Solid State Chemistry Meets Physcis: Thermoelectric Materials

AN INTERDISCIPLINARY COLLABORATION

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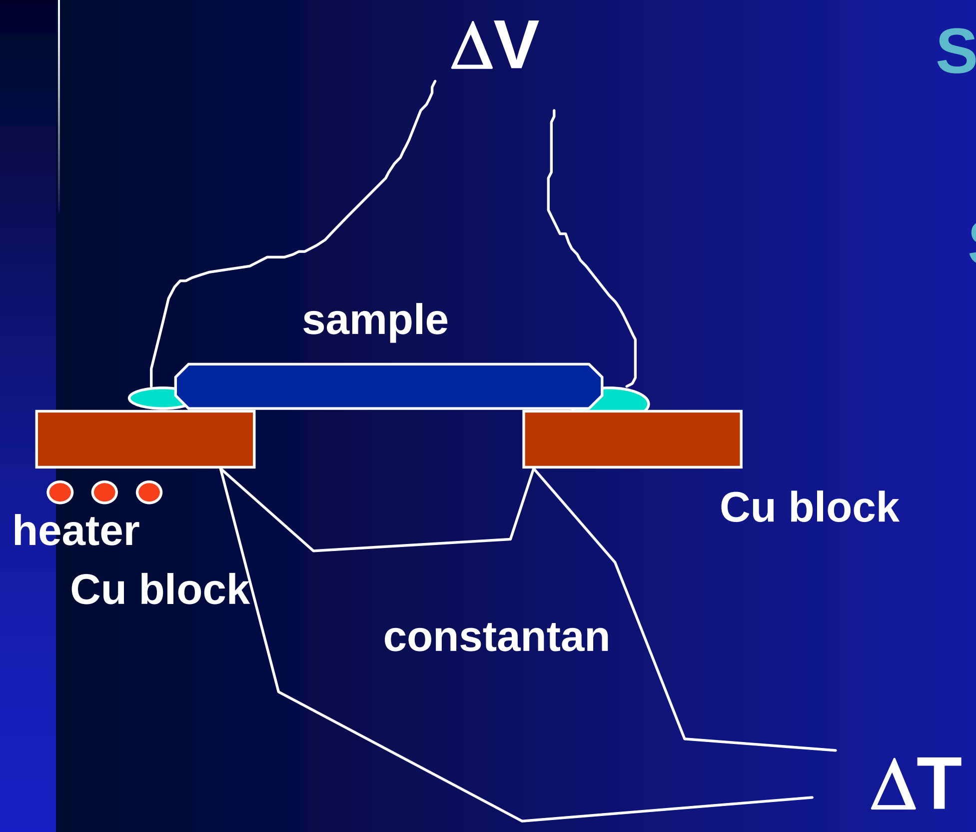
THERMOELECTRIC POWER
(Seebeck Coefficient)



$$S_{measured} = \frac{\Delta V}{\Delta T}$$

$$S_{measured} = S_{sample} - S_{Cu}$$

zero current technique:

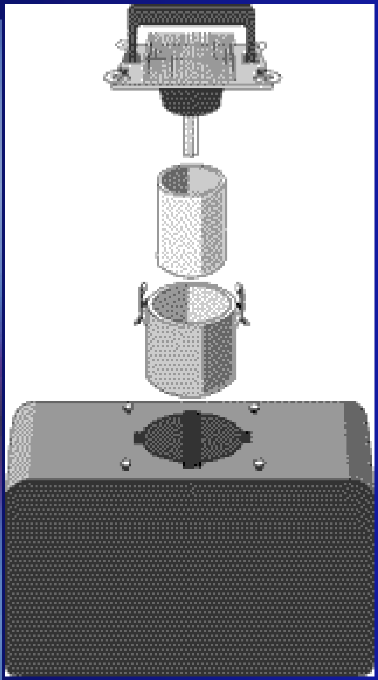
extremely useful probe for investigation of intrinsic conduction in granular or polycrystalline materials

Thermoelectric Applications

PRESENTS
The Cool World

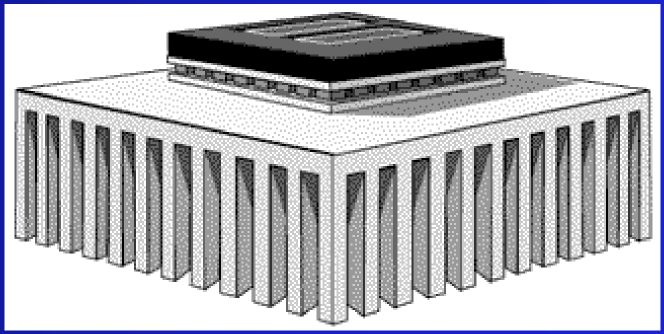
www.tellurex.com

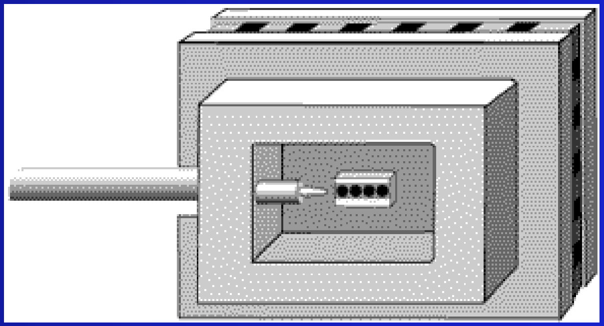
Beverage cooler



Biological samples

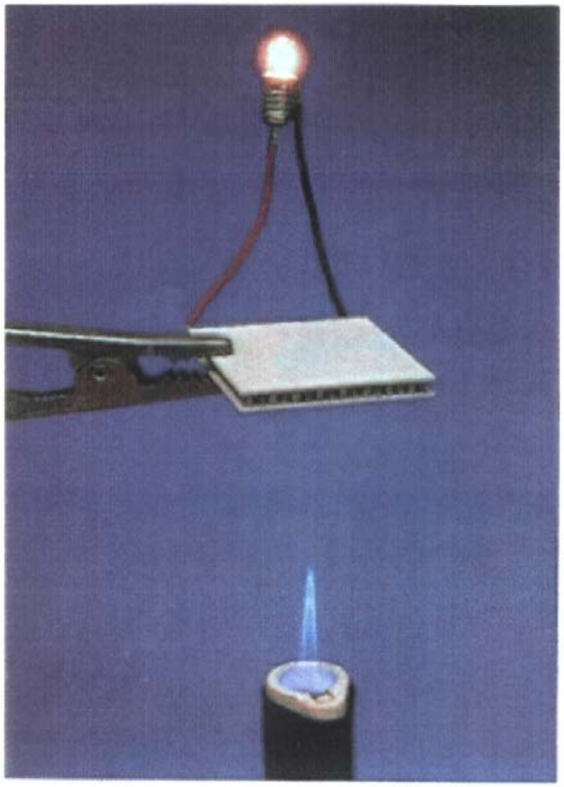
Microprocessor Cooler





LASER diode Cooler

Heat to Electric Energy



Electrical
Power Generation

Up to 20% conversion efficiency with right materials

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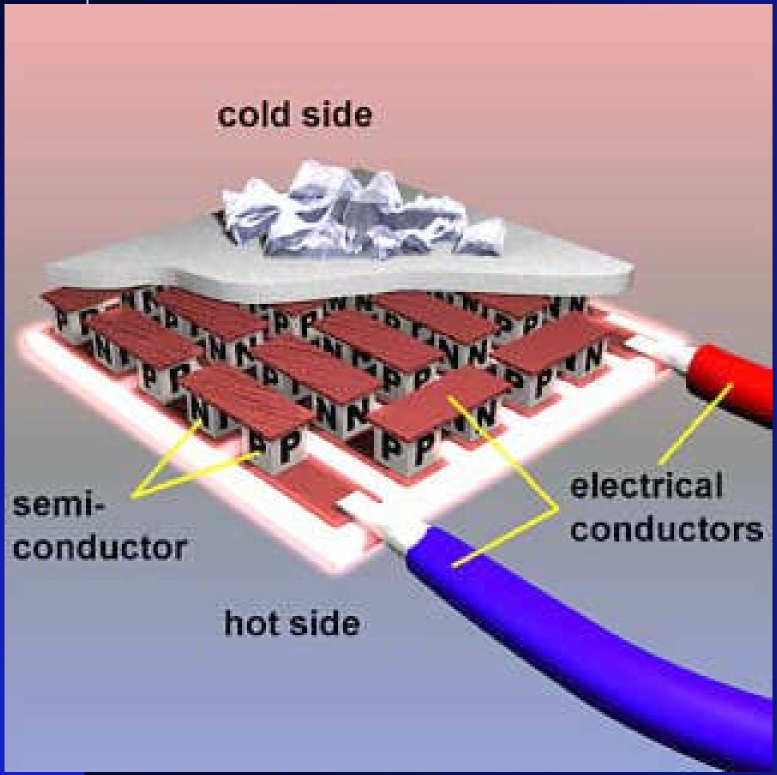
Thermoelectric Benefits

- TE coolers have no moving parts, need substantially less maintenance.
- Life-testing has shown the capability of TE devices to exceed 200,000 hrs. of steady state operation.
- TE coolers contain no chlorofluorocarbons.
- Temperature control to within fractions of a degree can be maintained using TE devices.
- TE coolers function in environments that are too severe, too sensitive, or too small for conventional refrigeration.
- TE coolers are not position-dependent.

How does it work?



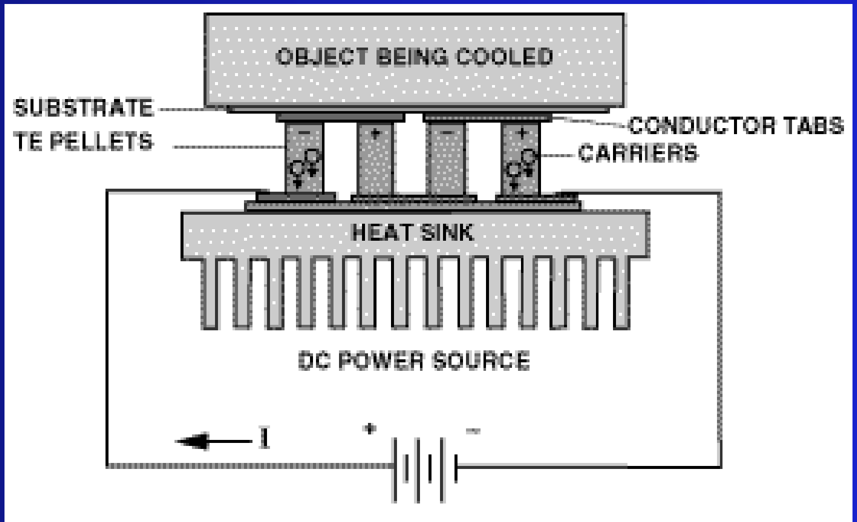


Figure 2

http://www.designinsite.dk

Thermoelectric applications

- Air conditioning (distributed, environmentally friendly)
- Spot cooling of electronic chips, superconductors etc.
- Thermal suits for fire-fighting, soldier etc
- Waste heat recovery (automobiles, utilities etc)
- Geothermal power generation

Figure of Merit

electrical conductivity

thermopower

$$ZT = \frac{\sigma \cdot S^2}{\kappa_{total}} \bullet T$$

Total thermal conductivity

Power factor

$$\sigma \cdot S^2$$

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Today's situation

- The most efficient materials today is Bi_2Te_3 alloy
- ZT~0.8-1.0
- Further improvements on Bi_2Te_3 are not expected.
- New materials are needed

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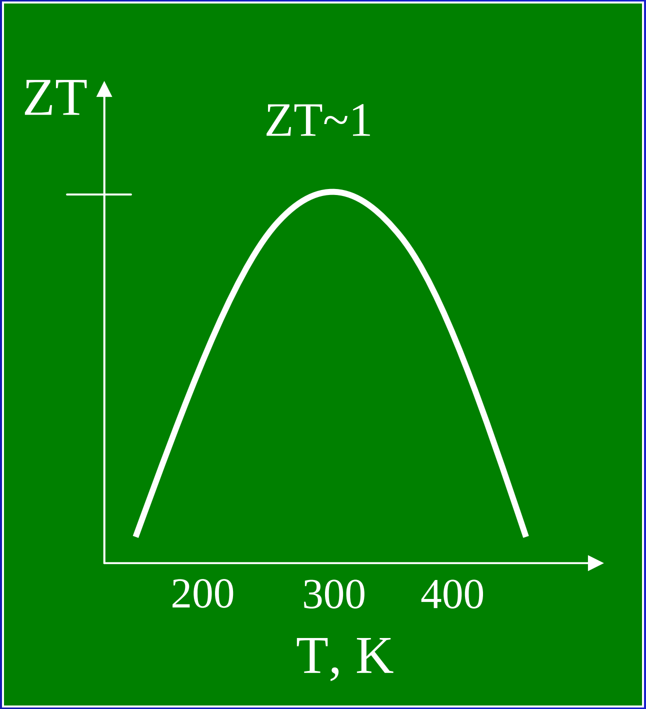
Thermoelectric Properties of Optimized Bi_2Te_3 (e.g. $Bi_{2-x}Sb_xTe_3$, $Bi_2Te_{3-x}Se_x$) at Room Temperature

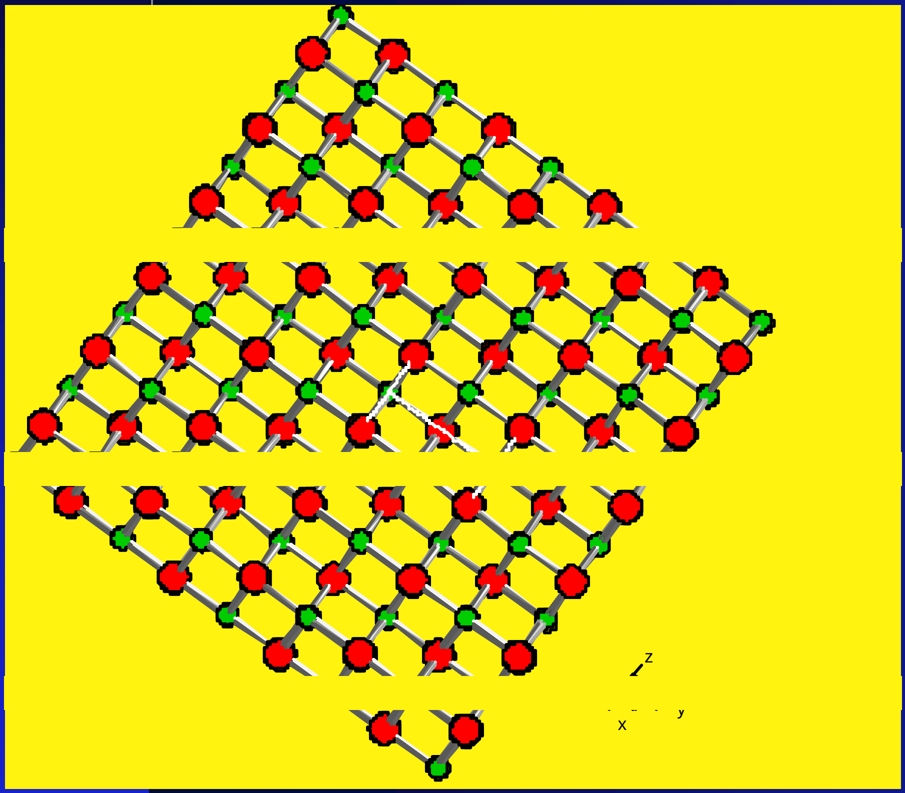
- $S \sim \pm 220\ \mu V/K$
- $\sigma \sim 950\ S/cm$
- $\rho = 1/\sigma \sim 1.1\ m\Omega \cdot cm$
- $\kappa \sim 1.5\ W/m \cdot K$

- $ZT \sim 1$!

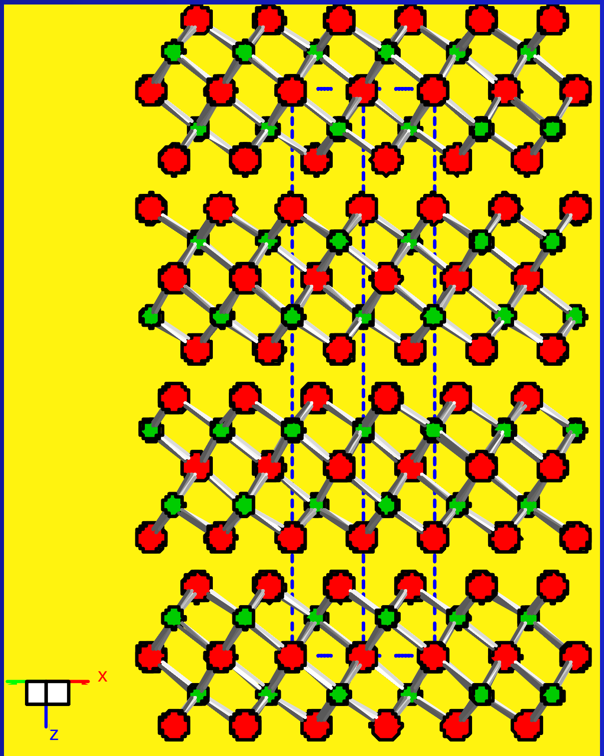


Structure of Bi_2Te_3 and NaCl

NaCl



Bi_2Te_3 defect NaCl



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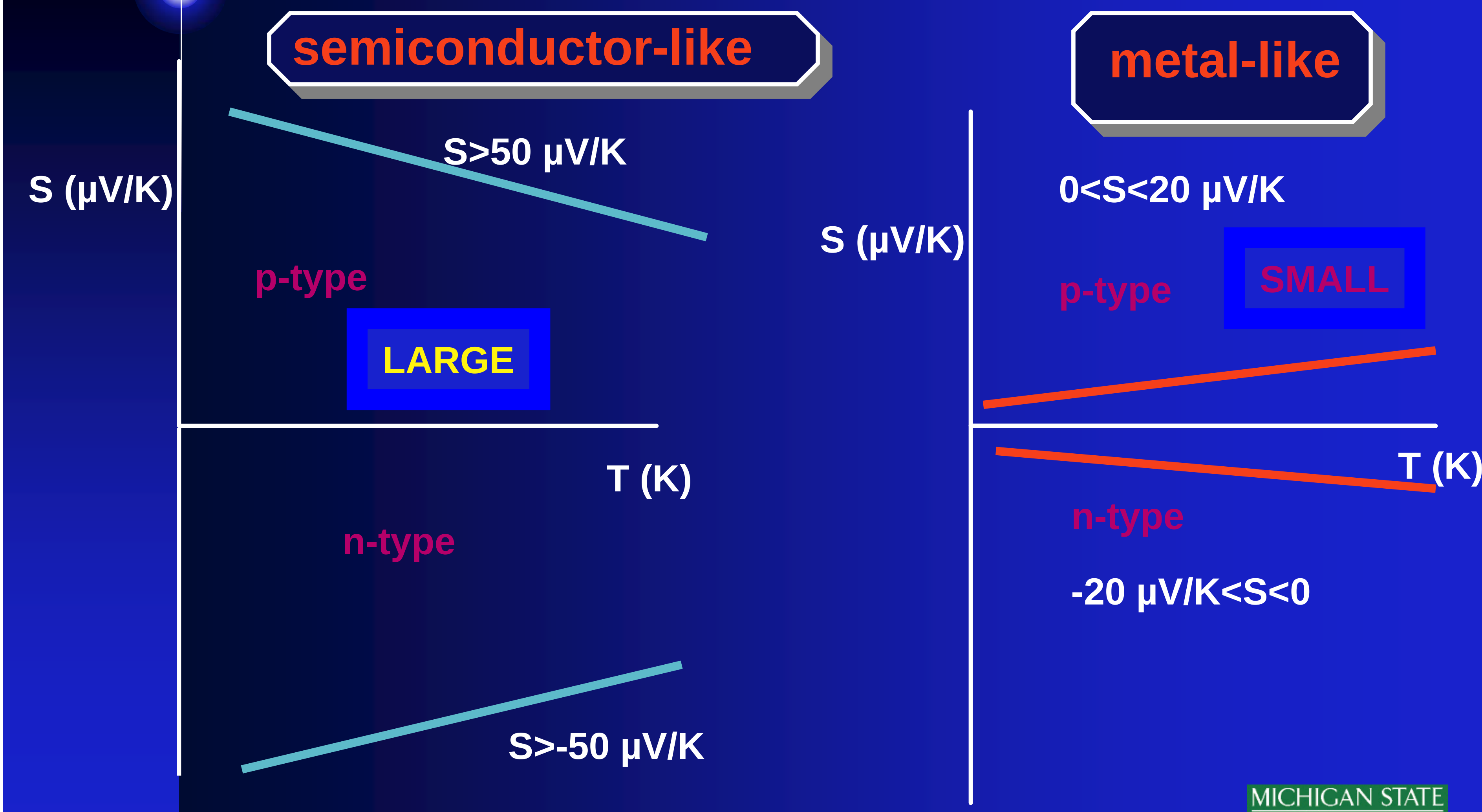
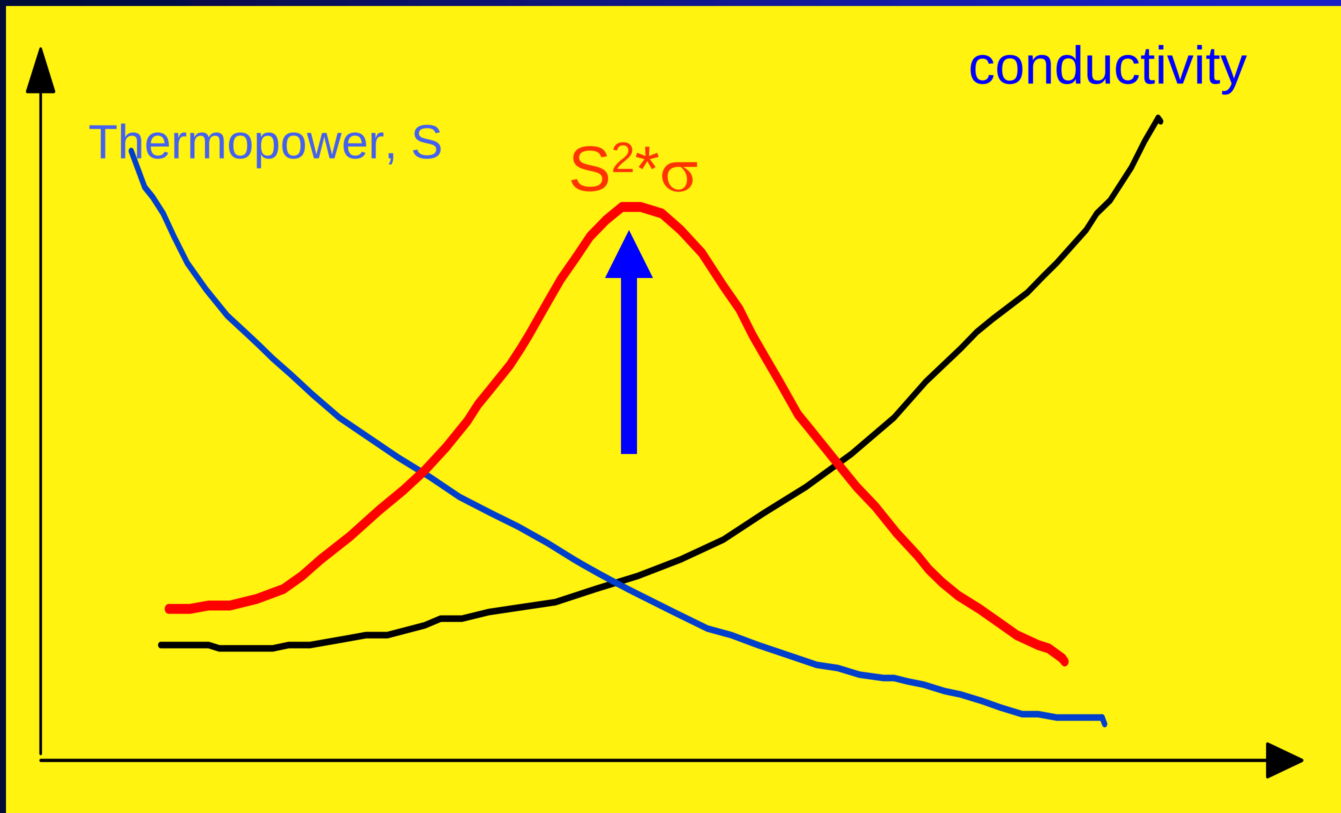
TYPICAL BEHAVIOR OF MATERIALS



Power Factor ($S^2*\sigma$) vs Carrier Concentration



10^{17} 10^{18} 10^{19} 10^{20} 10^{21}

Carrier Concentration, cm^{-1}

Thermopower and Electronic Structure

$$S = \frac{\pi^2 k_B^2 T}{3e} \frac{d(\ln \sigma(E))}{dE}\bigg|_{E = E_F}$$

Mott Equation

- $\sigma(E)$ is the electrical conductivity determined as a function of band filling or Fermi energy, E_F. If the electronic scattering is independent of energy, $\sigma(E)$ is just proportional to the density of states (DOS) at E_F.
- For maximum S, a large asymmetry in the DOS and/or scattering within a few kT above and below the Fermi energy is required.

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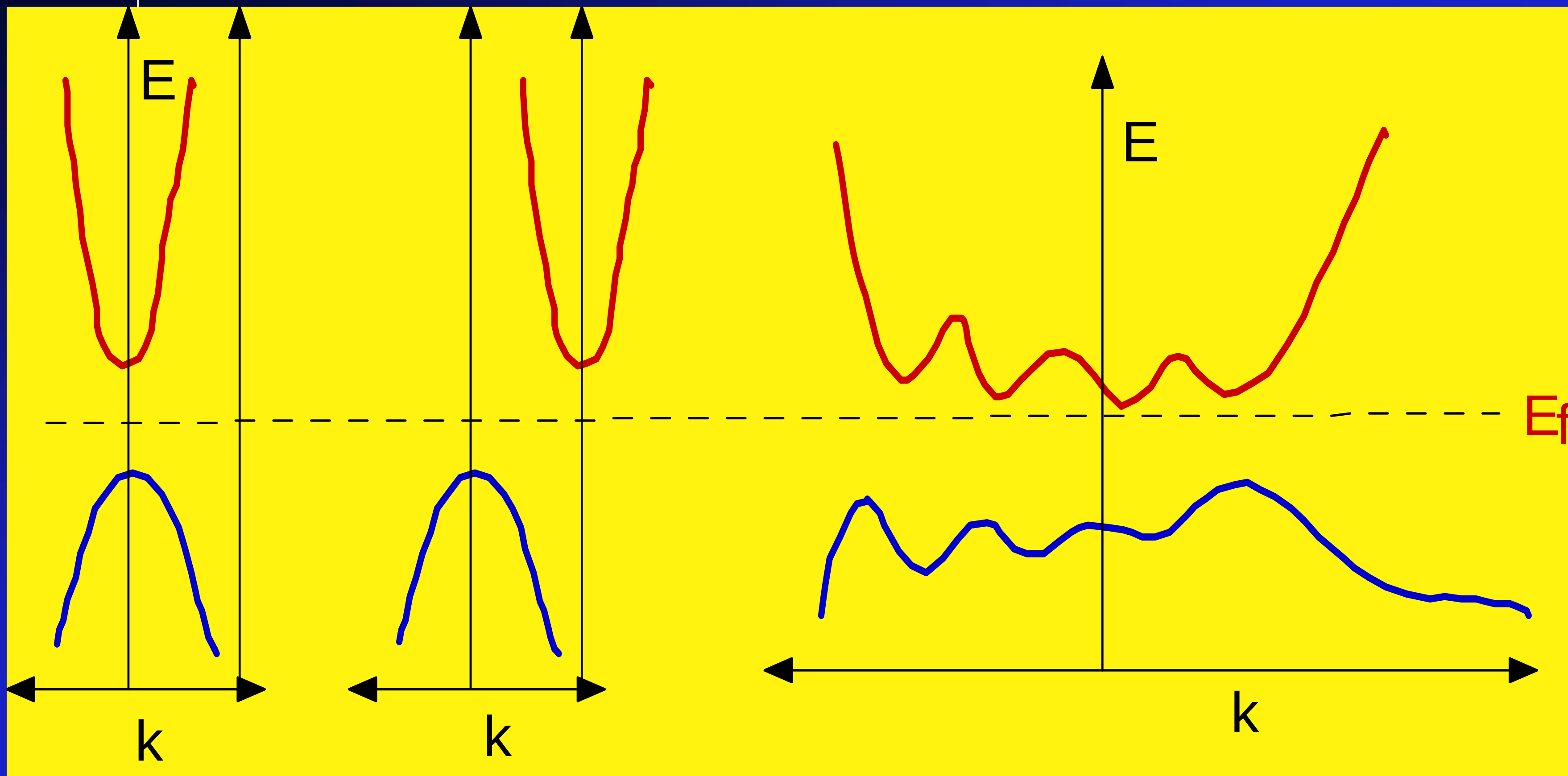
Band structure Types

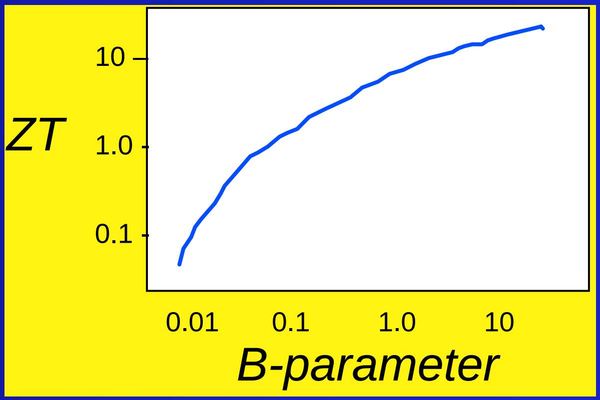


simple simple complex

ZT and Band Structure

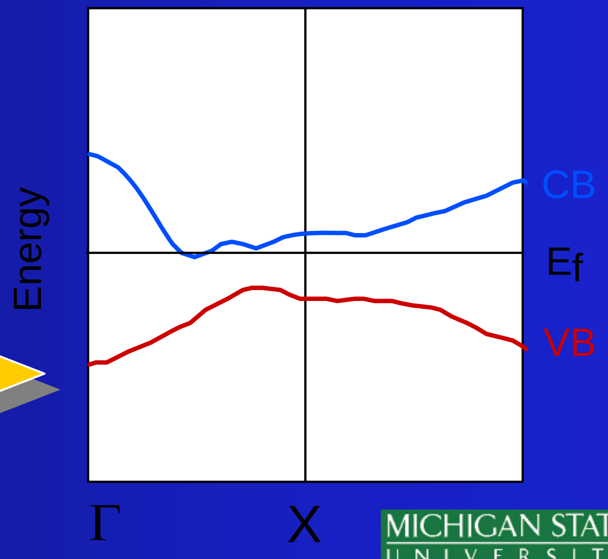
B- parameter

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



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



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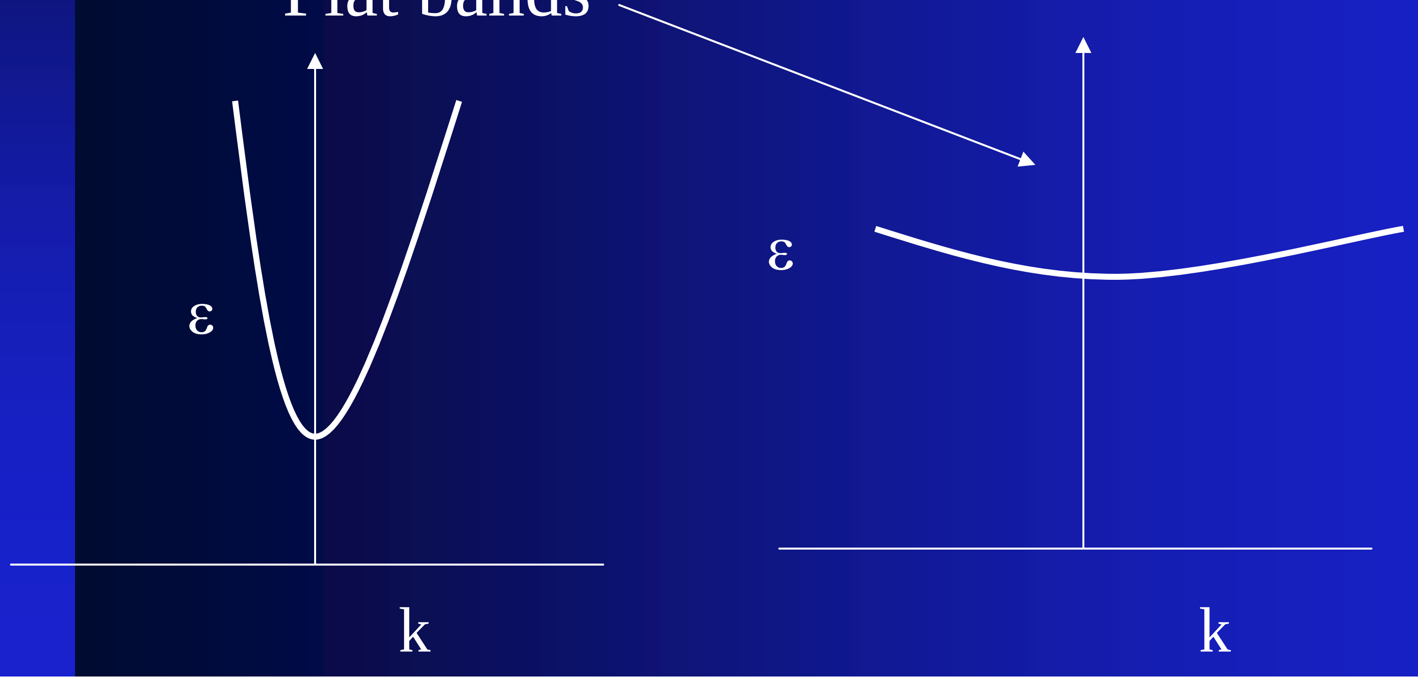
Desirable characteristics

- Multiple peaks and valleys in valence/conduction band
- Heavy carrier masses
  - Flat bands



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Selection criteria for candidate materials

- Narrow band-gap semiconductors
  - For operation at room temperature
- Heavy elements
  - High mobility, low thermal conductivity
- Large unit cell, complex structure
  - low thermal conductivity
- Highly anisotropic or highly symmetric
- Complex compositions
  - low thermal conductivity, electronic structure

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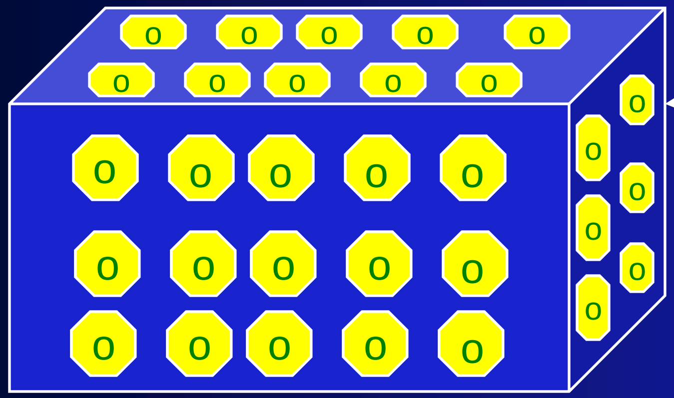
Important Issue: Thermal Conductivity

- Slack’s proposal: Phonon-Glass/ Electron-Crystal (PGEC)
  - Rattling Ions in the lattice: watch thermal displacement parameters



Rattling ions in cavities
or tunnels
scatter heat-carrying phonons

Crystalline solid

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Reaction Chemistry

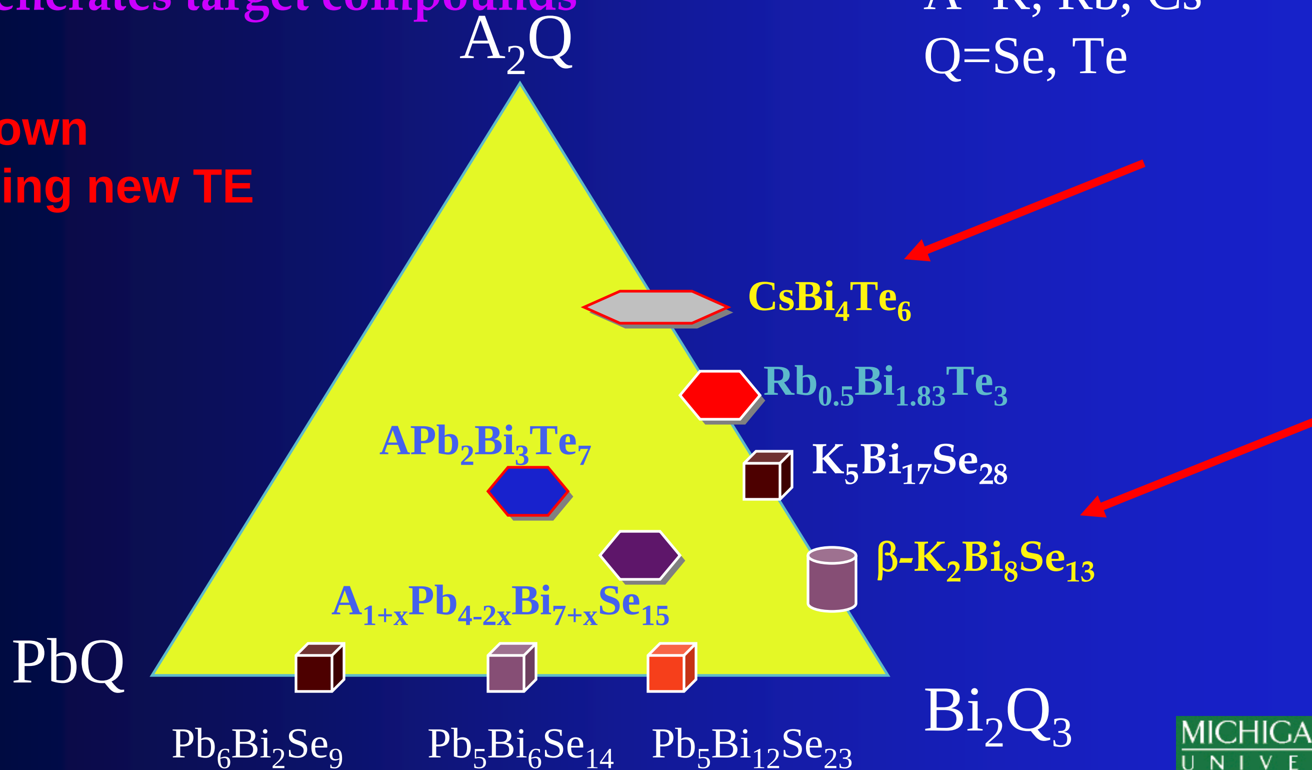
Investigating the System:

- $A_2Q + PbQ + Bi_2Q_3$ ———> $(A_2Q)_n(PbQ)_m(Bi_2Q_3)_p$

Map generates target compounds

A=K, Rb, Cs
Q=Se, Te

Phases shown are promising new TE Materials



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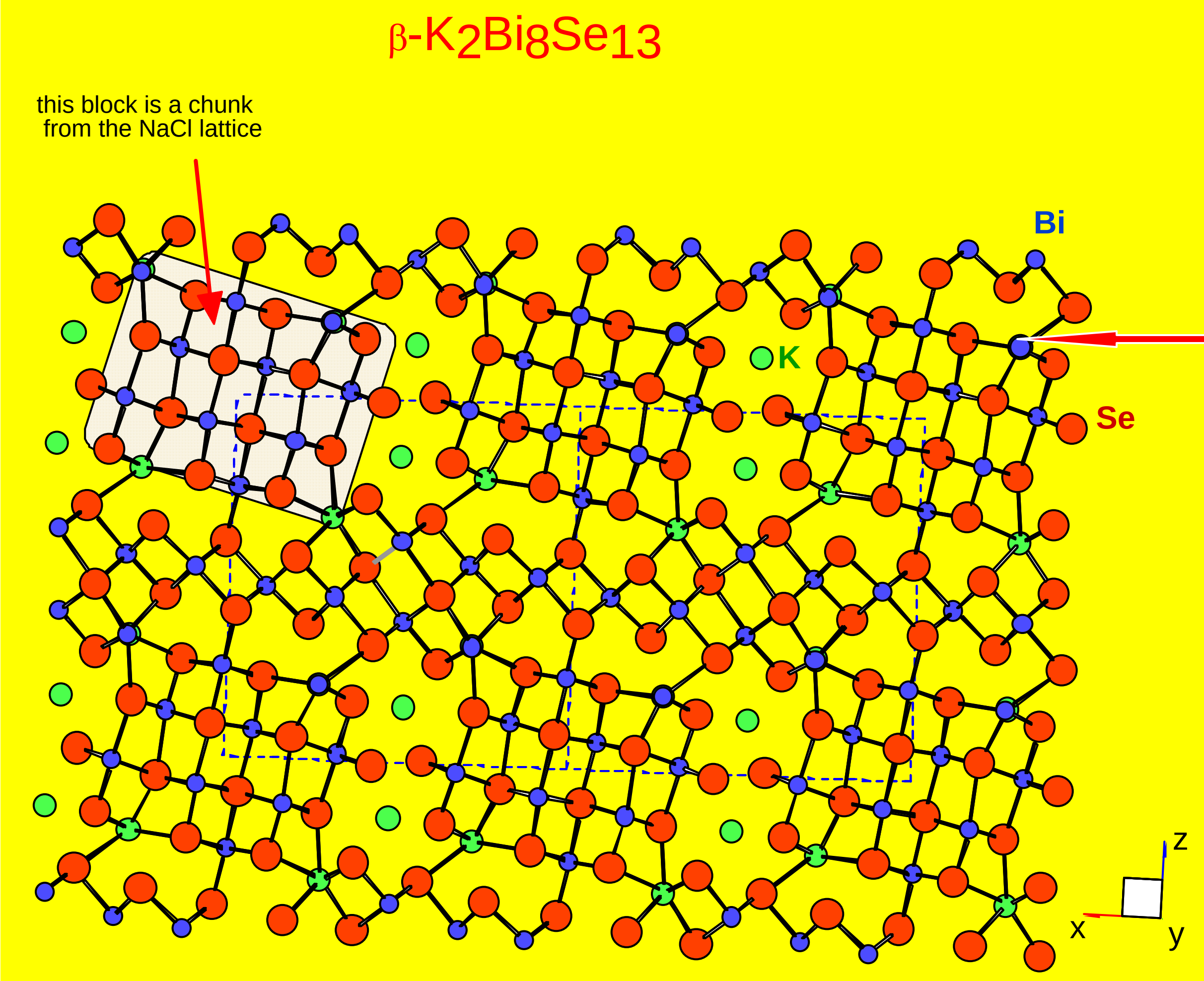
$K_2Bi_8Se_{13}$

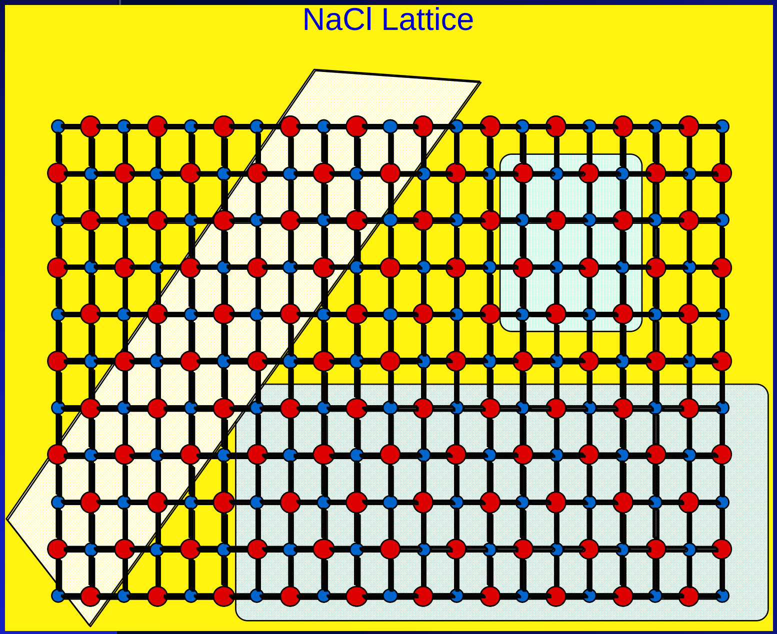


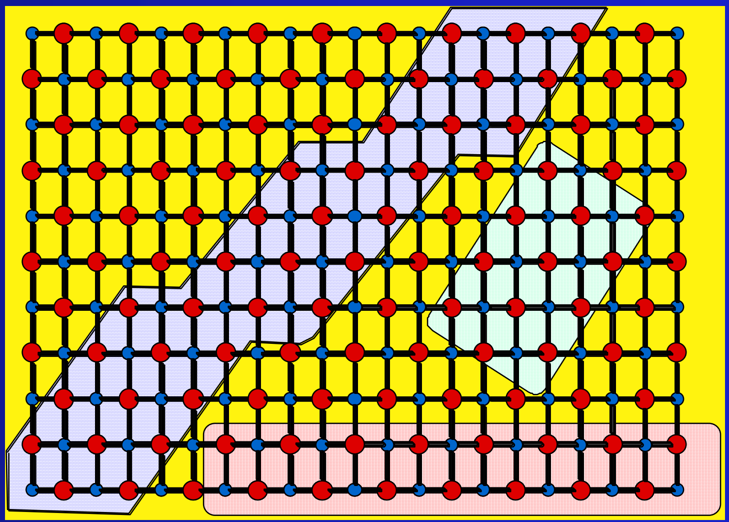
K ions possess ~2x the thermal displacement parameter of the Bi/Se framework

8,9-coordinate sites
K, Bi

NaCl Structure: The Basic "Raw" Material

"Modules" are cut out of NaCl stock





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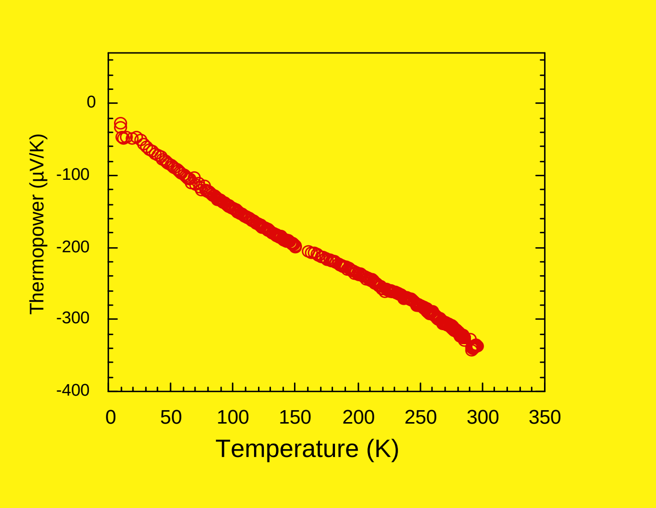
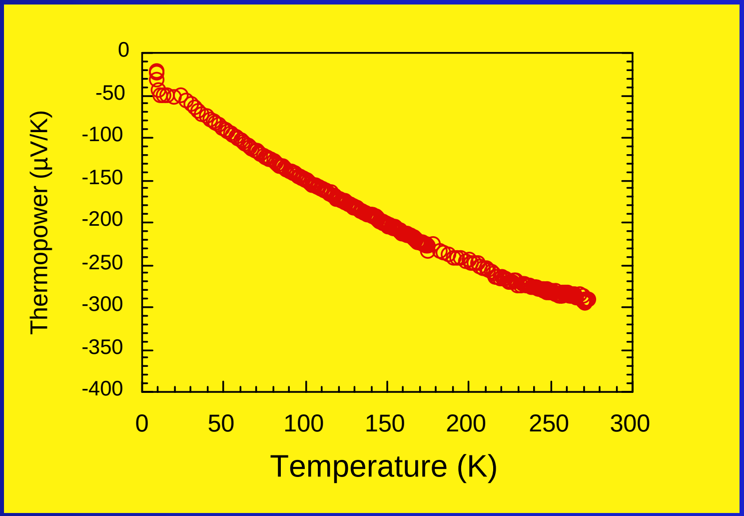
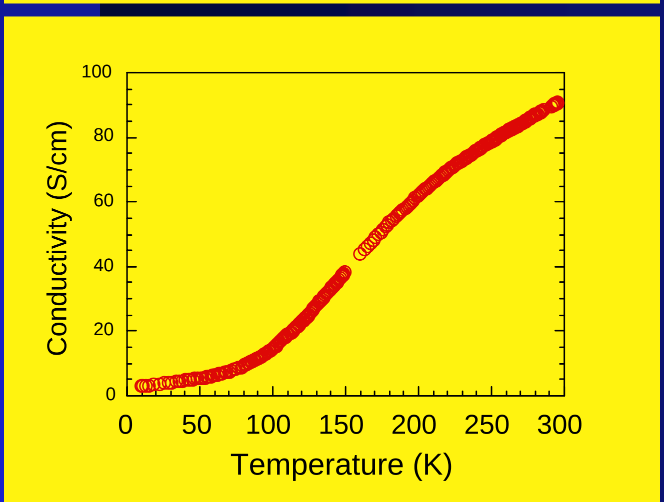
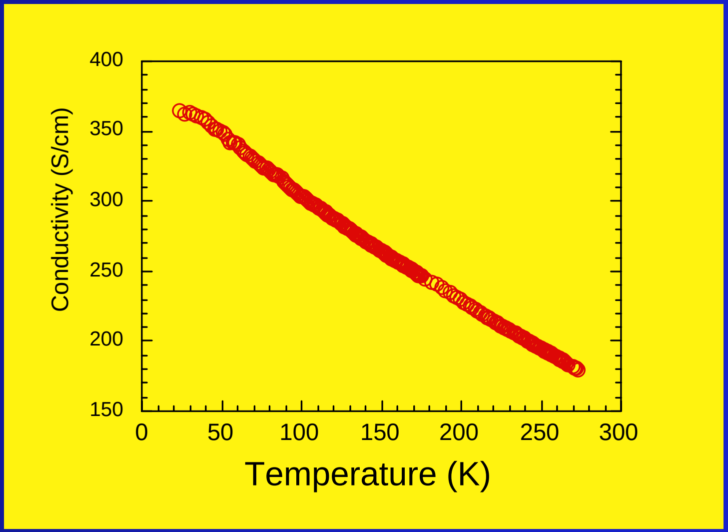
β-$K_2Bi_8Se_{13}$



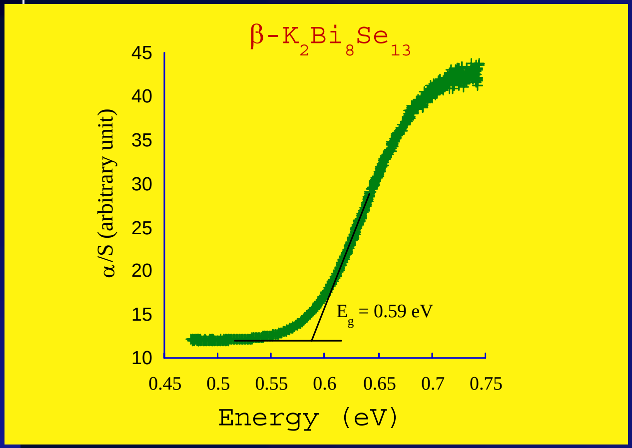
Sn Doped

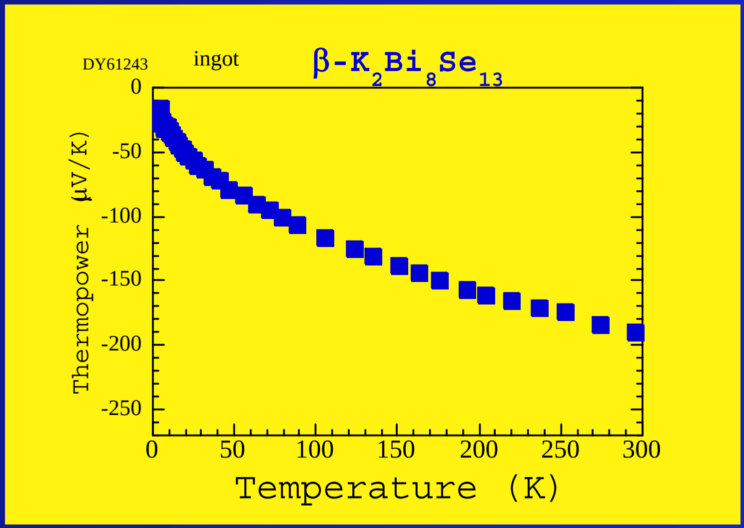


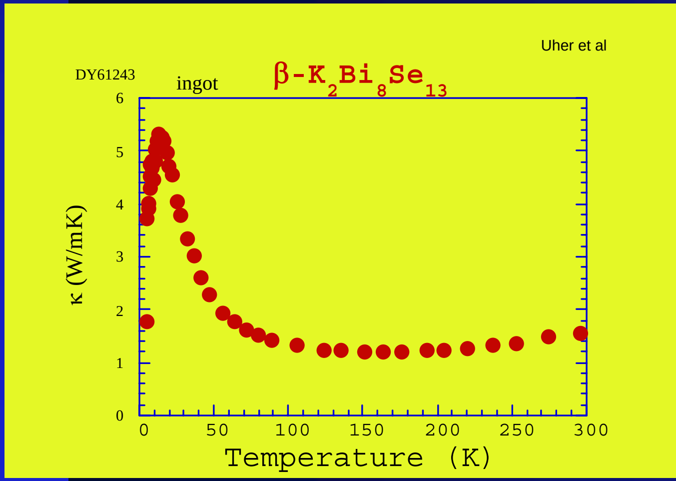


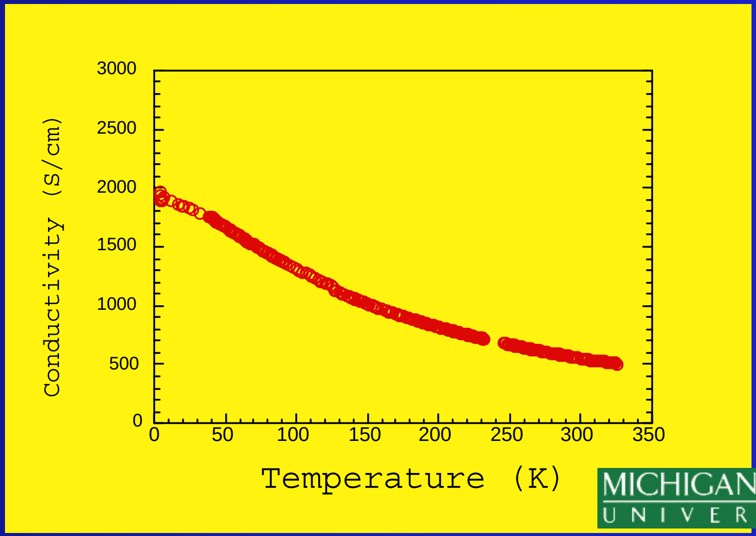


β-$K_2Bi_8Se_{13}$: Room temp ZT=0.9. At 600 K estimated at 1.5 (to be verified)









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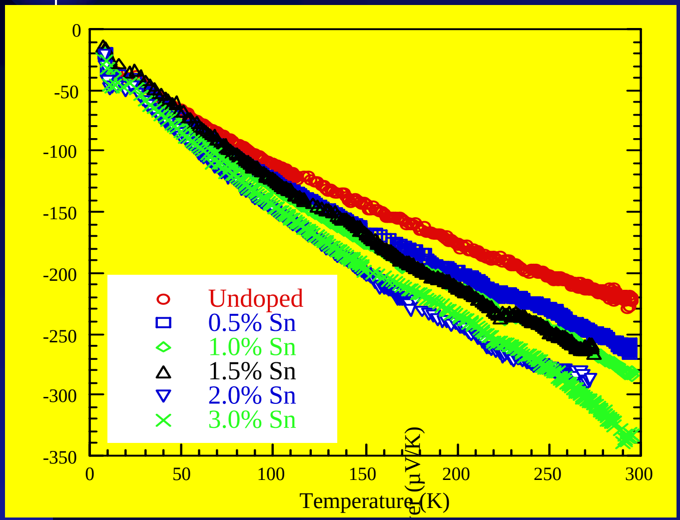
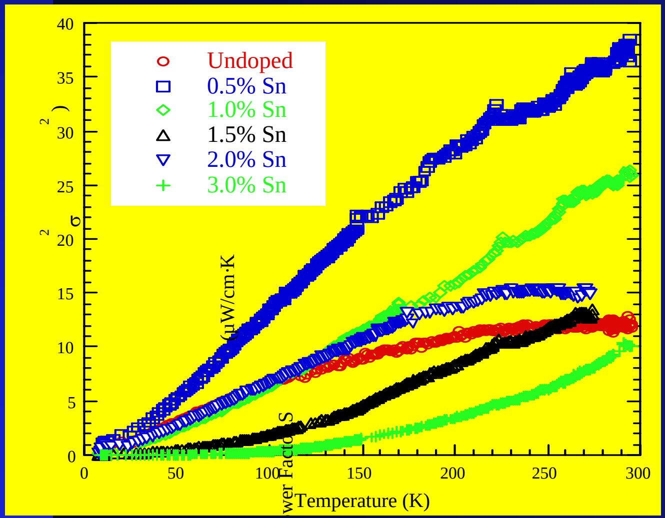
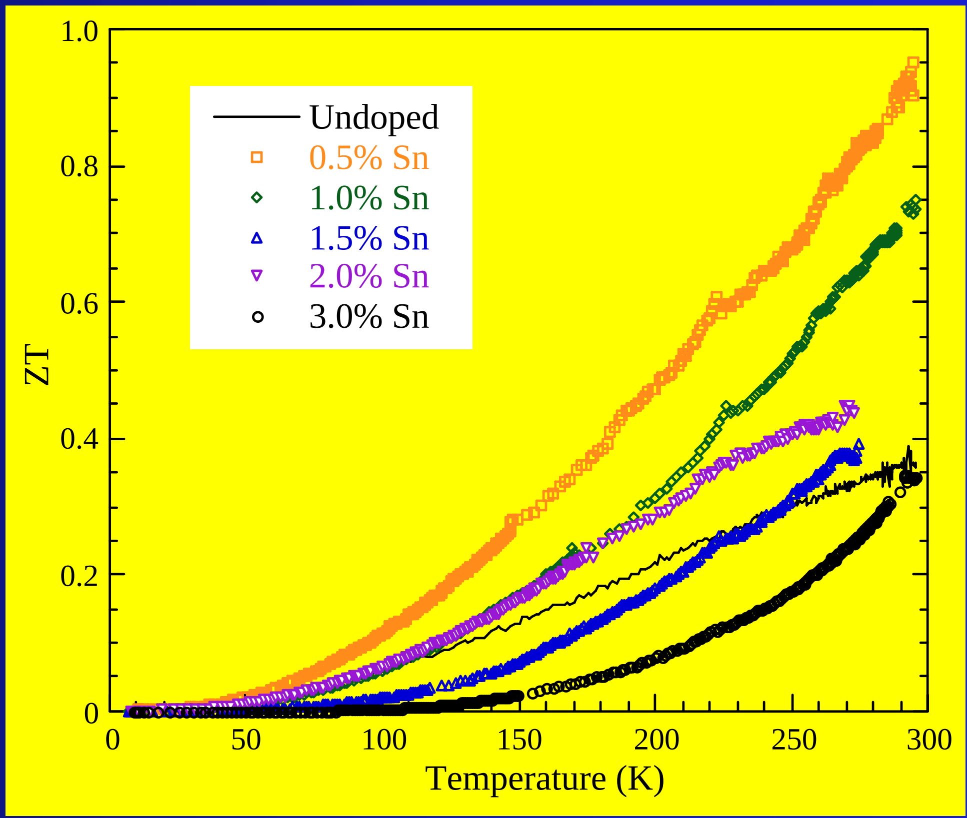
Sn Doping in β-$K_2Bi_8Se_{13}$







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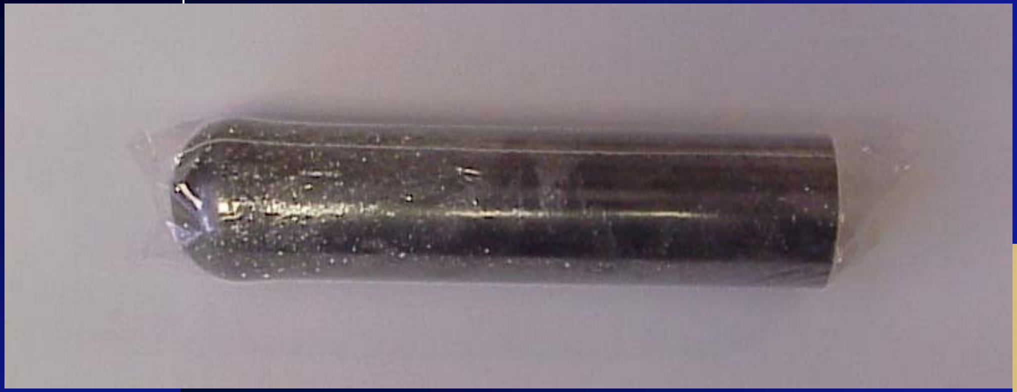
Michigan State University /Tellurex Corp. Collaboration



β-$K_2Bi_8Se_{13}$

New TE material grown at Tellurex

New TE material grown at MSU

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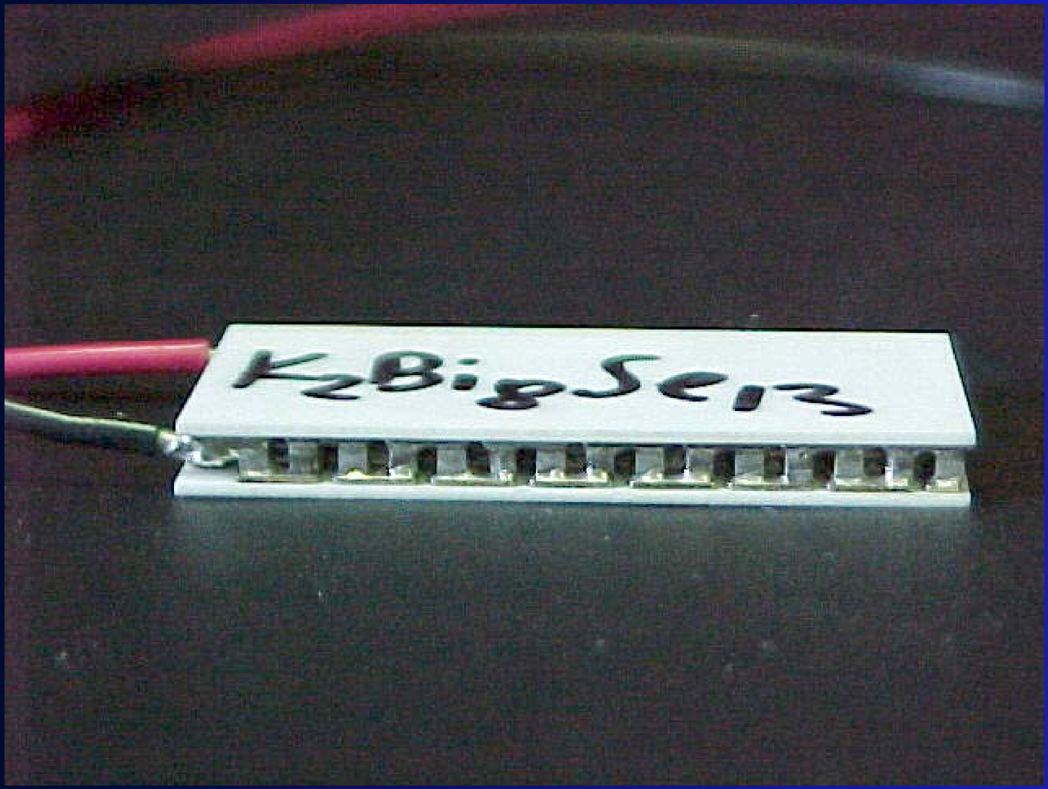
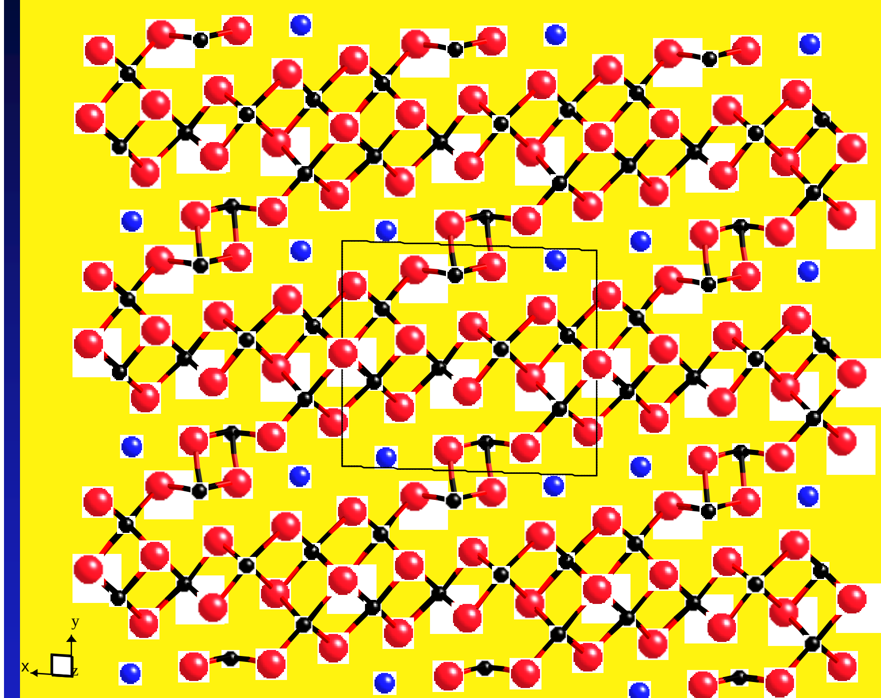
Photo of the first TE module containing 63 couples n-β-$K_2Bi_8Se_{13}$/p-Bi_2Te_3

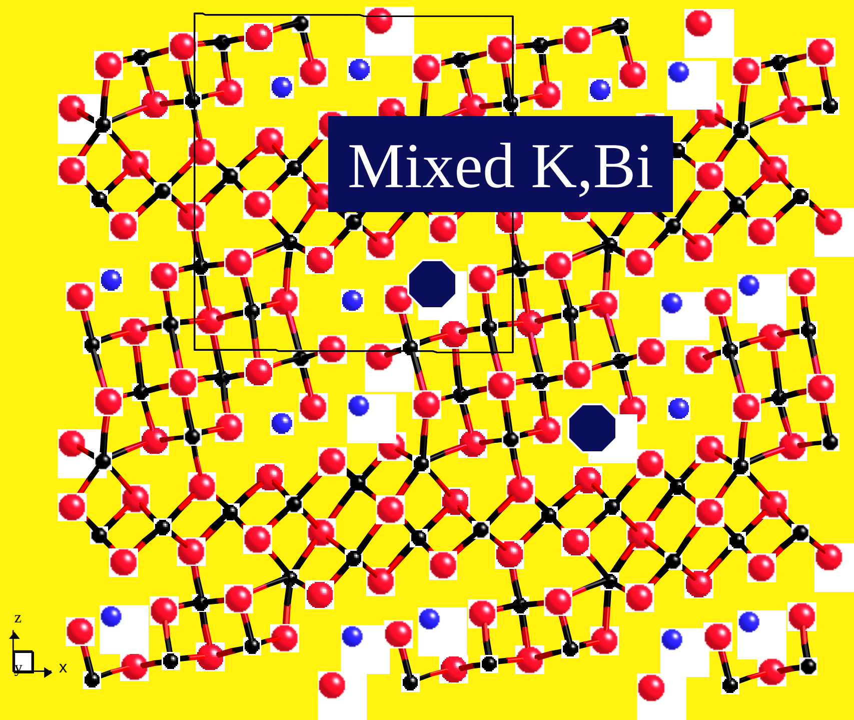


Unoptimized
$\Delta T = 36\ ^{o}C$
$T_h = 50\ ^{o}C$
All materials grown at Tellurex Inc

α-$K_2Bi_8Se_{13}$ versus β-$K_2Bi_8Se_{13}$

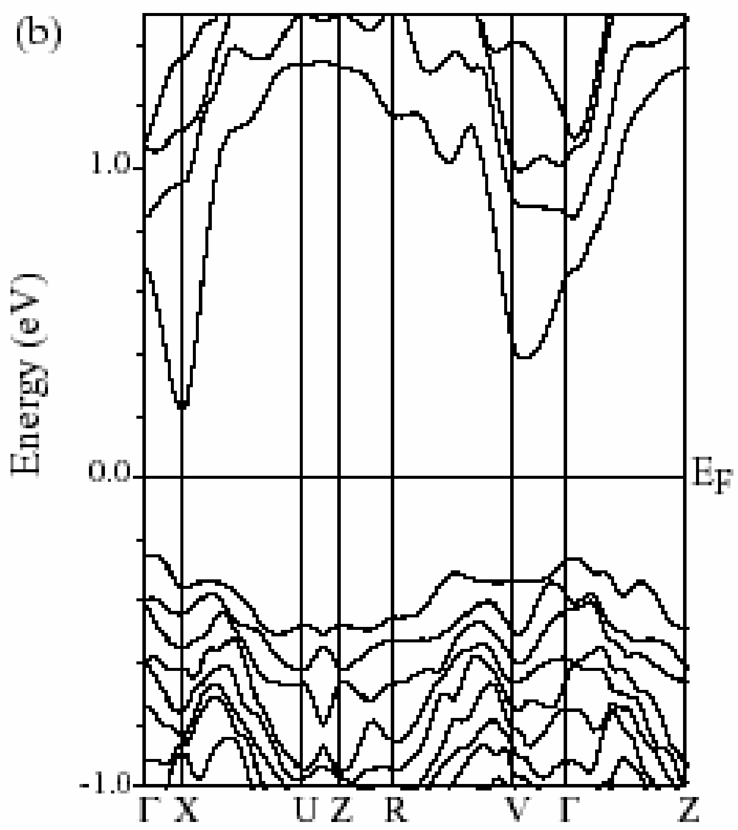


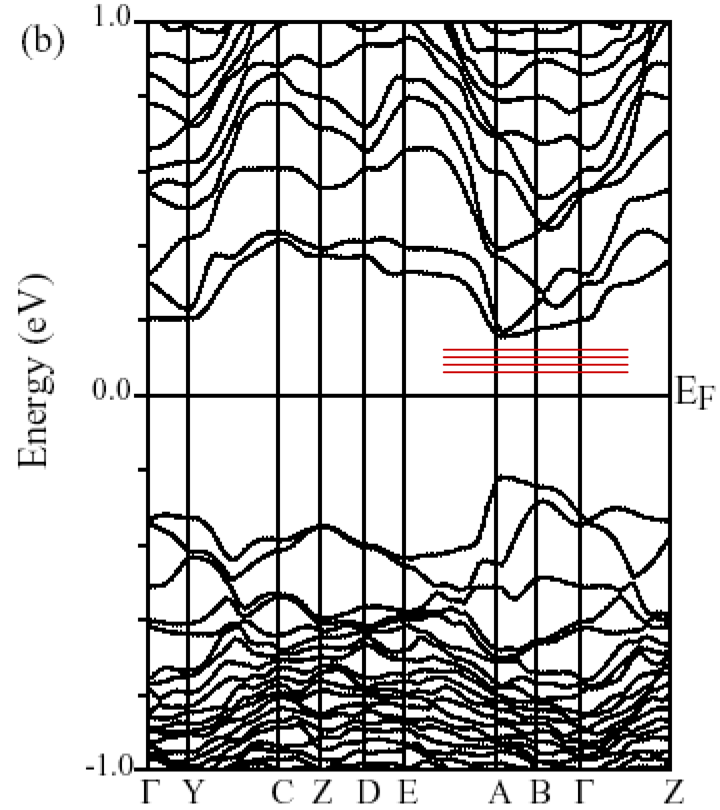
α-$K_2Bi_8Se_{13}$, E_g=0.76 eV



β-$K_2Bi_8Se_{13}$, E_g=0.59 eV

α-, β-$K_2Bi_8Se_{13}$: Electronic structure





n-type character

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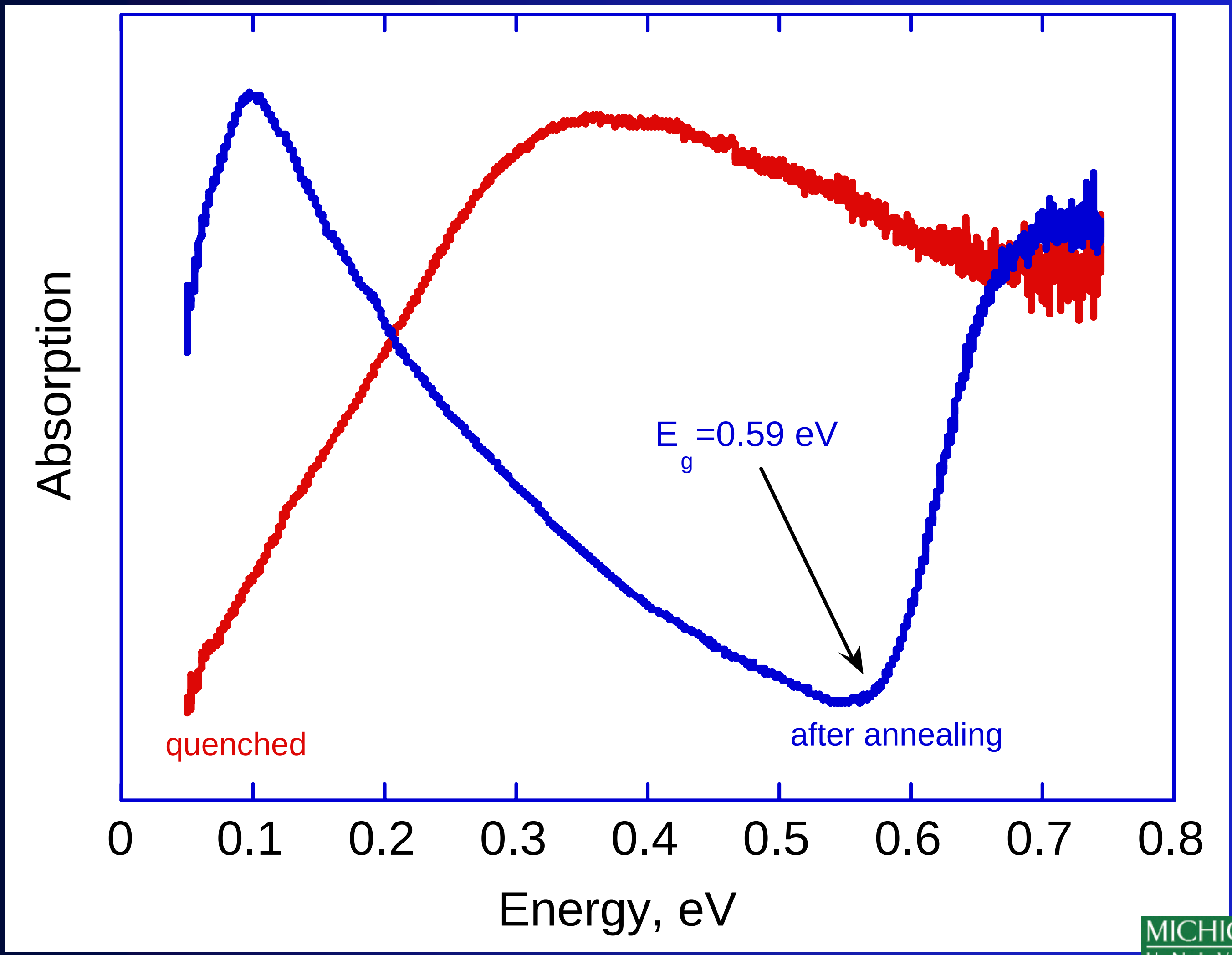
Quenched and annealed β-$K_2Bi_8Se_{13}$



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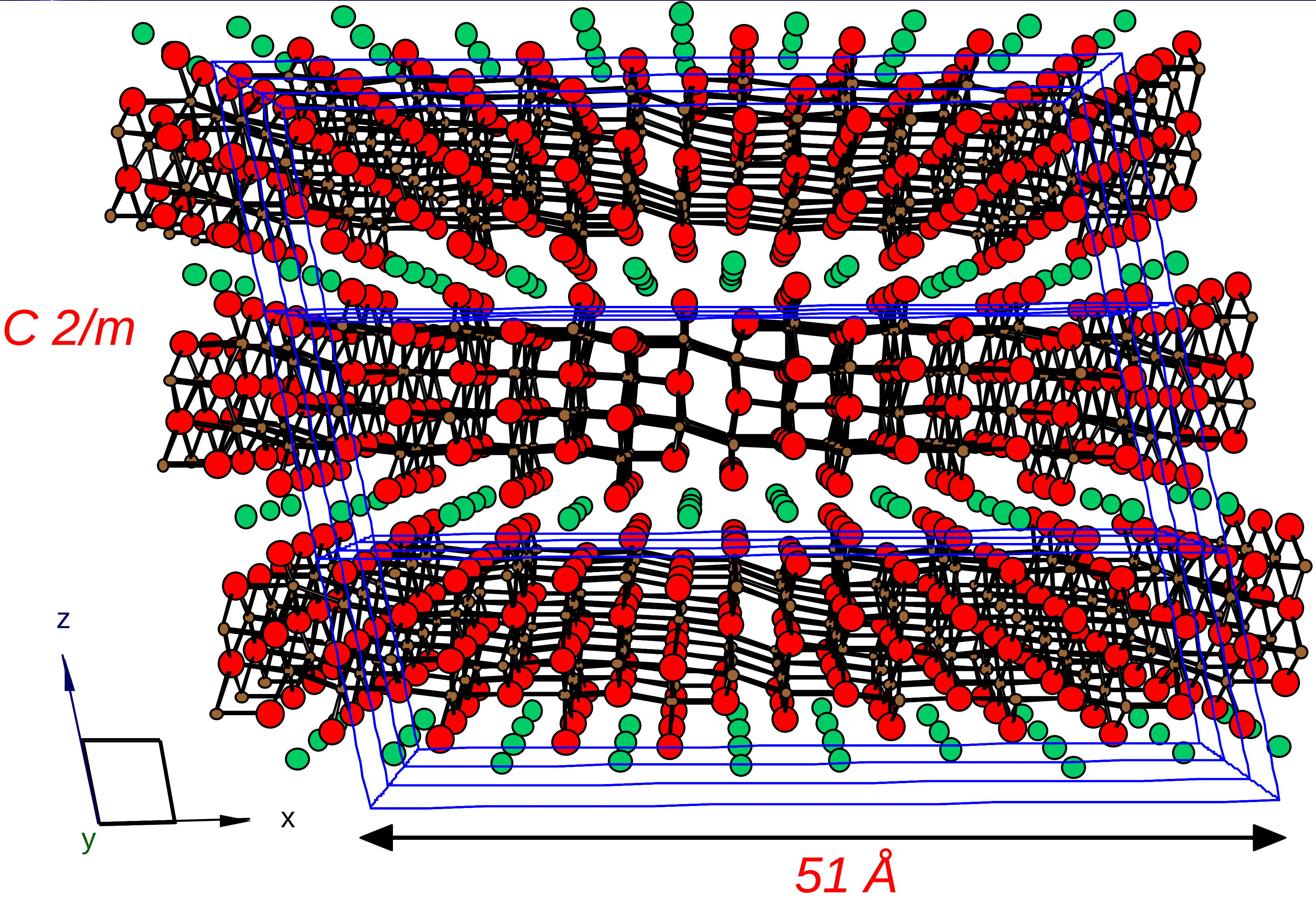
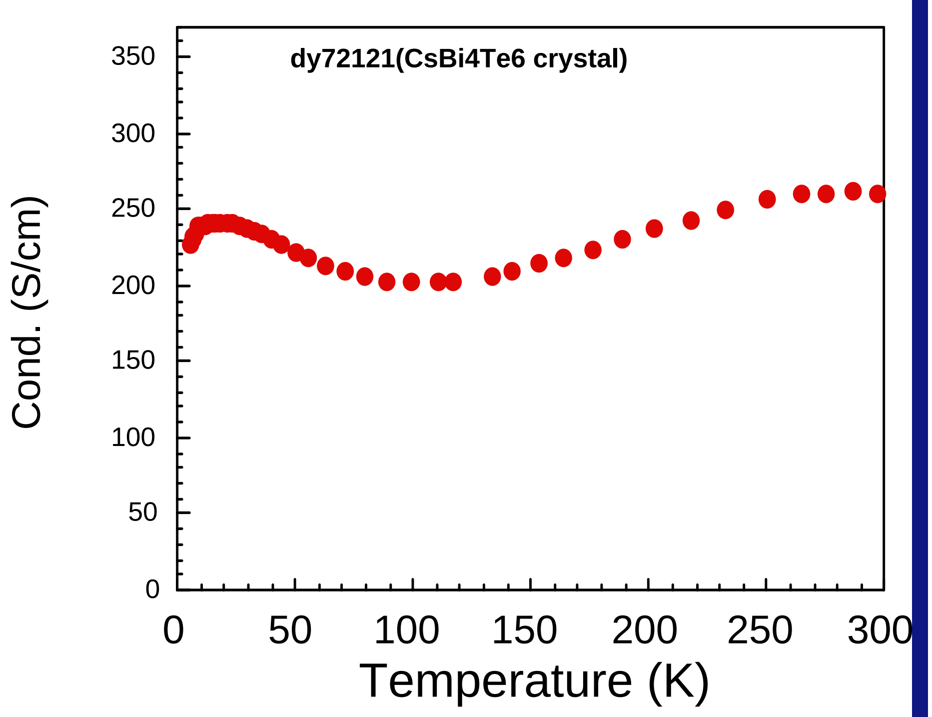
$CsBi_4Te_6$

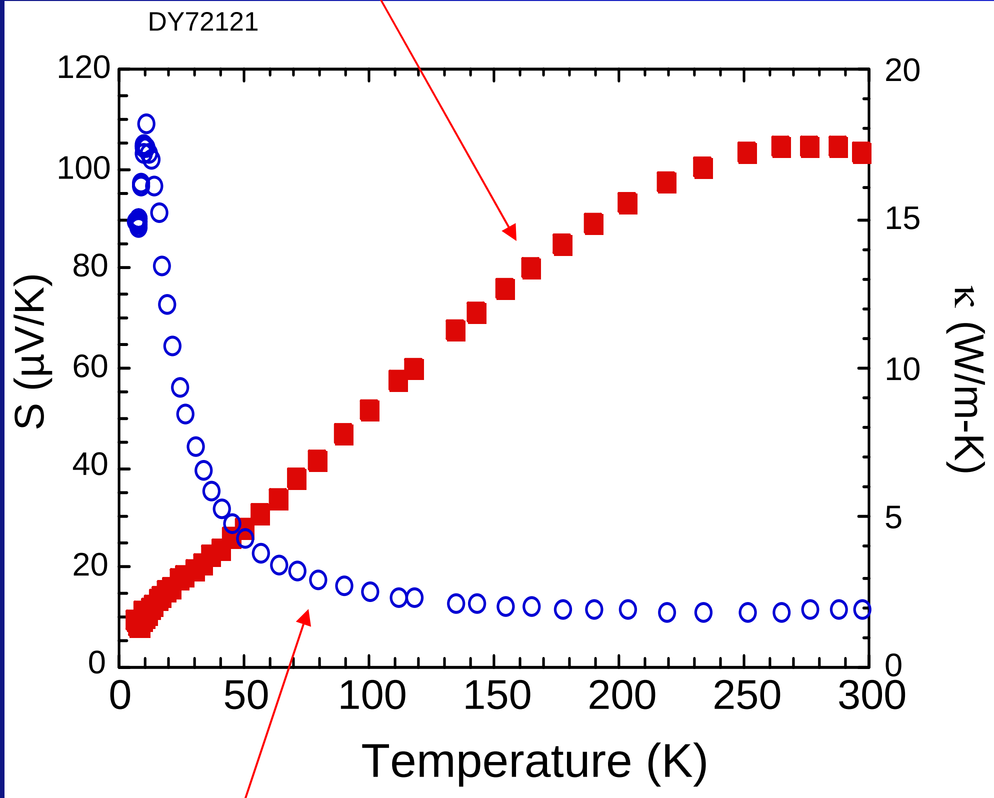


“Undoped” as-prepared material

conductivity



thermopower



Thermal conductivity

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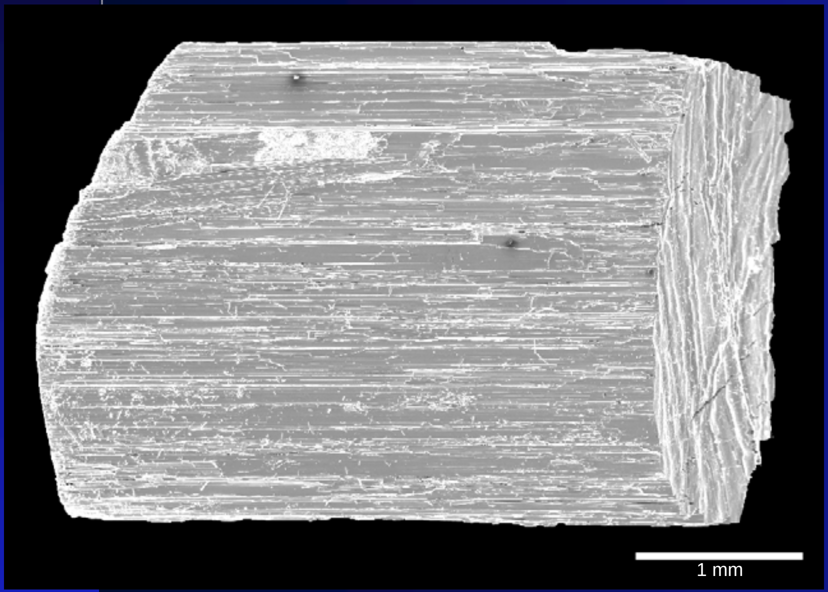
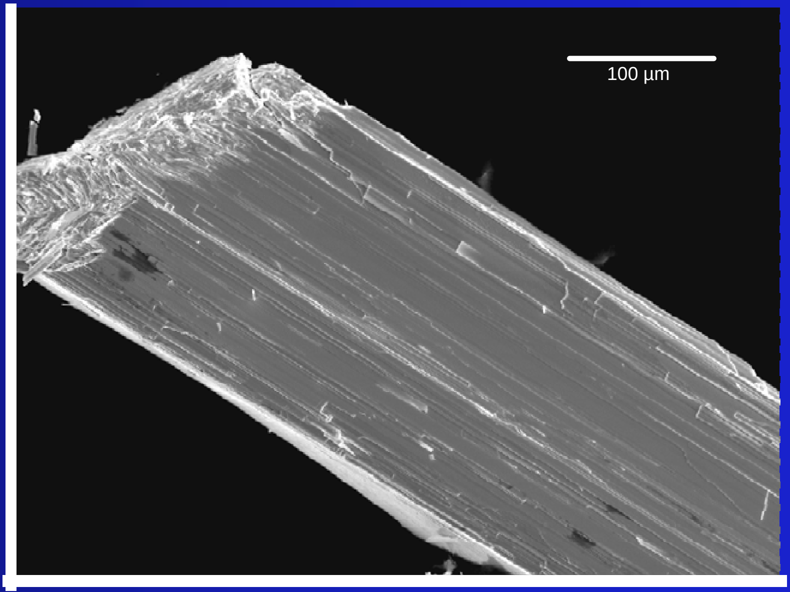
Crystals of $CsBi_4Te_6$





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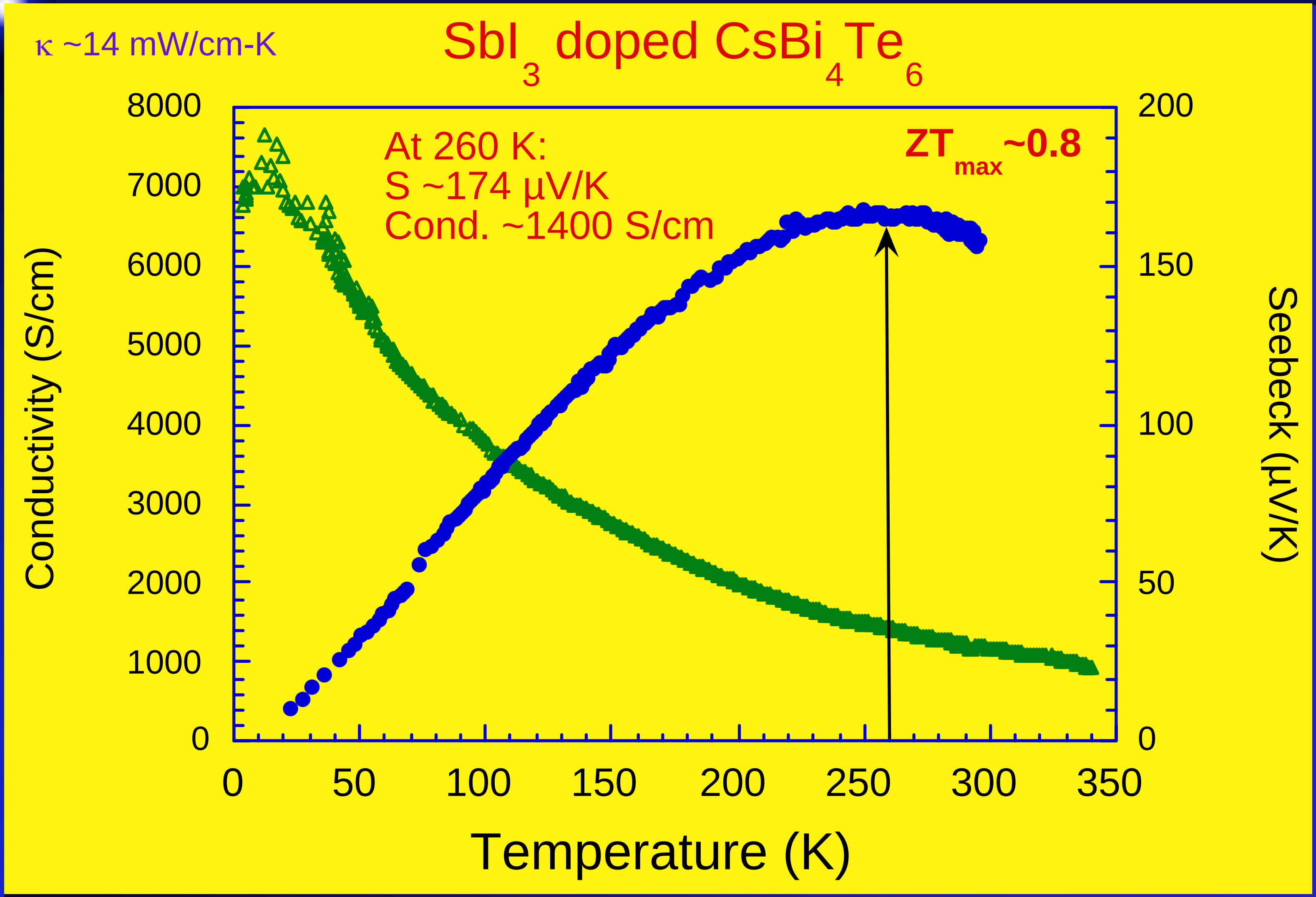
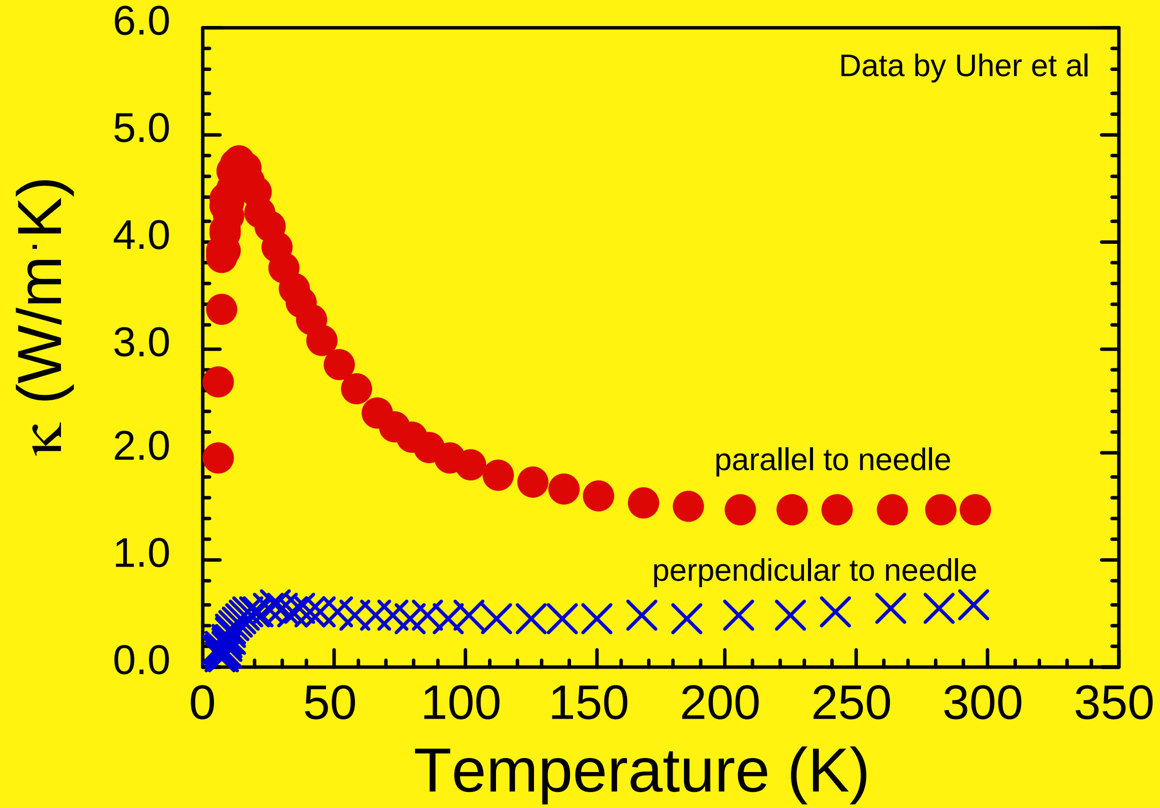
Doped $CsBi_4Te_6$



Thermal Conductivity of p-type $CsBi_4Te_6$



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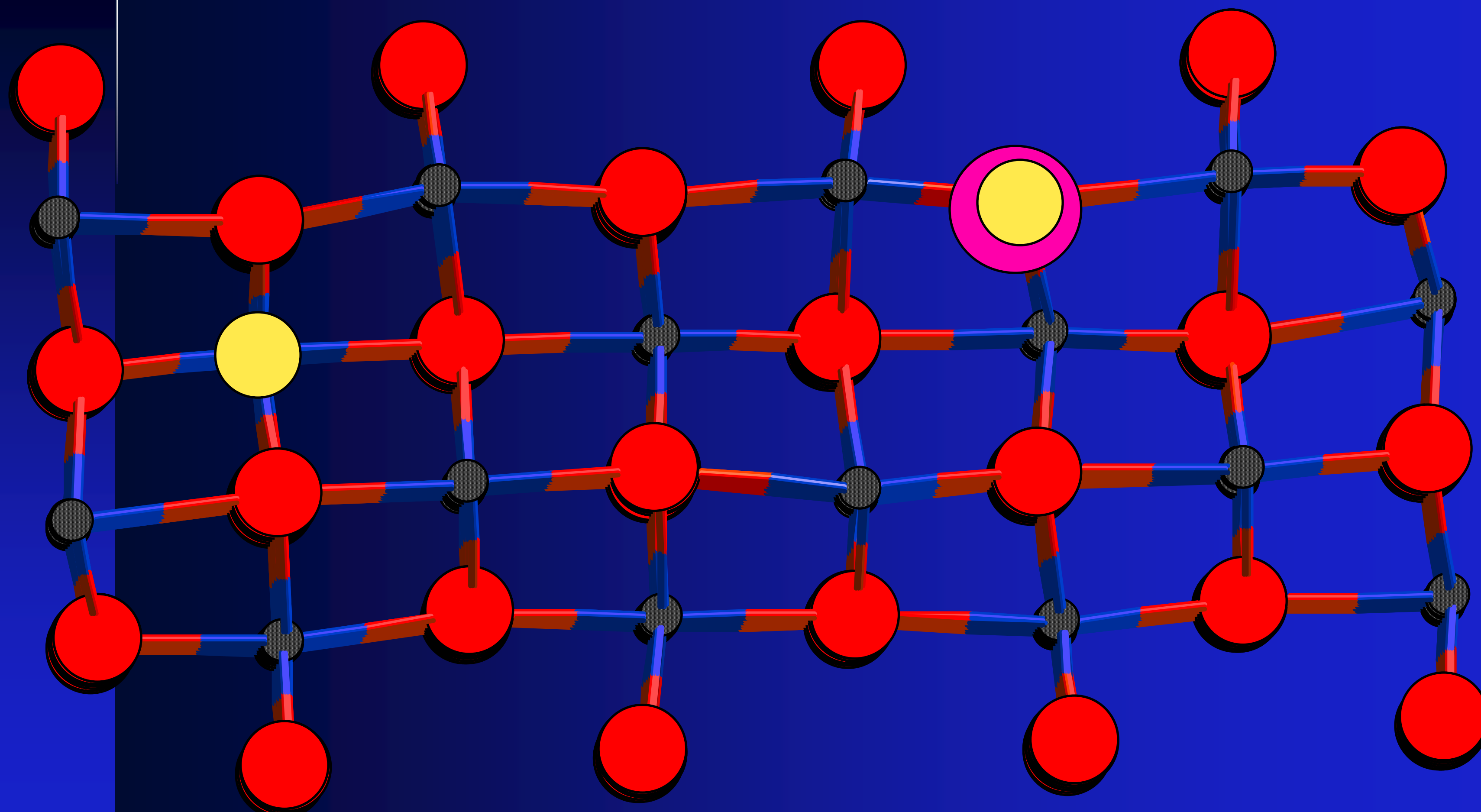
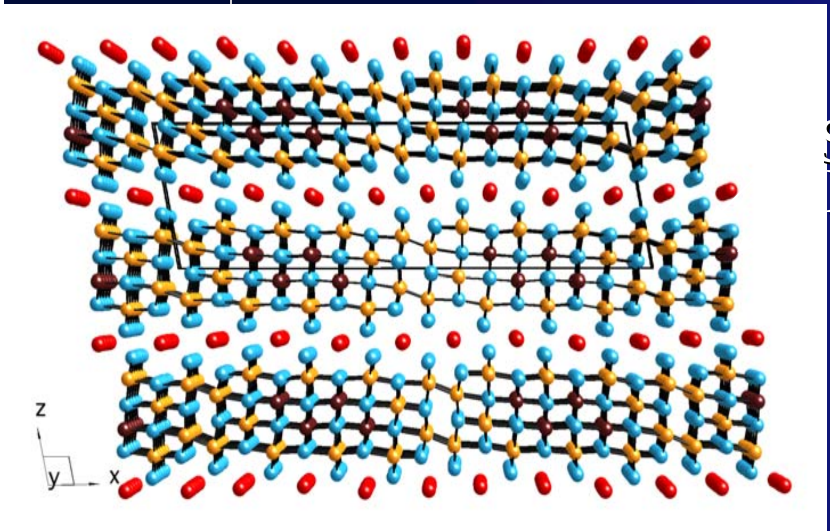
Doping with SbI_3

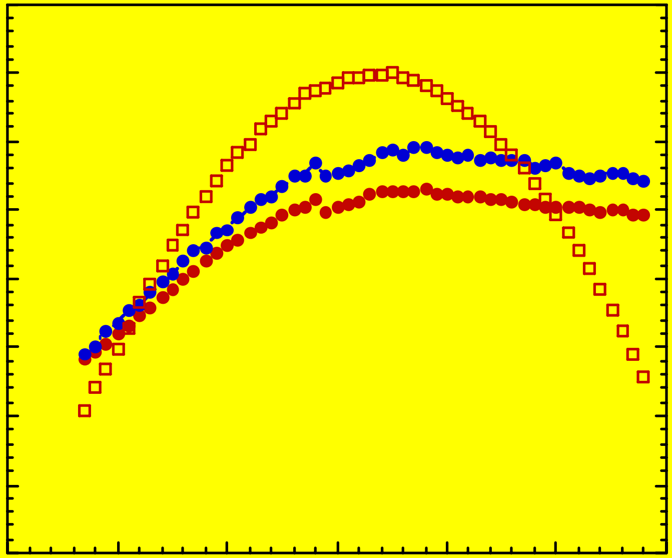


$CsBi_{4-x}Sb_xTe_6$

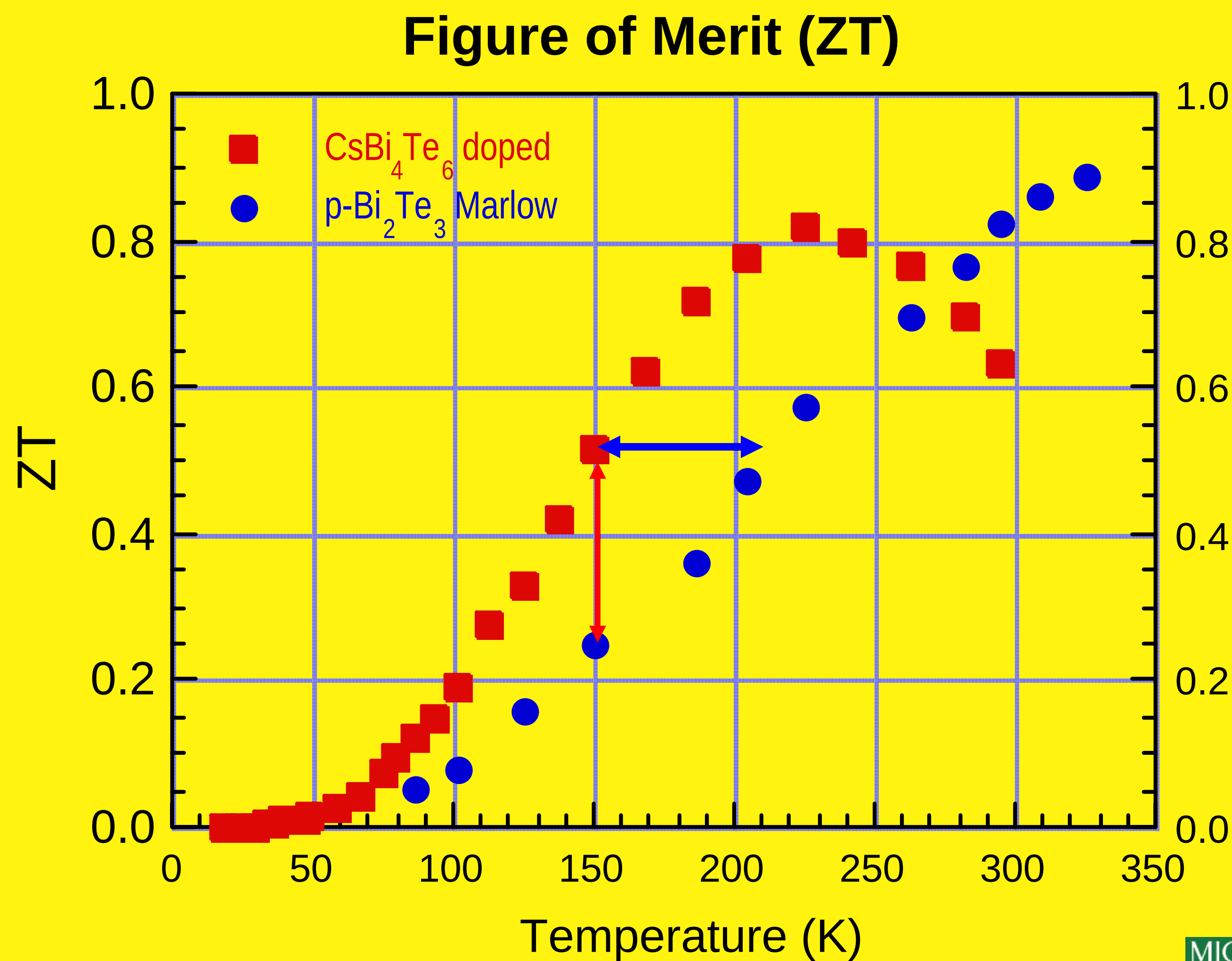
x = 0.3



Sb
Bi



$CsBi_4Te_6$



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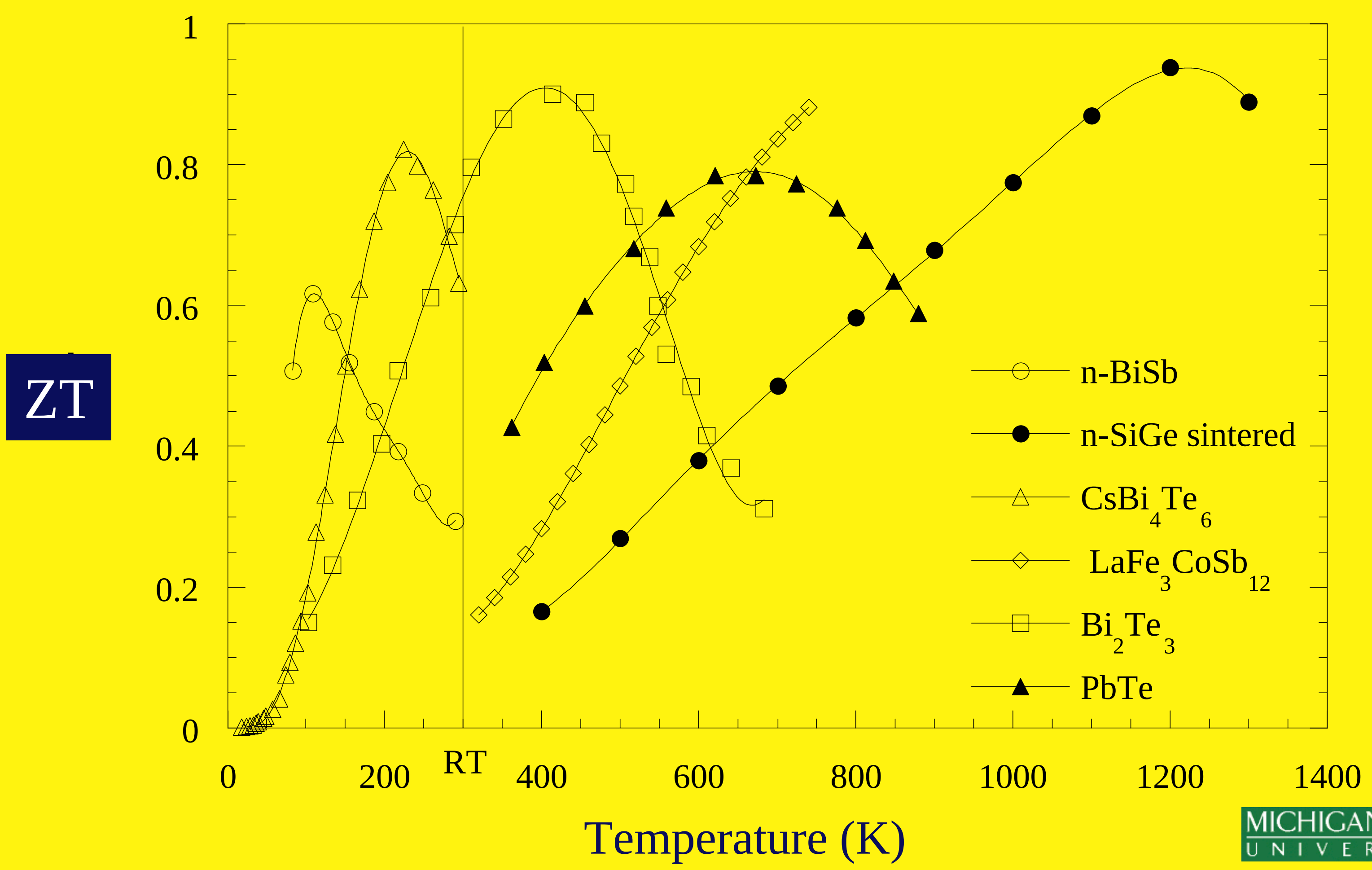
Best TE Materials



Conclusions

- The strategy to search for new materials in the $(A_2Q)_n(PbQ)_m(Bi_2Q_3)_p$ (Q=Se, Te) system is successful
- Many new promising compounds identified
- All compounds strongly anisotropic
- Doping studies are important in ZT optimization
- ZT for β-$K_2Bi_8Se_{13}$ ~0.7 at rt, higher at >400K

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- *Thermoelectric Materials 1998- The Next Generation Materials for Small-Scale Refridgeration and Power Generation Applications*, edited by Tritt, T. M.; Kanatzidis, M. G.; Mahan, G. D.; Lyon, Jr., H. B. *Mat. Res. Soc. Symp. Proc*. **1999**, *Vol. 545*, 233-246.

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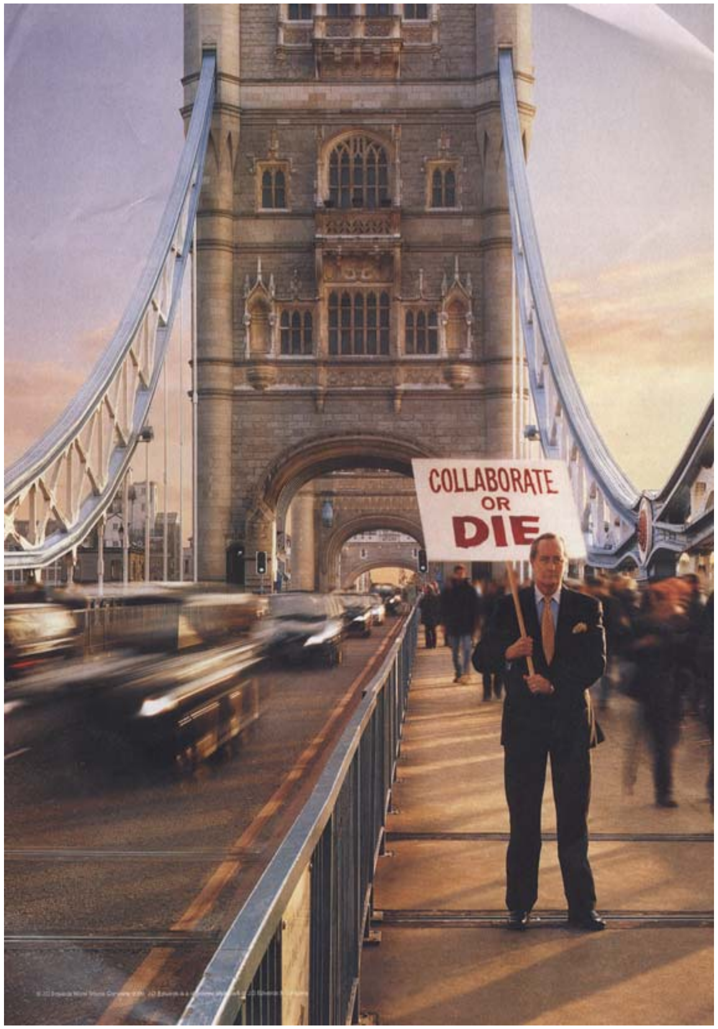

TE Research group

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- Sandrine Sportouch
- Rhonda Patschke
- Tim McCarthy
- Dr. Jun-Huan Do

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- Dr. Antje Mrotzek
- Lykourgos Iordanidis
- J. A. Aitken
- Jun-Ho Kim
- Joseph Wachter
- Marina Zhuravleva
- Xuini Wu
- Jim Salvador
- Brad Sieve
- R G Iyer
- Dr. Theodora Kyratsi
- Dr. J.-H. Do
- Dr. Duck Young Chung
- Dr. Servane Coste
- Dr. Pantelis Trikalitis
- Dr. Susan Latturner
- Dr. Kuei-fang Hsu