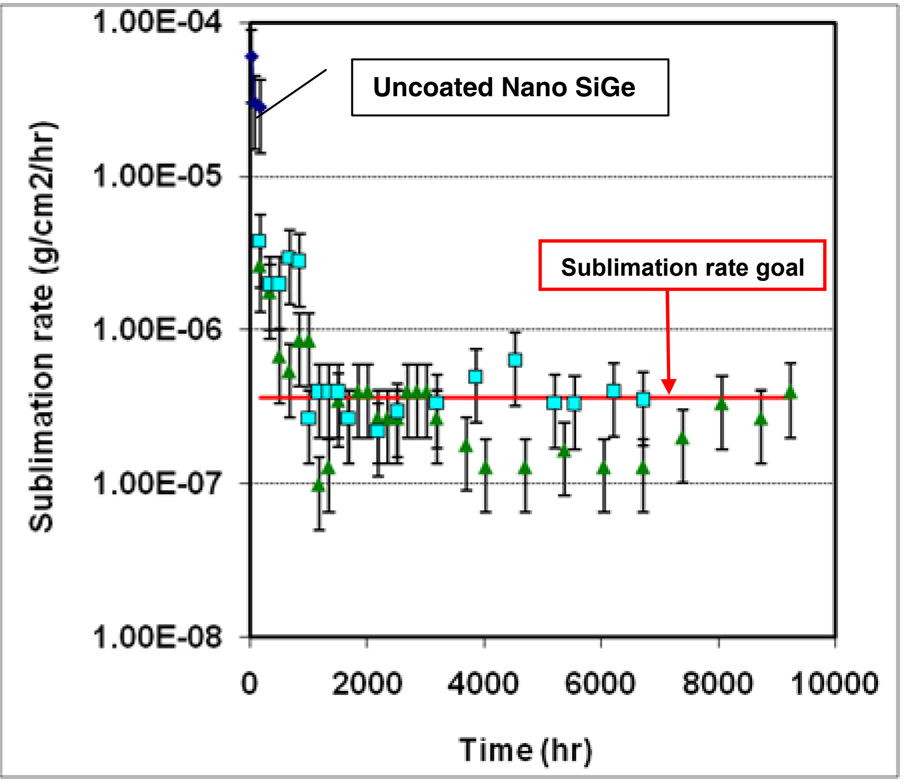
TE materials - Sublimation Rate Life Testing

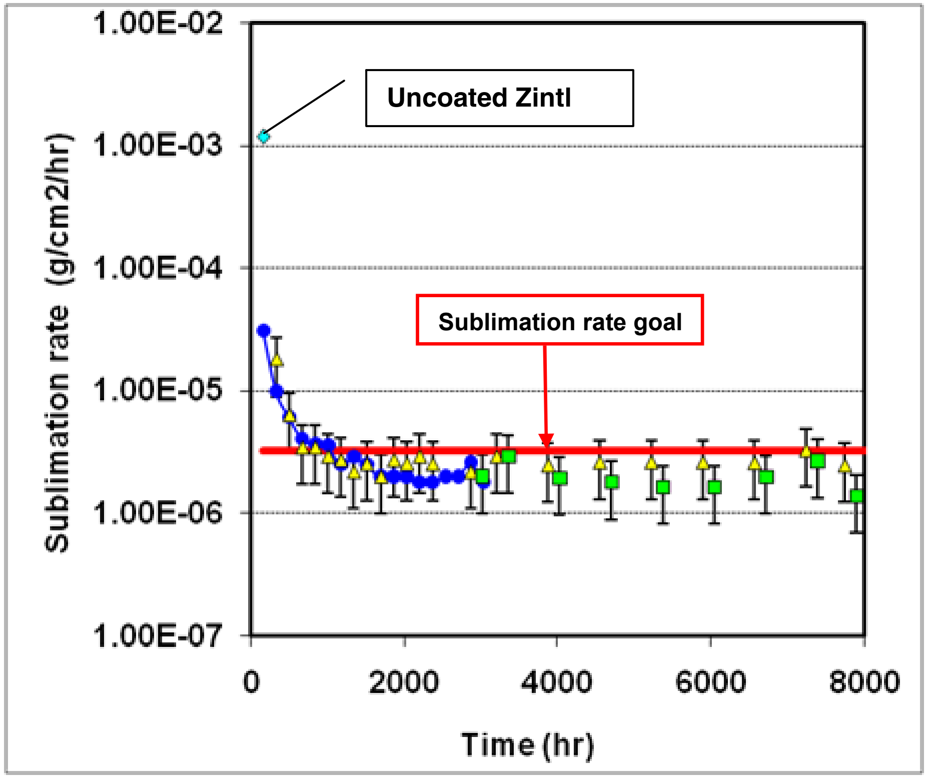


Coated Nano SiGe coupon coated after 9000 hrs of testing at 1273K



Coated Zintl coupon coated after 7000 hrs of testing at 1273K





Successfully developed coatings to control sublimation of Zintl and Nano SiGe materials <u>to the desired rates for a 14 year operation</u>

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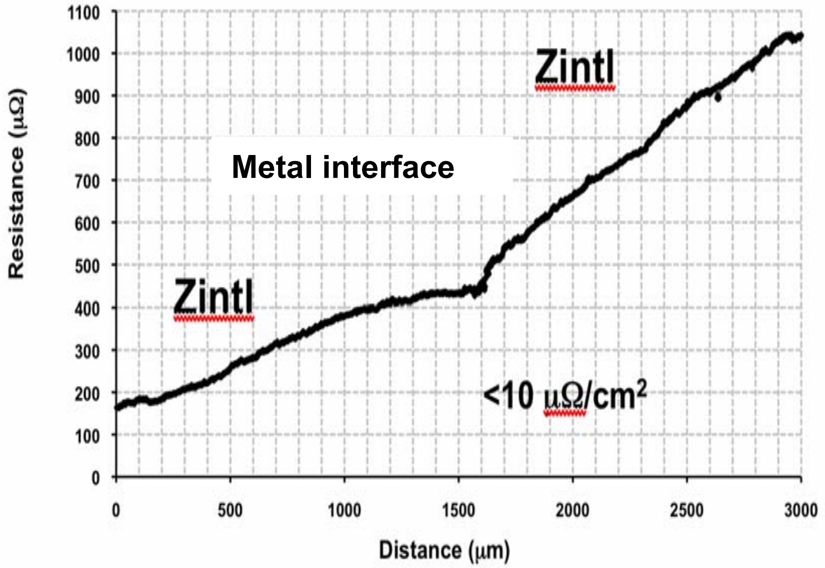
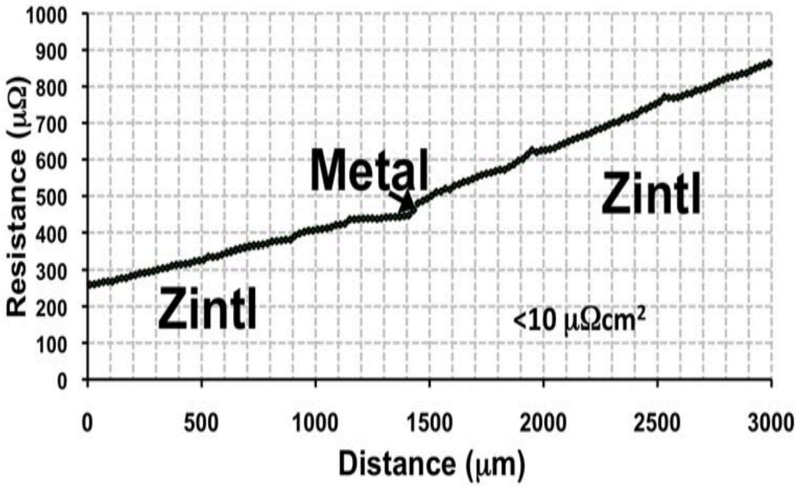
Couple Development – Stable Zintl metallization



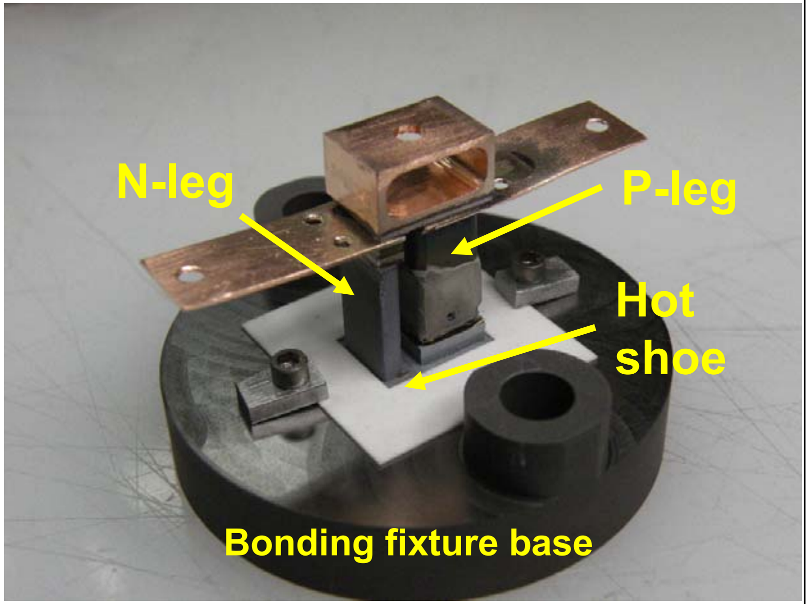
After aging for 1500 hrs at 1273 K

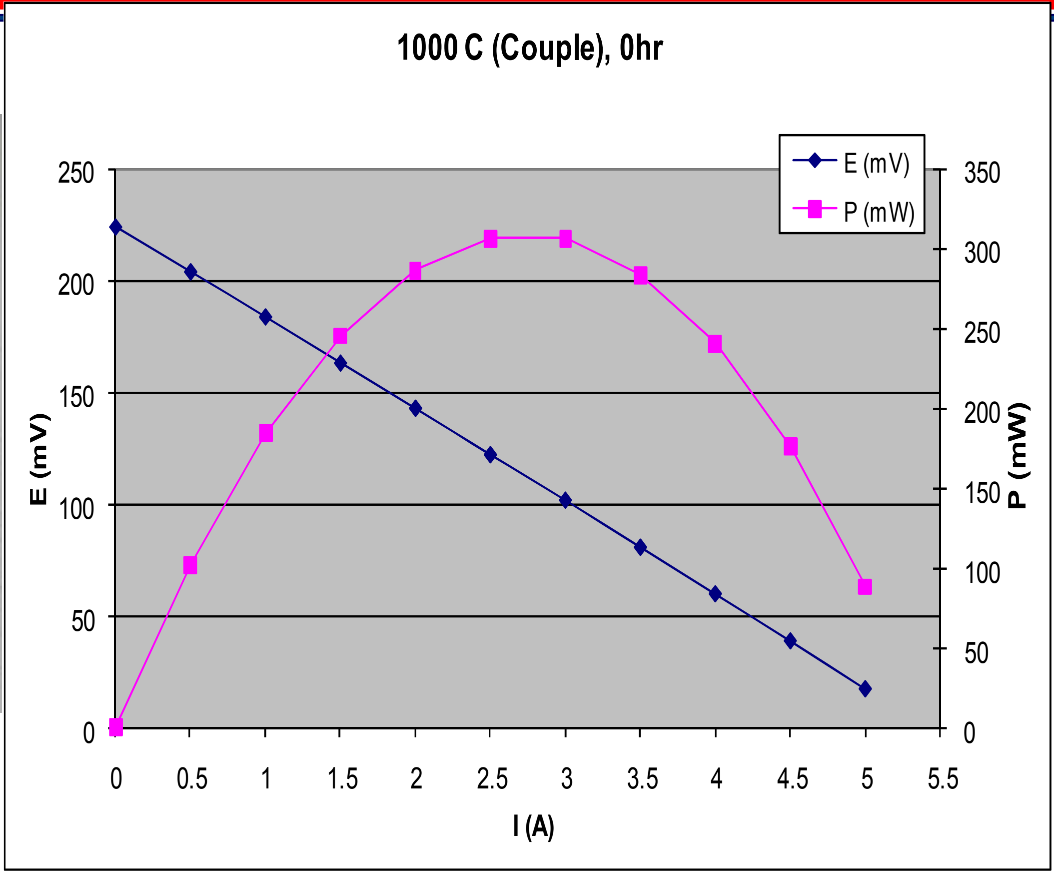


Metallized p-type $Yb_{14}MnSb_{11}$ (Zintl) leg

- Developed a metallization for Zintl and demonstrated stability of metallization for up to 1500hrs at 1273K
- Meets the goal of 25 μΩ-cm² or less for the interface electrical contact resistance

ATEC Baseline Couple Assembly

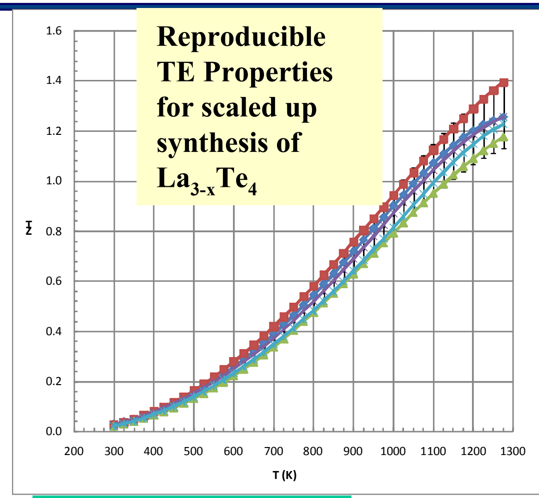


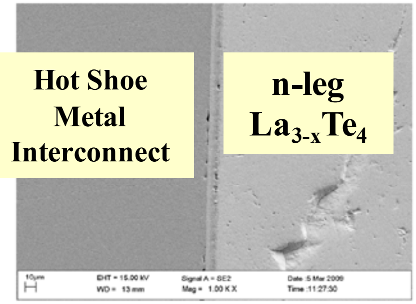


- Prototype couple assembly completed
- Employs a low modulus transition piece
- Minimize thermal stresses due to CTE mismatch between n and p-type legs

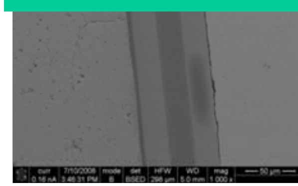
Zintl/$La_{3-x}Te_4$ Couple Development

- **Developed reproducible synthesis process for $La_{3-x}Te_4$**
  - Used ATEC process for Zintl
- **Developed low resistance thermally stable metallizations**
- **Built "Short" Couples**
  - Used for demonstrating bonding processes, couple assembly and mechanical compliance of high CTE components:
    - Negligible contact resistances
    - Survived several thermal cycles
- **"Tall" couples fabricated to operate across large temperature differential**
  - Conductively coupled configuration for short term testing
- **Initiated development of segmented legs for 2nd generation couple**
  - n-type $CoSb_3$/$La_{3-x}Te_4$ leg

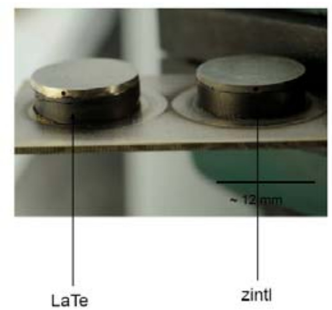


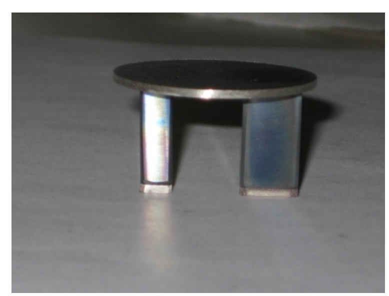


La$_{3-x}$Te$_4$ / metal/ Zintl Mechanically Strong Diffusion Bond



"Short" Zintl/$La_{3-x}Te_4$ couples





"Tall" Zintl/$La_{3-x}Te_4$ couple for conductive coupling to heat source

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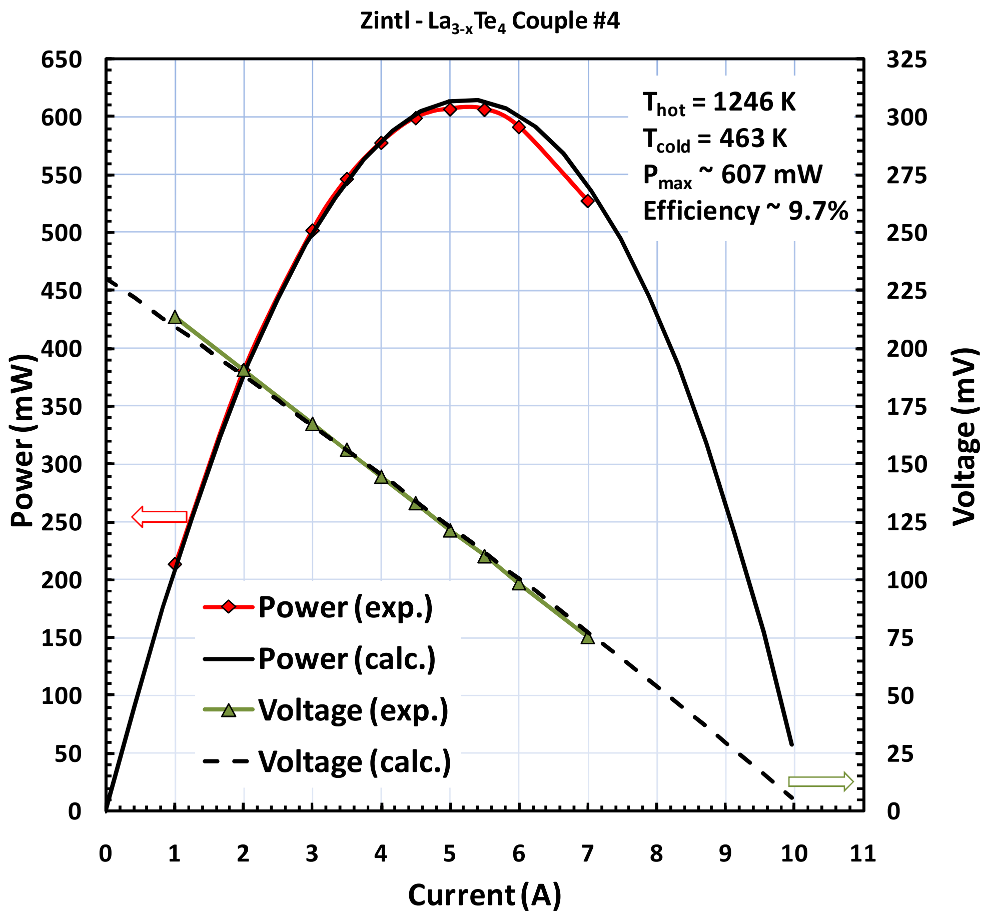
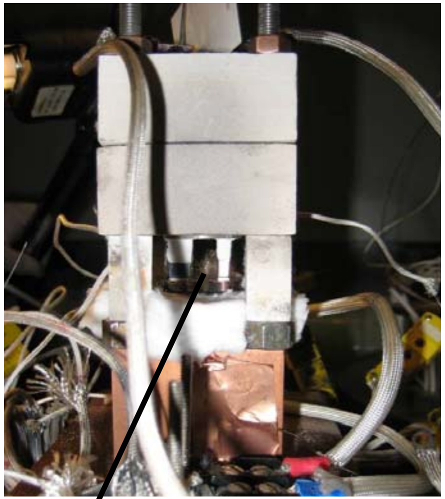
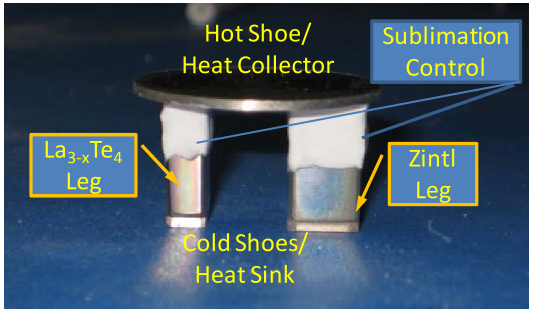
Advanced TE Couple Performance
(p-$Yb_{14}Mn Sb_{11}$ Zintl/n-$La_{3-x}Te_4$)

- *Performance within 3% of predictions (based on measured TE materials properties)*
  - *~ 30% better than "Heritage RTG" $Si_{0.8}Ge_{0.2}$ unicouple for same 700 K ΔT*
- *Achieved ~ 10% efficiency for 750 K ΔT*







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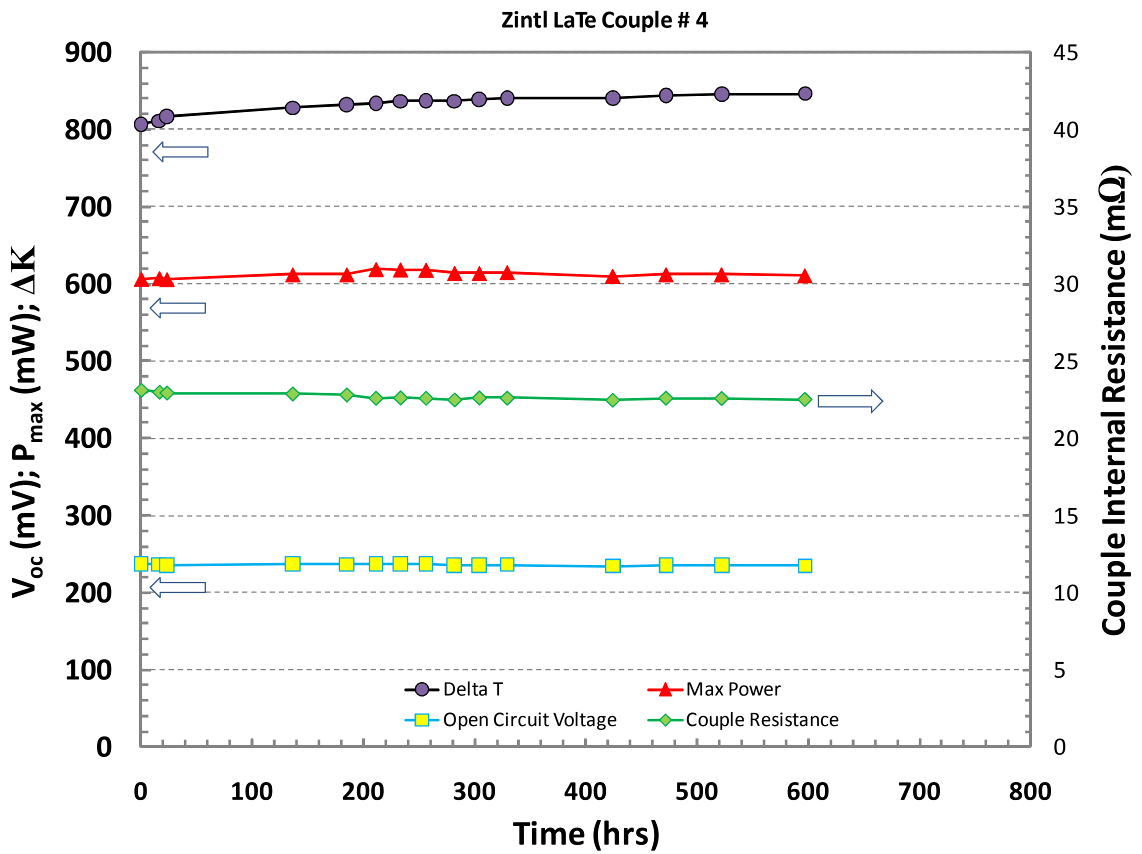
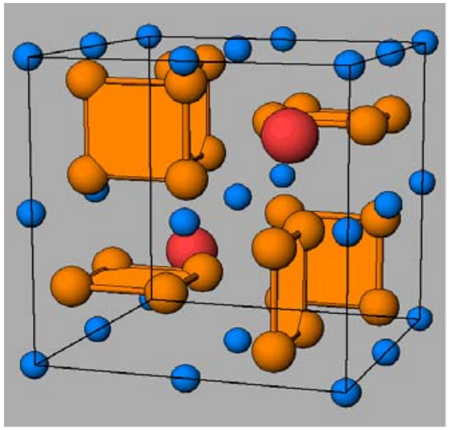
Advanced $Yb_{14}MnSb_{11}/La_{3-x}Te_4$ Couple – Life tests

- **Extended testing of spring loaded couples:**
  - Very stable performance for first 600 hours
    - Validates TE properties of Zintl and $La_{3-x}Te_4$ and their stability during in-gradient testing
    - Operated across ΔT as large as 850 K
  - Extended tests under way
    - Up to 1600 hours so far

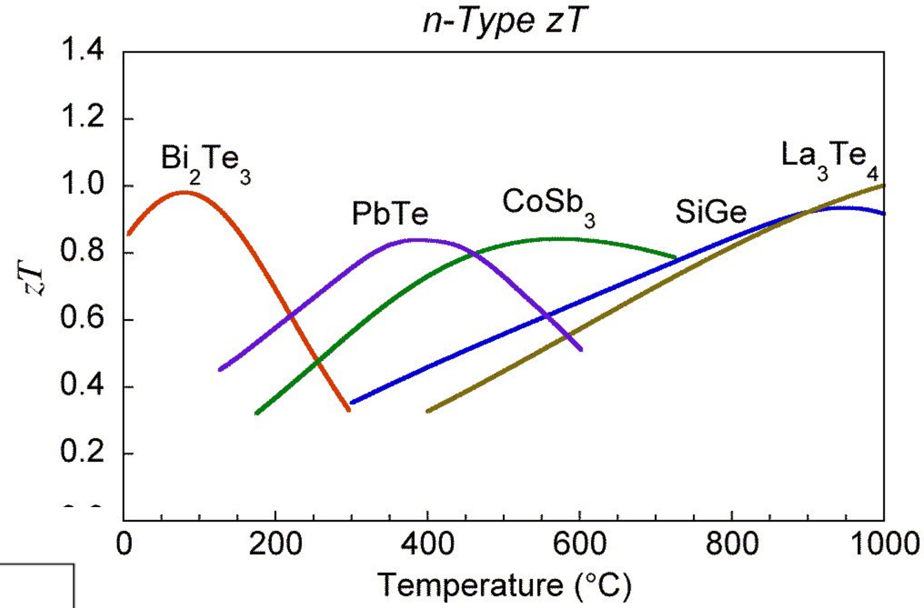
    (For RTG development >10,0000 hours of testing required)

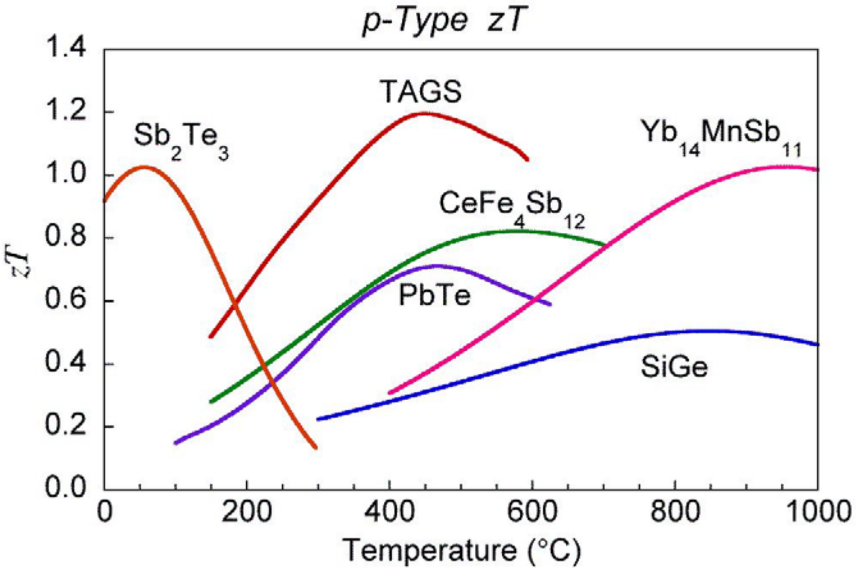


Skutterudites



Skutterudite crystal structure



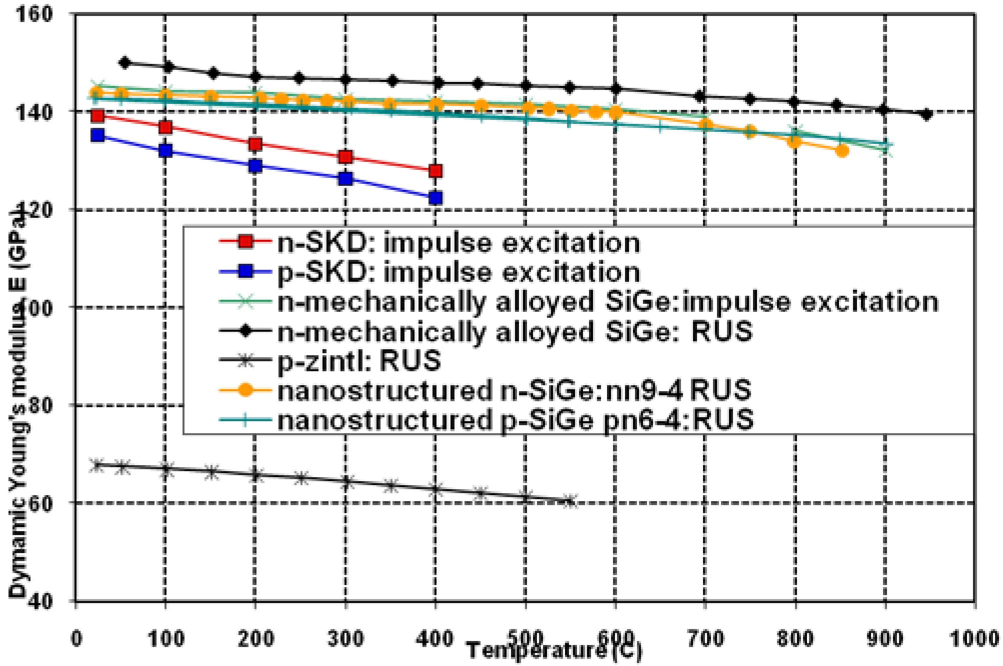


Skutterudite materials have relatively high TE efficiency in the 300-600C temperature range

Mechanical Properties

	Melting or Decomposition temperature (C)	Density (g/cm^3)	Dynamic Young's Modulus, E (GPa)	Dynamic Shear Modulus, G (GPa)	Poisson's Ratio	Modulus in Compression (GPa)	Compressive Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Fracture Toughness (MPa √m)	Average CTE (ppm/K)
P-SKD	825	7.92	133	54	0.22 – 0.29	115	657	~ 93	~ 37	~ 2.9 *	14.5 (200 – 600ºC)
N-SKD	876	7.61	136	60	~ 0.14 * 0.25***	92	766	~ 102	~ 86	1.6 *	12.2 (200 – 600º C)

* Preliminary Data   ** Estimated (not measured)   *** Calculated from speed of sound data



Skutterudite mechanical properties are acceptable for device integration

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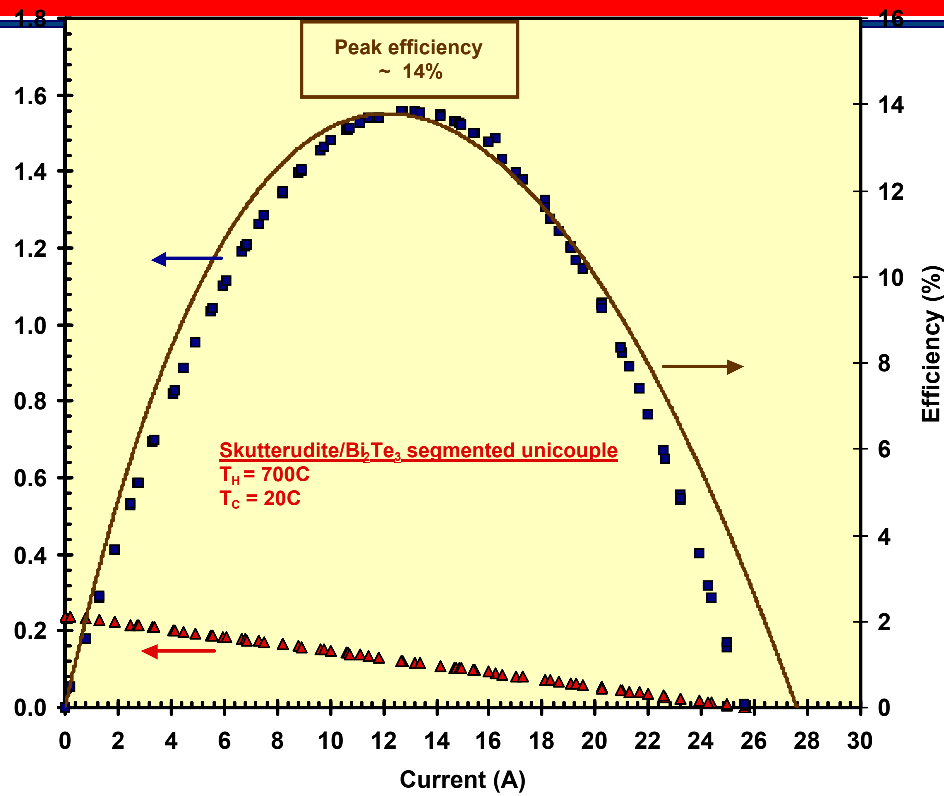
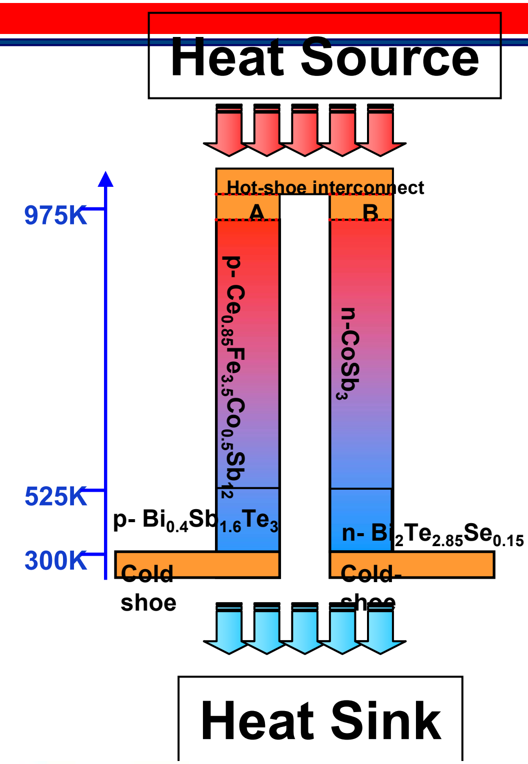
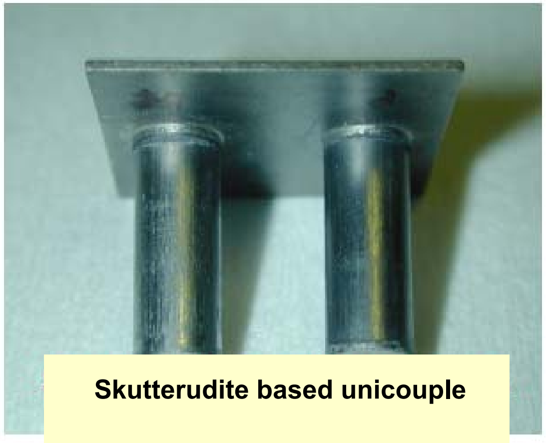
Skutterudite-based Segmented Unicouple Development at JPL





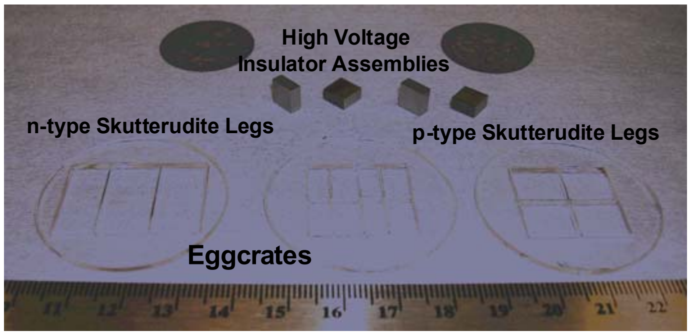


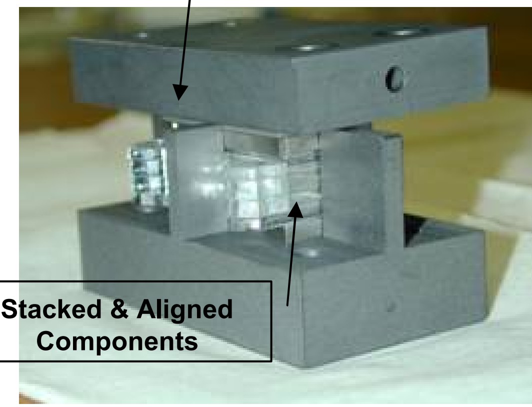
Skutterudite based unicouple

- **Skutterudites are among the few new materials developed since 1991 to have been integrated into unicouples**
- **Experimental I-P curves fully validated projected performance**
  - ~ 14% efficiency for 975K-300K ΔT
- **Results independently confirmed at the University of New Mexico**

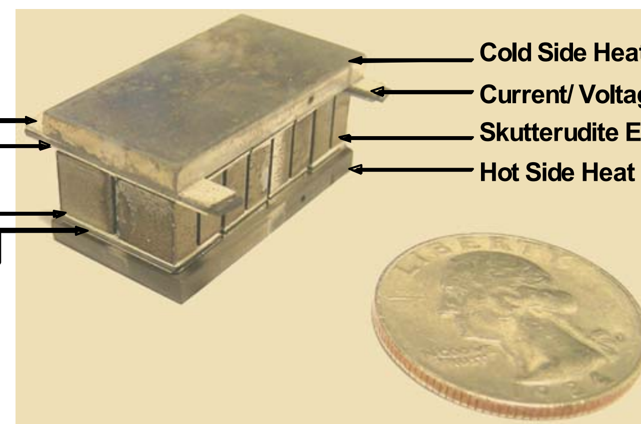
Assembly of Skutterudite TE Modules

Individual Module Component Technologies



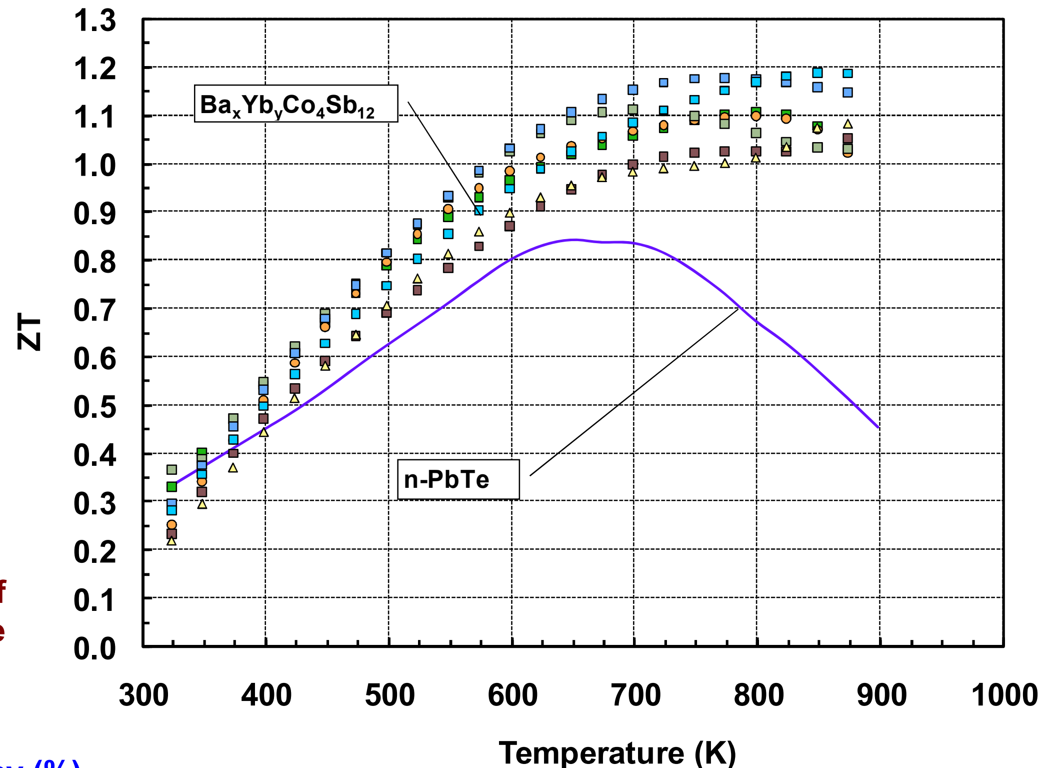


Assembled 2x4 Module after bonding cycle and egg-crate vaporized



$Ba_xYb_yCo_4Sb_{12}$: ZT

- **Ball milled $Ba_xYb_yCo_4Sb_{12}$**
  - ZT_{max} ~ 1.2 at 873K (consistent with previous reports)
  - ~ 40% improvement in ZT over n-type PbTe in the 873K-373K temperature range



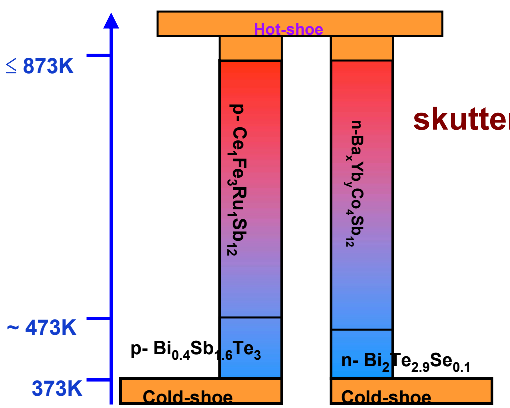


Illustration of skutterudite-Bi_2Te_3 couple

Couple efficiency (%)

	T_H= 873K - T_C= 373K	T_H= 773K - T_C= 373K	T_H= 673K - T_C= 373K
With Bi_2Te_3 segments	11.8	10.0	7.9
Without Bi_2Te_3 segments	10.7	8.8	6.8

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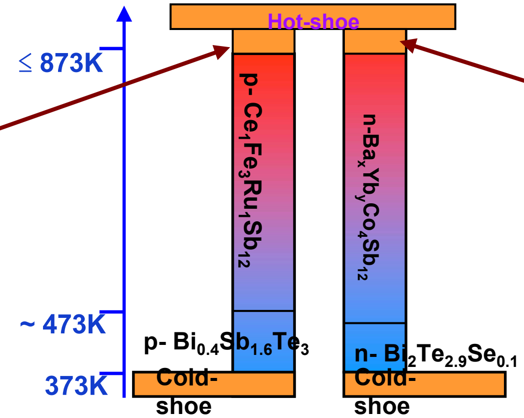
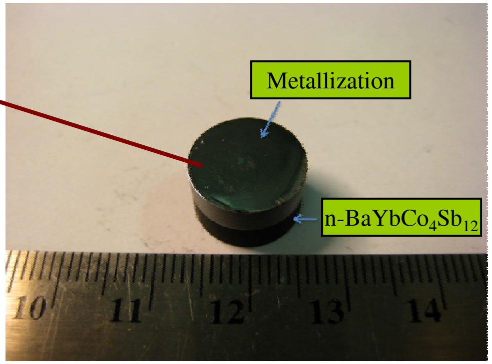
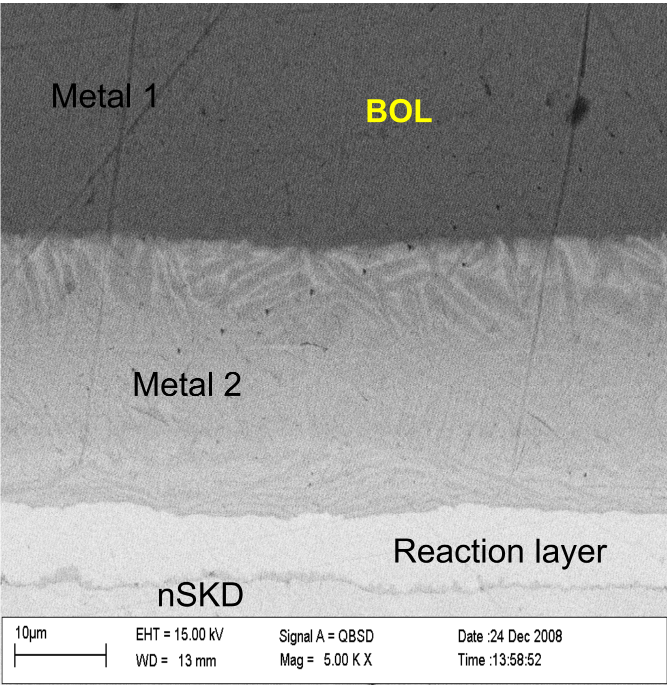
Metallization

- **Challenge: develop a chemically and mechanically stable metallization for operation up to ~ 600C**
- **JPL's experience is that Ti-based metallization do not work**

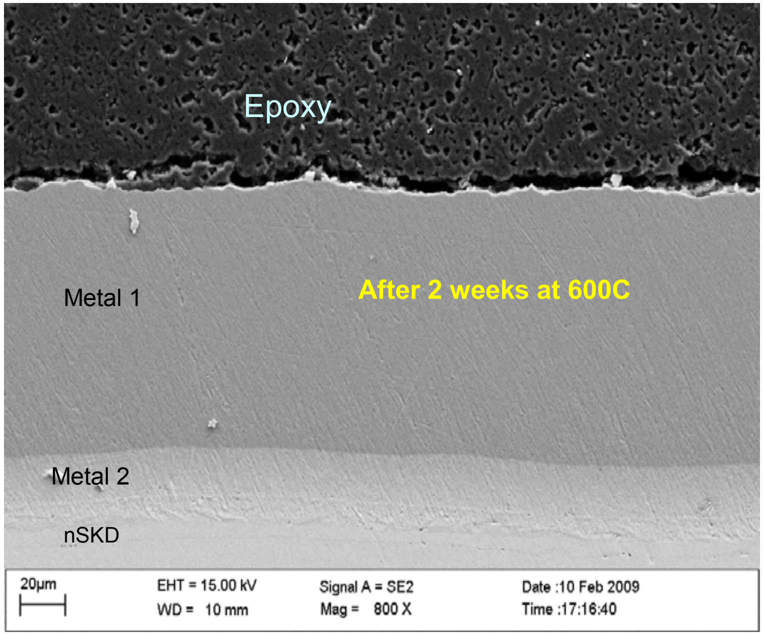




Metallized n-skutterudite puck

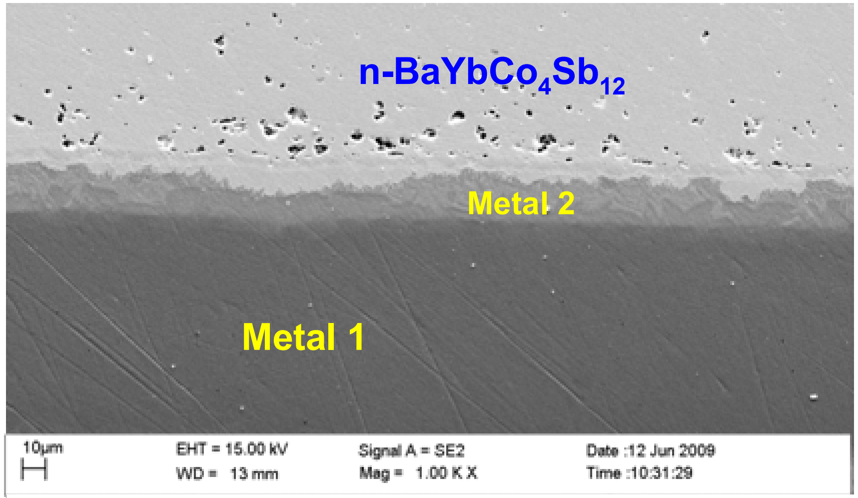


SEM images showing the SKD/metallization interface at beginning of life (BOL) and after 2 weeks aging at 600C. After aging, no degradation of the interface and no significant metal/SKD diffusion is observed.

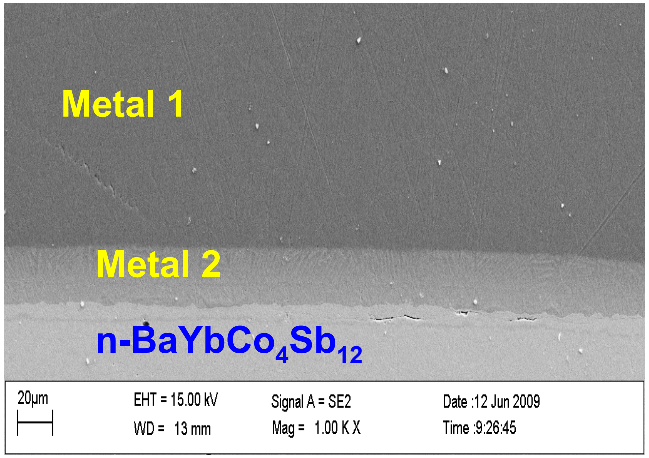


Metallization

SEM images showing the SKD/metallization interface at beginning of life (BOL) and after 2 weeks aging at 600C. After aging, no degradation of the interface and no significant metal/SKD diffusion is observed.



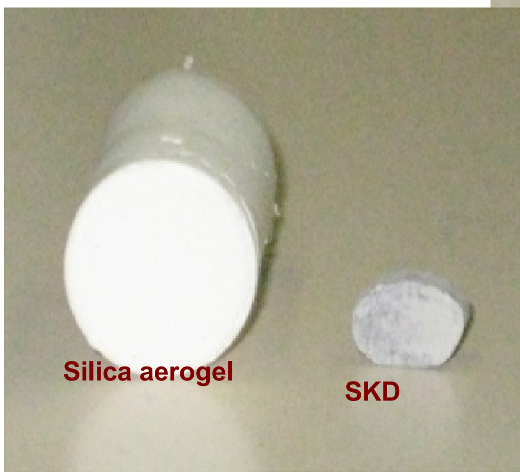
After 8 weeks of ageing at 600C



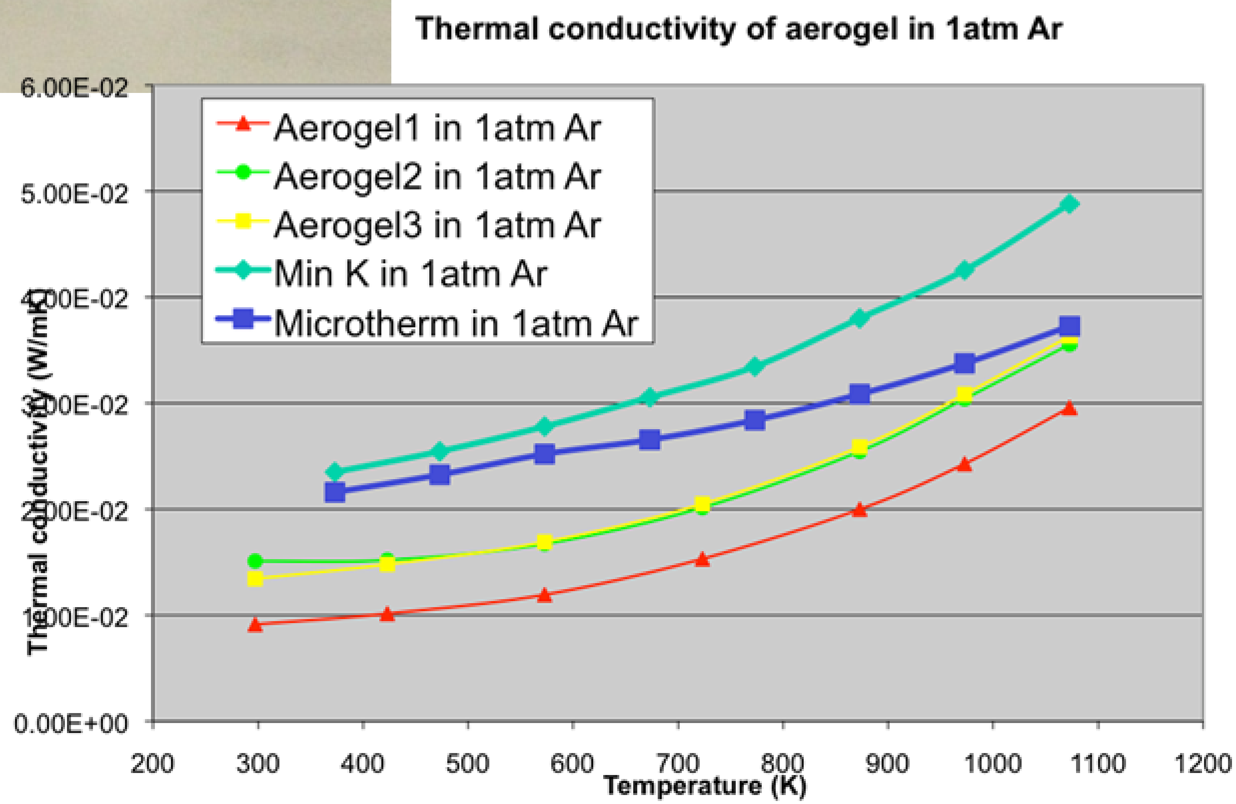
After 8 weeks of ageing at 500C

SEM images showing the SKD/metallization interface at beginning of life (BOL) and after 8 weeks of aging at 600C. After aging, no degradation of the interface and no significant metal/SKD diffusion is observed.

Aerogel for SKD



Sublimation

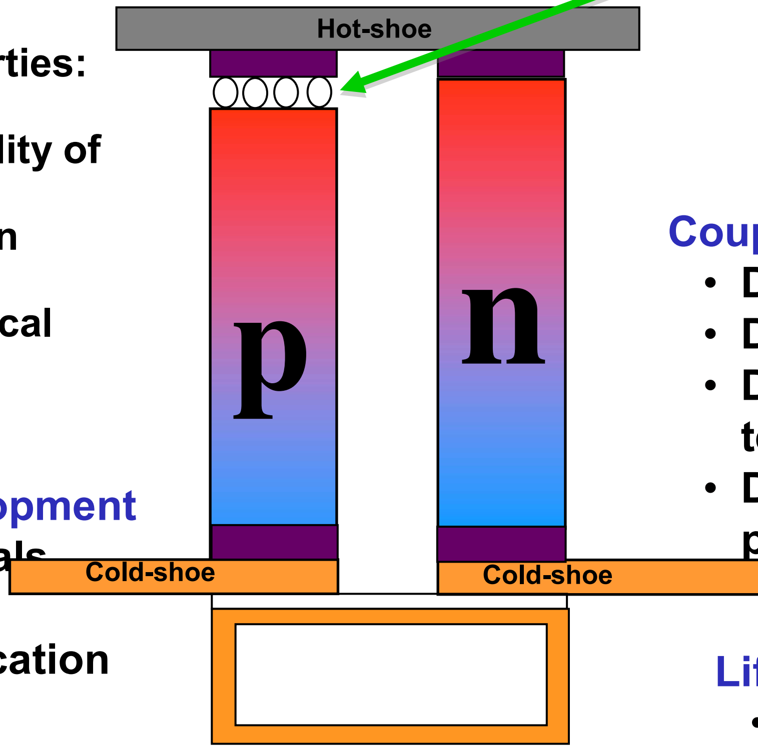


Thermal insulation

Summary

TE materials (n- and p-)
- Establish TE properties: ZT
- Establish repeatability of TE properties
- Develop sublimation control
- Determine mechanical properties

Bonds and legs development
- Develop TE materials metallization
- Develop legs fabrication and processing techniques
- Develop low electrical contact resistance bonds between the couple components
- Demonstrate mechanical and chemical stability at operating temperatures



Transition piece (as required - to mitigate CTE mismatch between n- and p-legs)

Couple assembly and testing
- Develop assembly procedure
- Develop tooling
- Develop couple performance test fixture
- Demonstrate BOL couple performance

Lifetime demonstration
- Test and demonstrate couple interface mechanical and chemical stability
- Demonstrate sublimation control efficacy over time
- Establish TE properties change over time
- Establish couple performance change

Significant progress achieved in the development of:

- Zintl/nano SiGe
- Zintl/LaTe
- SKD

couples

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