# Life testing of segmented high efficiency thermoelectric couples

**Jong-Ah (Jay) Paik, Samad Firdosy, Billy Li, Vilupanur Ravi, George Nakatsukasa, Leslie D. Zoltan, Chen-Kuo Huang, Bijiang Cheng, Erik Brandon, Richard Ewell, Thierry Caillat and Jean-Pierre Fleurial**

**Jet Propulsion Laboratory**
**California Institute of Technology**


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- Couple life test
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# The evolution of RTGs

**MHW-RTG**

*TRL 9-10*

158 We
4.2W/kg

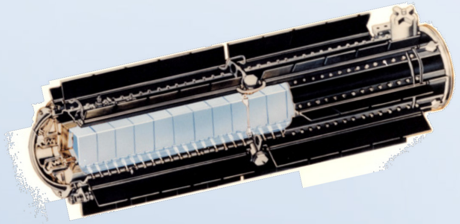
6. 6% Efficiency

> 30 Year life demonstrated

- *LES 8/9, Voyager 1 & 2*

**GPHS-RTG**

*TRL 9-10*



283We
5.1 W/kg
6. 8% Efficiency
> 18 Year life demonstrated

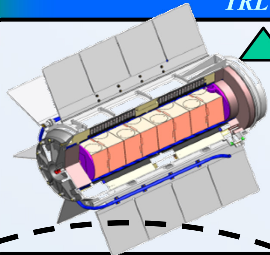
- *Ulysses, Galileo, Cassini, New Horizons*

*TRL 5-6* *TRL 7-8*

**MMRTG**

125 We
2.8 W/kg

6.3% Efficiency
- *MSL*



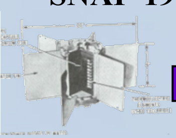
*TRL 1-2* *TRL 3-4* *TRL 5*

**ARTG**

6-8 W/kg
> 10% efficiency

Requires > 12% efficient couple technology

**SNAP-19**

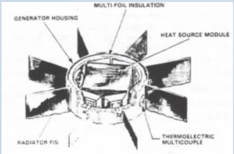


*TRL 9-10*

40 We
3 W/kg
6. 2% Efficiency
➢14 Year life
➢*Pioneer 10&11, Viking 1 & 2*

**MOD-RTG**

*TRL 3-6*




*Projected Performance*

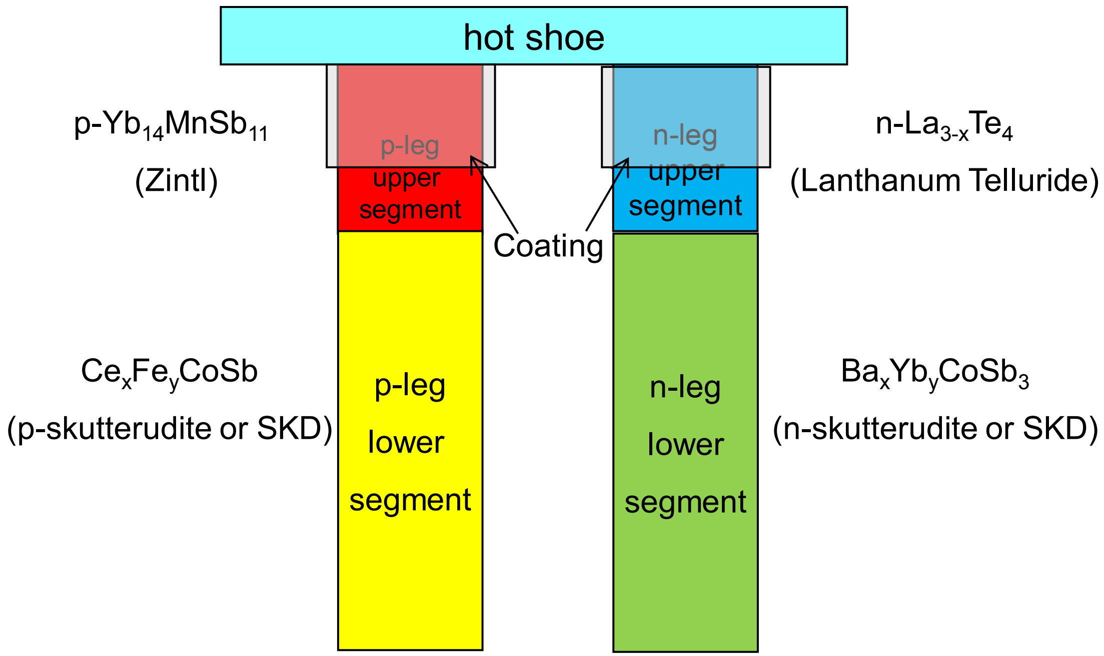
330 We
7.7 W/kg
6. 8% Efficiency (Si-Ge)
> 14 Year life

**1970 1980 1990 2000 2004 2006 2010**

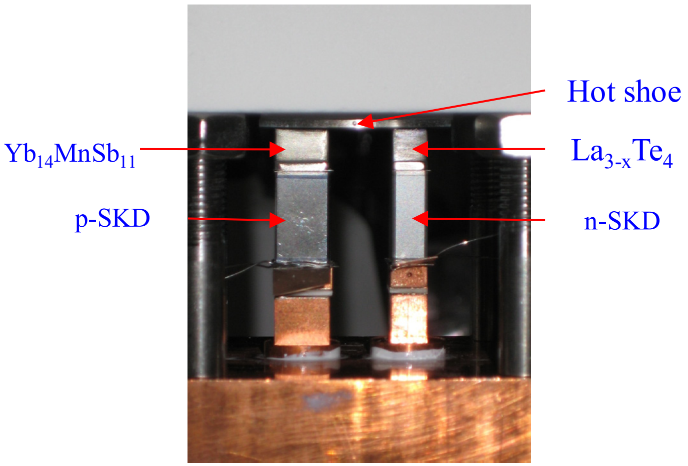


*NOTE: Graphics not to Scale*

# High efficiency thermoelectric couple




**Simplified scheme of a segmented couple**




**Segmented high efficiency thermoelectric couple**
**( up to 15% efficiency, up to 1273 K hot side operation)**

# What controls RTGs Lifetime Performance?

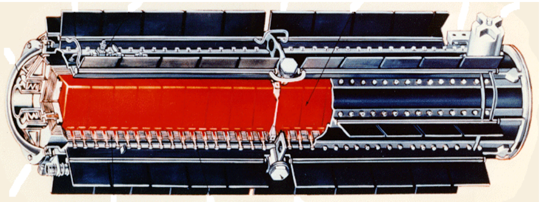
**Degradation mechanisms**

1. Fuel decay (Reduced heat from GPHS)

2. Decrease in hot-junction as a result of decreasing heat input
(smaller DT = lower Carnot efficiency)

3. Main other mechanisms dependent on time and temperature
   - Degradation of thermoelectric properties (lower ZT values)
   - Sublimation losses (increased TE leg electrical & thermal resistance)
   - Thermoelectric couple interfaces (increased electrical contact resistances)
   - Thermal insulation (reduced thermal efficiency)

**GPHS RTG**



~ 0.8%/year decrease in power output

+

~ 0.5%/year decrease in power output

+

Decrease in power output:
~ 0.3%/year

(~5% over 14 years)

=

Decrease in power output:
~ 1.6%/year total

(22% total over 14 years of operation)

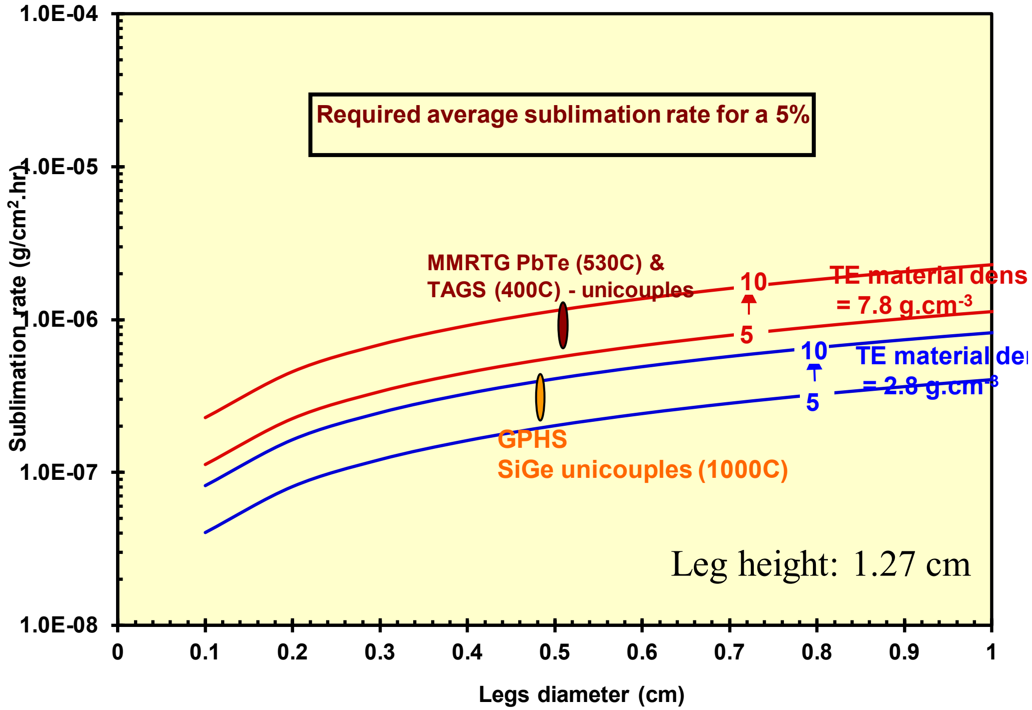
# Establishing life time performance

- Component life test
  - Subjects for component life test
    - Sublimation
    - Thermoelectric properties of materials
    - Bonding interfaces
  - Design, fabricate and test coupons to quantify each degradation mechanism and assess kinetics
  - Test duration will depend on kinetics
  - Develop models
- Couple life test
  - Steady state nominal and accelerated operating conditions
  - Prototypic single couple and multi-couple assembly
- Update performance model (DEGRA) and validate predictions

# Component life test
## (sublimation life test)

# Sublimation suppression

- **Sublimation suppression goal**
  - **10% cross sectional reduction at the hot end of the leg after 14 years operation (2~3% reduction in power output)**

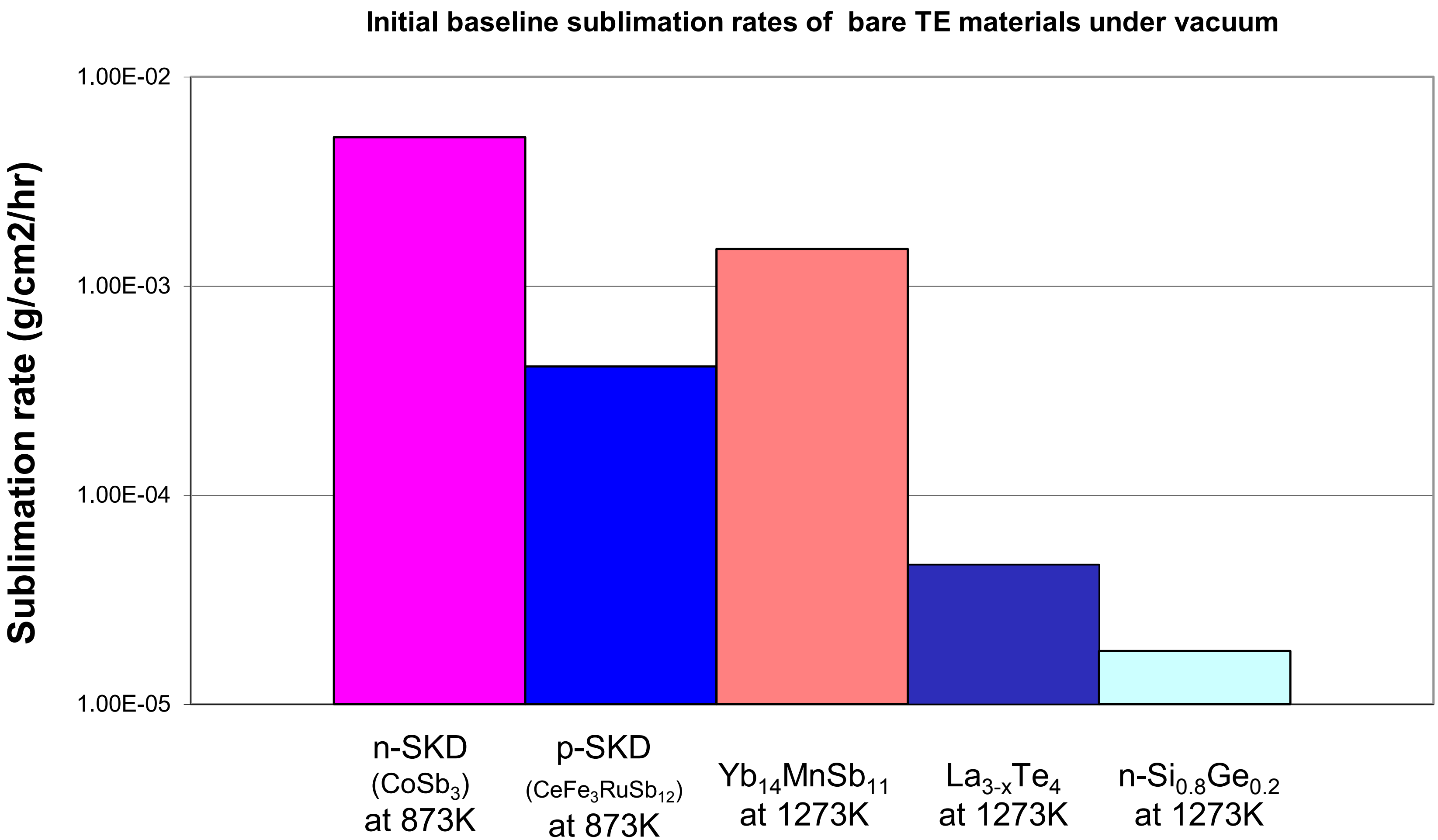



- **Sublimation phenomenon**
  - Most of TE materials used in power generation have peak figures of merit at the temperature where sublimation is a non-negligible mechanism
  - Sublimation leads to reduction of effective cross section, which leads to decrease in power output
  - Sublimed species can condense on cold side, which can cause short circuit on the device.
  - State of practice power generation thermoelectric couples have always some measure of sublimation control.

- **Background on previous sublimation suppression methods**
  - SiGe technology employed $Si_3N_4$ thin films
  - PbTe/TAGS technology employed an inert cover gas and solid insulation
  - Skutterudite technology uses opacified aerogel

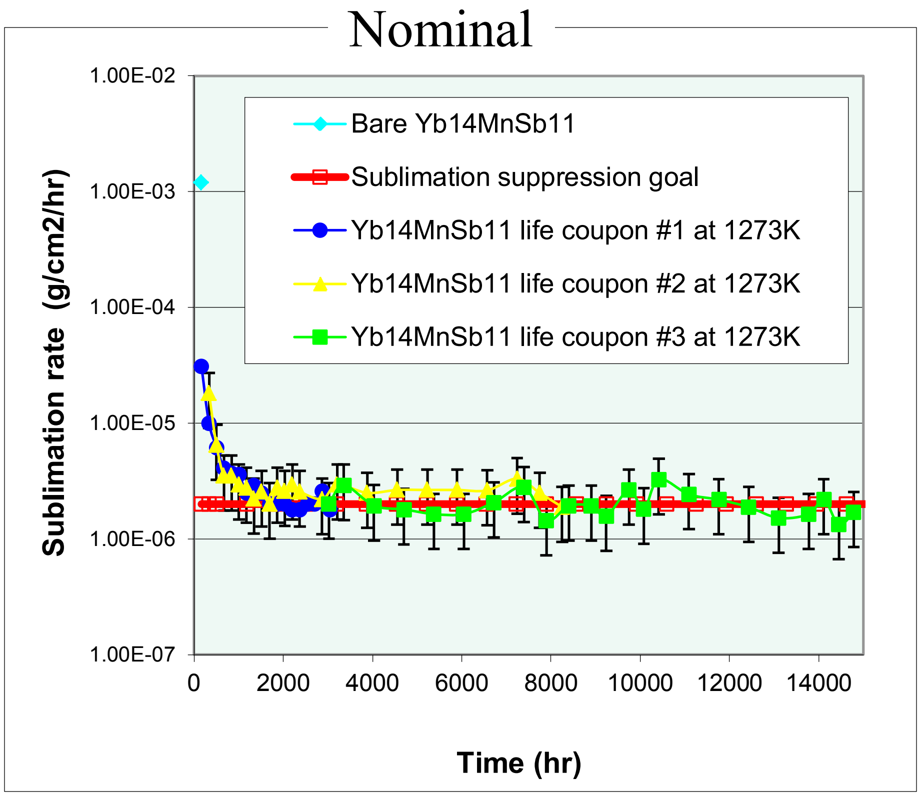
- **Requirements for sublimation suppression barriers**
  - Chemical stability against TE materials
  - Thermal stability at the operating temperature
  - Withstanding stress during thermal cycling
  - No significant effect on system performance

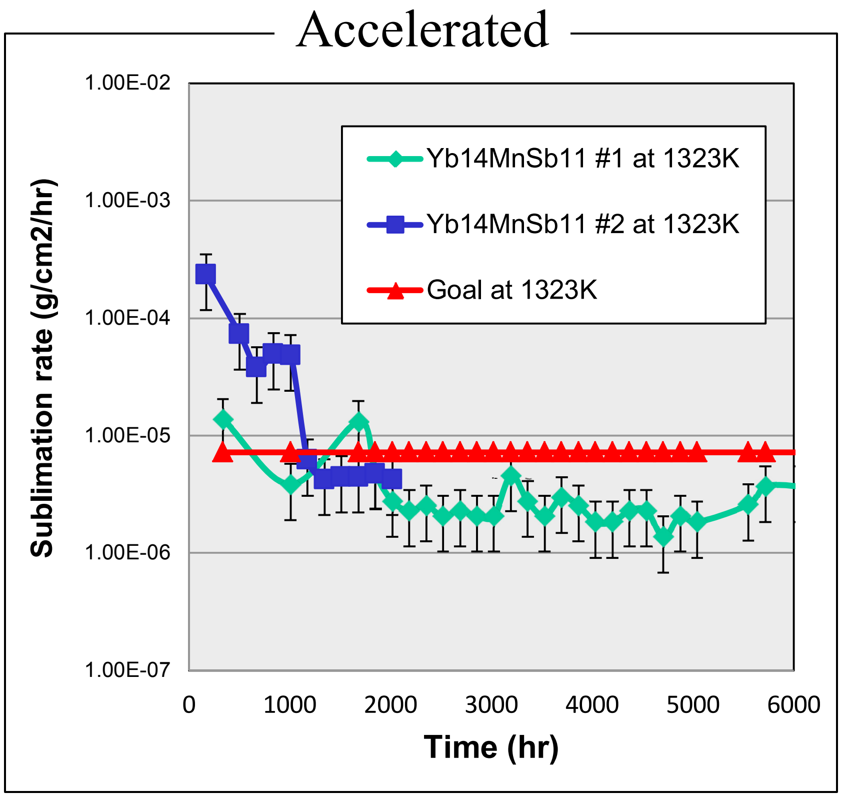
# Beginning of life sublimation rate of bare TE materials in vacuum




- **All the thermoelectric materials for RTG require some measure of sublimation suppression scheme (need $10^{-6}$ to $10^{-7}$ g/cm$^2$/hr)**

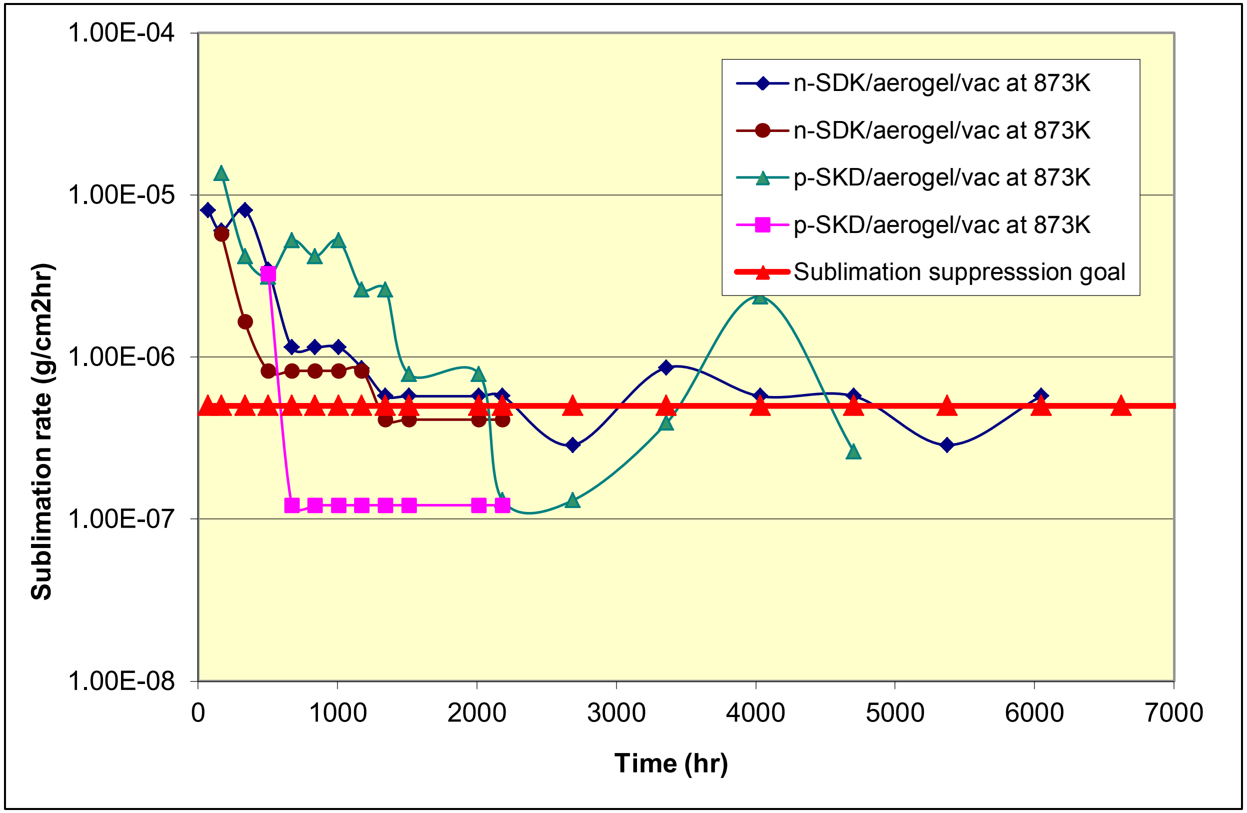
# $Yb_{14}MnSb_{11}$ sublimation life test with porous alumina layer at 1273K and 1323K




- **Sublimation rate continuously met the goal during 18 month coupon test.**
- **Accelerated test at 1323K also confirmed sublimation suppression of $Yb_{14}MnSb_{11}$ with alumina paste layer**
- **In spite of several thermal cycles, sublimation rates remained unaffected.**
- **<u>Successfully demonstrated</u> life time control of sublimation of $Yb_{14}MnSb_{11}$**

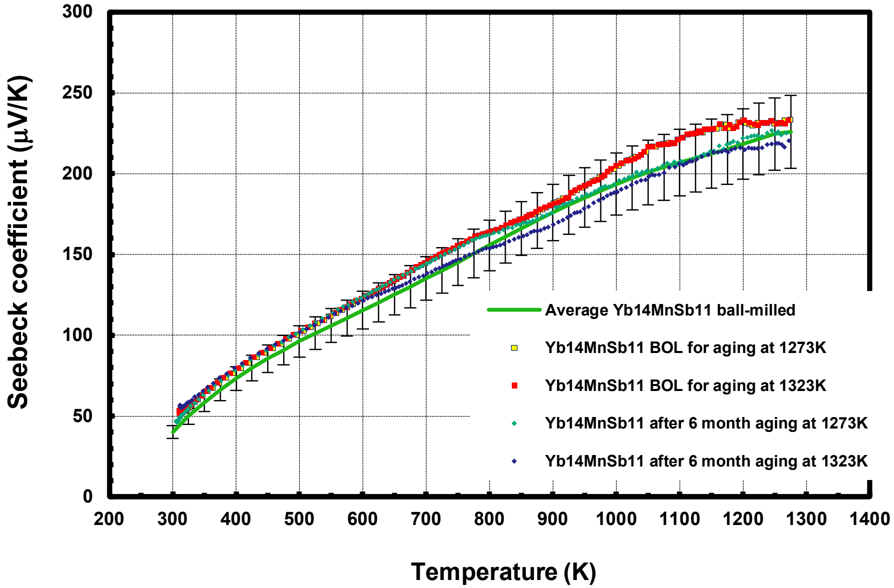
# Skutterudite sublimation life test with aerogel at 873K

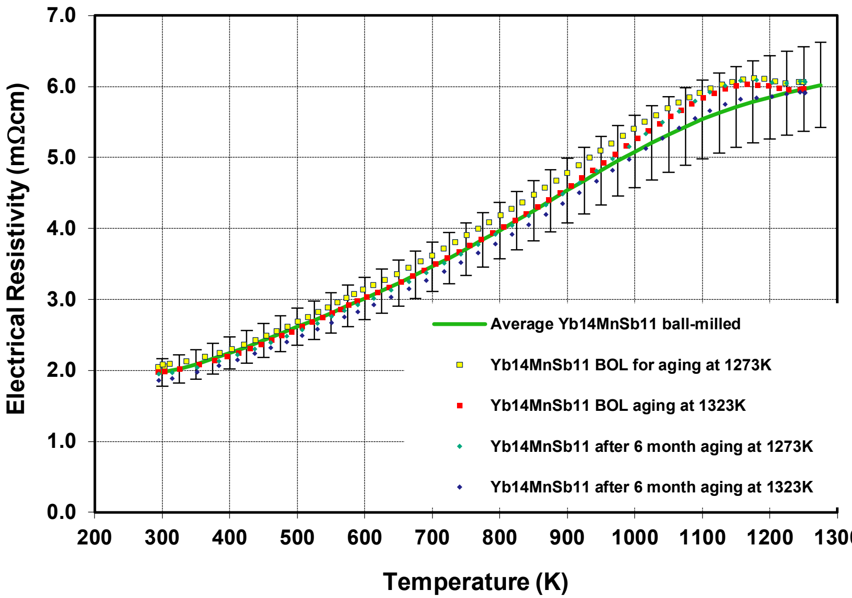


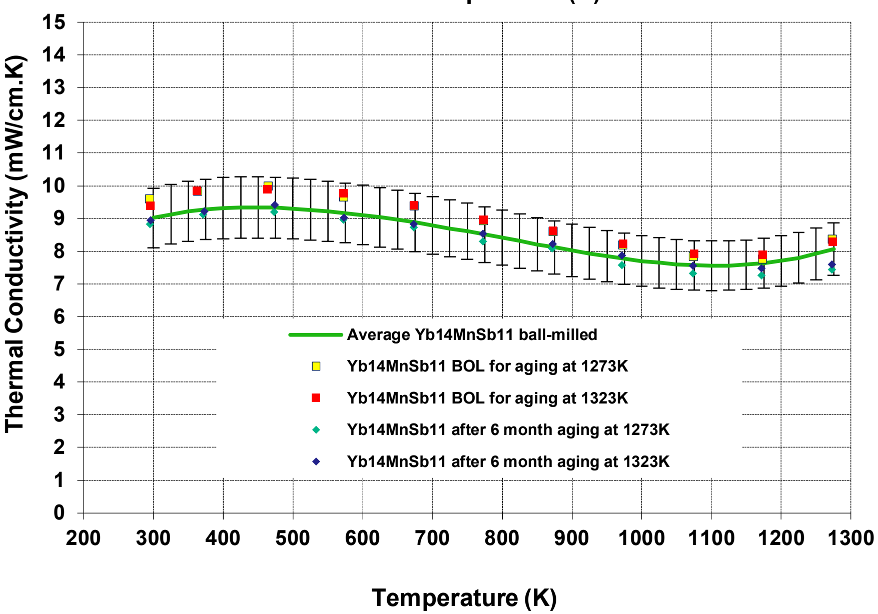

- **Sublimation rate continuously met the goal during 6 month coupon test.**
- **In spite of several thermal cycles, sublimation rates remained unaffected.**
- **<u>Successfully demonstrated</u> life time control of sublimation of skutterudite**

# Component life test
## (TE properties life test)

# Stable TE properties for $Yb_{14}MnSb_{11}$



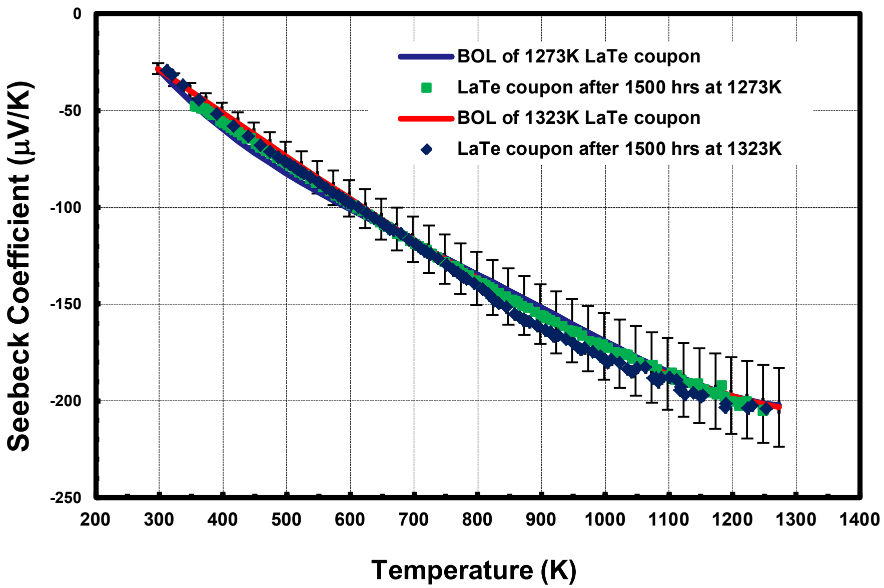



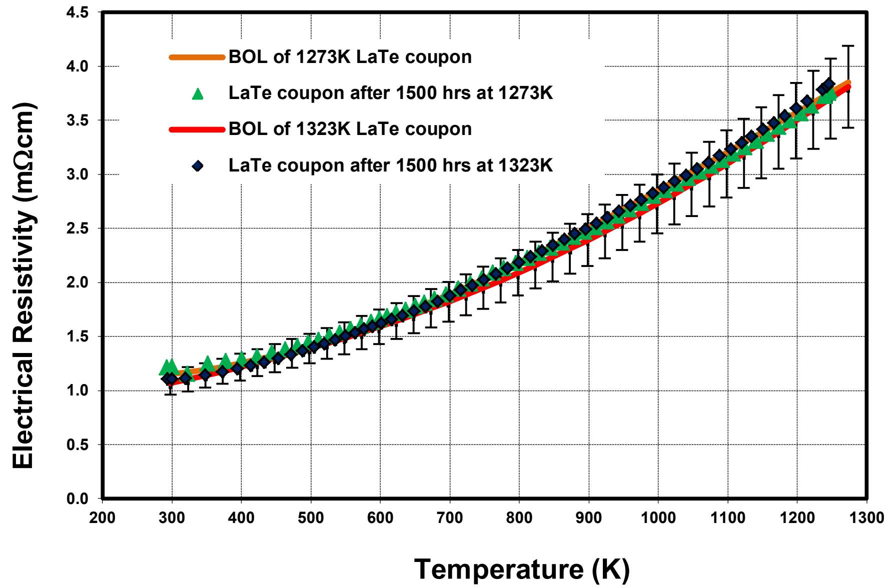



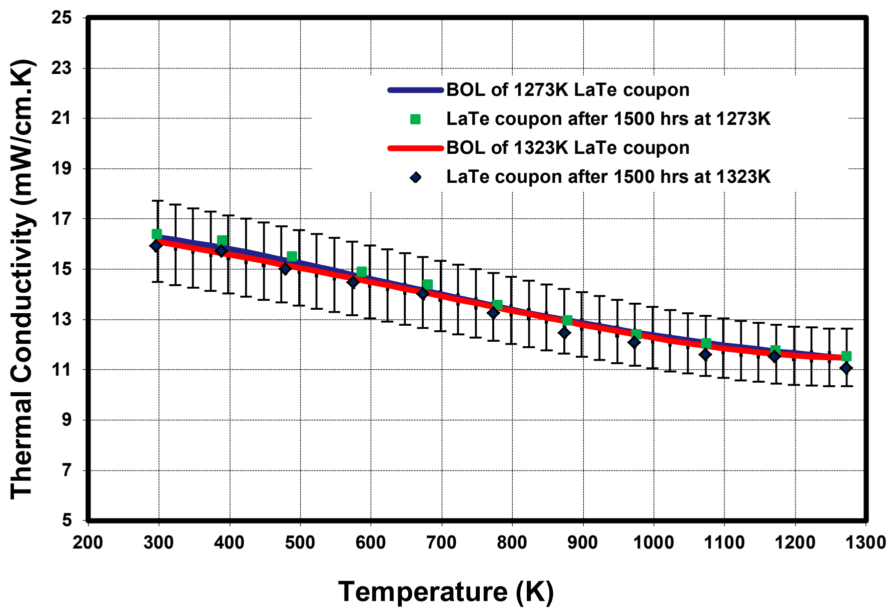

**5000hr – nominal and accelerated operating conditions (1273 K and 1323K)**

**All the three TE properties of $Yb_{14}MnSb_{11}$ (Seebeck coefficient, electrical resistance, and thermal conductivity) remained unchanged**

# Stable TE properties for $La_{3-x}Te_4$



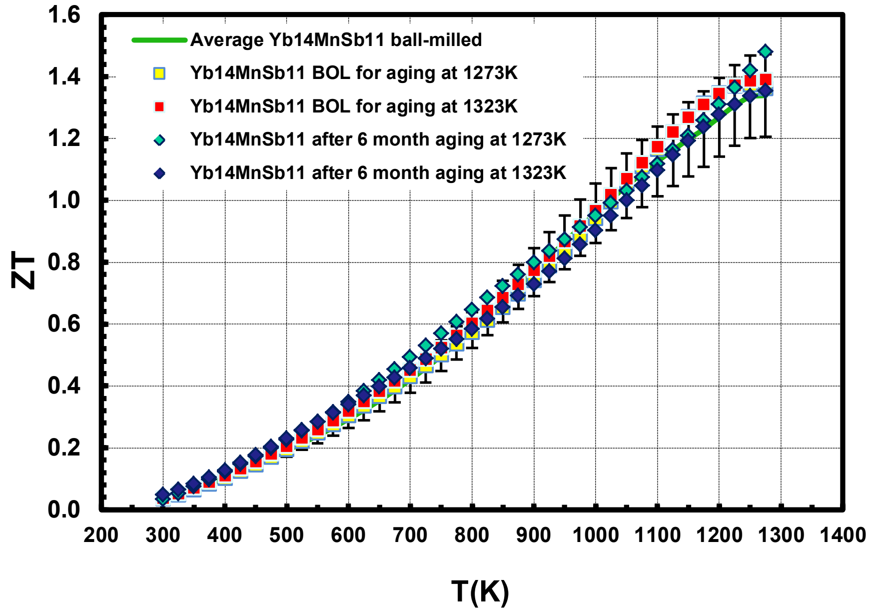




**1500hr – nominal and accelerated operating conditions (1273 K and 1323K)**

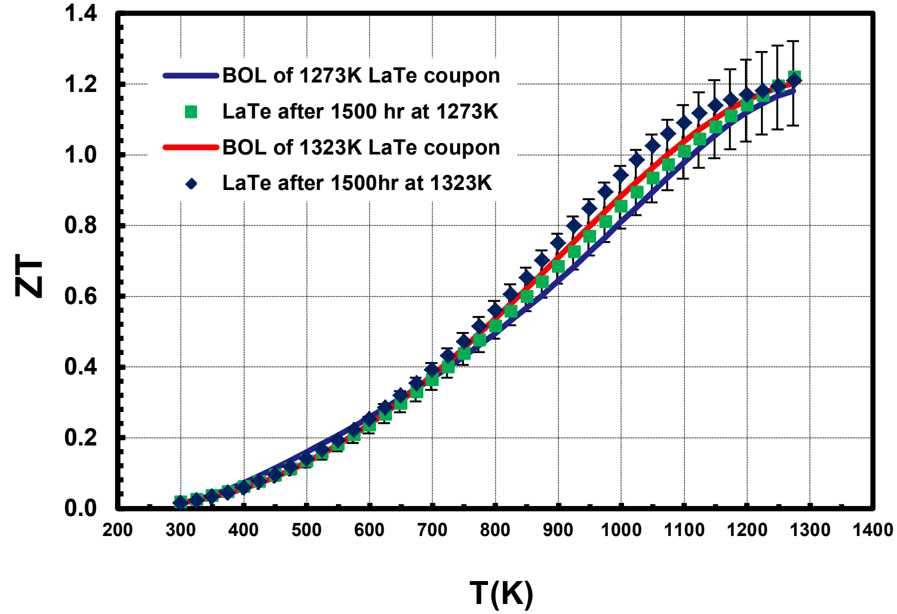
**All the three TE properties of $La_{3-x}Te_4$ (Seebeck coefficient, electrical resistance, and thermal conductivity) remained unchanged**

# Stable Figure of Merit of $Yb_{14}MnSb_{11}$ and $La_{3-x}Te_4$

## $Yb_{14}MnSb_{11}$ after 6 month aging




## $La_{3-x}Te_4$ after 2 month aging

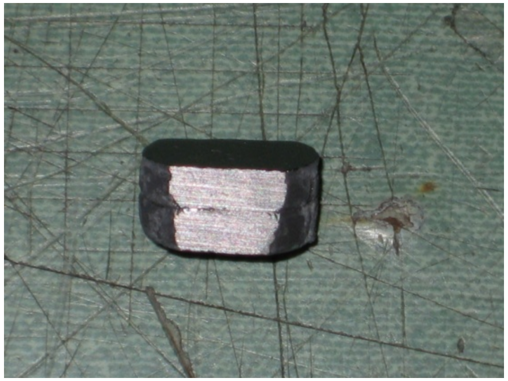



- Figure of merit was maintained after aging at either 1273K or 1323K
- There is no degradation on TE properties of $Yb_{14}MnSb_{11}$ and $La_{3-x}Te_4$ after aging at either 1273K or 1323K.
- Further life test is in-progress

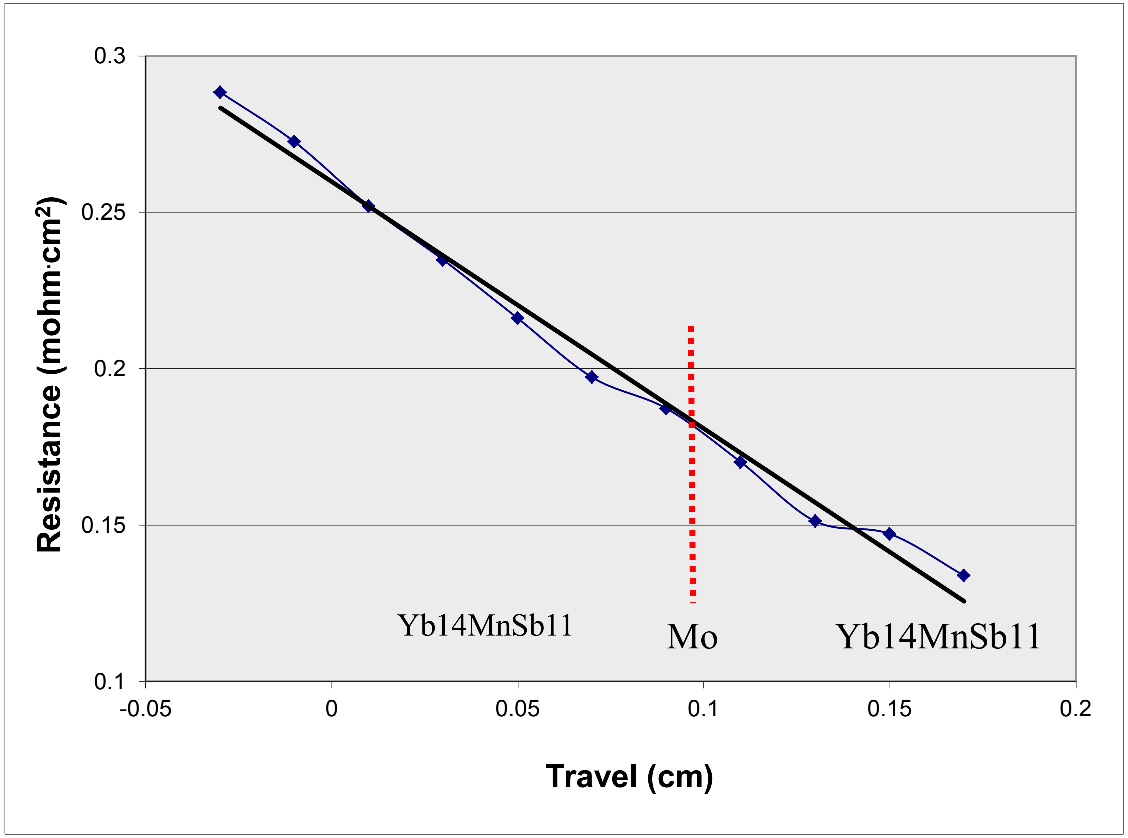
# Component life test

## (Contact resistance life test)

# $Yb_{14}MnSb_{11}$ Electrical Contact Resistance Life Test
# Stable Performance after 1500 hr aging at 1273K



$Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ coupon after 1500 hr aging at 1273K




- **A $Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ coupon showed no measurable contact resistance after 1500 hr at 1273K.**

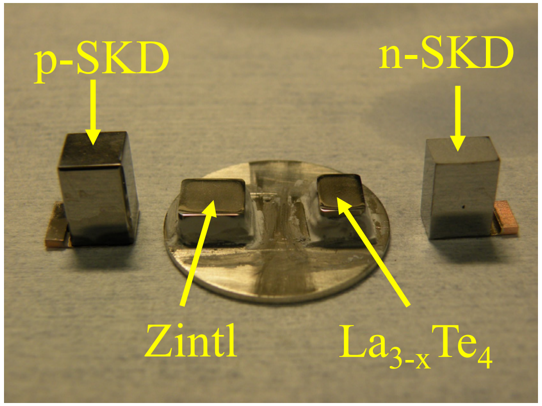
# Status of TE materials for high efficiency couples

| | n-type Skutterudite | p-type Skutterudite | $Yb_{14}MnSb_{11}$ (Zintl) | $La_{3-x}Te_4$ |
|---|---|---|---|---|
| Maximum operating temperature | 873K | 873K | 1273K | 1273K |
| Average ZT | 1.01 [873 to 473K] | 0.78 [873 to 473K] | 0.98 [1273 to 773K] | 0.88 [1273 to 473K] |
| TE Properties life test | >10,000 hrs at 873 K (from couple test) | | >5,000 hrs at 1273K and 1323K | > 1,500 hrs at 1273K and 1323K |
| Sublimation suppression | Demonstrated with aerogel ($5\times 10^{-7}$ g/cm$^2$/hr for 6000 hrs at 873K) | | Demonstrated with alumina paste ($2\times 10^{-6}$ g/cm$^2$/hr for >15,000 hrs at 1273K) | Not required up to 1173K |
| Contact Metallization | >1500 hr aging at 873 K | | >1500 hr aging at 1273K | >1000 hr aging at 1273K |

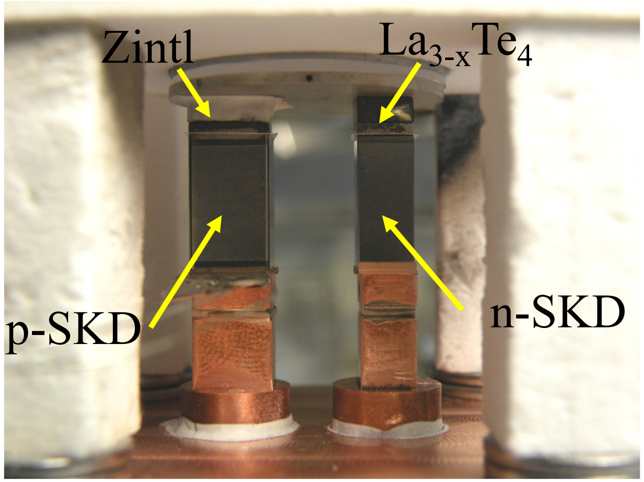
# Couple life test

# Couple Fabrication and Assembly

Fixturing for Couple Component Fabrication




Couple Fabrication – HT stage and LT segments

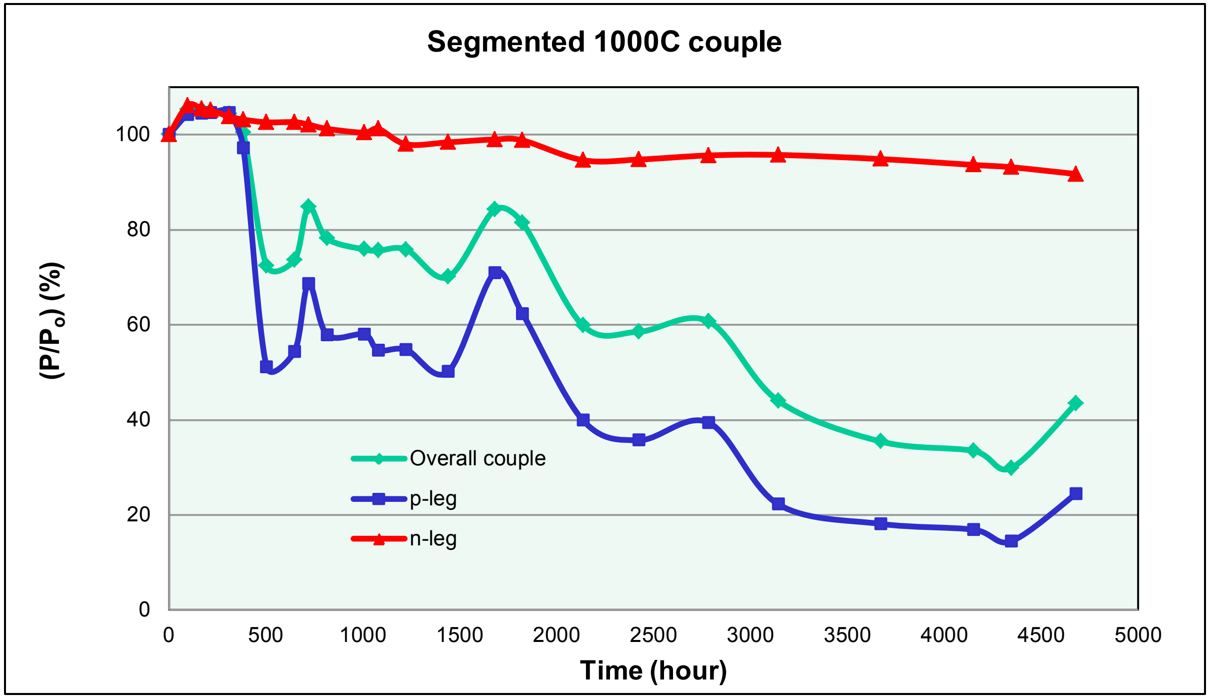



Couple assembled in test fixture

Sublimation coating applied & thermal insulation installation

# Extended Testing of 1000 C Couples

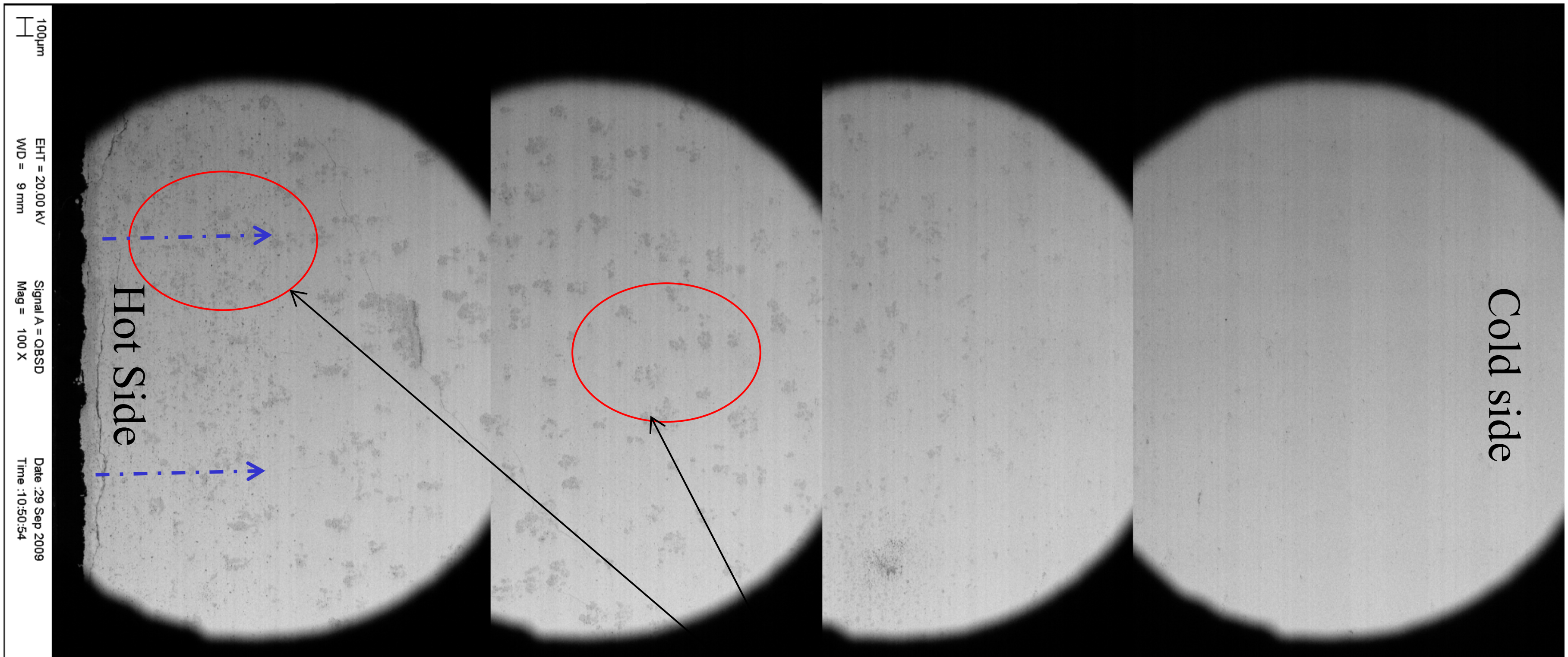
**Couple Performance vs. Time**




- **Extended testing performed on several segmented couples**
- **~95% of BOL power output was maintained after 5000 hr operation of 800C segmented couples.**
- **Performance decrease with time is highly dependent on maximum operating temperature**
- **Hot side interfaces are main root cause**
  - **Especially significant for Zintl p-leg**

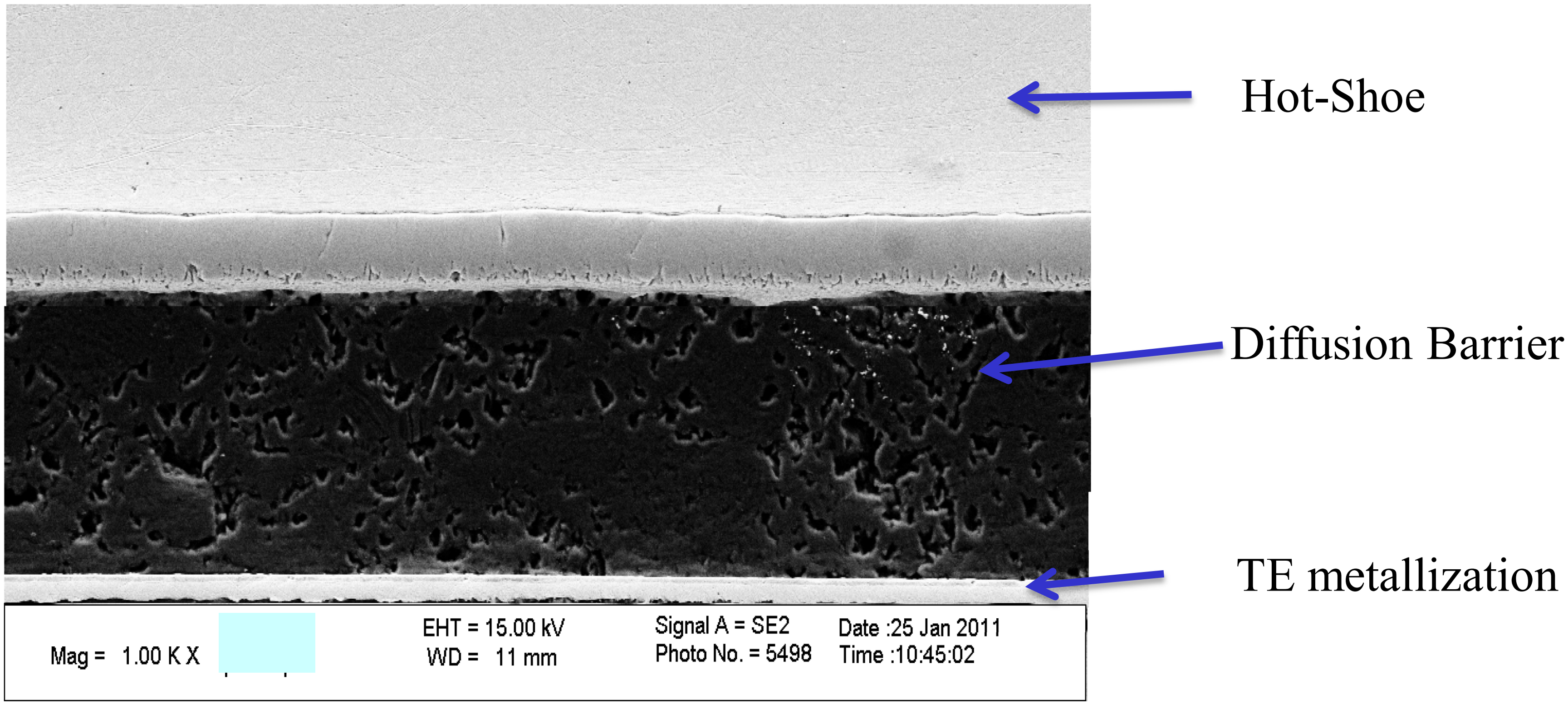
# Hot Side Interface Stability Challenges

- **Hot shoe interface degradation limits lifetime of current couple configurations operating above 1073K hot side temperatures**
- **Development of diffusion barriers to protect metal/TE contacts is required**



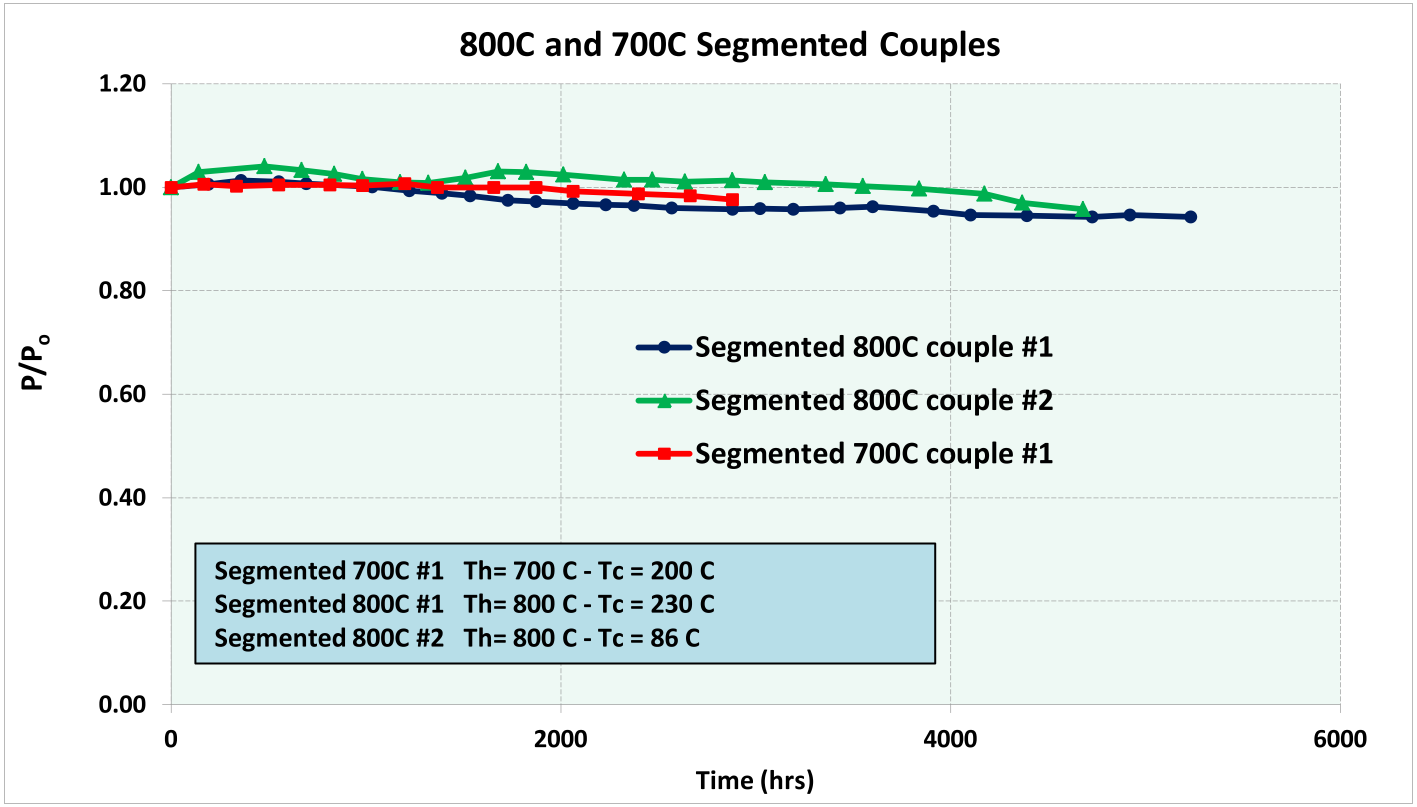

Hot shoe metal poisoning in p-Zintl leg of unsegmented couple after > 1000 hour operation at $T_h \sim 1273$ K (composite view)

# Hot Side Diffusion Barrier Development




- Several promising candidates have been identified
- Currently doing extended testing at the coupon level
- Planning on integrating diffusion barriers in next series of couples

# Extended Testing of 800C and 700C Segmented Couples




- **700C and 800C segmented couples maintained most of BOL power output during extended couple testing**
  - 800C segmented couples: ~95% of BOL power output after 5000 hr operation
  - 700C segmented couples: ~97% of BOL power output after 3000 hr operation
- **Degradation of p-leg (Zintl) from hot shoe metal poisoning is alleviated when the couples are operated at lower temperature.**

# Segmented Couples – Current Status

| | Segmented spring-loaded couple | | | |
|---|---|---|---|---|
| Upper segments | p-$Yb_{14}MnSb_{11}$ Zintl/n-$La_{3-x}Te_4$ | | | |
| Lower segments | p-SKD/n-SKD (Filled Skutterudites) | | | |
| Hot/ cold side temperature (K) | 1273/473 | 1173/473 | 1073/473 | 973/473 |
| | ($T_{SKD\text{-}interface}$ ~ 873K) | | | |
| BOL predicted couple efficiency | **13.7%** | 12.5% | **11.2%** | **10.0%** |
| Comments | Validated at BOL (**14.8%**) (1500 h to date) | Not fabricate d to date | Validated at BOL (**11%**)<br>Maintained ~95% of BOL power output after 5000hrs | Validated at BOL (**10%**)<br>Maintained ~97% of BOL power output after 3000hrs |

# Summary

- **Component life demonstrated that Skutterudites, $Yb_{14}MnSb_{11}$, and $La_{3-x}Te_4$ are acceptable for long life operation**
  - Vacuum or inert gas operation
  - Life test results to date indicate that these TE materials are ready for couple technology development (further verification is in-progress with extended life tests).
- **Developed effective sublimation suppression methods**
  - Porous coating on $Yb_{14}MnSb_{11}$
  - Aerogel on skutterudites
  - Assessment of sublimation kinetics indicates that the sublimation rate is likely to remain unchanged for the desired life time.
- **Segmented couple test demonstrated achieving predicted BOL efficiency**
- **Lower temperature segmented couples maintained BOL power output during life test**
  - 800C segmented couple : ~ 95% of BOL power output after 5000hr operation
  - 700C segmented couple : ~ 97% of BOL power output after 3000hr operation
- **On-going and future coupon and couples performance life tests will be used to verify degradation rates**

# Acknowledgements

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