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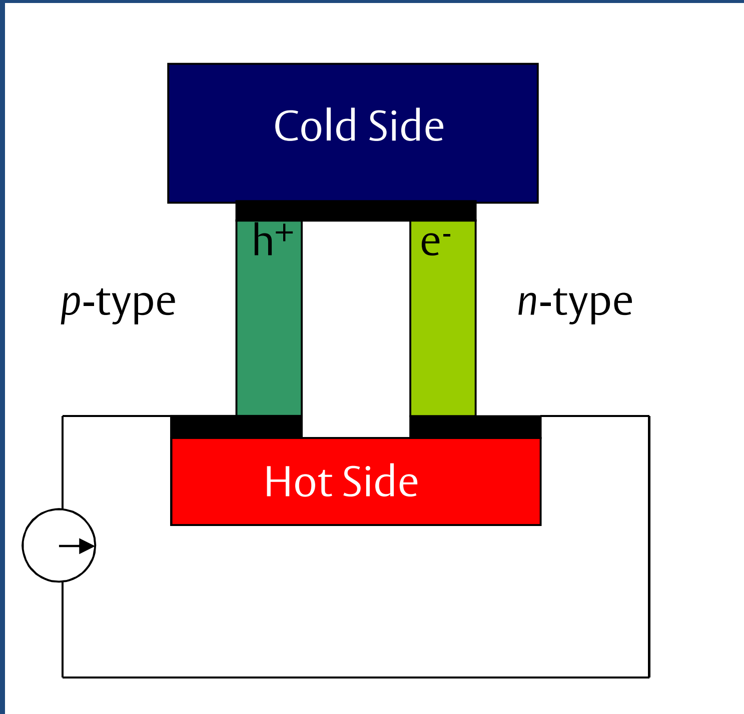
Traditional and Novel Thermoelectric Materials

Anthony Powell
Department of Chemistry
University of Reading
Reading RG6 6AD

a.v.powell@reading.ac.uk

Commercial Thermoelectric Devices



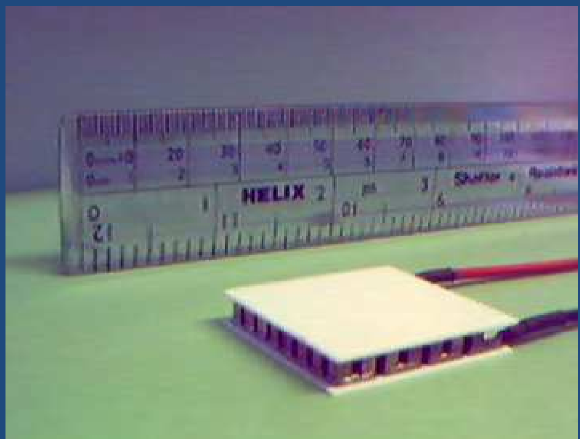
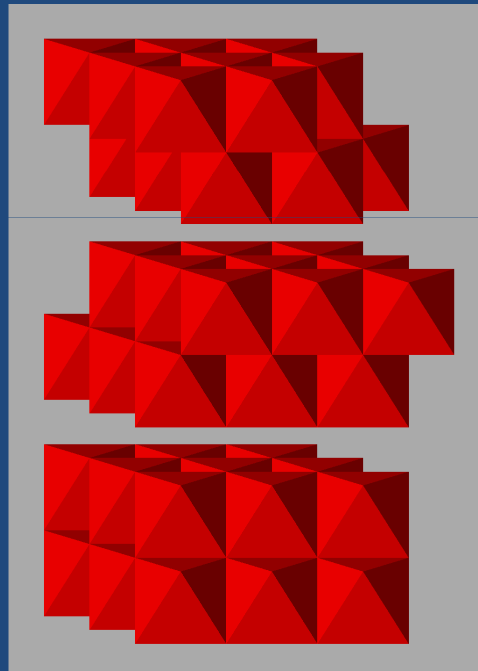


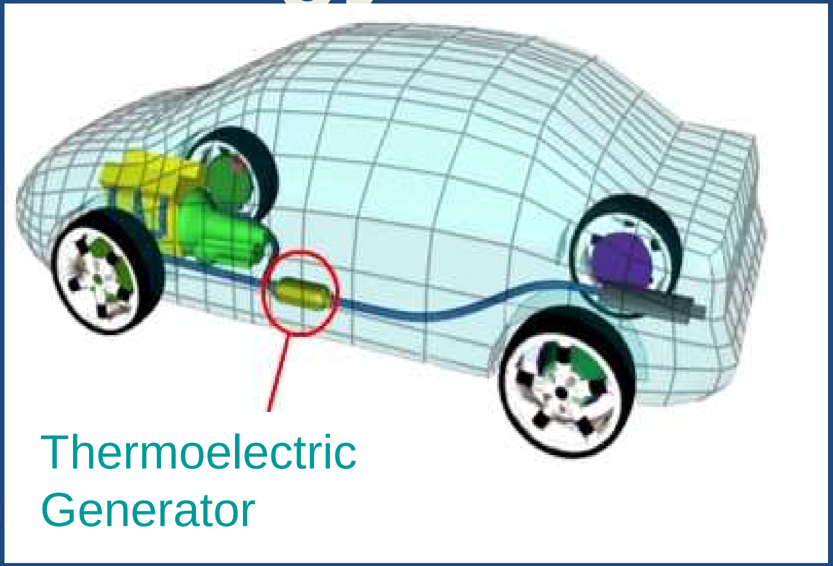
Figure of Merit: $$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$

Bi_2Te_3



$ZT \approx 0.9$ @ RT

Energy from Waste Heat



New car emission standards

160 g CO_2/km (2007)
130 g CO_2/km (2012)
95 g CO_2/km (2020)

Regulation (EC) No 443/2009 (2009)

80% reduction in greenhouse gas emissions(from 1990 levels) by 2050

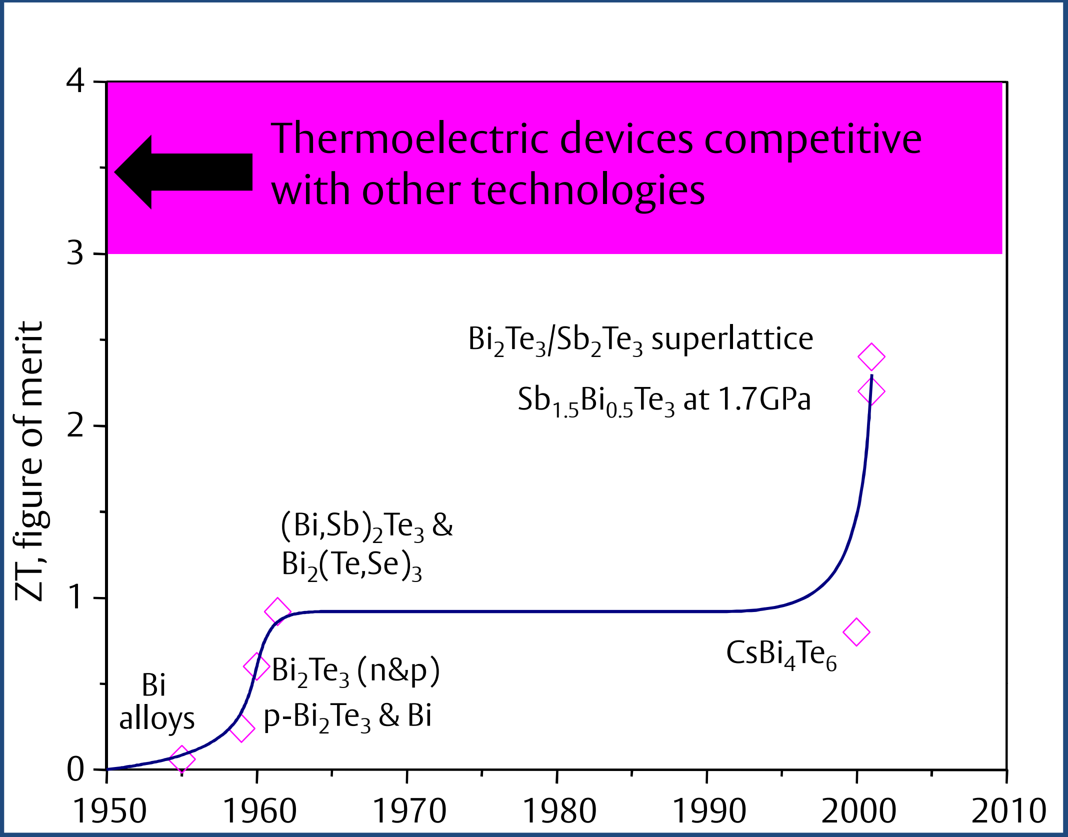
UK Climate Change Act (2008)

Recent programs:
GM
BMW
VW

200 - 600W TEG
ca. 5% Fuel Economy

Thermoelectric Materials

Figure of Merit: $$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$



TE couple	Tc/Th (K)	Efficiency (%)
PbTe *n/p*	547/866	5
PbTe/ TAGS-85	430/785	6.2
SiGe n/p	570/1273	6.6
SiGe *n/p*	300/973	7.4

Power densities ≤ 0.73 W cm^{-2}

Limitations of Current Materials

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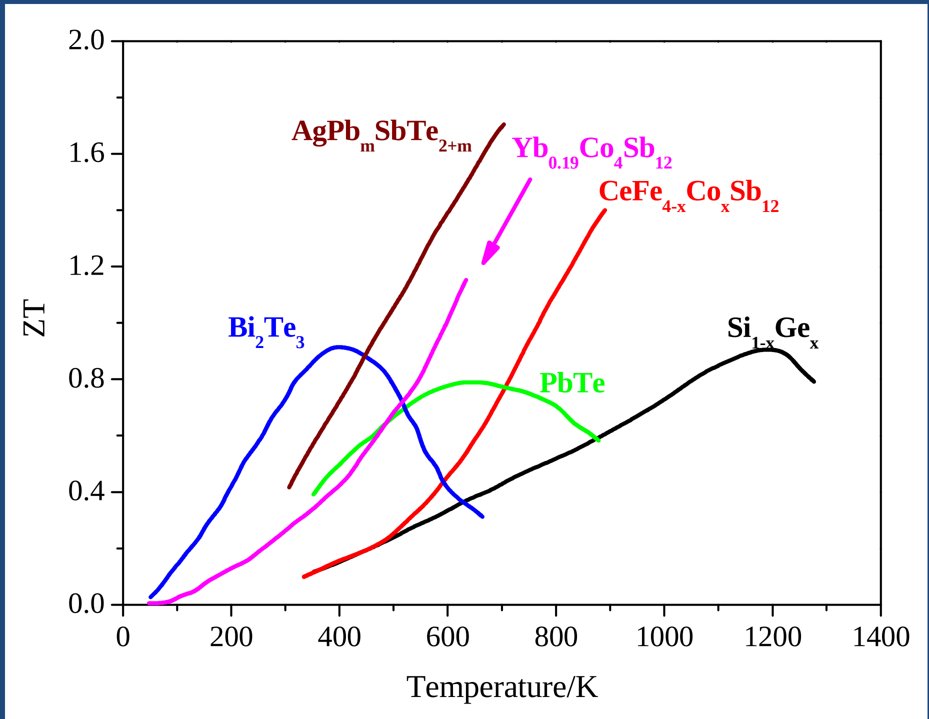
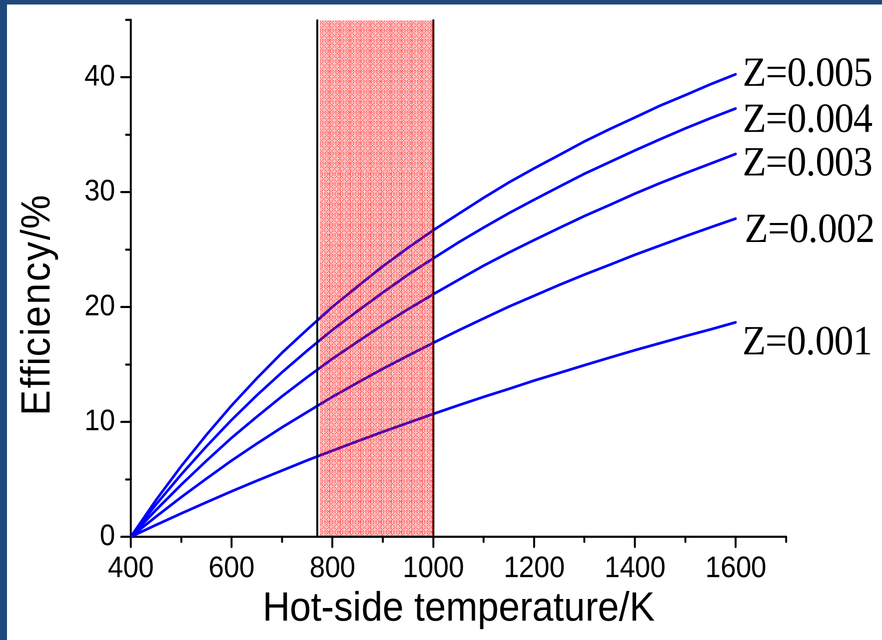
Figure of Merit: $$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$

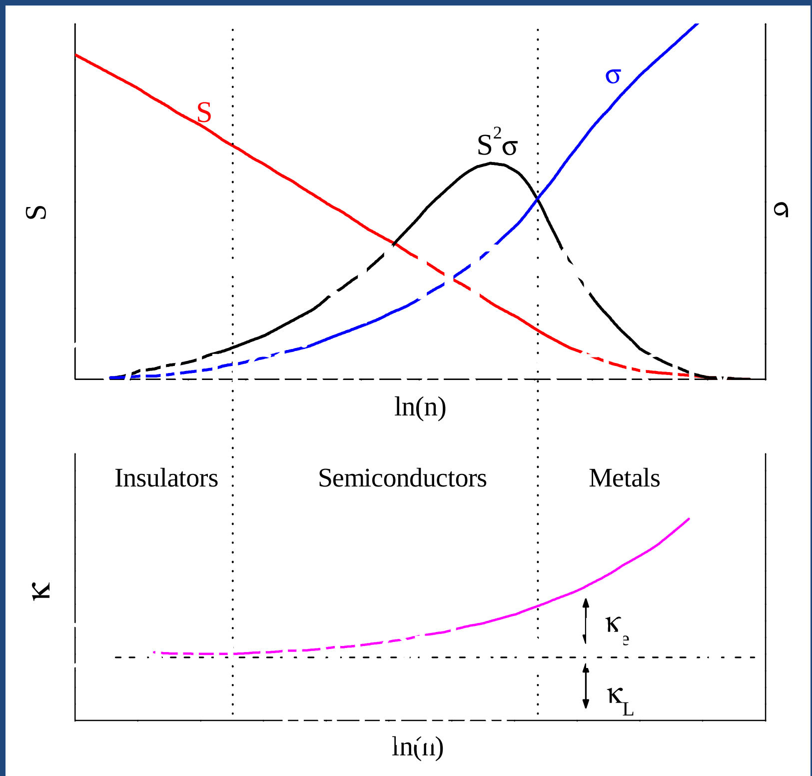




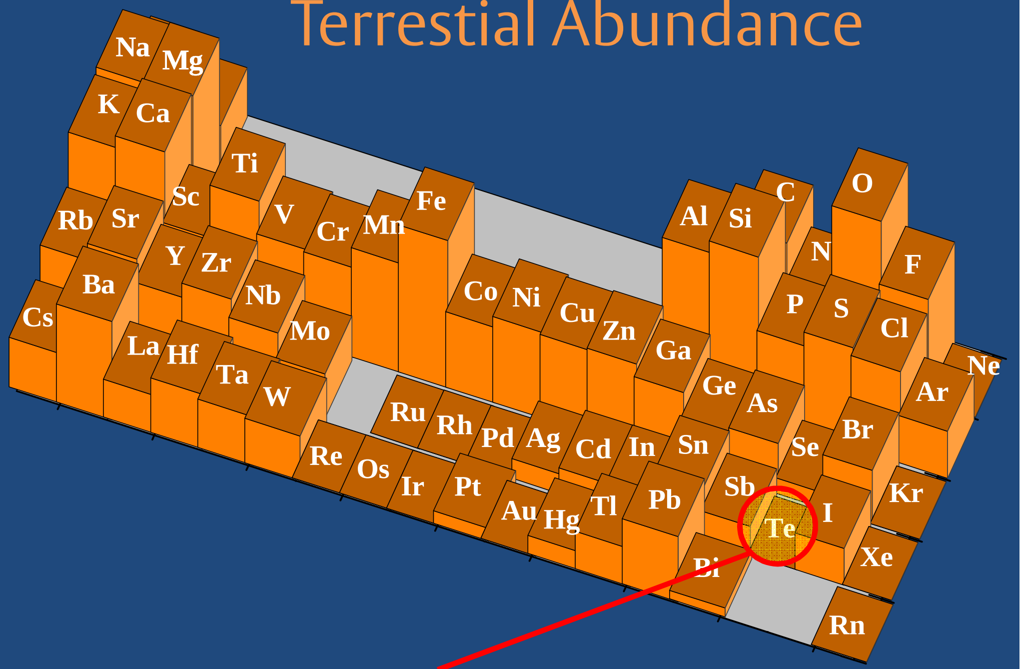
Materials Parameters

Figure of Merit: $$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$

- Electrical conductivity (s), Seebeck (S) and electronic thermal conductivity (k_e) all inter-dependent



Terrestial Abundance



Te: 1 ppb by weight

Materials Design 1:
Phonon Glass Electron Crystal

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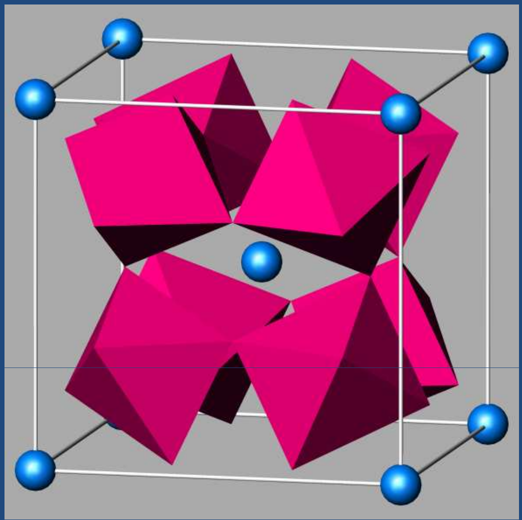
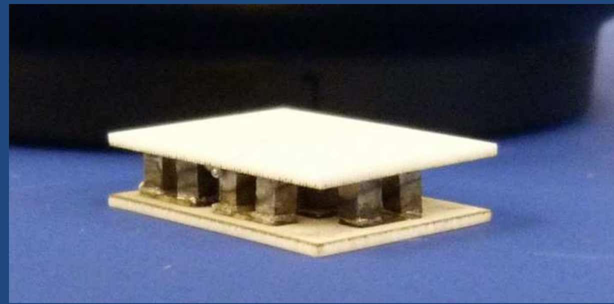
Filled Skutterudites

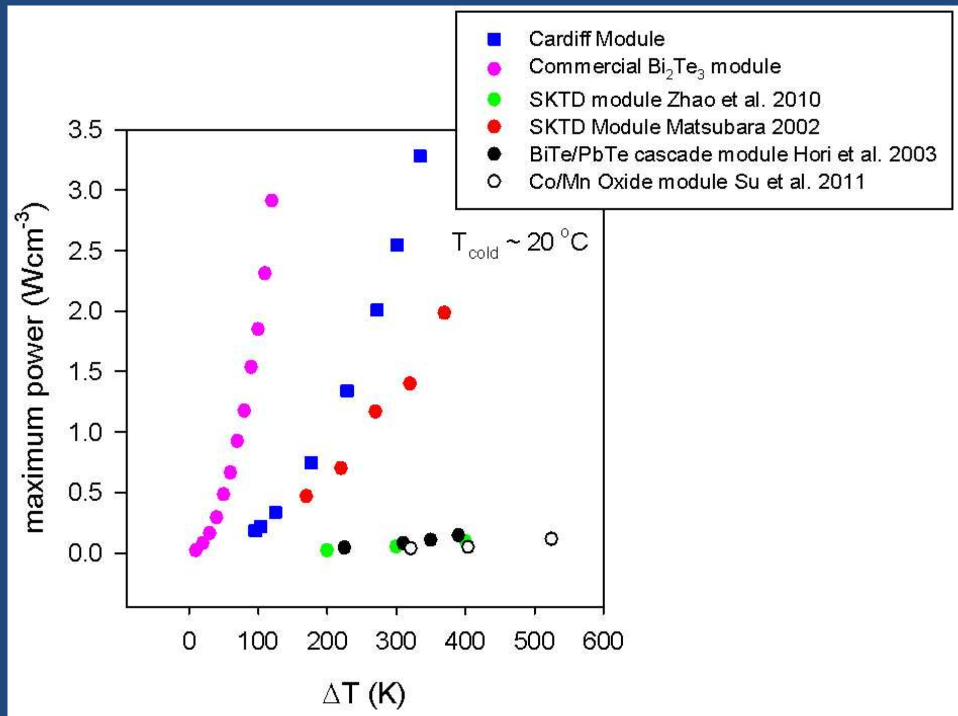


<u>HWU-Cardiff Skutterudite Module</u>

$Yb_xCo_4Sb_{12}$ (*n*-type)

$Ce_xFe_3CoSb_{12}$ (*p*-type)





Rattling vibrations reduce κ_{ph}

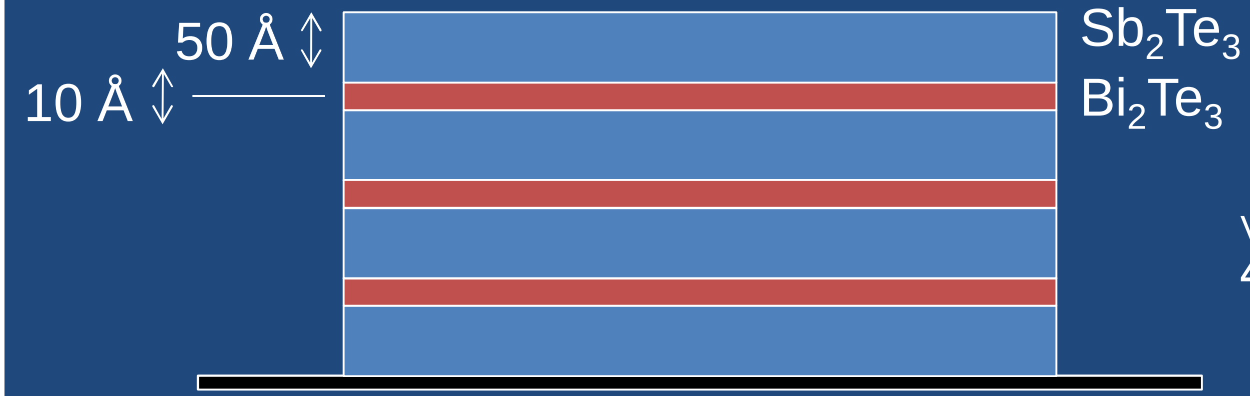
$CoSb_3$: 9 $Wm^{-1}K^{-1}$

$R(Fe_3CoSb_{12})$: 1.2 $Wm^{-1}K^{-1}$

J Garcia-Cañadas et al. J. ELectron Mater. ***42****, 1369, (2013)*

Materials Design 2: Reduced Dimensionality

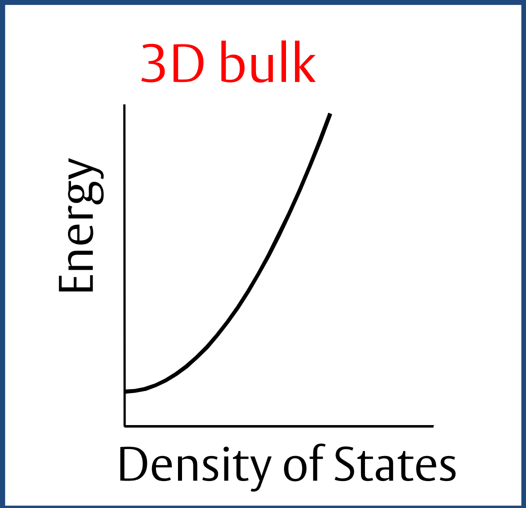
Thin-Film Superlattices

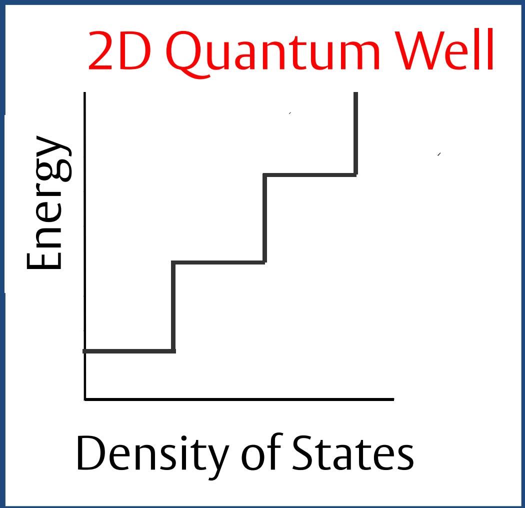


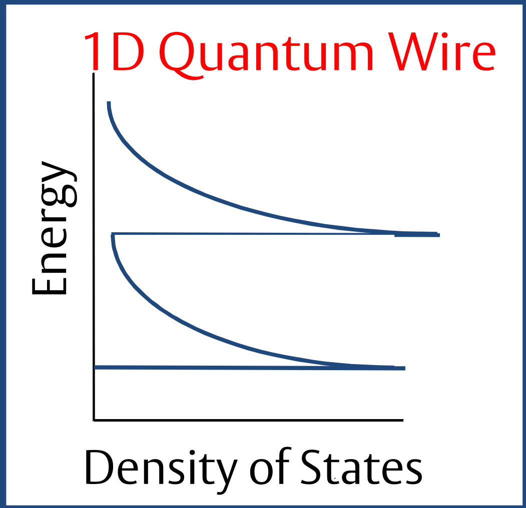
$\kappa = 0.22\ W\ m^{-1}\ K^{-1}$

$ZT = 2.4$ @ 330 K

Venkatasubramanian et al, *Nature*, **413**, 597, (2001)







- Quantum Confinement: Enhances S

Ordered Defect Phases as TEs

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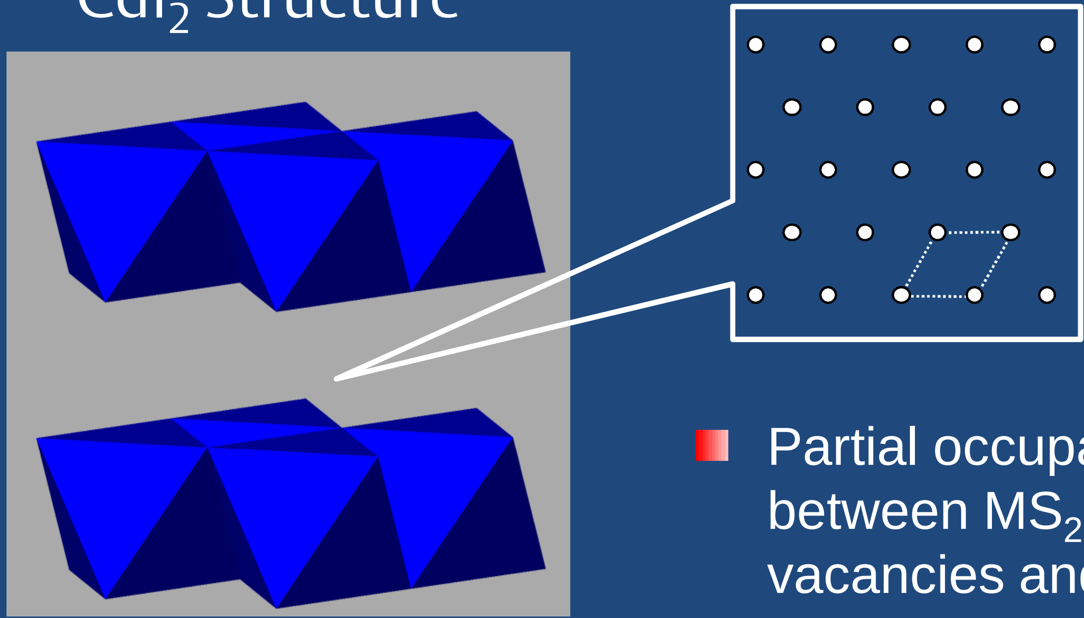
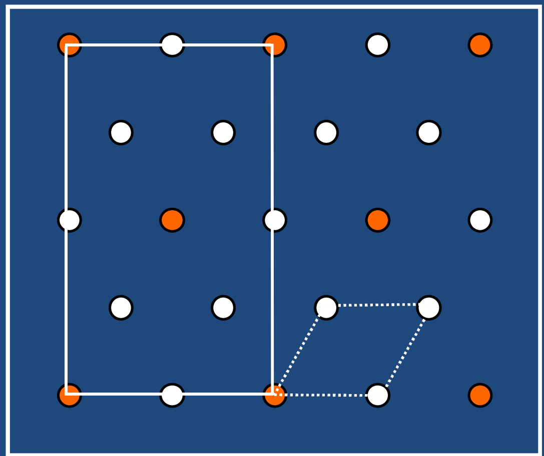
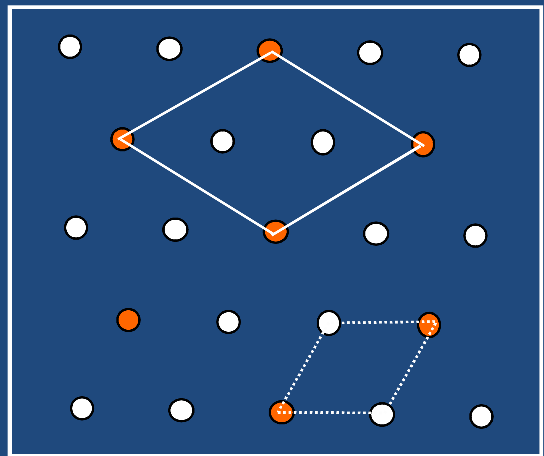
CdI_2 Structure

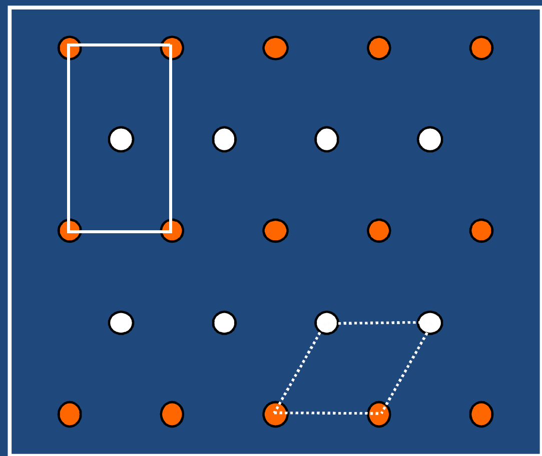


Network of vacant octahedral sites

- Partial occupancy of octahedral sites between MS_2 slabs leads to ordering of vacancies and formation of superstructures


x=1/4: M_5S_8


x=1/3: M_2S_3


x=1/2: M_3S_4

Compositional Dependence of Superstructure: Co_xTiS_2

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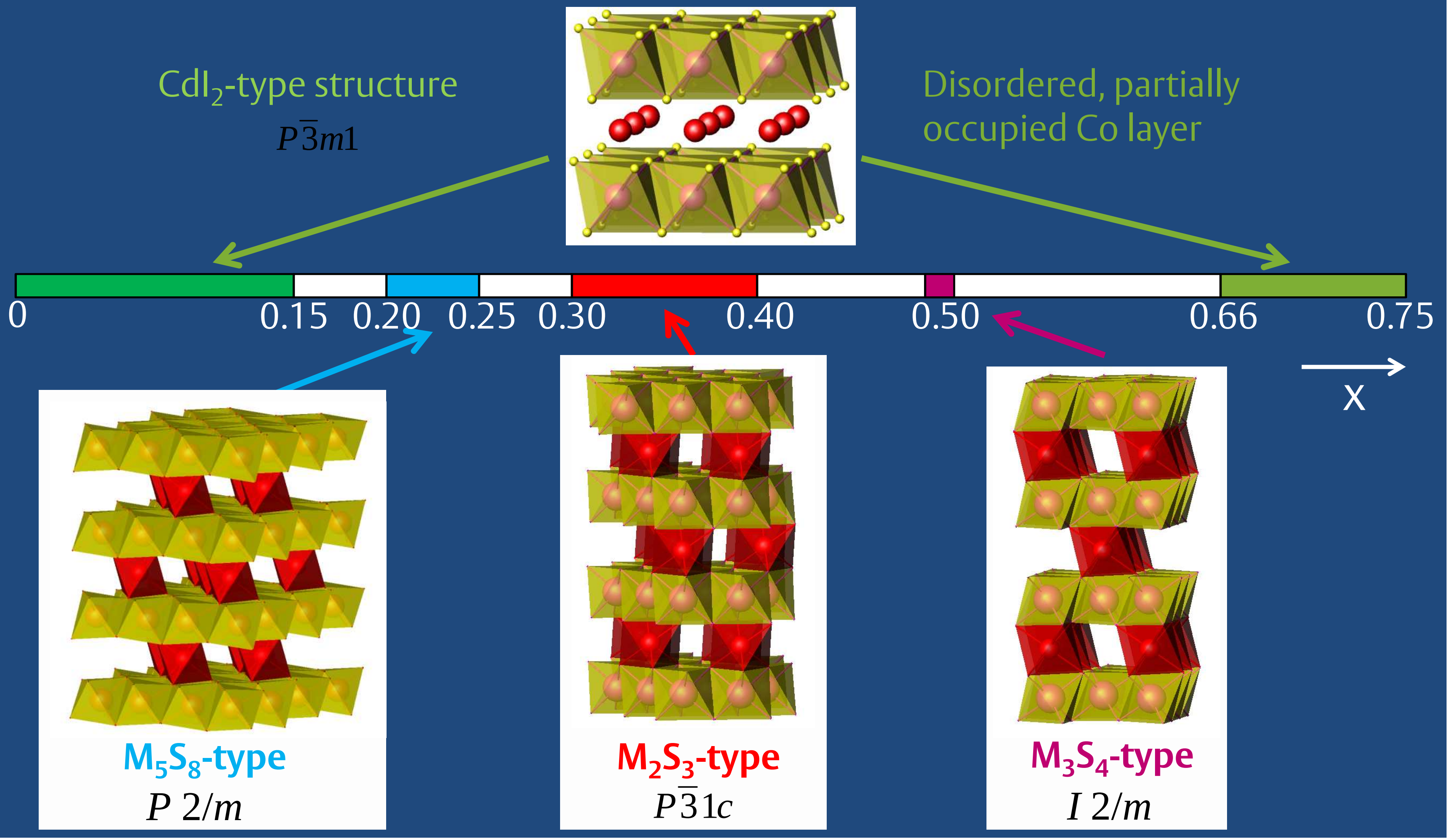
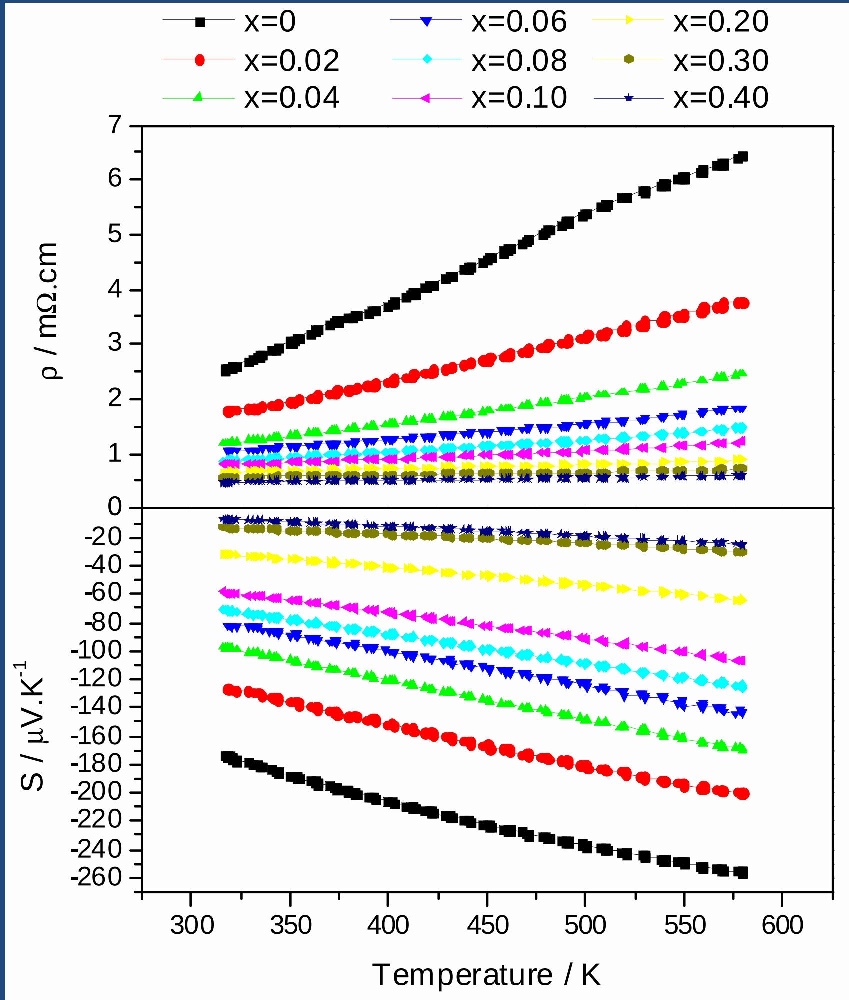
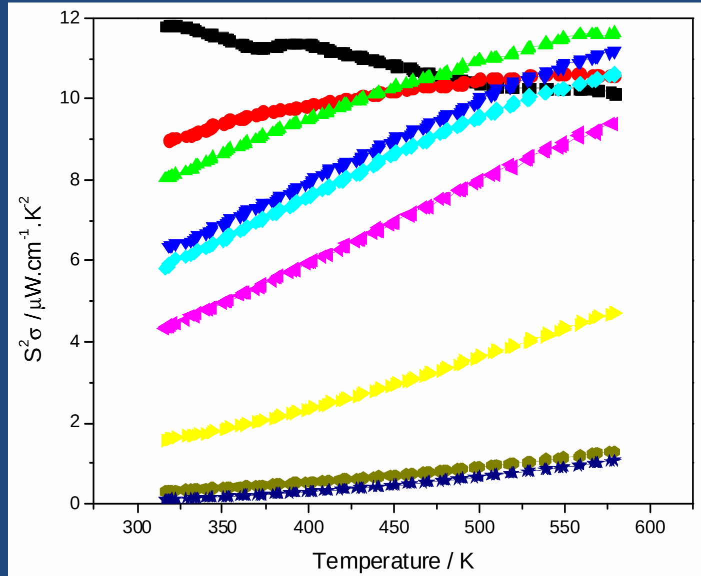
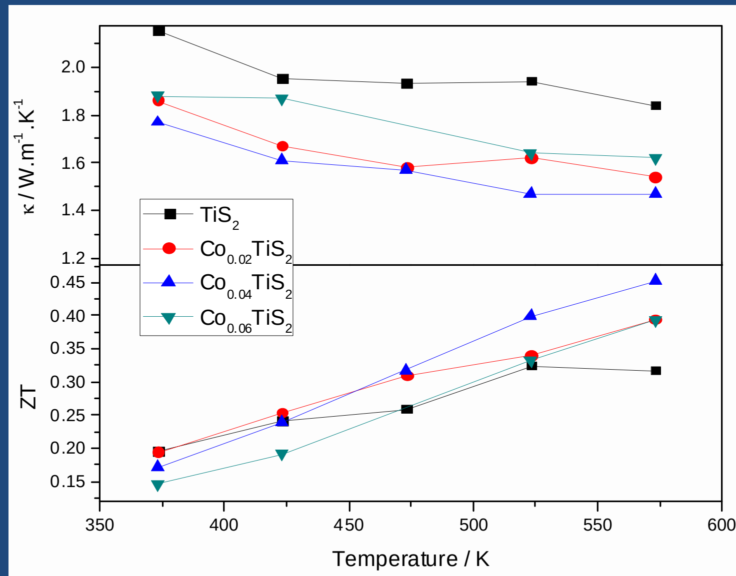


TE Properties of Co_xTiS_2





■ZT=0.45 @300°C



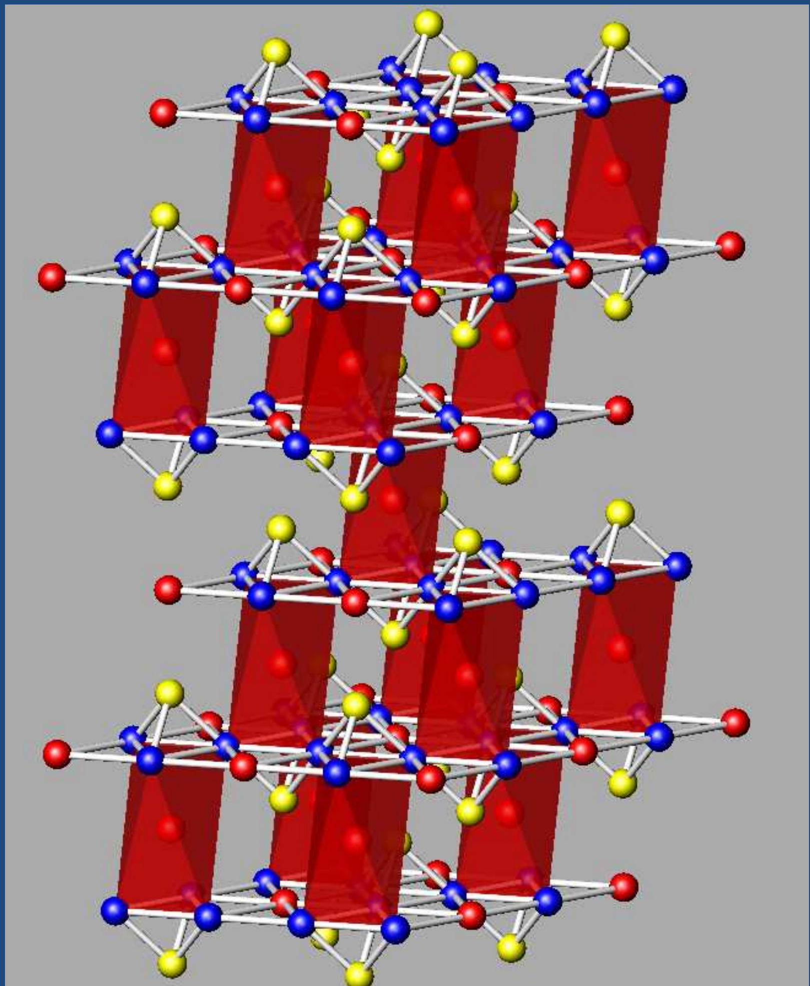
- Resistivity and Seebeck coefficient decrease with increasing x

G. Guelou poster at lunchtime

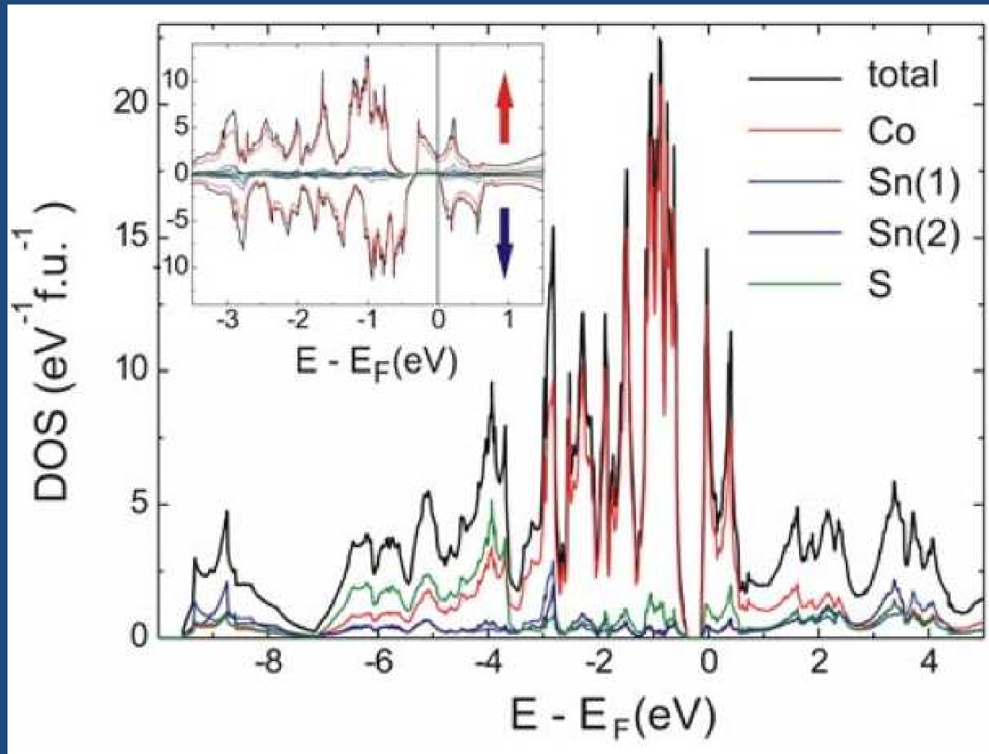
Materials Design 3: Fermi Level Tuning

Mott Relation:

$S \propto d\ln N(E)/dE$ @ $E = E_F$



Shandite: $Co_3Sn_2S_2$



Yu *et al. J. Phys. Conf. Ser.* **100** (2008) 072011

- $Co_3Sn_{2-x}In_xS_2$: Tune E_F – 2 e^- change

Compositional Dependence of S and ρ

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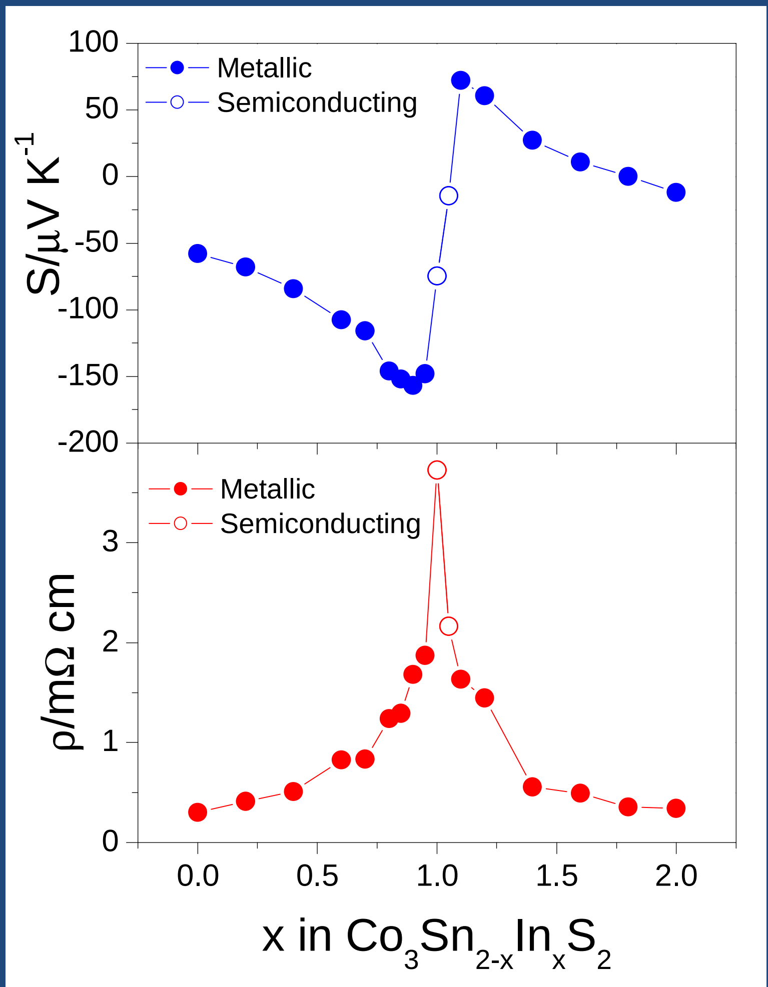
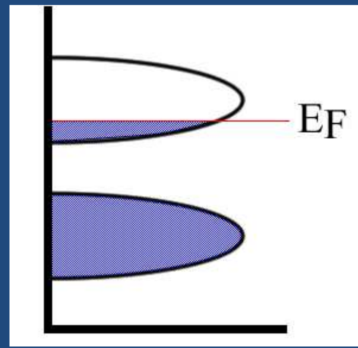
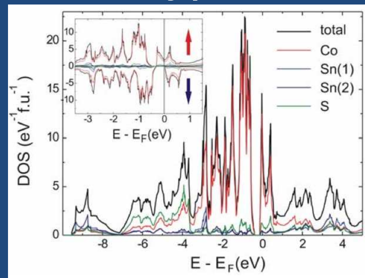
- Electrical properties at 360 K

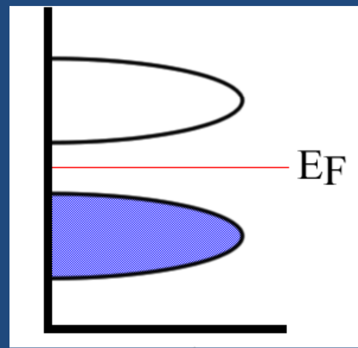


x=0: 47e$^-$
n-type metal

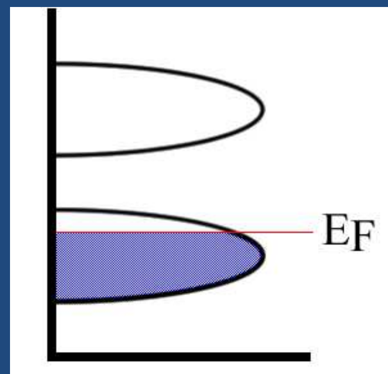




x=1.0: 46e$^-$
semiconductor



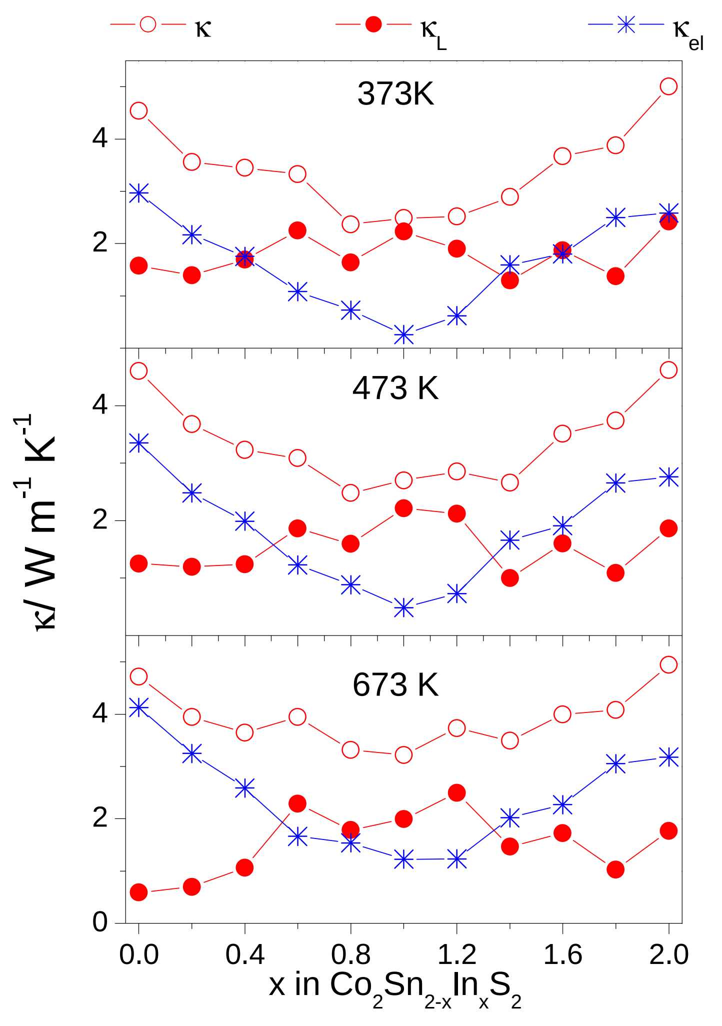
x=2.0: 45e$^-$
n-type metal

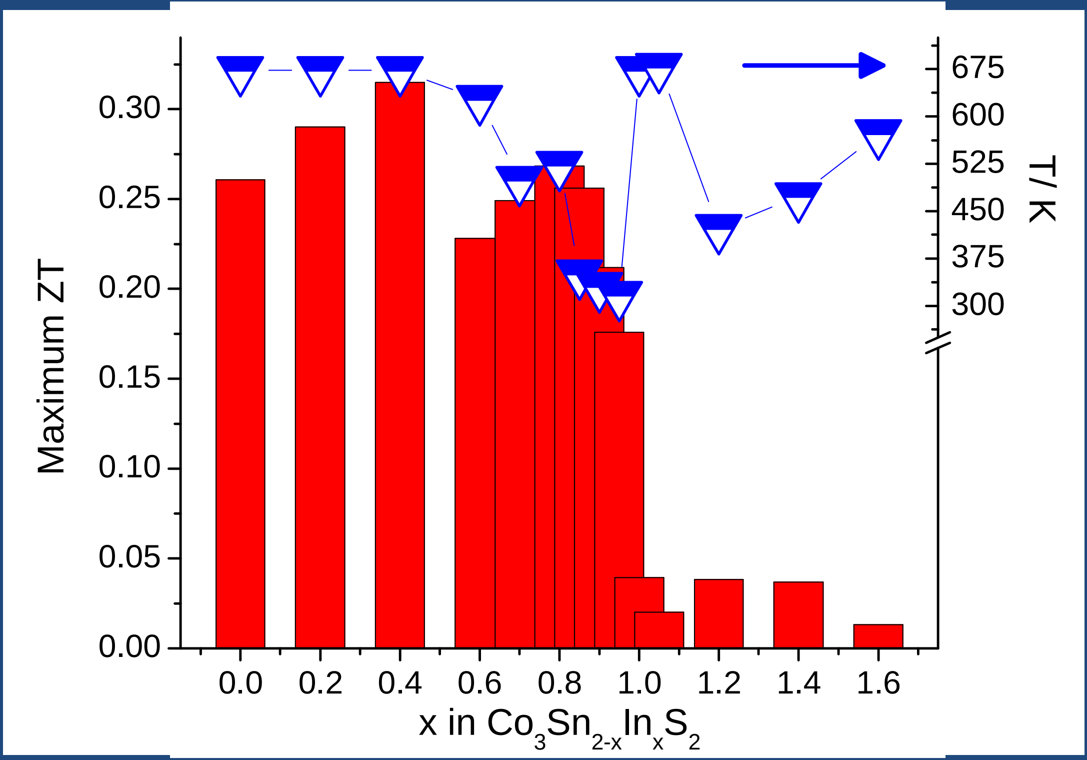


Increasing Indium Content

J. Corps et al, *J. Mater. Chem. A*, **1**, 6553, (2013)

TE Performance of $Co_3Sn_{2-x}In_xS_2$

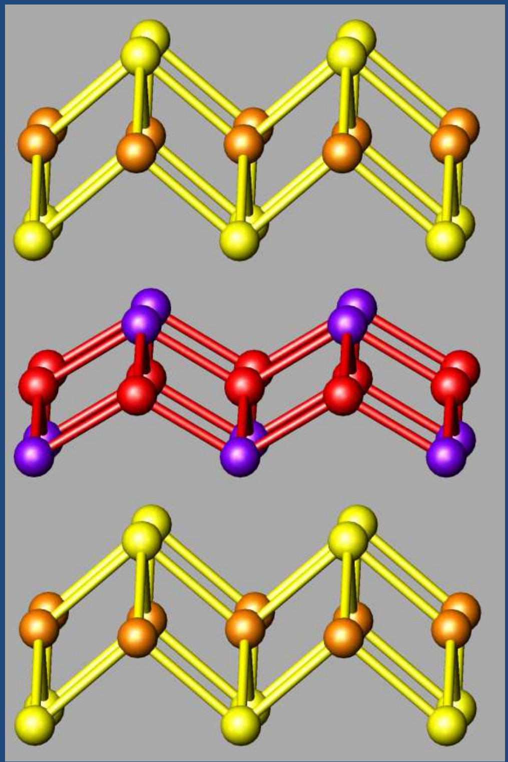




- ZT ≈ 0.2 at temperatures close to ambient.
- Max ZT = 0.32 at 400 °C

- Lattice contribution to thermal conductivity effectively independent of composition

Materials Design 4: Separation of $S^2\sigma$ and κ terms



Conducting $[Cu_2Q_2]^{2-}$ layer

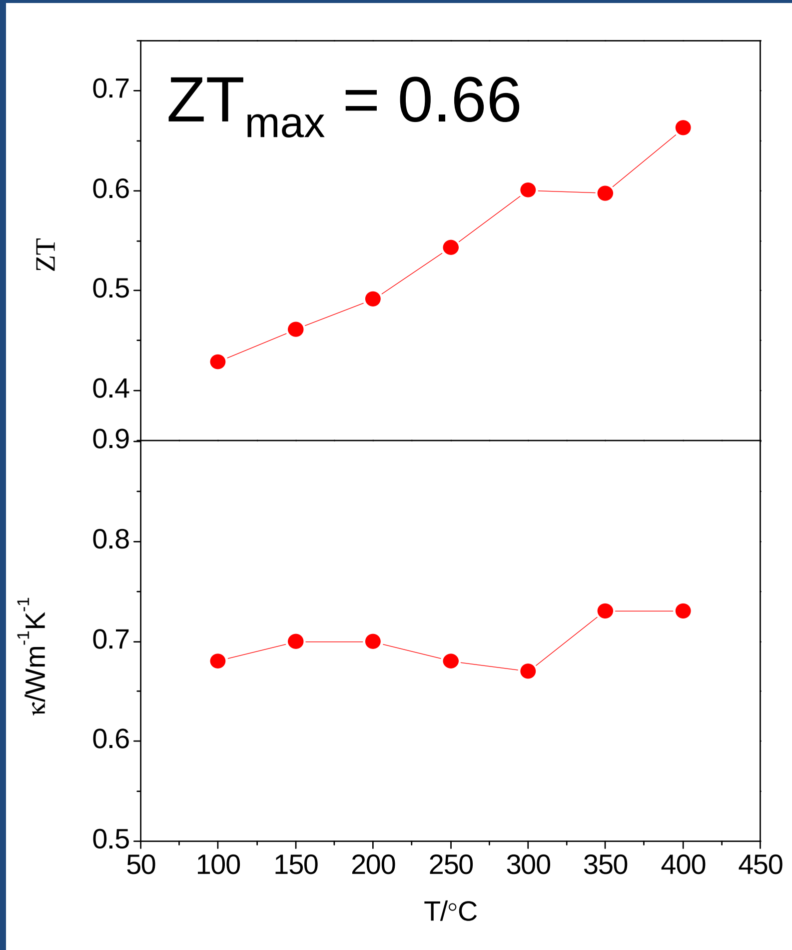
Insulating $[Bi_2O_2]^{2+}$ layer

$(Bi_2O_2)(Cu_2Q_2)$

$$ZT = \frac{S^2\sigma T}{\kappa}$$

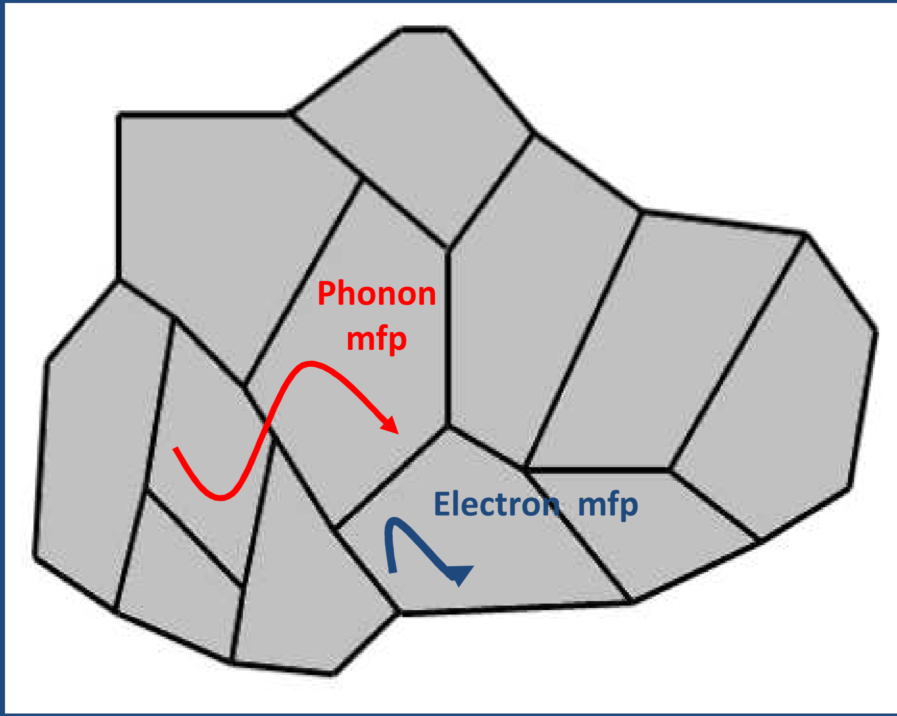
- Independent optimisation of $S^2\sigma$ (covalent) and κ_L (ionic)

BiOCuTe

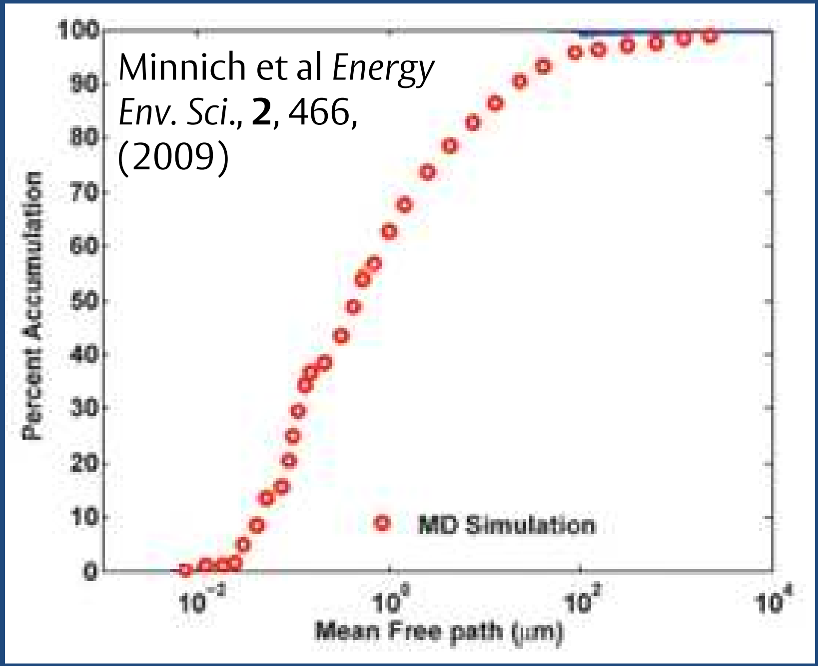


P. Vaqueiro et al: *J. Mater. Chem. A*, **1**, 520-523 (2013).

Materials Design 5: Nanostructuring



- Interface scattering: decreases κ_L
- Interface scattering when mean-free-path > interface spacing



Ball-Milled Thermoelectrics

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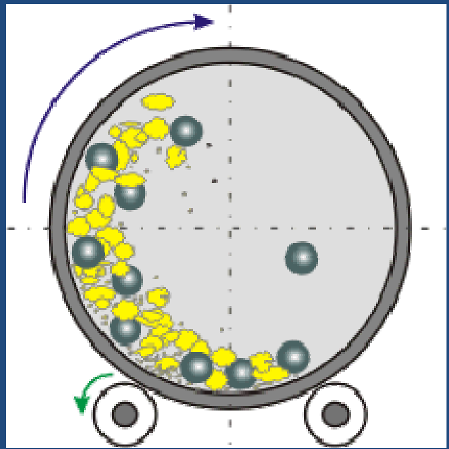
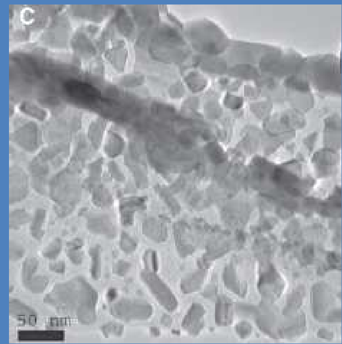
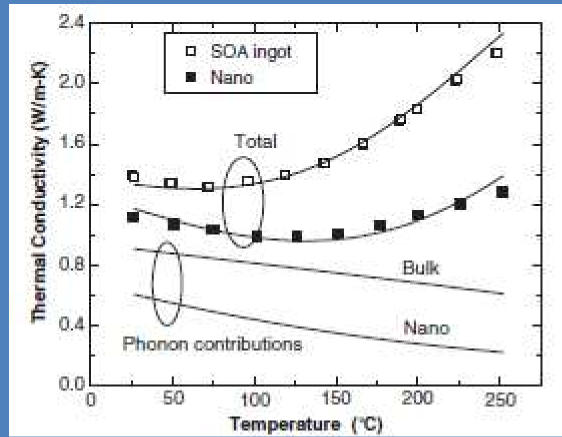


$(Bi,Sb)_2Te_3$





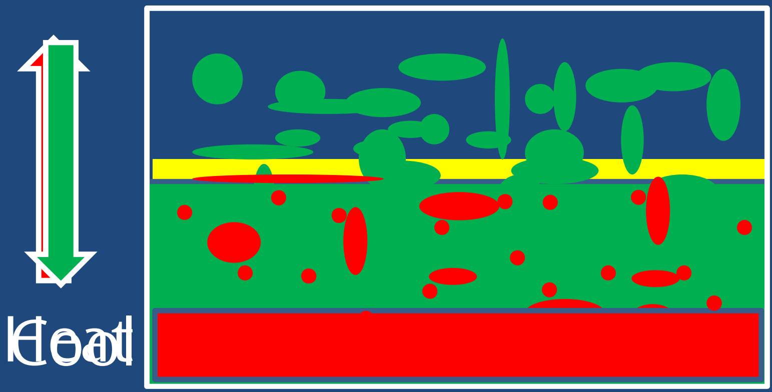
Poudel et al, *Science*, **320**, 634, (2008)

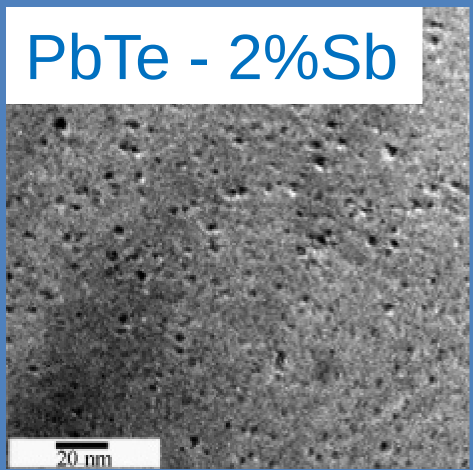
Material	Bulk		Nanostructured	
	ZT_{max}	Temperature at which ZT_{max} is observed	ZT_{max}	Temperature at which ZT_{max} is observed
Si	0.2	1200	0.7	1200
$Si_{80}Ge_{20}$ (n-type)	1.0	1200	1.3	1173
$Si_{80}Ge_{20}$ (p-type)	0.7	1200	0.95	1073
$(Bi,Sb)_2Te_3$	0.9	293	1.4	373
$CoSb_3$	0.45	700	0.71	700

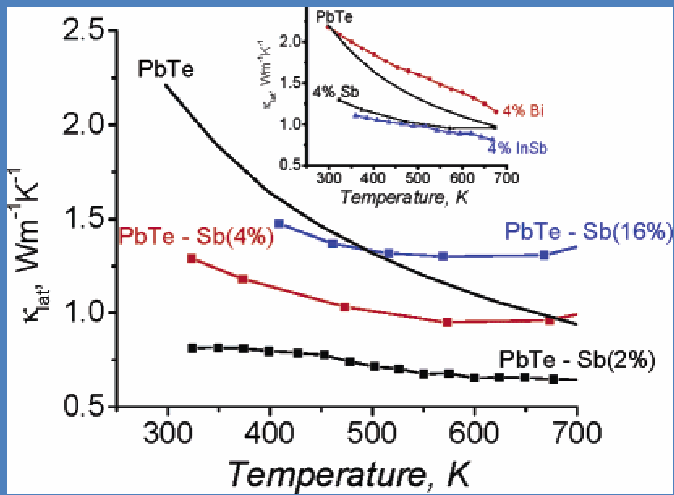
P. Vaqueiro and A.V. Powell, *J. Mater. Chem.*, **20**, 9577, (2010)

Nanocomposite TEs by Arrested Precipitation

Matrix Encapsulation





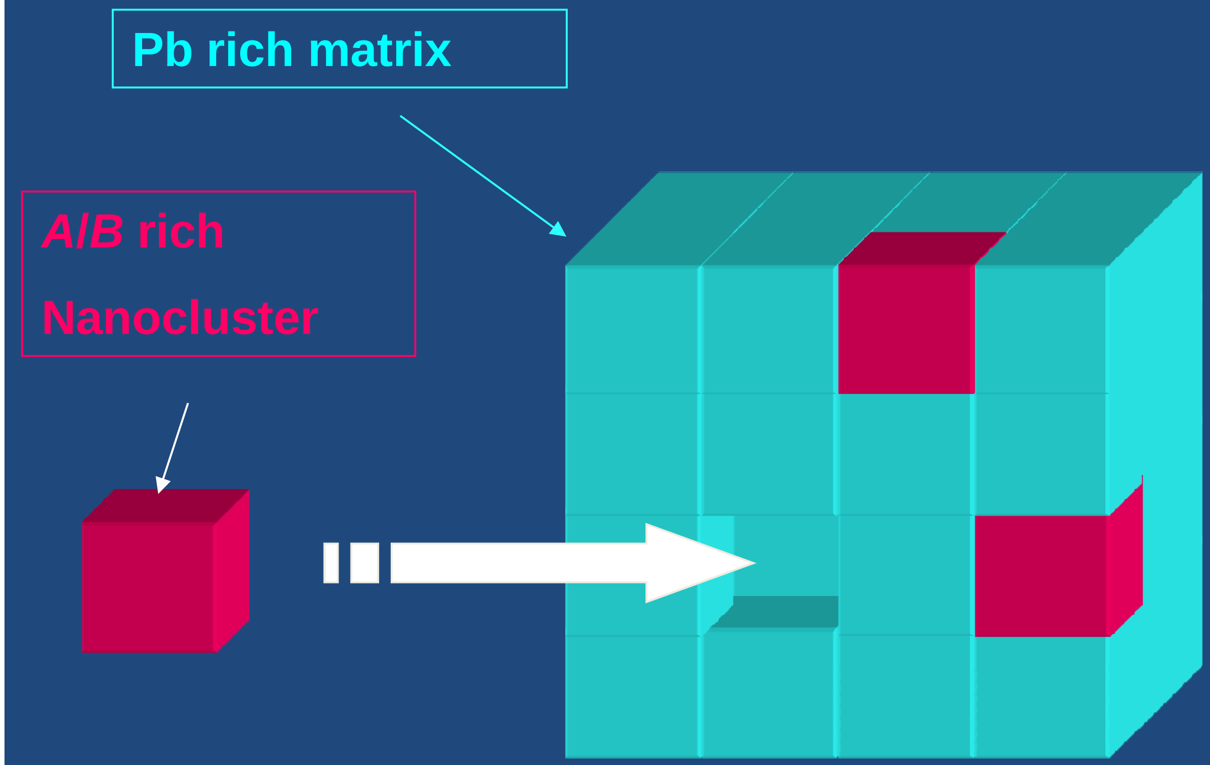


$k_L = 0.8\ W\ m^{-1}\ K^{-1}$

Sootsman *et al*, *Chem. Mater.*, **18**, 4994, (2006)

Nanoinclusions in *LAST*-type Phases

APb_mBTe_{m+2}



- Degenerate semiconductors
- Nanoinclusions
- Thermal conductivity reduced from PbTe

LAST=18

- *n*-type conduction
- ZT_{max} = 2.2 at 800K
- Silver deficient

Hsu et al, *Science*, **303**, 818, (2004)

Electrical Properties:
A = Tl, *B* =Bi Phases

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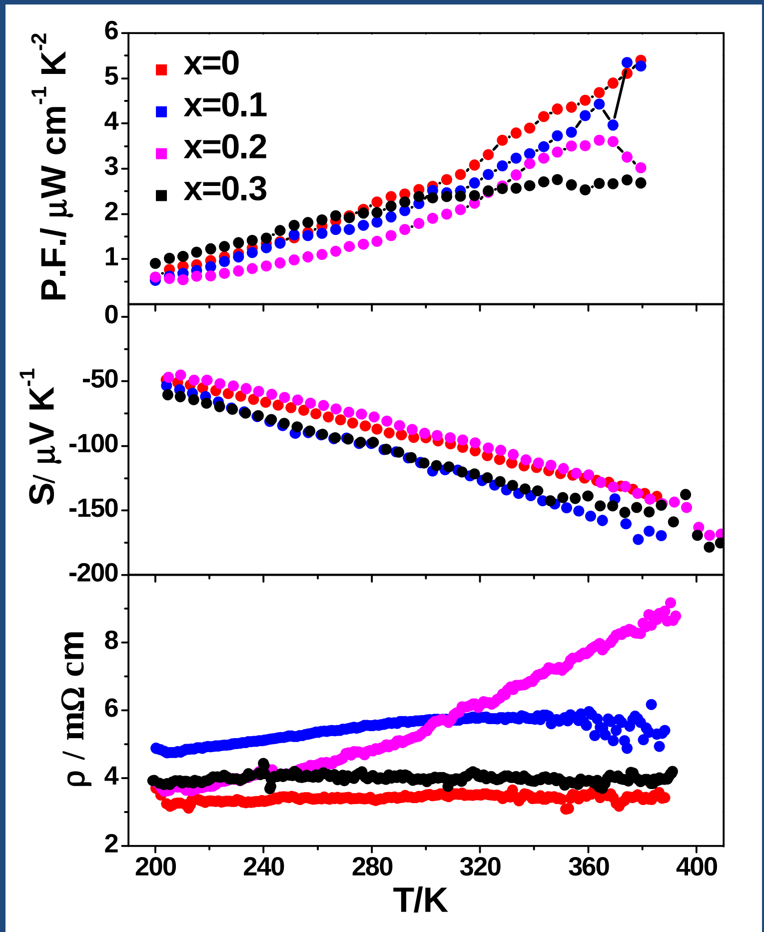
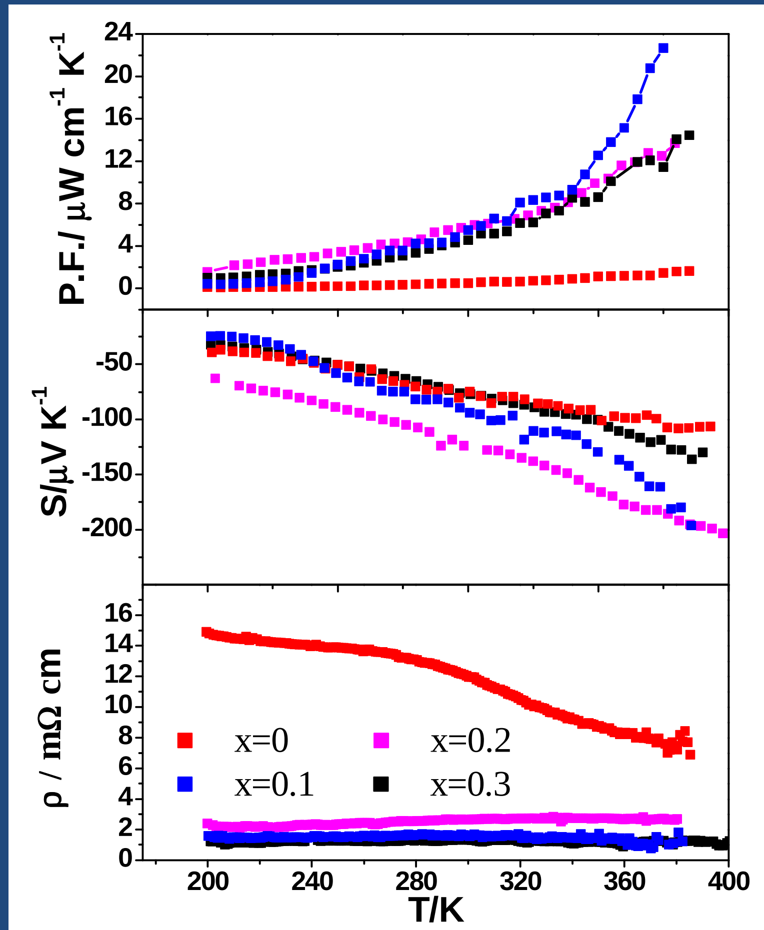
$Tl_{1-x}Pb_{10}BiTe_{20}$



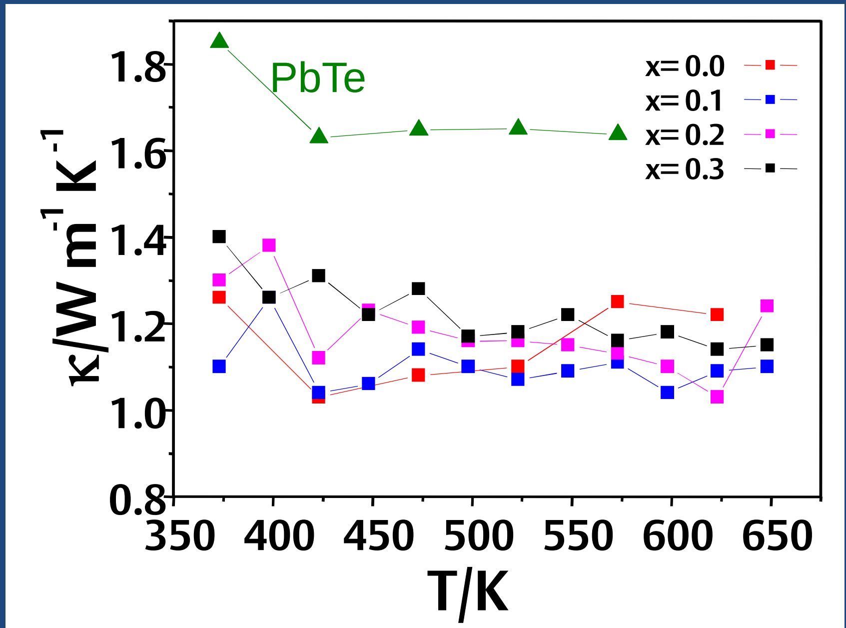
$Tl_{1-x}Pb_{18}BiTe_{20}$

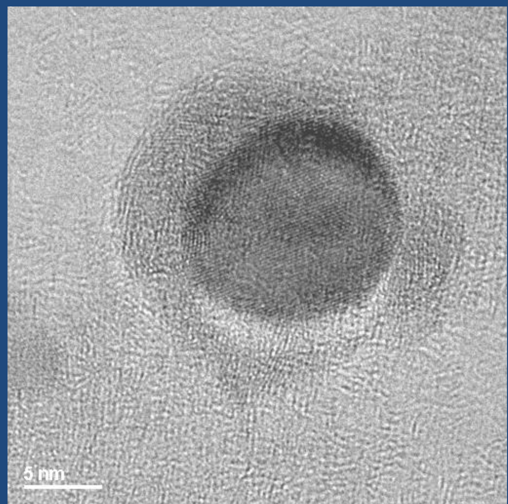


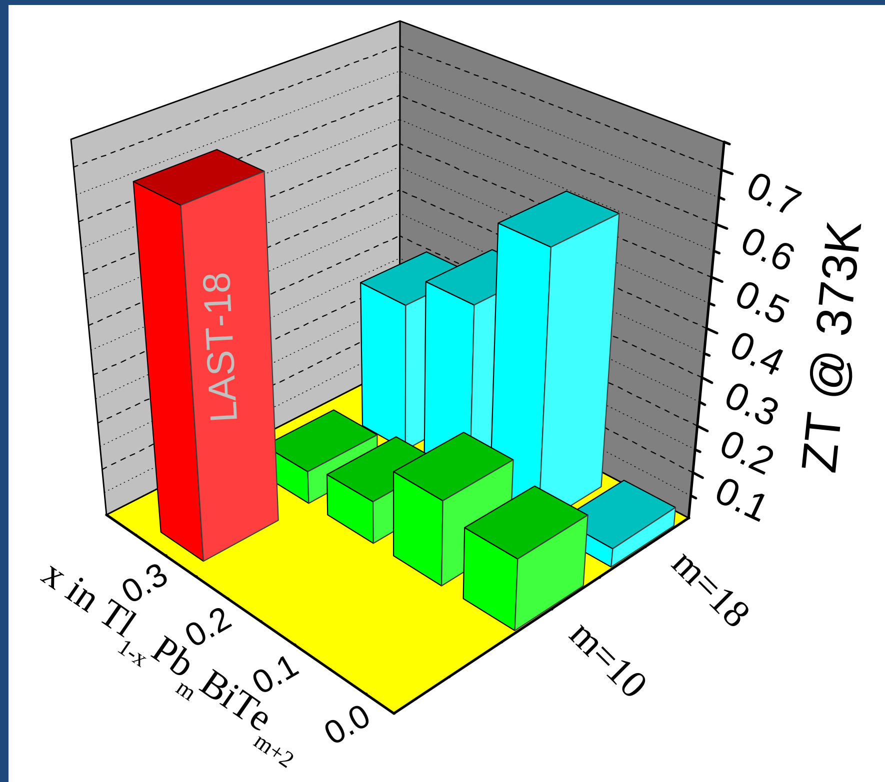
A.V. Powell et al, *MRS Proc*. 1044, U08-04, (2008)

TE Properties: $Tl_{1-x}Pb_mBiTe_{m+2}$

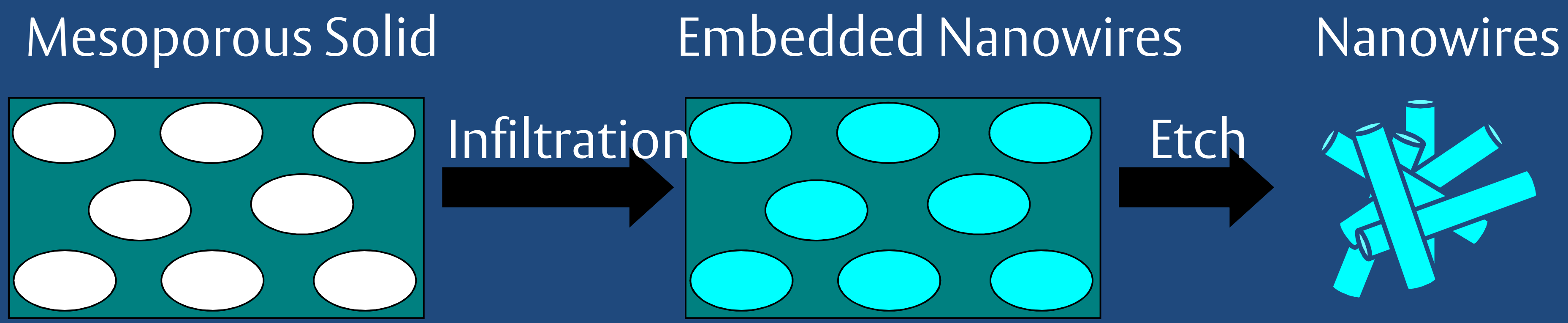
$Tl_{1-x}Pb_{18}BiTe_{20}$

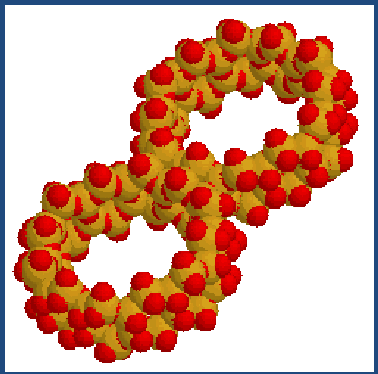






Nanocasting

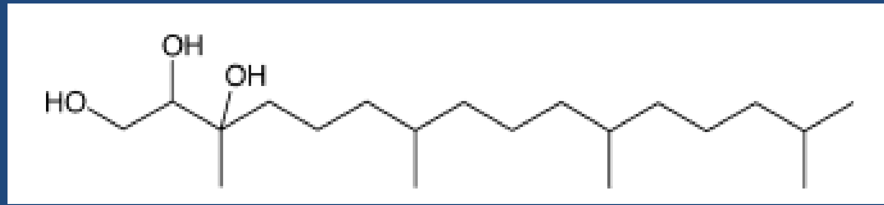


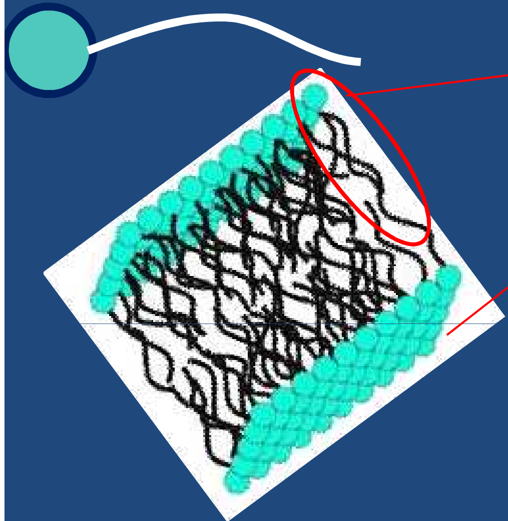


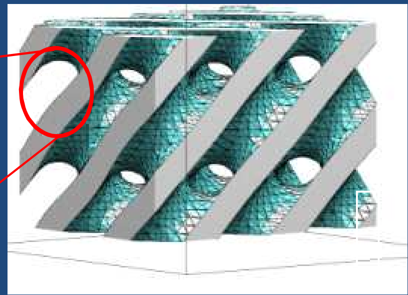
MCM-41

Template	Porosity	Average Pore Size/nm	Channel System
MCM-41	Mesoporous	2.2	1-D
MCM-48	Mesoporous	2.5	3-D
SBA-15	Mesoporous	7	1-D
SBA-16	Mesoporous	5.6	3-D
Zeolite VFI	Microporous	1.3	1-D
Zeolite LTL	Microporous	0.7	1-D

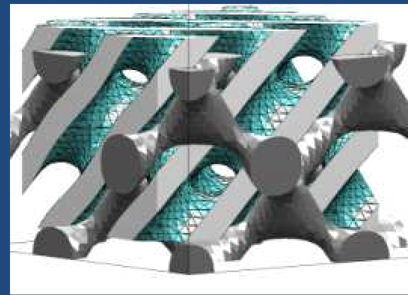
Soft Templating: Lipid self-assembly



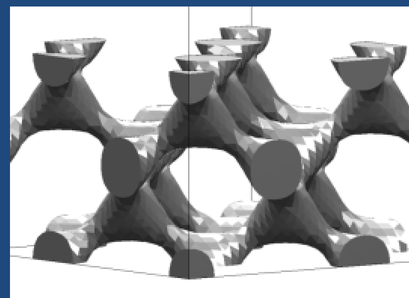




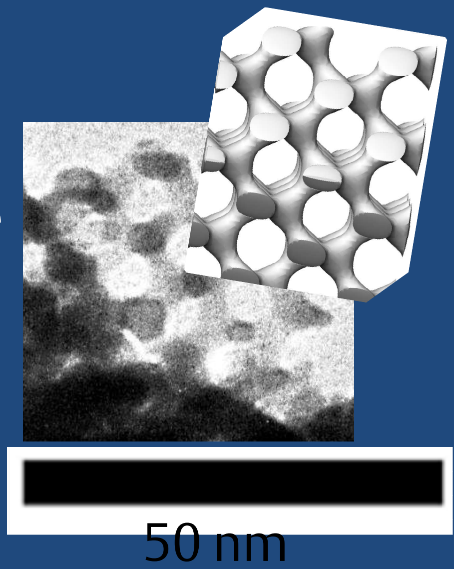
Deposition



Wash away template



Bicontinuous double diamond nanostructred Pt



S. Akbar et al, *Adv. Mater. 2013*, ***25***, *1160.*

Current Materials Challenges

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- Understanding:
  - New insights required into materials properties (especially at the nanoscale)
  - Design of new materials – portfolio of materials?
- Performance *vs* cost:
  - What performance is acceptable at what price?
  - To what extent does this vary with application?
- Sustainability:
  - Te-free thermoelectrics
- Manufacture:
  - Scaleability of synthesis
  - Consolidation – SPS, Hot Pressing, Microwave
  - Module design and fabrication, solders, barrier layers etc
  - Compatible n- and p-type materials
- Integration:
  - System-wide holistic approach

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Intelligent Thermal Management

anter corporation

[dstl]

EPSRC Engineering and Physical Sciences Research Council

Science & Technology Facilities Council

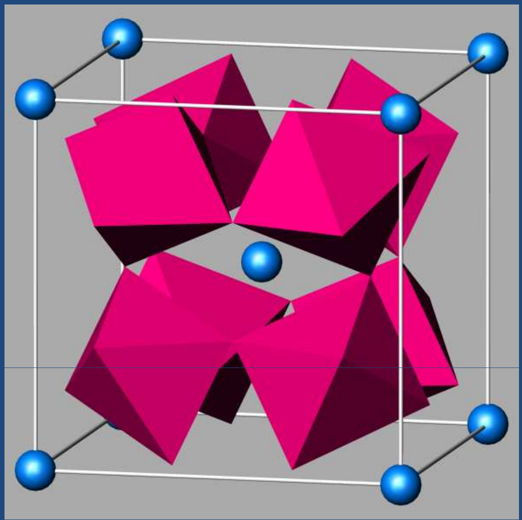
innovteg

SEVENTH FRAMEWORK PROGRAMME

Materials Design:
Phonon Glass Electron Crystal

University of Reading

Filled Skutterudites



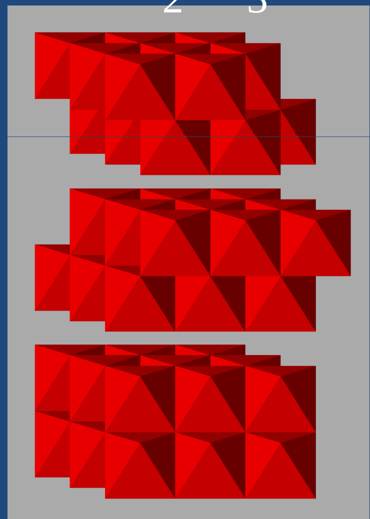
Rattling vibrations reduce κ_{ph}

$CoSb_3$: 9 $Wm^{-1}K^{-1}$

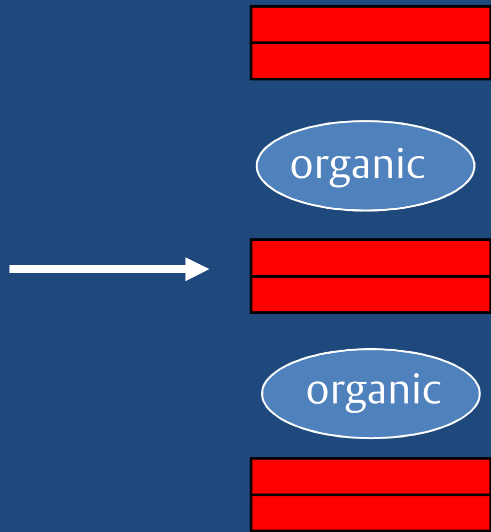
$R(Fe_3CoSb_{12})$: 1.2 $Wm^{-1}K^{-1}$

Organic-Inorganic Hybrids as Thermoelectrics

Bi_2Te_3

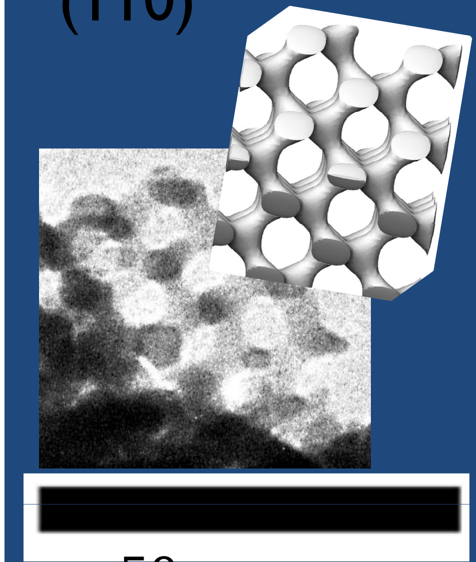


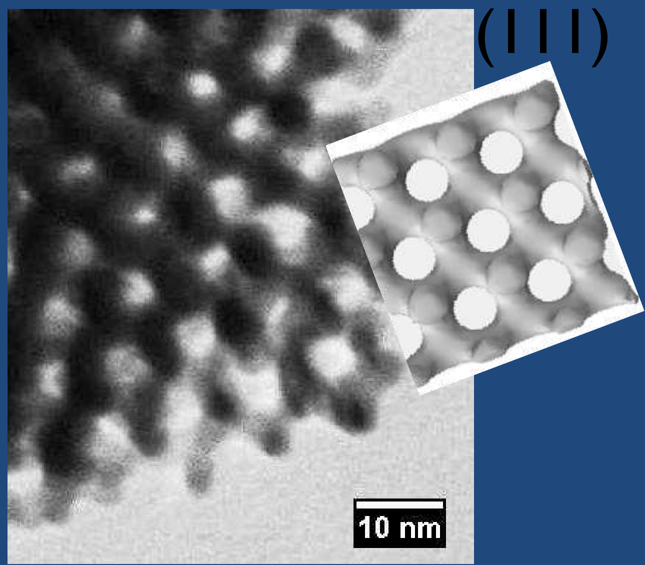
Layered semiconductor

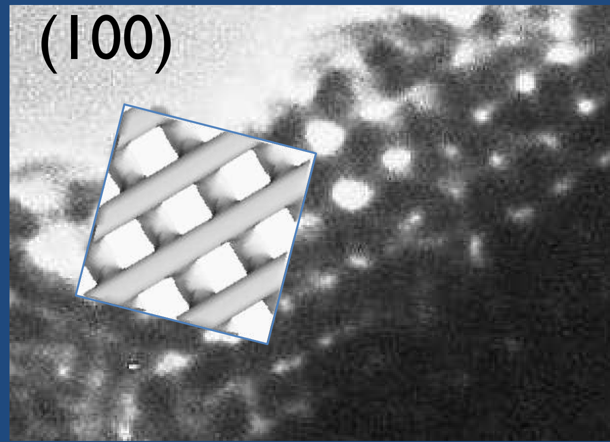


Organic-inorganic hybrid

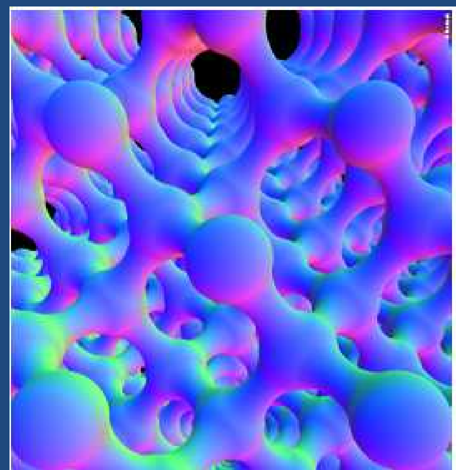
The "single diamond" nanostructure





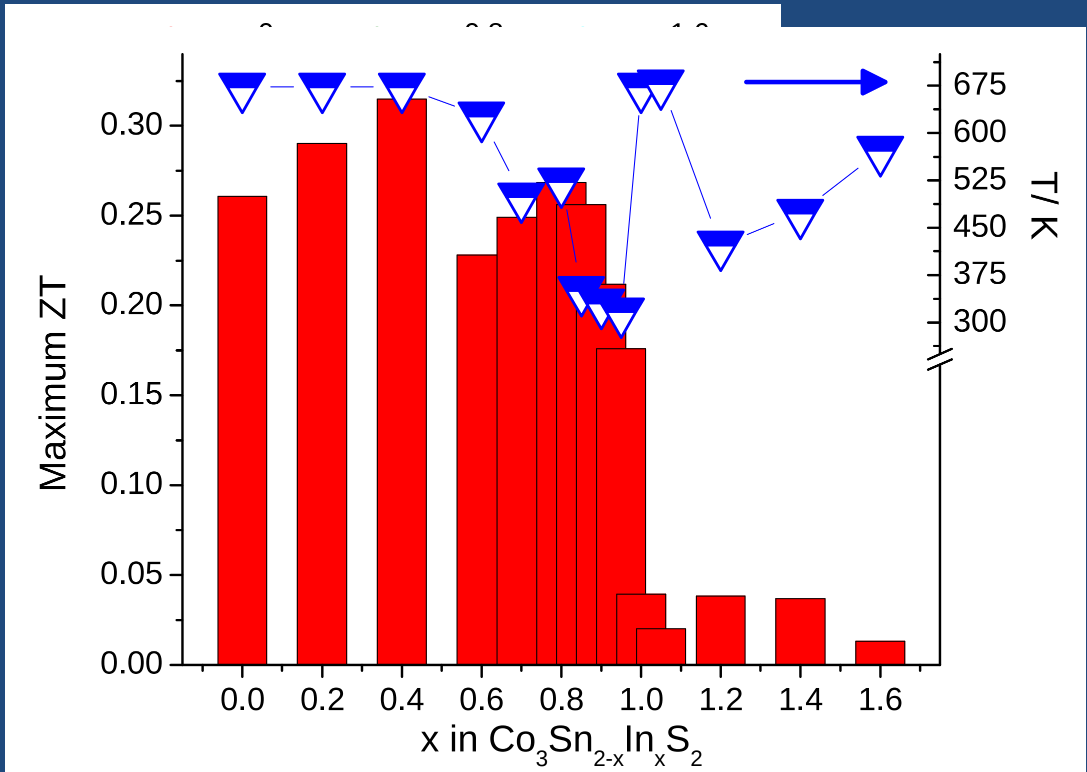


"The diamond structure… possesses the champion [photonic and phononic] band gap"
Gorishnyy et al, Physics World 2005

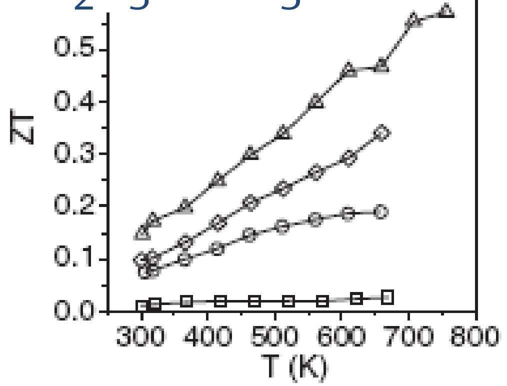


S. Akbar, J. Elliott*, M. Rittman & A. Squires*, *Advanced Materials 2013,*

Figures of Merit

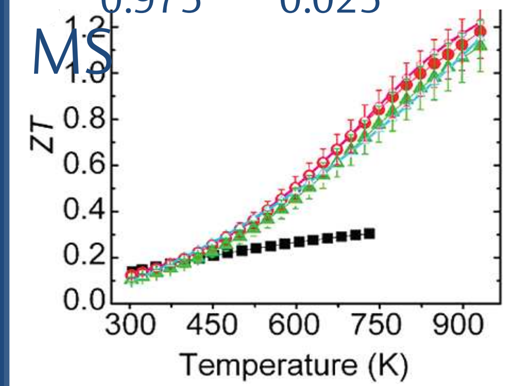


Bi_2S_3-$BiCl_3$



Adv Energy Mater. **2**, 634, (2012)

$Pb_{0.975}Na_{0.025}S$ - MS



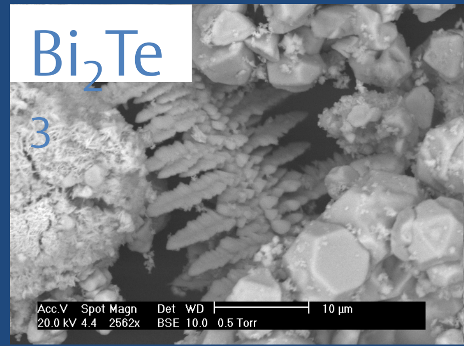
JACS, **134**, 7902, (2012)

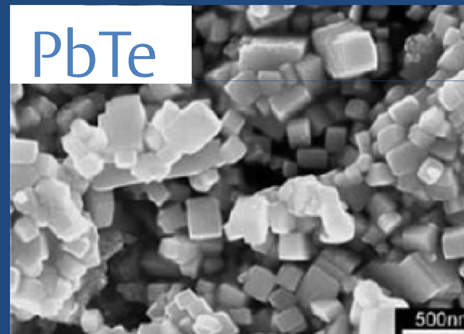
Solvothermal Growth of Nanoparticulate

Metal Salts,
Reducing agent
Solvent,
'Template
Molecule'

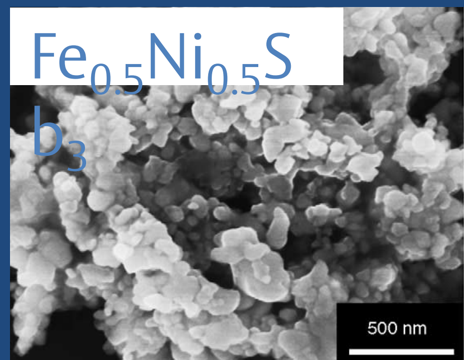
$T > T_{bp}$

$P \leq 200$ bar





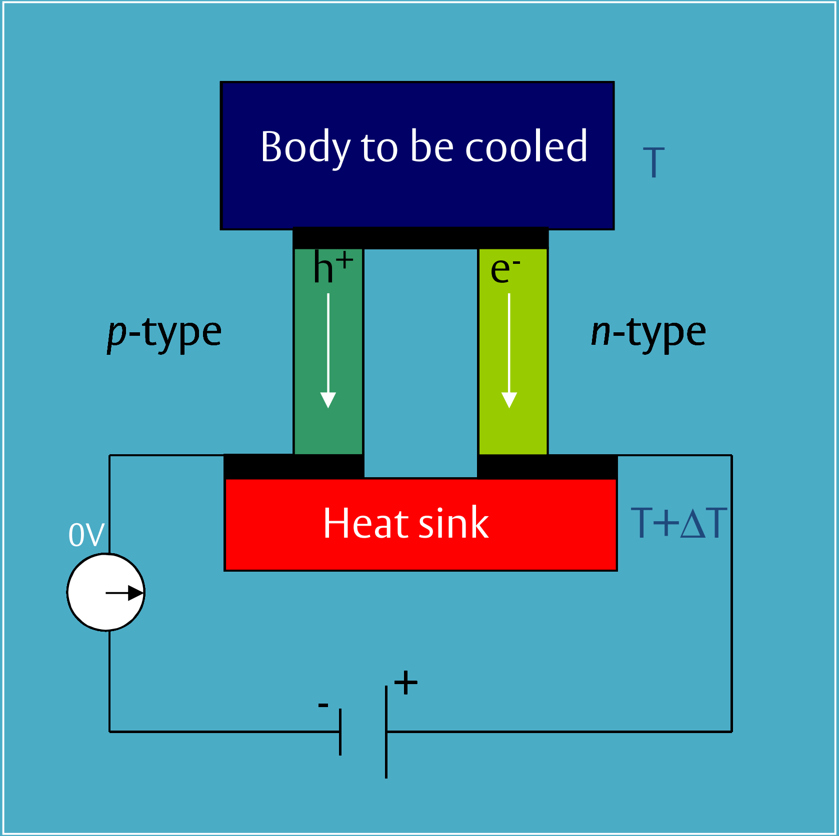
Ji *et al*. *J. Electron Mater.*, **36**, 271, (2007)



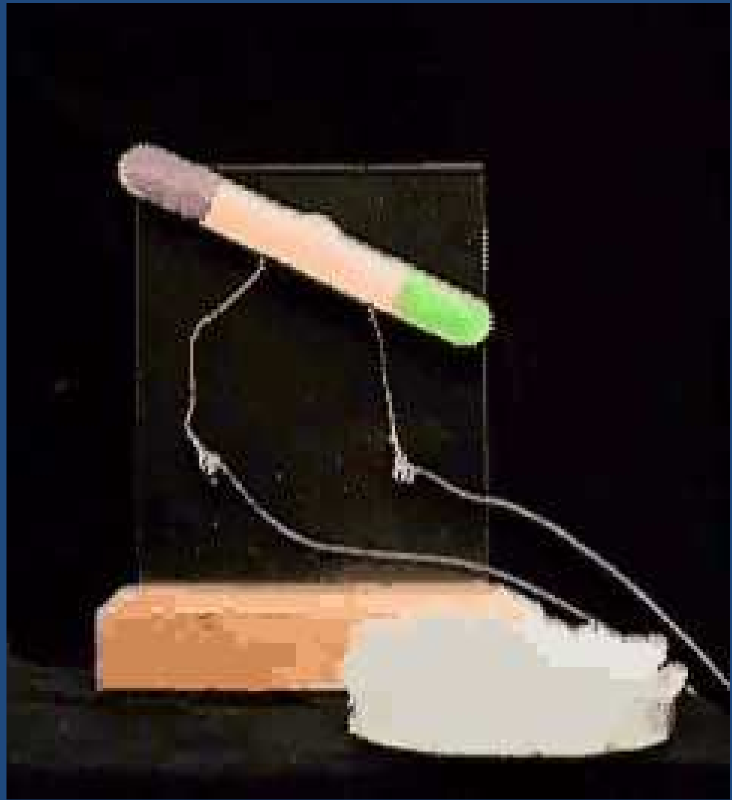
Mi *et al*. *JALCOM*, **399**, 260, (2005)

Thermoelectric Energy Recovery

Thermoelectric Couple

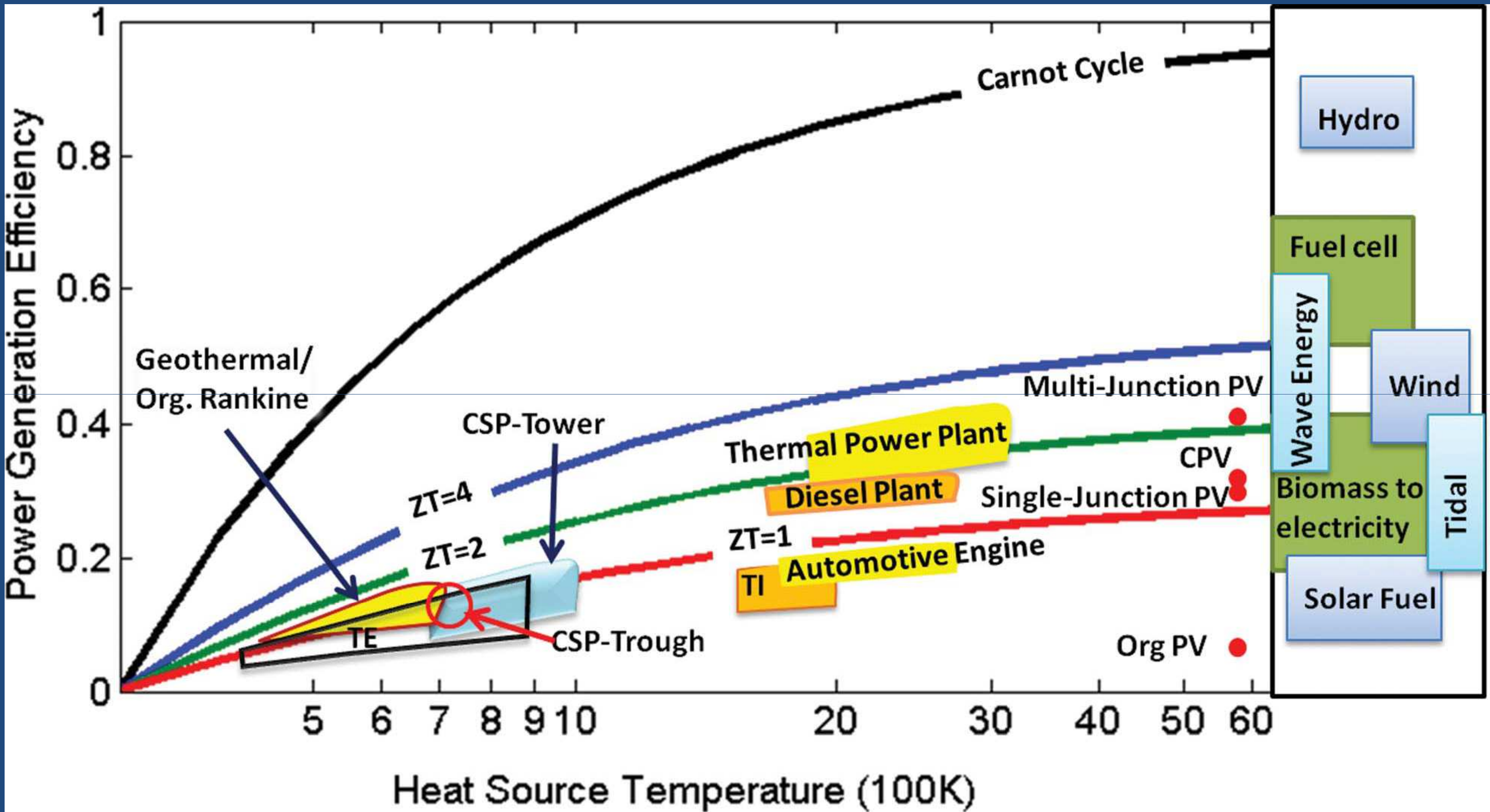


Power



- Lightweight and small
- Very reliable

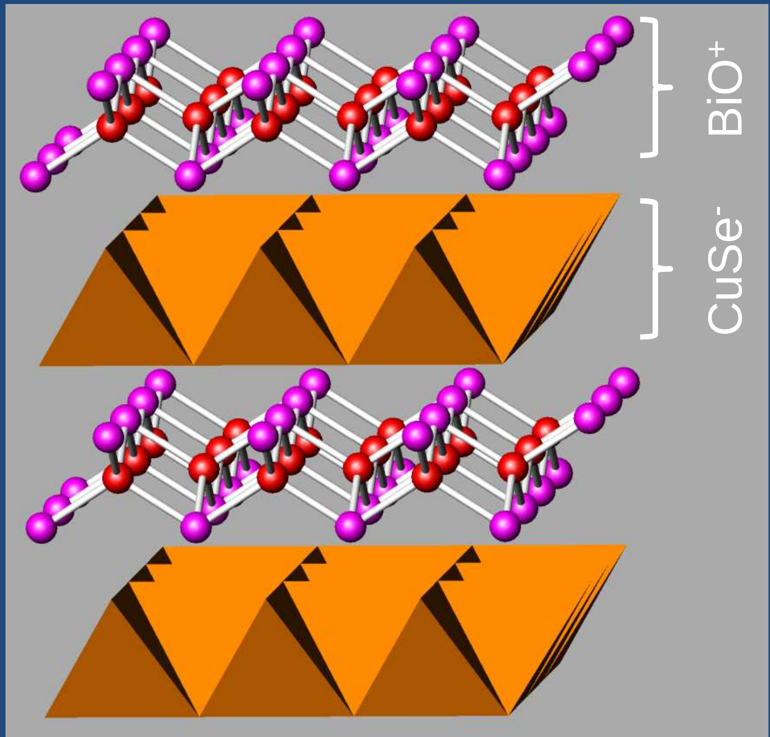
Energy Conversion Technologies



Zebarjadi et al, *Energy Env. Sci.*, **5**, 5147, (2012)

Materials Design 4: Separation of $S^2\sigma$ and κ terms

BiOCuSe



- Independent optimisation of $S^2\sigma$ (covalent) and κ_L (ionic)