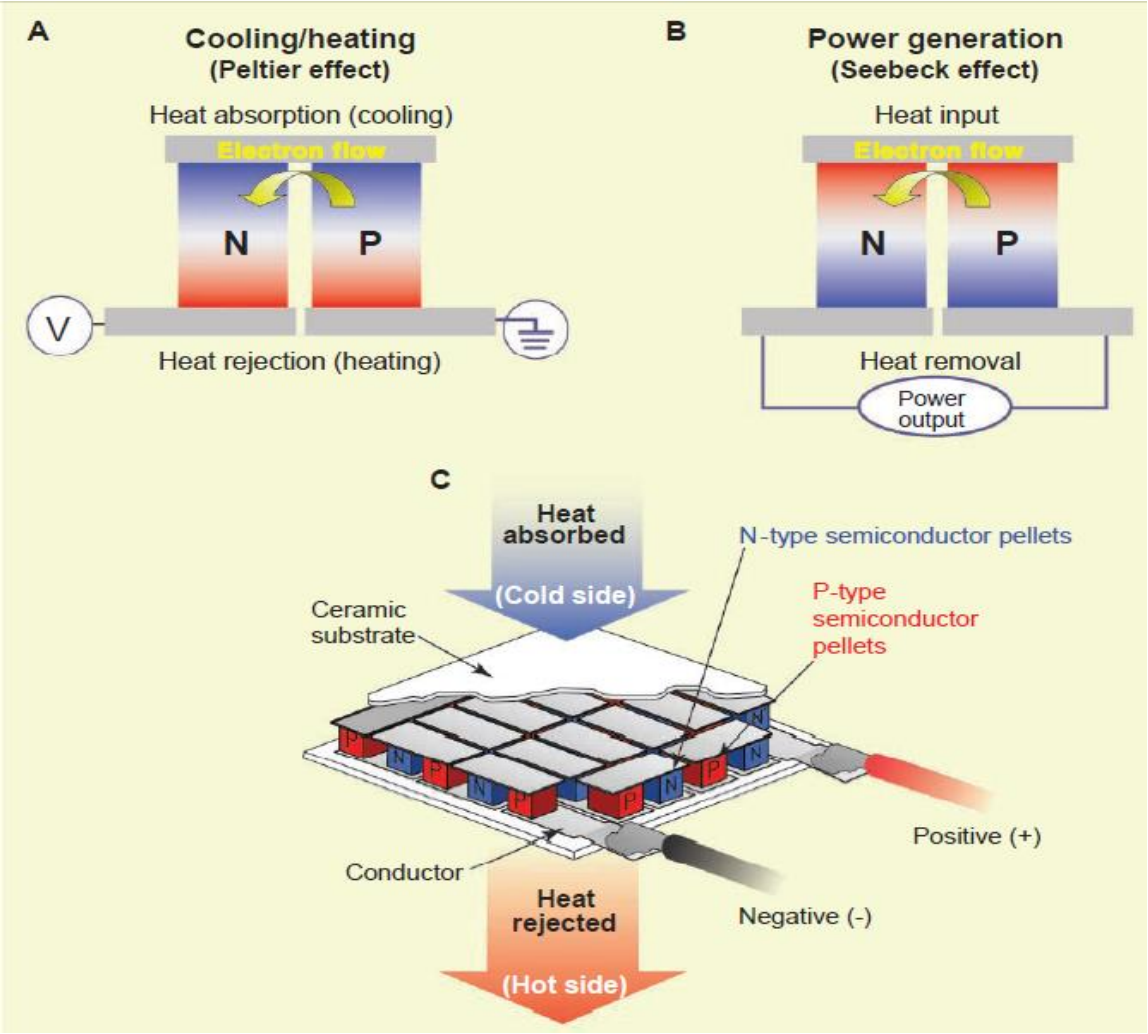
Semiconductor crystalline nanocomposites for novel thermoelectrics

Tomasz Story
Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

- **Thermoelectrics – the search for new materials**
- **New IV-VI semiconductor thermoelectrics: band structure engineering, crystalline nanocomposites, and quantum dot nanostructures**
- **Summary and outlook**

EAgLE
European Action towards Leading Centre for Innovative Materials

Thermoelectric p-n module



A: Peltier cooler

B: Thermoelectric Generator (TEG)

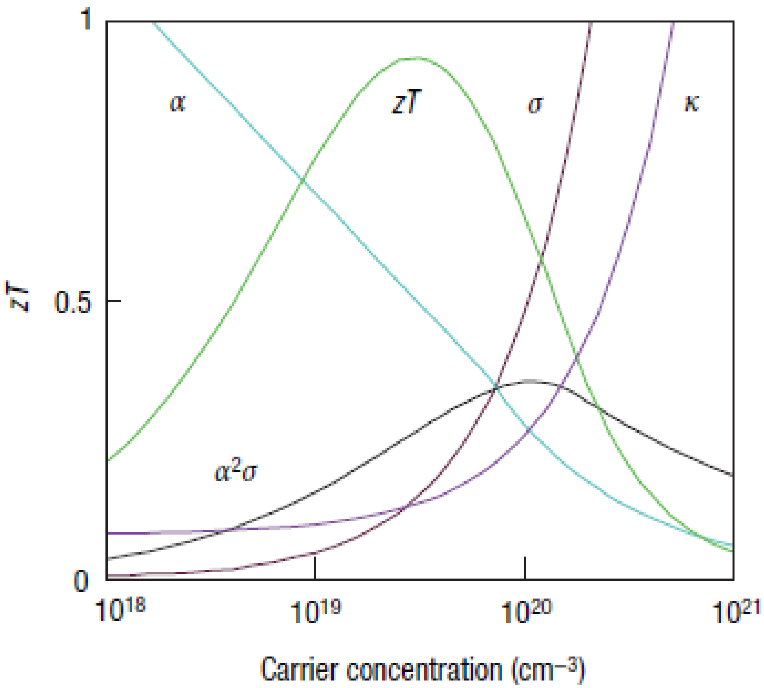
L.B. Bell,
Science 321, 1457 (2008)

Electronic, automobile, and military thermoelectric applications - examples

- **Climate control systems in cars**
- **Peltier refrigerators**
- **Power supplies for space missions, remote sensors, telecom facilites, etc.**
- **Energy harvesting systems**

Thermoelectric figure of merit parameter

"Electron Crystal - Phonon Glass"



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

$$S = \frac{2\pi^2 k_B^2 T}{3en} g(E)_{E=E_F}$$

$$\sigma = n e \mu$$

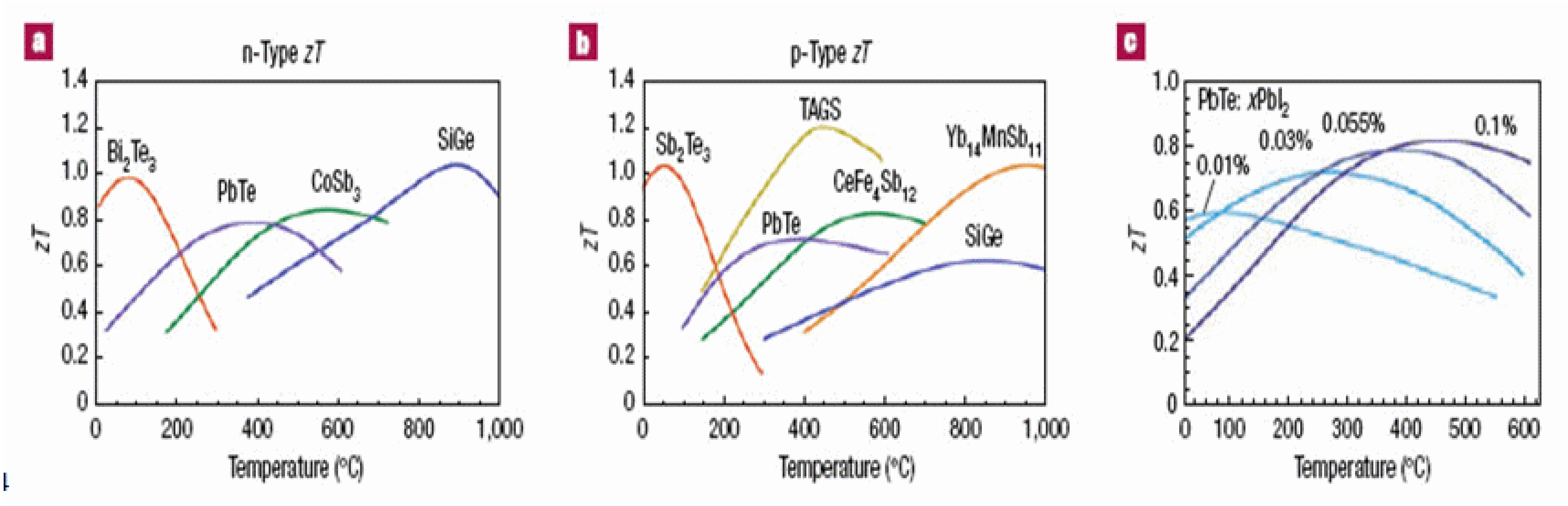
$$\kappa = \kappa_e + \kappa_L$$

$$\kappa_e = n e \mu L T$$

Complex thermoelectric materials

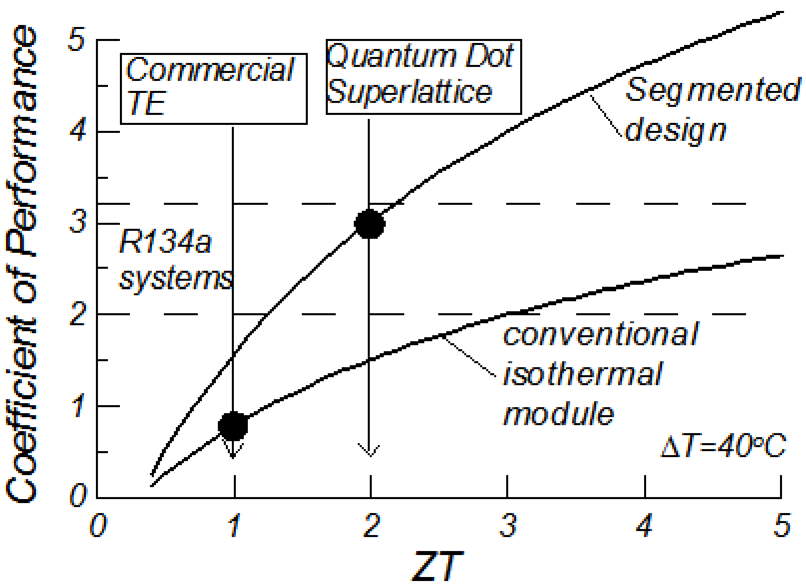
G. JEFFREY SNYDER* AND ERIC S. TOBERER Nature Materials 7, 105 (2008).

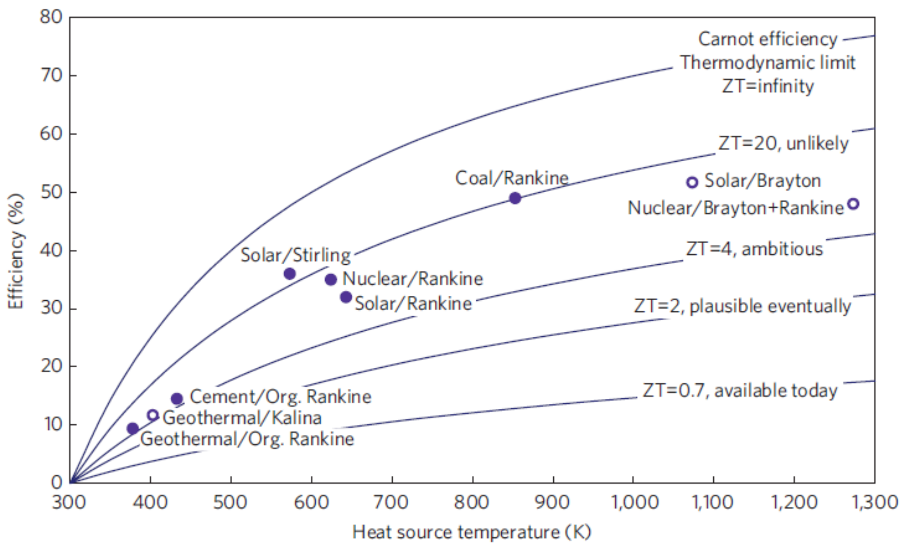
Thermoelectric materials



G.J. Snyder et al. Nature Materials 7, 105 (2008)

Thermoelectric vs classical generators and refrigerators





J.P. Heremans, Mat. Res. Soc. Symp. Proc. 793, 3 (2004).

B. Vining, Nature Materials 8, 83 (2009)

Search for new thermoelectrics

low dimensional semiconductor nanostructures of classical TE   PbTe, Si-Ge, Bi_2Te_3

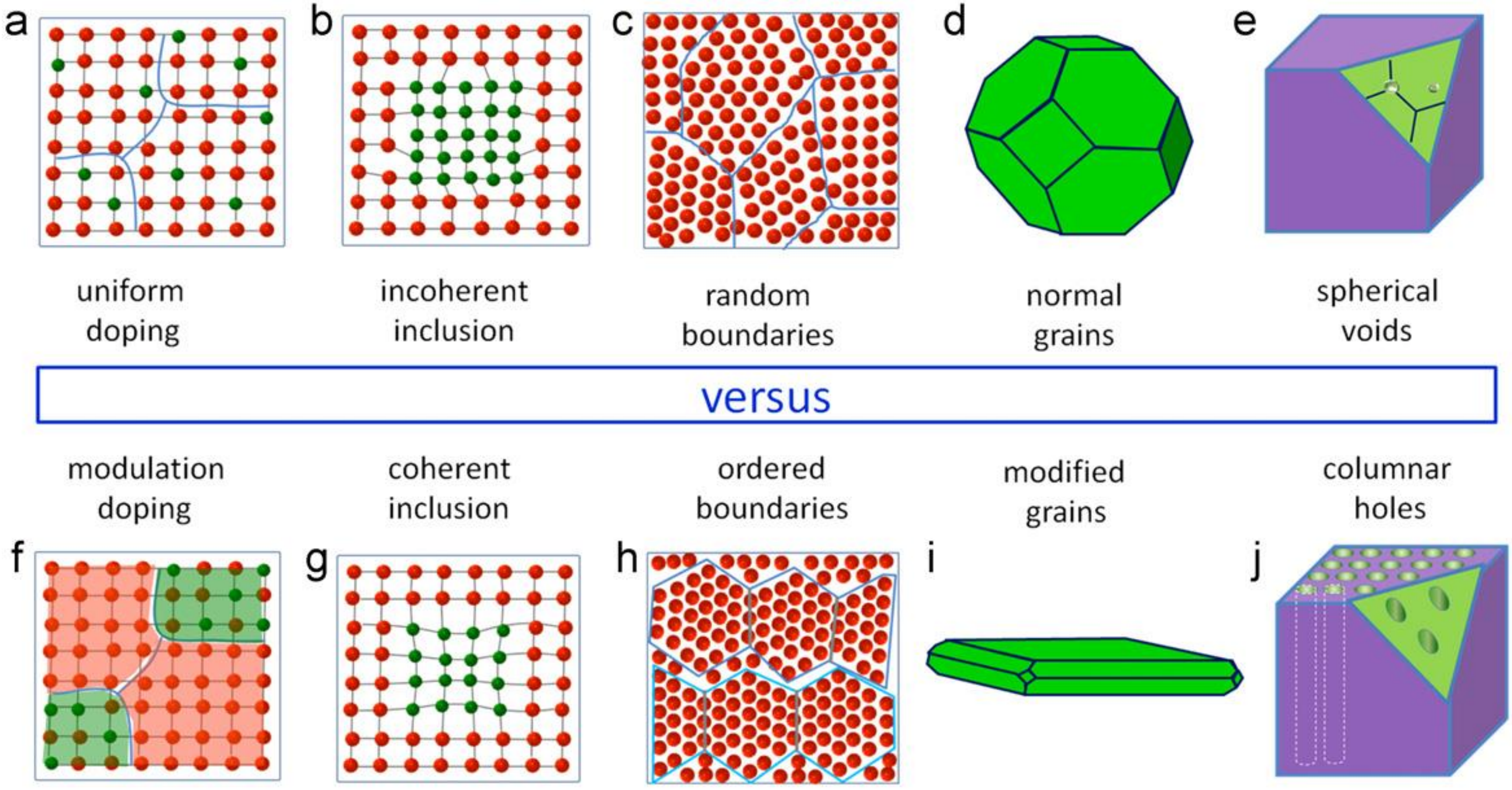
nanocomposites: electron crystal - phonon glass concept of new thermoelectrics

nonstandard metals or semimetals (resonant DOS features)

ultrapoor thermal conductors (rattling defects)

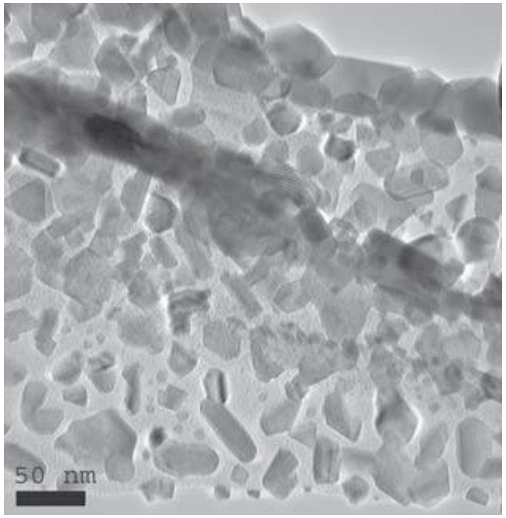
unconventional thermoelectrics - environmentally friendly/economically feasible: e.g. oxides, silicides

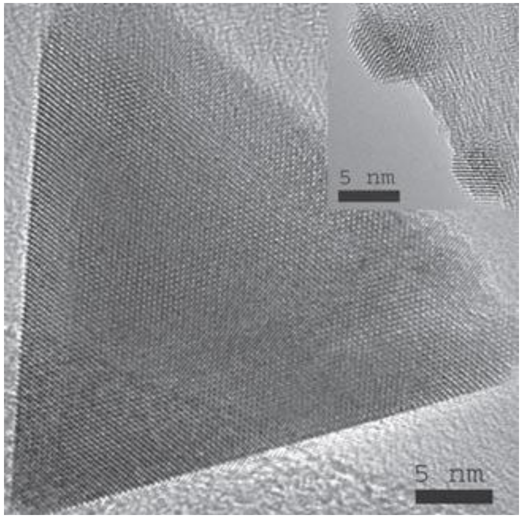
Electrical and thermal conduction in nanostructures

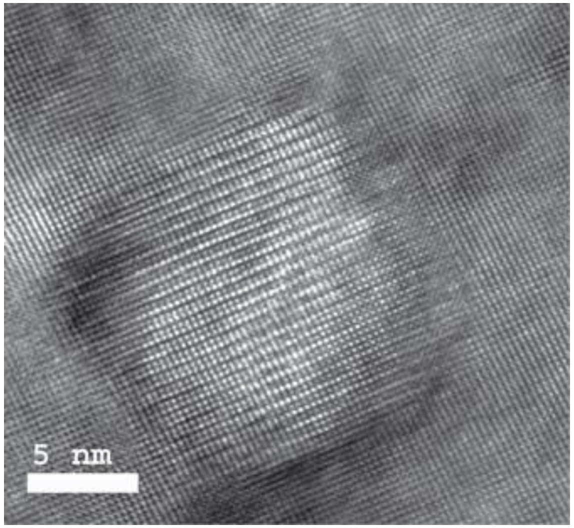


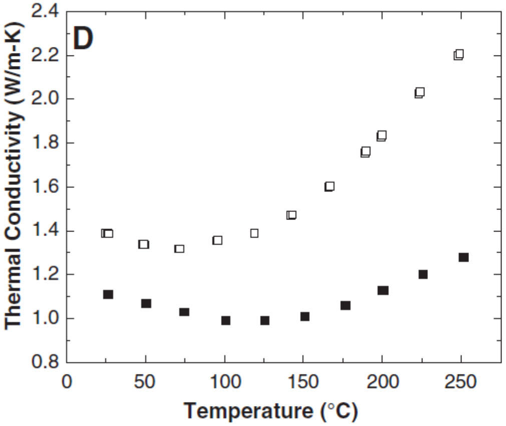
W. Lu, Nano Energy 1, 42 (2012)

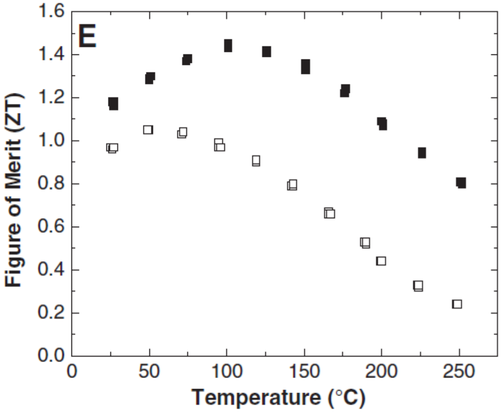
Nanocrystalline alloys - $(Bi,Sb)_2Te_3$











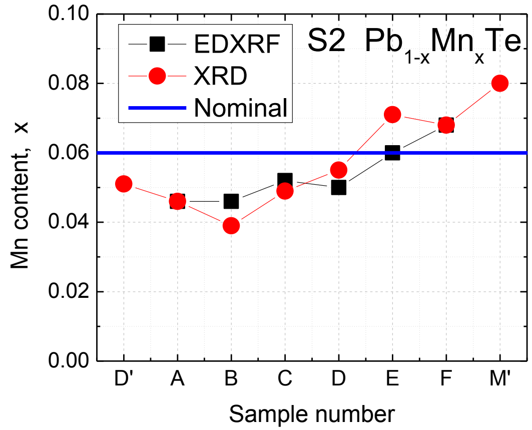
B. Poudel et al,
Science 320, 634 (2008)

$Pb_{1-x}Mn_xTe$ alloys - crystal growth and doping

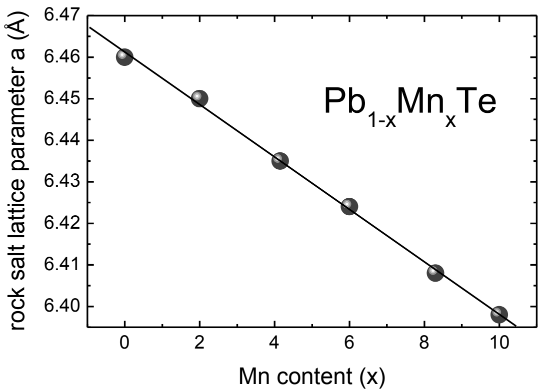
Structural and chemical characterization

- Bulk crystals (x <0.08) grown by standard Bridgman method
- Doped during growth : n-type with Bi or I; p-type with Na or Ag
- Single rock-salt phase (XRD analysis) with a moderate Mn segregation along an ingot

PbMnTe:Na bulk crystal ingot with Mn content x=0.01 grown by the Bridgman method (about half of the total length of a typical ingot shown).

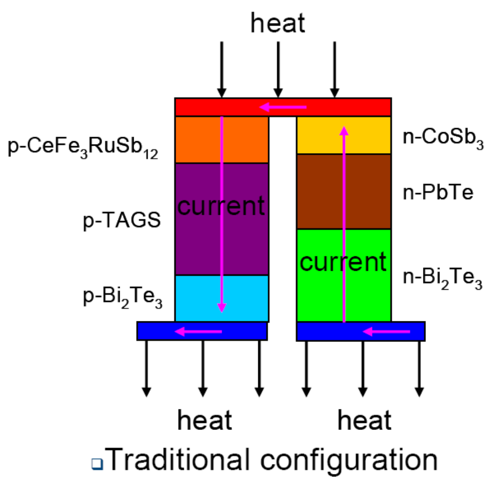


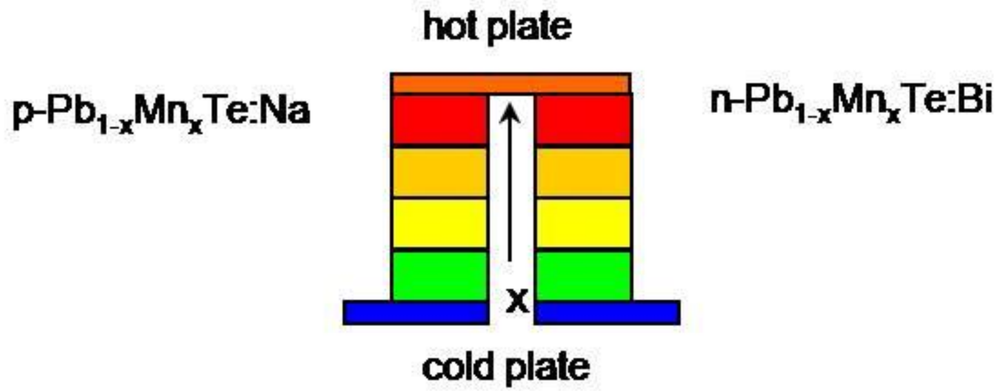
Manganese composition profile along the PbMnTe crystal ingot No S2 with nominal Mn content x=0.06 grown by the Bridgman method. D' corresponds to the first-to-grow part of the crystal. Total length of the ingot is about 5 cm. (x <0.1)

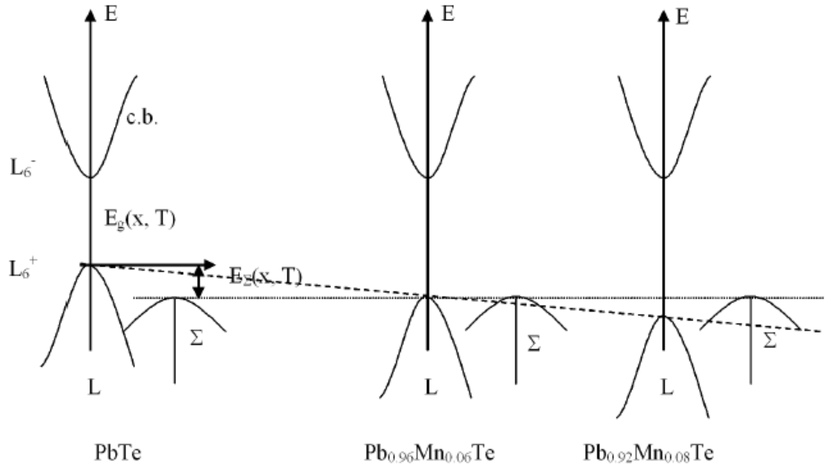


Manganese composition dependence of the rock salt lattice parameter of PbMnTe crystals grown by Bridgman method.

$Pb_{1-x}Mn_xTe$ bulk crystals - band structure model and thermoelectricity





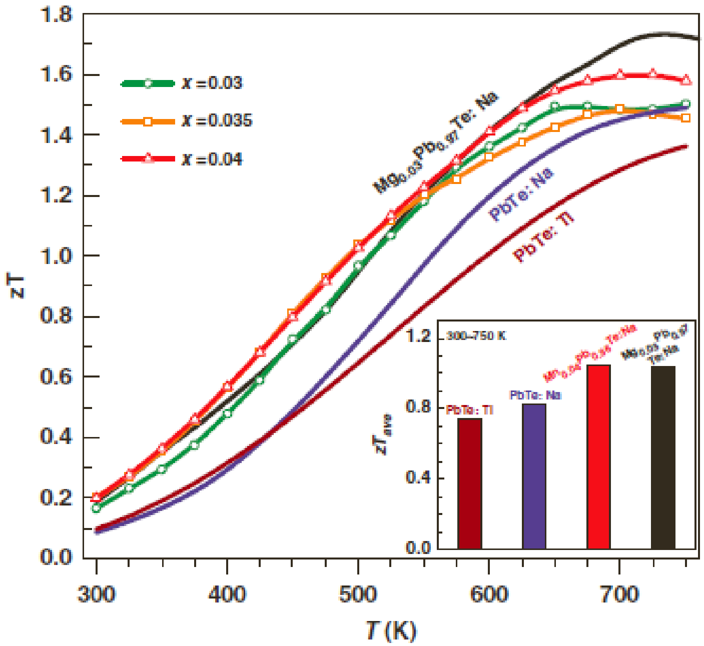


Compositionally graded thermoelectrics

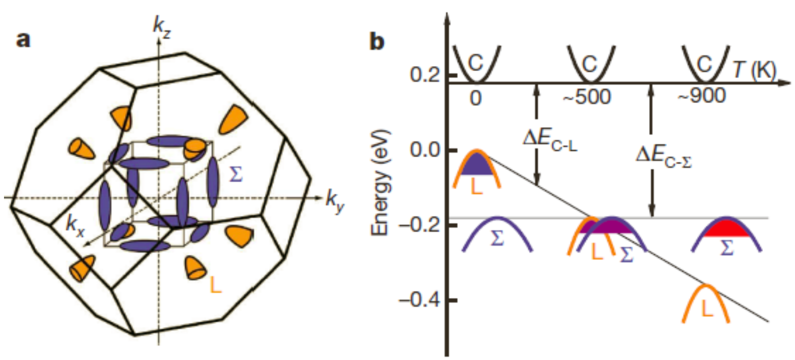
ZT(x) i T_{max} (x) Thermoelectric compatibility

V. Osinniy et al., Acta Phys. Pol. A 108, 809 (2005)
A. Łusakowski et al., Phys. Rev. B 83, 115206 (2012)
M. Bukała et al., Phys. Rev. B (2012)

$Pb_{1-x}Mn_xTe$ – high ZT parameter

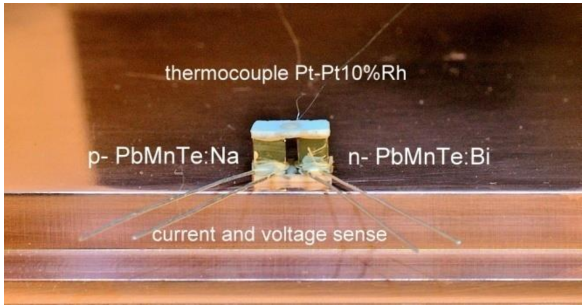


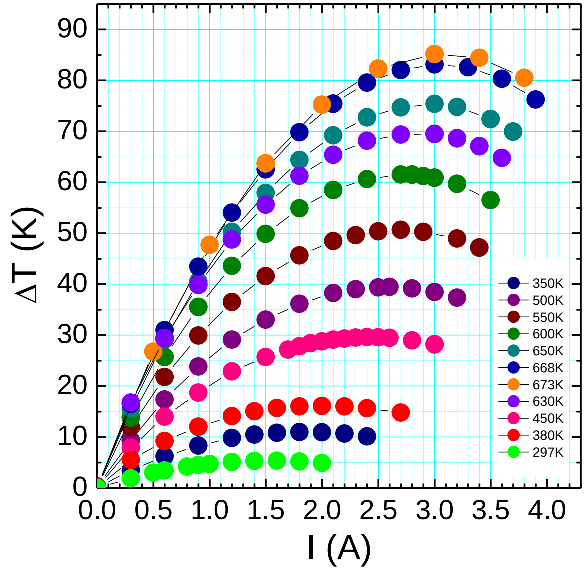
Y. Pei et al.,
NPG Asia Materials 4, e28 (2012)

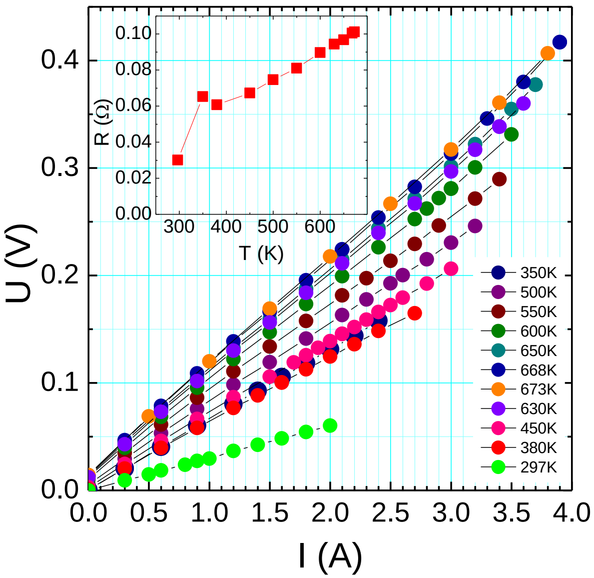


Y. Pei, …G.J. Snyder,
Nature 473, 66 (2011)

Thermocooler performance vs temperature



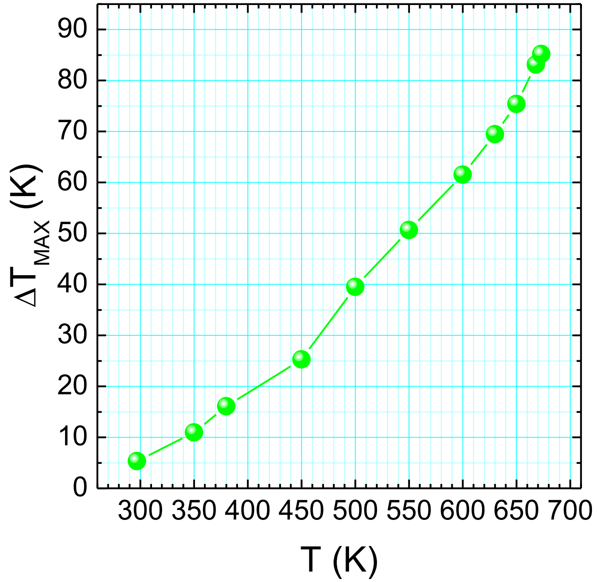


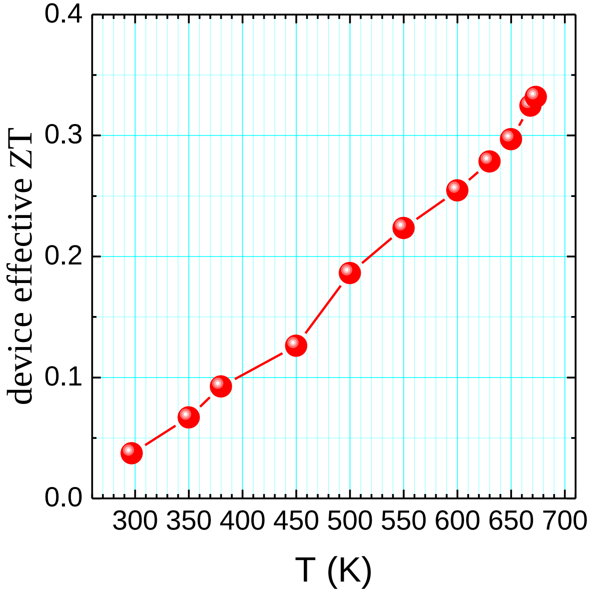


- n- and p- $Pb_{0.95}Mn_{0.05}Te$ bulk crystals of dimensions: 2x3x3 mm
- RuSi/Au metalization for ohmic contacts
- electrical contacts Ag-paste
- thermal contact Omegatherm 201 paste

$$\Delta T_{max} = 1/2\ ZT_c^2$$

K. Dybko, M Szot et al. (2013)





PbTe-CdTe bulk thermoelectric nanocomposite material

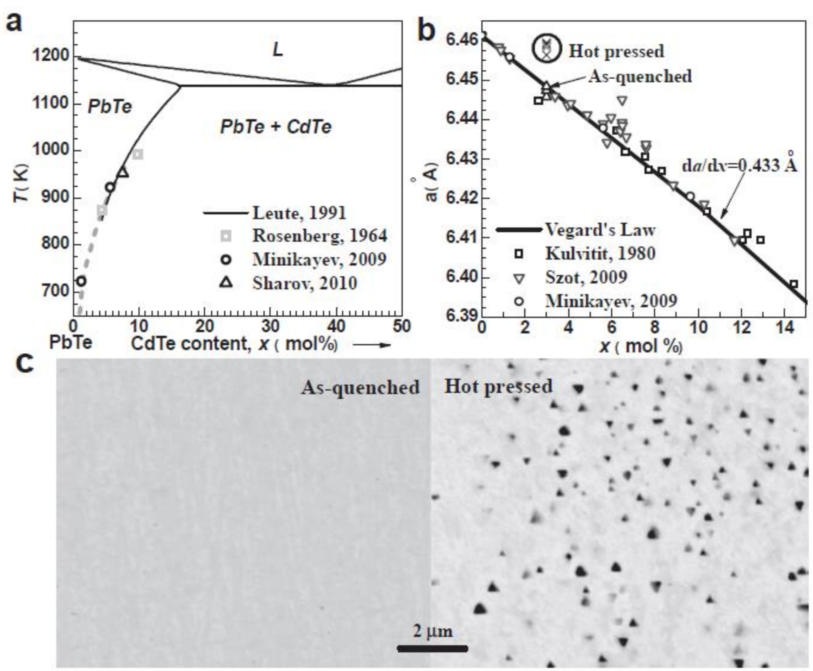
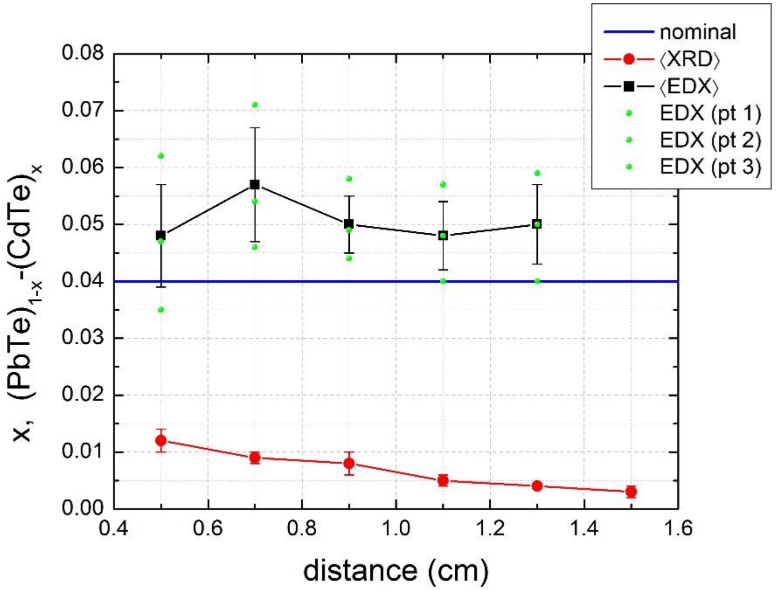


Figure 1. $(PbTe)_{1-x}(CdTe)_x$ phase diagram (a), the lattice parameter as a function of CdTe content (b) and the microstructure (c) in quenched ingots and hot pressed samples with $x = 0.03$ showing the presence of nanoparticles only after hot pressing at 823 K. Solubility decreases from 3 mol% in as-quenched to ~0.5–1 mol% in hot pressed samples, consistent with the phase diagram.

FULL PAPER

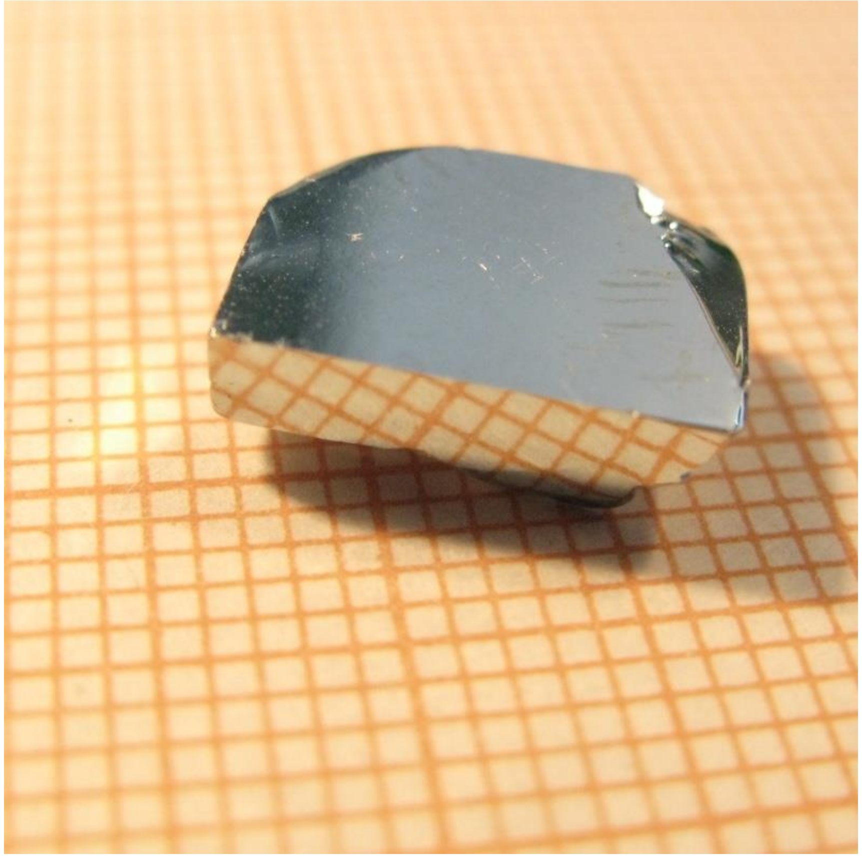
Y. Pei et al.., Adv. Energy Mater. (2012)

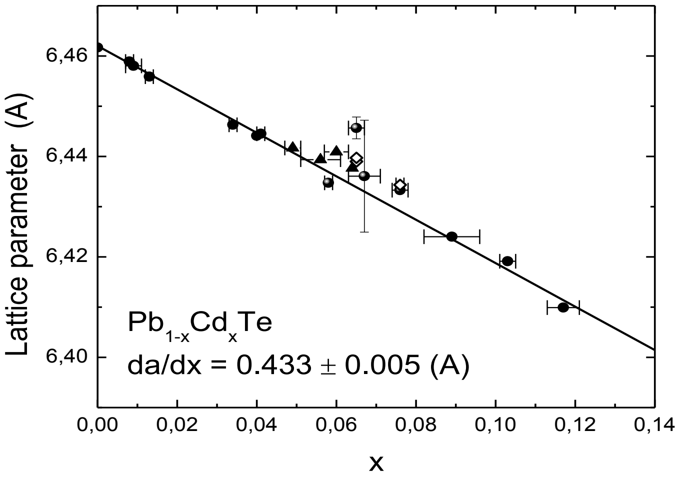
Two-phase crystalline composite - zinc-blende CdTe in rock-salt PbTe



Crystal growth - A. Mycielski (IF PAN)

$Pb_{1-x}Cd_xTe$ monocrystals

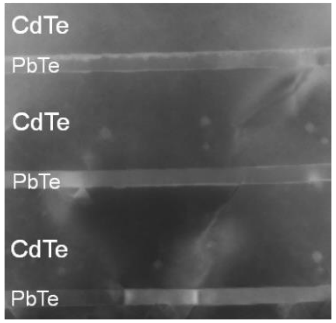


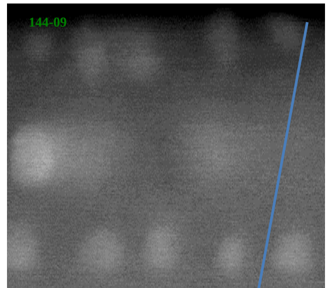


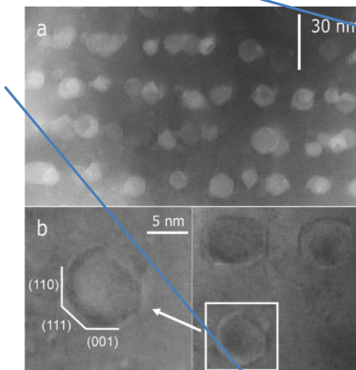
Vegard law a(x)

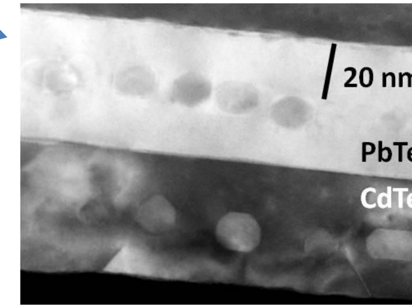
Self-selecting vapor phase growth by A. Szczerbakow

PbTe/CdTe epitaxial heterostructures

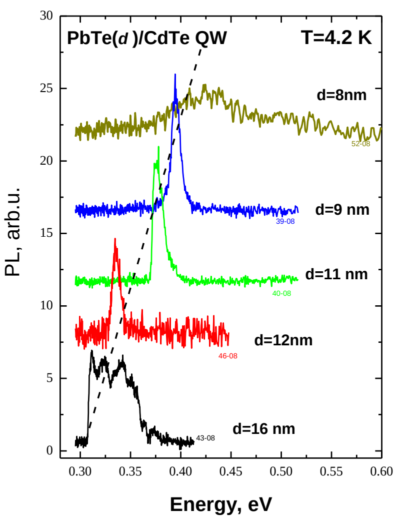


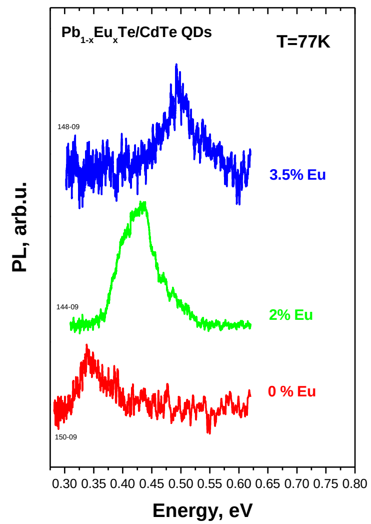


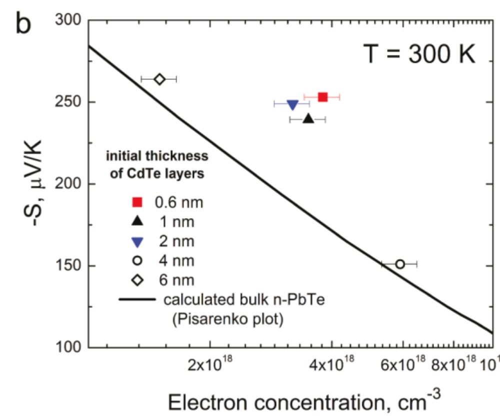




QDs+ADs







Quantum well

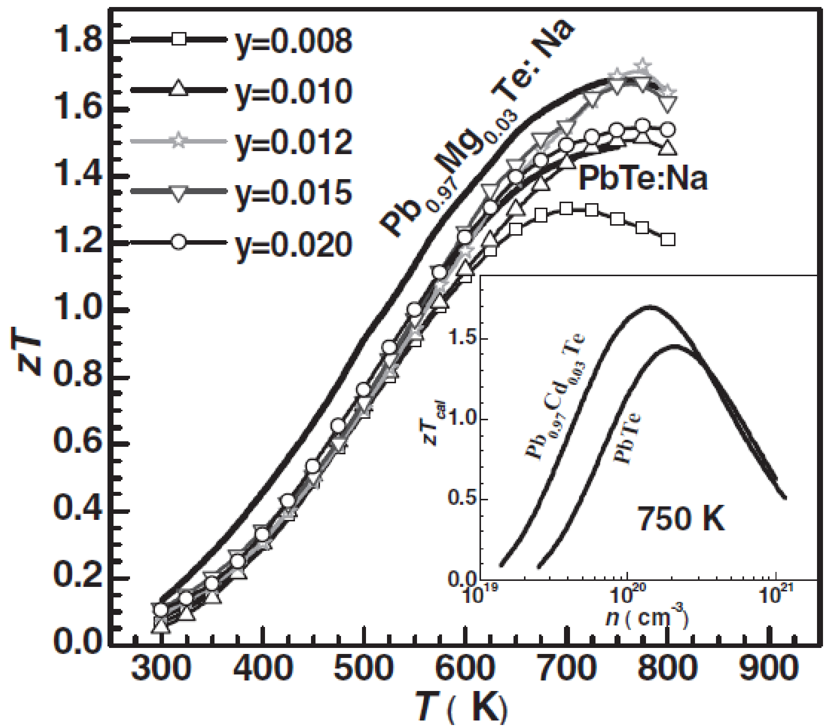
Quantum dot

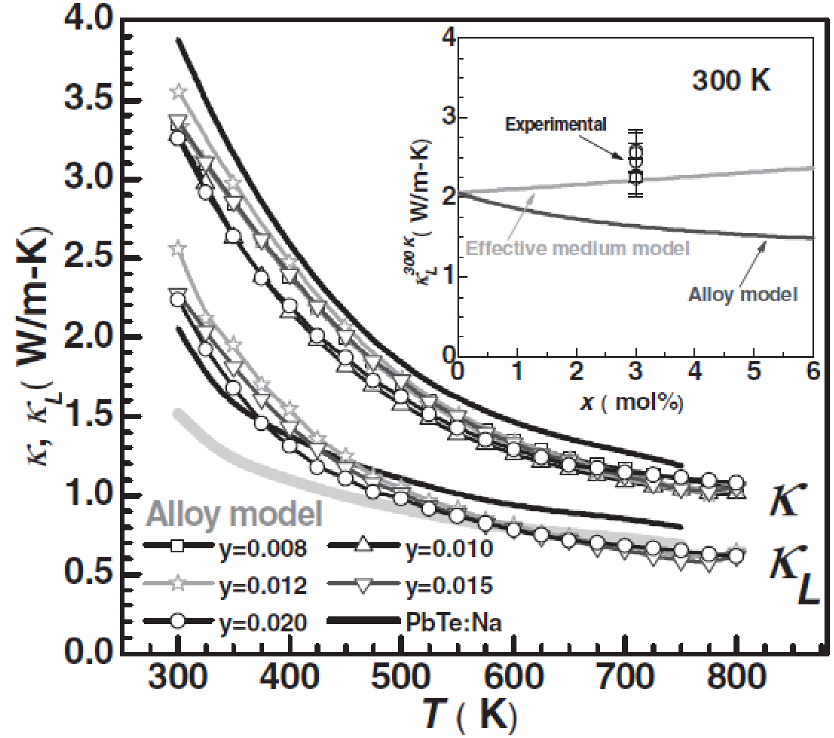
Anti-dots

E. Smajek, M. Szot et al. *J. Cryst. Growth (2011)*

M. Szot et al. *Cryst. Growth. & Design (2011)*

PbTe-CdTe bulk nanocomposite





Y. Pei et al.., Adv. Energy Mater. (2012)

Summary and outlook

1. **Thermoelectric generators may help to improve fuel economy by converting to electricity the waste heat produced during combustion engines' operation and industrial processing (3-10 %).**

2. **New ideas for better thermoelectrics: engineering of electronic and thermal properties of semiconductors and semimetals in the form of bulk nanocomposites (electron crystal - phonon glass type materials).**

3. **Thermoelectric project on PbTe-based alloys ($Pb_{1-x}Mn_xTe$) and nanocomposites (PbTe-CdTe): bulk crystal and thin layers growth, thermoelectric figure of merit parametr ZT=0.8 at T=700 K.**

4. **Showing thermoelectric functionalities and quantifying performance with simple demonstrator-devices.**

5. **Investigating new SnSe and SnS based thermoelectrics**