2012 THERMOELECTRICS APPLICATIONS WORKSHOP

High Reliability, High Temperature Thermoelectric Power Generation Materials and Technologies

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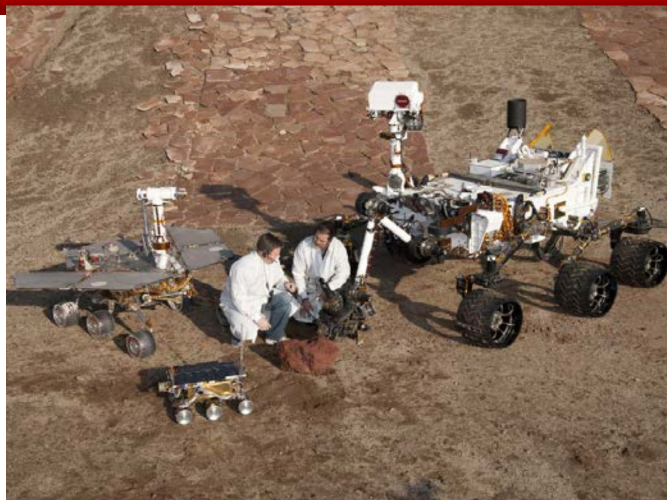
MMRTG-powered Mars Science Laboratory mission

Mars Science Laboratory

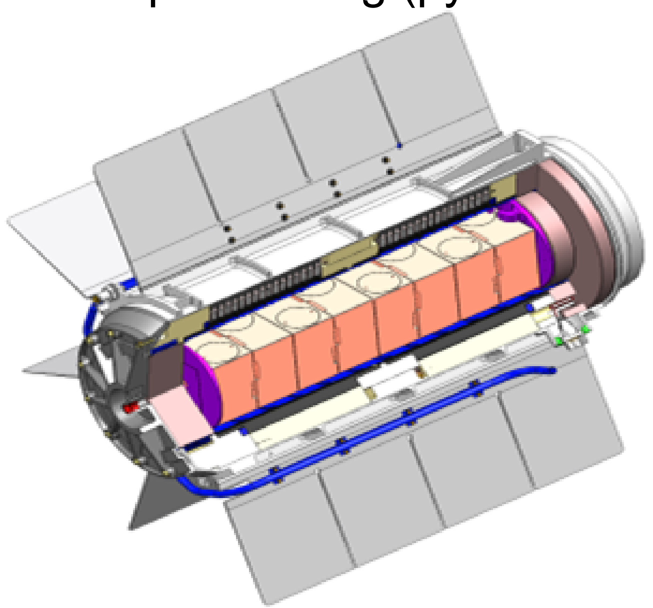


Launch - Nov. 26, 2011
Landing – Early Aug. 2012

Mars Science Laboratory is part of NASA's Mars Exploration Program, a long-term effort of robotic exploration of the red planet. Mars Science Laboratory is a rover that will assess whether Mars ever was, or is still today, an environment able to support microbial life. In other words, its mission is to determine the planet's "habitability."

Multi-Mission RTG Overview

- **Ability to operate in vacuum and planetary atmospheres**
  - 23-36 V DC capability, series-parallel circuitry
- **17 years lifetime requirement**
  - Up to 3 years of storage and up to 14 years of operation
- **Ability to withstand high mechanical loads**
  - ~ 0.3 g^2/Hz (random vibrations)
  - Up to 6000 g (pyrotechnic shock)



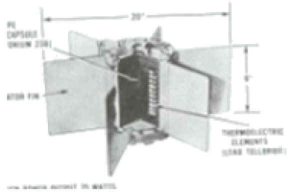
Beginning of Life Performance
~ 125 W
~ 2.8 W/kg

768 <PbTe + TAGS/PbSnTe> couples

RTG Technology - Missions

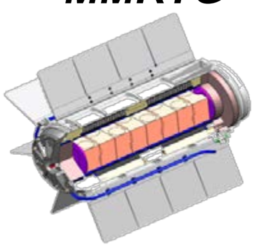
PbTe-based

SNAP-19



40 W_e, 3 W/kg
6.3% Efficiency
Deep space and planetary surface operation
➢ *30 Year life demonstrated*

MMRTG



120 W_e, 2.8 W/kg
6.3% Efficiency
Deep space and planetary surface operation

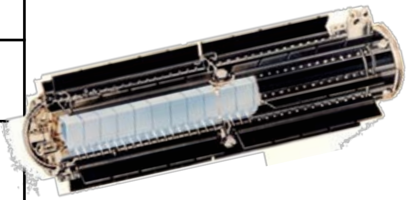
Mission	RTG	TE	Destination	Launch Year	Mission Length
Transit 4A	SNAP-3B7(1)	PbTe	Earth Orbit	1961	15
Transit 4B	SNAP-3B8 (1)	PbTe	Earth Orbit	1962	9
Apollo 12	SNAP-27 RTG (1)	PbTe	Lunar Surface	1969	8
Pioneer 10	SNAP-19 RTG (4)	PbTe/TAGS	Outer Planets	1972	34
Triad-01-1X	SNAP-9A (1)	PbTe	Earth Orbit	1972	15
Pioneer 11	SNAP-19 RTG (4)	PbTe/TAGS	Outer Planets	1973	35
Viking 1	SNAP-19 RTG (2)	PbTe/TAGS	Mars Surface	1975	4
Viking 2	SNAP-19 RTG (2)	PbTe/TAGS	Mars Surface	1975	6
LES 8	MHW-RTG (4)	Si-Ge	Earth Orbit	1976	15
LES 9	MHW-RTG (4)	Si-Ge	Earth Orbit	1976	15
Voyager 1	MHW-RTG (3)	Si-Ge	Outer Planets	1977	31
Voyager 2	MHW-RTG (3)	Si-Ge	Outer Planets	1977	31
Galileo	GPHS-RTG (2) RHU(120)	Si-Ge	Outer Planets	1989	14
Ulysses	GPHS-RTG (1)	Si-Ge	Outer Planets/Sun	1990	18
Cassini	GPHS-RTG (3) RHU(117)	Si-Ge	Outer Planets	1997	11
New Horizons	GPHS-RTG (1)	Si-Ge	Outer Planets	2005	3 (17)
MSL	MMRTG (1)	PbTe/TAGS	Mars Surface	2011	3

SiGe-based

MHW-RTG

158 W_e, 4.2 W/kg
6.5% Efficiency
Deep space operation
➢ *30 Year life demonstrated*

GPHS-RTG



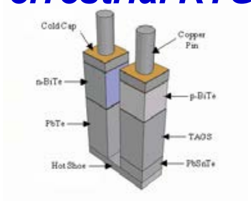
285 W_e, 5.1 W/kg
6.5% Efficiency
Deep space operation
> 18 Year life demonstrated

RTGs have been successfully used on a number of long-life missions

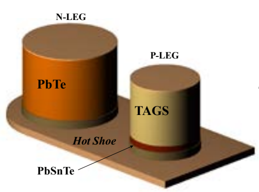
TE Converter Configurations

Couple Configuration	P-leg	N-leg	Heat Source Coupling	Program
Segmented Couple	Bi_2Te_3/TAGS/PbSnTe	Bi_2Te_3/PbTe	Conductive	Terrestrial RTGs
Segmented Couple	TAGS/PbSnTe	PbTe	Conductive	SNAP-19, MMRTG
Segmented Couple	$Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$	$Si_{0.63}Ge_{0.37}/Si_{0.8}Ge_{0.2}$	Radiative	MHW-, GPHS-RTG
Multicouple	$Si_{0.8}Ge_{0.2}$	$Si_{0.8}Ge_{0.2}$	Conductive, Radiative	SP-100, MOD-RTG
Segmented Couple	Bi_2Te_3/SKD*	Bi_2Te_3/SKD	Conductive	Segmented TE Couple (2002)
Multicouple	SKD (Skutterudites)	SKD	Conductive	STMC (2005)
Unsegmented Couple	Zintl	Nano $Si_{0.8}Ge_{0.2}$	Radiative	2008
Unsegmented Couple	Zintl	$La_{3-x}Te_4$	Conductive or radiative	2009 ATEC
Segmented Couple	SKD/Zintl	SKD/$La_{3-x}Te_4$	Conductive or radiative	2011
Segmented Couple	Adv. PbTe/Zintl	Adv. PbTe/$La_{3-x}Te_4$	Conductive	2012
Segmented Multicouple	SKD/Zintl	SKD/$La_{3-x}Te_4$	Conductive or radiative	2012 Small FPS

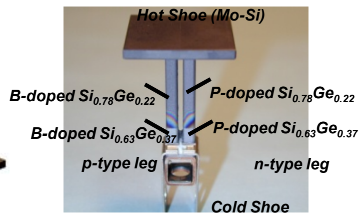
Terrestrial RTG



MMRTG



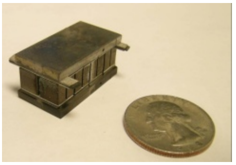
MHW-RTG



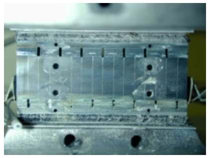
ATEC

Segmented HT Couple

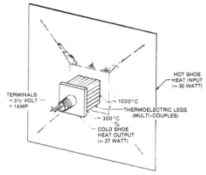
STMC



SP-100



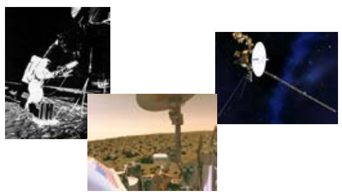
MOD-RTG



Multicouples developed for higher power systems (space reactor, terrestrial)
Arrays of discrete couples typically used for RTGs

High Temperature TE Materials
RTG Technology Development Timeline

Timeline	1960s	1970s	1980s	1990s	2000-2009	2010-2019	2020-2030

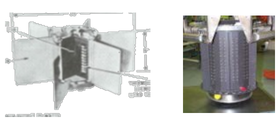
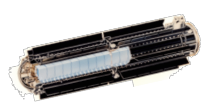
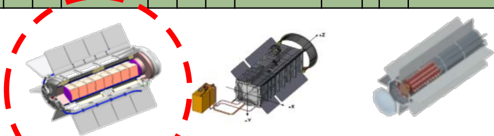



Mission

Mission	Pioneer 11 (1972-73)	Viking (1975)	Voyager (1977)	Galileo (1989)	Ulysses (1990)	Cassini (1997)	New Horizons (2005-2006)	MSL (2011)	Discovery (2016-17)	OPFM 1 (>2020)	Discovery & NF (2026)	OPFM 2 (2027)

Generator

Generator	SNAPs (1961-1970)	MHW (1975)	GPHS (1985)	MMRTG (2009)	ASRG (>2016)	ARTG (>2020)

Technology

(~7 to 7.5 %)

PbTe (1958)	TAGS (1965)	SiGe (1968)	"Fine-grained" Si-Ge, Rare earth chalcogenides and Boron Carbide	Skutterudites (1991-)	Nano Bulk Si-Ge	14-1-11 Zintls, $La_{3-x}Te_4$ and Adv PbTe
PbTe couples	SiGe "unicouples" (1968)	MOD-RTG SiGe Multicouples	No Development	MMRTG couple (2003)	1st Gen Unsegmented ATEC couples	1st Gen Segmented ATEC Couples
ARTG	2nd Gen Advanced TE	2nd Gen Advanced TE				

Segmented couples (10-15%)

>20%

?

Timeline	1960s	1970s	1980s	1990s	2000-2009	2010-2019	2020-2030

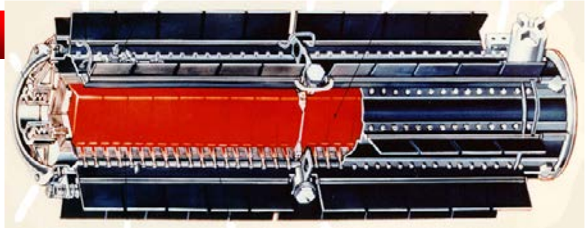
DOE TEAW 03/21/2012

Lifetime Performance Validation

What controls RTGs Lifetime Performance?

Degradation mechanisms

1. Fuel decay
2. Decrease in hot-junction as a result of decreasing heat input
3. Thermoelectric materials-related mechanisms



GPHS RTG

~ 0.8%/year decrease in power output

+

~ 0.5%/year decrease in power output

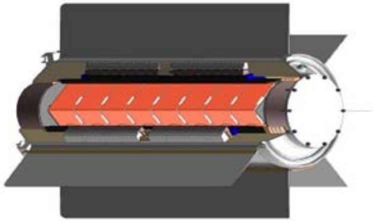
+

Decrease in power output: ~ 0.3%/year

=

Decrease in power output: ~ 1.6%*/year total

* Averaged to 14 years operation



MMRTG

~ 0.8%/year decrease in power output

+

~ 0.5%/year decrease in power output

+

Decrease in power output: ~ 2.5**/year

=

Decrease in power output: ~ 3.8**/year total

** Rate estimation based on ~ 2 years MSL EU test data and averaged to 14 years operation

TE-related degradation mechanisms can represent a significant fraction of the overall RTG degradation over time

Impact of key TE-related degradation mechanisms on RTG performance

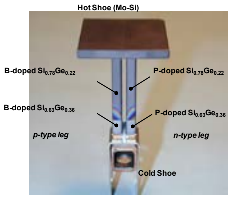
Degradation mechanism	Key potential impact(s)	Impact(s) on RTG performance
Sublimation of TE materials *(A major concern for most TE materials…)*	• Increase in electrical resistance • Electrical and thermal shorts • Promote the degradation of couple interfaces at the hot-junctions • Potentially impact all other mechanisms	• Reduced power • Electrical isolation
Changes in TE properties *(can be due to dopant precipitation, structural phase changes, phase segregation, electromigration, etc…)*	• Can reduce thermoelectric efficiency if lower ZT • Lower temperature gradient across TE elements if increased thermal conductivity	• Reduced power
Increase in electrical & thermal contact resistances at interfaces *(can be due to interdiffusion, microcrack propagation, etc…)*	• Increase in electrical resistance • Lower temperature gradient across TE elements	• Reduced power
Increased conductance of thermal insulation *(can be due to interactions between insulation packaging, TE materials and sublimation products, etc…)*	• Increased heat losses • Reduced heat flux through the thermoelectric couples	• Reduced power • Thermal management

Each TE-related degradation mechanism can have a significant impact on overall RTG degradation over time; must be tested for, quantified and modeled

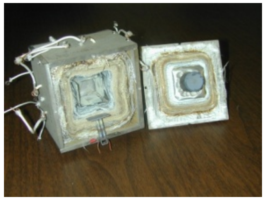
Life Testing & Performance Validation

- **Materials (TRL 1-3)**
  - Stable TE properties vs. time & temperature demonstrated over > 1 year of testing
  - Control of sublimation rates down to 10^{-6} to 10^{-7} g.cm^2/hr, verified over > 1 year of testing

- **Couples TRL (2-4)**
  - Stable electrical contact metallizations
  - Stable interfaces to hot and cold shoes, between TE segments
  - Maintain mechanical, thermal and electrical integrity
  - Greater than 5 years life predicted based on normal and accelerated testing

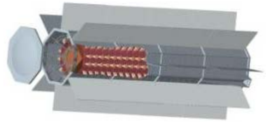


- **Couple Arrays (TRL 3-5)**
  - Use of prototypic couples
  - No interaction with thermal insulation, verification of mechanical integrity
  - Greater than 3 years of testing



- **Electrically heated Power Demonstrator (EPD, 18-couple) (TRL 4-5)**
  - Demonstration of thermal and electrical efficiencies at subscale system level

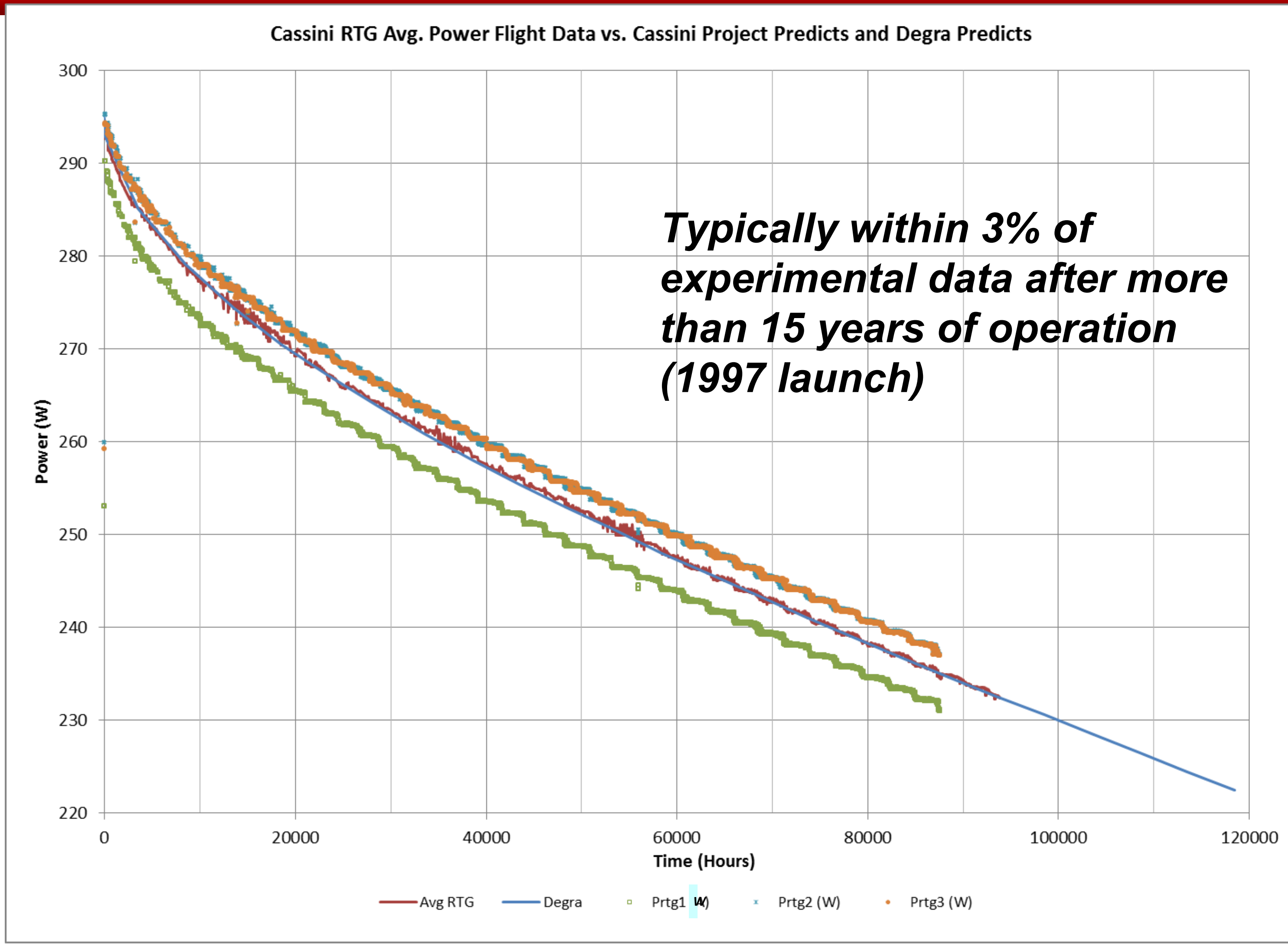
- **ETG (TRL 6)**
  - Validation of thermal and electrical efficiencies at full scale system level
  - Qualification testing



- **Life Performance Model**
  - Materials properties and test data used to predict long term performance
  - Provide Mission planners with performance profile during various scenarios and operation phases

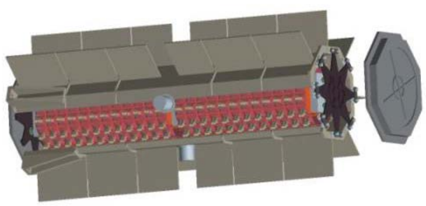
Well defined technology development roadmap to establish lifetime performance of RTGs

GPHS-RTG Data & Lifetime Performance Predictions



High Temperature TE Couple Technology Development for Next Generation Space Power Systems

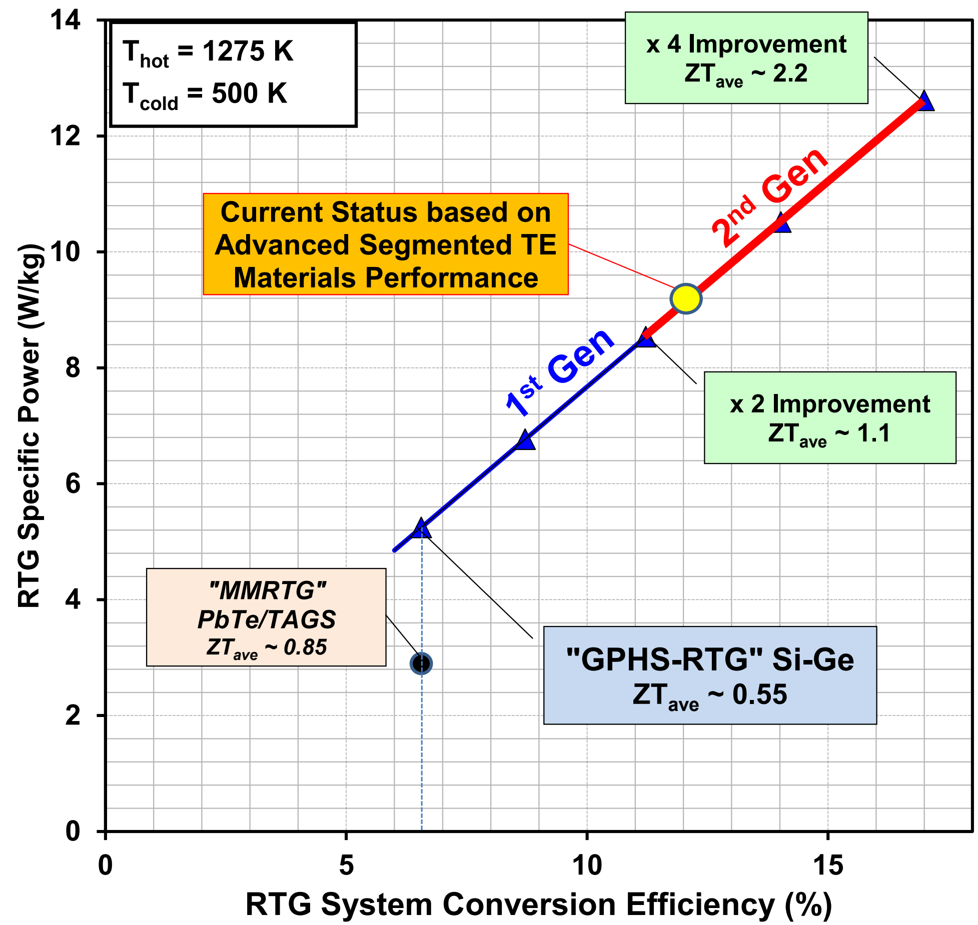
Impact of Higher Performance Materials on Thermoelectric Power Systems for Space Exploration



T_{hot} = 1100 K to 1275 K

(higher is better!)

Lower System Mass and Higher Conversion Efficiency Needed (x2 to 4)

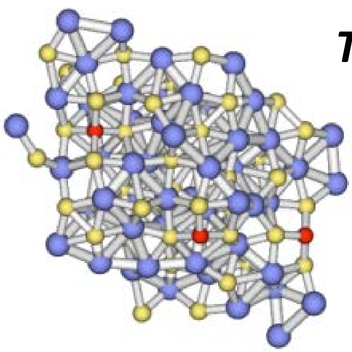


Advanced RTG Specific Power vs. System Conversion Efficiency
(Based on radiatively coupled vacuum operation unicouple based RTG concept)

Ultimate goal: > 15% efficient, >10 W_e/kg Advanced RTGs

Advanced RTG Technology Development Path

ATEC



TRL 1-2

High ZT TE materials

TRL 2

Component Development

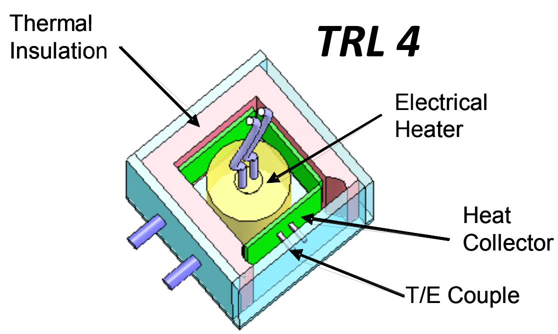
TRL 3

Couple Dev. & Performance Validation
Initial life testing

Advanced TE materials & Devices Task

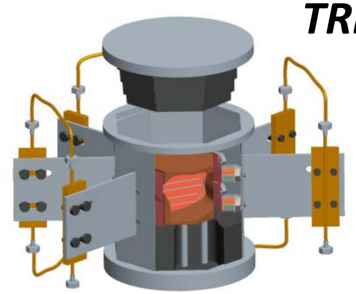
Advanced Thermoelectric Couple (ATEC) project

TRL 4

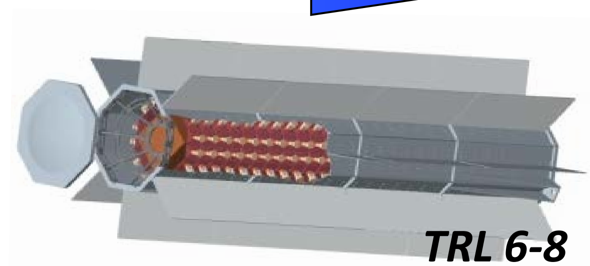


4-couple/module development
Life testing, demo and modeling

TRL 5



Converter (EPD) Development
Life & Performance Validation



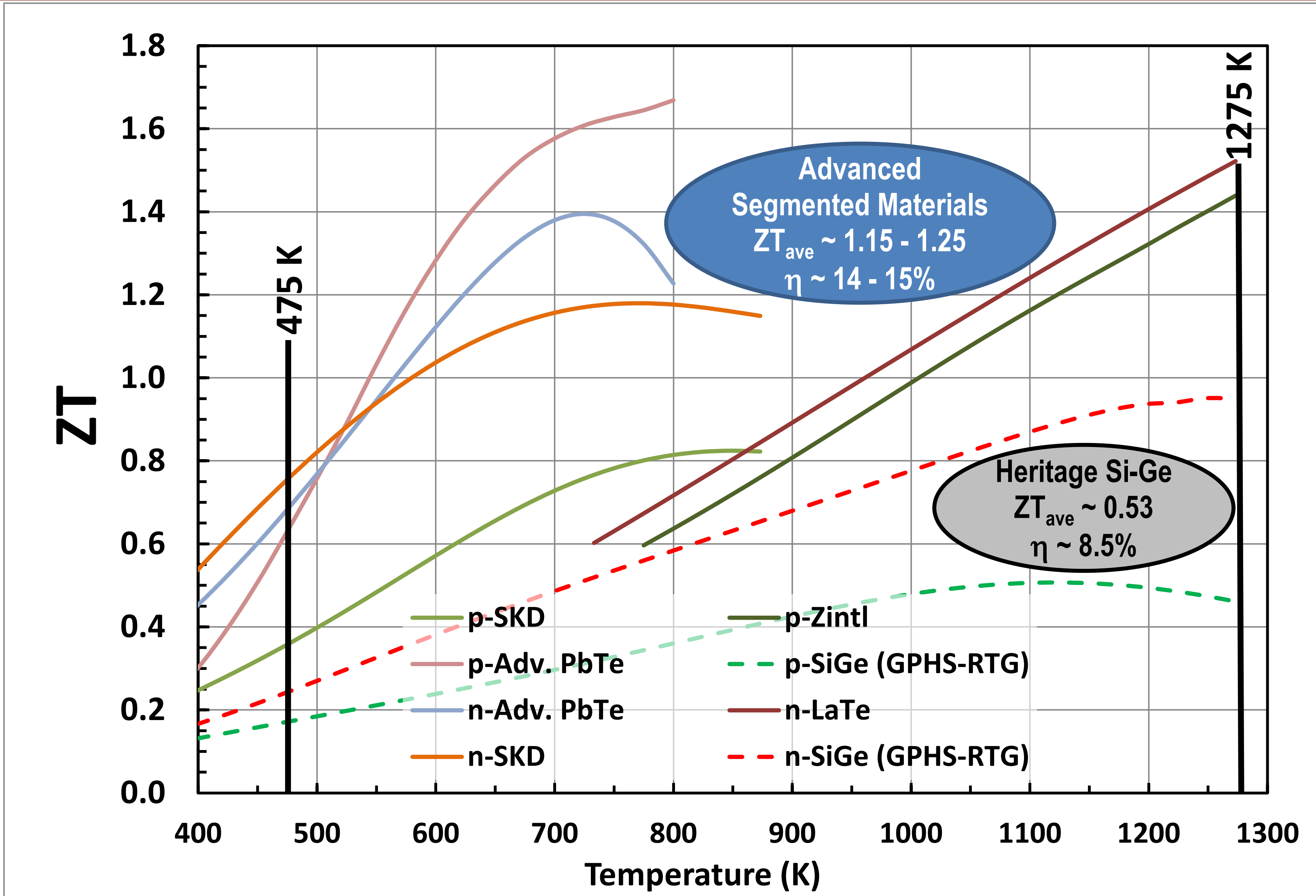
TRL 6-8

Engineering & Qualification
ARTG development & performance validation

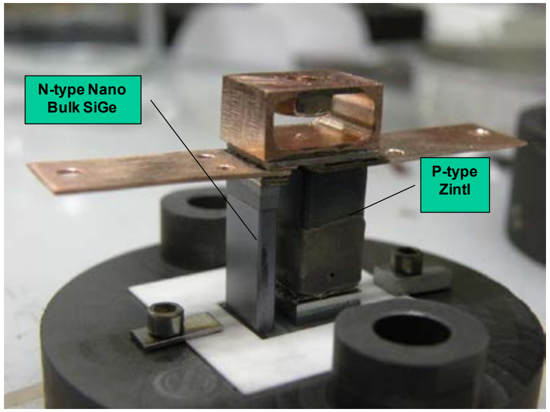
Advanced Thermoelectric Couple (ATEC) project

DOE/Industry

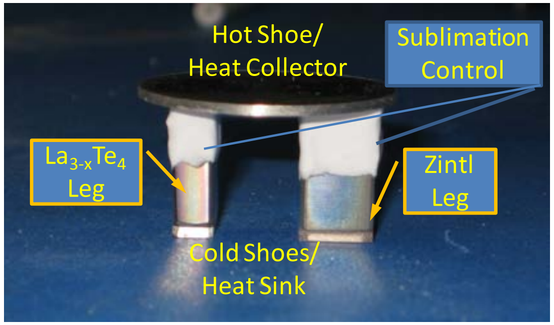
Baseline ATEC advanced TE Materials
Large performance gains over heritage Si-Ge alloys



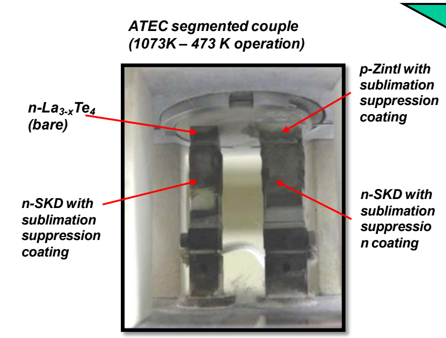
Couple Configurations in Development



Zintl ($Yb_{14}MnSb_{11}$) / NanoSiGe Couple (2007-2009)

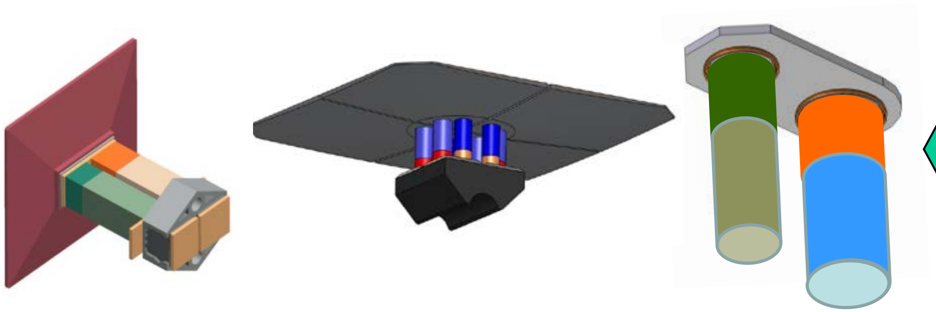


Zintl ($Yb_{14}MnSb_{11}$) / $La_{3-x}Te_4$ Couple (2009-2010)



Zintl/SKD // $La_{3-x}Te_4$/SKD Segmented Couple (2010-)

Zintl/Adv.PbTe // $La_{3-x}Te_4$/Adv.PbTe Segmented Couple (2012 -)



Zintl // $La_{3-x}Te_4$ Cantilevered and Spring-loaded Segmented Couples for Life Performance validation(2012-2014)

Materials, Components & Couple Development Challenges

Materials

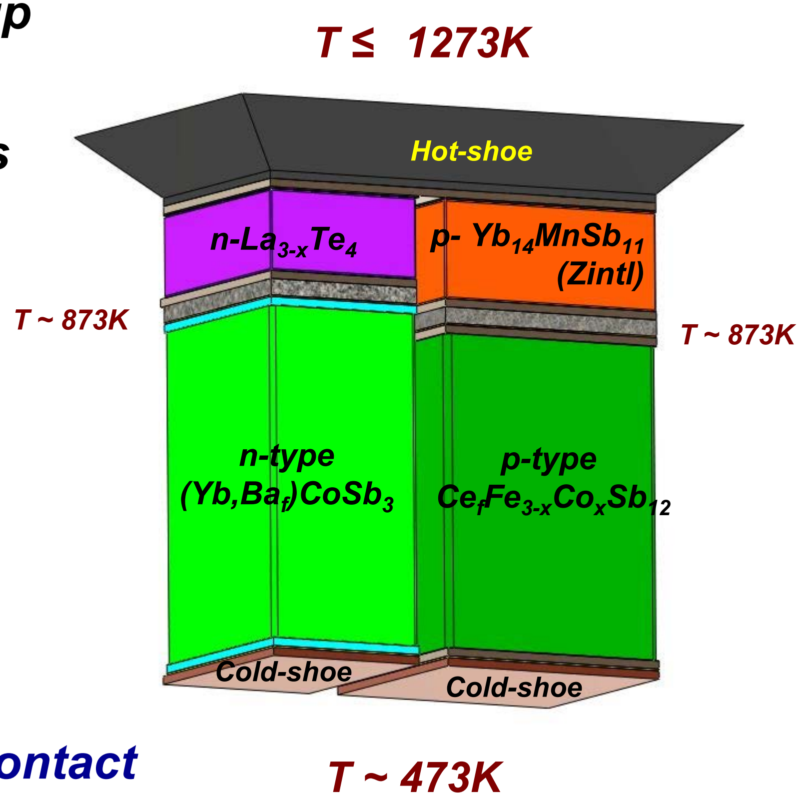
TE materials
- Batch Synthesis Scale-up
- Reproducibility and stability of TE Properties

Components

Leg segments
- Machining
- Stable metallization
- Sublimation control

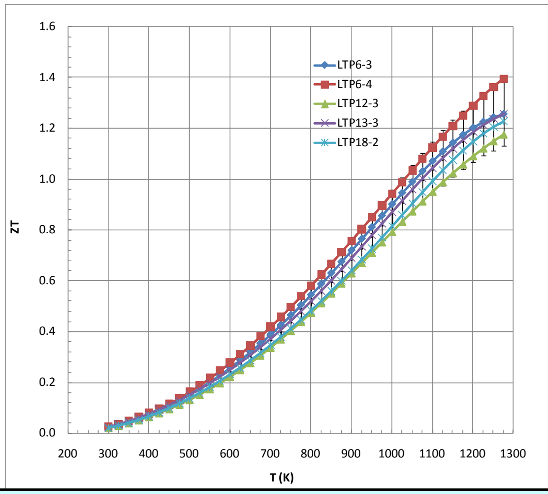
Couples

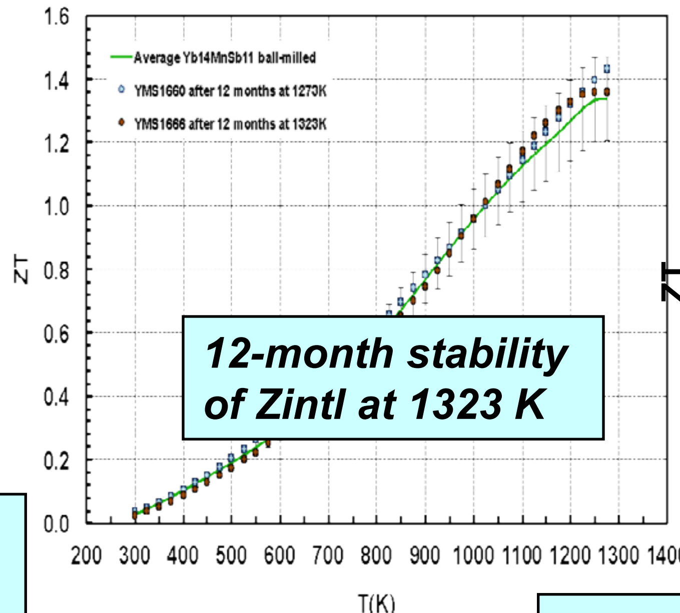
Design, Fabrication Assembly & Testing
- Robust design
- Stable, low electrical contact resistance interfaces
- Couple Assembly
- Thermal Insulation
- Life demonstration



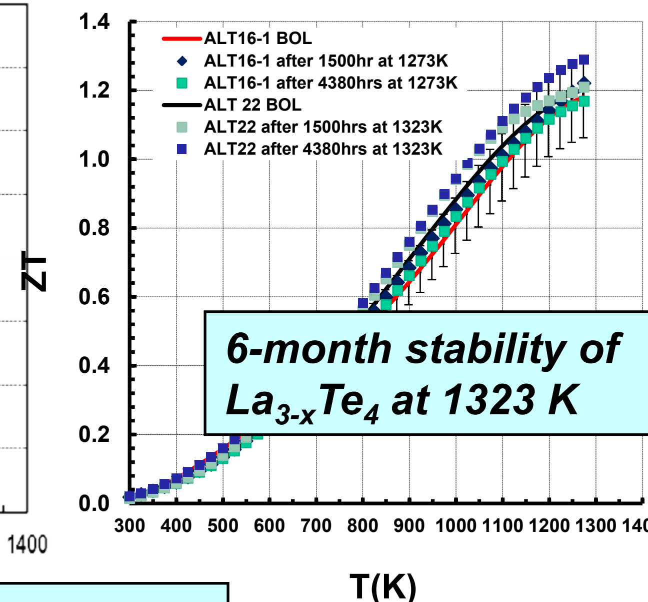
Segmented $Yb_{14}MnSb_{11}/La_{3-x}Te_4$ High Temperature TE Couple Technology Development

Powder Metallurgy Synthesis Scale-up and Reproducible TE properties





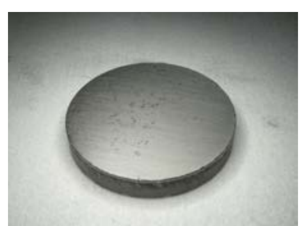
12-month stability of Zintl at 1323 K



6-month stability of $La_{3-x}Te_4$ at 1323 K

Reproducible BOL properties for $Yb_{14}MnSb_{11}$, $La_{3-x}Te_4$ and filled skutterudites produced in 100- to 200 g batches

$Yb_{14}MnSb_{11}$

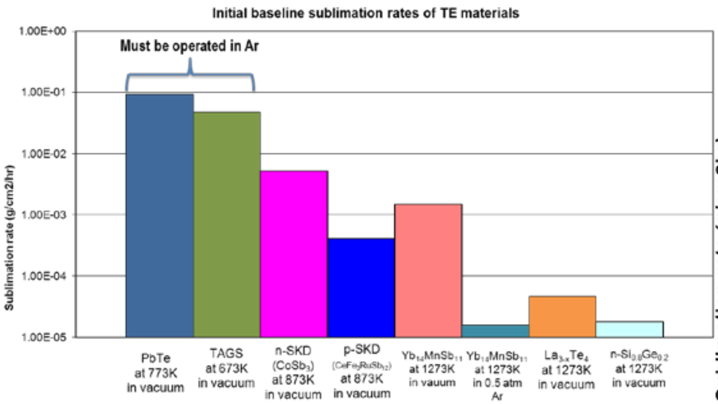


$La_{3-x}Te_4$

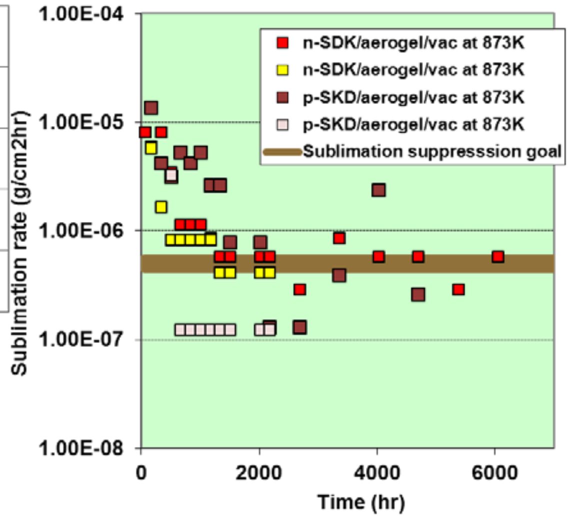
Filled Skutterudites

Segmented $Yb_{14}MnSb_{11}/La_{3-x}Te_4$ High Temperature TE Couple Technology Development

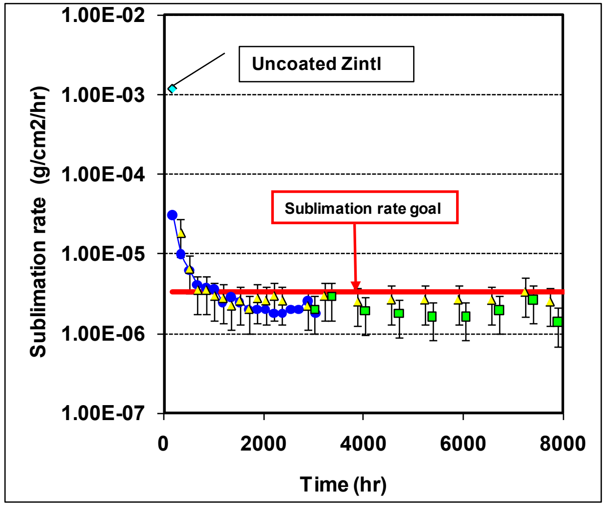
Sublimation Control for TE Materials and Thermally Stable Low Electrical Contact Resistance Metallizations



12-month stability of SKD Sublimation Control at 873 K

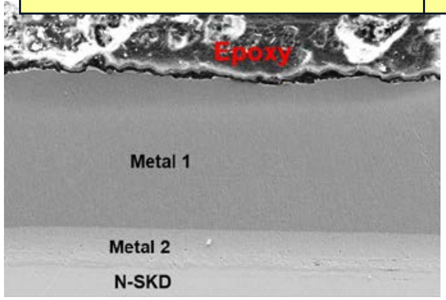


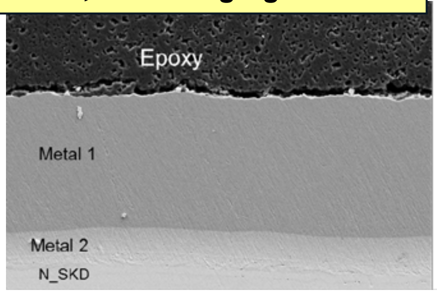
18-month stability of Zintl Sublimation Barrier Coating at 1273 K



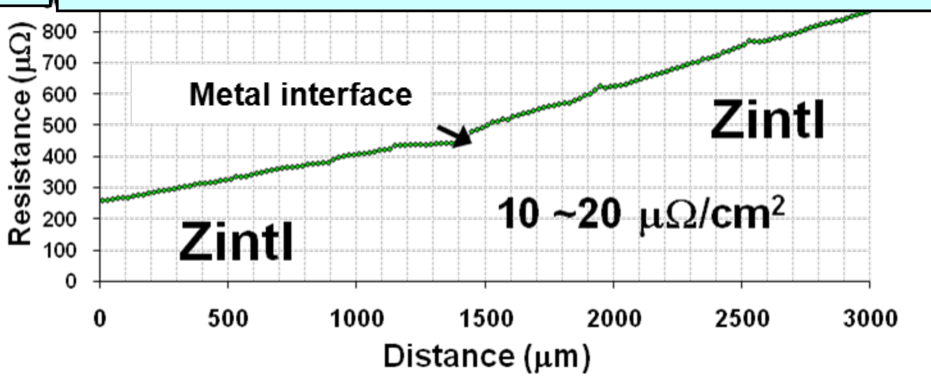
12-month stability of SKD Metallization at 873 K

As-fabricated	*After 5,000 hrs aging at 600C*



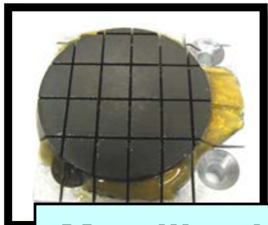
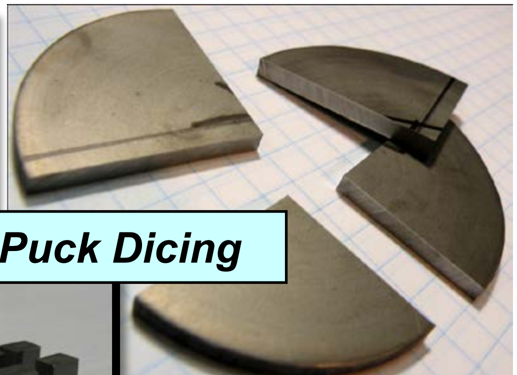


2-month stability of Zintl Metallization at 1273 K

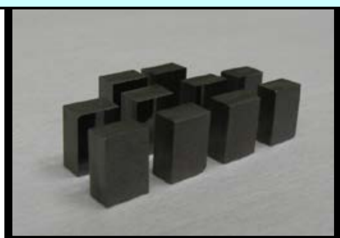


Segmented $Yb_{14}MnSb_{11}/La_{3-x}Te_4$ High Temperature TE Couple Technology Development

Metallized TE Segment Fabrication

Metallized Puck Dicing



$La_{3-x}Te_4$

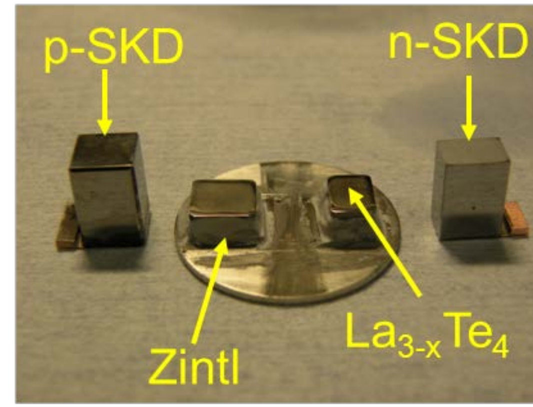
$Yb_{14}MnSb_{11}$ Zintl


Filled Skutterudites

Couple Assembly and Test

Stand-alone Segmented Legs

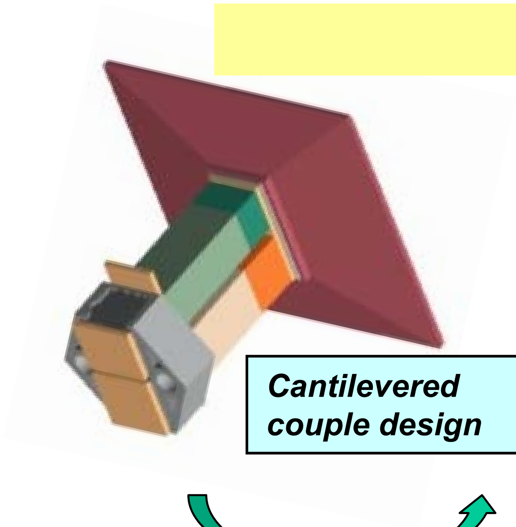
Full couple assembly



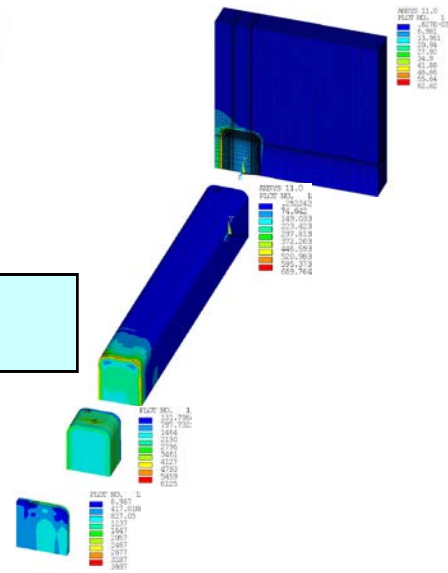
Sublimation Control and Thermal Insulation Packaging into Spring-loaded Test Fixture

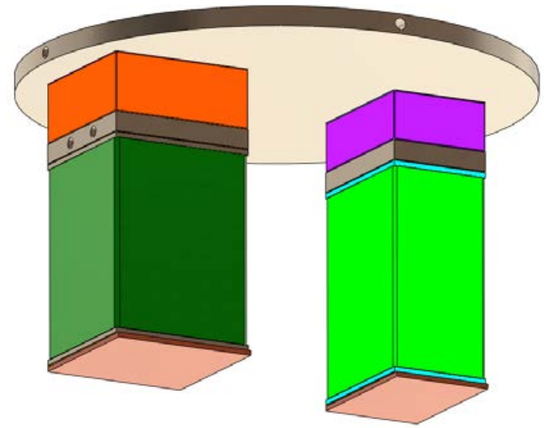
Segmented $Yb_{14}MnSb_{11}/La_{3-x}Te_4$ High Temperature TE Couple Technology Development

Design of Robust HT Segmented Couples

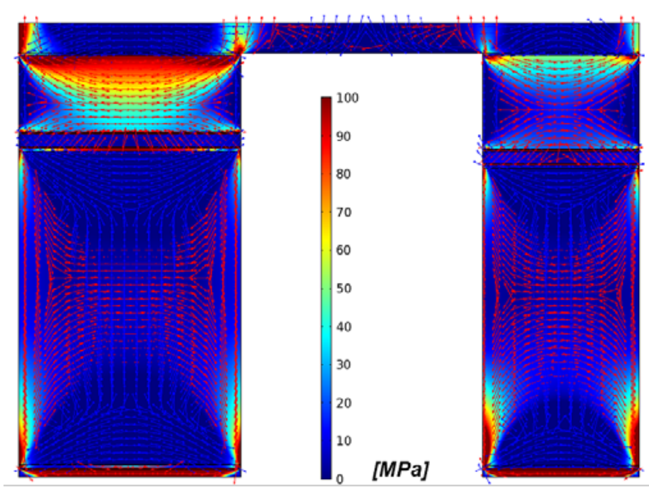


Cantilevered couple design



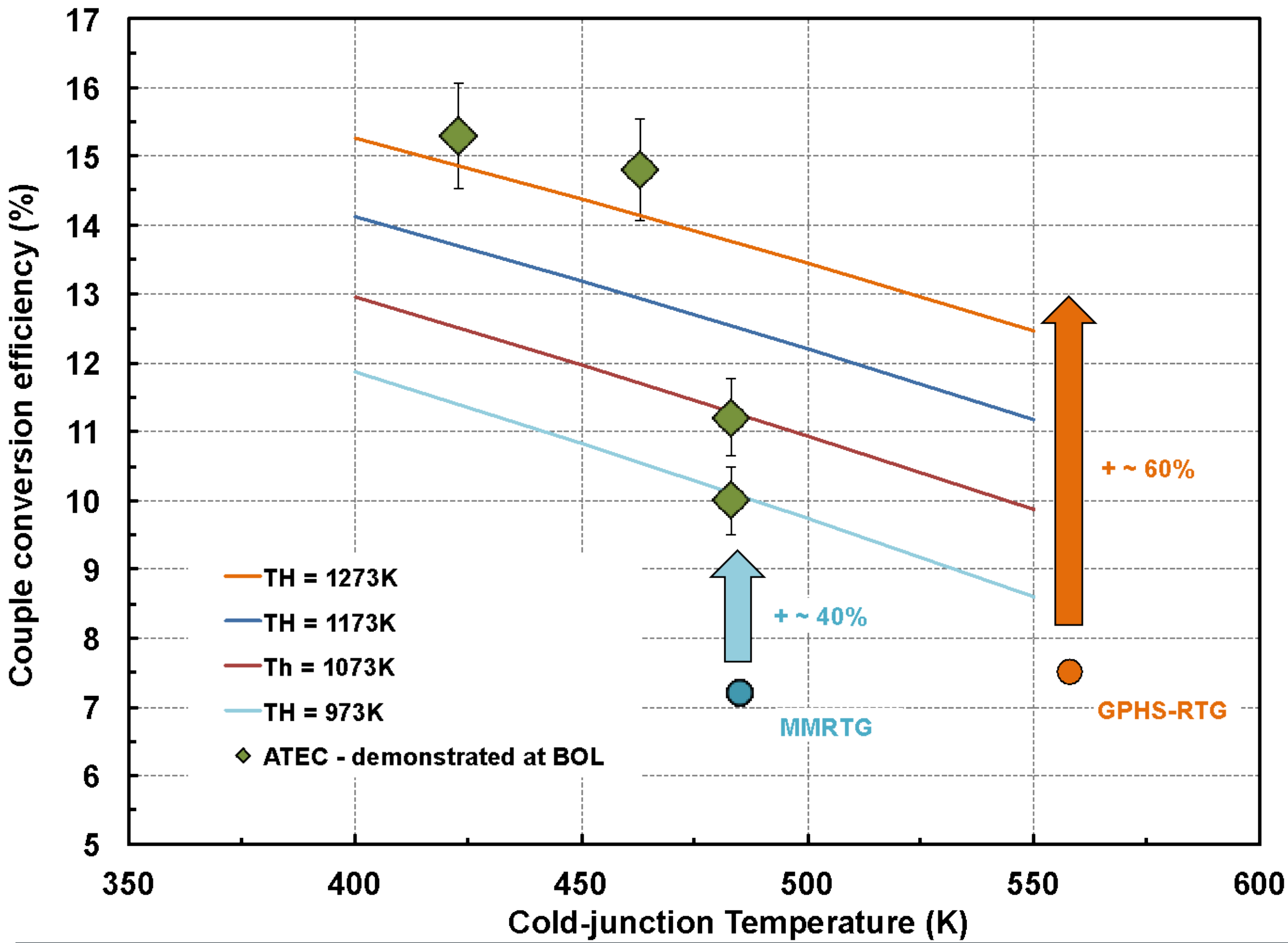


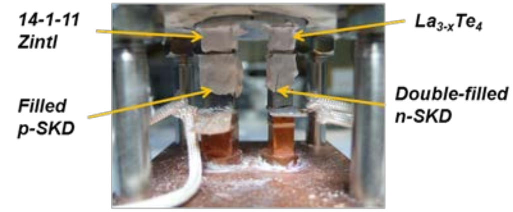
Spring-loaded couple design



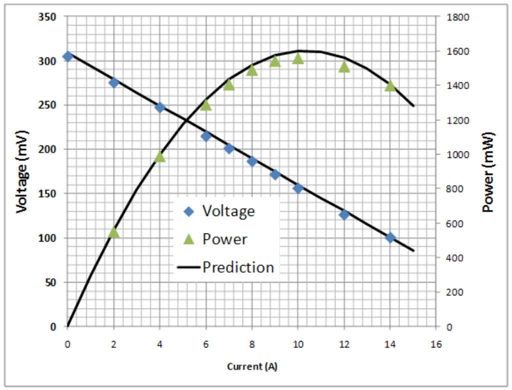
- **Detailed Finite Element Analysis (ANSYS, COMSOL)**
- **Supported by experimental data on temperature dependent mechanical and thermal properties on TE materials, electrical and thermal interfaces**
- **Coupon-level demonstrations**
- **Couple-level validations**
- **Extensive life testing**

1st iteration for 1st Gen Segmented Couple testing – Demonstrated BOL efficiency –





High Temperature Segmented Zintl/$La_{3-x}Te_4$/SKD Couple Spring-loaded Performance Test Configuration

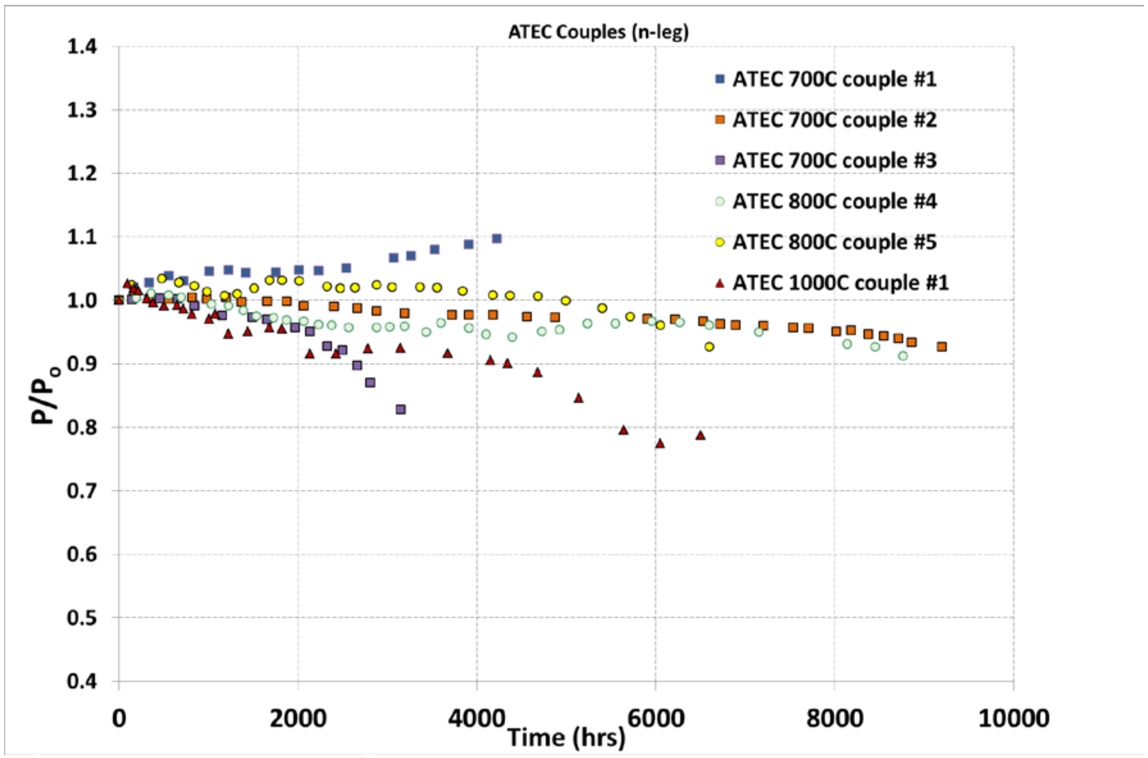


Beginning-of-Life (BOL) Experimental vs. Predicted I-V and I-P curves For Advanced TE Couple

- ***Demonstrated large increases in couple efficiency over MMRTG and GPHS couples. ~ 15% efficiency for 1273 -463 K operating temperature range***

1st iteration for 1st Gen Segmented Couple testing – Preliminary Life Assessment–

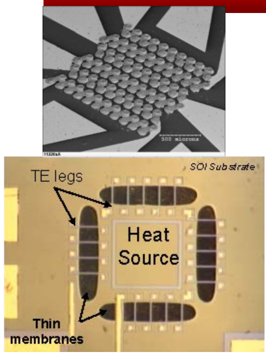
- Several couples have now been tested for up to 9,000 hours and at hot side operating temperatures ranging from 973 K up to 1273 K
- Long term performance degradation mechanisms have been identified; next iteration of couples will integrate small modifications to minimize degradation
  - Will be implemented later in FY12



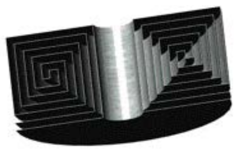
Changes in maximum Power output for n-leg of ATEC couples normalized to BOL performance

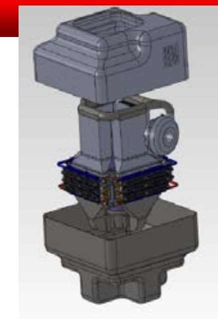
Potential for Terrestrial High Grade Waste Heat Recovery Applications

Advanced TE Power Systems



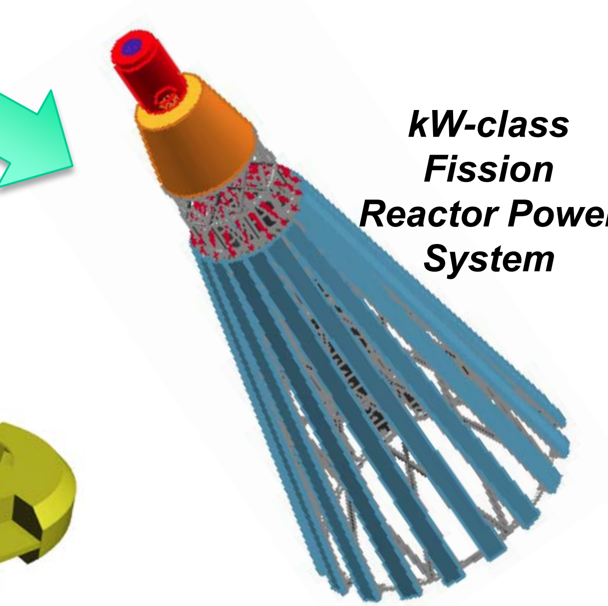
Miniaturized devices and energy harvesting systems



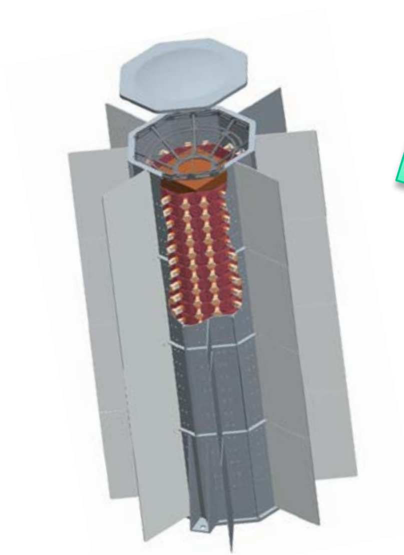


Auxiliary and waste heat recovery power systems

Advanced TE Technology

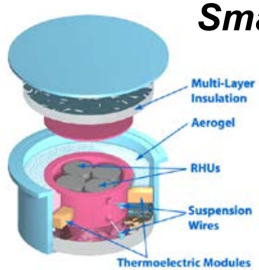


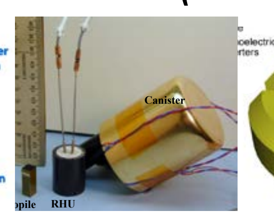
kW-class Fission Reactor Power System

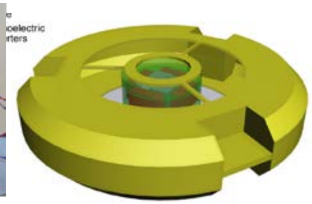


Advanced RTGs (100's W)

Small RTGs (10's W)



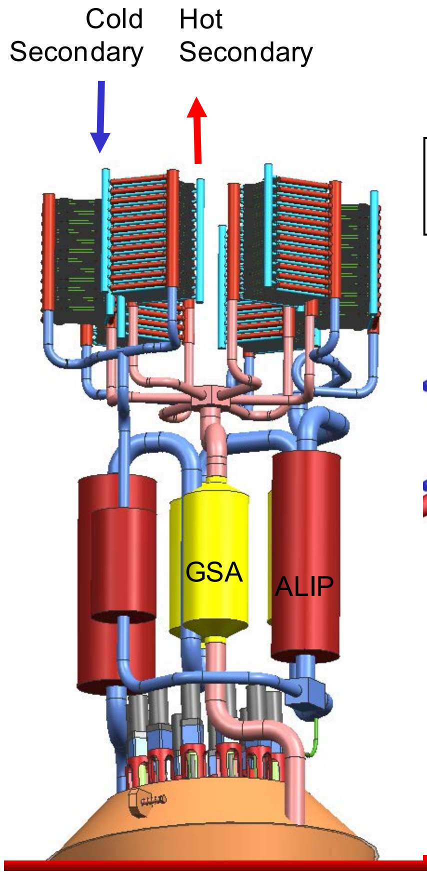


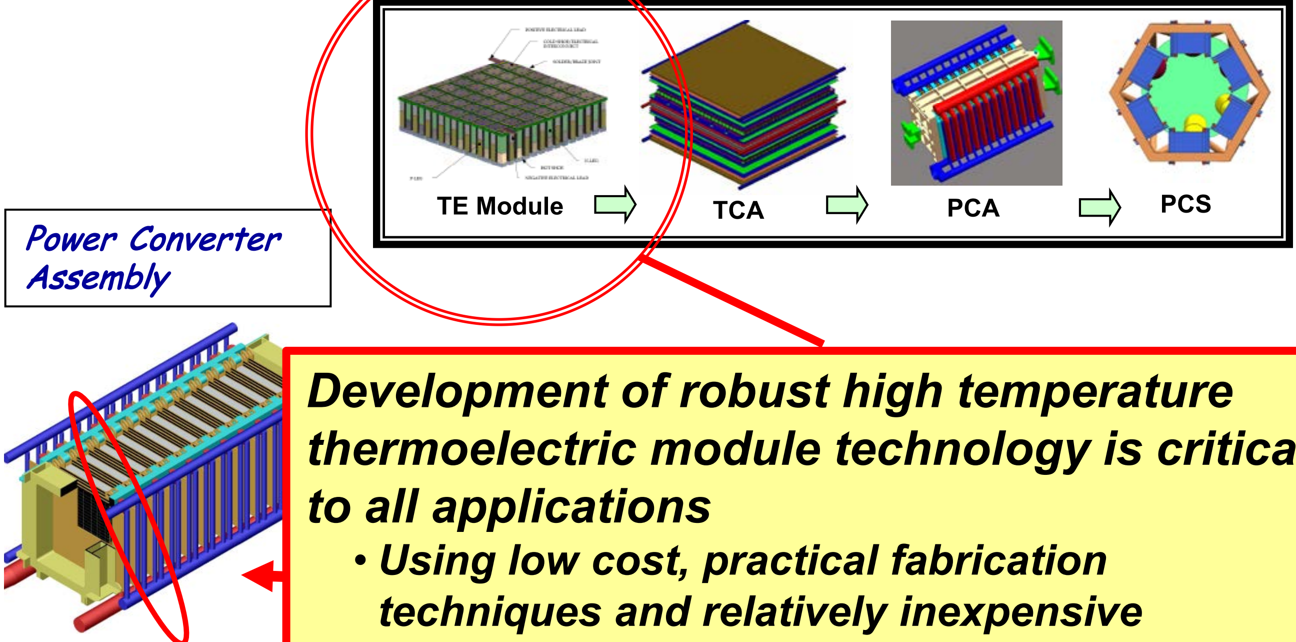


Advanced high temperature TE technology being developed for space power systems could also be applied to terrestrial Waste Heat Recovery and auxiliary power systems

Nuclear Electric Propulsion or Primary Power for Space Exploration and Science Missions

- Technology development was focused on arrays of thermoelectric couples grouped into power converter assemblies
- Used liquid metal heat exchangers to interface with reactor heat source and radiator heat sinks





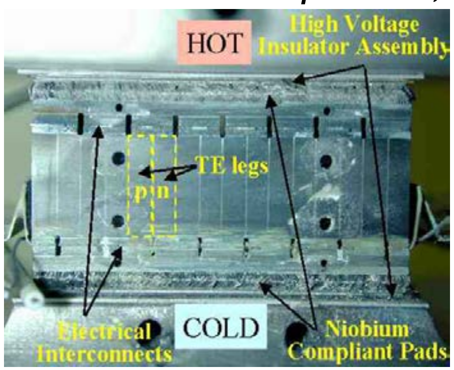
Development of robust high temperature thermoelectric module technology is critical to all applications

- ***Using low cost, practical fabrication techniques and relatively inexpensive materials (including thermoelectrics)***
- ***Ability to integrate with various heat exchangers***
- ***Ability to reliably survive thermal/mechanical stresses***

Mechanically Compliant High Temperature TE Module Technologies at NASA/DOE/JPL

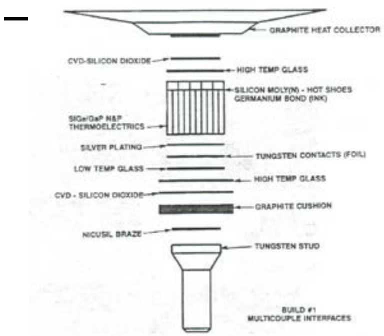
SP-100 SiGe Multicouple (1990s)

- *Conductively coupled on hot side with built in compliant pads*
- *Tested for up to 25,000 hours*



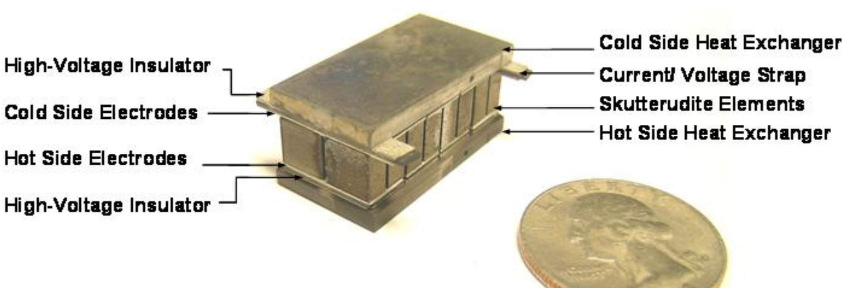
Designed for integration with flat plate HXs, 873 K - 1273 K Steady State Hot Side operation

MOD-RTG SiGe Multicouple Technology (1980s)

- *Graphite heat collector, bolted on radiator side*
- 

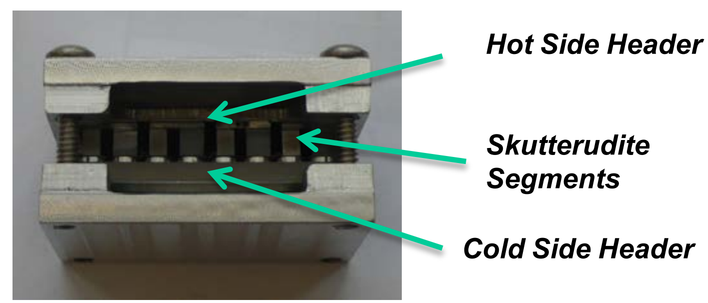
Designed for radiative coupling in RTG, 573 K - 1273 K Steady State operation

Skutterudite Module Developed at JPL under NASA/SMD In-Space Propulsion Program (2004-2005)



Designed for integration with flat plate HXs, 473 K - 873 K Steady State operation

Segmented Module under development for portable power system (2011-2012)



Designed for integration with high efficiency HXs, 400 K - 1223 K operation with multiple thermal cycles in vacuum or atmospheric environments

Summary

- **Successfully completed the development of first generation Advanced High Temperature TE materials**
  - Developed first generation TE materials with x2 ZT_{ave} improvement
  - Transitioned several first generation TE materials for engineering development of couples
- **The majority of risks at the first generation TE materials and components levels have been retired**
  - Demonstrated long term stability of first generation TE materials
  - Components-level life demonstrated through extended tests (up to 11,600 hours)
- **Demonstrated up to 15% BOL efficiency with segmented TE couples**
  - Work is in progress to demonstrate life performance capabilities
    - Without life, high ZT does not matter!
  - Fabricated and conducted up to 9,000 hrs of life assessment for 1st iteration ATEC couples
    - Still some work to be done to retire most significant degradation mechanisms but there are no “show stoppers” so far
- **New technology could be applied to selected high temperature waste heat recovery applications**
  - Availability of rugged TE couple & modular devices <u>is a must to enable new applications</u>

Acknowledgments

- **This work was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration**

- **The work presented here benefited from contributions from a number of collaborators in the past few years**
  - California Institute of Technology
  - University of California at Los Angeles, University of California at Davis
  - California State Polytechnic University, Pomona
  - Ole Miss, University of Southern California
  - Michigan State University
  - ATA Engineering
  - Teledyne Energy Systems
  - HS Rocketdyne