Materials, Modules, and Systems: An Atoms to Autos Approach to Automotive Thermoelectric Systems Development.

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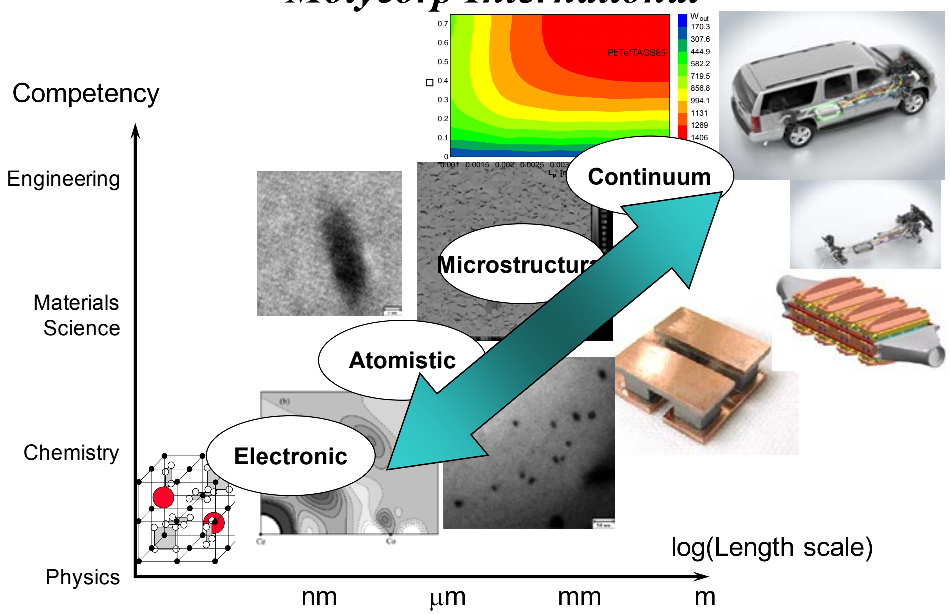

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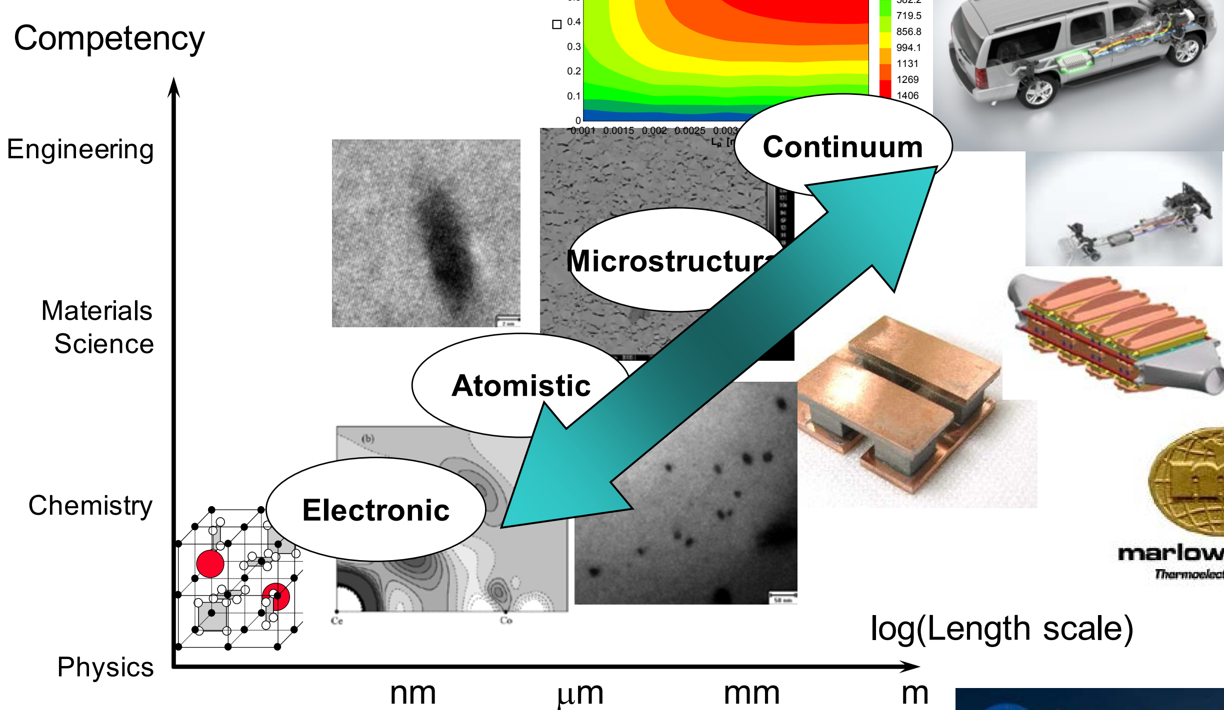
Development of Cost-Competitive Advanced Thermoelectric Generators for Direct Conversion of Vehicle Waste Heat into Useful Electrical Power

Target: 5% fuel economy improvement using thermoelectrics.

Molycorp



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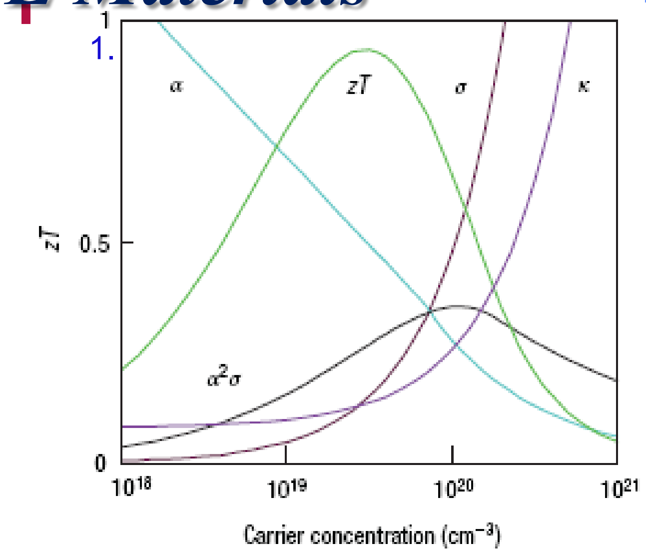
Efficiency of Energy Conversion for TE Materials

$$ZT = \left(\frac{S^2}{\rho \cdot \kappa}\right) T$$ Figure of Merit

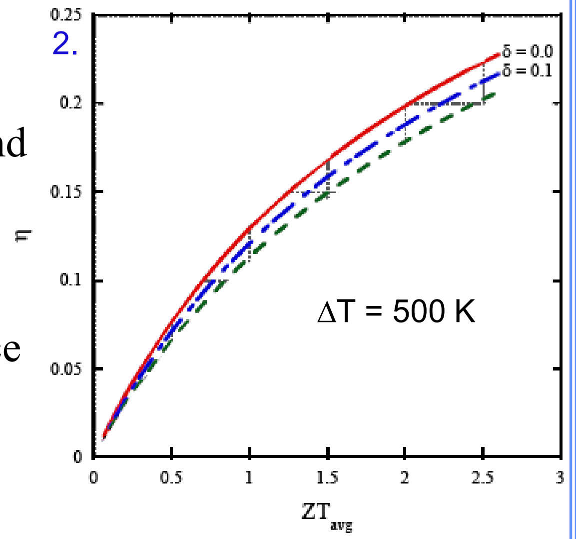


Optimization of ZT is challenging since all parameters are interrelated

Decreasing ρ by doping decreases S due to the changes in Fermi-level

Decreasing ρ by doping increase κ due to increased carrier contribution.

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



The conversion efficiency stated here is based on the TE materials only and represents an upper limit of the generator efficiency. Factors which will impact the efficiency include:

Thermal losses due to poor heat transfer from exhaust gas to solid interface

Parasitic thermal losses and electrical contact resistances.

1. G.J. Snyder E.S. Toberer *Nature Mater.* **7**, 105 (2008)
2. T.M Tritt, M.A. Subramanian *MRS Bull*. **31**, 188 (2006)

ZT and Module Level Performance

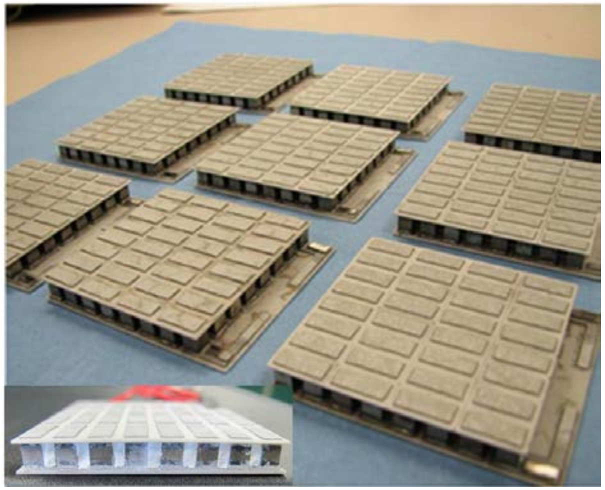
$$V_{OC} = n\int_{T_c}^{T_h} S(T)_p dT - n\int_{T_c}^{T_h} S(T)_n dT$$

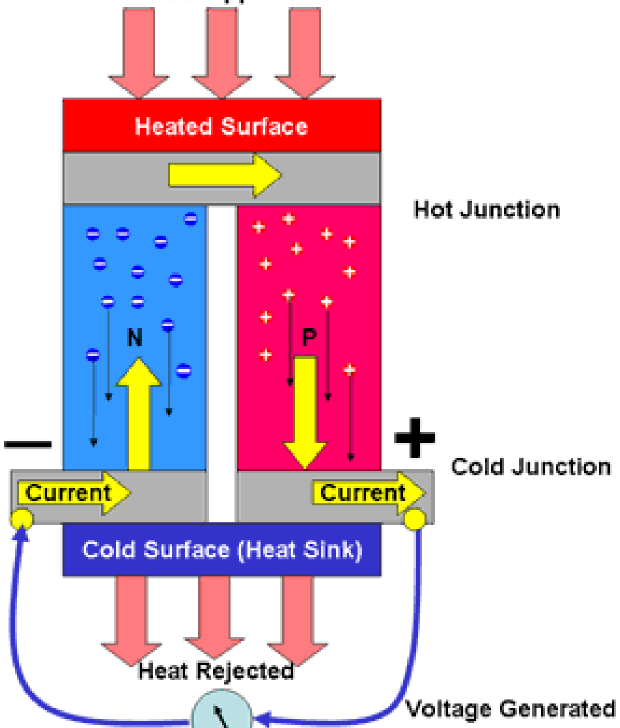
$$I = \frac{V_{OC}}{(R_{int} + R_{Load})}$$

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

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

Efficiency = P_{out}/Q_H





Semiconductor Thermocouple
Seebeck Effect

Thermoelectric Generators in the Vehicle

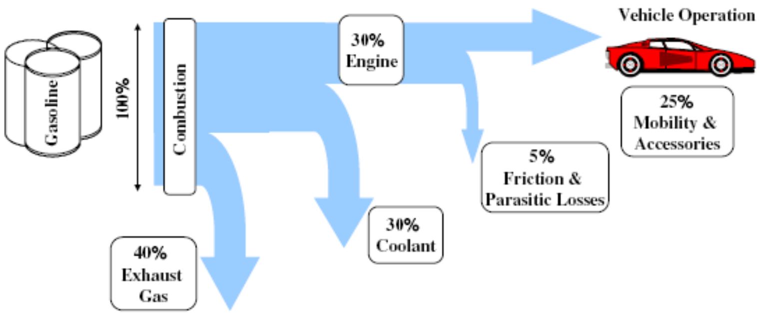
The primary purpose of the TEG is to recuperate waste heat from the exhaust gas and convert to electricity.

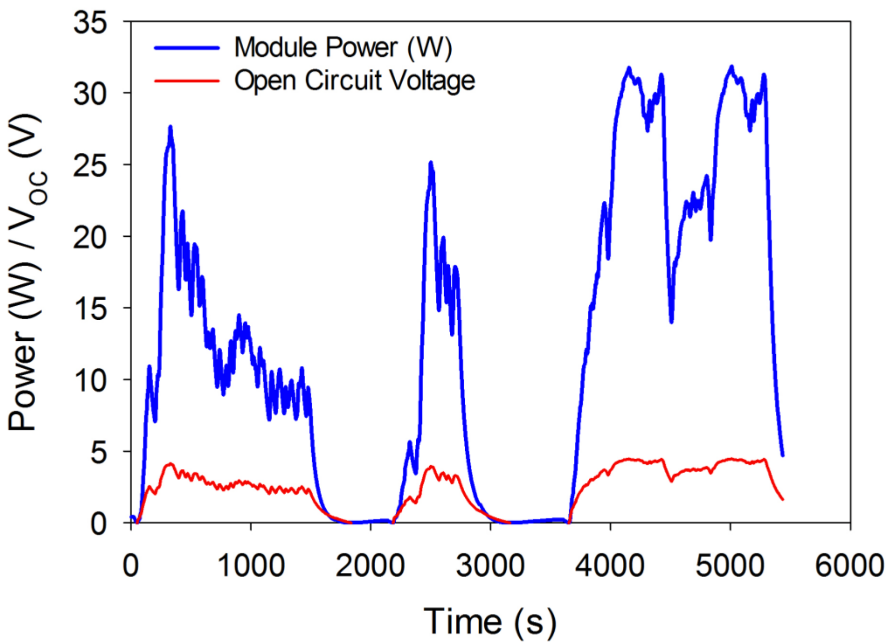
There are other advantages and opportunities that exist by virtue of having a heat exchanger scavenging waste exhaust energy.

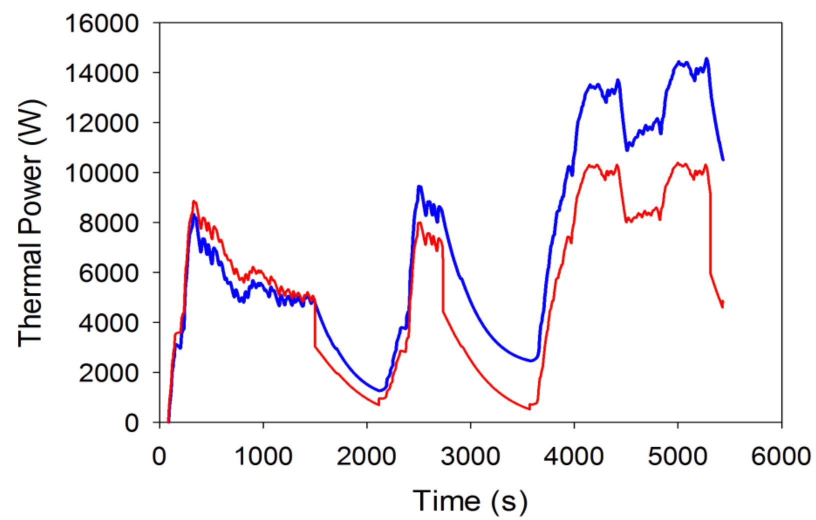
- Faster engine warm-ups for improved FE and passenger comfort.
- Use of rejected waste heat to warm other PT components during operation.

Thoughtful thermal management is a must otherwise too much heat will likely need to be rejected by radiator Upsizing a radiator is likely not feasible due to cost, packaging and aerodynamics considerations.

Thoughtful electrical power management is also a necessity .







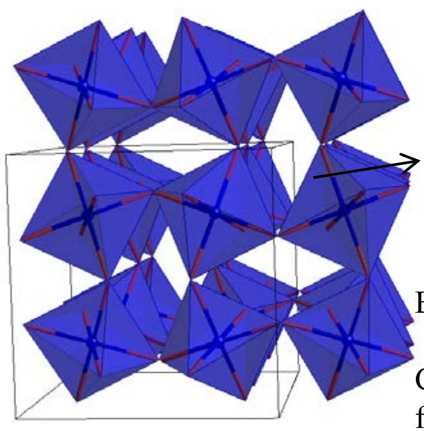
Development of TE Materials and High Throughput Production Methodology.

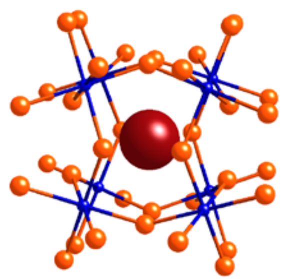
In our first program we were interested in developing skutterudite based TE materials
Advantages of Skutterudites.

- Thermal conductivity can be reduced by the incorporation of fillers into the crystallographic voids
- Can be made n- or p- type. Carrier concentration and type can be controlled by compositional changes.
- Reasonably good tensile fracture strength

Disadvantages:

- The peritectic decomposition of the material below the composition's melting point precludes simple melt cast techniques and requires potentially time consuming and energy intensive power metallurgy.
- Antimony is prone to sublimation. Need to be encapsulated.
- Skutterudites are prone to oxidation at high temperatures, and will need to be isolated from the environment.





Base compound $CoSb_3$

Can be made n-type through filling electropositive elements

Can be made p-type by substituting Fe on the Co site

		[111]		*[100]*	
R	Mass (10^{-26} Kg)	k (N/m)	ω_0 (cm^{-1})	k (N/m)	ω_0 (cm^{-1})
La	23.07	36.10	66	37.42	68
Ce	23.27	23.72	54	25.18	55
Eu	25.34	30.16	58	31.37	59
Yb	28.74	18.04	42	18.88	43
Ba	22.81	69.60	93	70.85	94
Sr	14.55	41.62	90	42.56	91
Na	3.819	16.87	112	17.18	113
K	6.495	46.04	141	46.70	142

Traditional preparation of n-type filled-skutterudites

Co and Sb shot pre-melted by induction at 1400°C in a ratio of 1:3 in BN. Followed by adding Ba, Yb and Sb to the desired composition and re-melting at 1200°C for 5 min.

The resulting ingot is not the desired skutterudite phase since skutterudites decompose above 840°C; products are: $CoSb_2$ + Sb+ $YbSb_2$

2 weeks annealing at 750°C

After annealing the product is $Ba_yYb_xCo_4Sb_{12}$

Annealed samples are ground into powder for hot pressing or spark plasma sintering

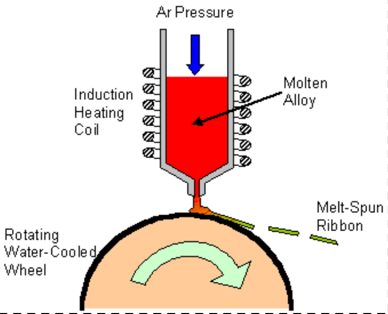
Resulting billets are >98% fully dense pure phase skutterudite

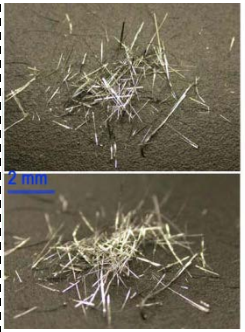
For traditional method 2 weeks preparation time used

Proposed melt-spin preparation of n-type filled-skutterudites

Co and Sb shot pre-melted by induction at 1400°C in a ratio of 1:3 in BN. Followed by adding Ba, Yb and Sb to the desired composition and re-melting at 1200°C for 5 min.

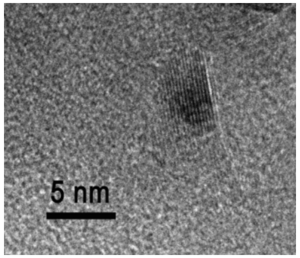
Resulting ingot melt-spun using specified temperature, ejection pressure, and wheel speed





Ribbon product: not the desired skutterudite phase

Fine-grain structure of the rapidly cooled ribbon product facilitates solid-state reaction, eliminating need for lengthy annealing

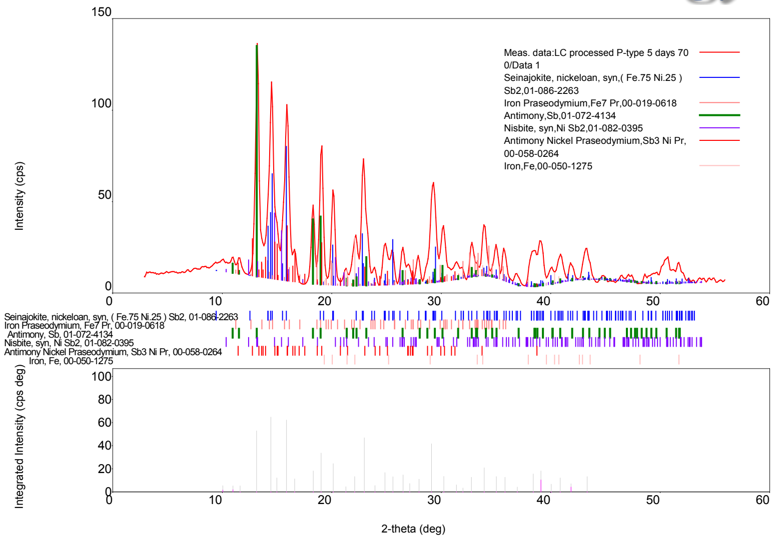


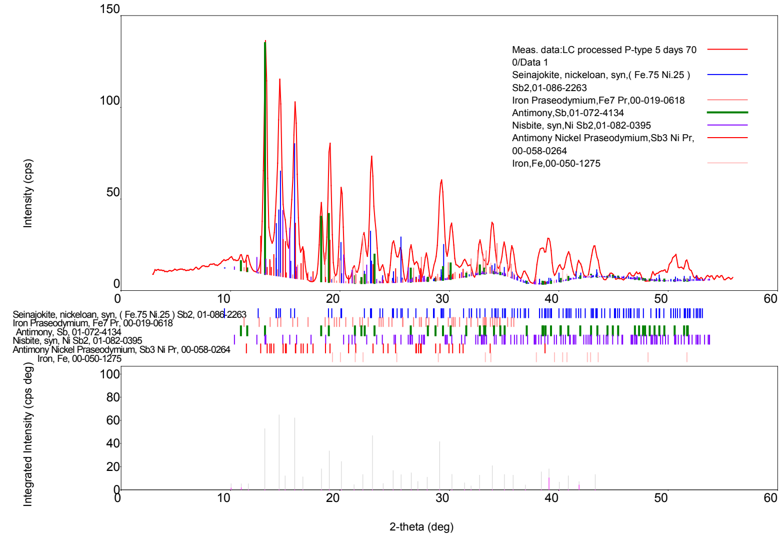
Ribbons are ground into powder for spark plasma sintering

Resulting billets are >98% fully dense pure phase skutterudite

For melt spinning method preparation time is reduced to 4-5 hours

Development of TE Materials and High Throughput Production Methodology





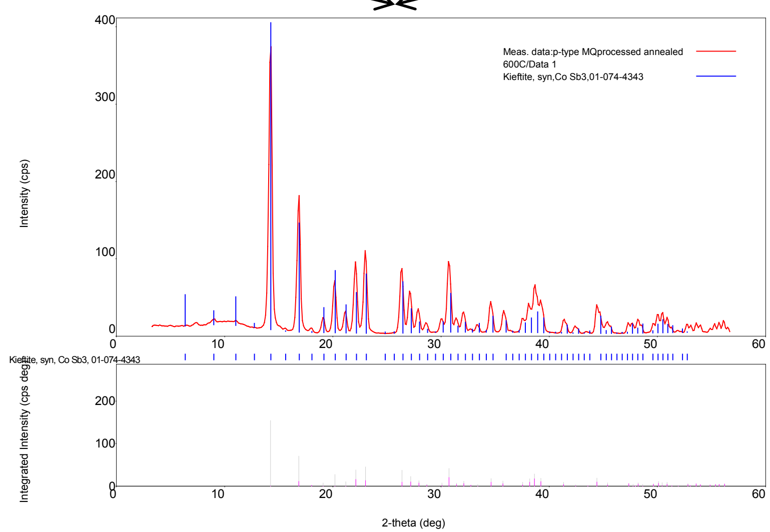
SPS for 20 min.

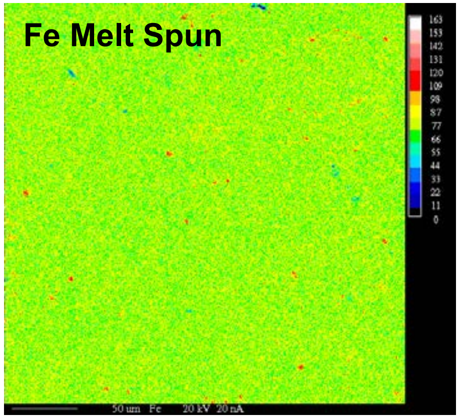
Annealed for 1 week at 650^{o}C

This was found to be true for both n- and p-type skutterudite materials and did not matter if the materials were rapidly quenched (higher wheel speed) or slow quenched.

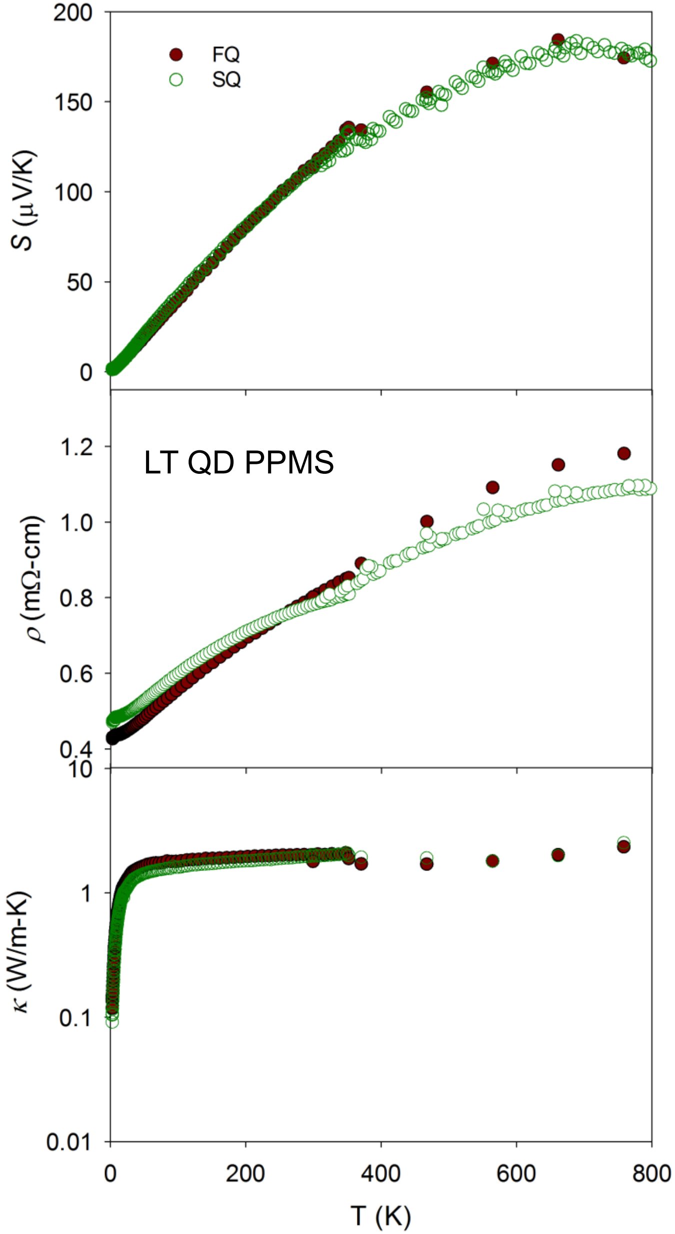
N-type materials are more stable at higher temperatures.

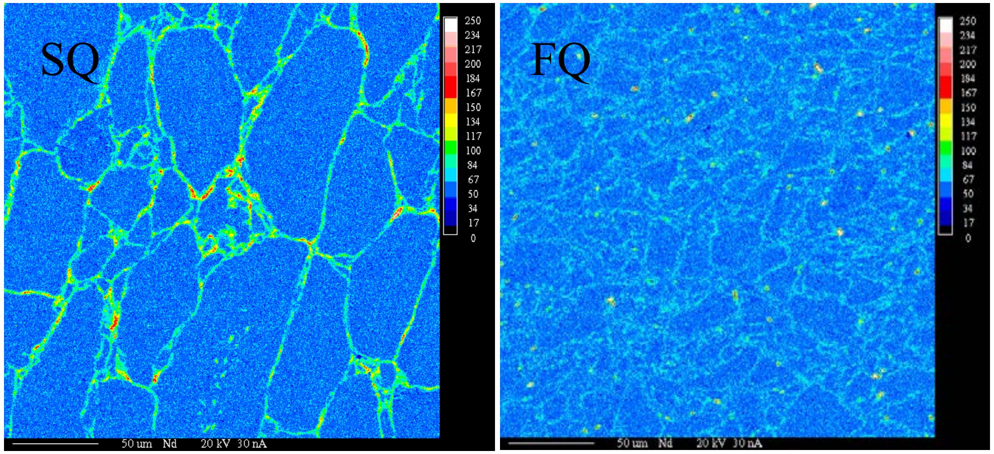
P-type tended to decompose in the SPS if sintering temperature exceeded 600 ^{o}C.



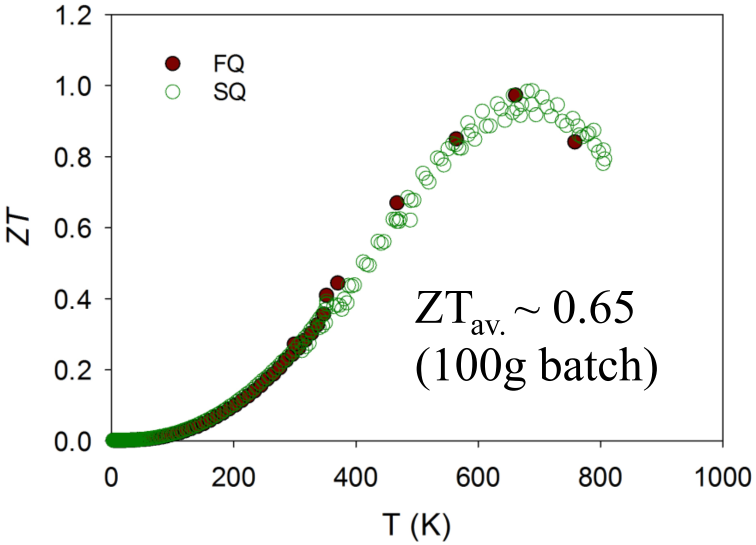


High Temperature Transport Properties and Composition

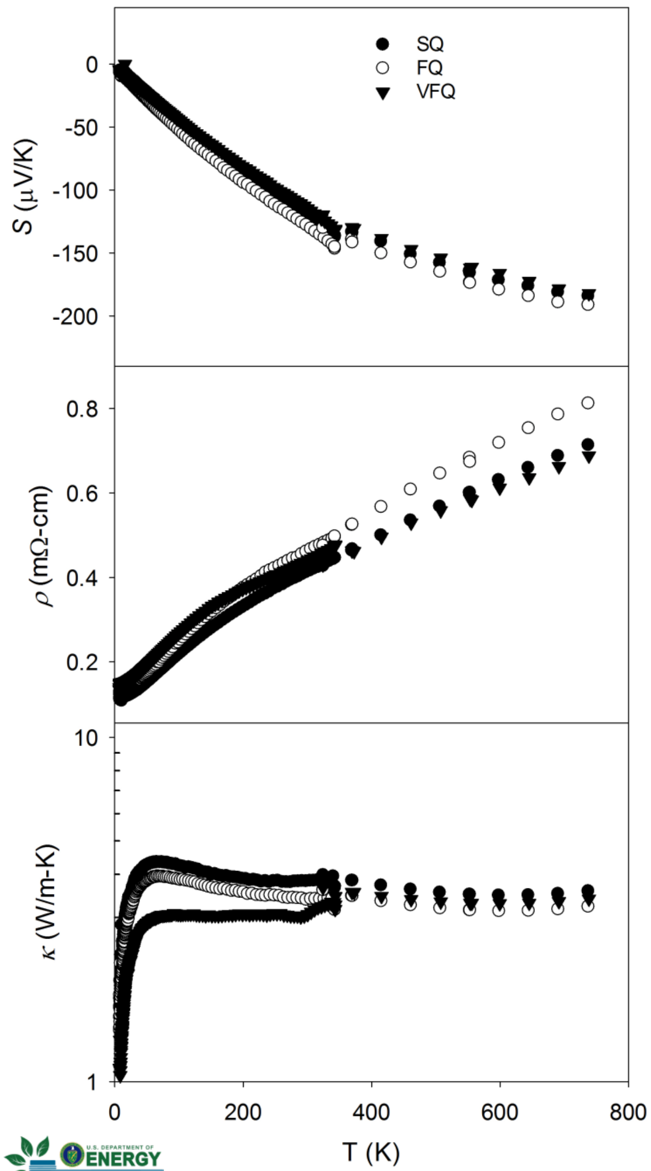


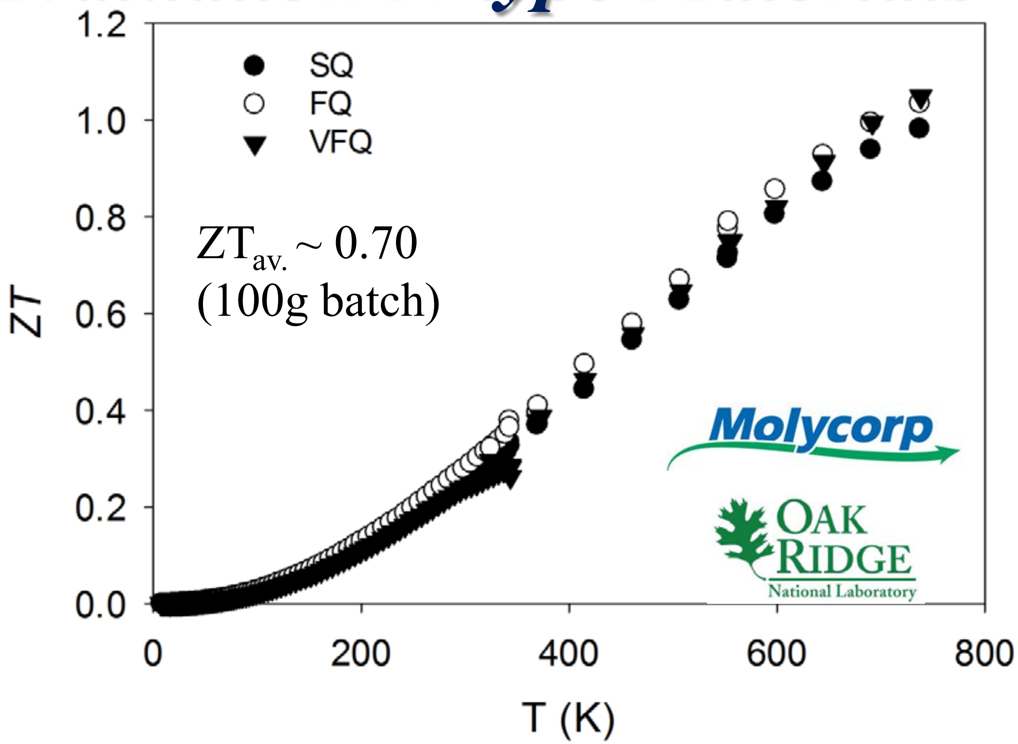


$Pr_{0.176\pm0.004}Nd_{0.50\pm0.01}Fe_{3.41\pm0.02}Ni_{0.588\pm0.007}Sb_{12.09\pm0.02}$



Transport Property Evaluation N-type Materials



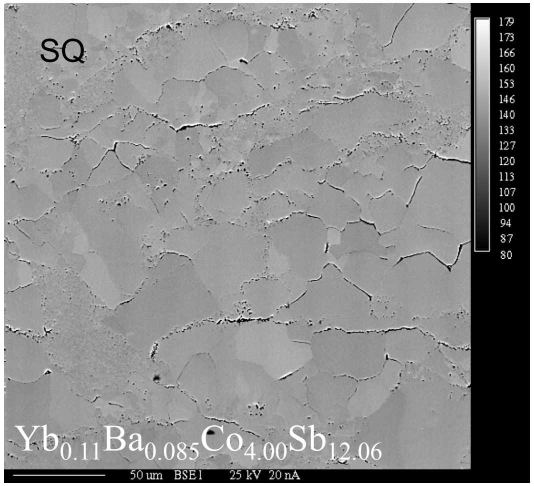


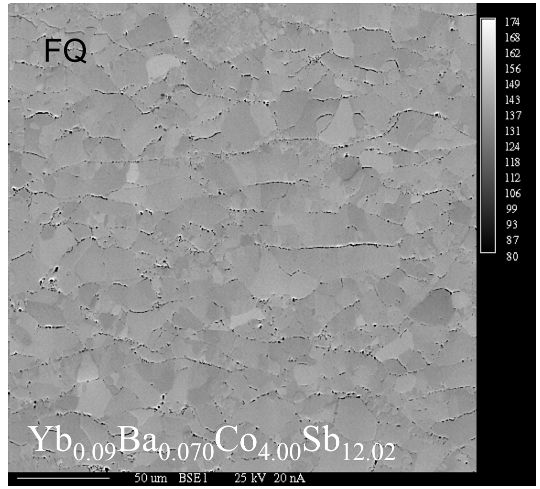
A small and likely statistically insignificant improvement in ZT with a faster quench rate:
(ZT= 0.97 for SQ vs. ZT =1.05 for FQ and VFQ at 740 K)

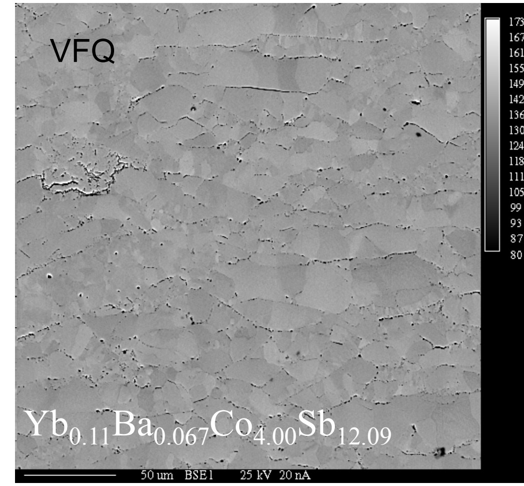
Sample transport properties were repeatable over the heating and cooling cycle.

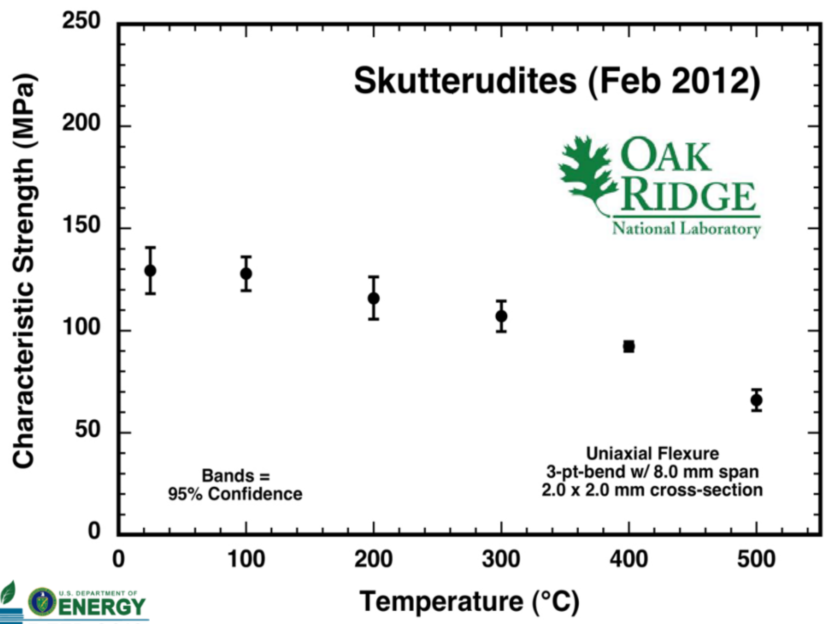
Tests are underway to look at cycling reproducibility.

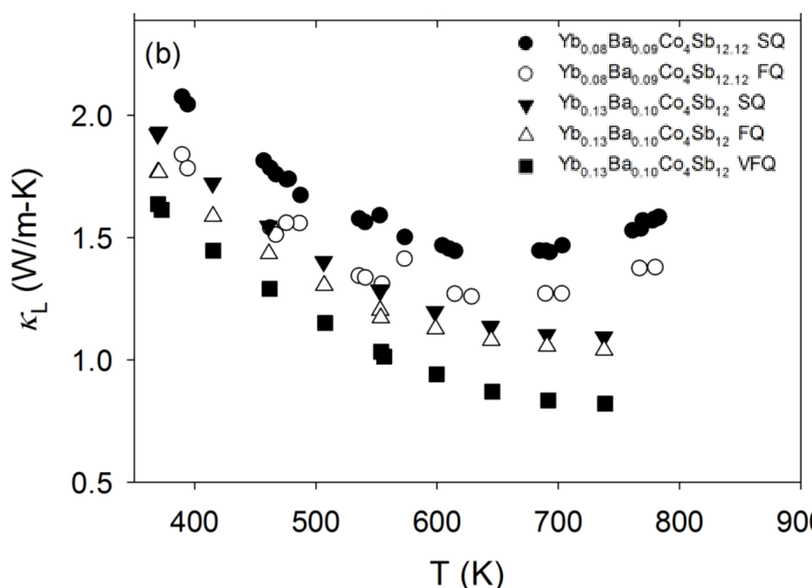
Composition and Microstructure of N-type Materials











Materials Passivation

Sublimation of Sb from the hot side leads to a gradual increase in the module's internal resistance. This is caused by changing carrier concentration and necking at the TE material/metal interconnect junction.

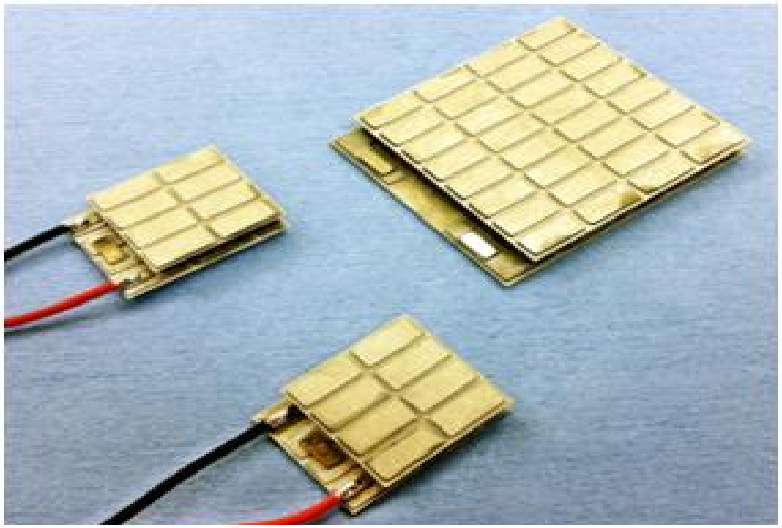
Oxidation is also a concern. It is likely not feasible to hermetically seal the entire generator so individual modules or legs will need to be encapsulated in an inert atmosphere.

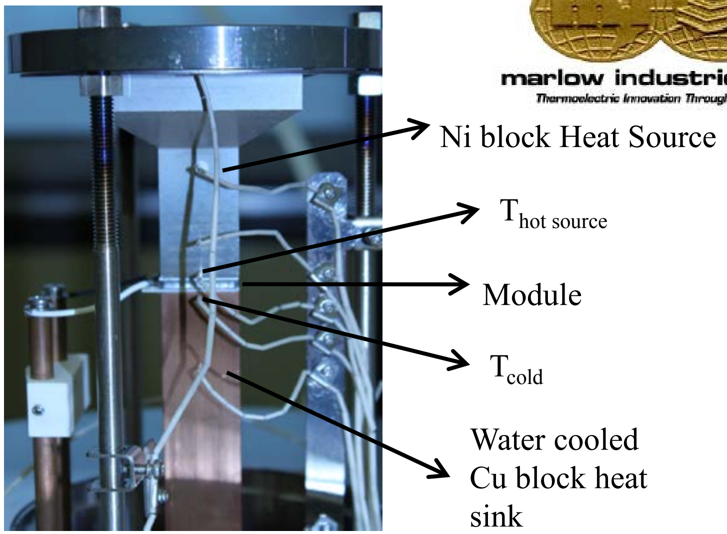
Results of several measurements performed in a poor vacuum atmosphere

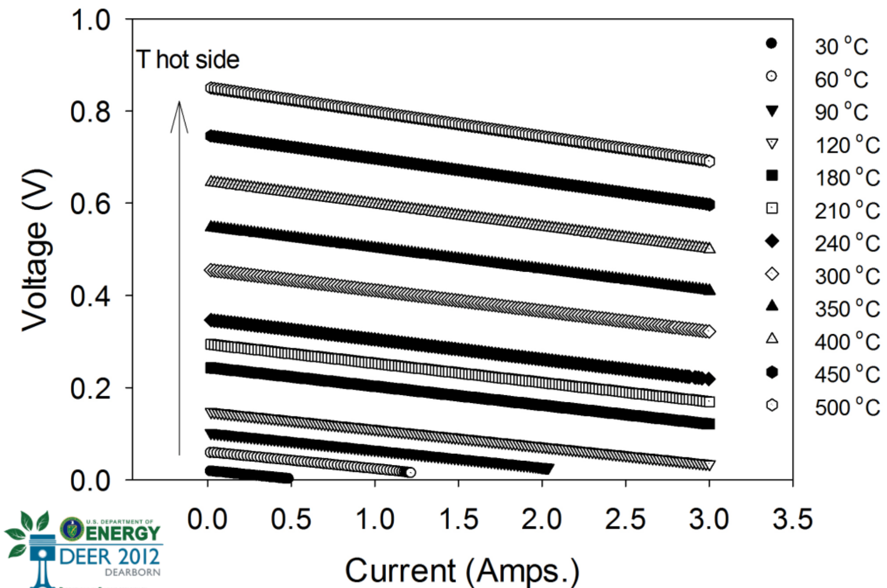
Castable ambiently dried aerogel for sublimation suppression and thermal insulation.

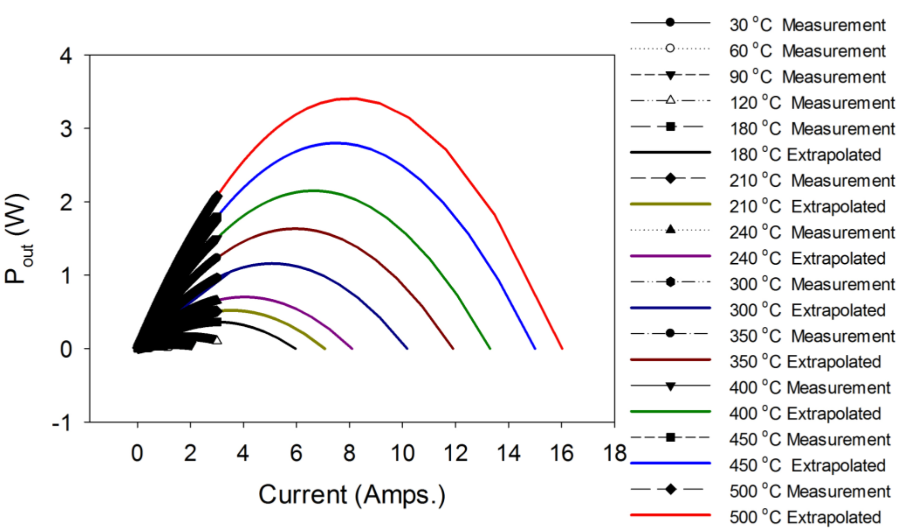
Modules from Melt Spun Skutterudites

marlow industries, inc.
Thermoelectric Innovation Through Research

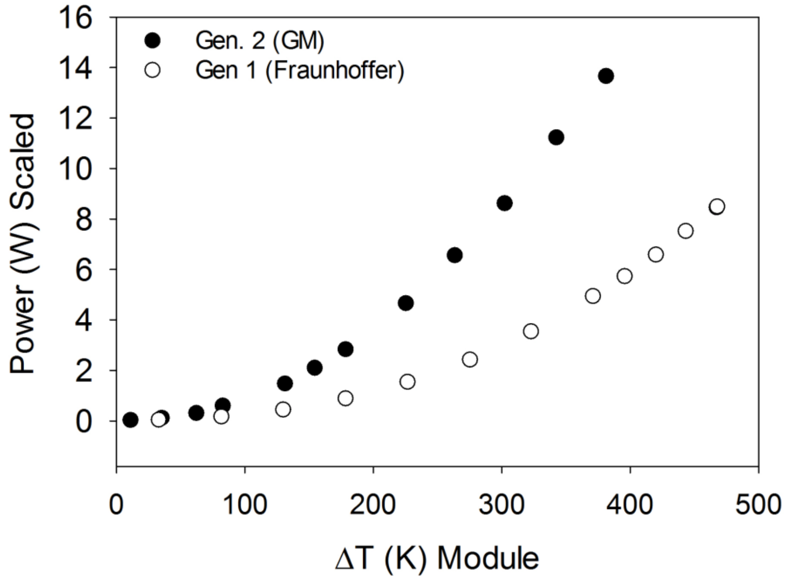


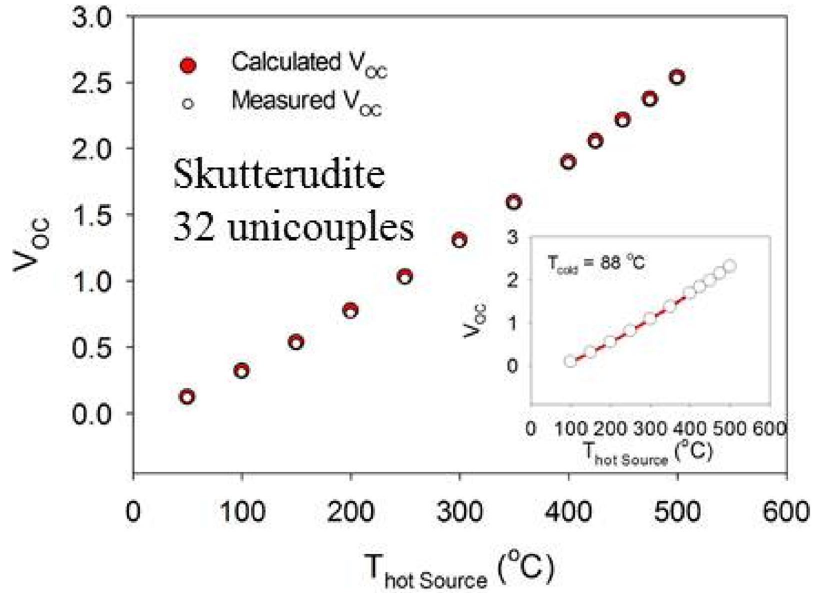


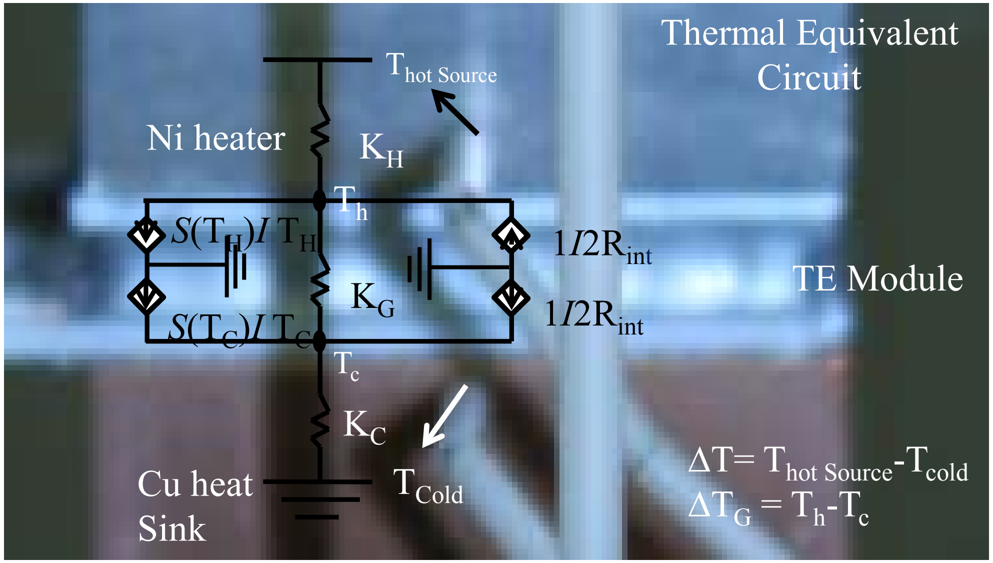


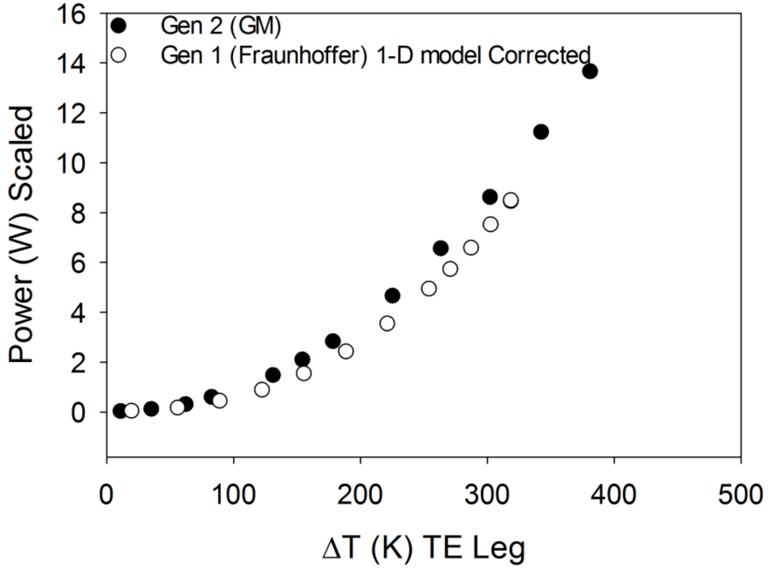


Comparison of Gen 1 and Gen 2 Skutterudite Modules

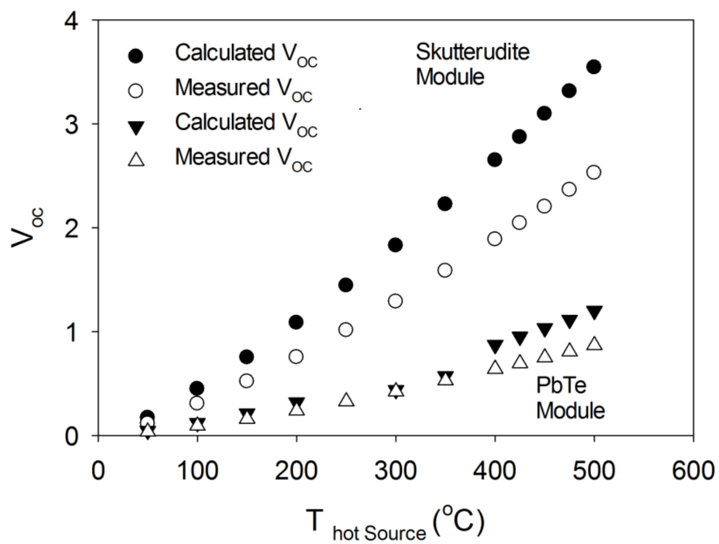


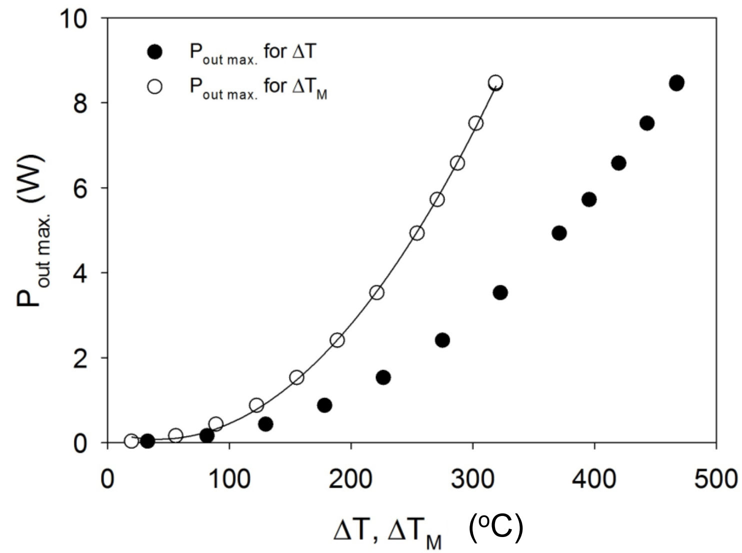




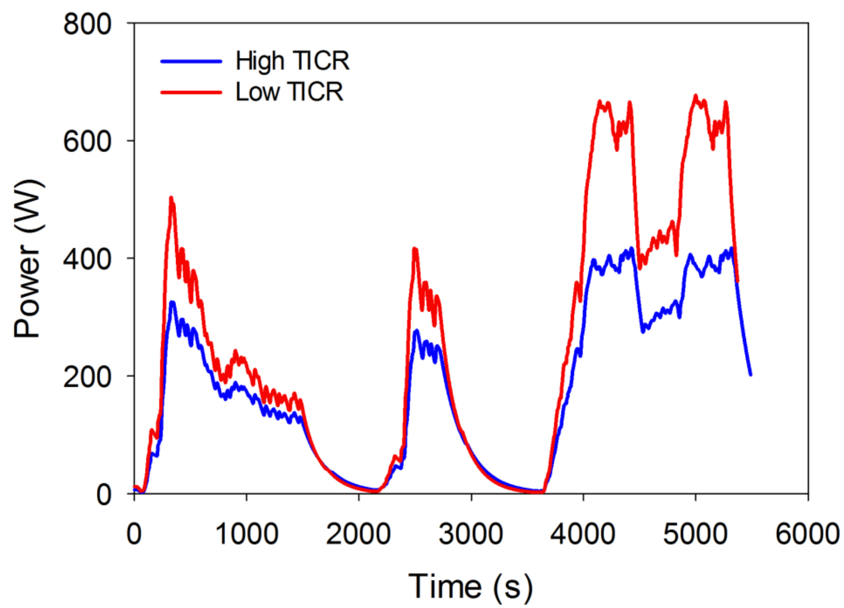


Effects of Thermal Interface Contact Resistance on Generator Power





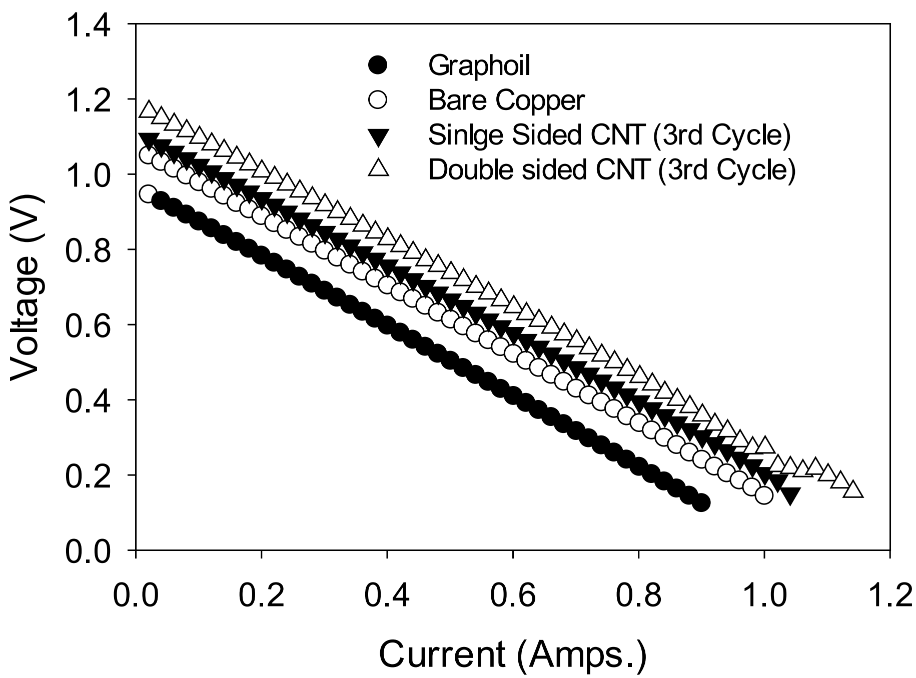
$$P_{out} = V_{OC}^2 \frac{R_{Load}}{(R_{Load} + R_{Int})^2}$$

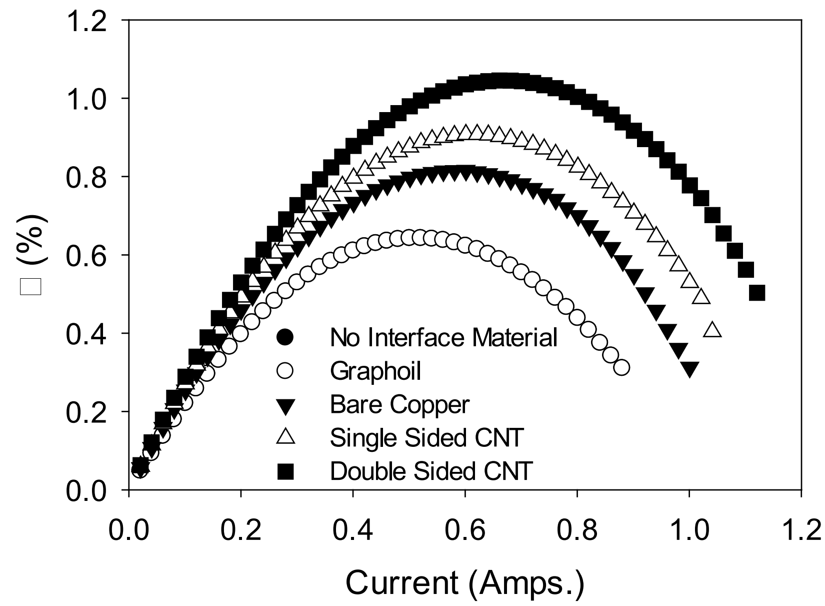


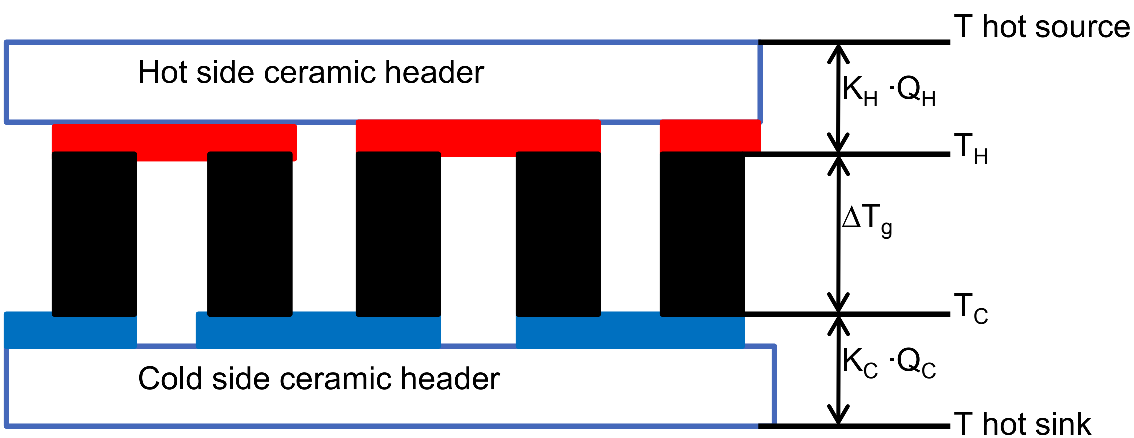
The presence of thermal interface contact resistance and alumina ceramics greatly reduce the ΔT experienced by the TE elements.

This is particularly severe under high large temperature gradients (high heat flux conditions.

Efforts to Reduce Thermal Interface Contact Resistance







Summary ,Conclusions, and Future Directions

- We have demonstrated that a combination of melt spinning combined with consolidation techniques such as SPS or hot pressing is a scalable and potentially high throughput method for skutterudite thermoelectric materials production. ZT values compare favorably with literature values for Yb and Ba filled skutterudites .

- Three point tensile fracture testing finds that most samples failed from edge or surface flaws indicating that MS-SPS processing is a mature powder processing technique that leads to low number of volume flaws.

- High temperature TE modules were made from these MS-SPS materials and the modules were characterized. Despite the superior TE performance of the p-type material used in the Gen-2 the internal resistance is still quite high due to larger electrical contact resistance.

- Thermal contact resistance, at least in test stand measurements, seem to have been reduced with the smaller Gen.-2 module leading to superior module level performance.

- We are in the process of investigating low cost sustainable filler elements for skutterudite materials that are compatible with MS-SPS processing to reduce materials costs reduce utilization of high priced rare-earth elements.

- Efforts are underway to reduce electrical contact resistance in the new p-type formulation.

- Efforts to reduce thermal interface contact resistance are also ongoing as well as metrology to characterize these value to assist in generator modeling.

Thank You !