Evaluation of Thermal to Electrical Energy Conversion of High Temperature Skutterudite-Based Thermoelectric Modules

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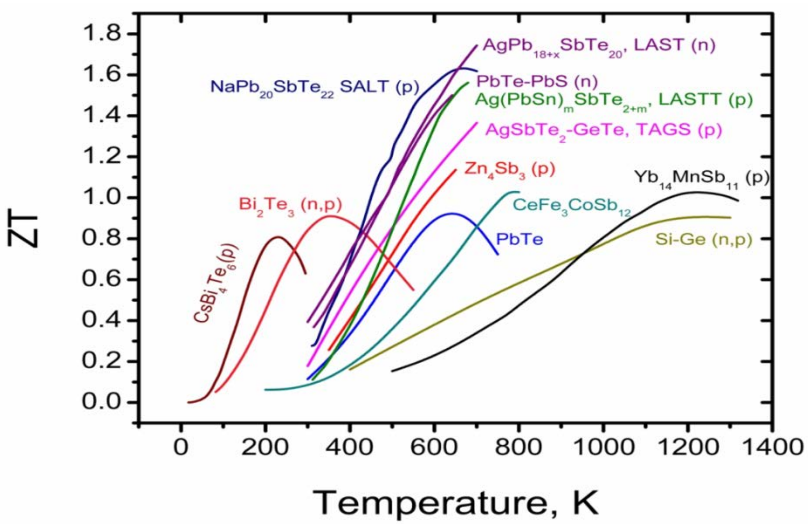
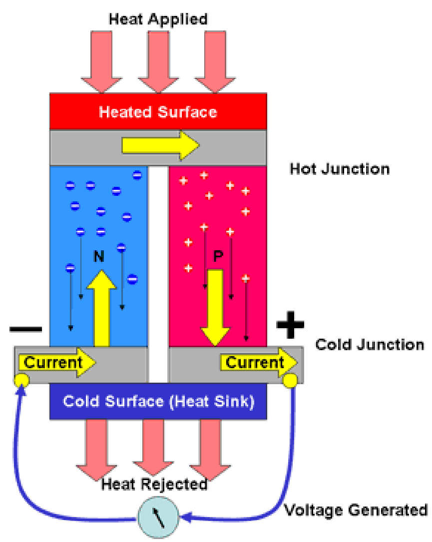
Transitioning Lab Scale to Large Scale: Challenges

In the last two decades numerous University labs have demonstrated significant improvements in *ZT,* nearly doubling the value.

Despite this progress no new materials have transitioned to new products such as high temperature modules or power generation devices.





Semiconductor Thermocouple
Seebeck Effect

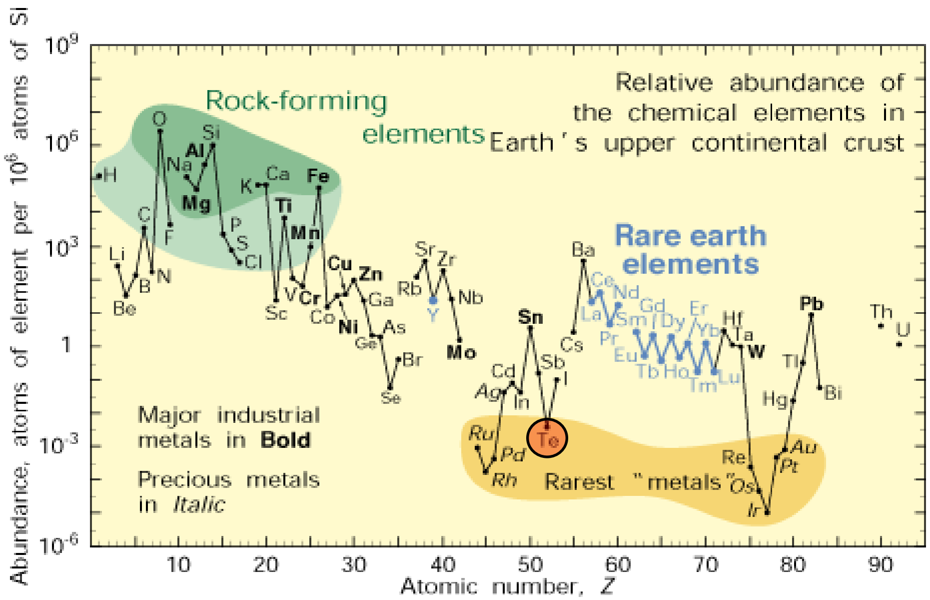
$$ZT = \frac{S^2}{\rho \cdot \kappa} T$$

$$Q = \frac{-A(T_2 - T_1) \times \kappa}{x}$$

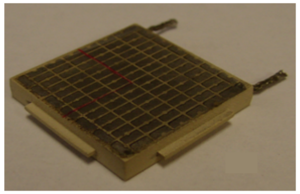
$$P_{Joule} = V_{OC}^2 \frac{R_{Int}}{(R_{Load} + R_{Int})^2}$$

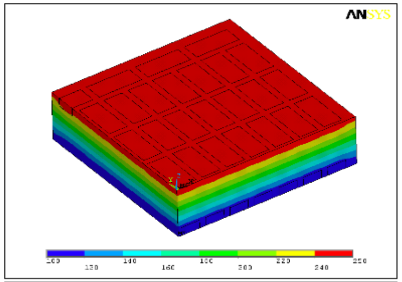
Transitioning Lab Scale to Large Scale: Challenges

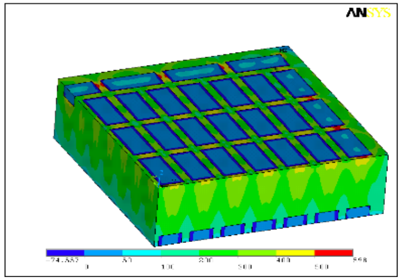
ZT is only part of the story: Raw material cost and availability as well as mechanical strength and chemical stability need consideration.

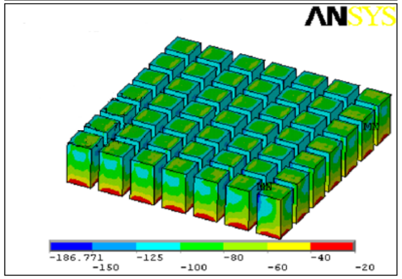


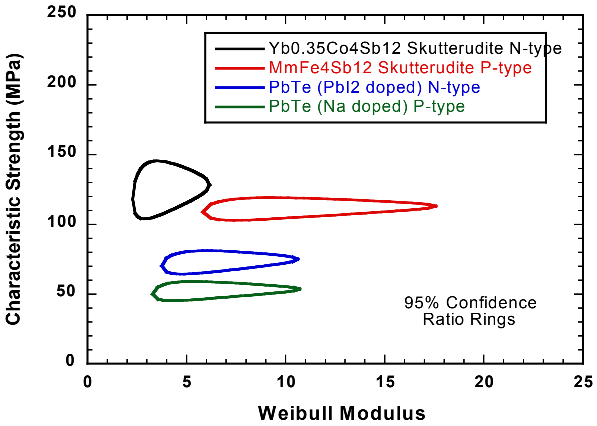
For perspective in 2008, (mainly due to refining shortages) 1 kg of solar grade polycrystalline silicon $450.00 [2]







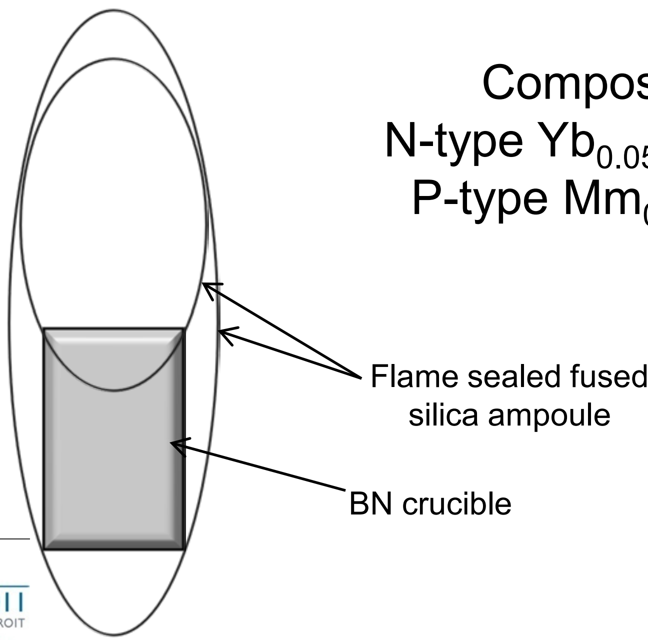




Preparation of Skutterudites

Co(and Fe) and Sb shot were pre-melted by induction at 1400 °C in a ratio of 1:3 in BN

Filler species and melt Combined in BN crucible. Induction melted at 1200 °C 5min. Followed by annealing at 700 °C for 1 week.



Compositions Targeted

N-type $Yb_{0.05}Ba_{0.08}La_{0.05}Co_4Sb_{12}$

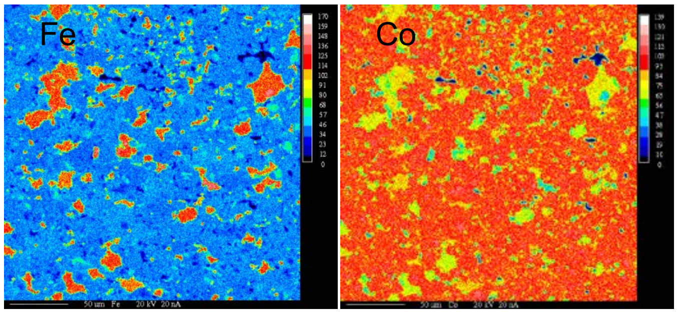
P-type $Mm_{0.28}Fe_{1.52}Co_{2.48}Sb_{12}$

Resulting melt was ground, cold pressed and annealed for an additional week

Annealed pellets were reground sieved and consolidated by SPS typical grain size ~3µm

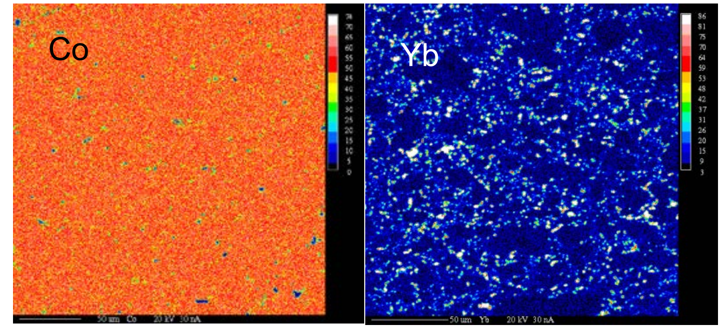
Ingot 98.5% or higher of theoretical density

3.0 kg of n- and p-type Skutterudites Prepared

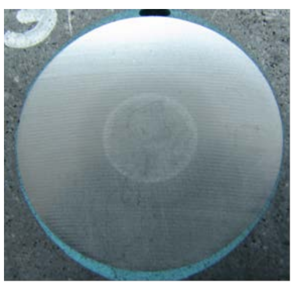


P-type material was grossly inhomogeneous

Refinement of skutterudite preparation will be required going forward.

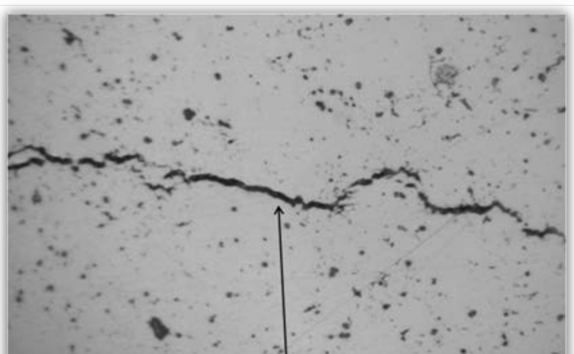


N-type material was homogenous but contained significant amounts of Yb-oxide. It does not seem to affect transport. Its just wasteful.



3.0 cm puck

Significant difficulty in powder processing

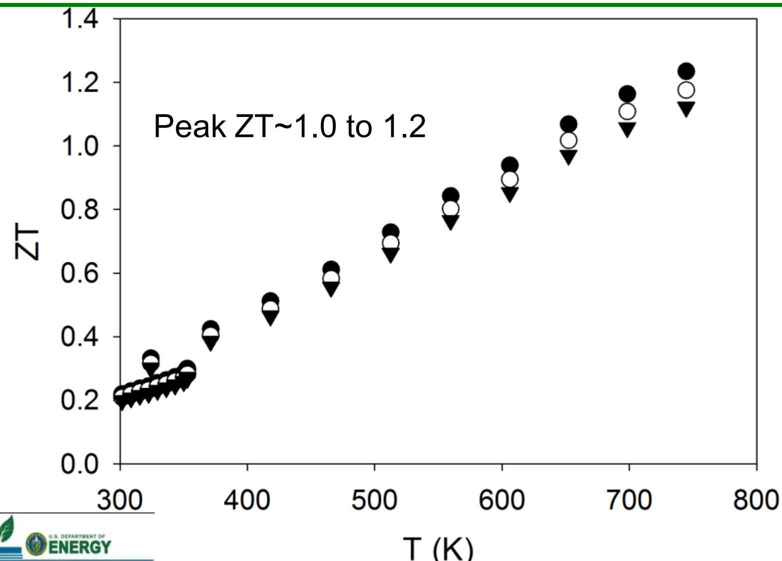


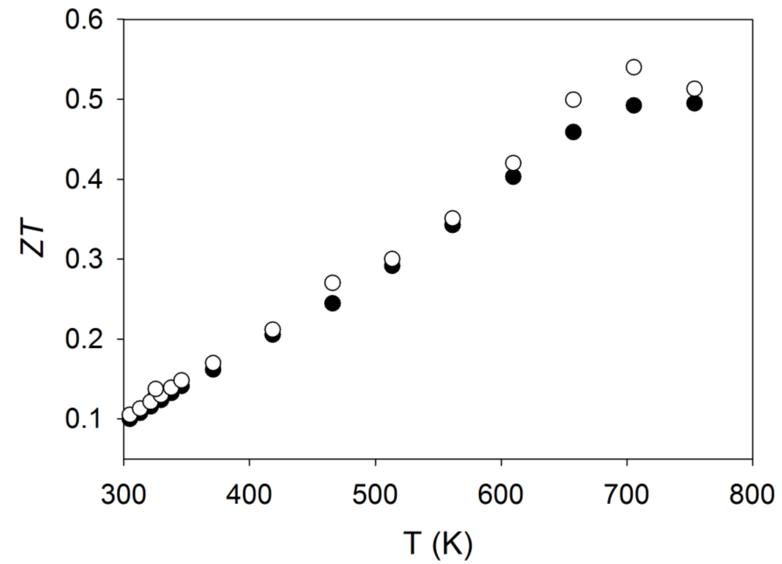
Vacated Vein Post 475C Heat Treat, 67 hours

Scaled up Synthesis and Skutterudite Module Fabrication

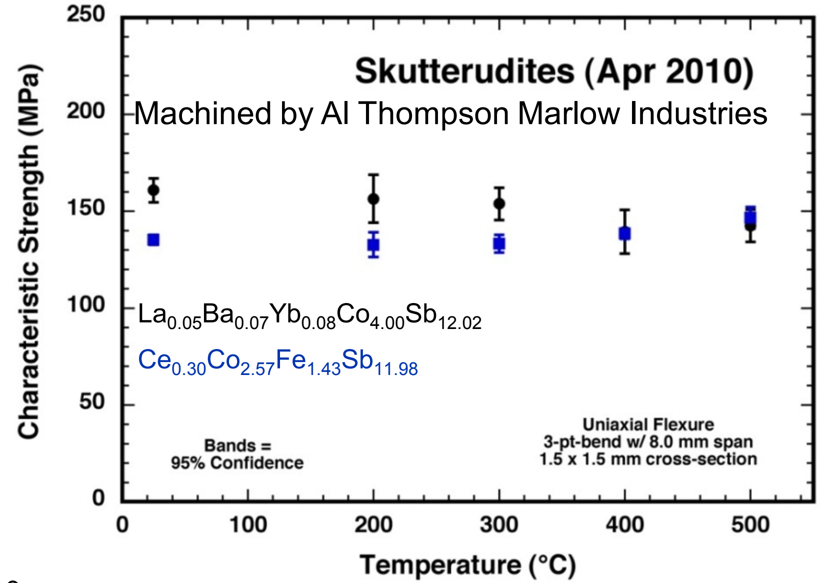
Lot # N-type	κ (W/m·K)	ρ (mΩ·cm)	S (μV/K)
1	3.5	0.45	-115
2	3.6	0.45	-112
3	3.7	0.40	-111
4	3.5	0.35	-110
5	3.8	0.3	-100
6	3.8	0.33	-100

Lot # P-type	κ (W/m·K)	ρ (mΩ·cm)	S (μV/K)
1	2.77	1.13	89
2	2.70	1.18	87
3	2.75	1.27	100





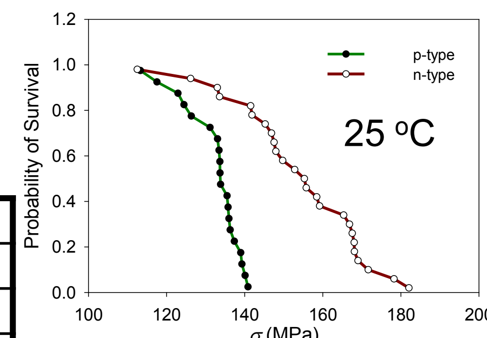
Temperature Independent Characteristic Strength

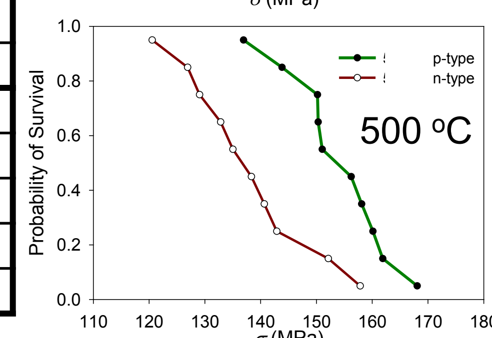


Results are for large scale (1.0 kg batches and 3.0 cm (80 g billets).

Material	Temp (°C)	# of Tests	|------- 2- parameter Weibull -------| Characteristic Strength* (MPa)	Weibull Modulus*	|-- Gaussian --| Ave. Strength (MPa)	Std. Dev. (MPa)
(n-type)	25	25	160	10.6	154	17
	200	14	156	6.7	148	20
	300	15	154	9.6	147	16
	400	15	139	6.4	130	25
	500	15	143	8.8	135	17
(p-type)	25	20	135	24.2	132	8
	200	14	133	10.8	127	21
	300	15	133	15.0	129	11
	400	15	138	28.4	136	7
	500	15	147	13.4	142	12

* Values in parenthesis = ± 95% confidence interval





Scaled up Synthesis and Skutterudite Module Fabrication

Module #	Module Impedance(Ω) Lot #1	Module Impedance (Ω) Lot #2	Module Impedance (Ω) Lot #3	Module Impedance(Ω) Lot #4
1	0.143	0.146	0.146	0.232
2	0.142	0.151	0.148	0.186
3	0.143	0.148	0.150	0.224
4	0.142	0.153	0.148	0.223
5	0.142	0.150	0.146	
6	0.143	0.148		
7	0.143	0.147		
8	0.143	0.148		
9	0.145	0.147		
10		0.156		
11		0.145		

Module Performance: Governing Equations

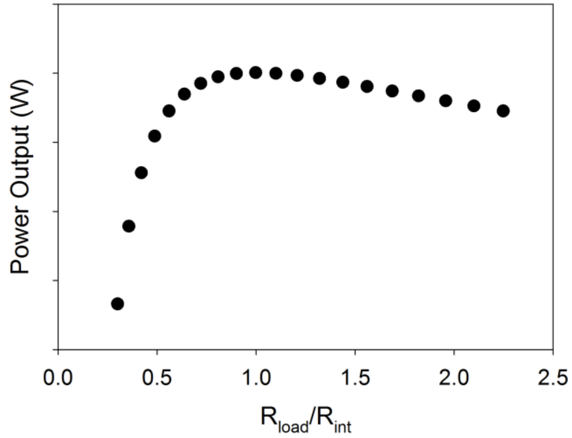
$$V_{OC} = n\int_{T_c}^{T_h} S(T)_p dT - n\int_{T_c}^{T_h} S(T)_n dT$$

$$I = \frac{V_{OC}}{(R_{int} + R_{Load})}$$

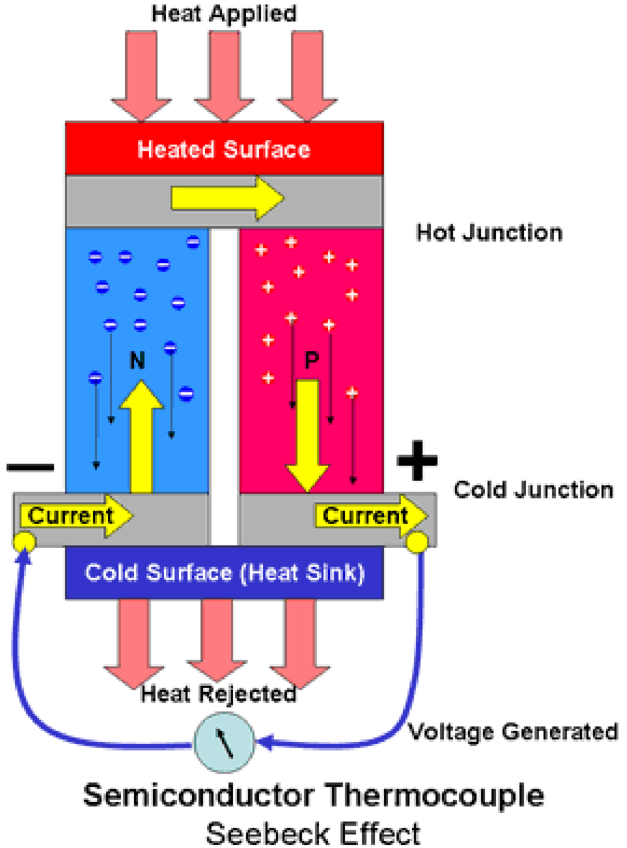
$$P_{out} = V_{OC}^2 \frac{R_{Load}}{(R_{Load} + R_{Int})^2}$$

$$Q_H = \kappa_n l_n \frac{dT}{dx} + \kappa_p l_p \frac{dT}{dx} + IT_H S - I^2 R$$

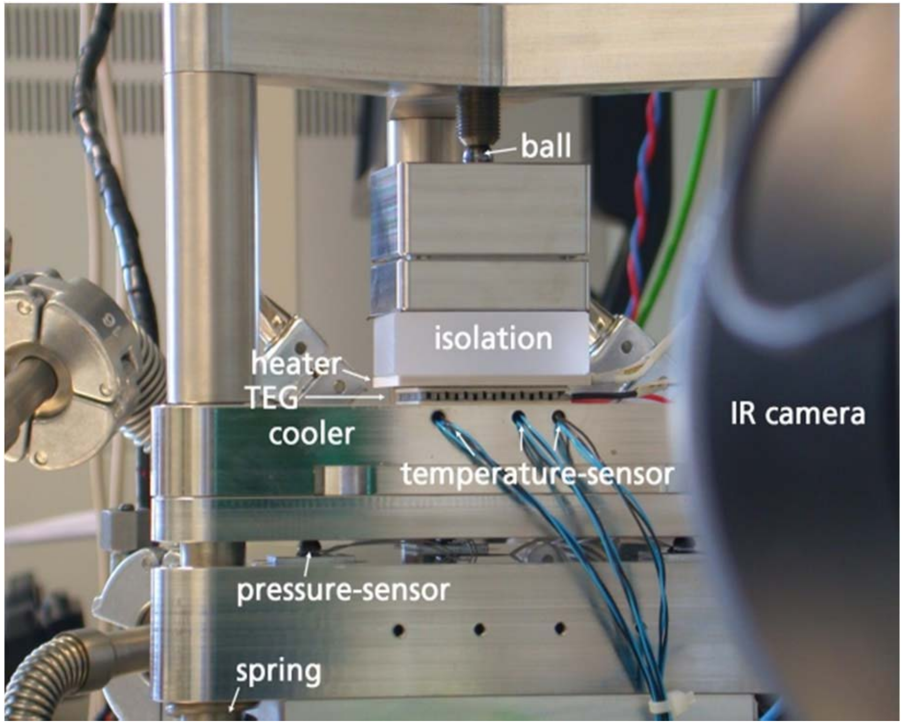
$$Q_c = \kappa_n l_n \frac{dT}{dx} + \kappa_p l_p \frac{dT}{dx} + IT_C S + I^2 R$$

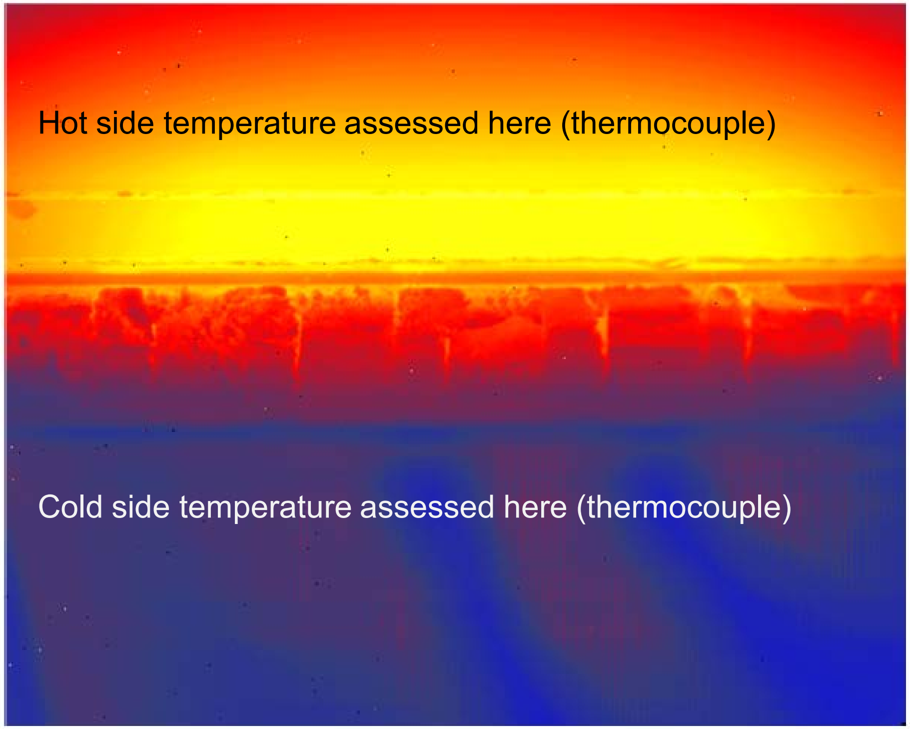


$$\text{Efficiency} = P_{out}/Q_H$$



Module Performance Evaluation





A temperature gradient is applied using a heater at the top of the module and a circulating cooling bath at the bottom. Specific temperatures are thereby maintained for the hot and cold sides of the module.

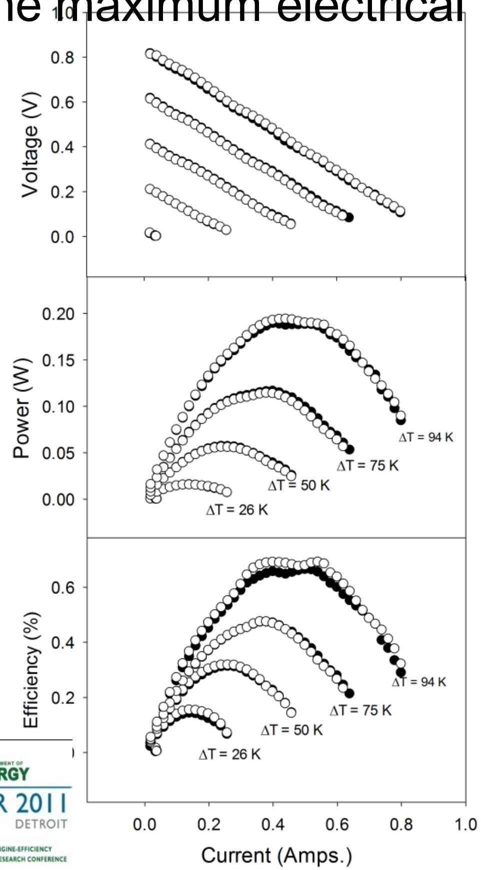
Thermography indicates that the module temperature gradient is not uniform.

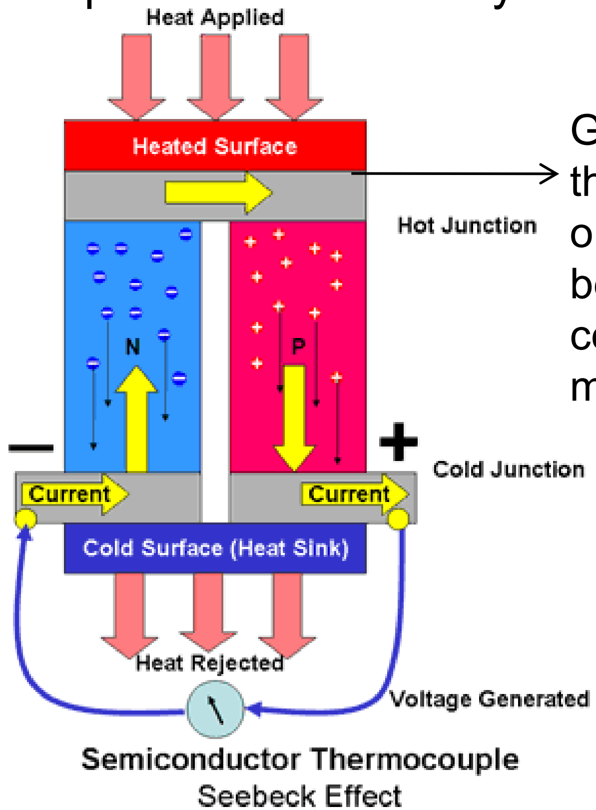
Module Performance Evaluation

The measurement : A temperature gradient is applied across the module by the establishment of a steady state heat flow Q.

The open circuit voltage is measured then current is allowed to flow and a load resistance is adjusted to trace a V and current curve.

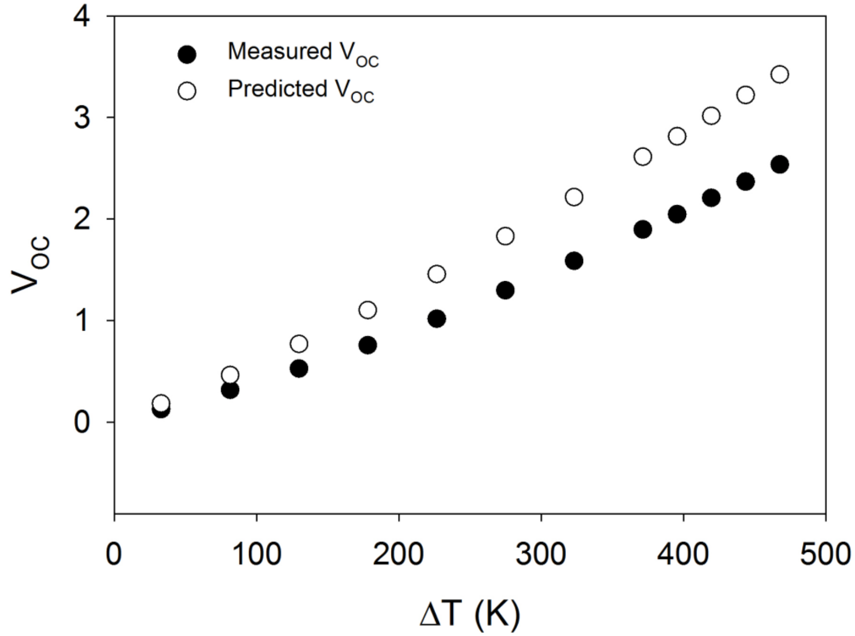
The maximum electrical power output is determined by this scanning

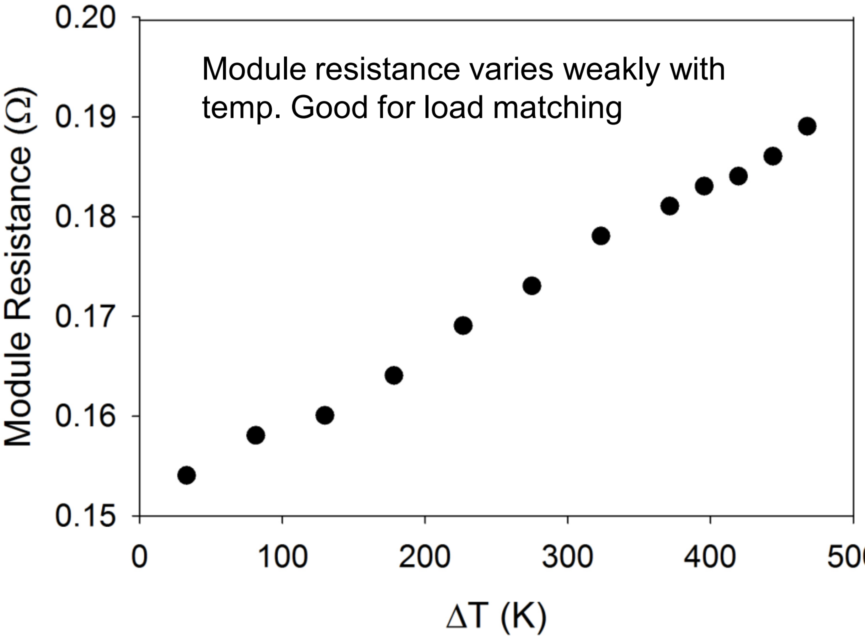




Grafoil was used as a thermal interface material on the hot and cold side between the hot source, cold sink and the ceramic module headers

Open Circuit Voltage and Module Resistance





$$V_{OC} = n\int_{T_c}^{T_h} S(T)_p\,dT - n\int_{T_c}^{T_h} S(T)_n\,dT$$

We estimate nearly 100°C temperature drop between the measurement position and the predicted hot side temperature at the top of the thermal elements. Likely a smaller temperature gap exists at the cold side. Very high thermal contact resistance reduces efficiency.

$$R_{Int} = R_{TE} + R_{CH} + R_{CH}$$

Based on the resistivities of the materials comprising the modules and their temperature dependencies, we can estimate the contact resistance to range from 26 to 40 $\mu\Omega$-cm^2 for low temperature and high temp. respectively.

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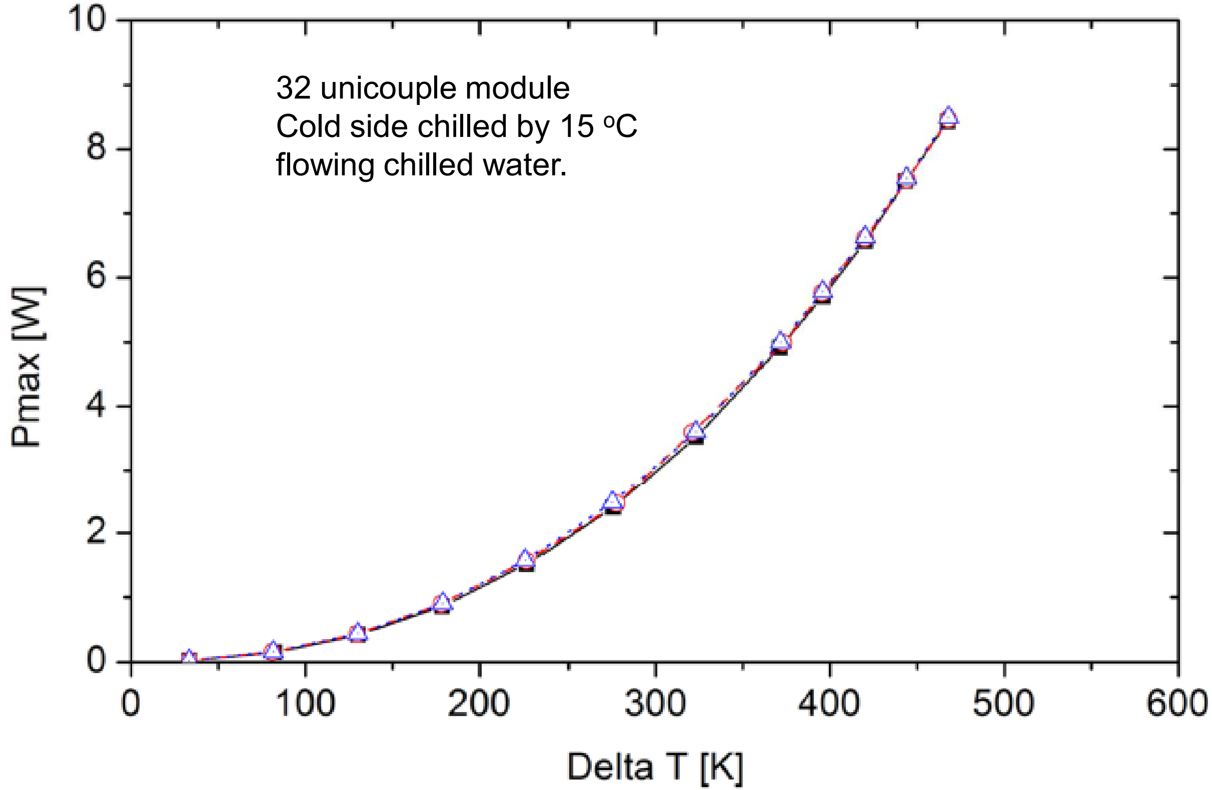
Measured Power Output at a Given ΔT



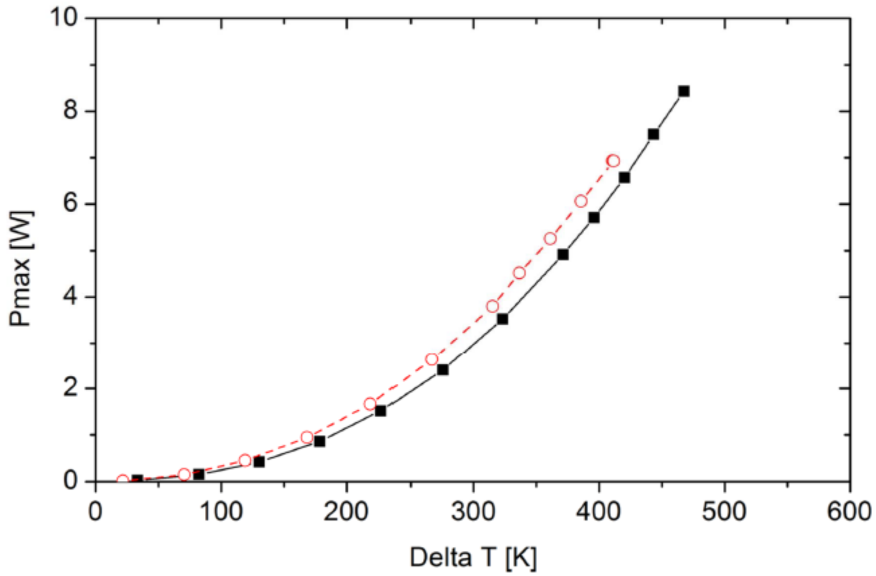
Power output is stable over the 3 thermal cycles performed.

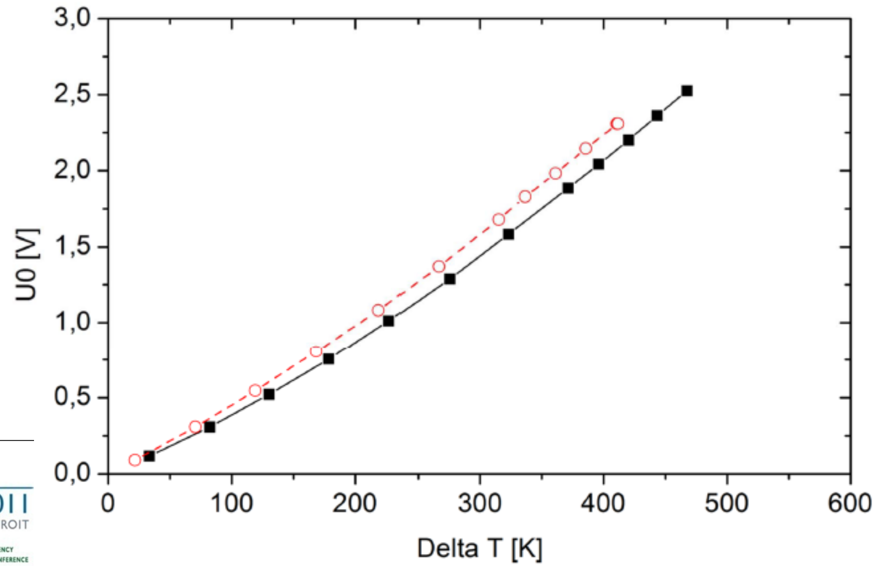
Heated hot side to 500 °C (773K), while performing measurements at 50°C increments .

Cooled hot side while performing measurements.

Finally heated hot side again to 500 °C in 50 °C increments.

Performance with Higher Cold Side Temperatures





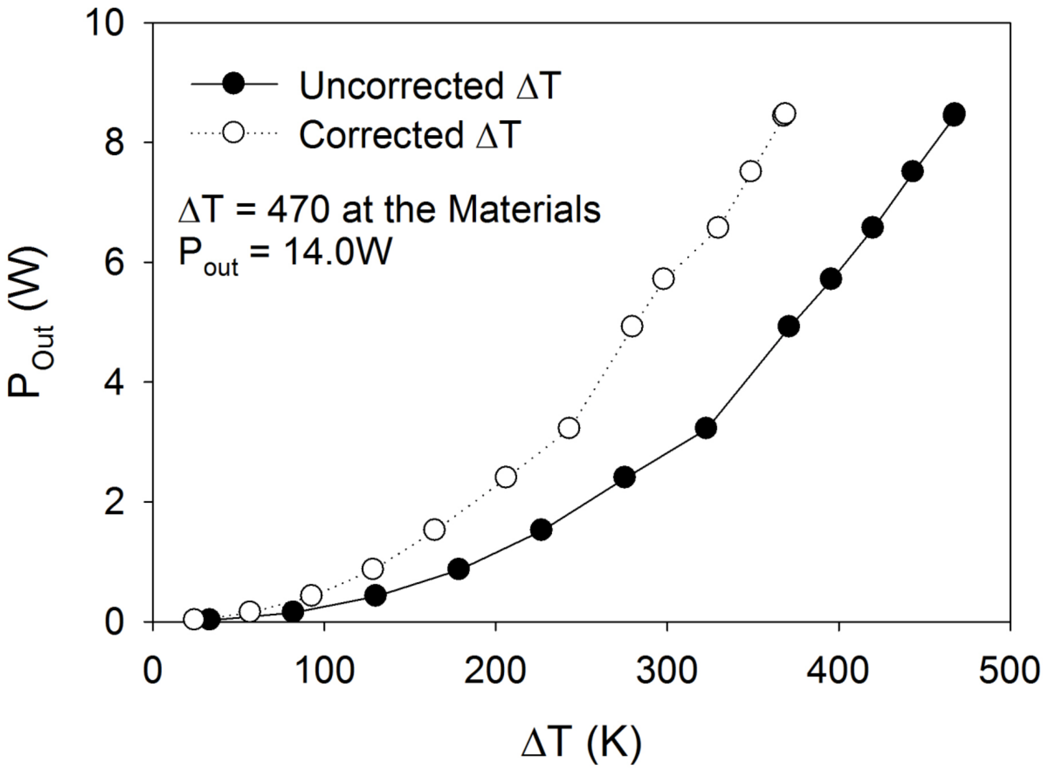
As the ZT values increase with temperature the power output is improved for a given ΔT at a higher cold side temperature .

These measurements were performed on the same module after the lower cold side temperature measurements were run.

Power Output with Corrected ΔT

We know from the V_{OC} measurements that there is a significant discrepancy between the temperatures measured at the for the hot and cold side and actual temperature of the hot and cold side of the legs.

For the sake of making a conservative estimate we assume the temperature discrepancy is all at the hot side. Based on this assumption and the V_{OC} equation adjusted ΔT can be calculated.



Estimates of Thermal Efficiency

$$\eta = \left(\frac{T_H - T_c}{T_c}\right) \cdot \frac{\sqrt{1 + Z\overline{\overline{T}}} - 1}{\sqrt{1 + Z\overline{\overline{T}}} + {}^{T_c}/_{T_H}}$$

Theoretical conversion efficiency for the materials only

Taking the ZT values we have for the materials, and the largest ΔT for the study (T_H = 773K and T_C = 305 K)

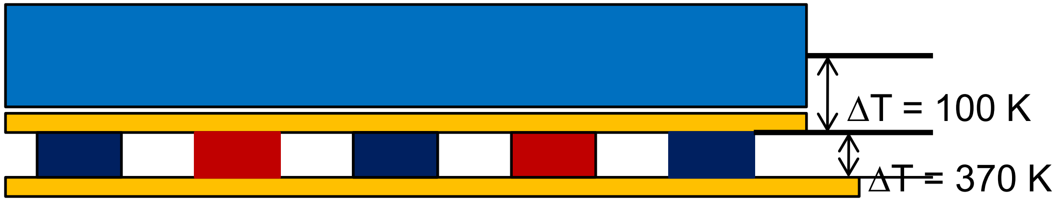
The average ZT for both materials in this temperature range is ZT = 0.47

η= 8% for the materials.

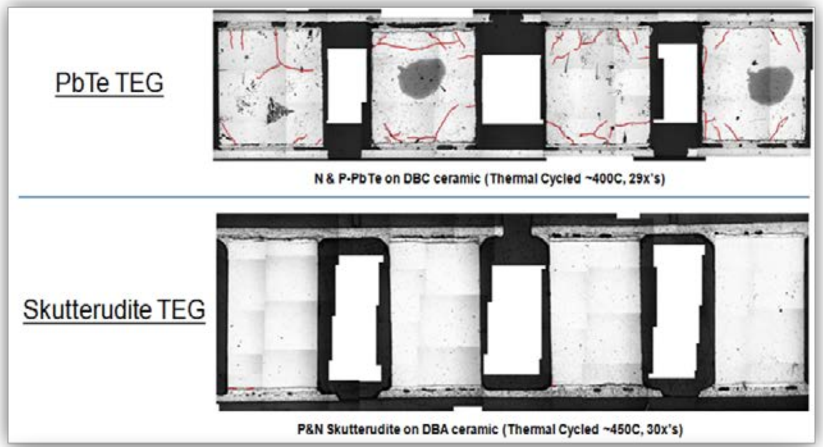
If we use Fourier's law for the average thermal conductivities, cross sections and number of legs for the projected ΔT(468 K) =179 W of heat passes through the legs and 14 W of electricity is produced ~7.8% conversion. Excellent agreement.

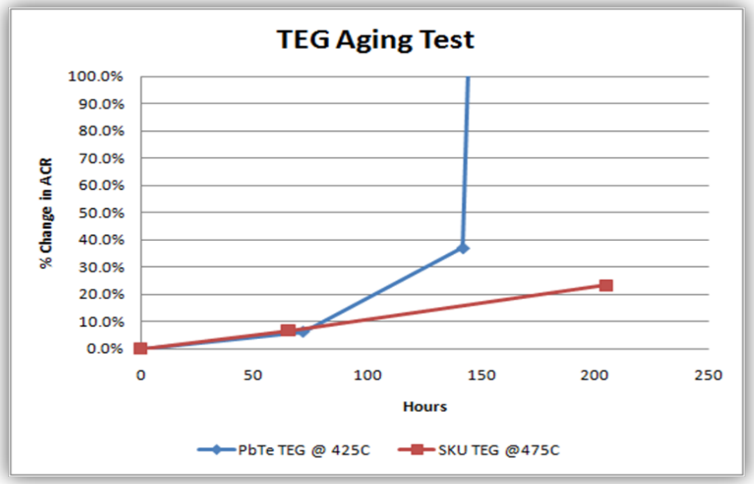
Similar analysis can be done for the apparent ΔT and the measured P_{out}, lower average ZT value of 0.4 η= 6.1% from the above relation and 6.0% obtained by Fourier's law.

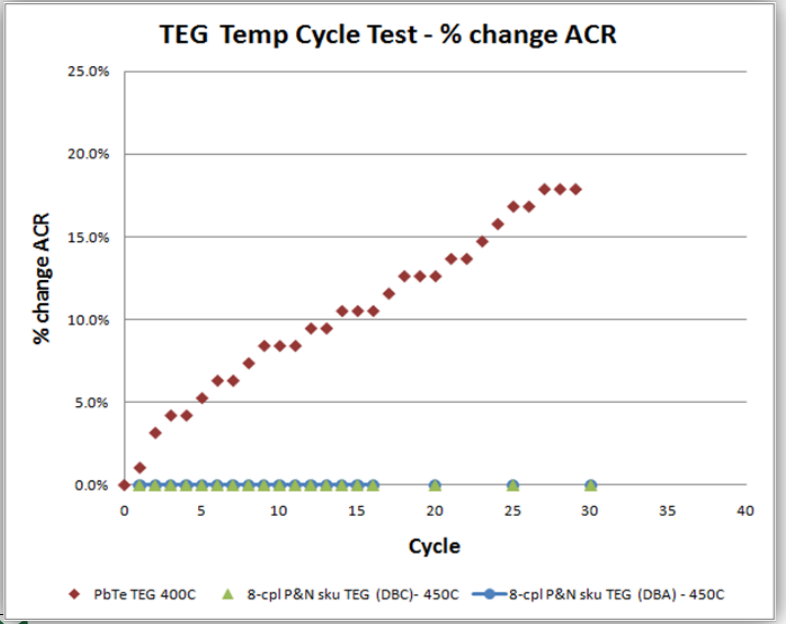
But much more power is being delivered to the module (how much is difficult to estimate)



Results of Initial Durability Studies







Skutterudite materials show good stability with thermal cycling and soak.

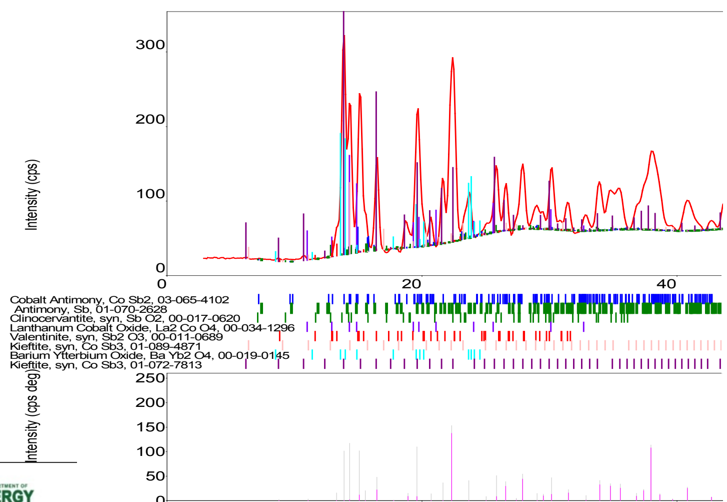
Increase in resistance in soak likely due to sublimation and oxidation of junctions

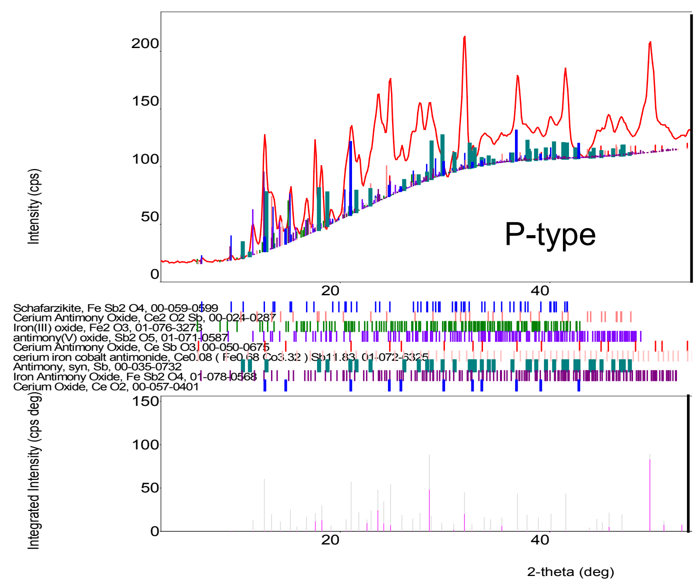
Modules will Need Protection From the Environment

Products of oxidation:

N-type	P-type
$CoSb_2$	$FeSb_2O_4$
Sb	Fe_2O_3
SbO_2	Ce_2O_2Sb
La_2CoO_4	Sb_2O_3
Sb_2O_3	Skutterudite
$CoSb_3$	Sb
$BaYb_2O_3$	CeO_2

Results of several measurements performed in a poor vacuum atmosphere





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Summary and Conclusions

- While not terribly flattering, the results shown here are likely representative of actual operating conditions, without significant improvement in thermal contact resistance.
- Skutterudite modules presented have demonstrated reasonable durability. Certainly superior to comparable test modules based on PbTe.
- Both skutterudite and PbTe materials are highly susceptible to oxidation and measures will need to be taken in order to protect them while in service. Significant challenge with hot side temperatures around 500°C .
- Significant improvement can be made by getting p-type materials to state of the art levels. (ZT=1 at 750 K) would improve P_{out} to 12 to 13 W under the same operating conditions.
- Thermal efficiencies are difficult to estimate as at this point. Thermal contact resistance is not well characterized in the test cell.