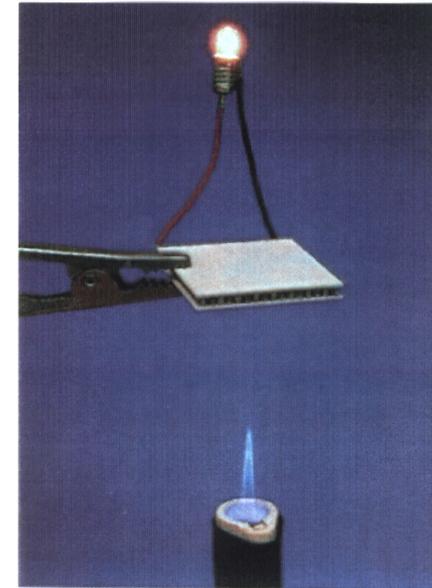


New thermoelectric materials and devices at Michigan State University

- Mercuri G. Kanatzidis, Chemistry
- Timothy Hogan, E.Engineering
- S. (Bhanu) D Mahanti, Physics
- Other Collaborators
 - Ctirad Uher, Univ. of Michigan, Physics
 - Kannewurf, Northwestern
 - Tellurex Corp., Traverse City MI



Electrical
Power Generation



Reaction Chemistry

Investigating the System:

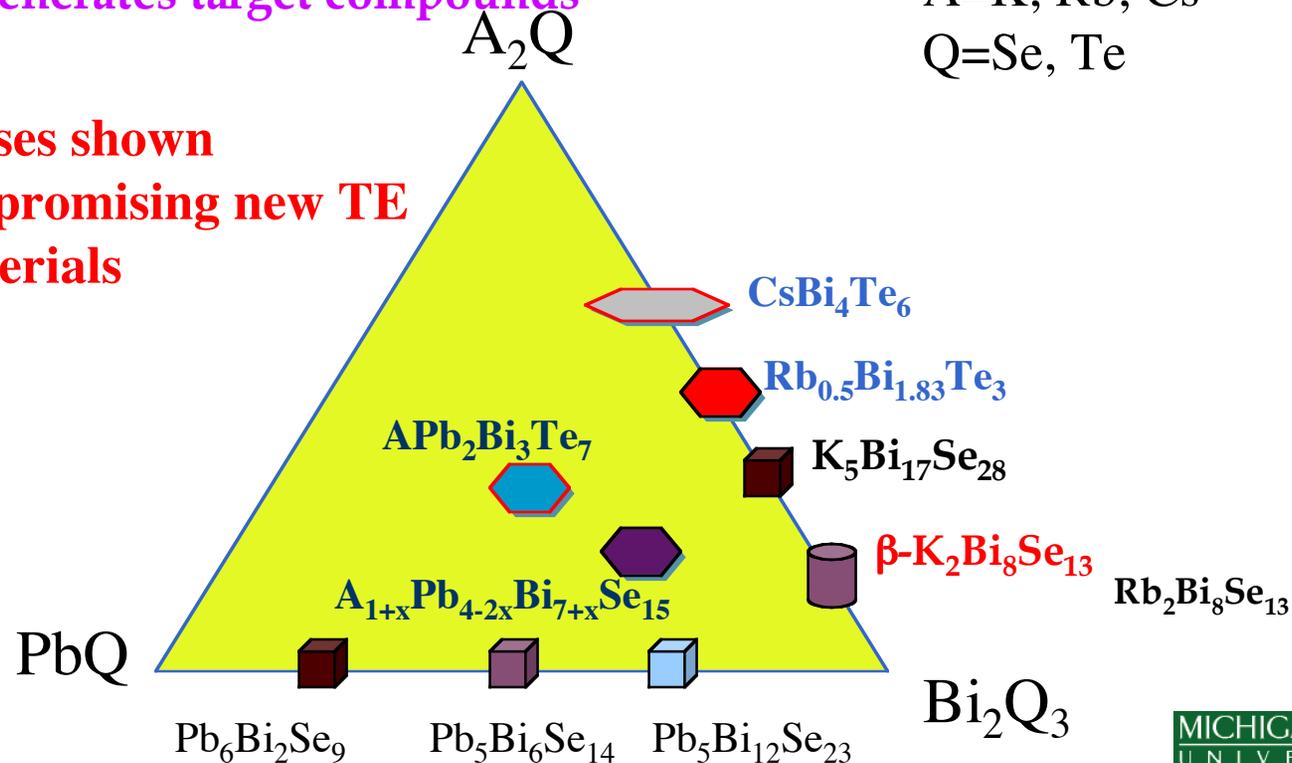


Map generates target compounds

A=K, Rb, Cs

Q=Se, Te

Phases shown
are promising new TE
Materials



ZT and Band Structure

B- parameter

$$B = \frac{CT^{5/2}\gamma\sqrt{m_x m_y m_z}\mu_x}{\kappa_{latt}}$$

m= effective mass

μ = mobility

κ_{latt} = lattice thermal conductivity

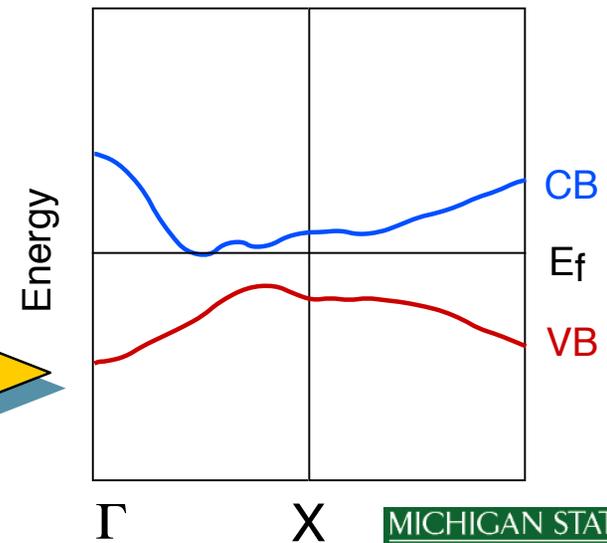
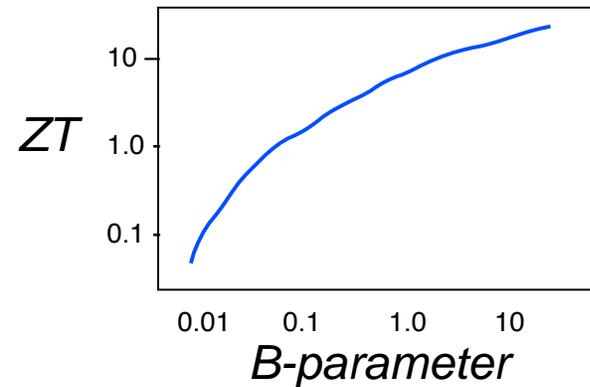
T = temperature

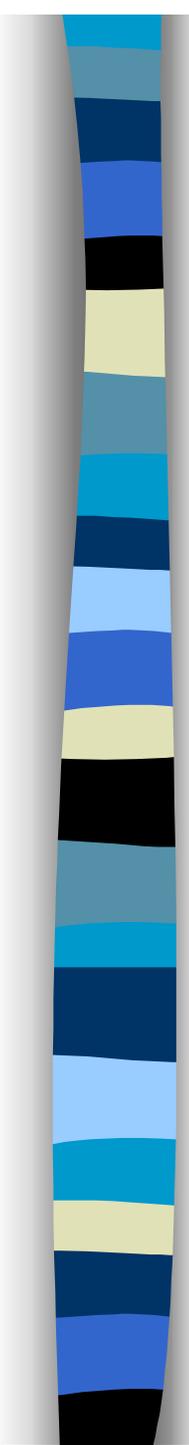
γ = band degeneracy

High γ comes with

(a) high symmetry e.g. rhombohedral, cubic

(b) off-center band extrema





New Materials for Thermoelectric Applications

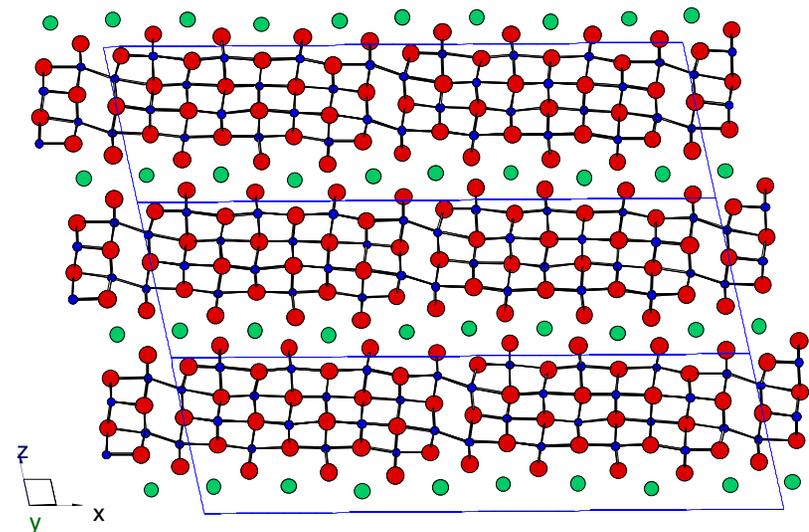
- CsBi_4Te_6
- $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ and its derivatives
- Cubic Chalcogenides
- New compounds
 - New Super Series
$$\mathbf{A}_m[\mathbf{M}_{1+l}\mathbf{Se}_{2+l}]_{2m}[\mathbf{M}_{2l+n}\mathbf{Se}_{2+3l+n}]$$
 - **A=alkali, M=Sn, Pb, Bi, Sb**

New Bismuth Chalcogenide Thermoelectric Materials

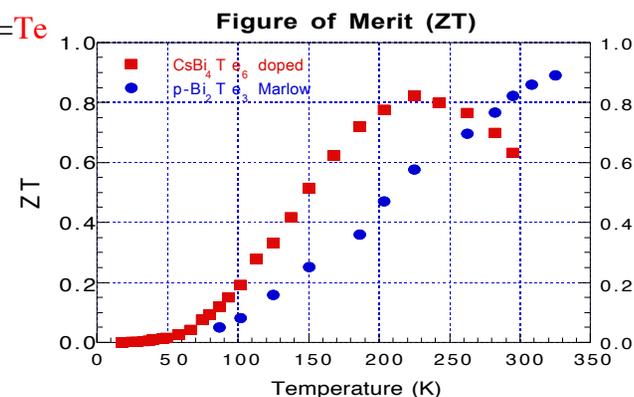
CsBi_4Te_6 was found to be a low temperature material with a ZT at 240 K of ~ 0.8 (p-type). (*Science*, **2000**, 287, 1024)

CsBi_4Te_6 could function in a temperature range where $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ quits being effective. Thus in a segmented configuration CsBi_4Te_6 and $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ may significantly lower the minimum achievable cooling temperature of TE devices, enabling various cooling applications.

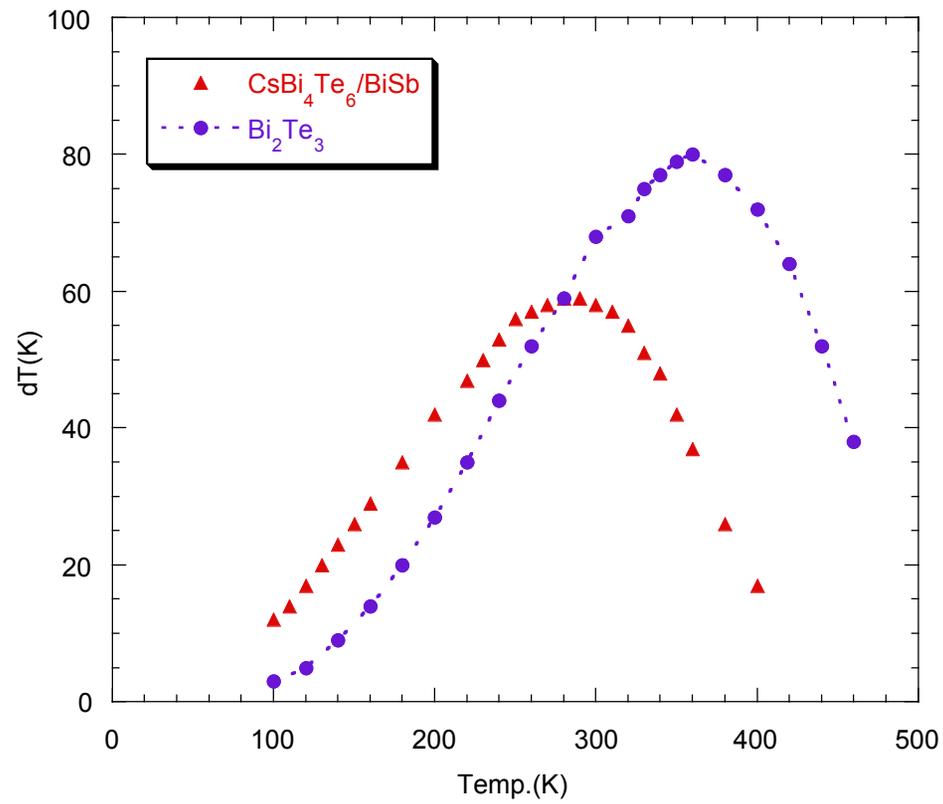
$\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ is another new material with potential to outperform all others at high temperatures (300-700 K)



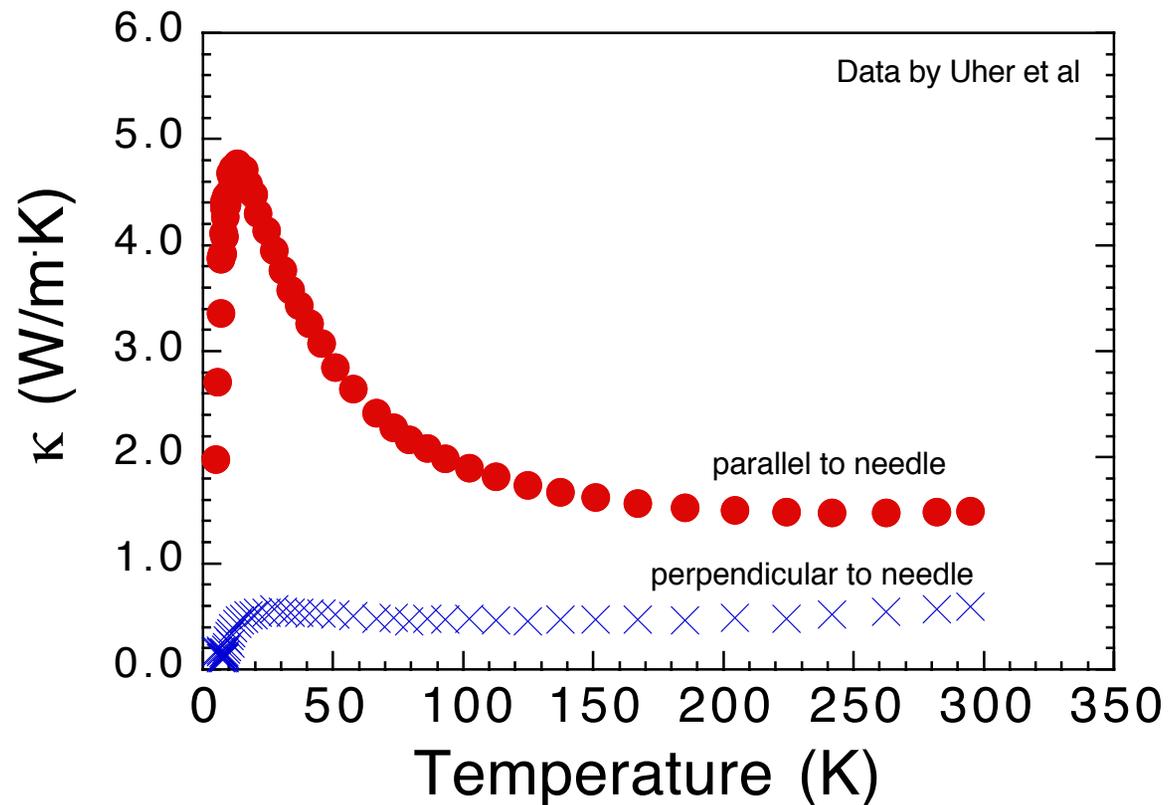
red circles=Te
black=Bi
green=Cs



Module data



Thermal Conductivity of p-type CsBi_4Te_6



BiI₃ Doping of CsBi₄Te₆

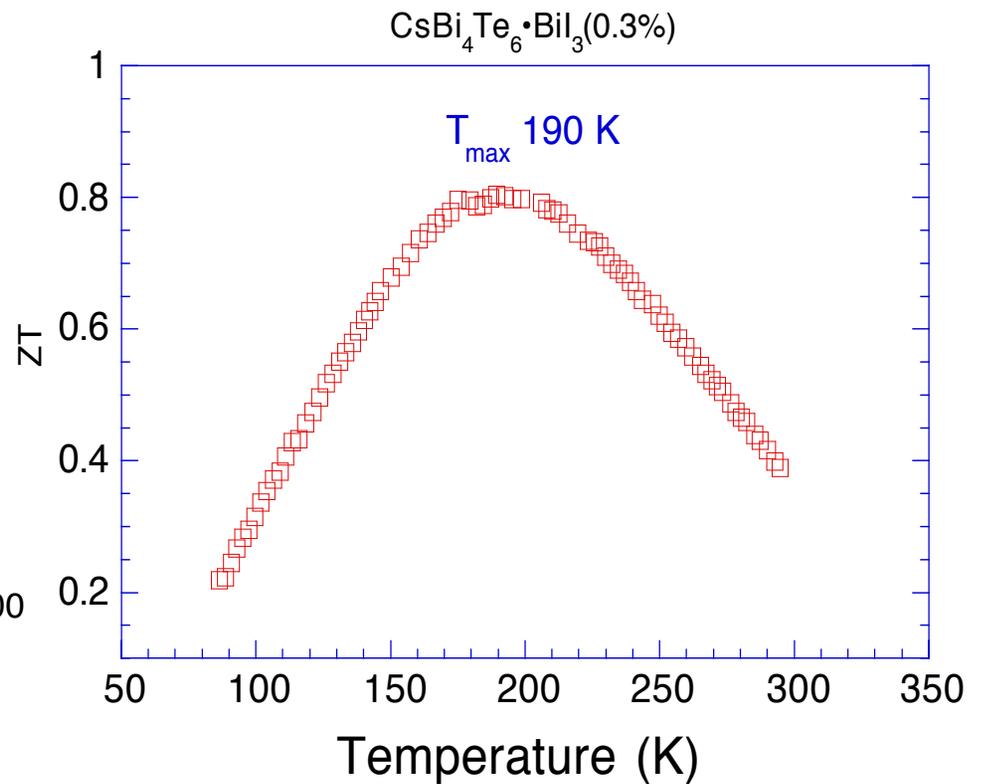
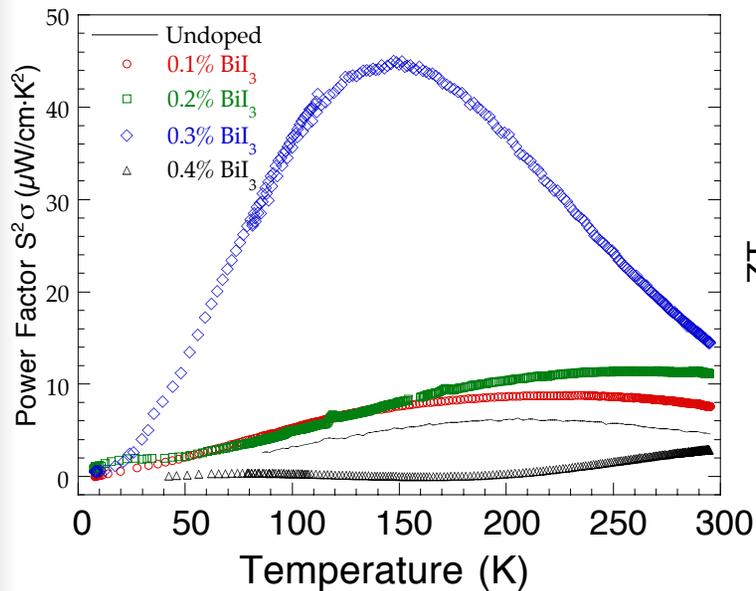
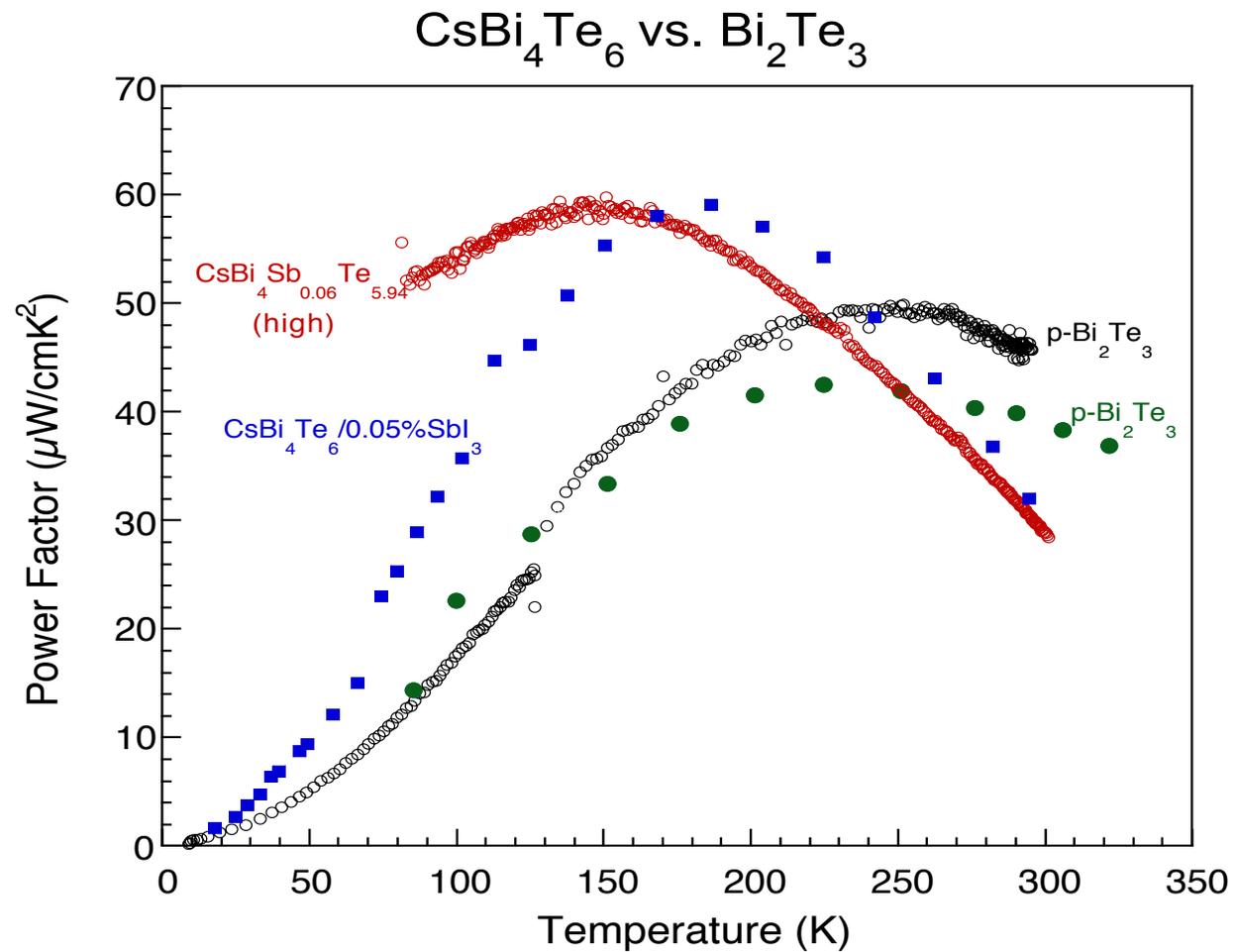


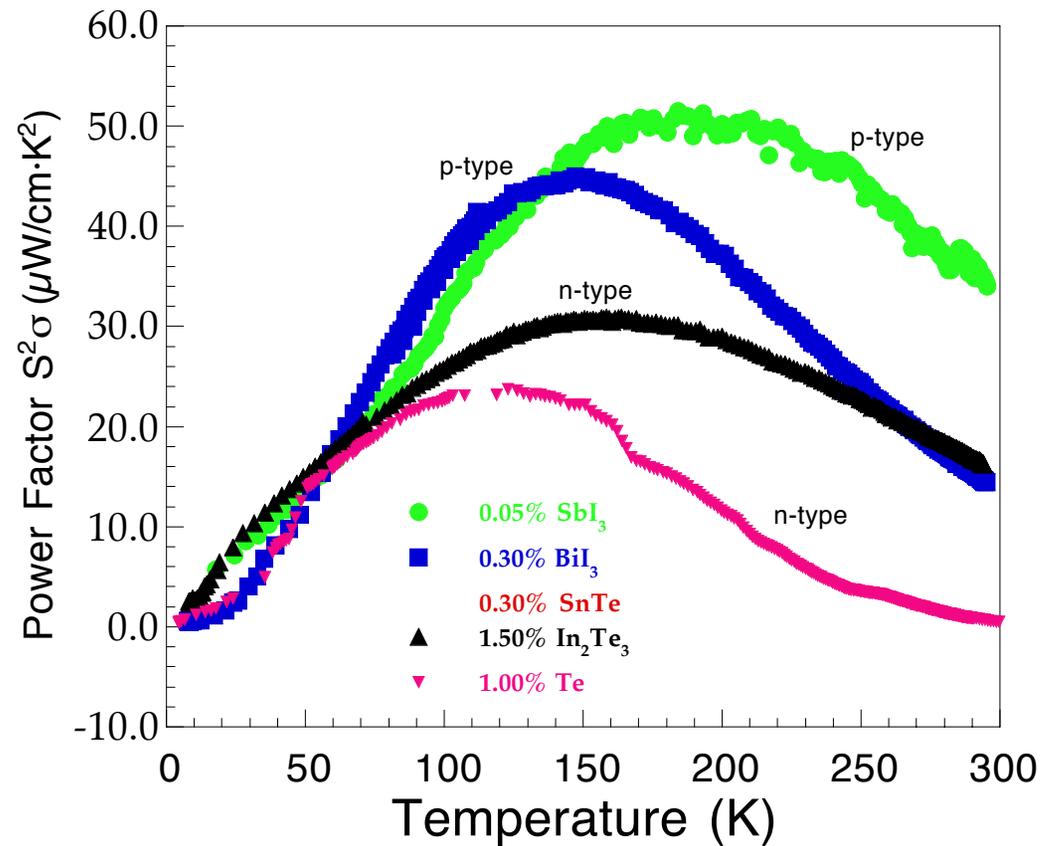
Table II. PF values for each dopant at room temperature and maximum value. Maximum PF observed for each dopant shown in boldface.

Dopant	Concentration, %	$S^2\sigma$ at 295 K, $\mu\text{W}/\text{cm}\cdot\text{K}^2$	Maximum $S^2\sigma$, $\mu\text{W}/\text{cm}\cdot\text{K}^2$
Undoped ^a	—	31.7	45.4 @ 186 K
Undoped ^b	—	4.82	6.40 @ 211 K
SbI ₃	0.02	26.7	28.8 @ 235 K
	0.05	34.0	51.5 @ 184 K
	0.1	11.0	22.1 @ 165 K
	0.2	8.95	13.9 @ 165 K
	0.3	4.98	7.14 @ 214 K
	0.4	6.28	7.19 @ 248 K
	BiI ₃	0.1	7.62
0.2		11.2	11.5 @ 270 K
0.3		14.5	45.0 @ 147 K
0.4		2.95	2.95 @ 295 K
SnTe	0.3	9.45	11.9 @ 229 K
	0.6	7.82	7.91 @ 272 K
	1.0	4.94	5.14 @ 258 K
	1.5	3.43	3.53 @ 282 K
In ₂ Te ₃	0.6	9.20	10.3 @ 282 K
	0.9	16.2	22.3 @ 204 K
	1.5	22.4	32.1 @ 188 K
	2.0	1.58	1.58 @ 295 K
	3.0	0.034	9.55 @ 136 K
	4.0	1.68	3.44 @ 111 K

Power factors

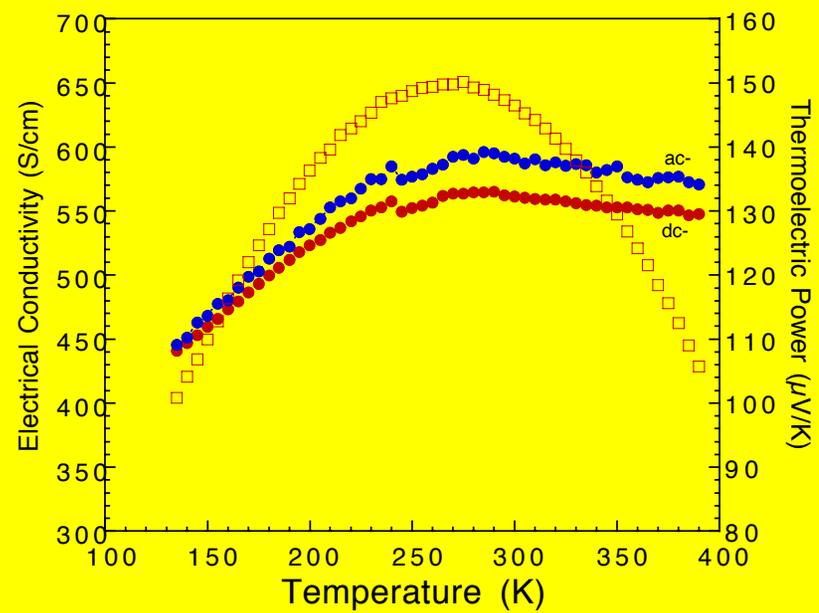
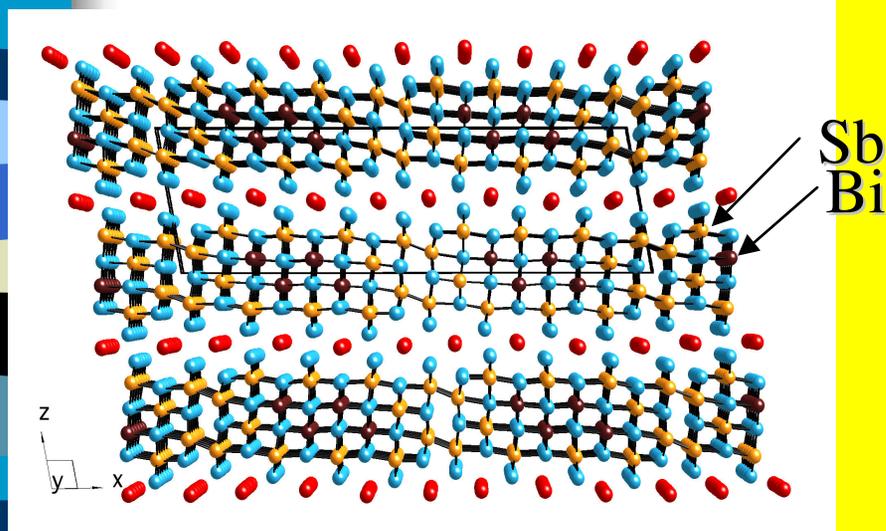


Dopants for CsBi₄Te₆ (both n- and p-type)





$x = 0.3$

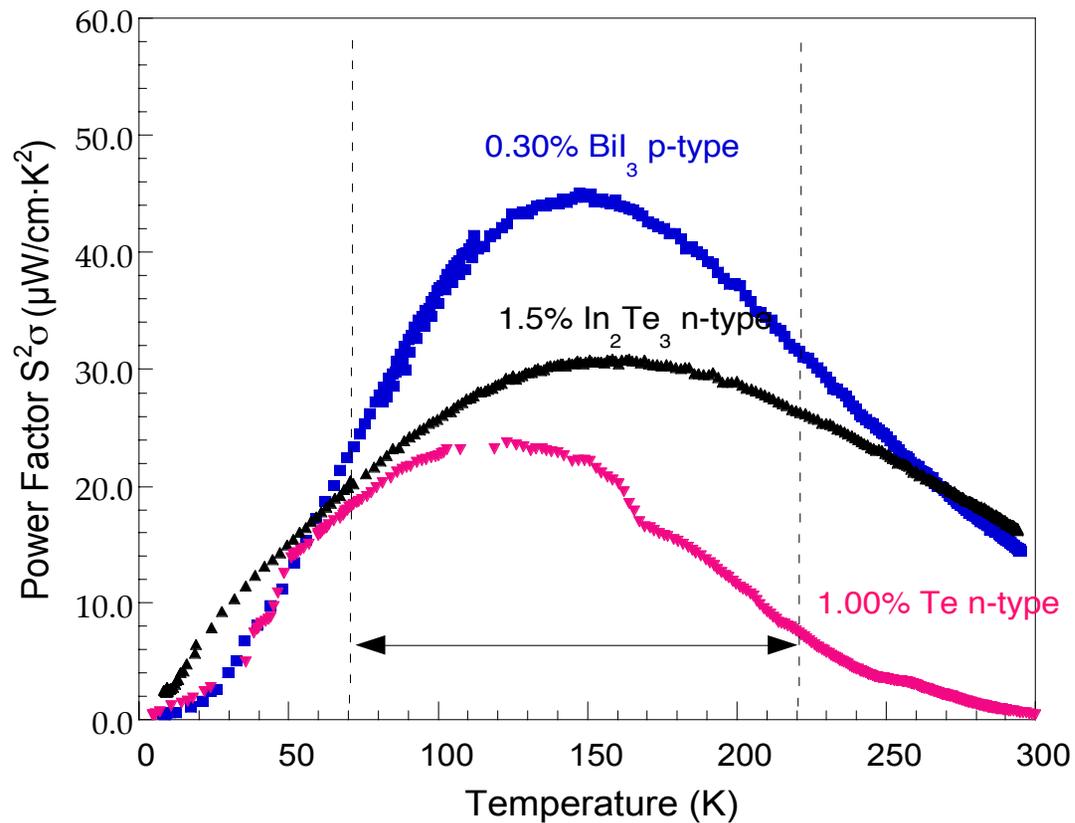


CsBi₄Te₆ ingot

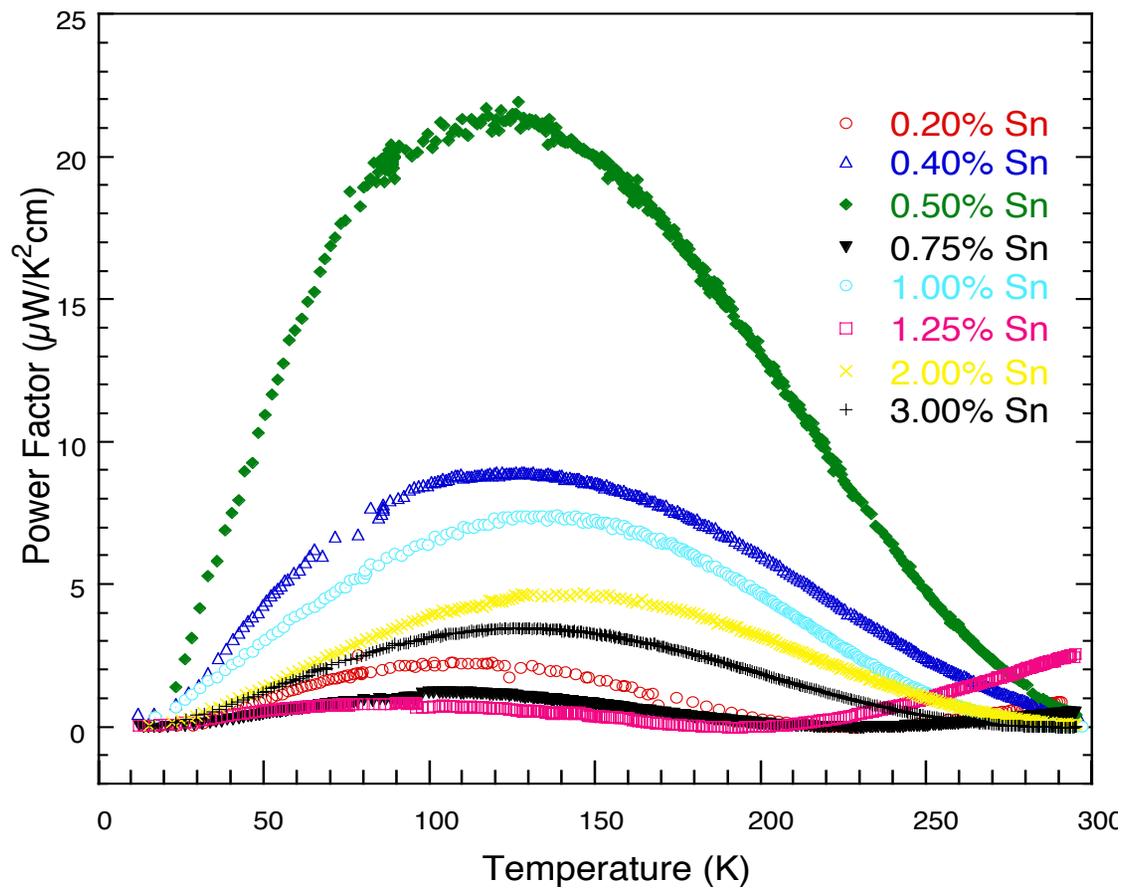


1 cm

. CsBi_4Te_6 : Power factor values for the best concentrations of the dopants BiI_3 , In_2Te_3 and Te .

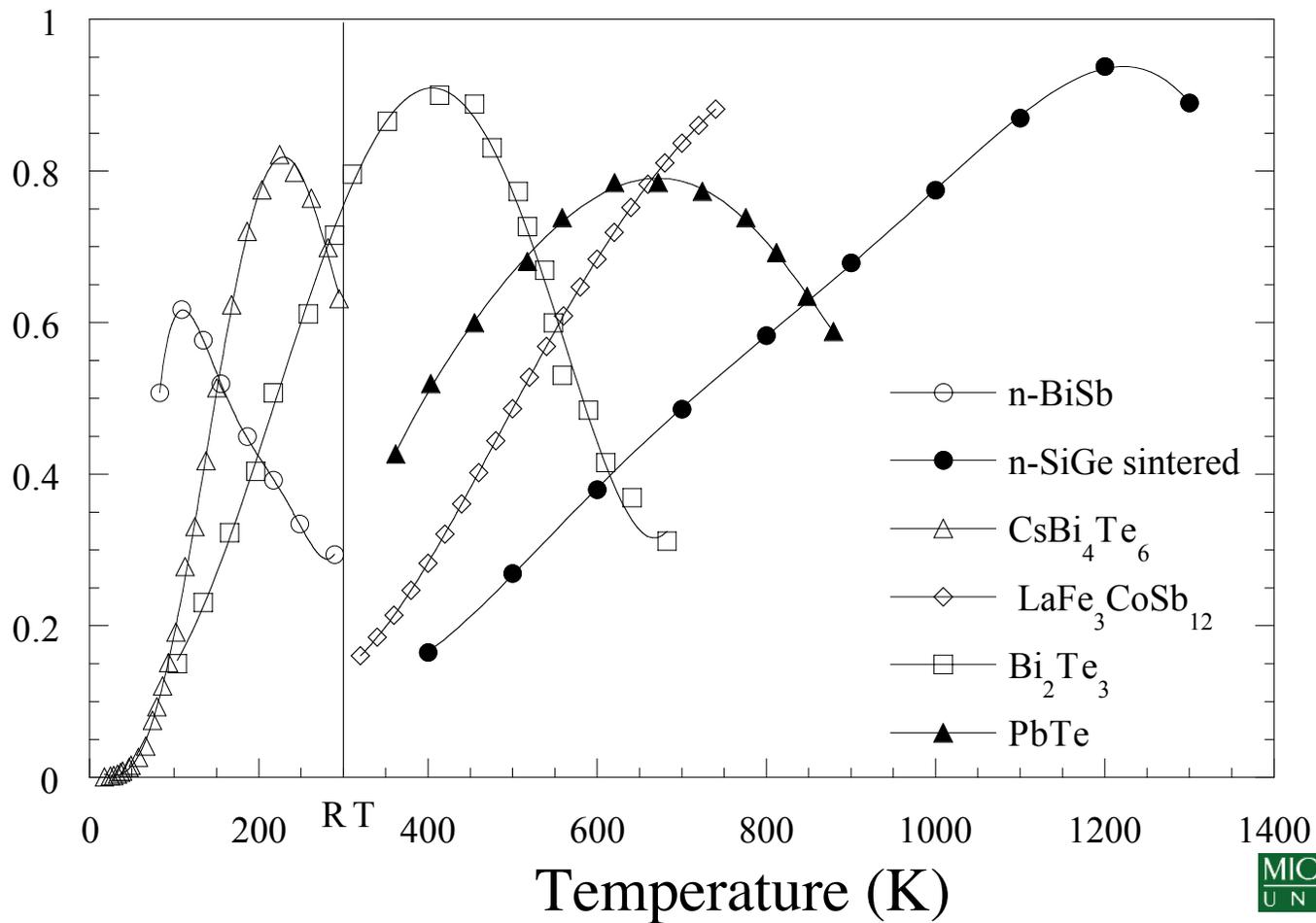


CsBi₄Te₆: Power factor values a series of concentrations of Sn.



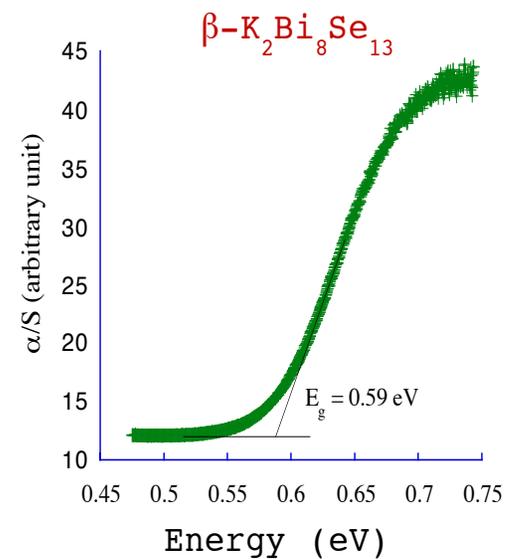
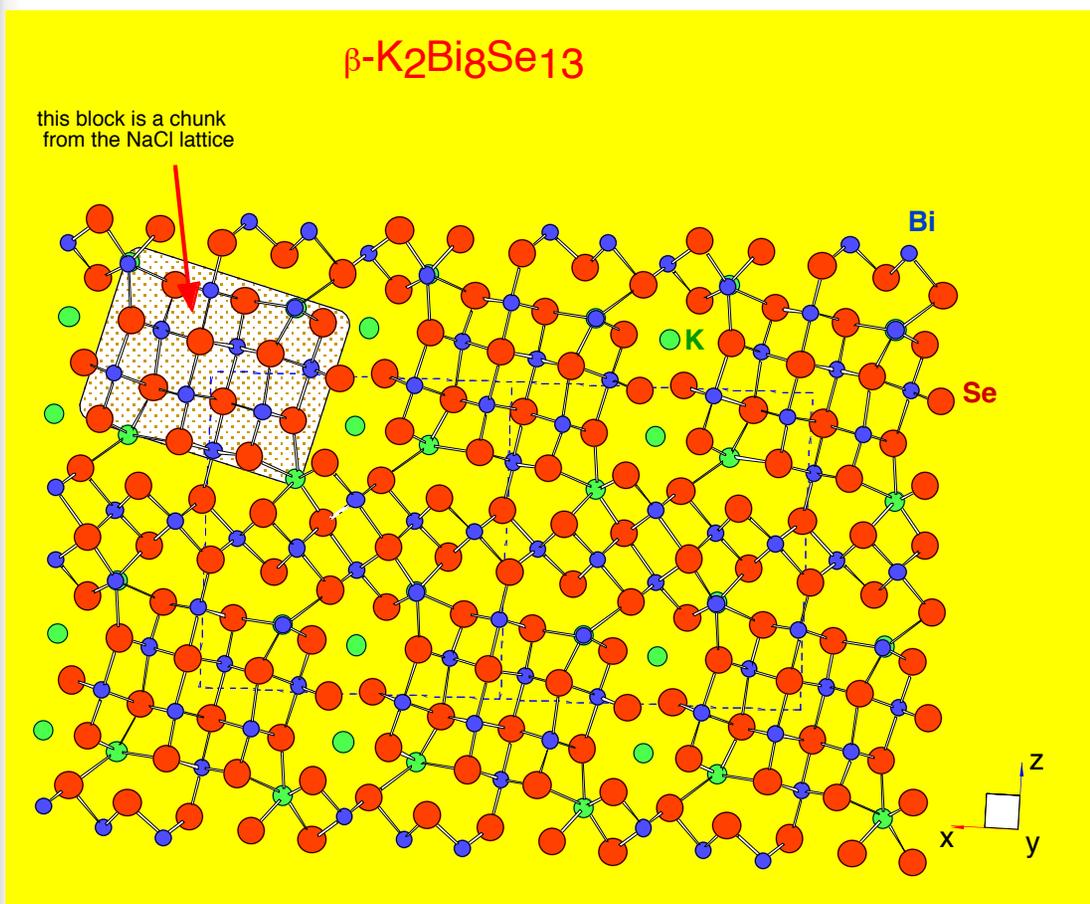
Best TE Materials

ZT

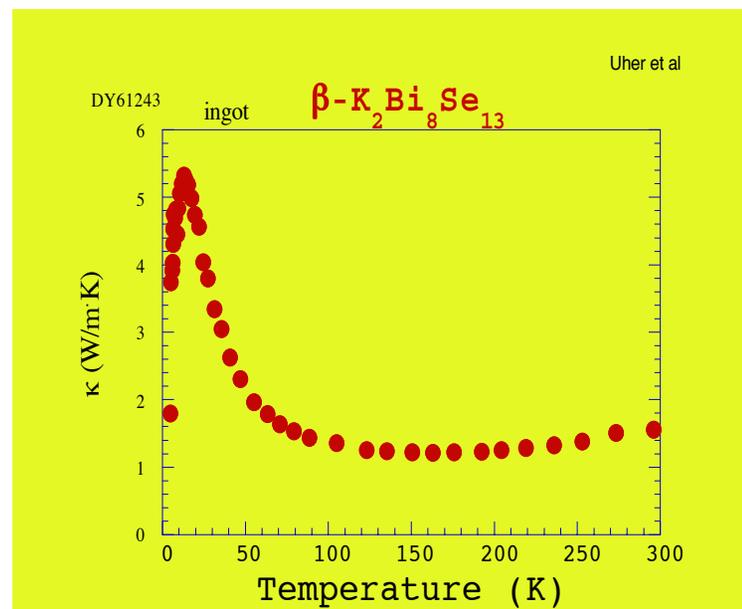
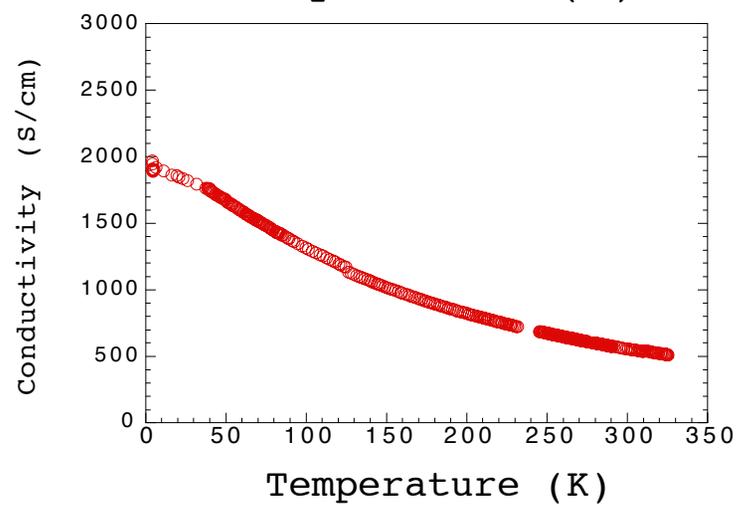
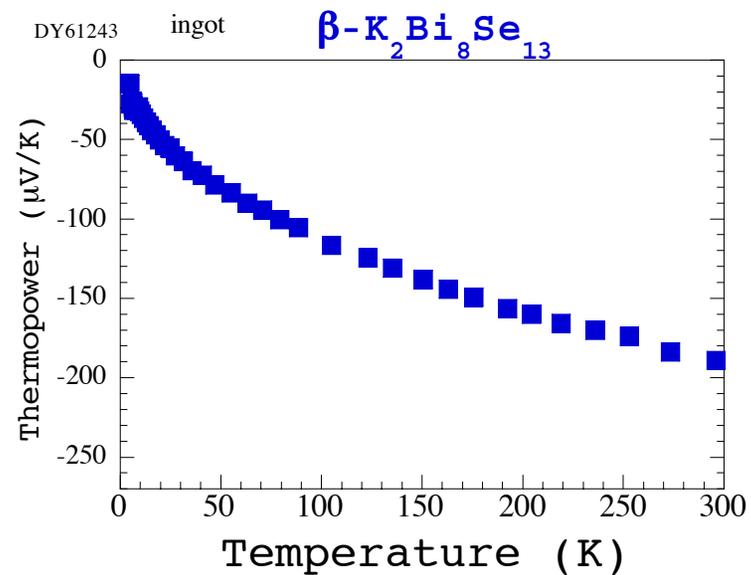


$K_2Bi_8Se_{13}$

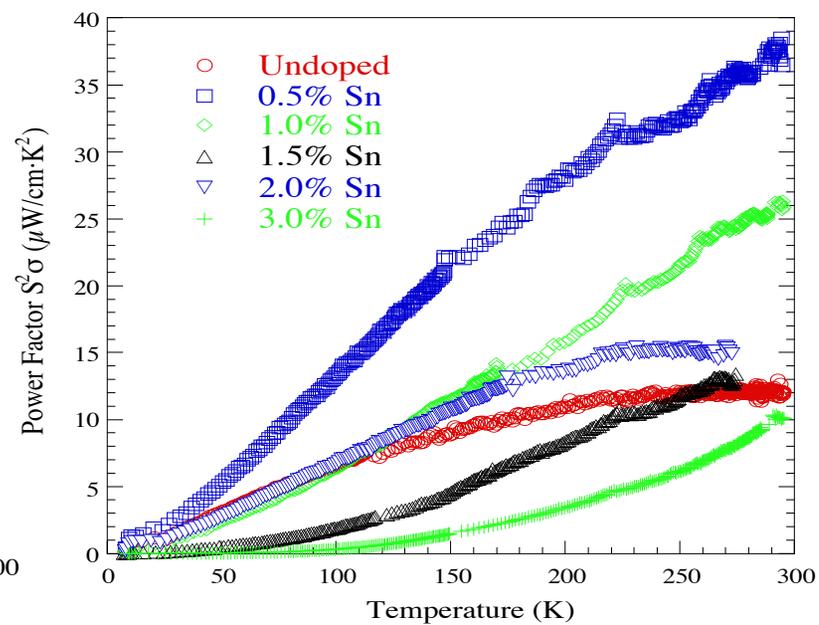
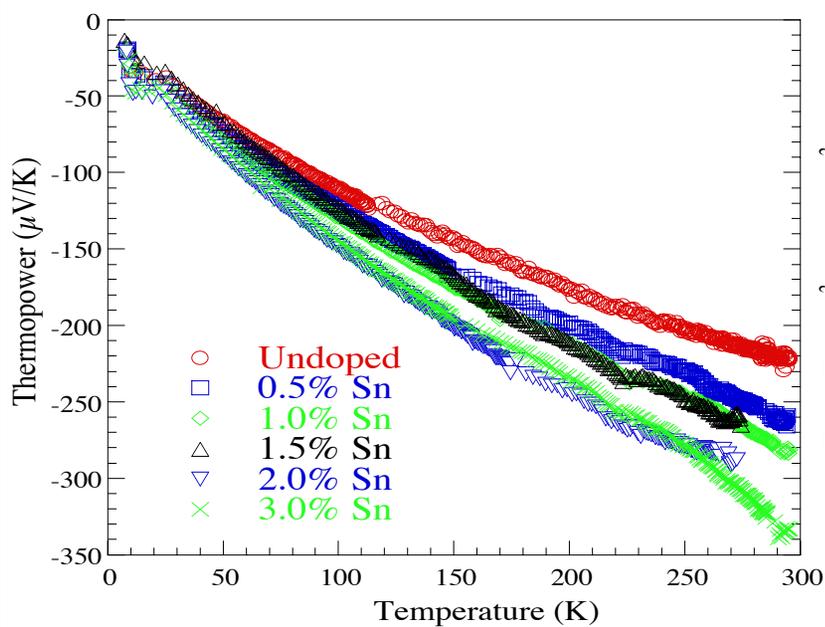
K ions possess $\sim 2x$ the thermal displacement parameter of the Bi/Se framework



$\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$

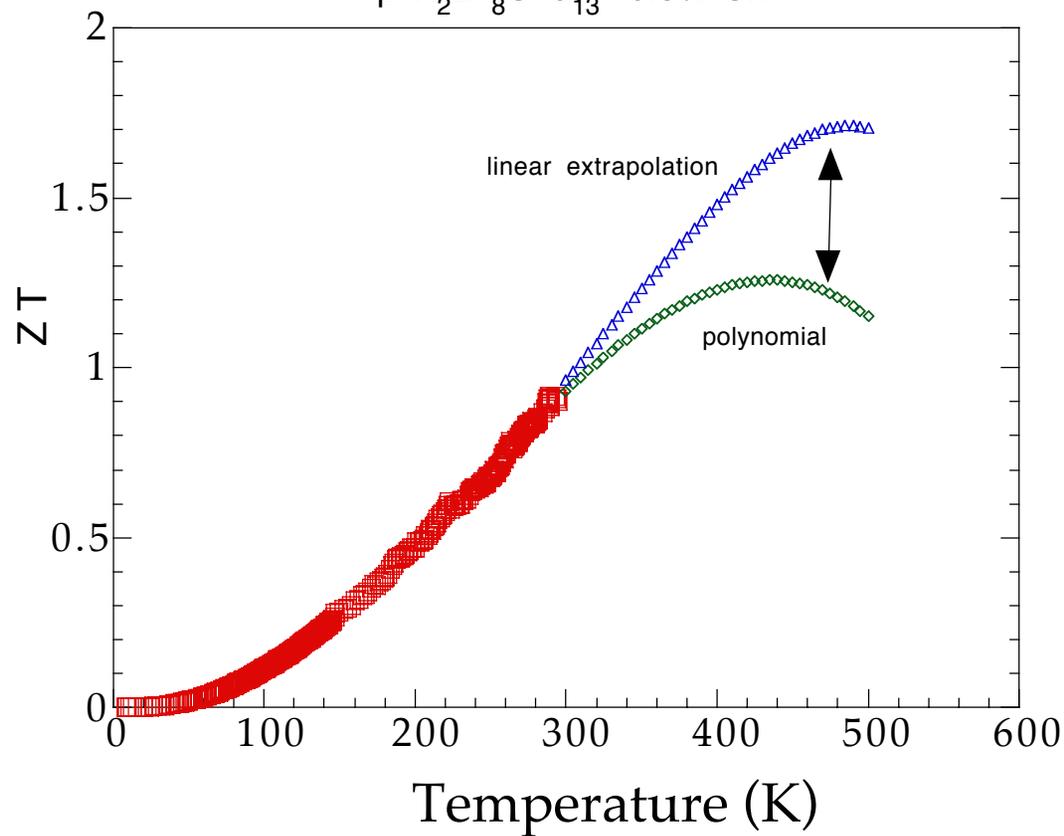


Sn Doping in β -K₂Bi₈Se₁₃



$\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$

$\beta\text{-K}_2\text{Bi}_8\text{Se}_{13} \cdot 0.5\% \text{ Sn}$



Michigan State University /Tellurex Corp. Collaboration

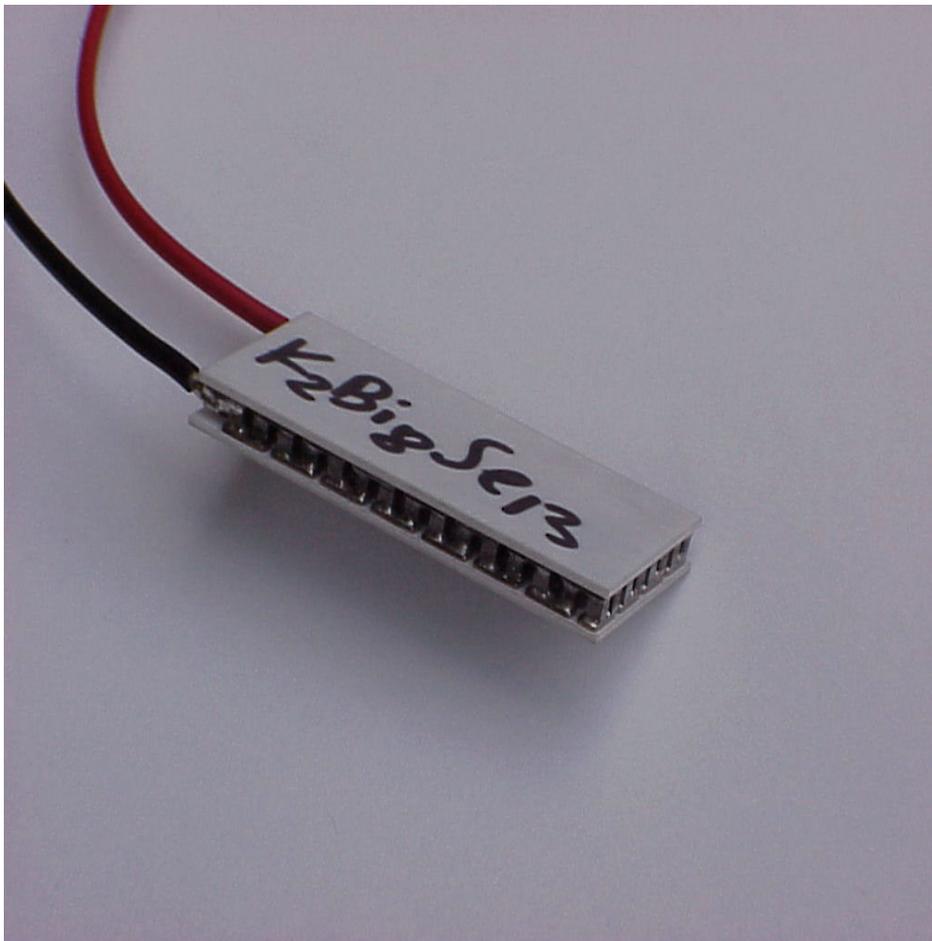


Material grown at Tellurex



New TE material grown at MSU

Photo of the first TE module containing 63 couples $n\text{-}\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}/p\text{-Bi}_2\text{Te}_3$



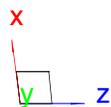
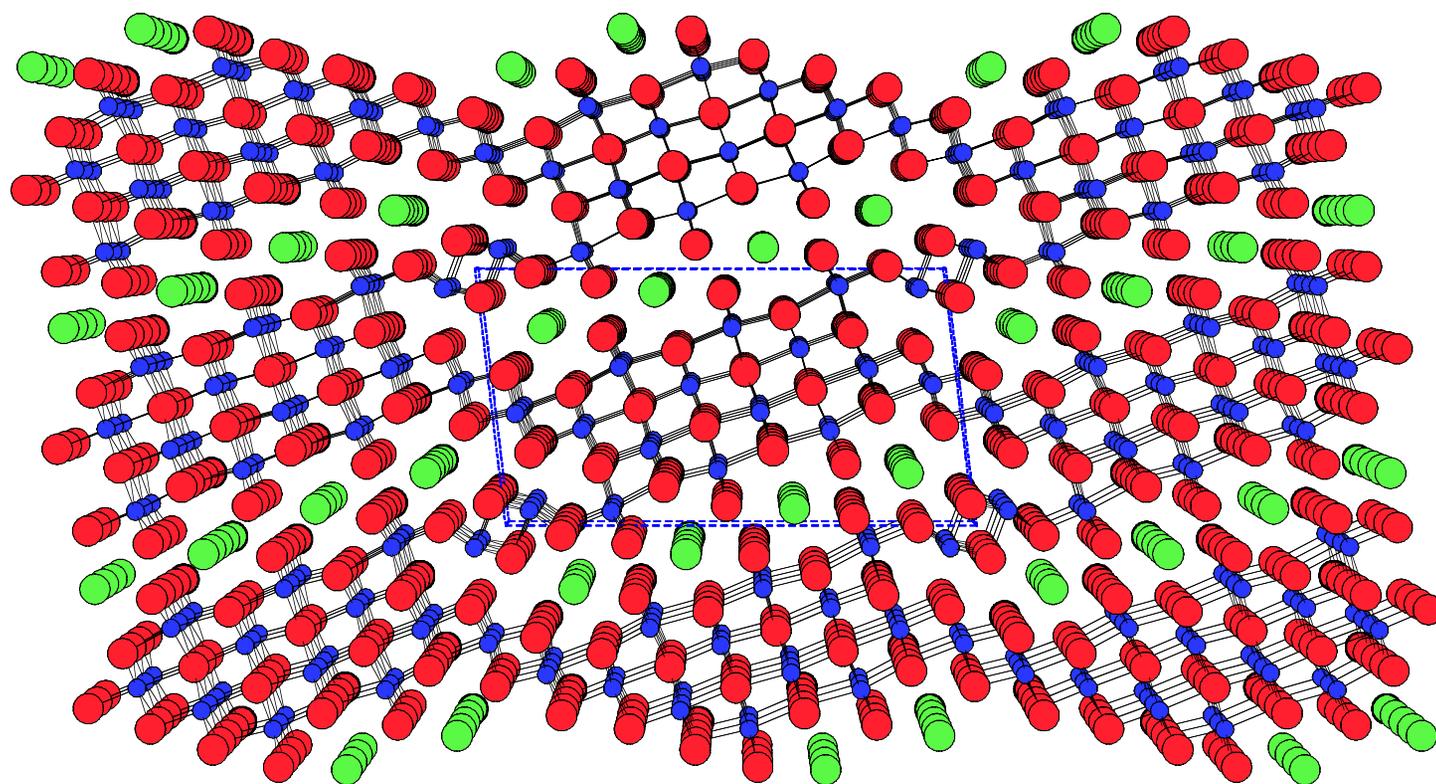
Unoptimized

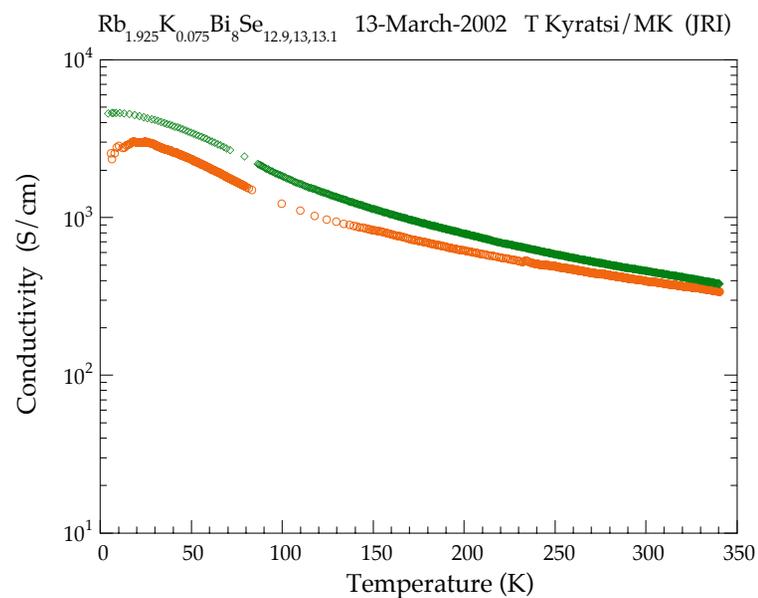
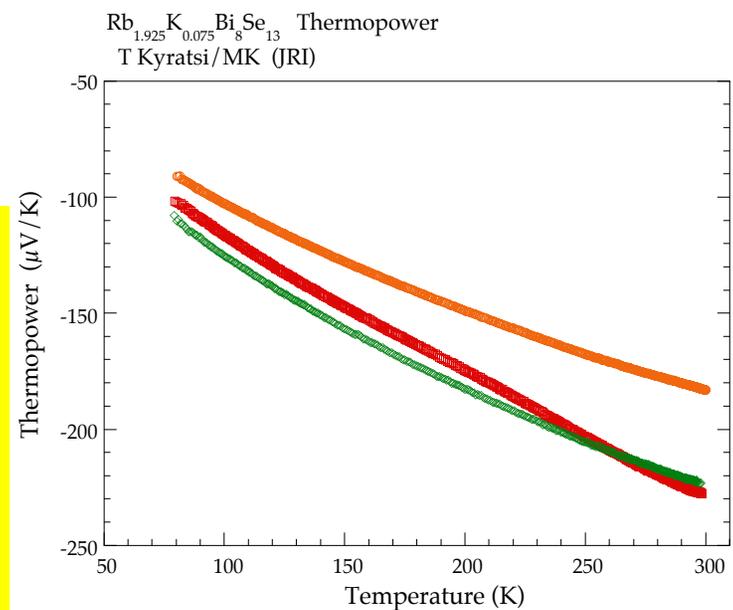
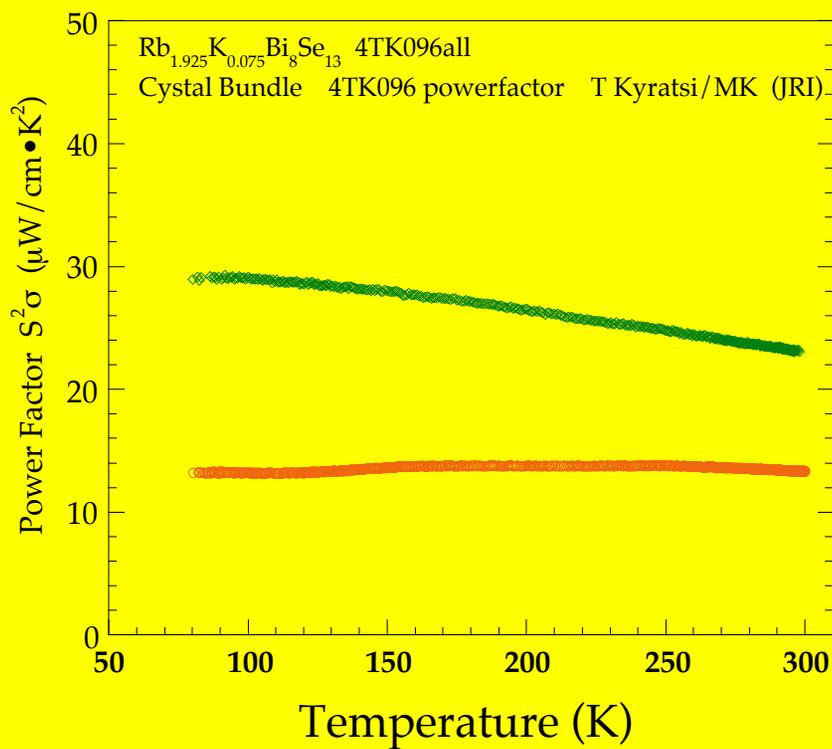
$\Delta T = 39\text{ }^\circ\text{C}$

$T_h = 50\text{ }^\circ\text{C}$

All materials grown
at Tellurex Inc

New material $\text{Rb}_2\text{Bi}_8\text{Se}_{13}$





ZT and Band Structure

B- parameter

$$B = \frac{CT^{5/2}\gamma\sqrt{m_x m_y m_z}\mu_x}{\kappa_{latt}}$$

m= effective mass

μ = mobility

κ_{latt} = lattice thermal conductivity

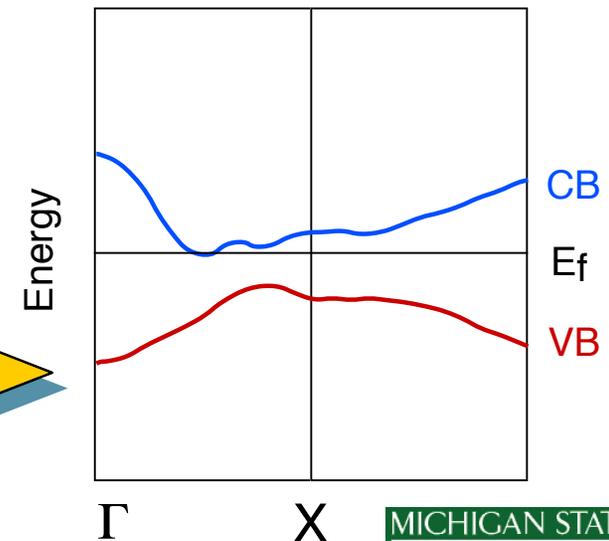
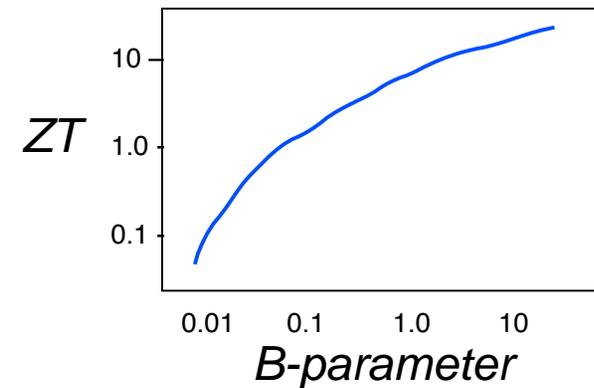
T = temperature

γ = band degeneracy

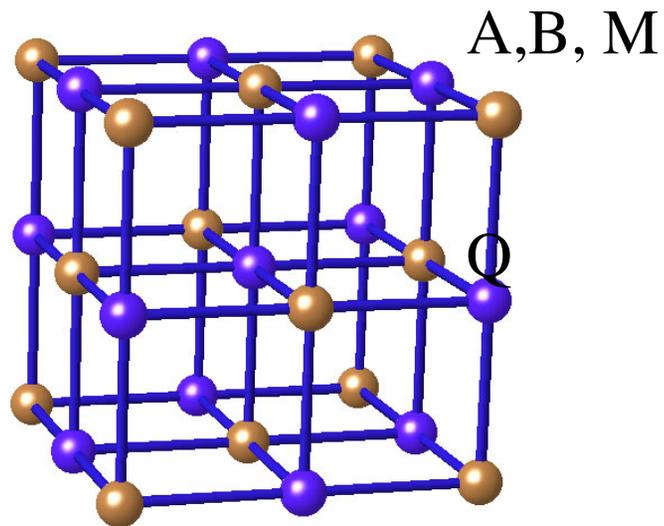
High γ comes with

(a) high symmetry e.g. rhombohedral, cubic

(b) off-center band extrema



$A_m B_n M_m Q_{2m+n}$ System



NaCl structure type $Fm\bar{3}m$

Cationic positions

A: +1 (K, Ag)

B: +2 (Pb, Sn)

M: +3 (Bi, Sb)

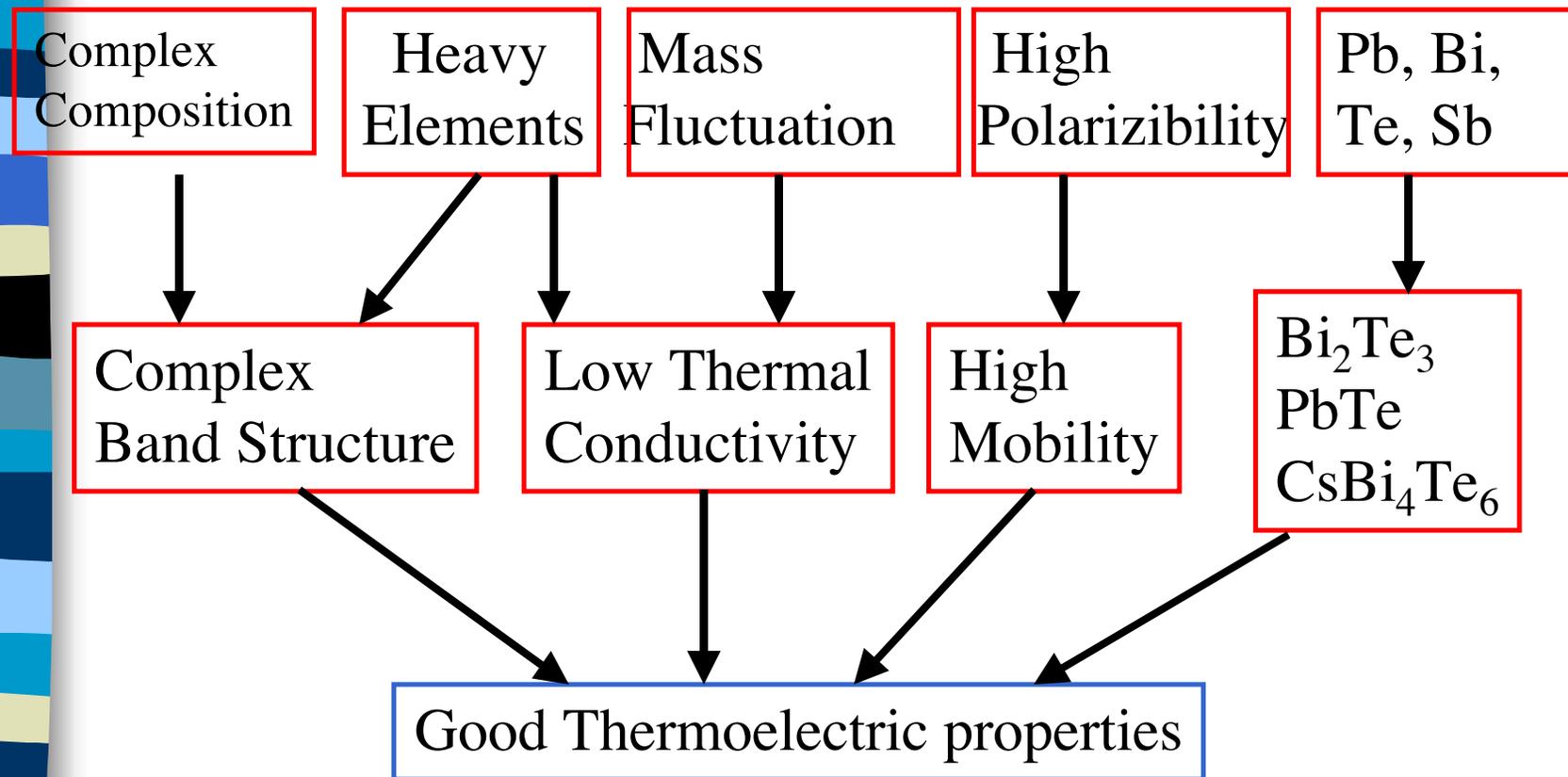
Anionic positions

Q: -2 (S, Se, Te)

Charge balance equation:

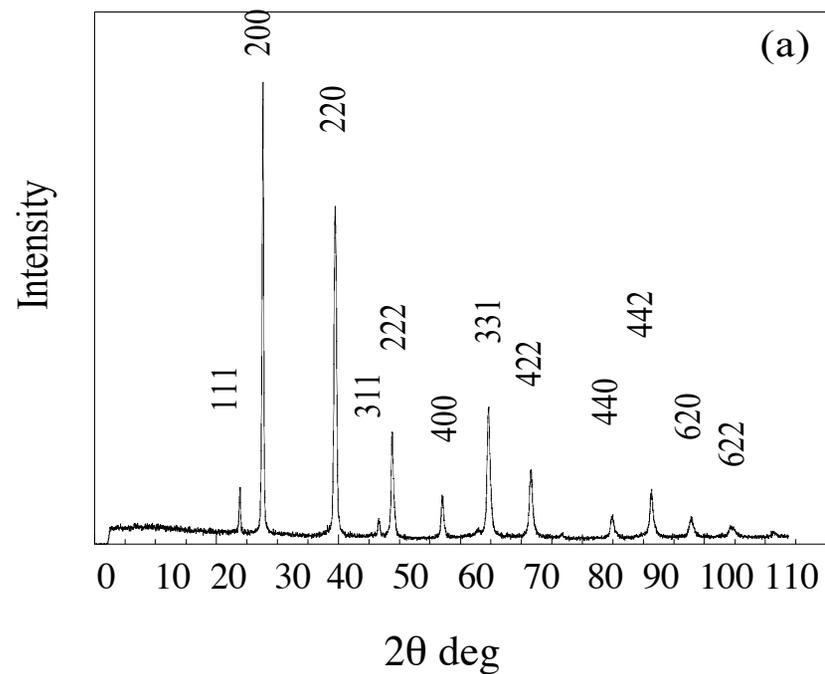
$$m(\text{charge A}) + n(\text{charge B}) + m(\text{charge M}) = (2m+n)(\text{charge Q})$$

Advantages



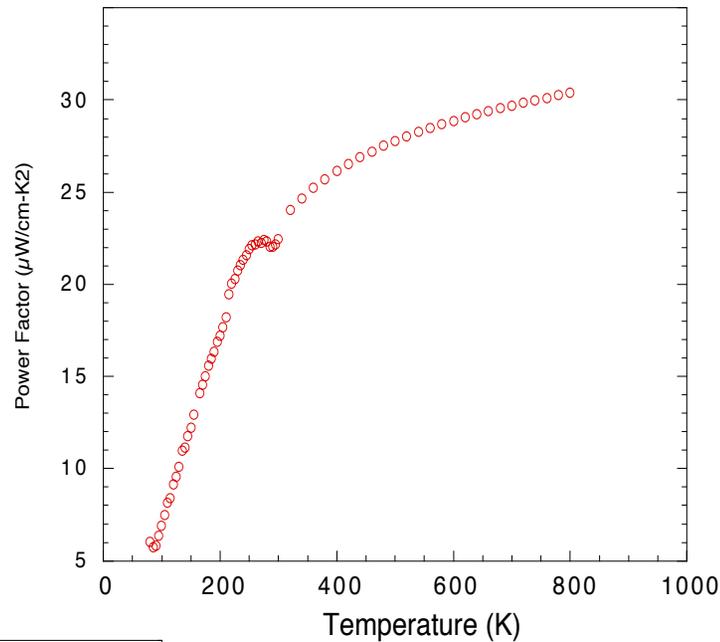
X-ray Powder Diffraction

Typical cubic NaCl powder diffraction pattern

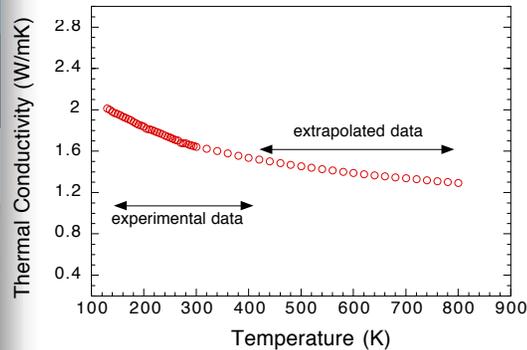


Patent application filed

ZT and power factor (LAST-85)



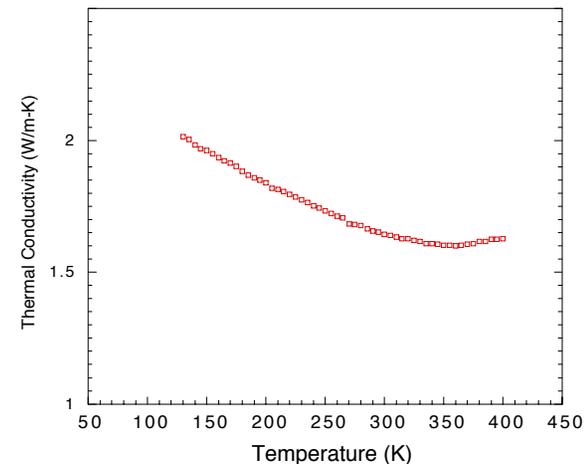
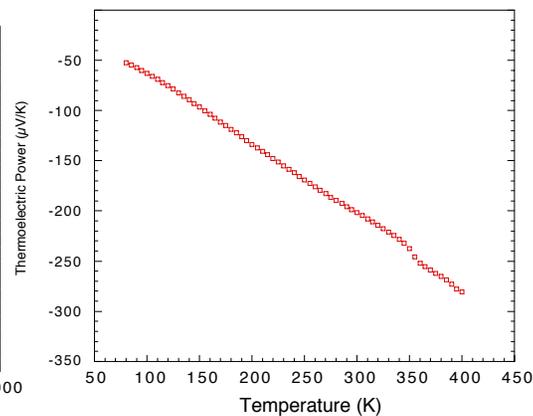
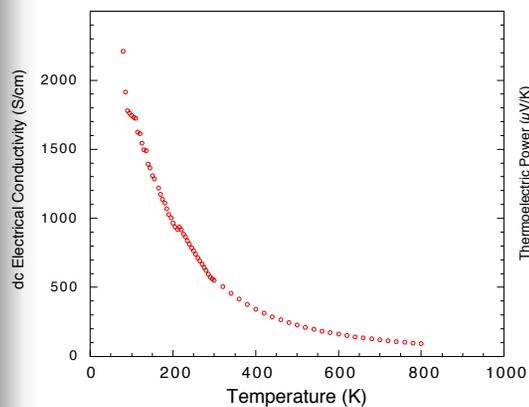
LAST-80: best sample



Thermal cond. data extrapolated
> 400 K
Resistivity and thermopower
extrapolation trend checked with
actual measurements at 500-600 K

ZT = 2 at 700 K
ZT was calculated
with real experimental data
for cond. and Seebeck. Only the
Thermal conductivity data were
extrapolated from 400-800 K

LAST-85 composition



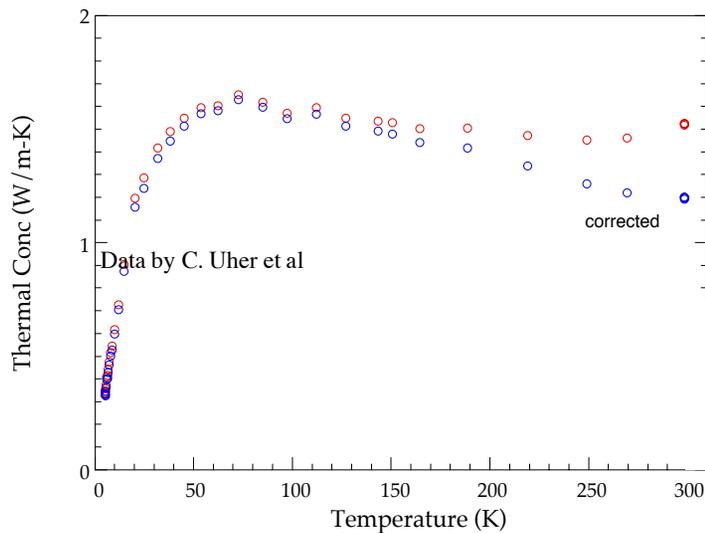
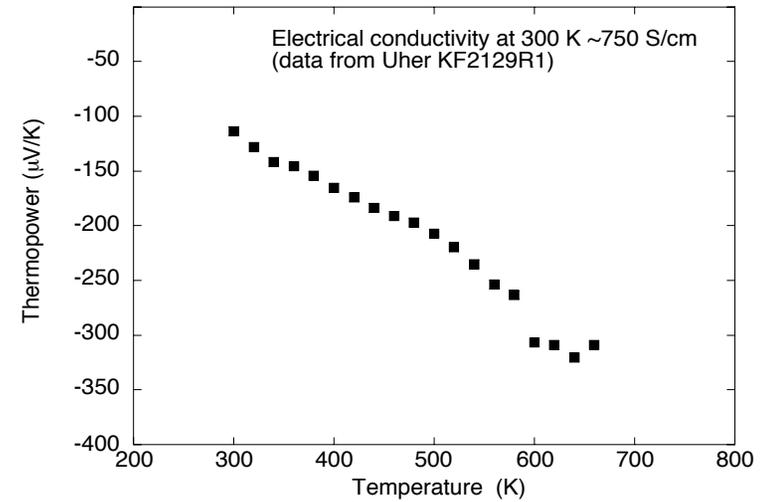
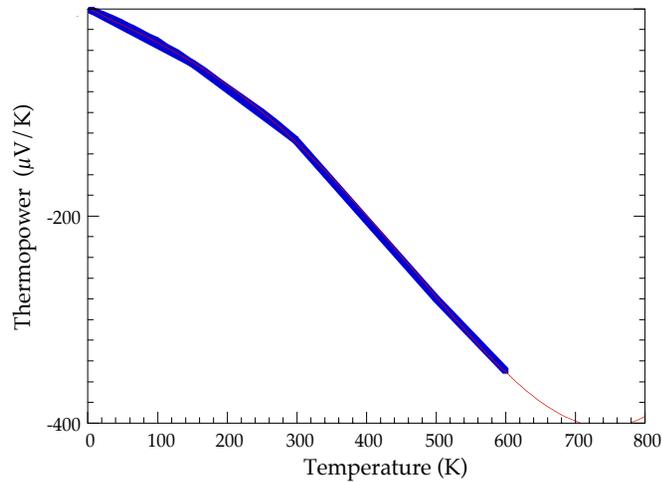
LAST-90: ingot grown
at Tellurex Inc



Est ZT @ >600 K
To exceed 1.0 in
this system

BLAST: Bismuth-Lead-Antimony-Silver-Tellurium

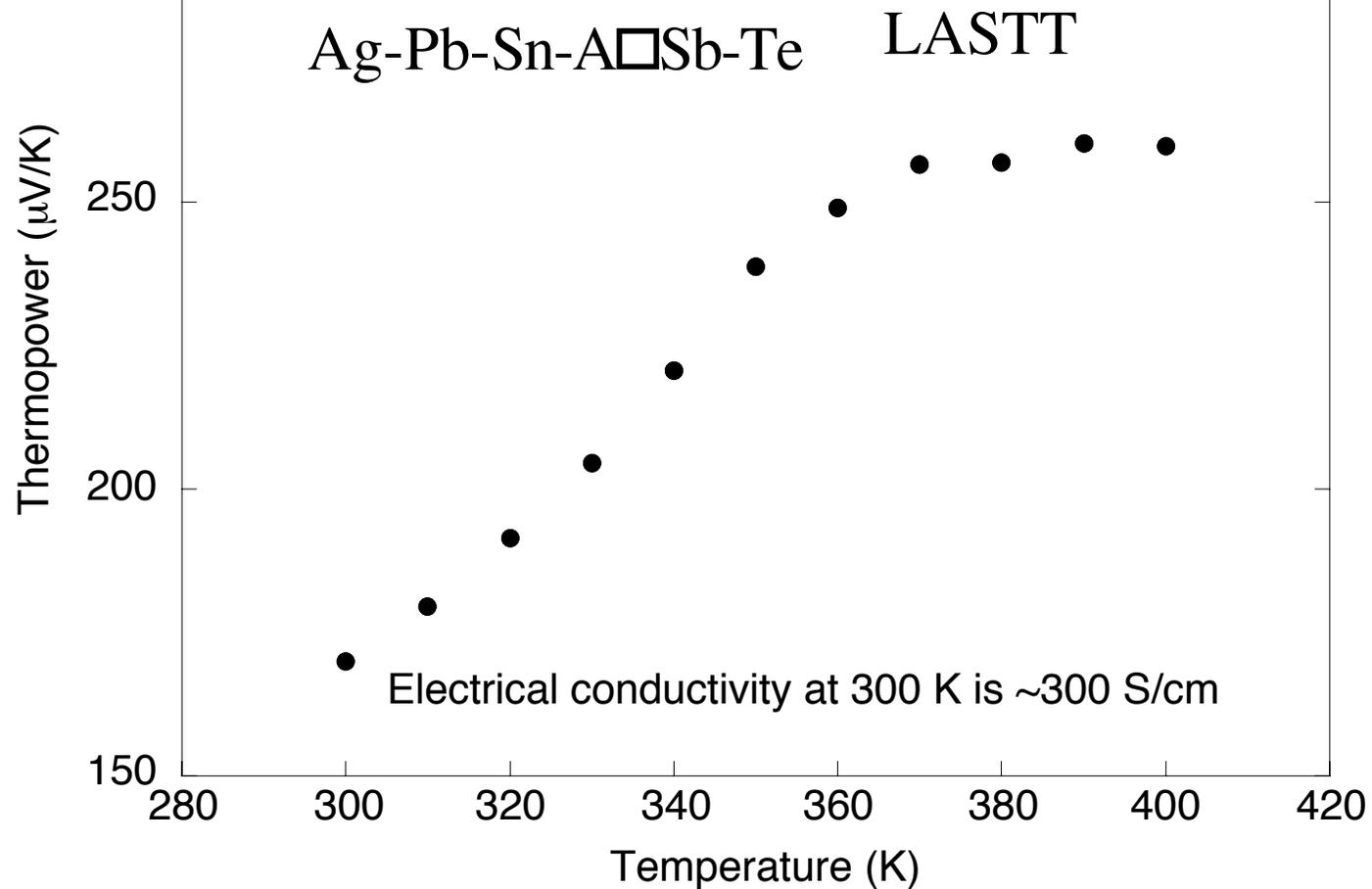
BLAST-92



Example: with a $ZT=1.8$
 a hot source at 800 K
 and a cold side of 300 K,
 $\eta \sim 20\%$

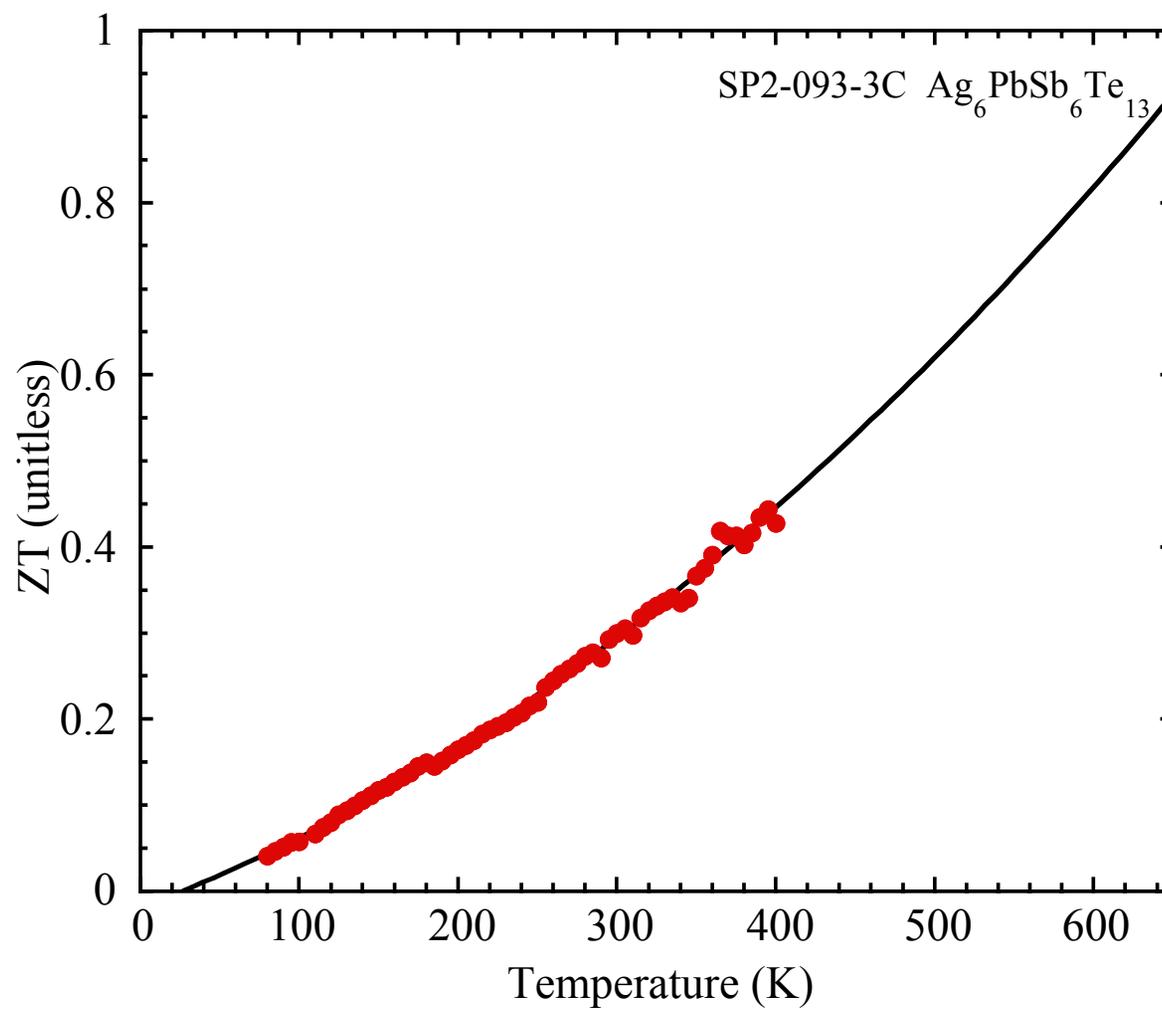
$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H}$$

P-type systems possible



Work on p-type systems is in its infancy

Cubic $\text{Ag}_6\text{PbSb}_6\text{Te}_{13}$



P-type

TEM: concentration gradients

