Nanopowder thermoelectrics: improved energy conversion by nanostructuring

Sabine Schlecht

DFG-JST Workshop Kyoto, 20.- 23. January 2009

Thermoelectric effects

interconversion of thermal and electrical energy

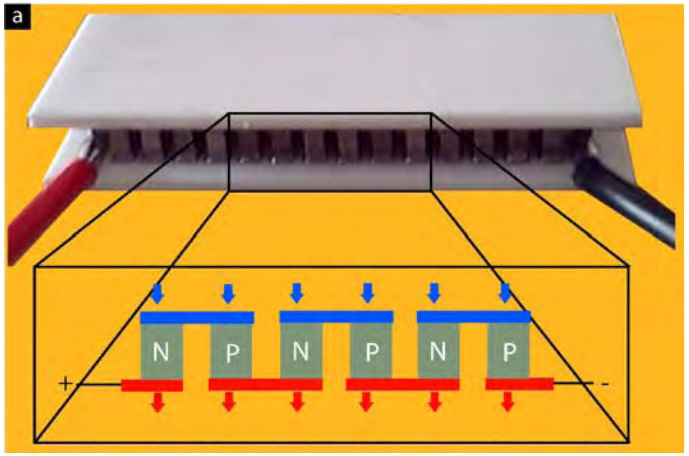
Seebeck 1821:

difference in potential from a difference in temperature (TE generator)

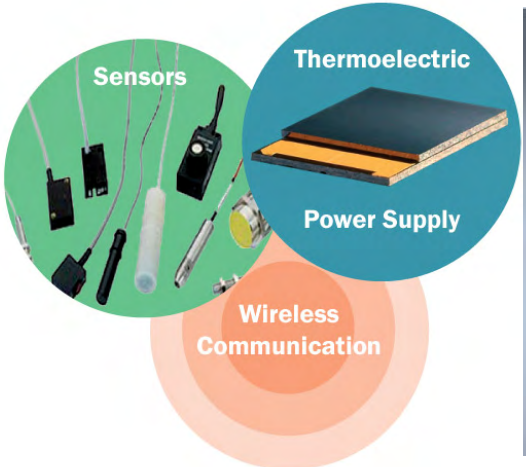
Peltier 1834:

difference in temperature from a difference in potential (cooling)

Fields of application for TE converters



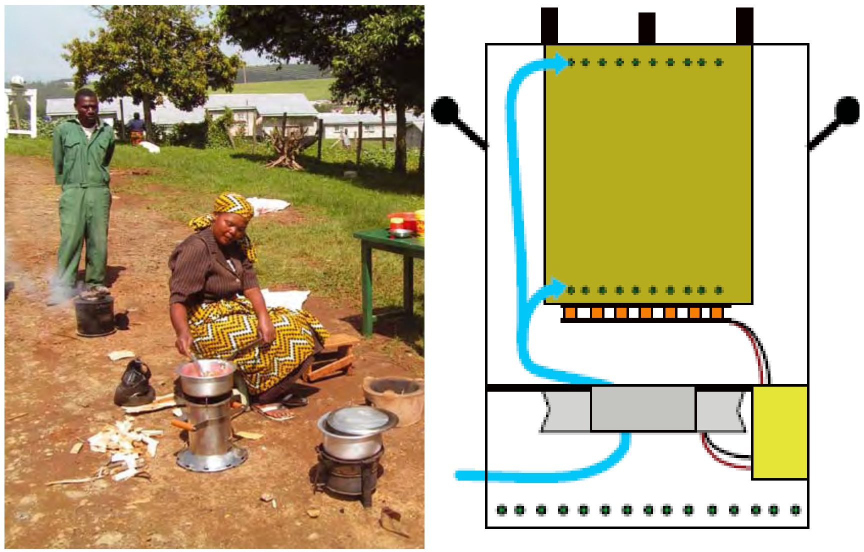
Peltier element



TEG for sensing

TEG for vehicles

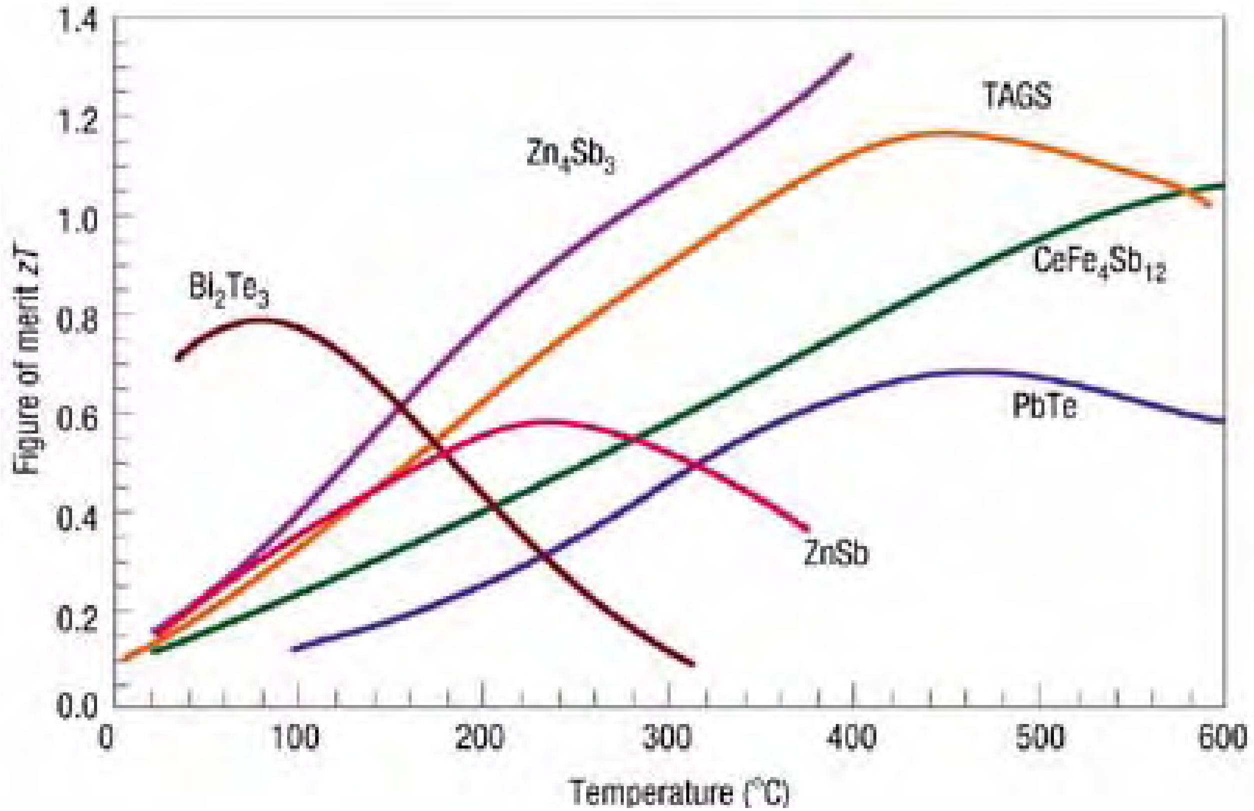
RTG-New Horizons



Woodstove with TEG

Nanoscale Thermoelectrics

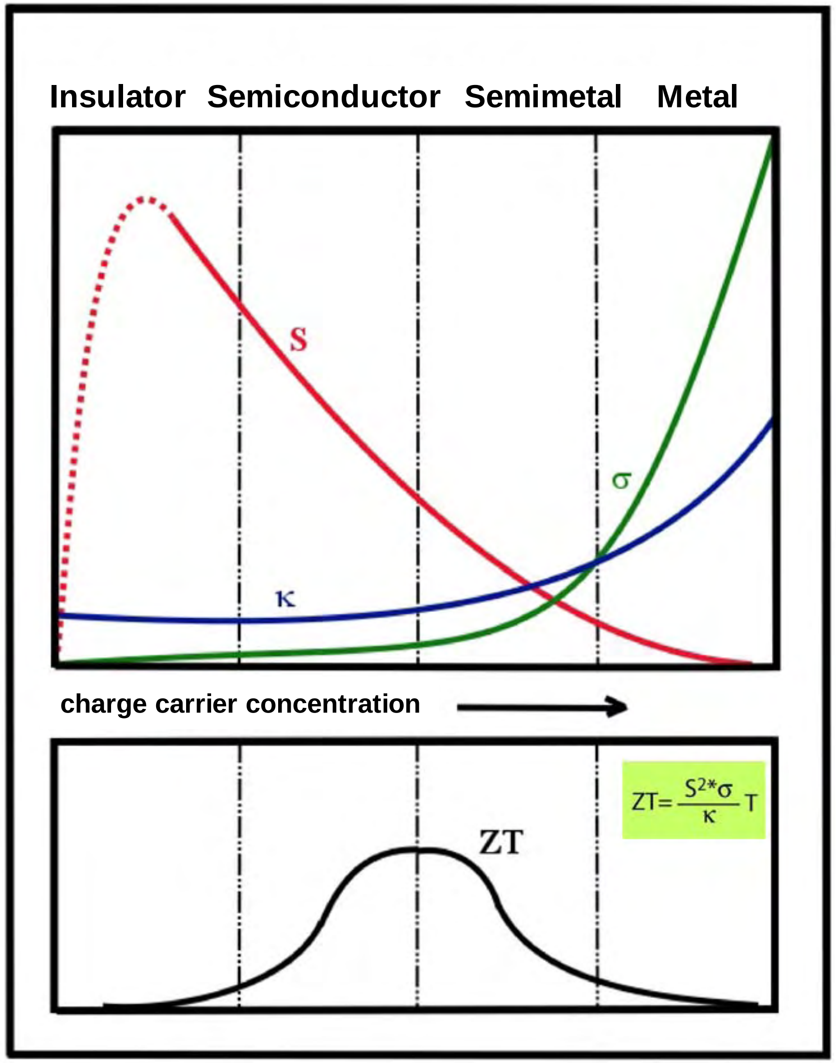
Efficiency of TE conversion (Altenkirch 1909):
figure of merit ZT= $(S^2 \cdot \sigma)/\kappa$



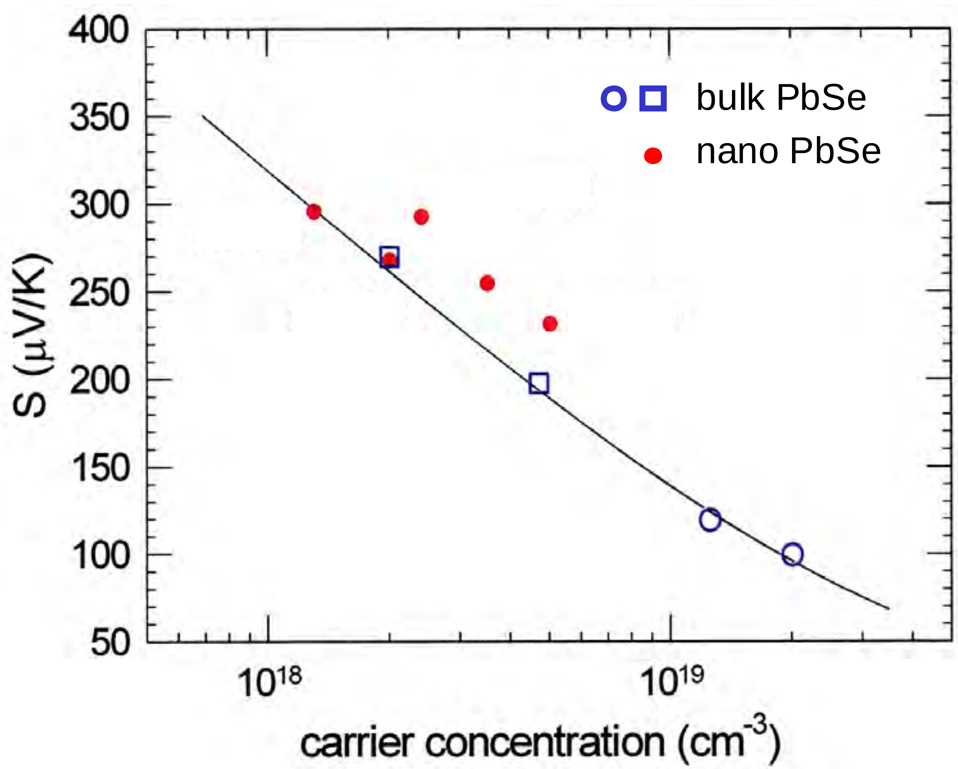
Why nano ?

- **reduction of κ**
- **Influence on S and σ ?**
- **concept of ‚electron crystal' and ‚phonon glass'**

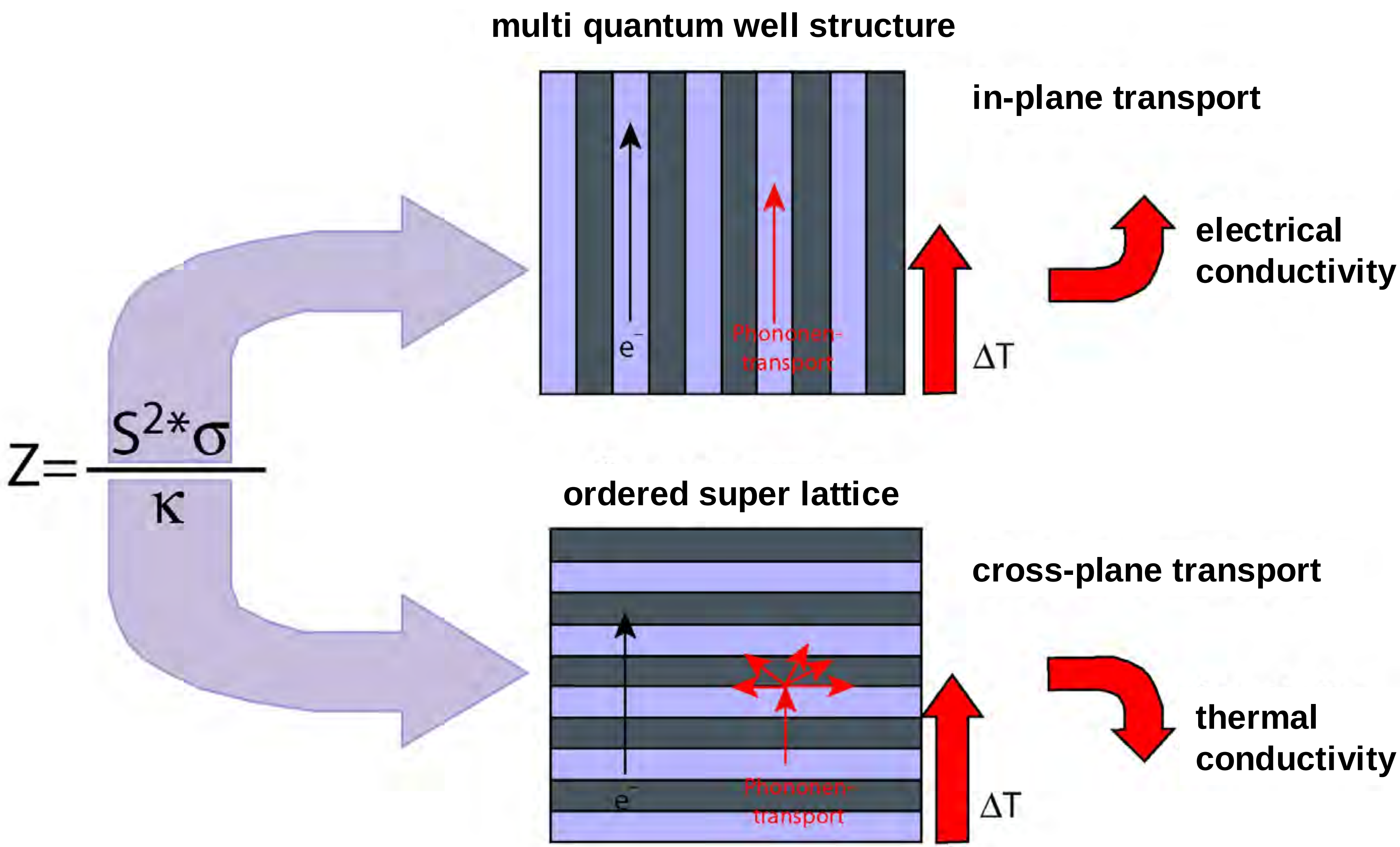
Changes of TE parameters on the nanoscale



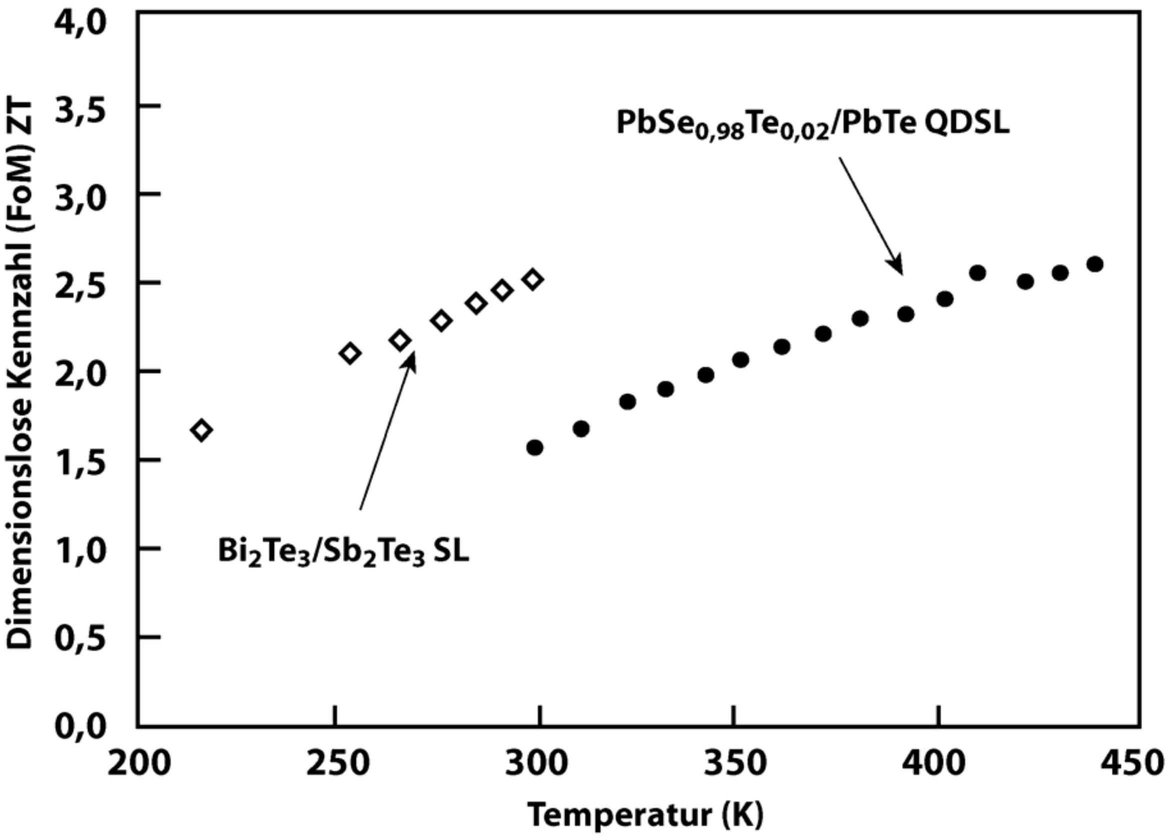
S for nanoscale PbSe films

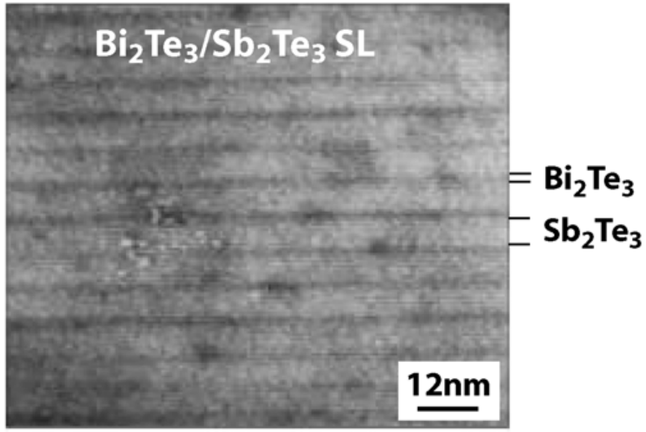


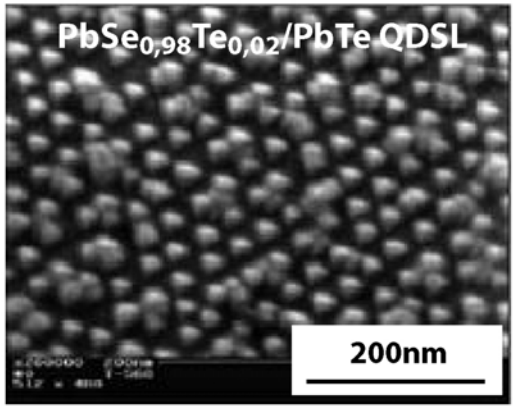
Effects of nanostructuring on ZT



Super lattices of layers and quantum dots

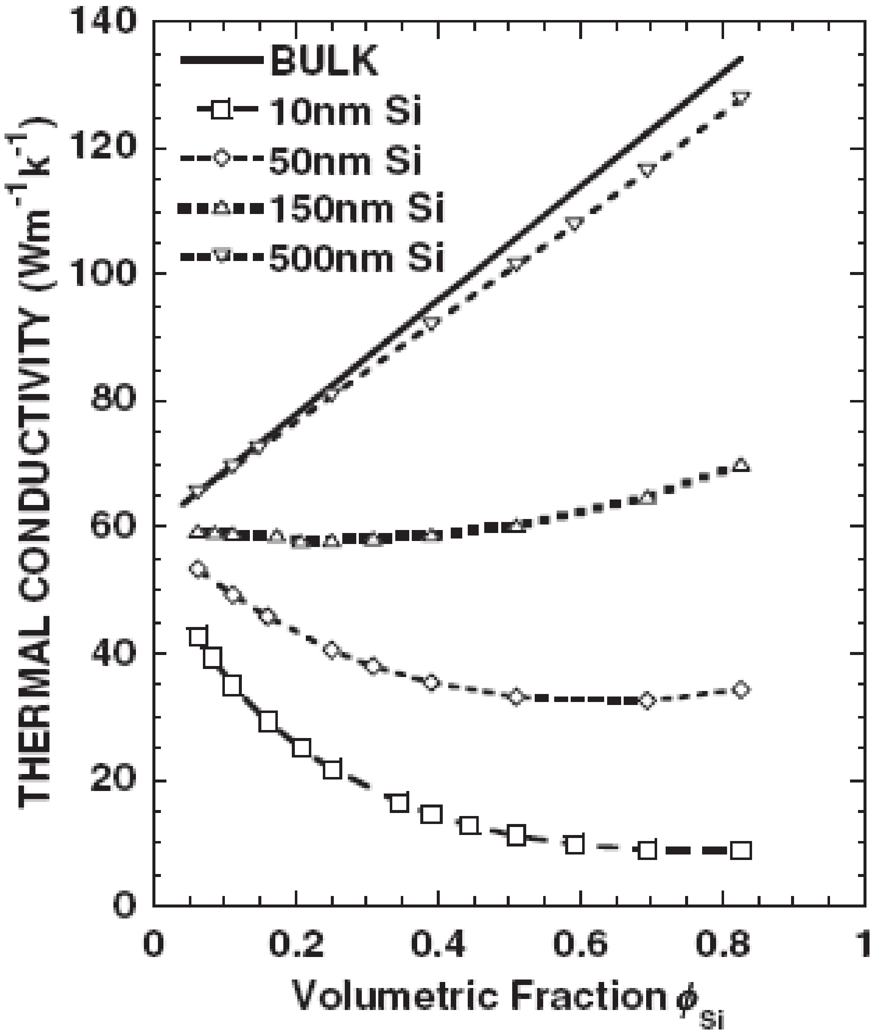


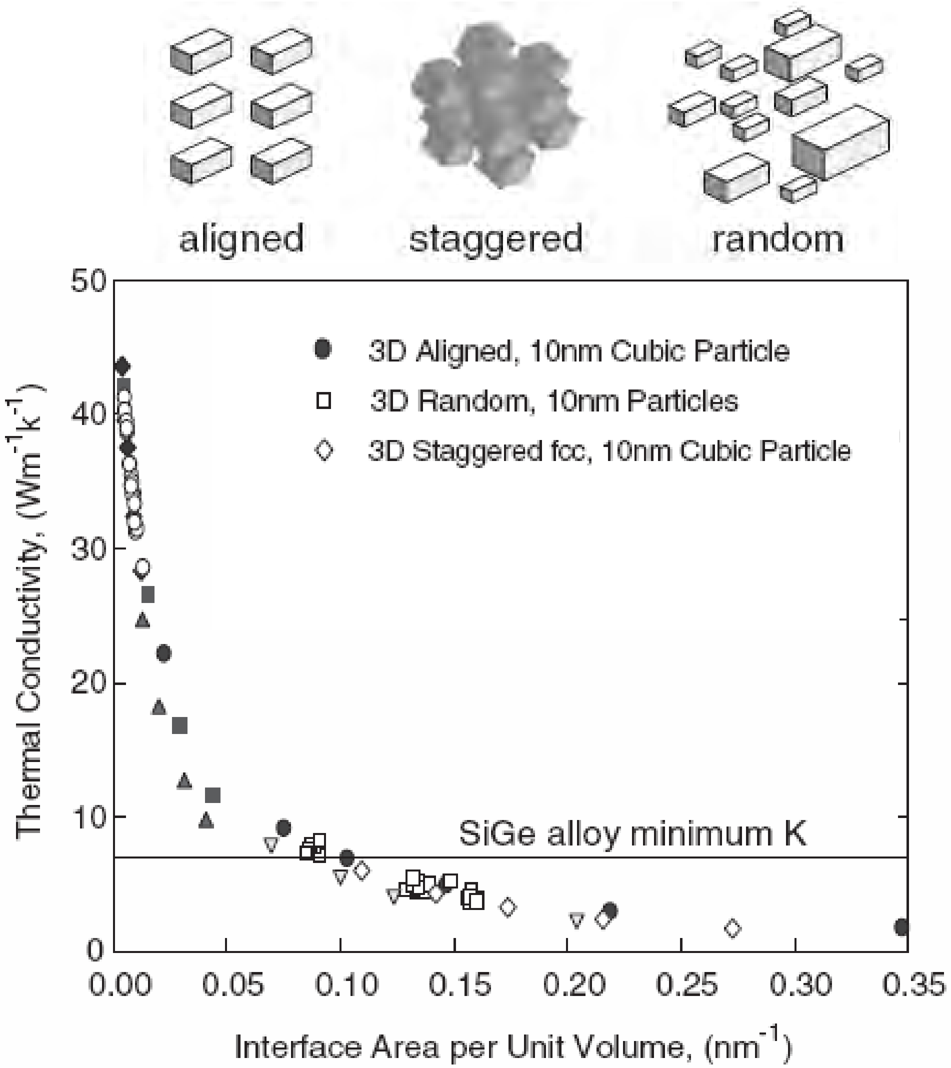




pioneered by Harman, Venkatasubramanian

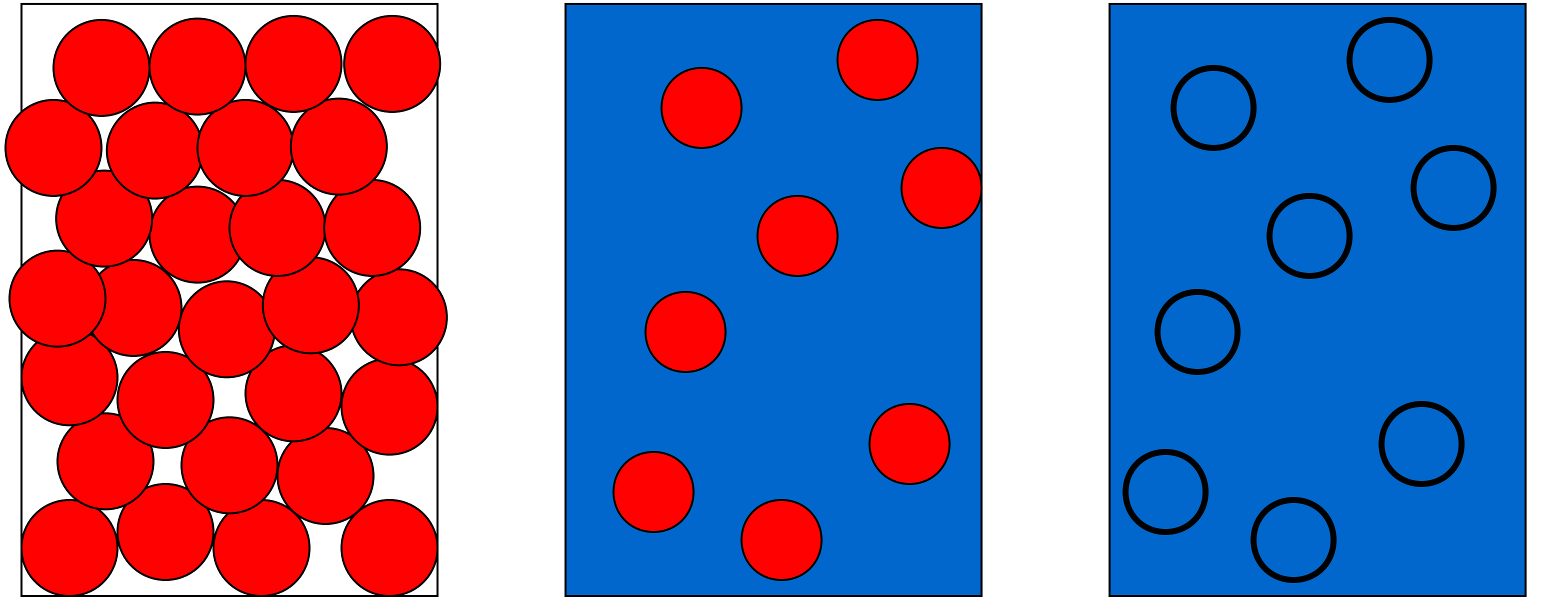
Reduction of the thermal conductivity by phonon scattering





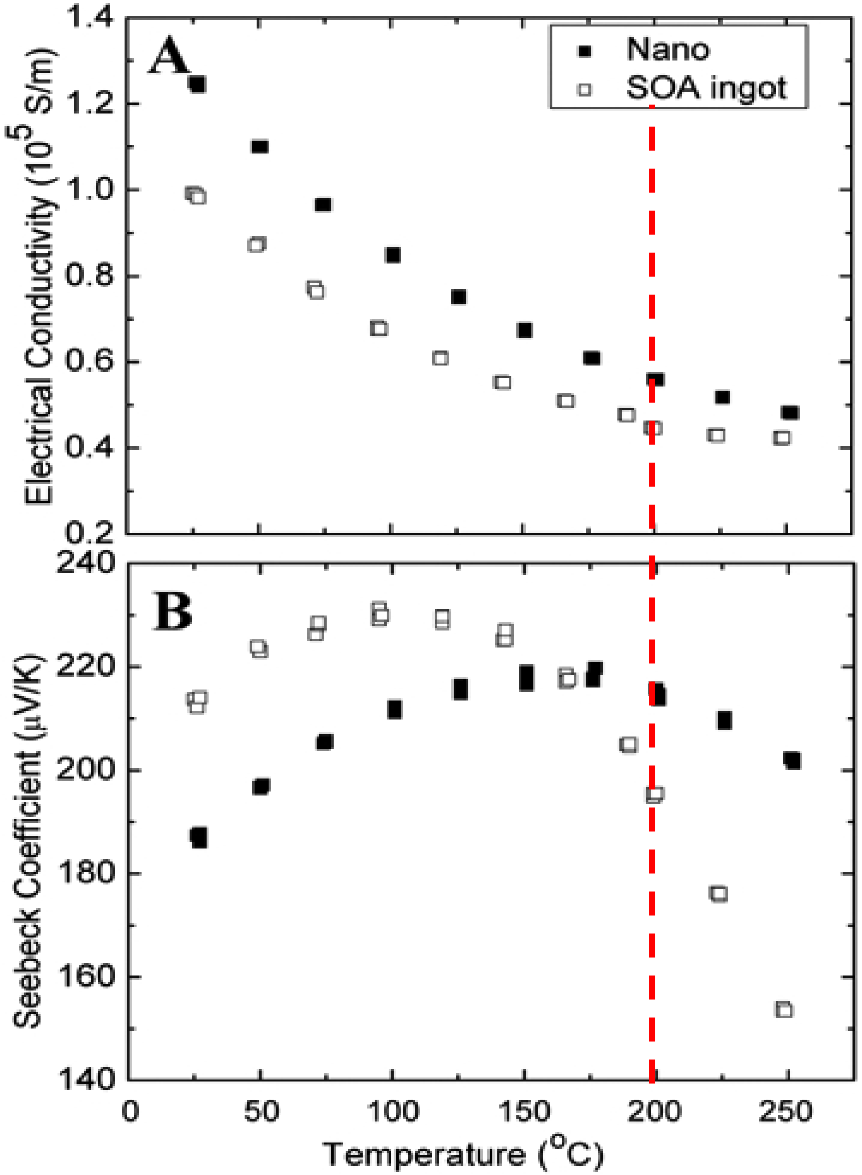
R. Yang, G. Chen, M. S. Dresselhaus

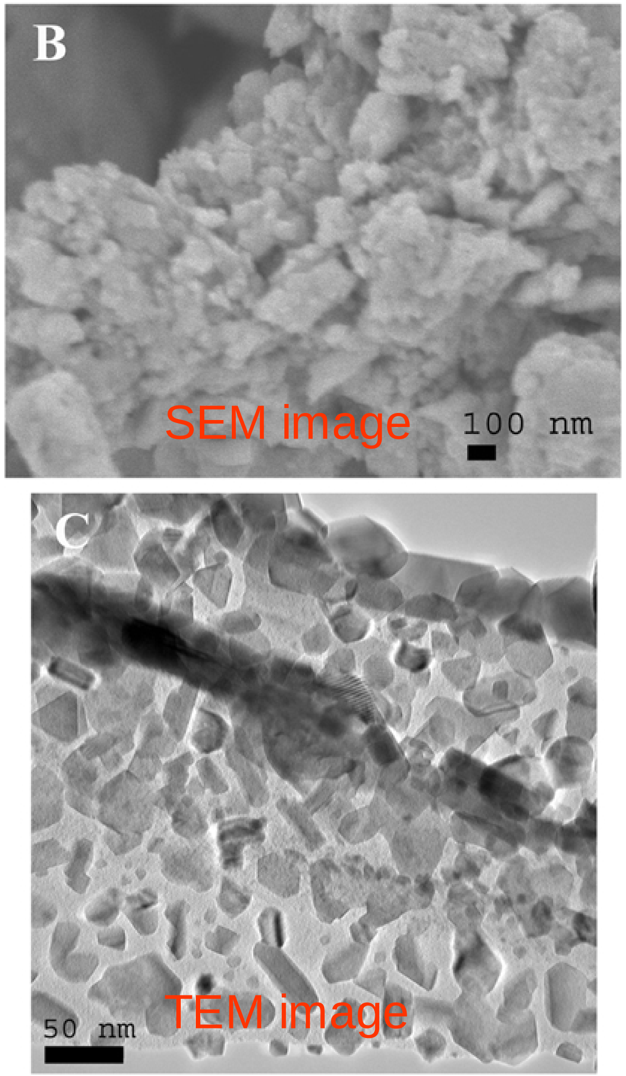
Types of nanocomposite powders



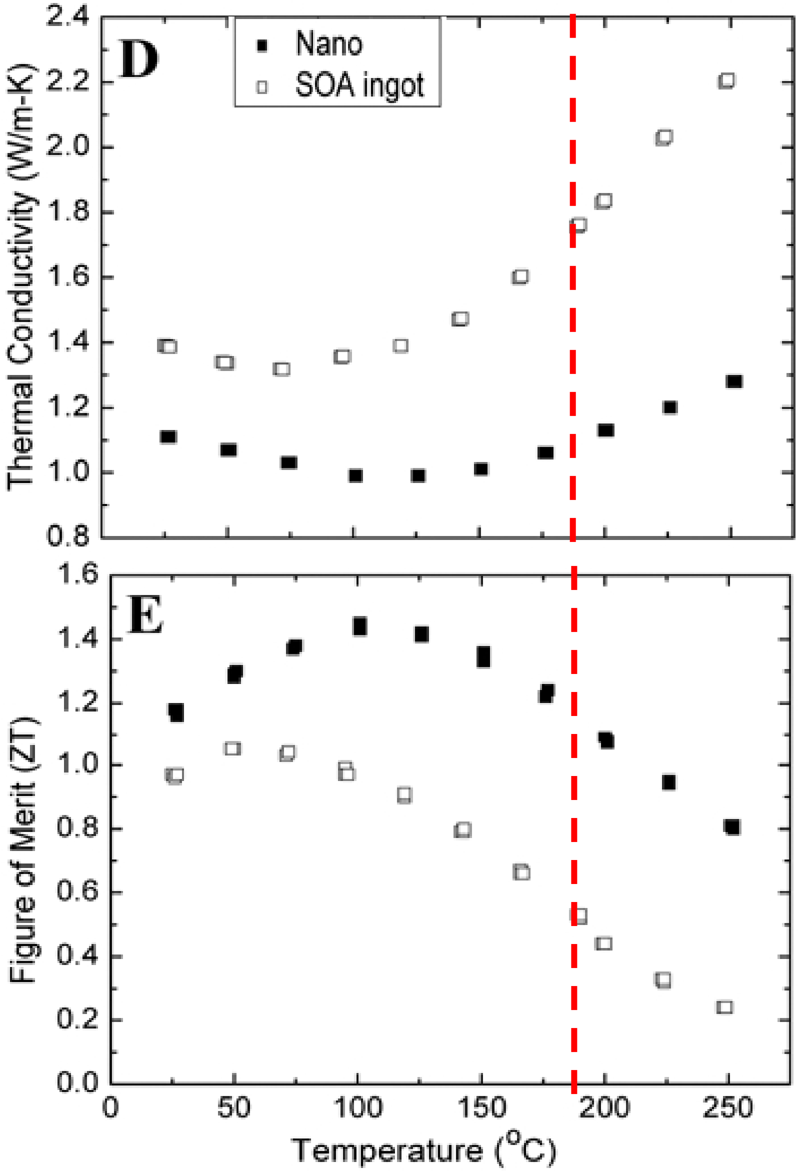
A B C

TE data for nano-$Bi_{0.5}Sb_{1.5}Te_3$





TE data for nano-$Bi_{0.5}Sb_{1.5}Te_3$



→ σ (nano) slightly higher than σ (bulk)

→ κ (nano) significantly lower than κ (bulk)

- effective phonon scattering at a large number of grain boundaries

- doping level and structural defects

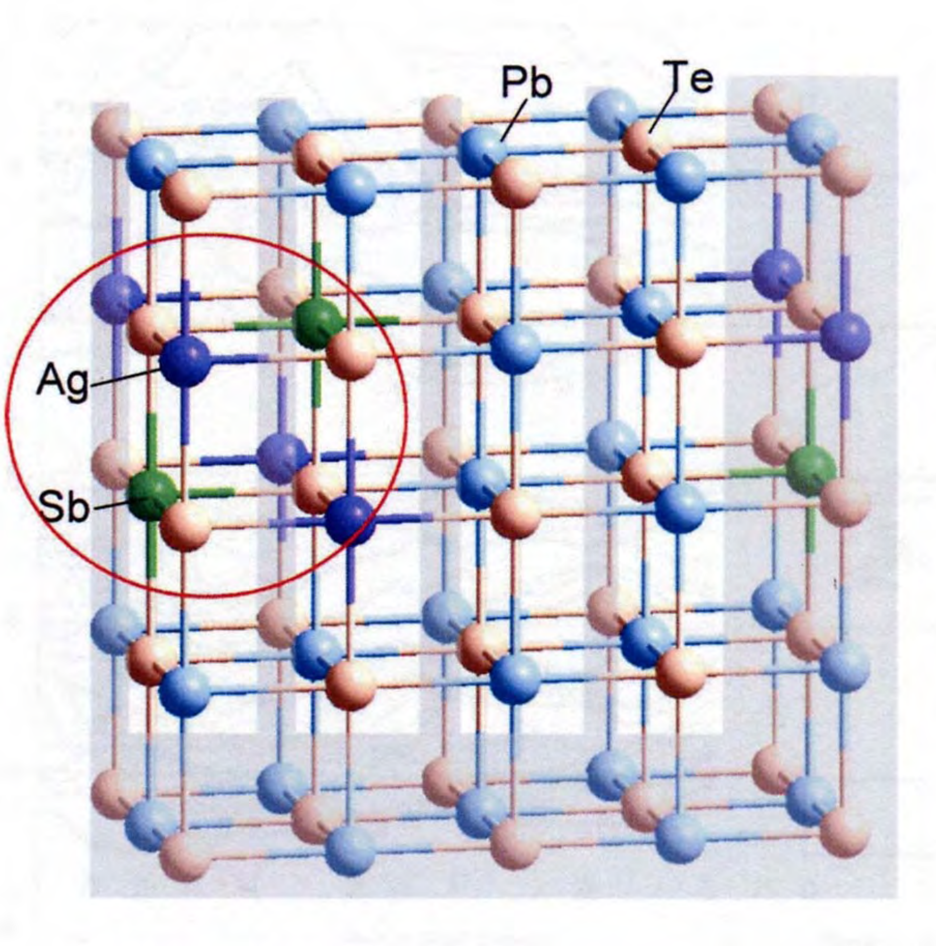
→ Improvement of the figure of merit

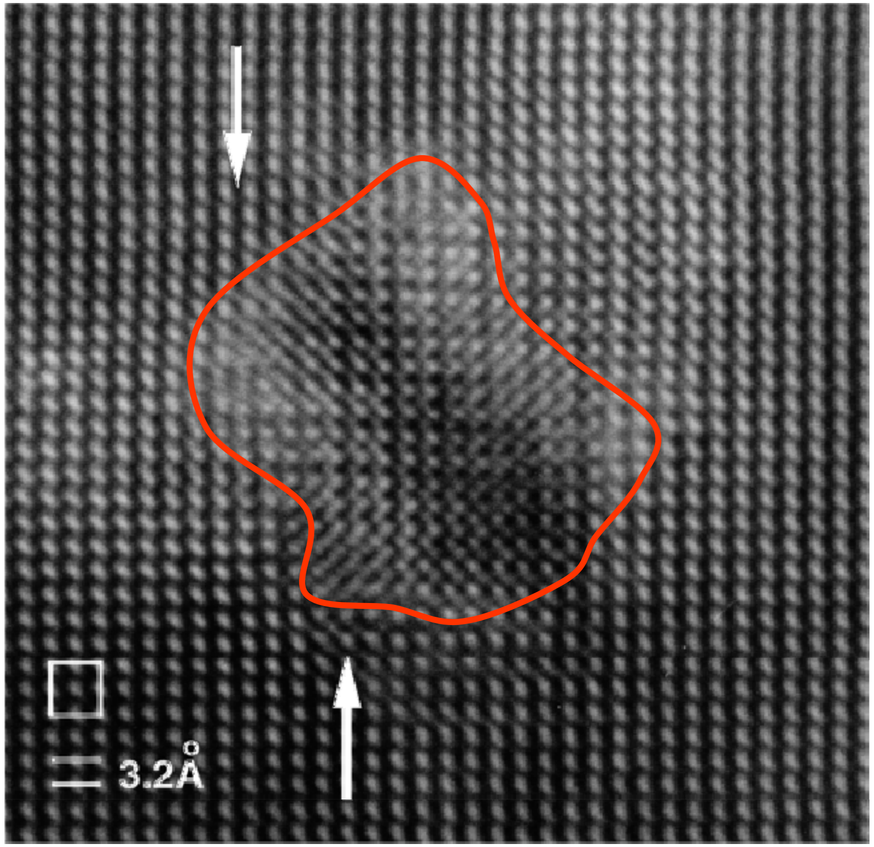
ZT (nano) (200° C) = 1.1

ZT (bulk) (200° C) = 0.4

B. Poudel, Q. Hao, Y. Lan, A. Minnich, Z. Ren, *Science*, **2008**, *305*, 638.

Nanoscopic de-mixing: formation of a nanocomposite (LAST materials)





M. G. Kanatzidis, Michigan State

Syntheses from activated elements

Tellurides

$$Pb^* + Ph_2Te_2 \xrightarrow[\text{diglyme}]{165^\circ\text{ C}} \text{nc-}PbTe + Ph_2Te$$

$$2\ Sb^* + 3\ Ph_2Te_2 \xrightarrow[\text{diglyme}]{165^\circ\text{ C}} \text{nc-}Sb_2Te_3 + 3\ Ph_2Te$$

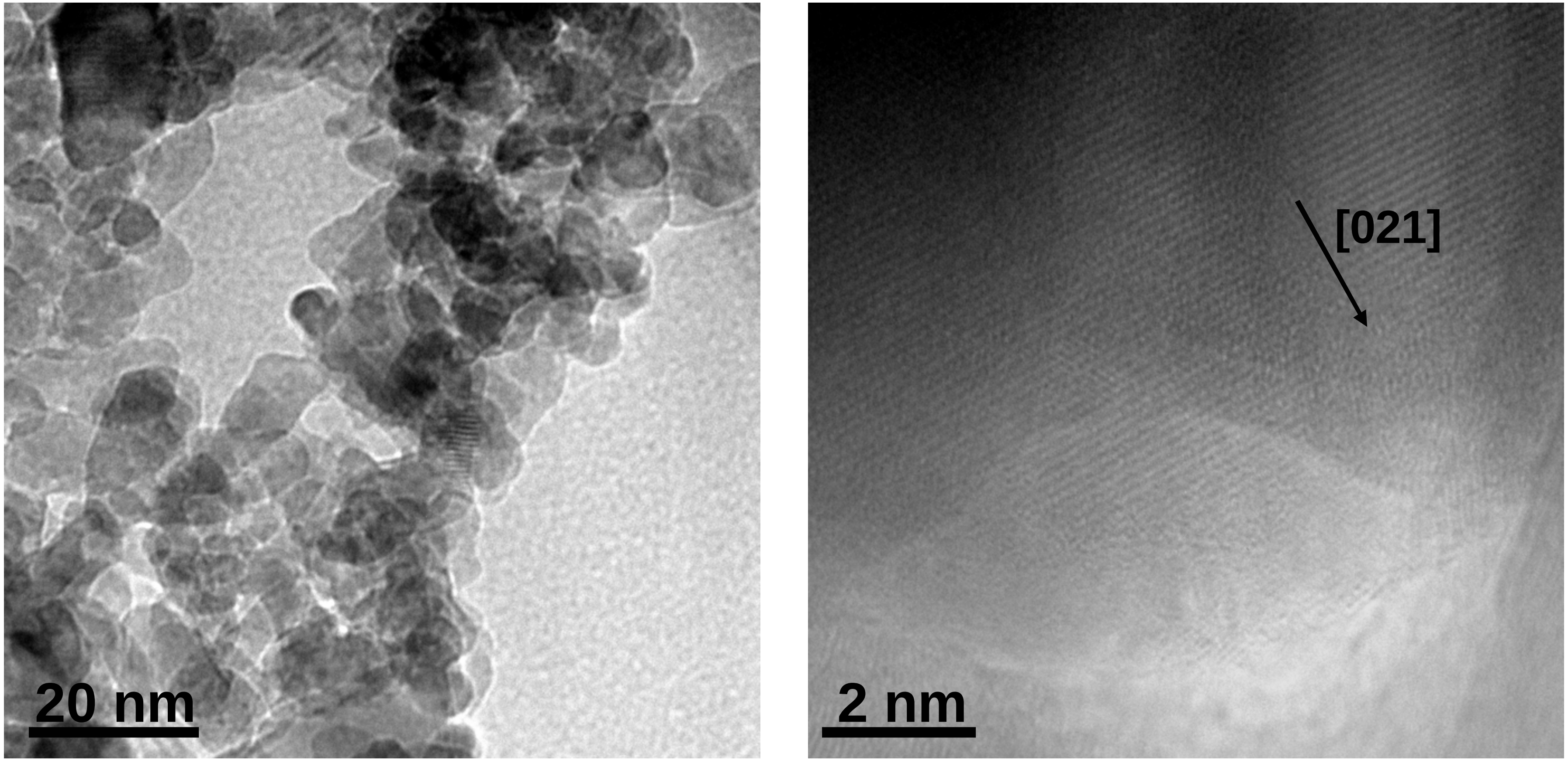
Antimonides (solid-solid reactions)

$$4\ Zn^* + 3\ Sb^* \xrightarrow{300^\circ\text{ C}/275^\circ\text{ C}} \text{nc-}Zn_4Sb_3$$

$$Zn^* + Sb^* \xrightarrow{300^\circ\text{ C}} \text{nc-}ZnSb$$

$$Co^* + 3\ Sb^* \xrightarrow{300^\circ\text{ C}} \text{nc-}CoSb_3$$

ZnSb nanopowders (13 nm)

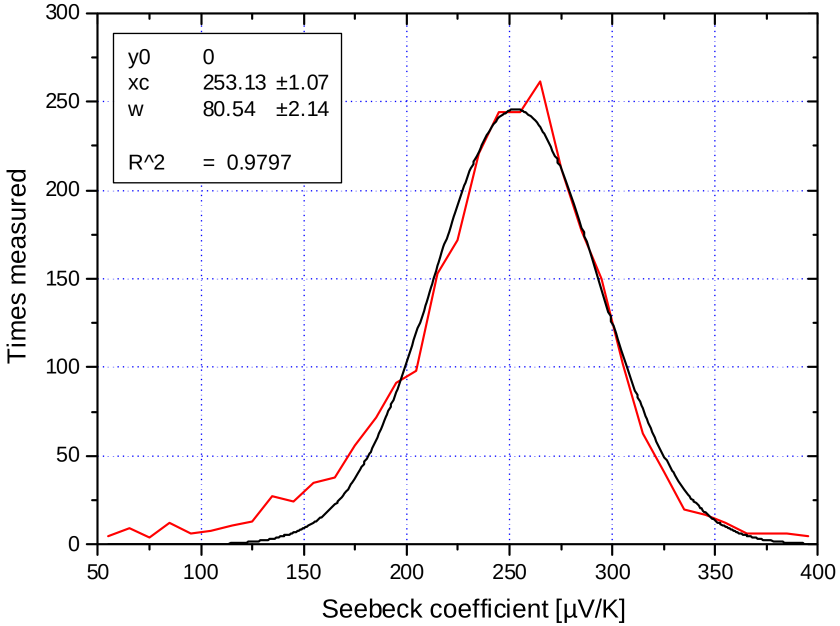


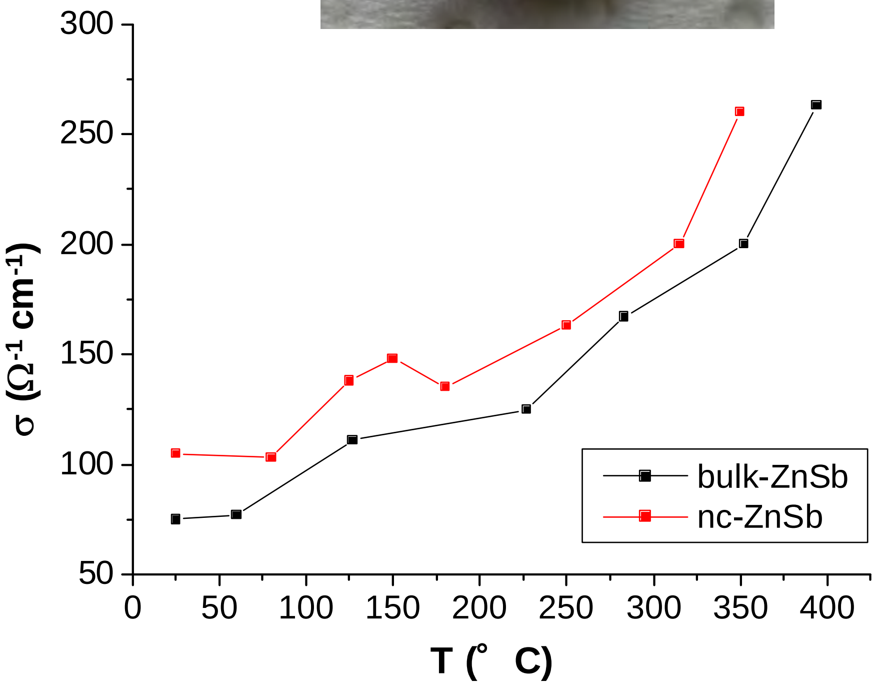
particle size ~ 13 nm

Compacting and TE data for nc-ZnSb

- Uniaxial hot-pressing (450° C, 100 MPa): stable samples with a density of 4.9 g/cm^3

- Seebeck coefficient S = 253 ± 2 μV/K (bulk: 196 μV/K)[1]





$S^2\sigma$ = 6.8 μW/(K^2 cm) nc-ZnSb

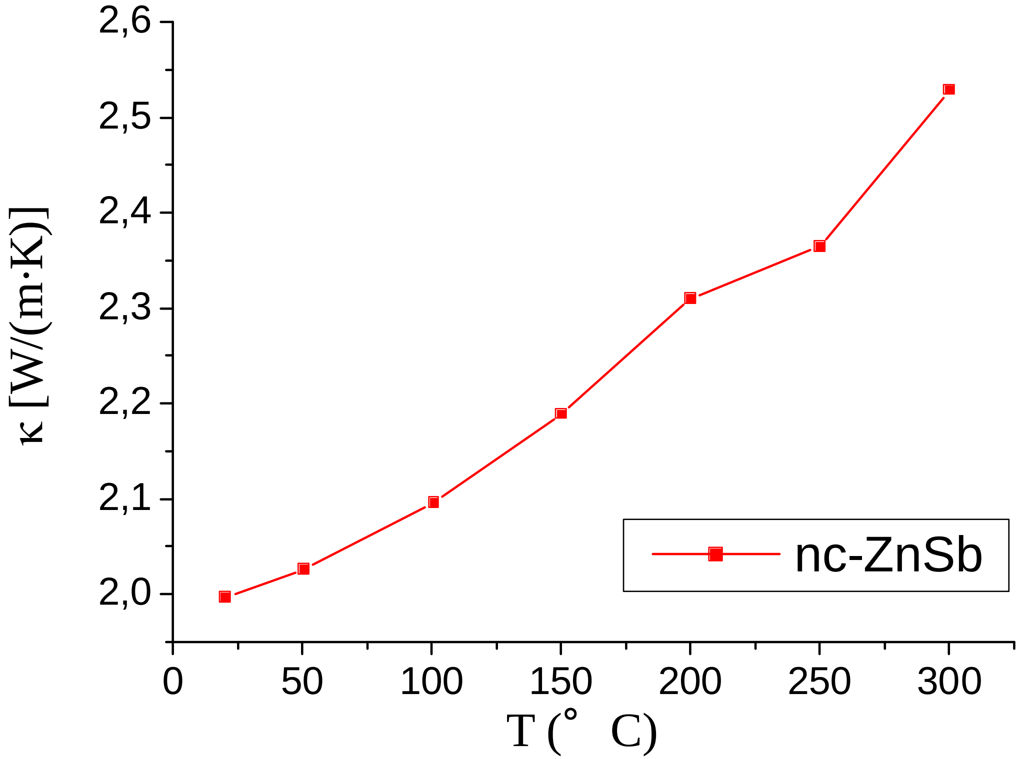
$S^2\sigma$ = 3.5 μW/(K^2 cm) bulk-ZnSb[1]

[1] P. J. Shaver, J. Blair, *Phys. Rev*. **1966**, *141*, 649.

Compacting and TE data for nc-ZnSb

- Uniaxial hot-pressing (450° C, 100 MPa): stable samples with a density of 4.9 g/cm^3

- Seebeck coefficient S = 253 ± 2 μV/K (bulk: 196 μV/K)[1]



ZT (293 K) = 0.100 nc-ZnSb

ZT (293 K) = 0.044 bulk-ZnSb

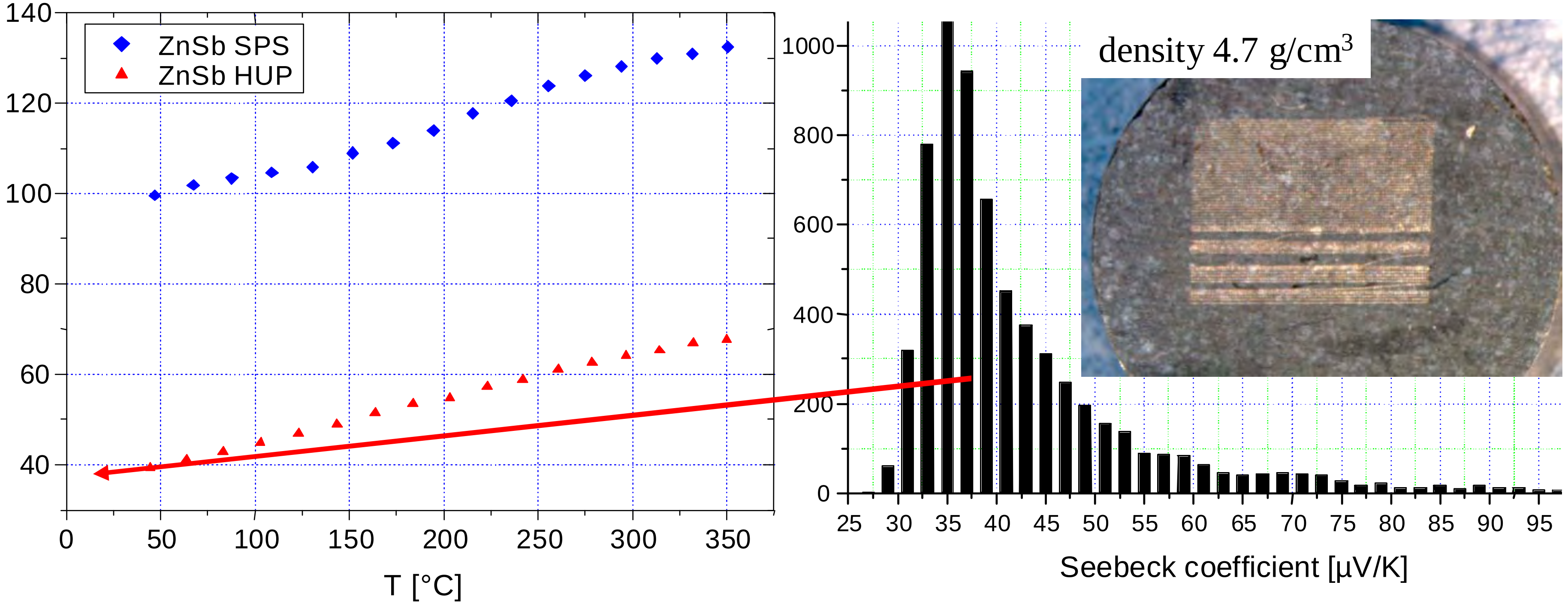
ZT (nano) = 2.2 *ZT* (bulk)

[1] P. J. Shaver, J. Blair, *Phys. Rev.* **1966**, *141*, 649.

[2] L. T. Zhang, M. Tsutsui, *J. All. Comp.* **2003**, *358*, 252.

Influence of the method of compacting: ZnSb (20 nm)

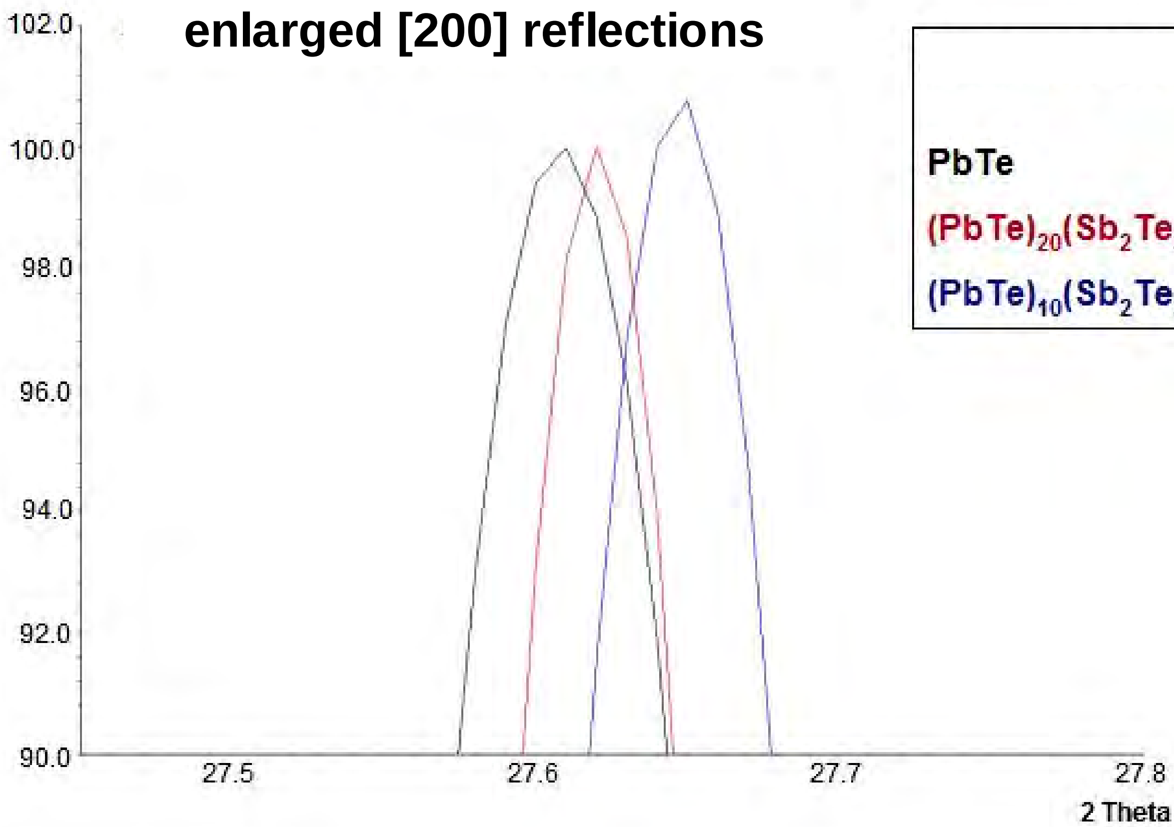
S(T) for HUP and SPS **S-scan after one thermal cycle**



→ Improved stability of data with prolonged synthetic procedure

Ternary Phases in the System PbTe - Sb_2Te_3

$$x\ \text{nc-PbTe} + \text{nc-}Sb_2Te_3 \xrightarrow[\text{quenched}]{400°C,\ 17\ h} Pb_xSb_2Te_{x+3} \qquad (x = 20,10)$$



	a
PbTe	6.456 Å
$(PbTe)_{20}(Sb_2Te_3)_1$	6.454 Å
$(PbTe)_{10}(Sb_2Te_3)_1$	6.447 Å

Summary and Outlook

→ Thermoelectric energy conversion shows excellent potential for future recovery of waste heat in industry, vehicles and household

→ current and further miniturizarion allow the use of TE converters for sensing, communication, integrated systems and in biomedical industries

→ nanostructuring of good TE semiconductors has already shown the potential for a ZT of 2 that is required for widespread application

→ the need for more efficient energy recycling will also lead to relevant discoveries in the field of fundamental research (natural sciences and engineering)

Acknowledgement

Coworkers

D. Petri
I. B. Angelov
M. Artamonowa
C. Erk
M. Roskamp
W. Meng
B. N. Ghosh
C. Rohner

Cooperations

Dr. M. Steinhart (MPI Halle)
Prof. Dr. B. Koksch (FU Berlin)
Prof. Dr. H.-U. Reißig (FU Berlin)
Dr. J. Dernedde (Charité, Berlin)
Dr. H. Böttner, Dr. D. Ebling (Fraunhofer IPM, Freiburg)
Dr. E. Müller, C. Stiewe (DLR Köln)

Funding

Deutsche Forschungsgemeinschaft (SFB 765, SPP 1165, SPP 1386)
Fonds der Chemischen Industrie (to C.E.)