

Commercialization of Bulk Thermoelectric Materials for Power Generation Applications

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- Update on ZT Plus activities
- Experimental approaches to accelerate bulk materials R&D
- ZT data analysis approaches

ZT Plus develops and produces *high performance* thermoelectric materials for efficient energy conversion for mid temperature waste heat recovery and power generation applications.

ZT Plus is a division of Amerigon Inc.

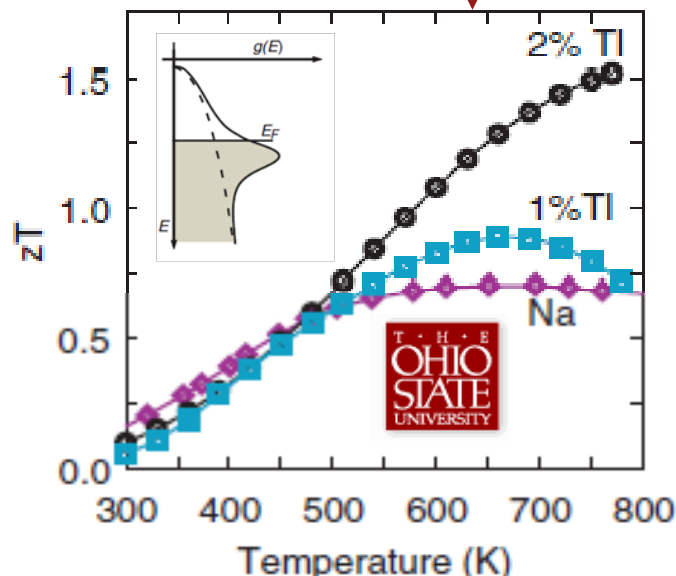
ZT Plus Genesis

- BSST has been funding internal Materials Research Program since 2006, establishing Emerging Materials Department in 2008.
- In 2009 BSST formed ZT Plus to commercialize improvements in bulk TE material performance demonstrated by Ohio State, Michigan State and Northwestern Universities.
- Formation and funding of ZT Plus was partially made possible by ONR's long term support of academic research, DARPA's targeted research and DOE sponsored vehicle research and development initiatives.
- DOE sponsorship of device-level development has been, and continues to be, of paramount importance for TE market development.

Material Improvement

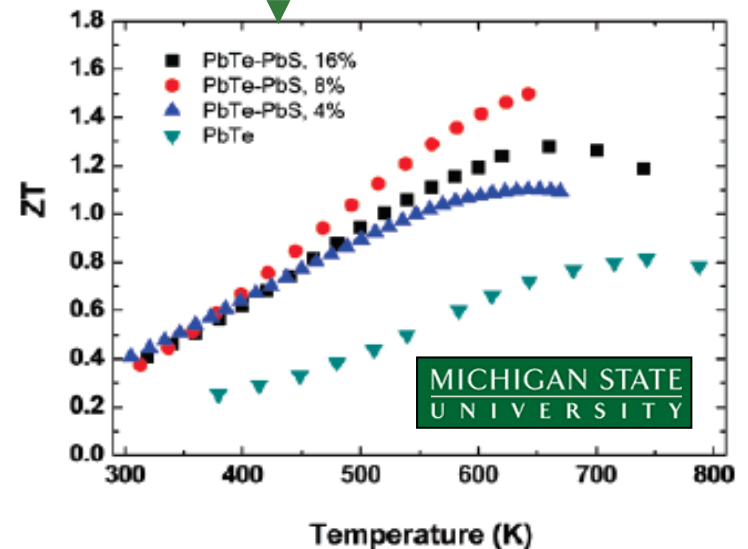
$$ZT = \frac{\alpha^2 \sigma}{(k_e + k_{ph})} T$$

P-type



Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States
Joseph P. Heremans, et al.
Science 321, 554 (2008);

N-type



Spinodal Decomposition and Nucleation and Growth as a Means to Bulk Nanostructured Thermoelectrics: Enhanced Performance in $Pb_{1-x}Sn_xTe-PbS$

John Androulakis,[†] Chia-Her Lin,[†] Hun-Jin Kong,[‡] Citrad Uher,[‡] Chun-I Wu,[§]
Timothy Hogan,[§] Bruce A. Cook,[‡] Thierry Caillat,[¶]
Konstantinos M. Paraskevopoulos,[‡] and Mercouri G. Kanatzidis^{*,†,‡}
J. AM. CHEM. SOC. 2007, 129, 9780–9788

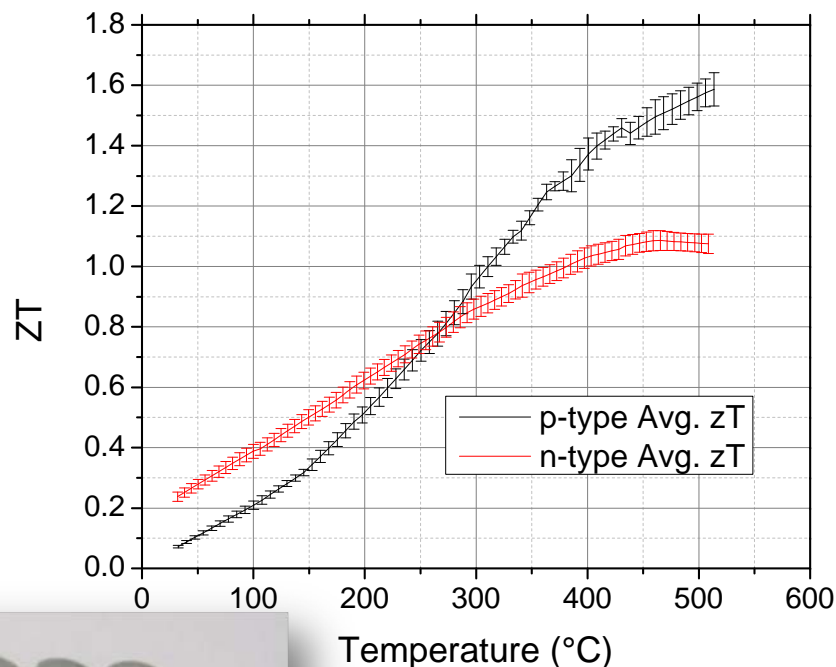
ZT Plus Capabilities Update



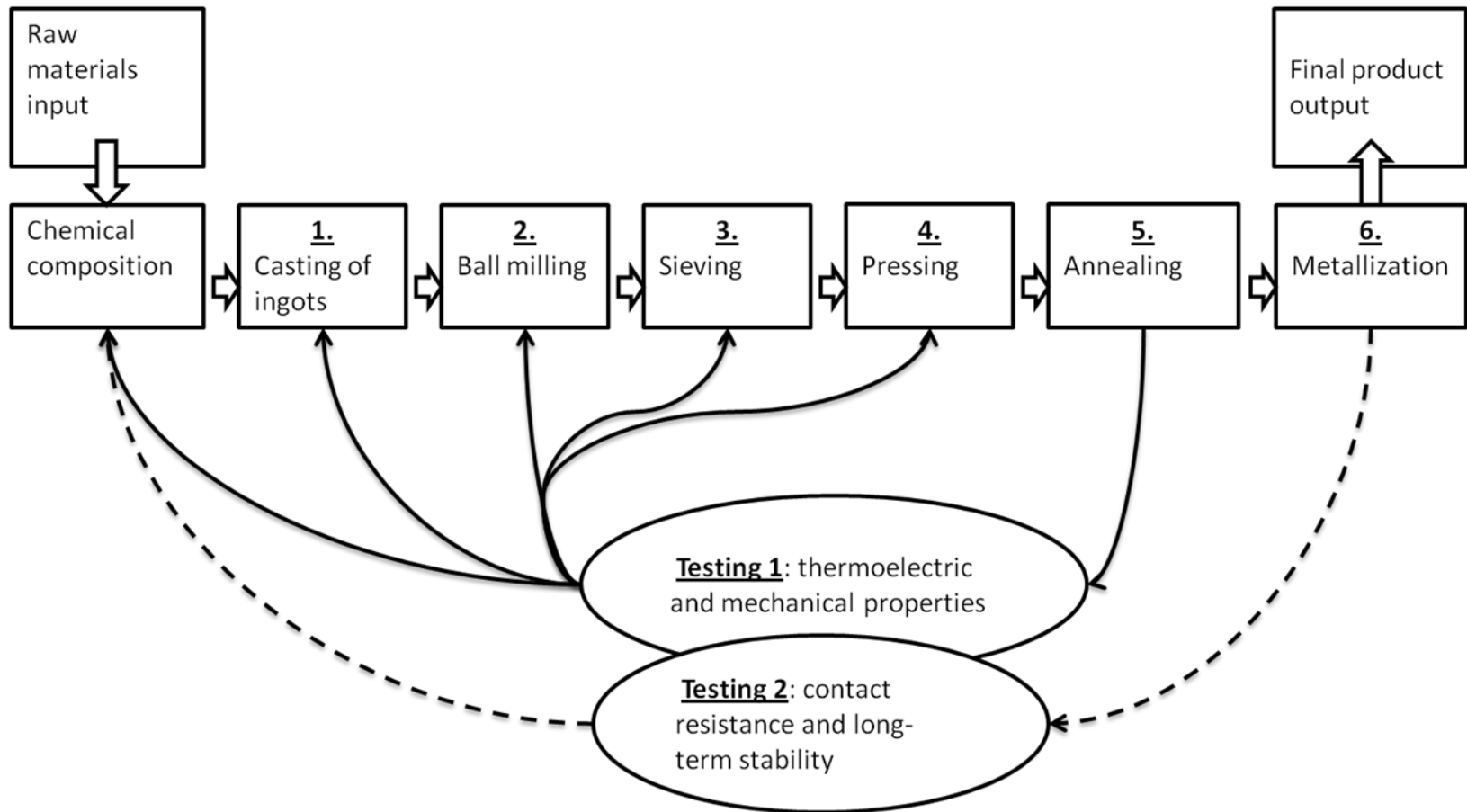
- New facility in operation since Nov. '09
- Proximity to Amerigon/BSST, Caltech and JPL
- 10,000 sq.ft., all operations are in clean room space
- R&D and pilot manufacturing capabilities
- Ingot casting, powder metallurgy
- Metallization
- Materials metrology to 600°C

ZT Plus Materials

- Currently sampling to select customers: high performance PbTe (no Thallium)
- Ongoing testing: mechanical, thermocycling
- Future plans:
 - PbTe production scale up
 - Pb and Te-free materials



Technology Commercialization



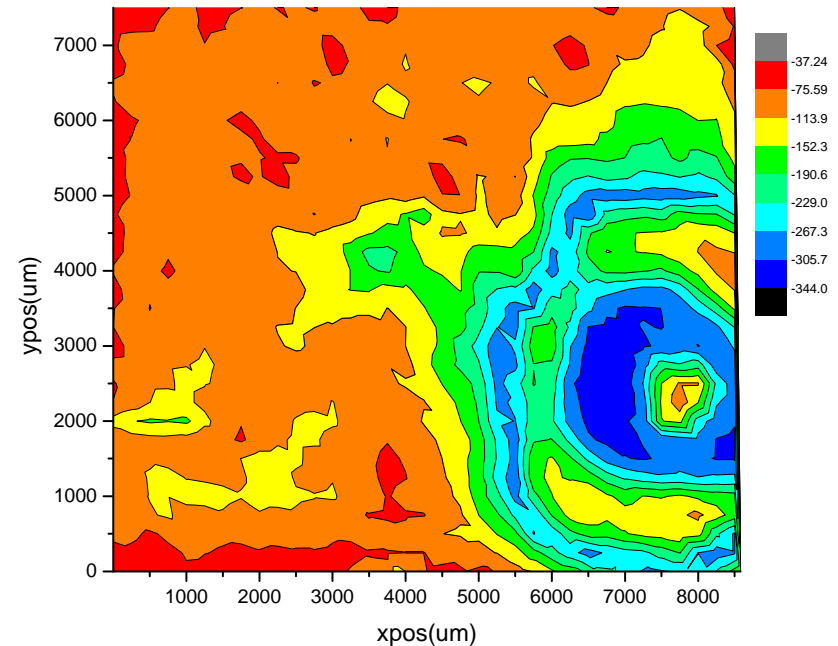
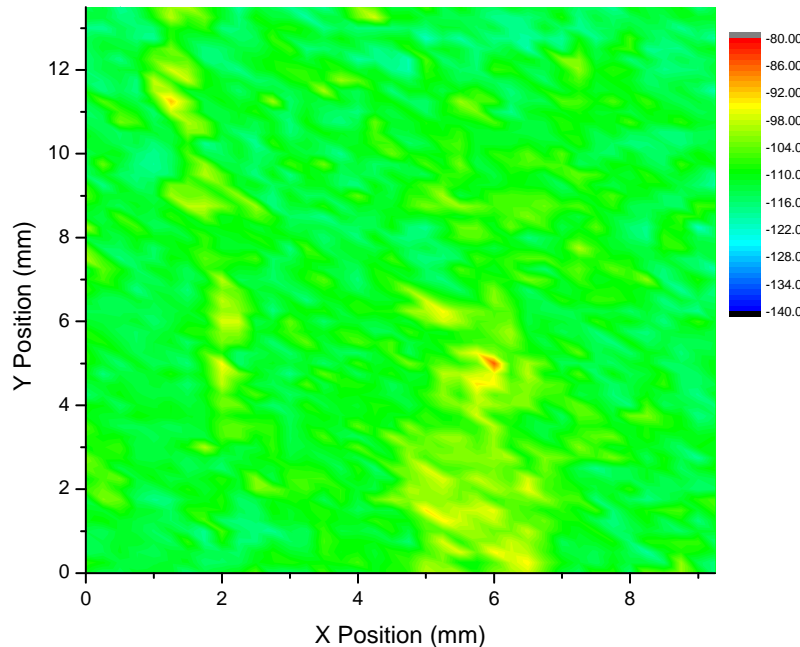
Long feedback loops are prohibitive!

Development Acceleration

1. Implement Design of Experiments methodology → reduces time by shrinking the experimental space.
2. Matching throughput of metrology with that of synthesis is a critical enabling feature for shortened information feedback loops.
3. Use fast, but not necessarily precise, tools for material screening → allows to arrive to negative results faster, thereby reducing the bottleneck of slow metrology.
4. Track and eliminate sources of variability → results have high robustness and reproducibility.

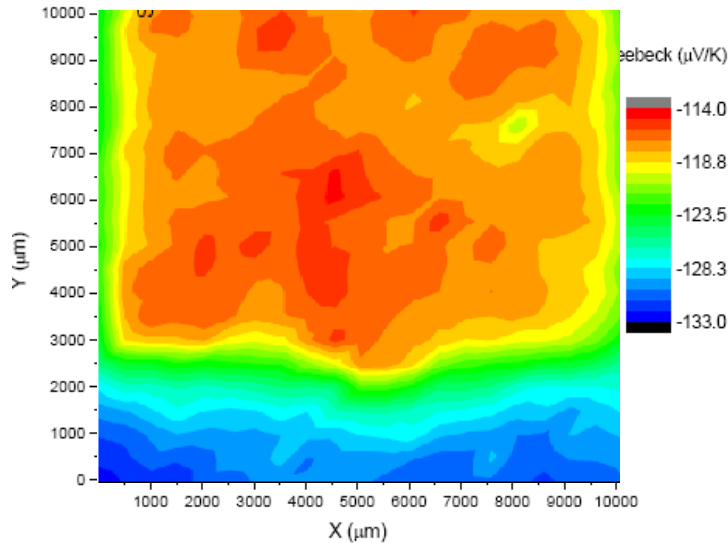
Rapid Screening – Scanning Seebeck

Uniform vs. Non-Uniform Cast Ingots



Measurements take tens of minutes instead of tens of hours. Experimental feedback is drastically reduced.

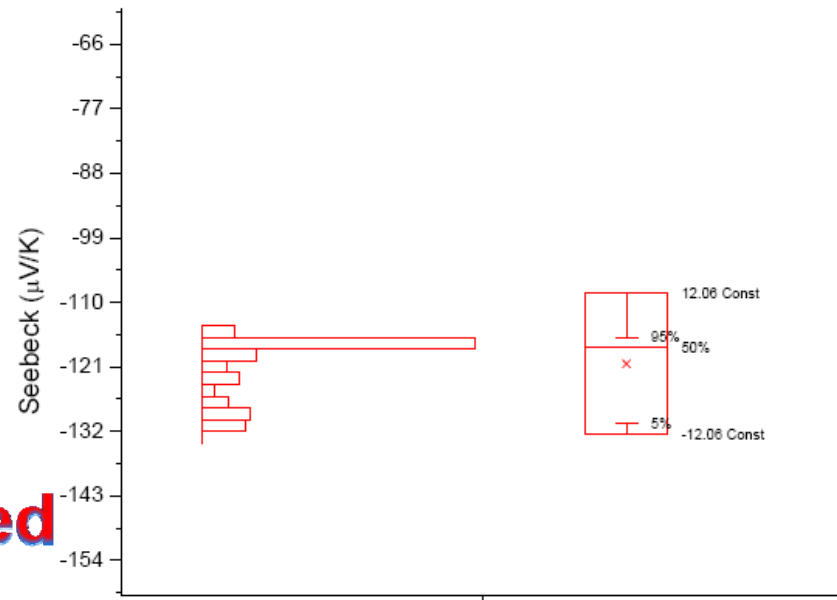
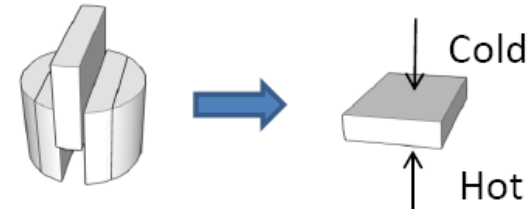
Example: Non-Uniform Pressed Coin



Fails 'Gaussian Distribution' Test

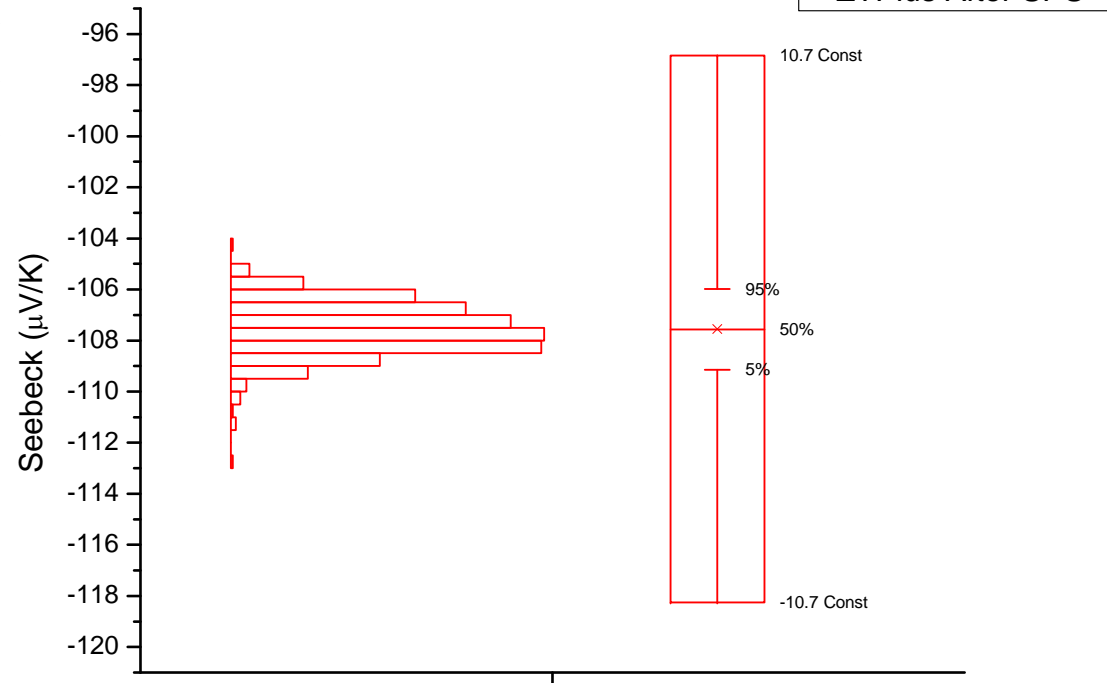
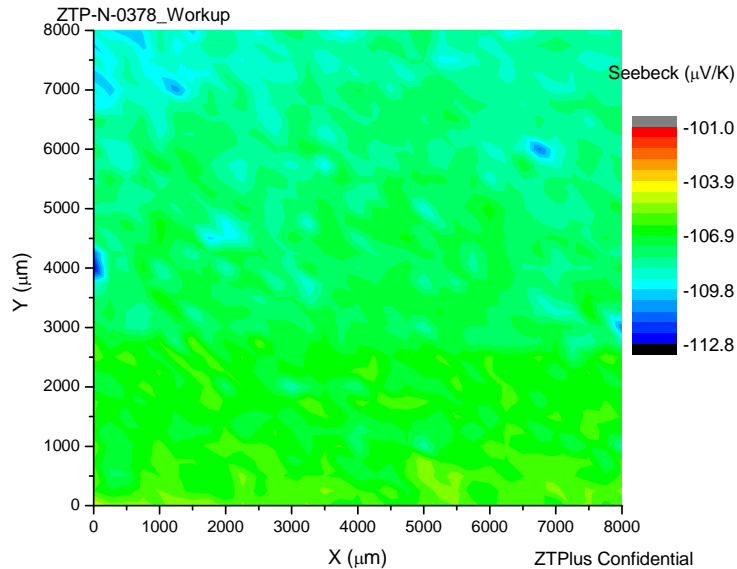
Bimodal – Seebeck changes within the ingot

Scanning Seebeck Analysis
of remaining ingot



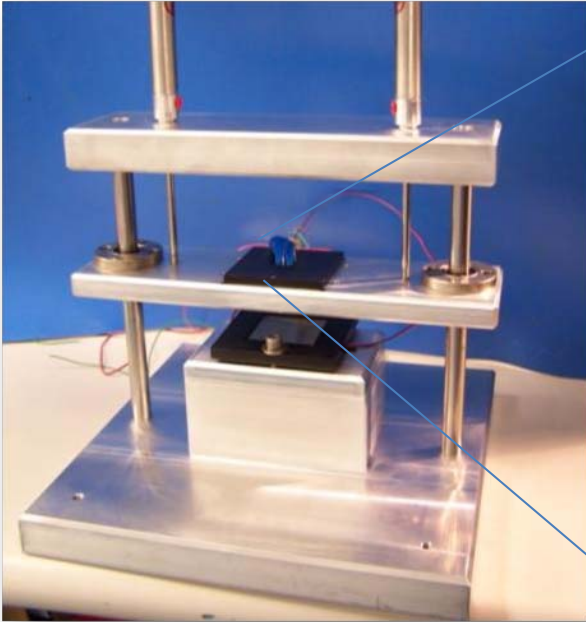
**Scanning Seebeck
uncovers process-induced
material variation**

Example: Uniform SPS Coin



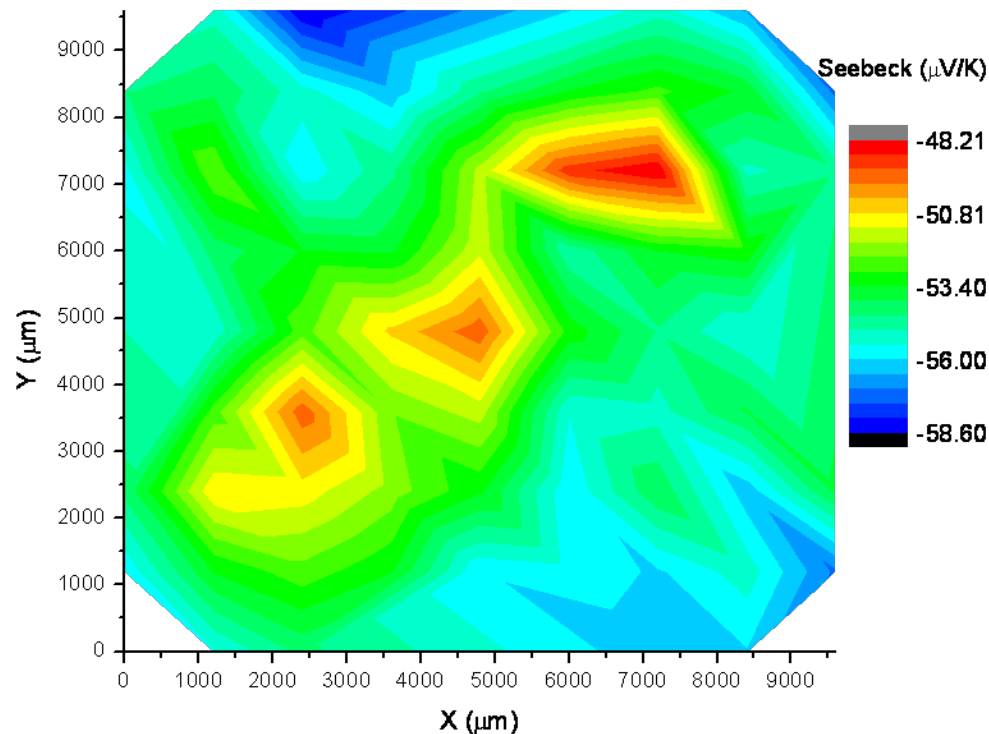
Passes '10% of Mean' Test
Passes 'Gaussian Distribution'
Test

Even Faster Screening – Multi-probe Seebeck: Simultaneous Measurement with 60 Probes



60 voltage probes and 4 thermocouples

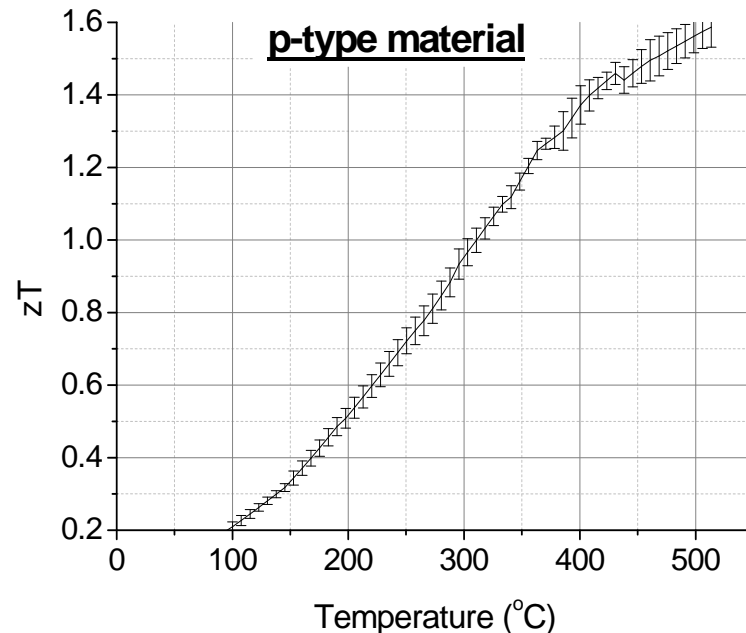
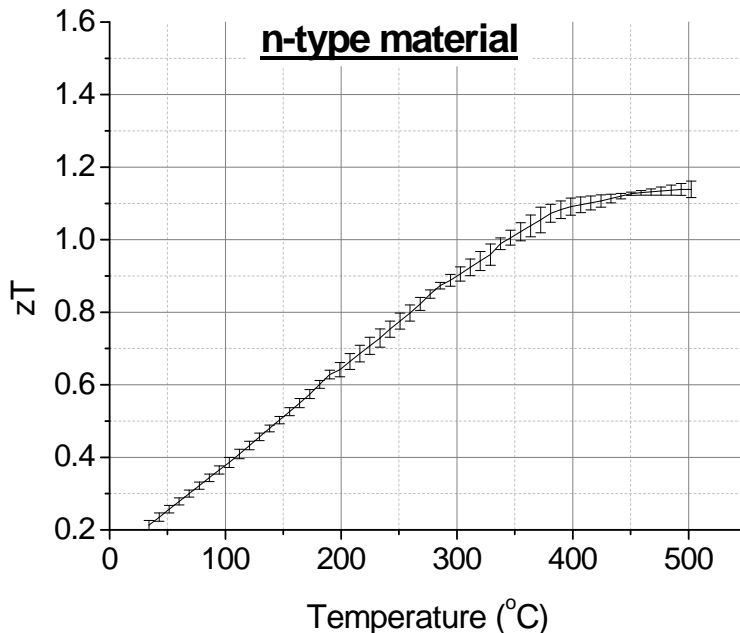
Even Faster Screening – Multi-probe Seebeck: Simultaneous Measurement with 60 Probes



Measurements take ~~tens of~~ minutes instead of tens of hours.

<ZT> Analysis

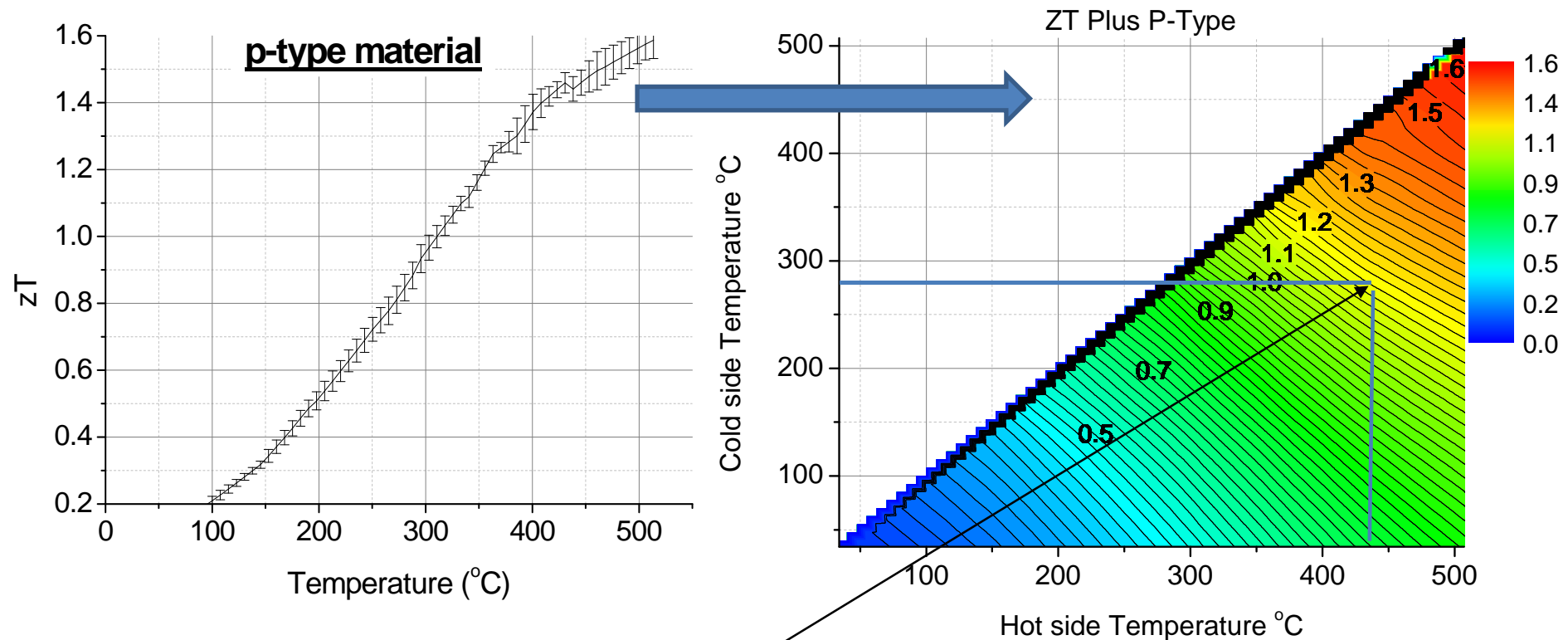
- Not only material development cycle is long, but also device optimization is complex. Simple tools are desirable to compare the benefits of variations of material properties.
- Average ZT is the property that is being used extensively for performance estimates.
- Average ZT is a function of temperature range.



Which material is better?

<ZT> Plots

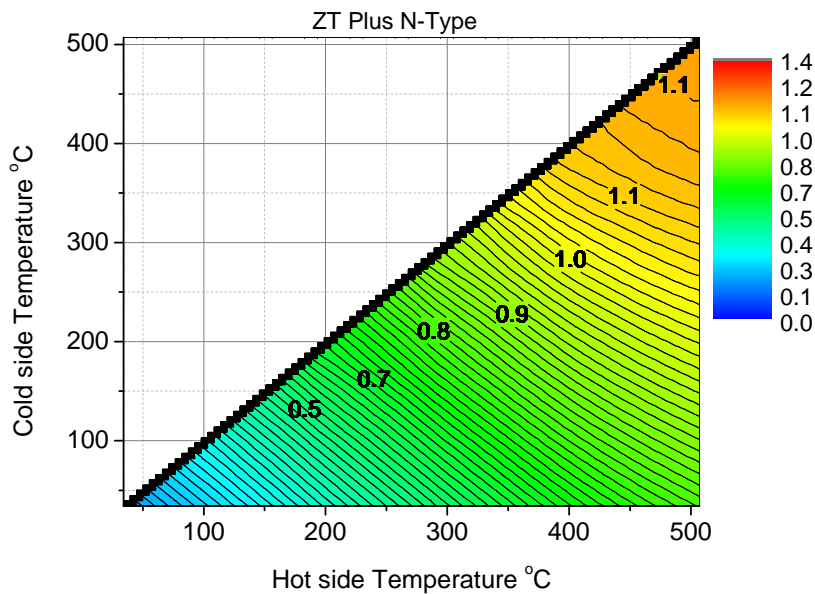
Convert $ZT(T)$ plot into $\langle ZT \rangle (\Delta T)$ contour map



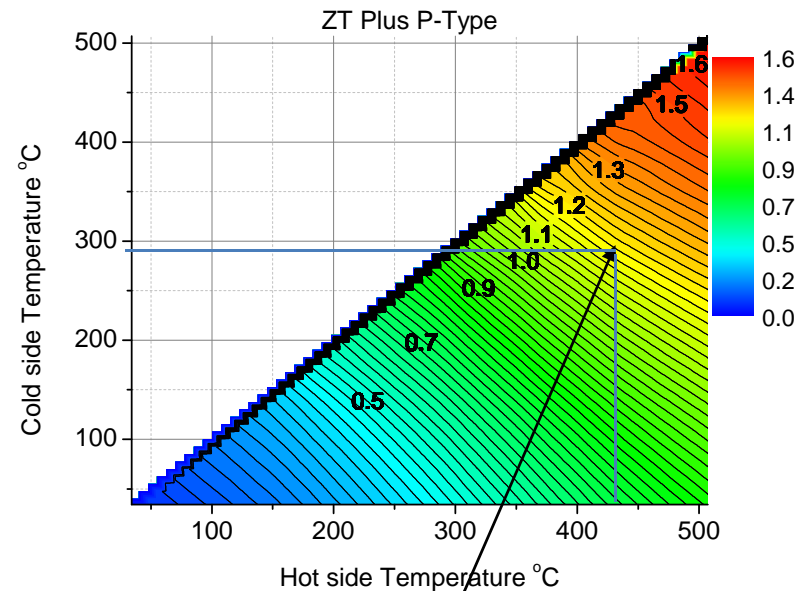
Example: $\langle ZT \rangle$ between 280 and 430 $^{\circ}\text{C}$ is 1.15

<ZT> Plots

N-type



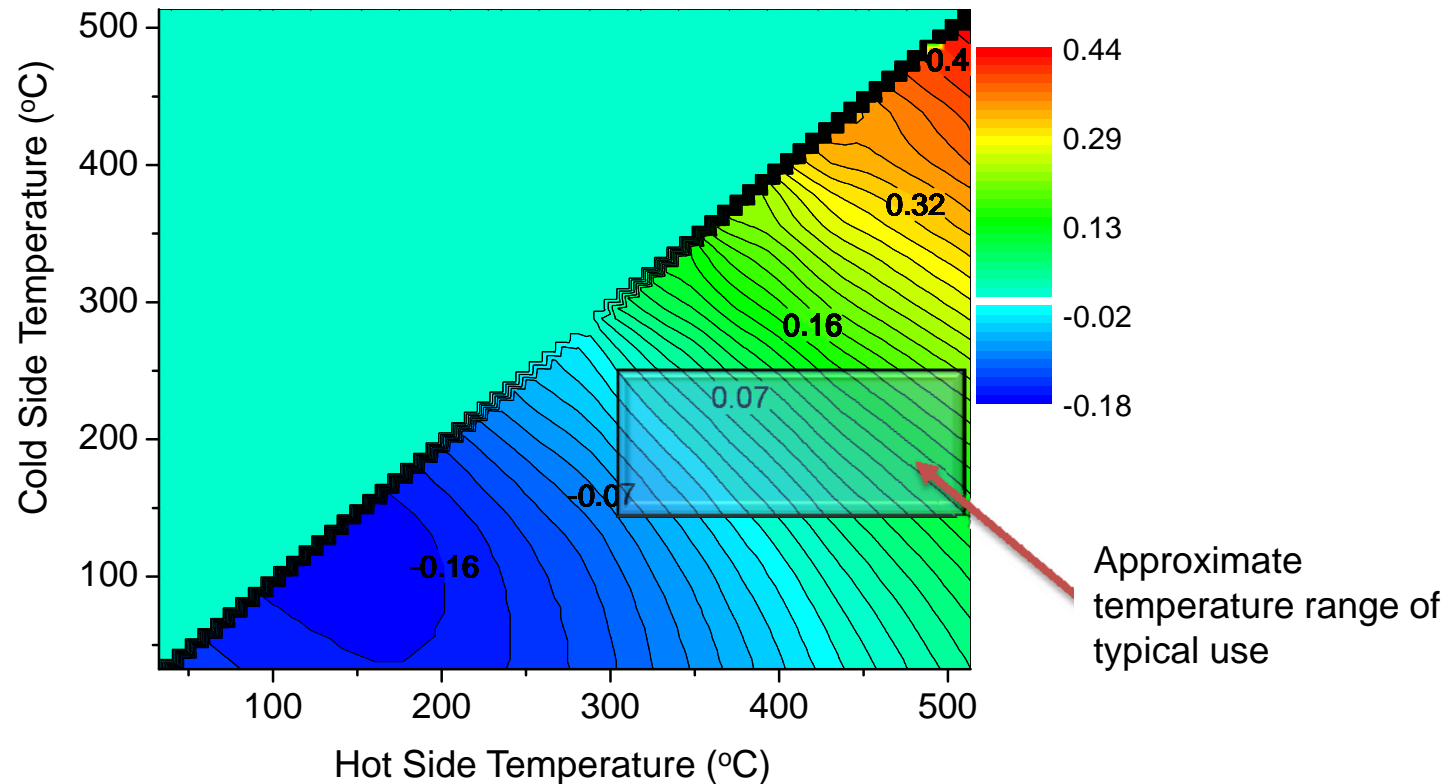
P-type



Example: <ZT> between 280 and 430 °C is 1.15

Differential $\langle ZT \rangle$ Plot

$$\text{Average } P, N \text{ differential } zT = \frac{\int_{T_1}^{T_2} [zT(T)_{P\text{-type}} - zT(T)_{N\text{-type}}] dT}{T_2 - T_1}$$

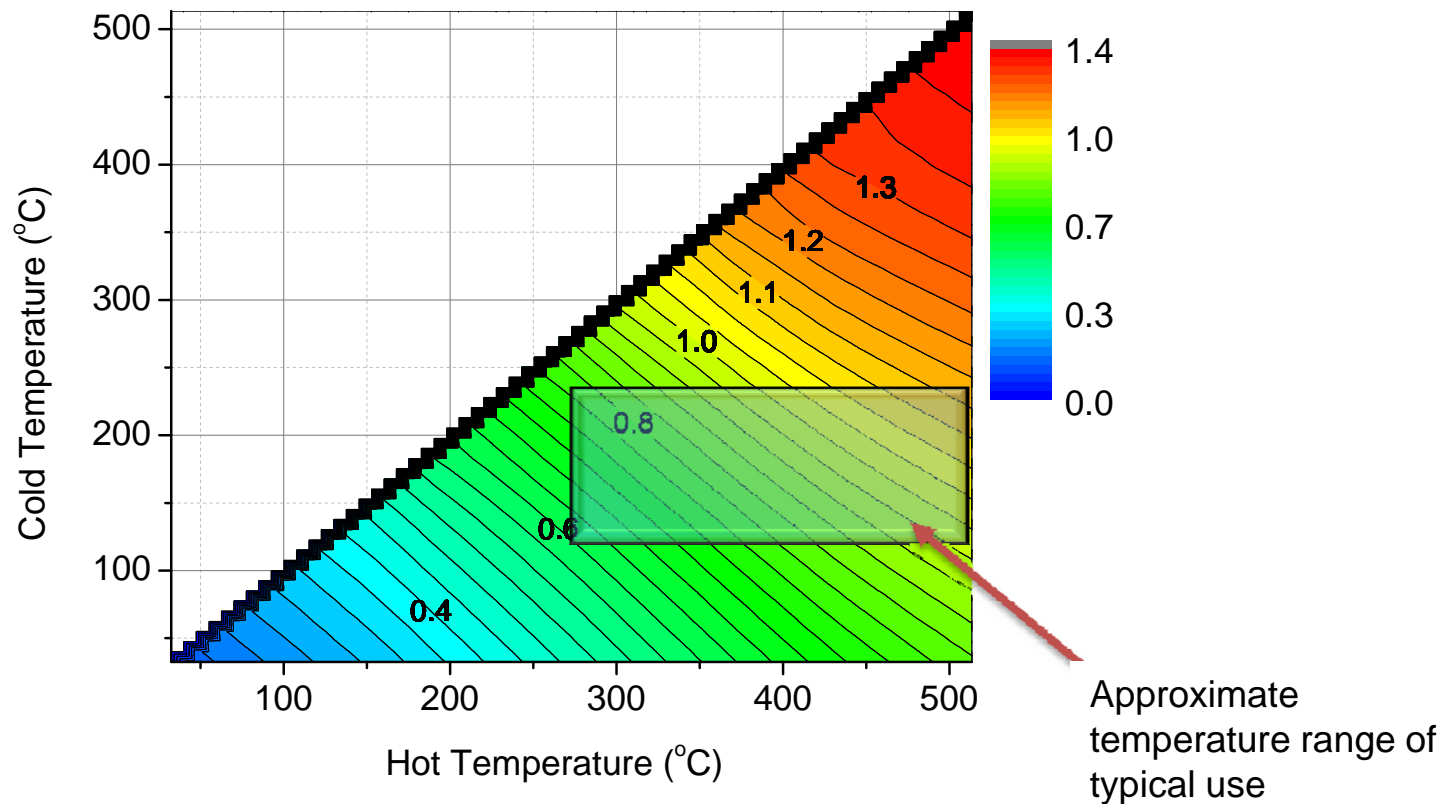


Which material is better?

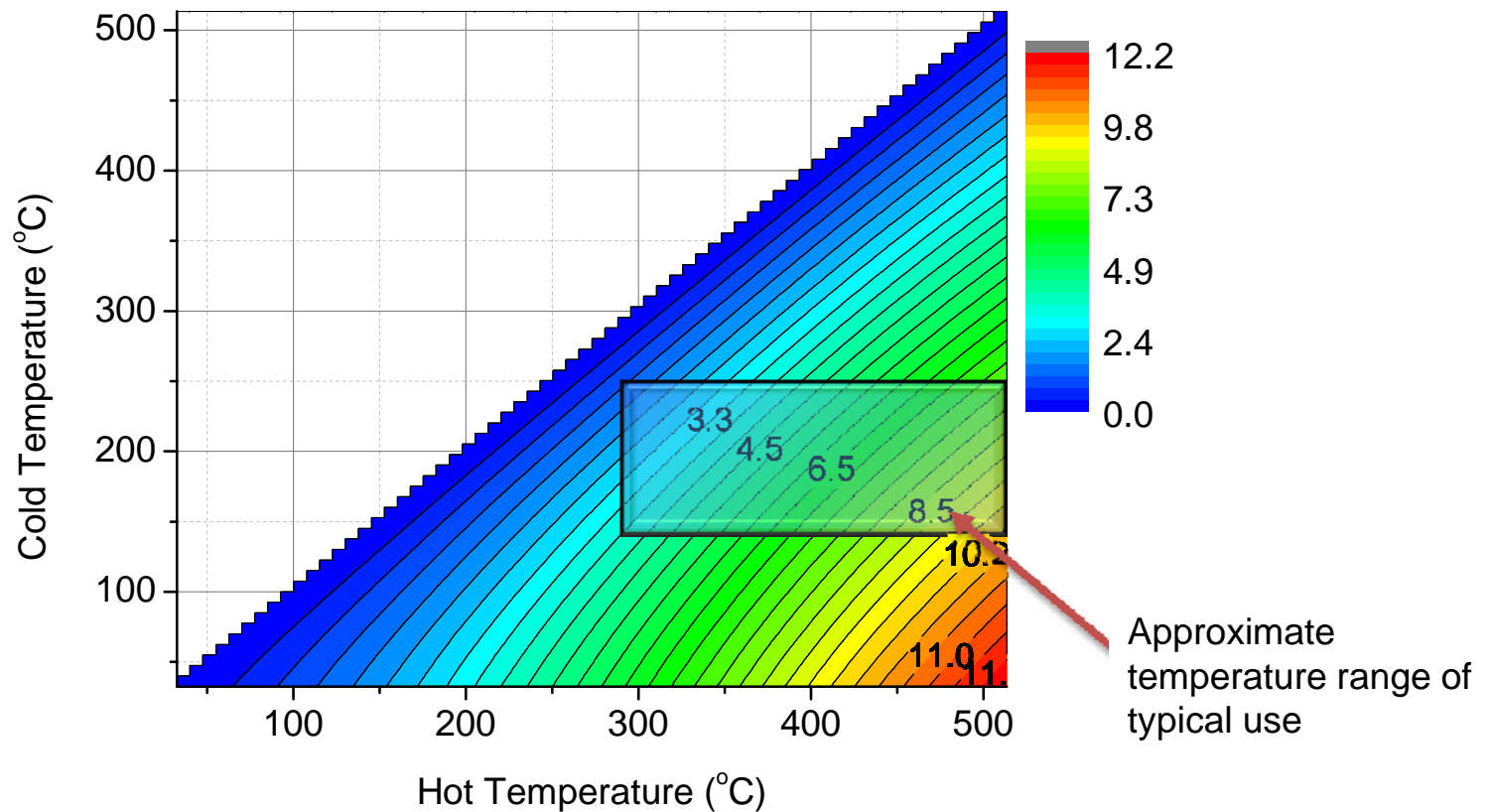
Judging by average $\langle zT \rangle$ these materials are relatively well matched.

$\langle ZT \rangle$ of a Couple

$$\text{Average } P, N \text{ pair } zT = \frac{\frac{1}{2} \int_{T_1}^{T_2} [zT(T)_{P\text{-type}} + zT(T)_{N\text{-type}}] dT}{T_2 - T_1}$$



Ideal Efficiency of a Couple



Assumptions: no parasitic losses; not accounting for material self-compatibility.

Conclusions

- ZT Plus has successfully transitioned advanced PbTe materials from academic laboratories to pre-production sampling; currently gearing up for scale-up.
- Experimental cycle of material development needs to be fast and robust for optimization experiments targeting production-viable materials.
- Careful selection of measurement and analysis tools need to be employed for rapid characterization of TE materials.
- Sore issue – universally acceptable metrology of TE materials, especially for power generation applications.

Acknowledgments

- Government support – DOE, DARPA, ONR
- OEM and T1 partners – BMW, Ford, Faurecia
- Academic partners – OSU, Northwestern University
- Colleagues at ZT Plus, BSST and Amerigon