Mechanical and Elastic Property Evaluation of n- and p-type Skutterudites

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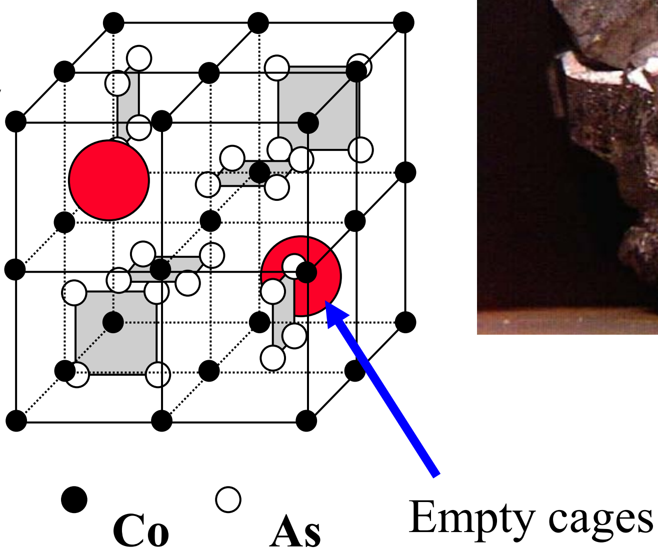
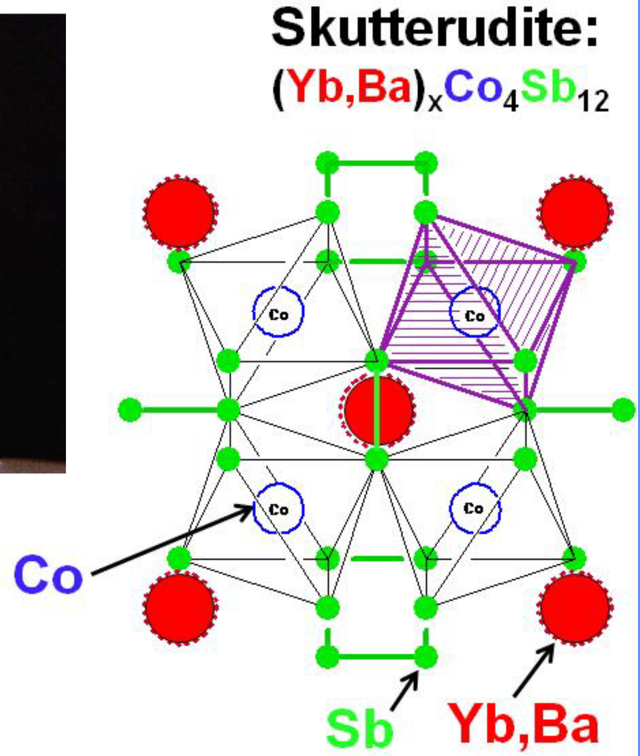
Filled Skutterudites: Technologically Important and Scientifically Fascinating Materials

Skutterudite: a $CoAs_3$ mineral found near Skutterud, Norway, in 1845, and compounds with the same crystal structure (body-centered cubic, *Im3,* Oftedal, I. (1928): *Zeitschrift für Kristallographie* 66: 517-546) are known as "skutterudites"

□Co_4As_{12}





W. Jeitschko, D. J. Braun, Acta Crystallogr. 1977, B33, 3401: Filled Skutterudite Crystal Structure for $LaFe_4P_{12}$.

Fracture and Failure in Ceramics : Battling Flaws

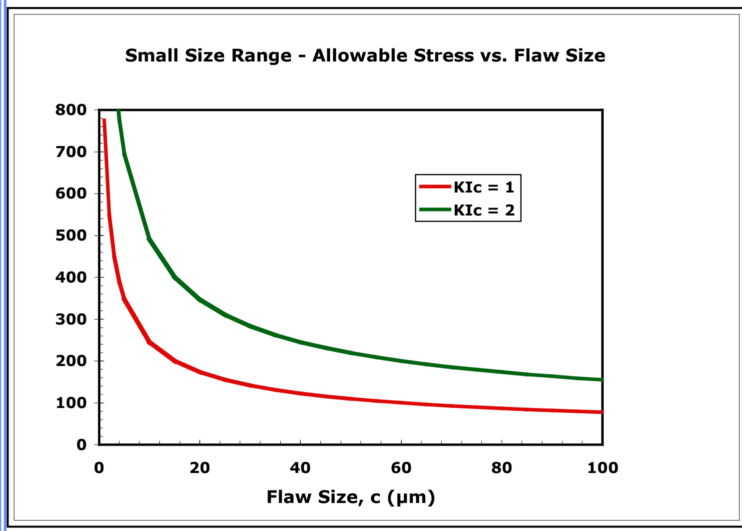
Fracture toughness $K_{IC} = Y\sigma\sqrt{a \cdot \pi}$.

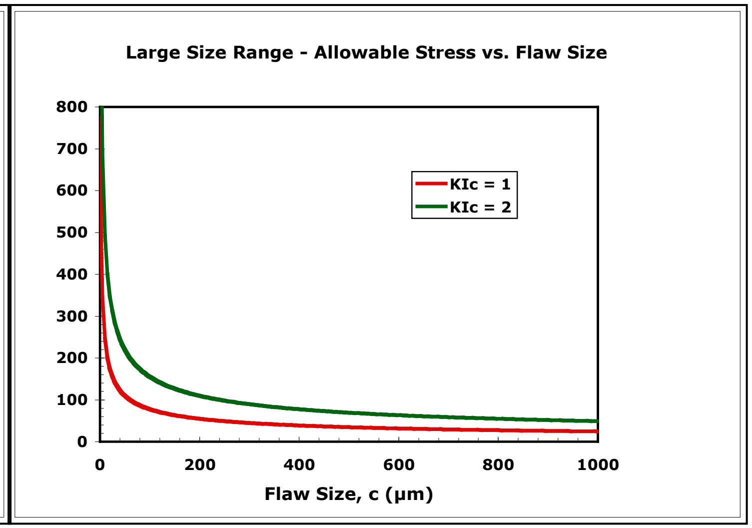
Mode I fracture Y is a crack shape factor and is larger for surface and edge cracks.

$$a_c = \frac{1}{\pi}\left(\frac{K_{IC}}{\sigma Y}\right)^2$$

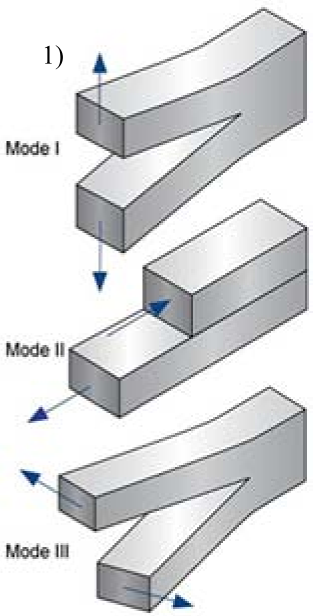
a is the crack length for edge cracks

or one half crack length for internal cracks.





1)

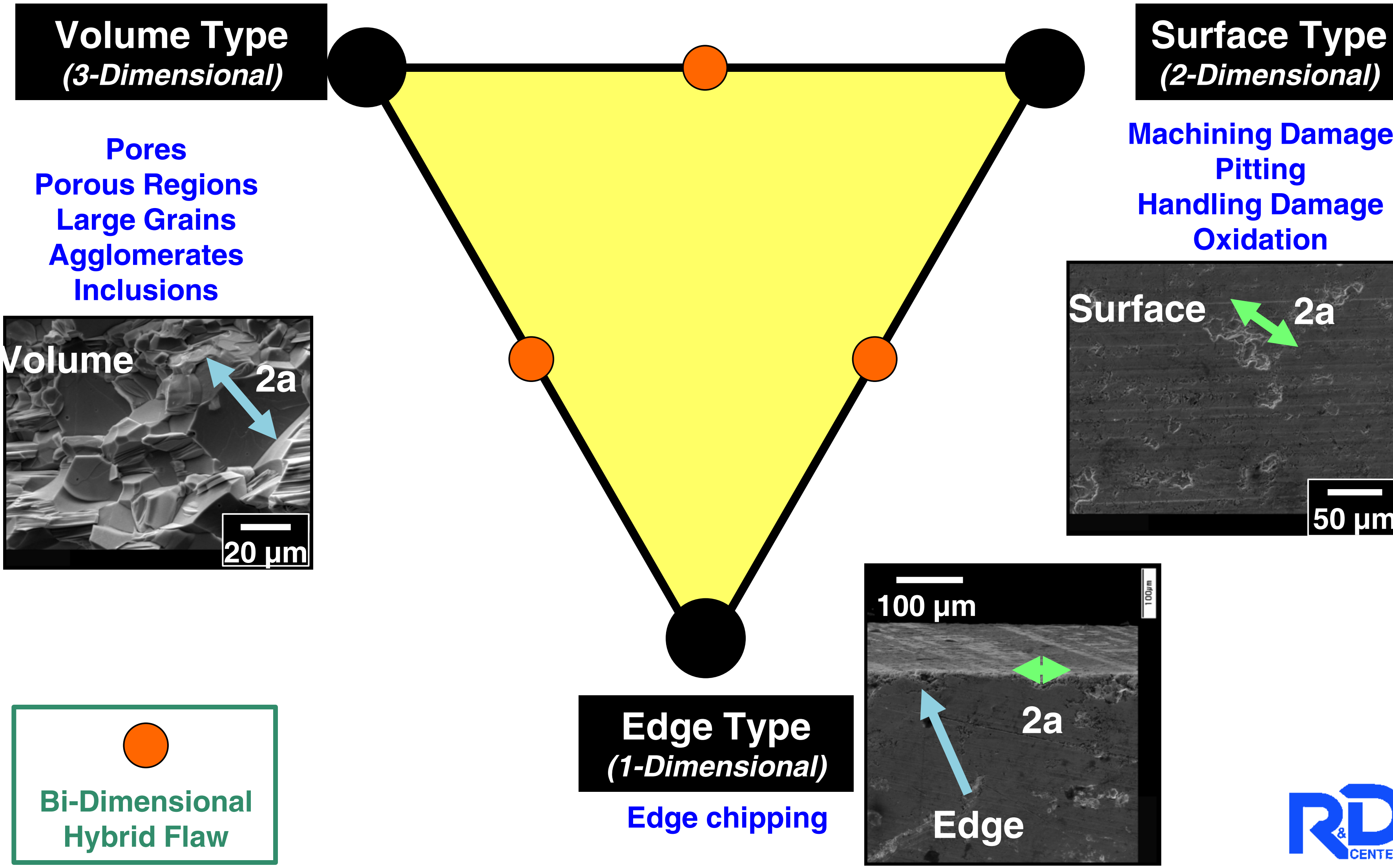


[2] $K_{Ic} = 1.1 - 2.2 \text{ Mpa} \cdot \text{m}^{1/2}$

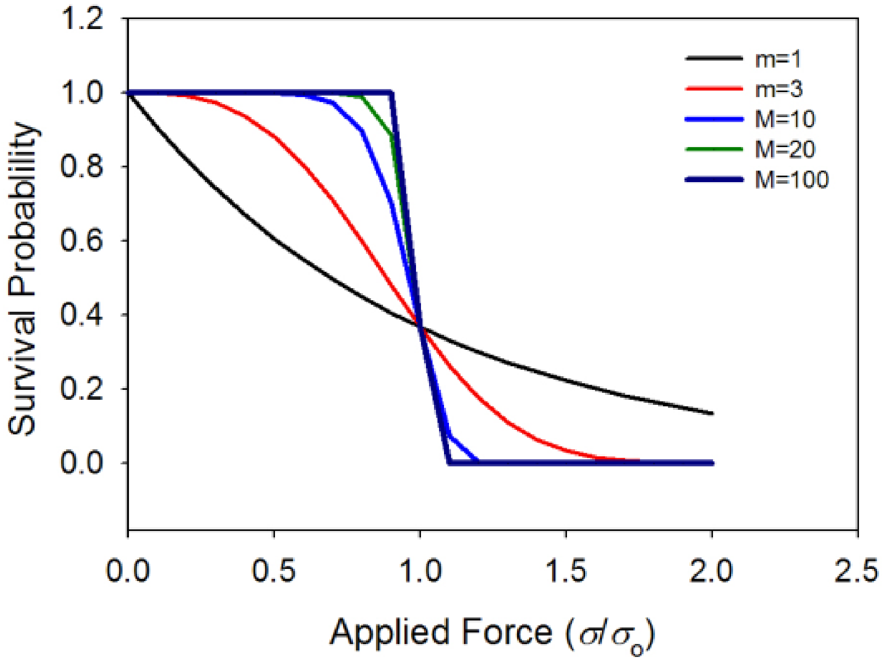
1) http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Mechanical/FractureToughness.htm

2) V. Ravi, S. Firdosy, T. Caillat, B. Lerch, A. Calamino, R. Pawlik, M. Nathal, A. Sechrist, J. Buchhalter, and S. Nutt. Mechanical Properties of Thermoelectric Skutterudites, Proceedings of the American Institute of Physics Conference, Space Technology and Applications International Forum, (2008) February 10-14; Albuquerque, NM.

Strength-Limiting Flaw Classification For Brittle Materials.



Fracture and Failure in Ceramics : A Statistical Problem



$$\Phi = e^{-(\sigma/\sigma o)^\wedge M}$$

The Weibull Modulus (M) is a measure of the scatter of data in a Weibull distribution

It is analogous to the standard deviation in a Gaussian distribution.

For ceramic fracture and failure M is a measure of the flaw population distribution.

Controlling fracture is controlling or eliminating the outliers in the flaw population

Thermal Shock Resistance Parameter For Thermoelectric Materials in Operation

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

Steady State Heat Flow *Q*

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

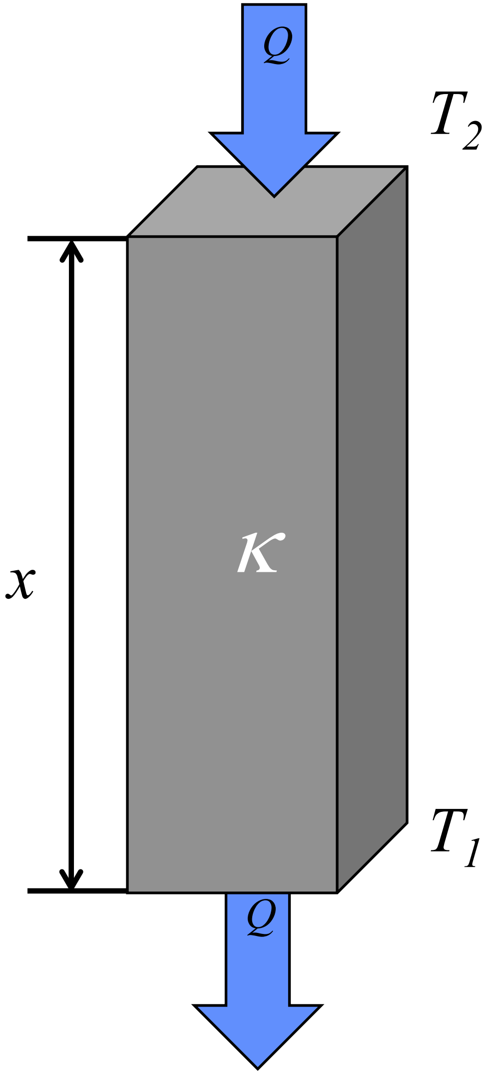
Temperature Gradient as a result of heat flow

$$\sigma = \frac{(T_2 - T_1) \times E \times CTE}{(1 - \upsilon)}$$

Stress as a result of a temperature gradient

$$QF = \frac{(1 - \upsilon) \times \kappa \times \sigma}{E \times CTE}$$

Maximum allowable heat Flow



Of Concern is the Long Term Survival of the TE Legs Under Normal Operating Conditions.

$$R_{Therm} = \frac{\sigma_{Tens}(1-\nu)\kappa}{CTE \bullet E}$$

Kingery, J. Am. Cer. Soc., 38:3-15 (1955).

R_{Therm} = Thermal shock resistance parameter (the larger the better)
σ_{Tens} = Tensile stress or strength
ν = Poisson's ratio
κ = Thermal conductivity
CTE = Coefficient of thermal expansion
E = Elastic modulus

Griffith Criterion

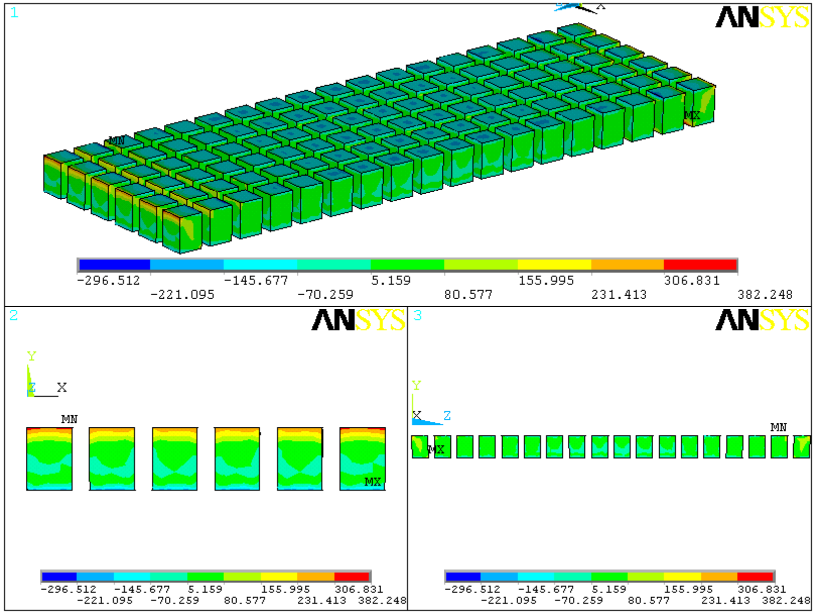
$$\sigma_{Tens} = \frac{K_{Ic}}{Y\sqrt{a}}$$

K_{Ic} = Fracture toughness
Y = Crack shape factor
a= Griffith flaw size

Tensile Strength << Compressive Strength
Manage tensile stress for conservative design

Must seek to minimize c!

Thermal Stress Experienced by a TE Module During Operation.



FEA finds that stress is particularly concentrated at edges and corners under 500 °C thermal gradient.

The stresses calculated by FEA for a module are quite sensitive to:

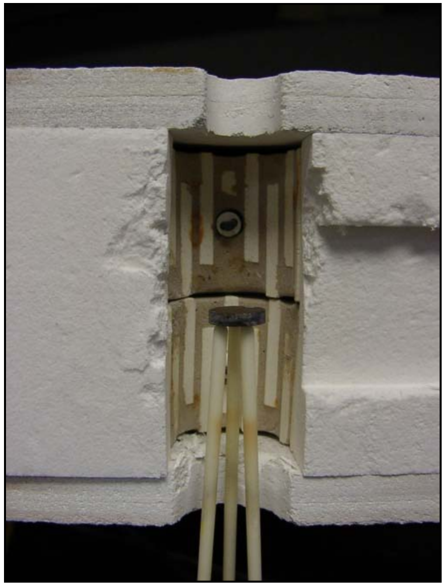
(a) CTE, E inputs

(b) Boundary Conditions (these presented here are very strenuous).

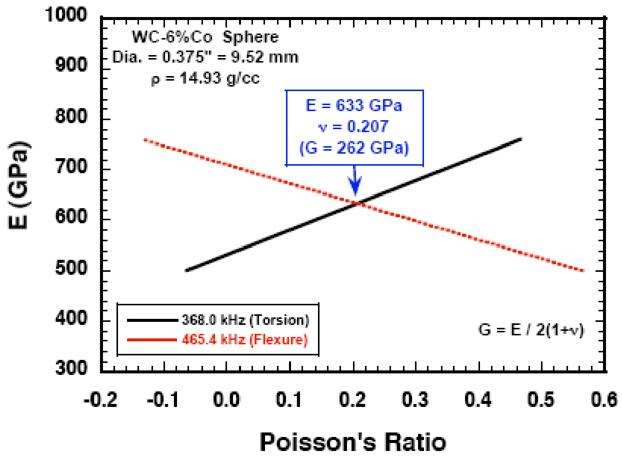
When these mismatched CTE's (stainless steel contacts and Al_2O_3 insulators are accounted for tensile stresses in the legs climb to greater than 300 MPa via FEA modeling.

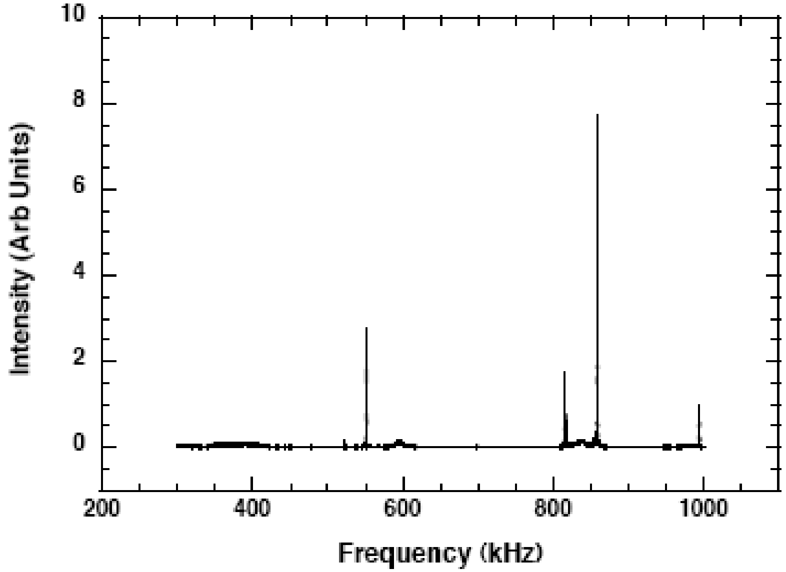
1) O. M. Jadaan and A. A. Wereszczak, "Probabilistic Design Optimization and Reliability Assessment of High Temperature Thermoelectric Devices," Ceramic Engineering and Science Proceedings, 29, [3], 157-172 (2008).

Elastic Property Measurements



Elastic Modulus and Poisson's ratio were determined by Resonant Ultrasound Spectroscopy (RUS).





$$f_{tors} = A_t + B_t \bullet E + C_t \bullet \nu \quad \text{and}$$

$$f_{flex} = A_f + B_f \bullet E + C_f \bullet \nu$$

Summary of Elastic Properties

Sample type	E (Gpa)	G (Gpa)	B (Gpa)	ν	V_T ($x10^3$ m/s)	V_L ($x10^3$ m/s)
n-type	135	55	80	0.20	2.69	4.50
p-type	123	50	73	0.20	2.56	4.29

n-type $La_{0.05}Ba_{0.07}Yb_{0.08}Co_{4.00}Sb_{12.02}$

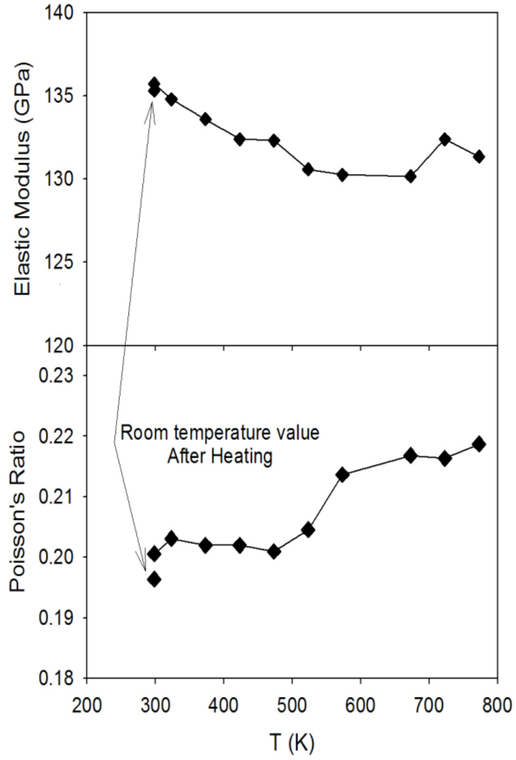
p-type $Ce_{0.30}Co_{2.57}Fe_{1.43}Sb_{11.98}$

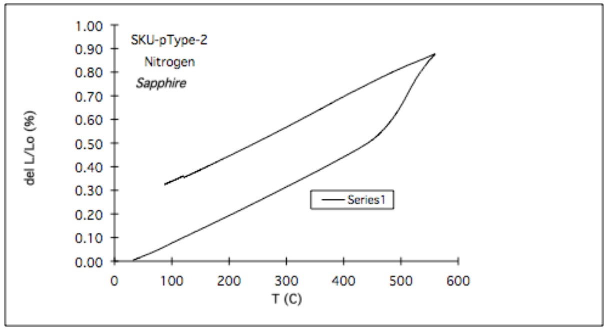
$$B = \frac{E}{[(1+\upsilon)\cdot 2]}$$

$$G = \frac{E}{[(1-2\upsilon)\cdot 3]}$$

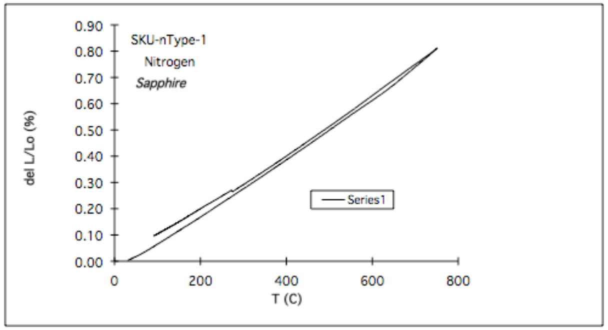
$$\upsilon_T = \sqrt{\frac{G}{\rho}}$$

$$\upsilon_L = \sqrt{\frac{E}{\rho} \times \frac{1-\upsilon}{(1+\upsilon)(1-2\upsilon)}}$$



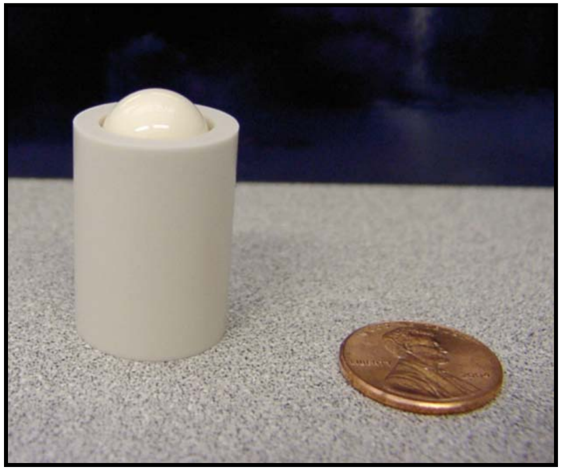


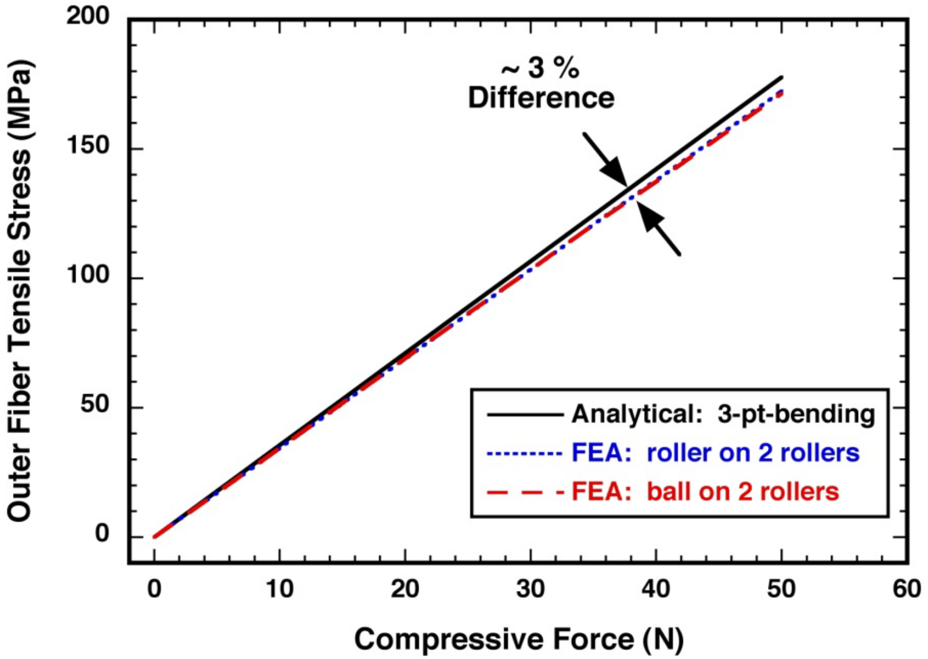
CLTE = 11.5 ppm to 450°C



CLTE = 10.1 ppm

An All-Alumina High-Temperature "3-Point" Bend Fixture Was Developed and Used For Strength Testing



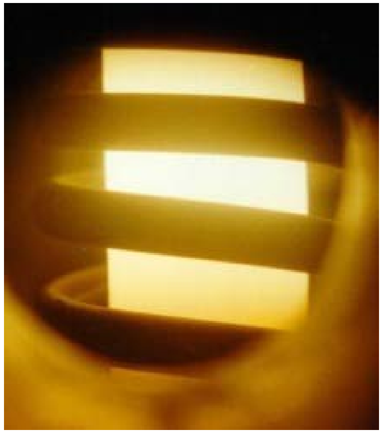


$$\sigma_{ten} = \frac{3PL}{2bh^2}$$

Comparison of the outer-fiber tensile stress as a function of 3-point-bend force for the analytical case (black), its finite element analysis (blue), and the case for the bend fixture shown in Fig. 3 (red). Difference was small (~3%), so the analytical expression was used to estimate failure stresses in this study.

This is actually a "Ball on Two Rollers" 3-Point Bend Fixture. The self aligning nature allows high sample throughput. The close contact between the ball and cylinder make for a virtually oxygen free environment .

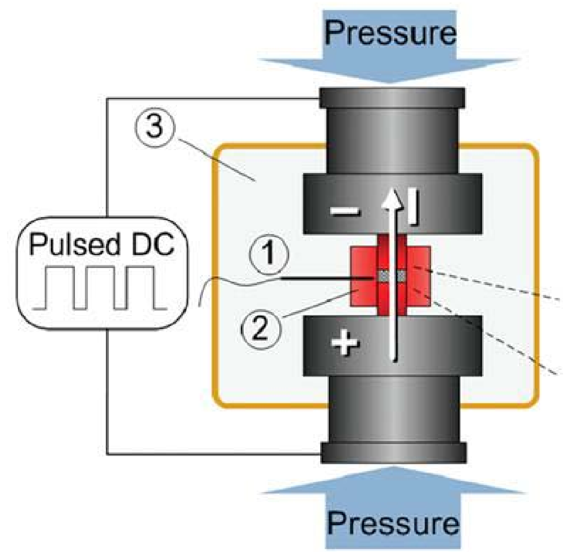
Preparation of Filled Skutterudites.



Induction melting of the elements. Sealed vessel required for n-type

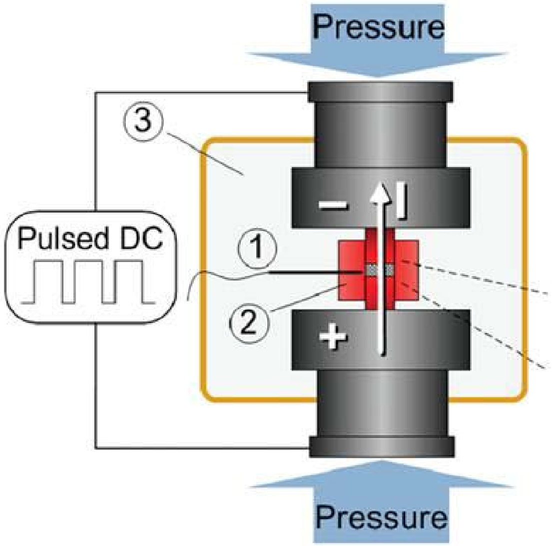
The melt is annealed at 750 °C for 1 week

Annealed charge was milled by HEBM and sieved to 60 μm



Diced by low speed diamond saw

Prototypical Graphite Die and to Create Test Specimens

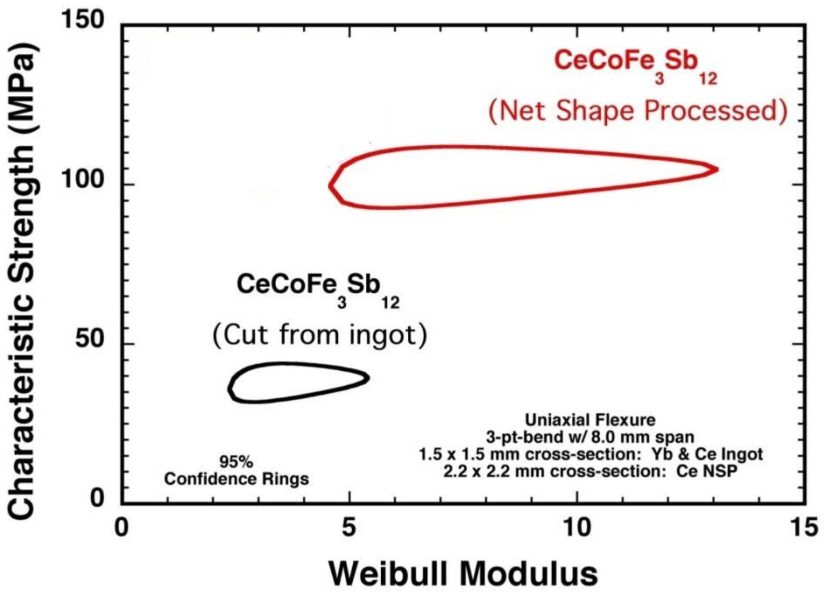


SPS

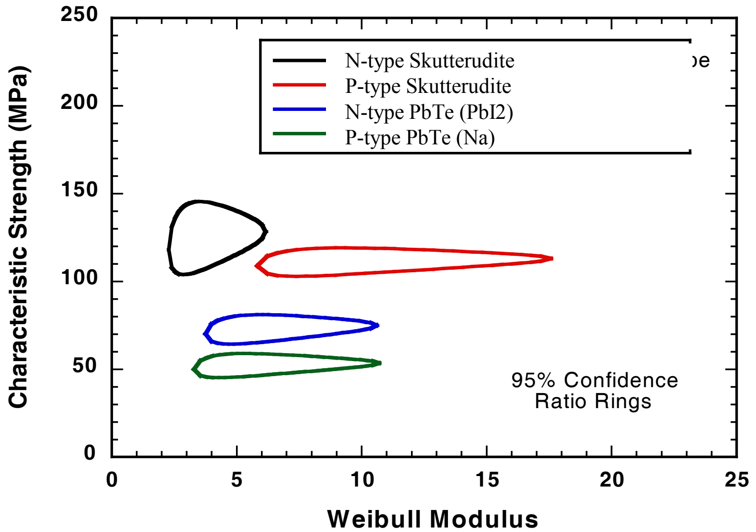
Sintering

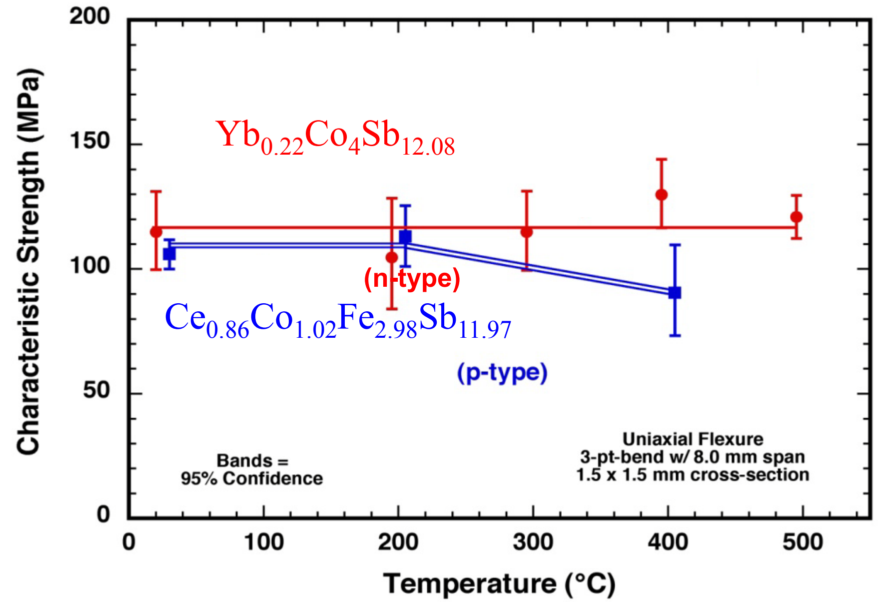
Room Temperature Strength of Diced and NSS Test Coupons

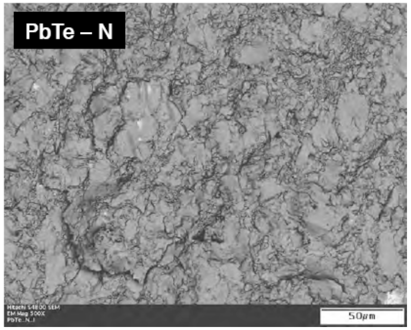
- Edge type (1-D), extrinsic, typically a machining effect
  - *e.g.,* edge chipping or chamfering (TE elements can be cast as cylinders)
- Surface type (2-D), can be extrinsic or intrinsic
  - *e.g.,* machining damage, reaction layer, oxidation layer
- Volume type (3-D), usually intrinsic
  - *e.g.,* pores, agglomerates, large grains, etc.
  - Improvement in material processing will lessen their effect

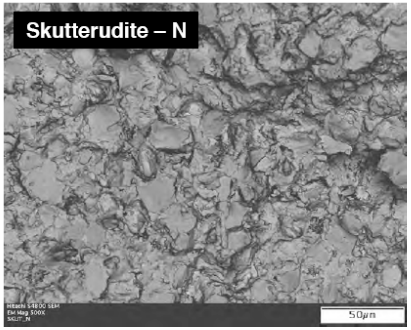


Strength as a Function of Temperature







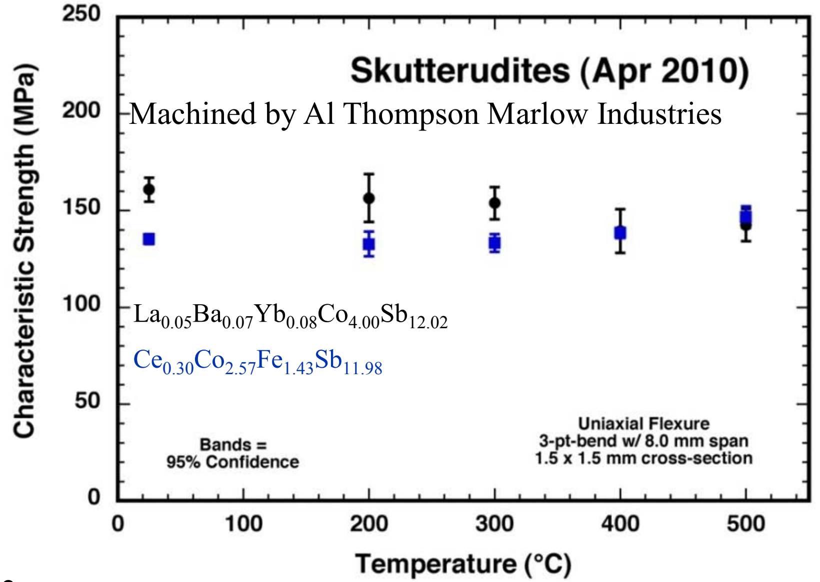


Results are for small scale reactions (60g) and ½ in. billets

The characteristic strength of skutterudites is twice that of the PbTe based materials with similar microstructures that we have tested. Samples prepared by SPS and cut parallel to pressing axis

J.R. Salvador et. al. Philo. Mag. 89, 1517 (2009).

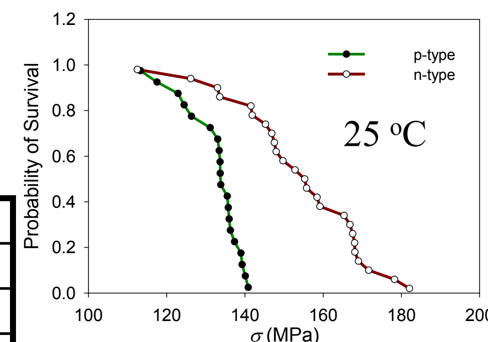
Incremental Improvement in Characteristic Strength

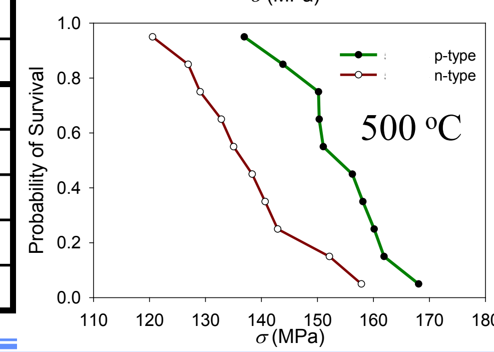


Results are for large scale (1.0 kg batches and 3.0 cm (80 g billets).

Material	Temp (°C)	# of Tests	2- parameter Weibull: Characteristic Strength* (MPa)	2- parameter Weibull: Weibull Modulus*	Gaussian: Ave. Strength (MPa)	Gaussian: 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

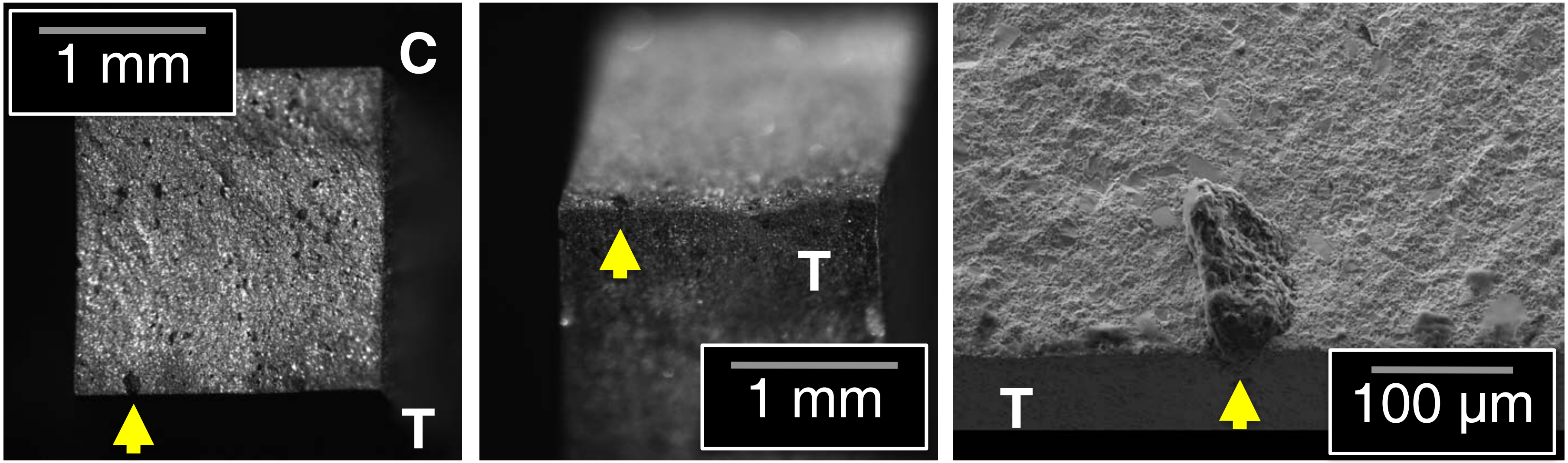
* Values in parenthesis = ± 95% confidence interval

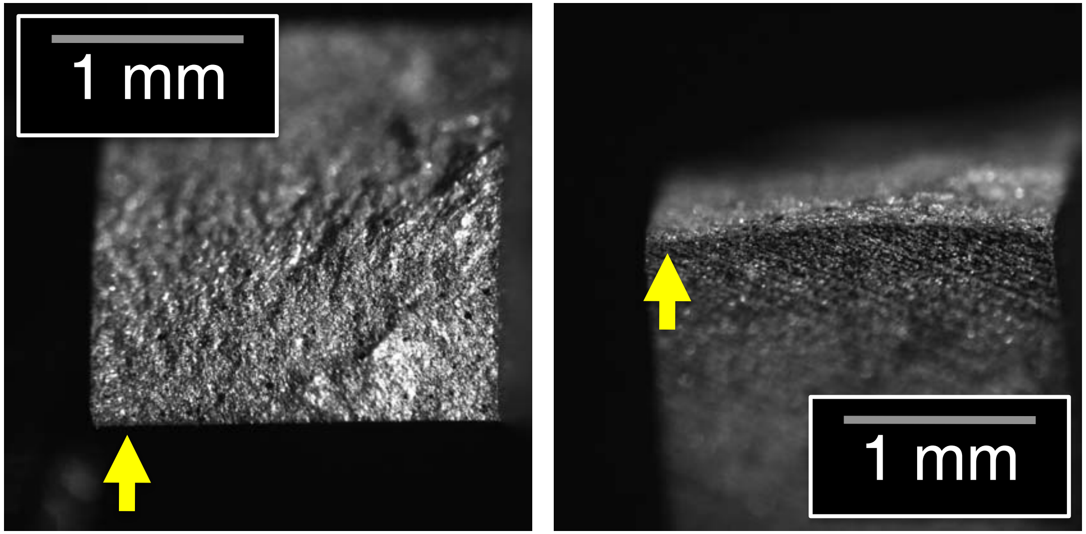




Representative Flaws of Large Scale Materials

Volume-Type Flaw (SKN-3)

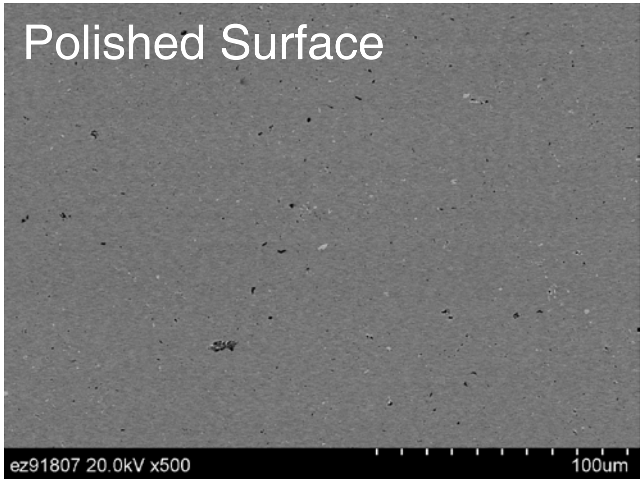


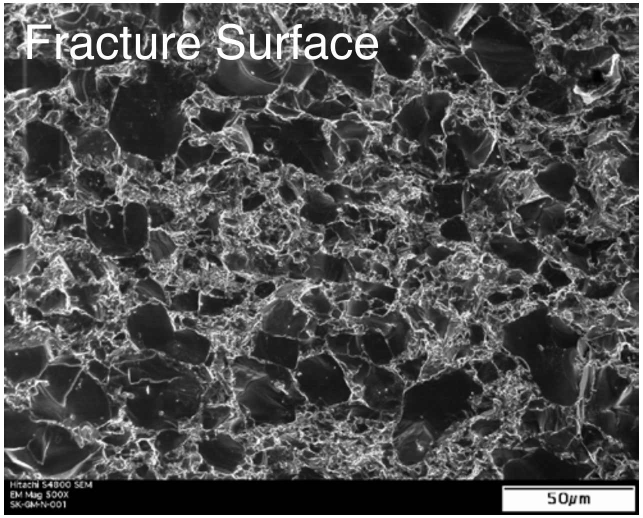


Surface-Type Flaw (SKN-17)

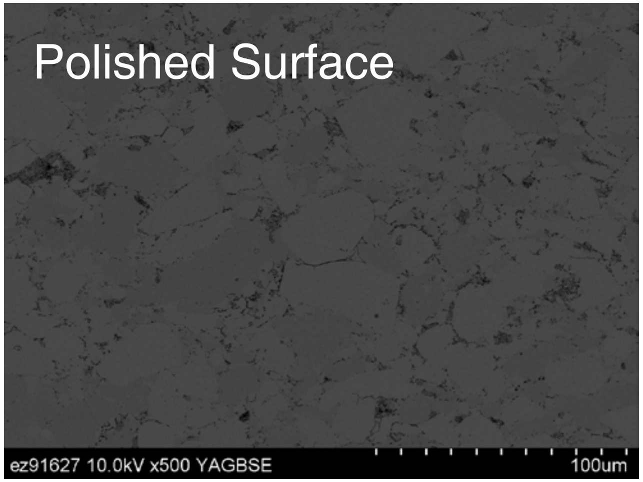
Source of Persistently Lower Weibull Modulus in n-Type Materials?

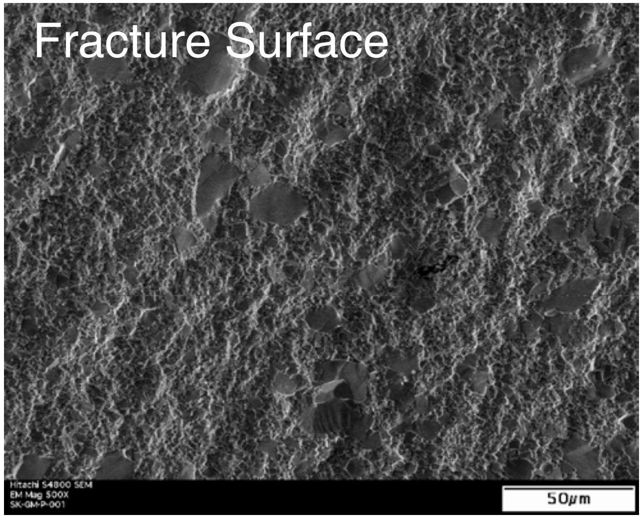
N-Type





P-Type





Conclusions

- Demonstrated incremental improvement in the fracture strength of skutterudite materials by flaw mitigation.   Characteristic strengths for skutterudites are twice that of PbTe and Bi-Te based materials.

- Fracture strength of both n- and p-type skutterudites is nearly temperature independent and characteristic strength magnitude is encouraging from a durability standpoint.

- Weibull modulus (increased uncertainty) of the n-type material still lags p-type due to the larger distribution of volume flaws (larger grain distribution).

- There is significant room for improvement in the control of microstructure by optimizing powder metallurgical techniques.

Thank You !