New developments in the research of thermoelectric materials

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CiQUS

Nanofabrication: concepts, techniques and applications in Nanotechnology

Jaca, July 2013

Outline

I.- Brief introduction to thermoelectricity

II.- Applications of thermoelectric systems

III.- Theoretical approach to thermoelectric phenomena

IV.- Old thermoelectric materials and approaches

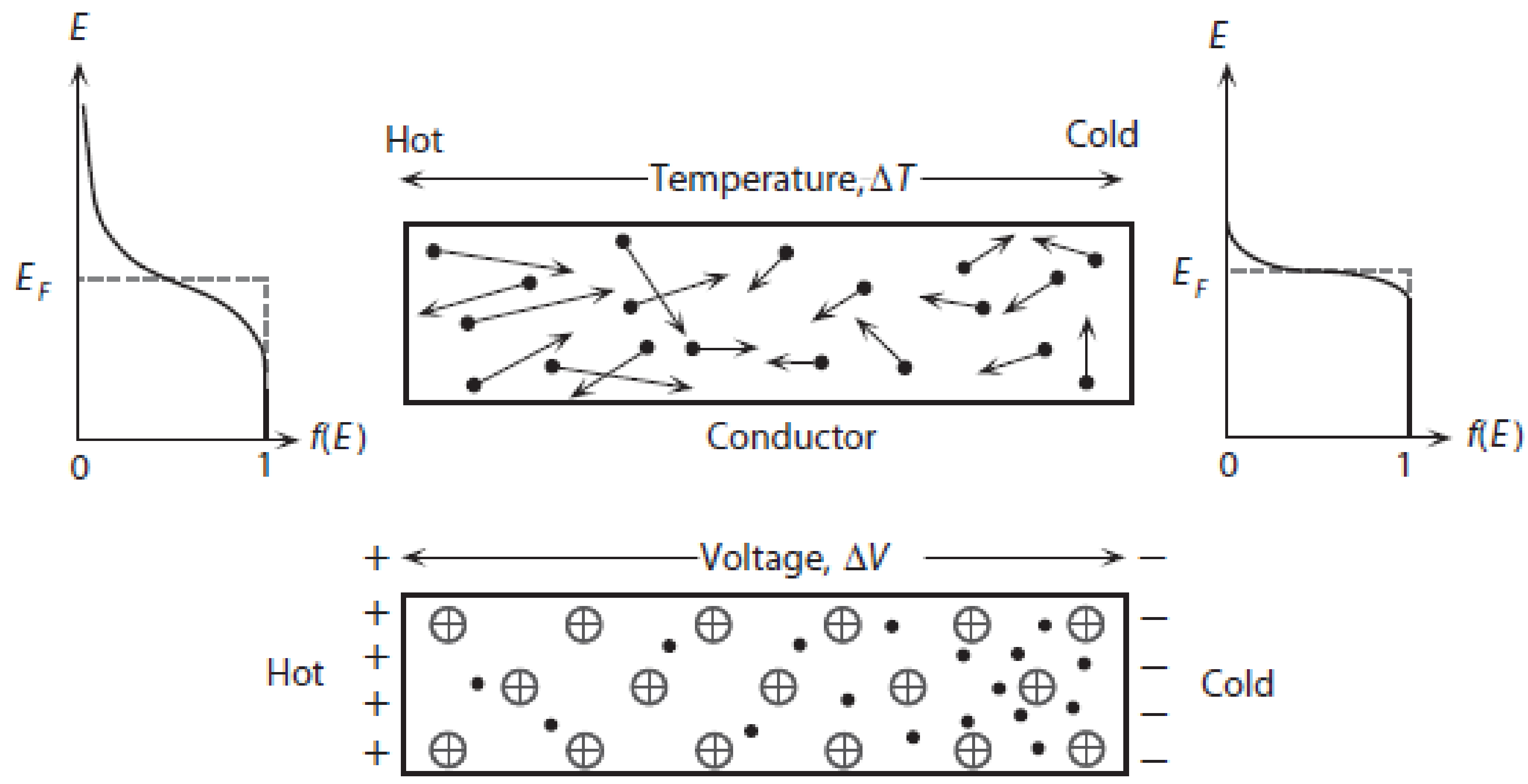
V.- New approaches to an old problem: nano-TE

VI. Challenges in the characterization of nano-TE materials

I. What is thermoelectricity ?

The generation of an electrical voltage from a temperature gradient and vice versa.

$$\Delta V \Leftrightarrow \Delta T$$



I. What is thermoelectricity ?

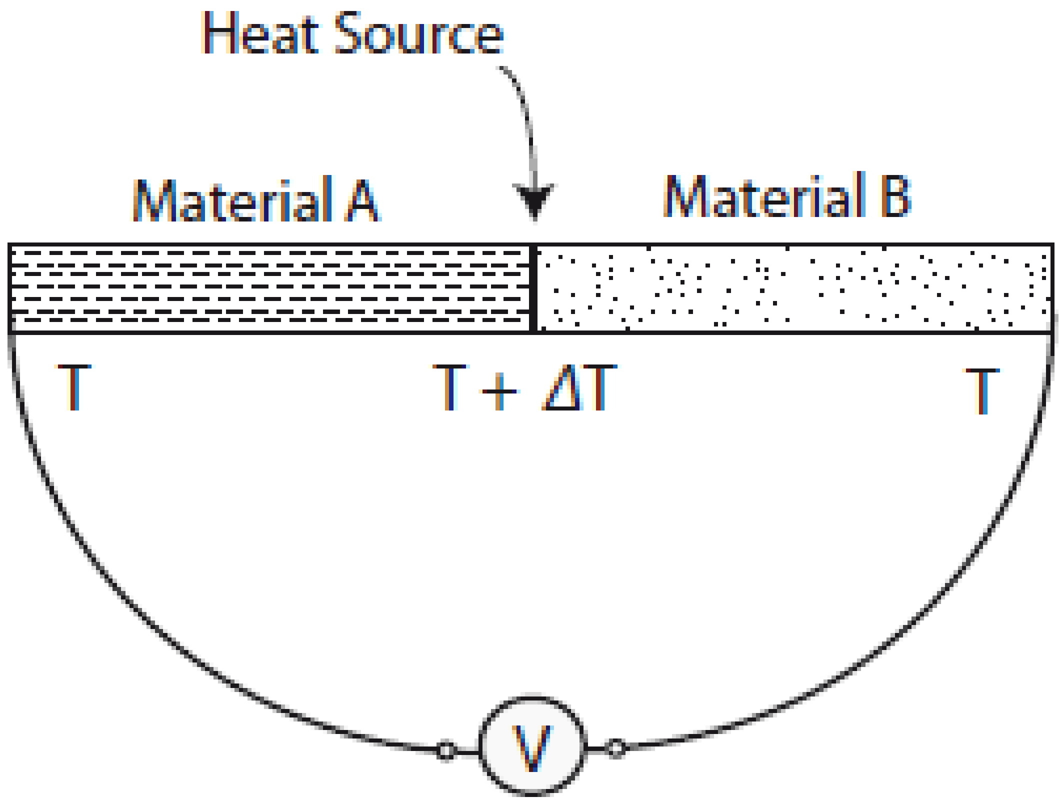
The generation of an electrical voltage from a temperature gradient and vice versa.

$$\frac{\Delta V}{\Delta T}$$

$$[V/K] \times Q = [J/K]$$

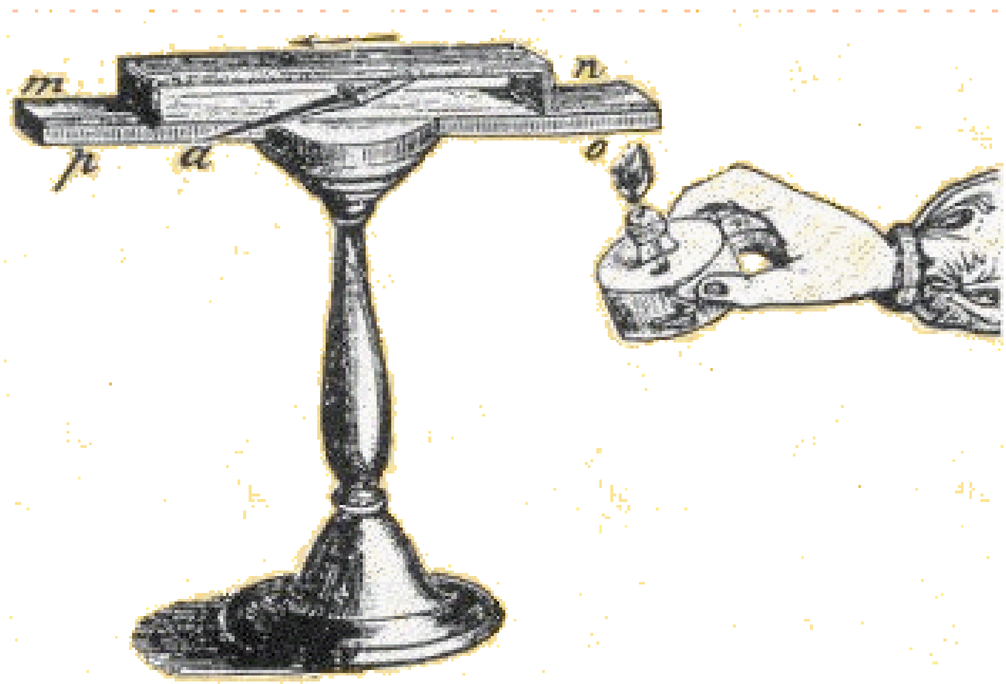
Entropy per charge carrier

$$\approx \mu V/K$$

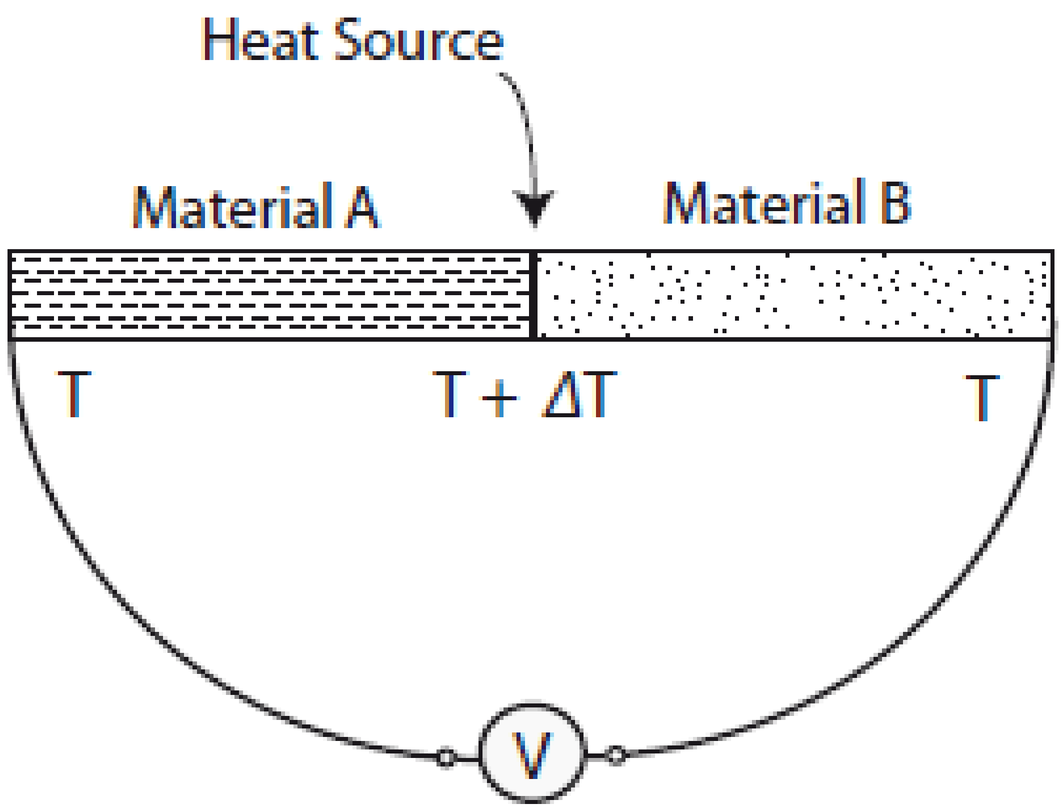


The Seebeck effect

$$S = \frac{\Delta V}{\Delta T}$$



Thomas Johan Seebeck (1821)



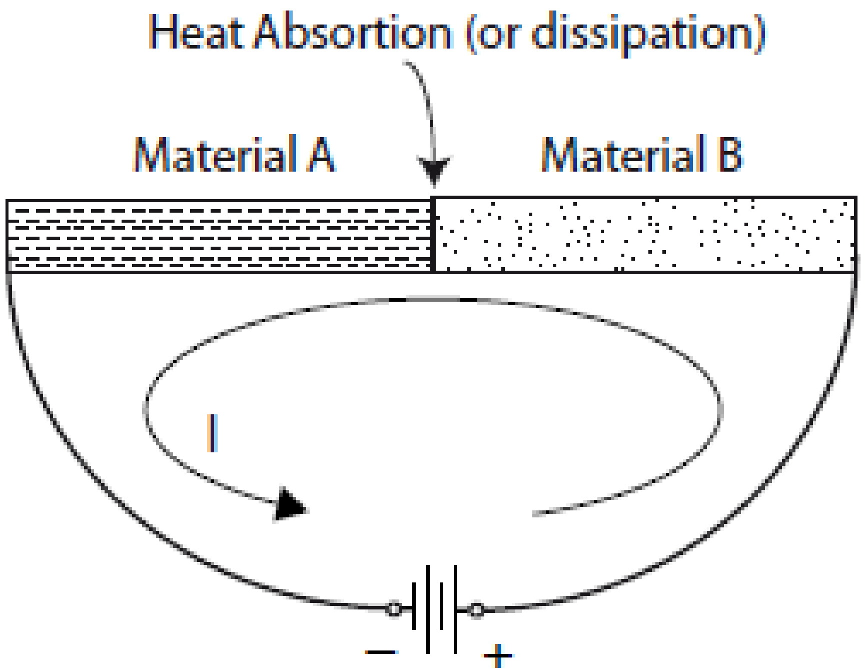
I. Seebeck coefficient of some representative systems

Material	Seebeck Coefficient (μv/K)
Se	900
Si	440
Sb	47
Pt	-5
Ni	-1.5
Te	500
Pb	4.0
CrN	-150
$SrTiO_{3-\delta}$	-800

I. Basic thermoelectric phenomena

The Peltier effect

$$Q = \Pi_{AB} J$$



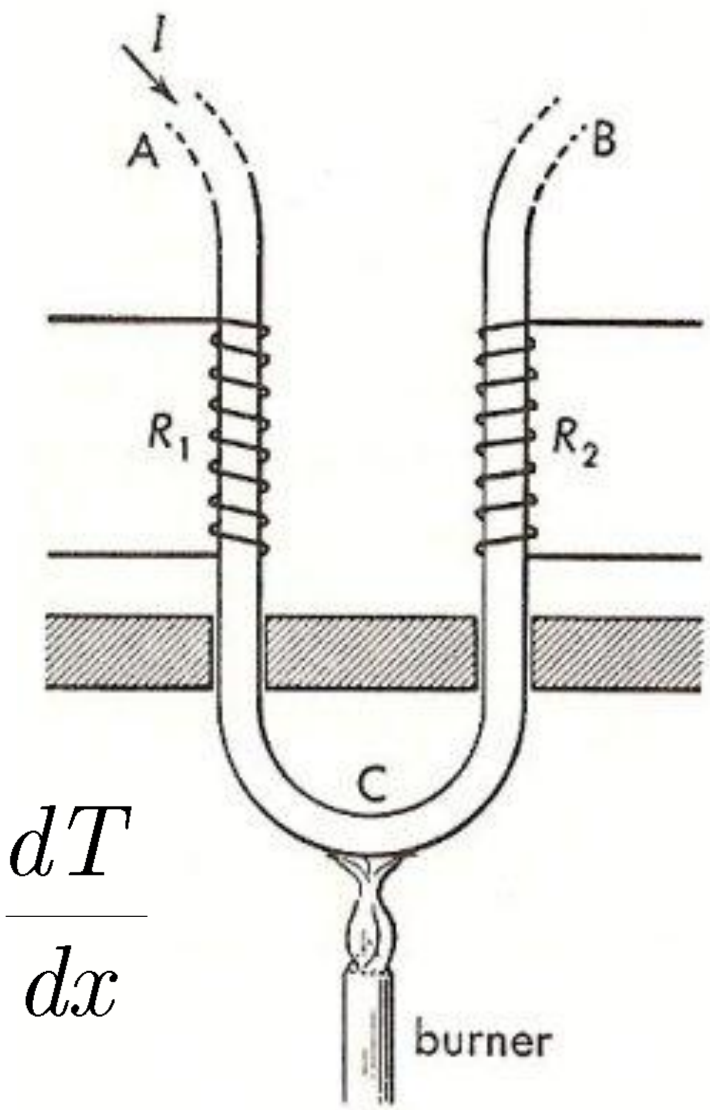
Jean Charles Peltier (1834)

The Thomson effect

$$\tau = \frac{TdS}{dT}$$

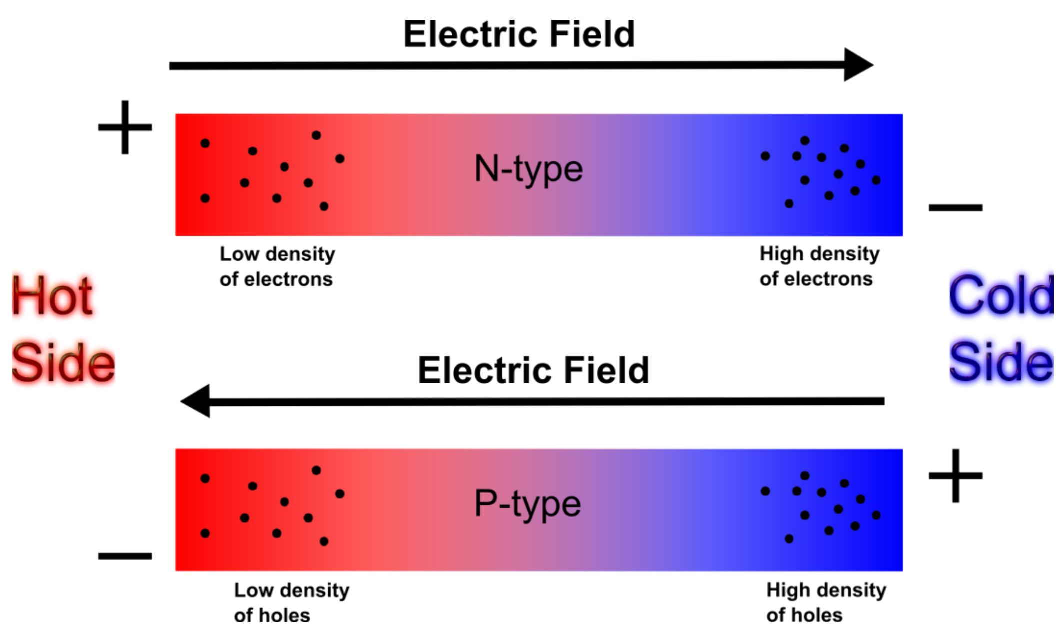
$$\Pi = ST$$

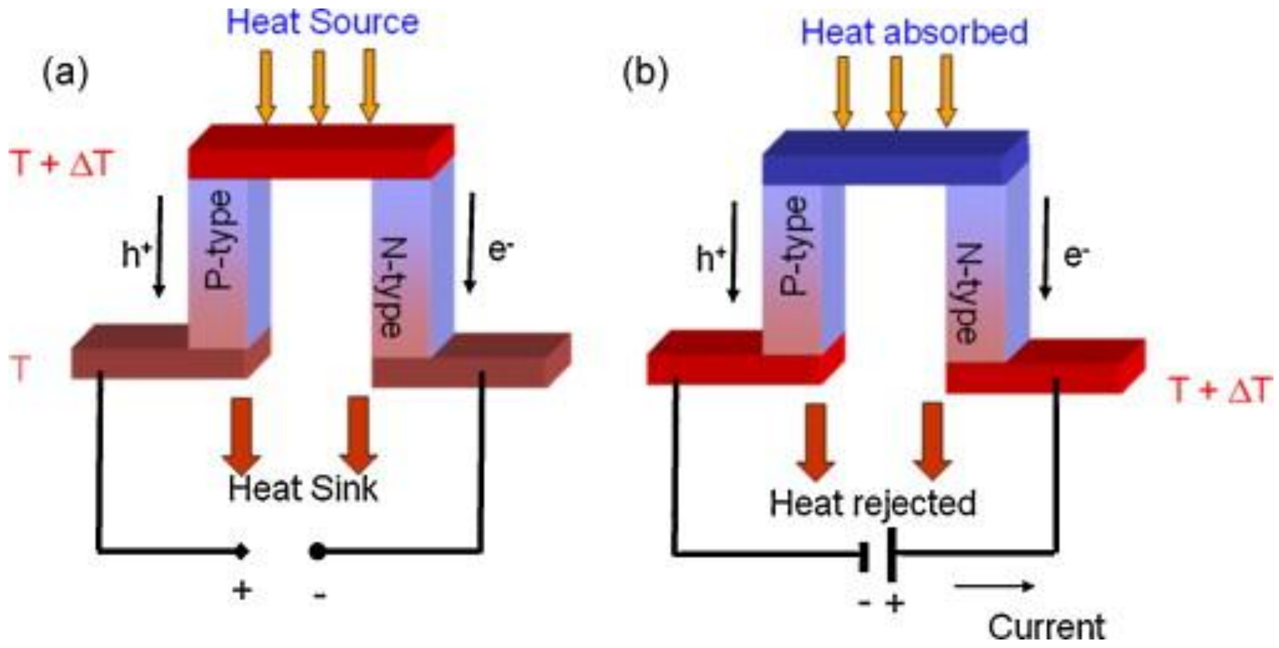
$$Q = \rho J_x^2 - \tau J_x \frac{dT}{dx}$$

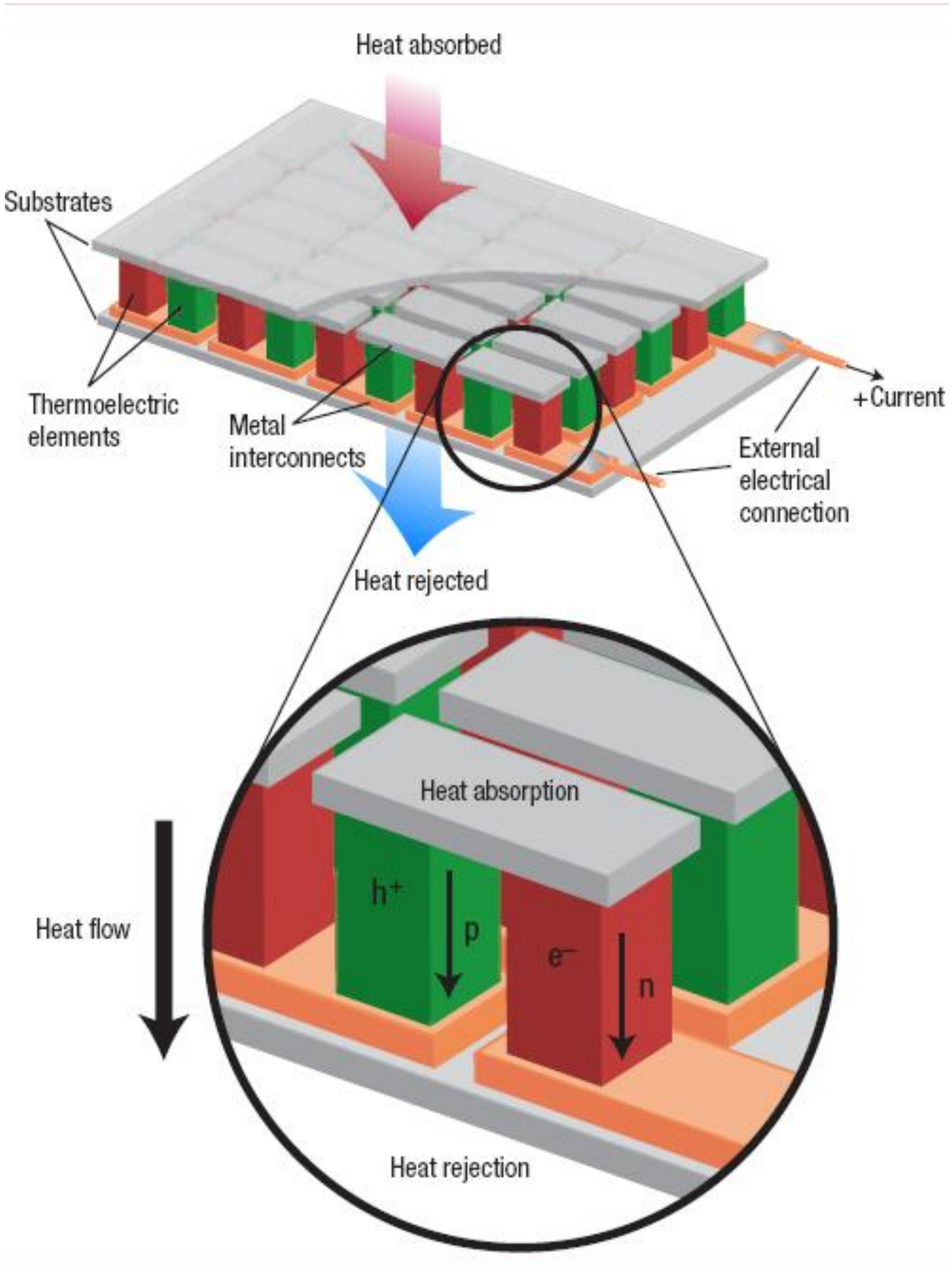


Willian Thomson (Lord Kelvin) (1854)

From TE materials to devices







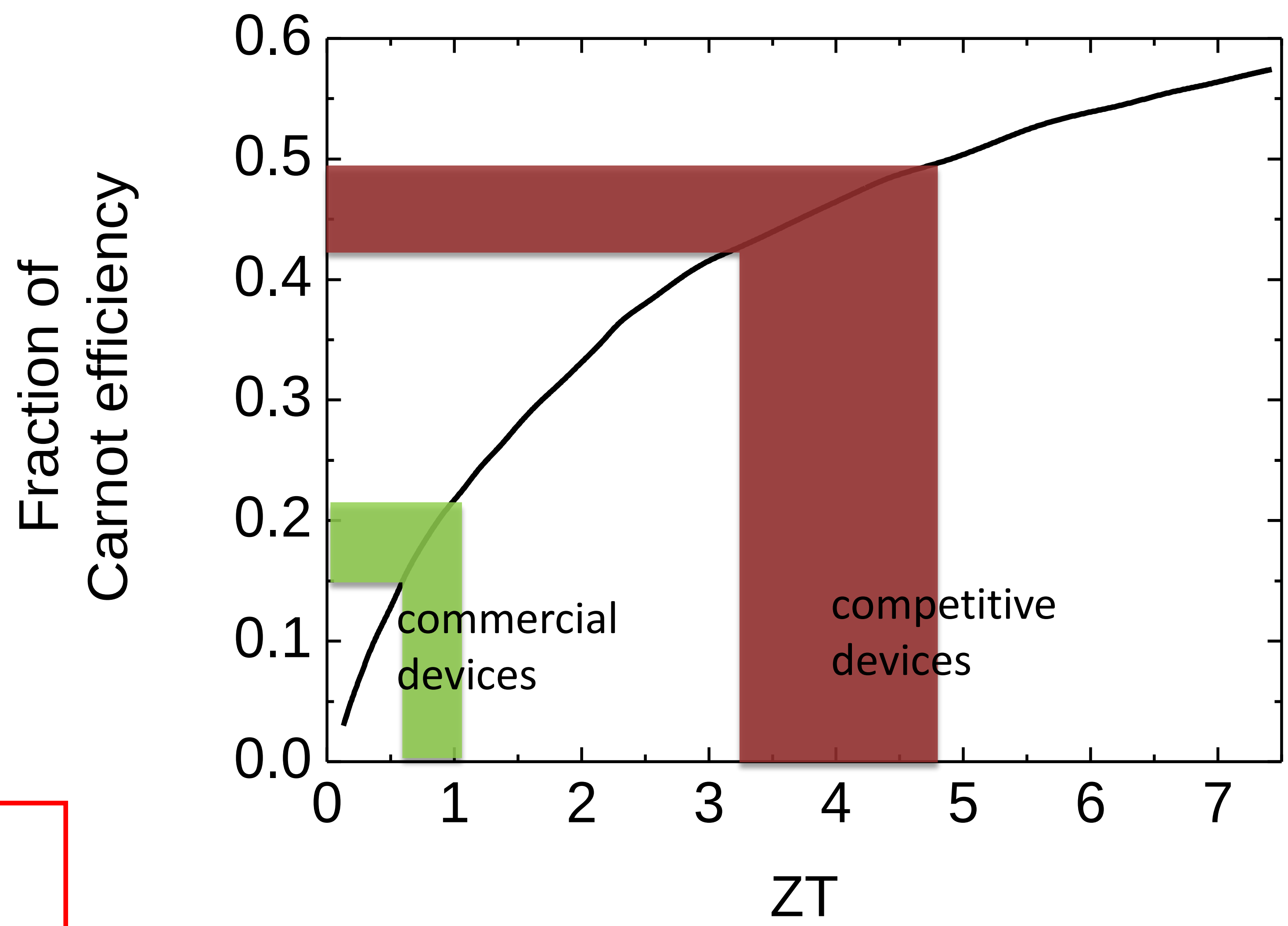
Efficiency of a TE device

Thermoelectric Figure of Merit

$$Z = \frac{S^2\sigma}{\kappa}$$

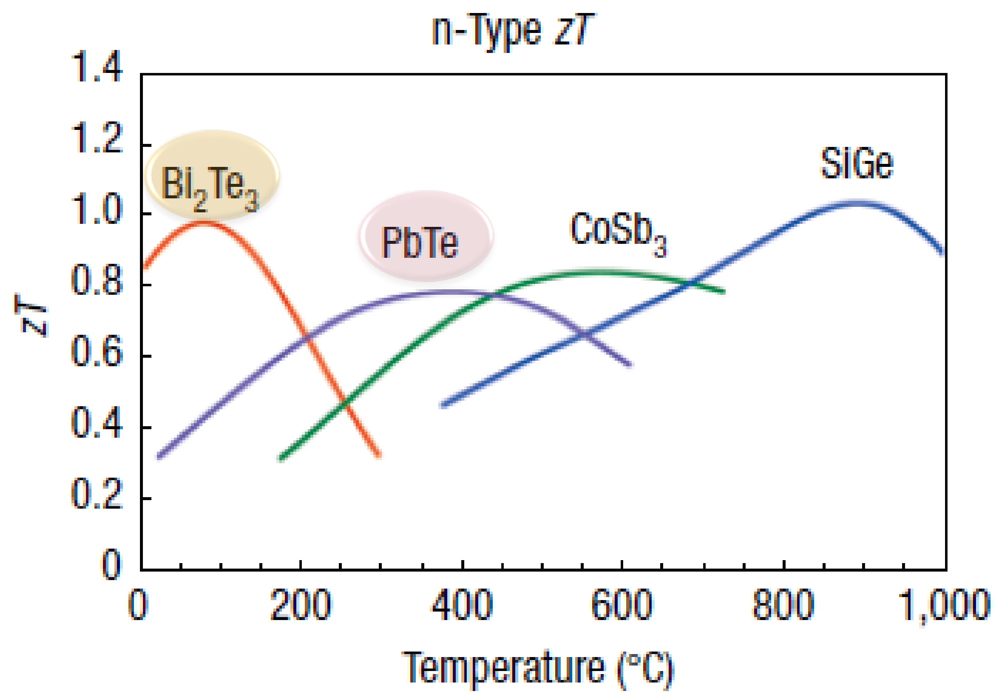
Carnot Efficiency

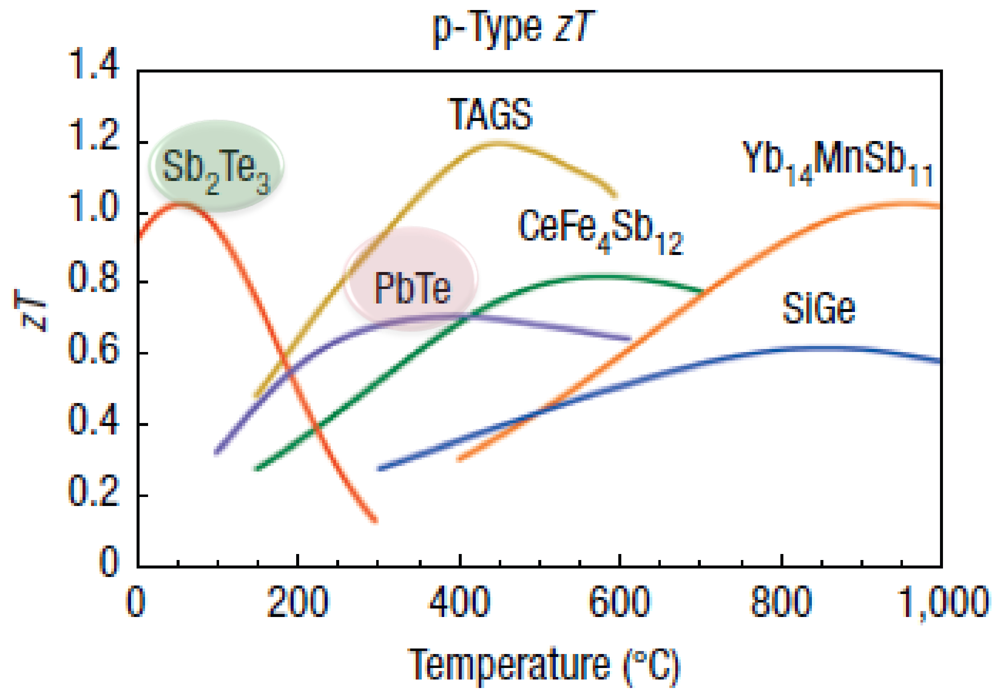
$$\eta = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1+ZT_{avg}}-1}{\sqrt{1+ZT_{avg}}+\frac{T_{cold}}{T_{hot}}}$$



I. Efficiency of TE materials

Best “**classic**” thermoelectric materials



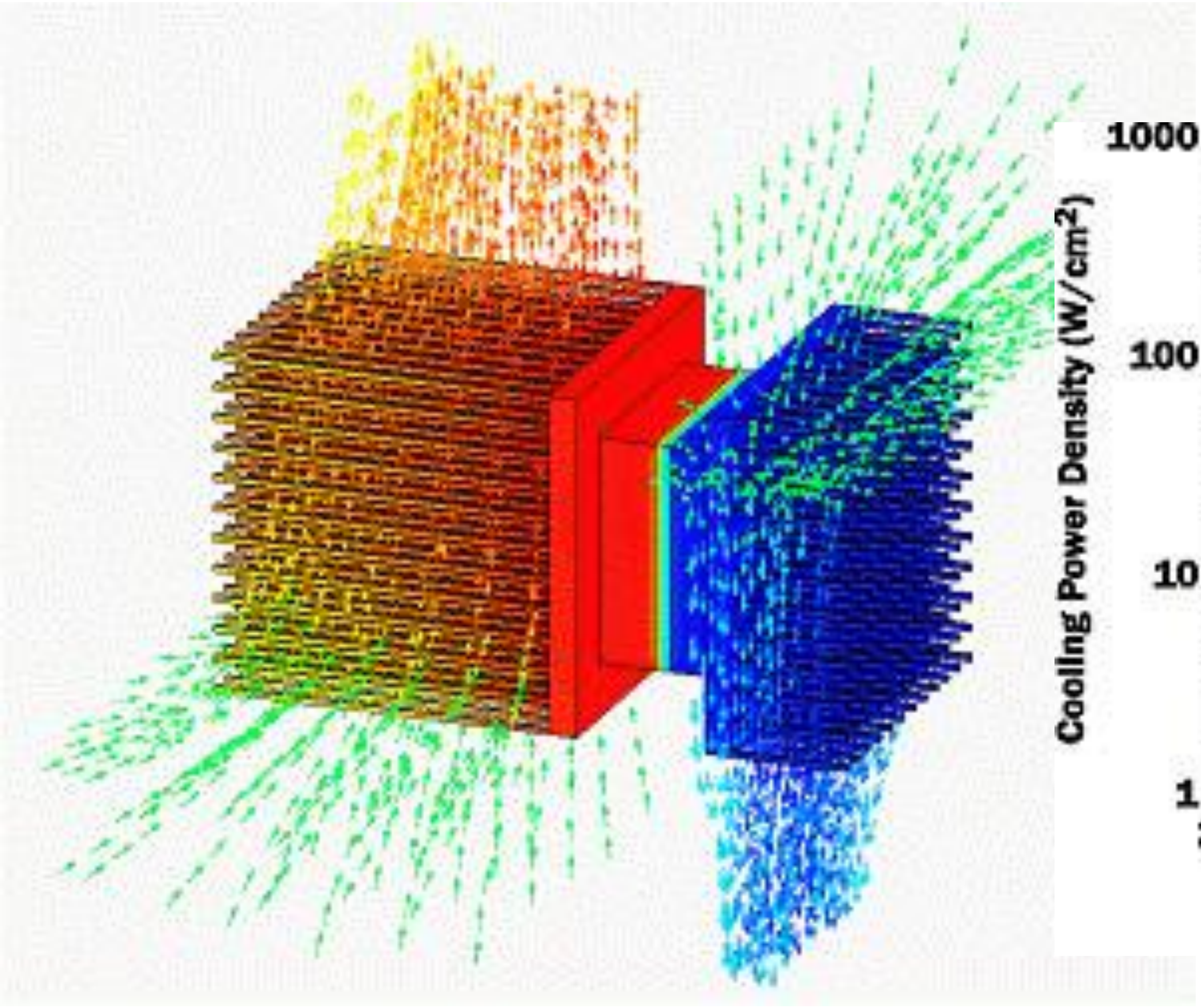


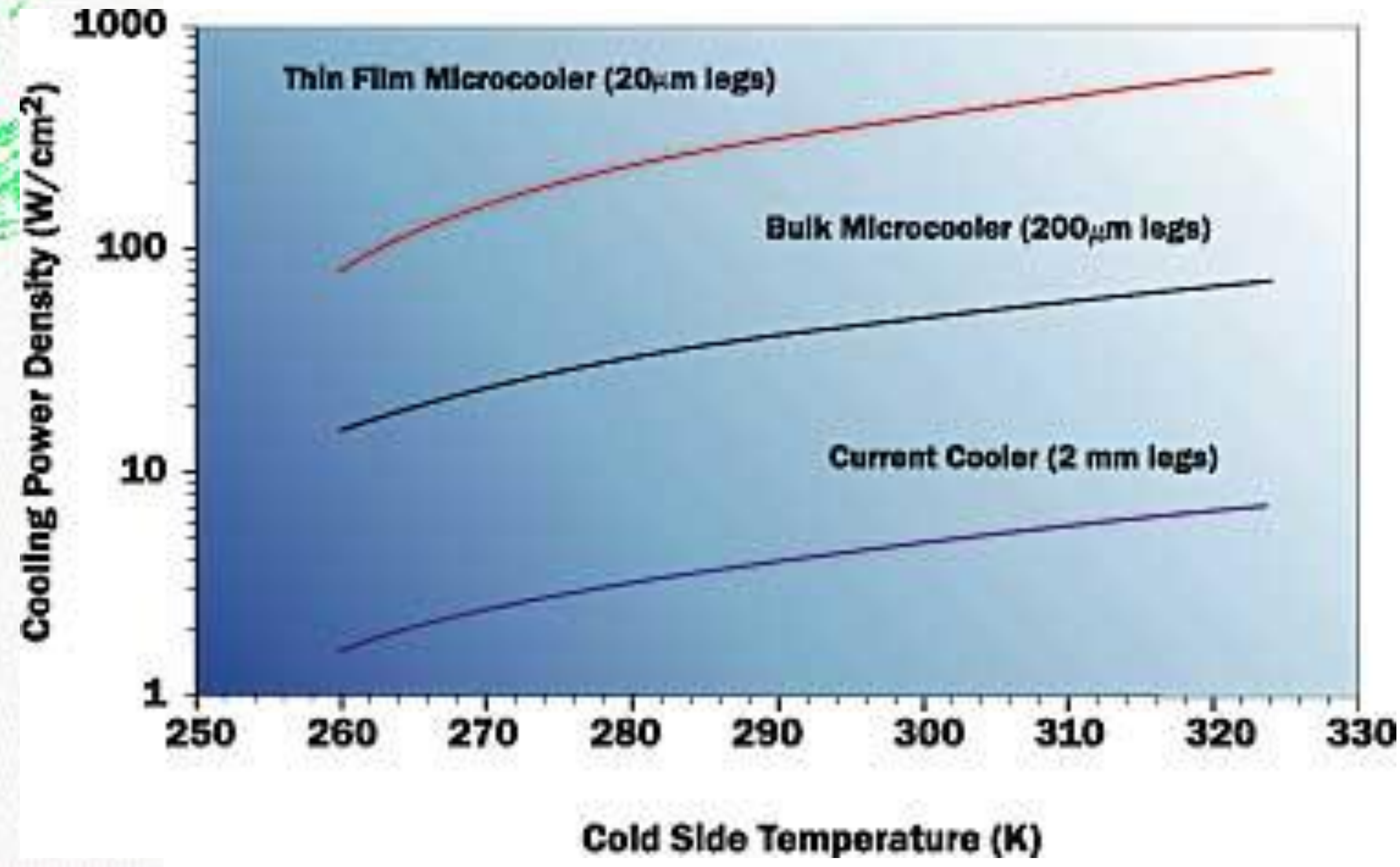
II. Applications of TE systems

Applications of TE systems

- Energy Harvesting
- Cooling (electronics, etc)

II. Cooling (electronics)





II. Temperature control

today…

POWER SOURCE
- Batteries

CLIMATE CONTROL
- None

Enabled by
Thermoelectrics (TE)

…tomorrow

POWER SOURCE
- Logistic fuel based system

CLIMATE CONTROL
- Thermoelectric based cooling/heating
- On-demand

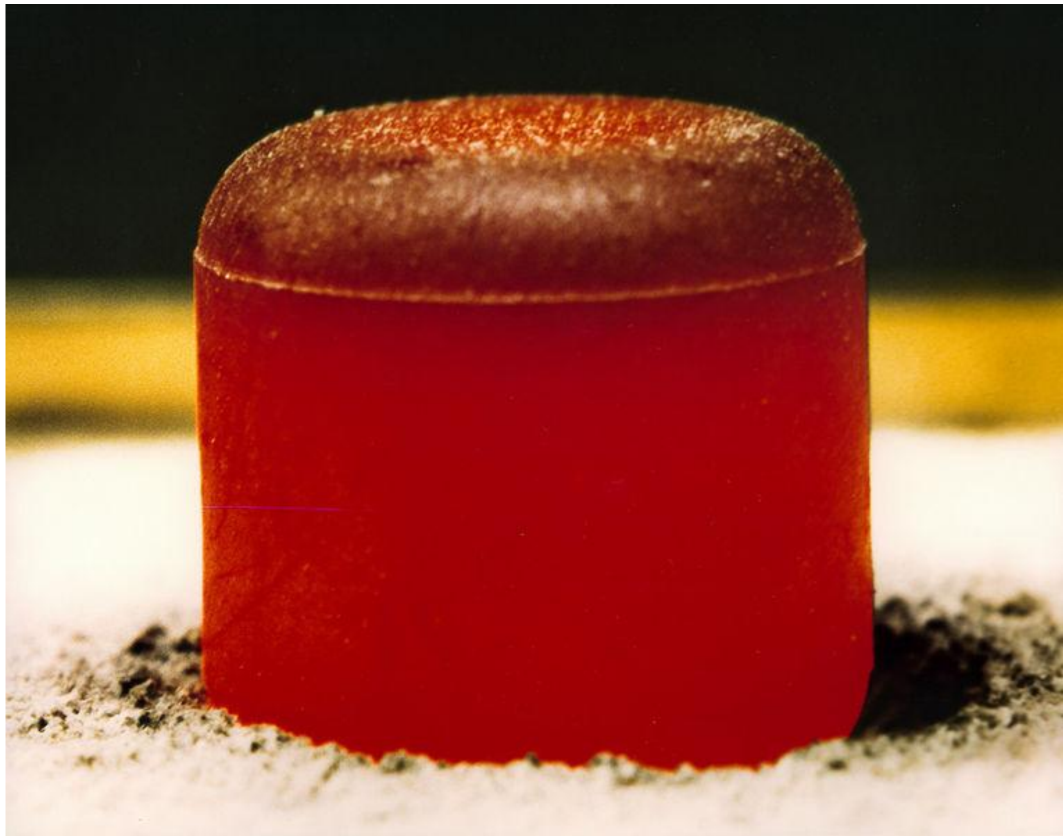
IMPACT
- >30% weight savings over existing systems

Assumptions
12 hour mission @ 110°F ambient temperature

DARPA TTO Program Manager: Ed van Reuth

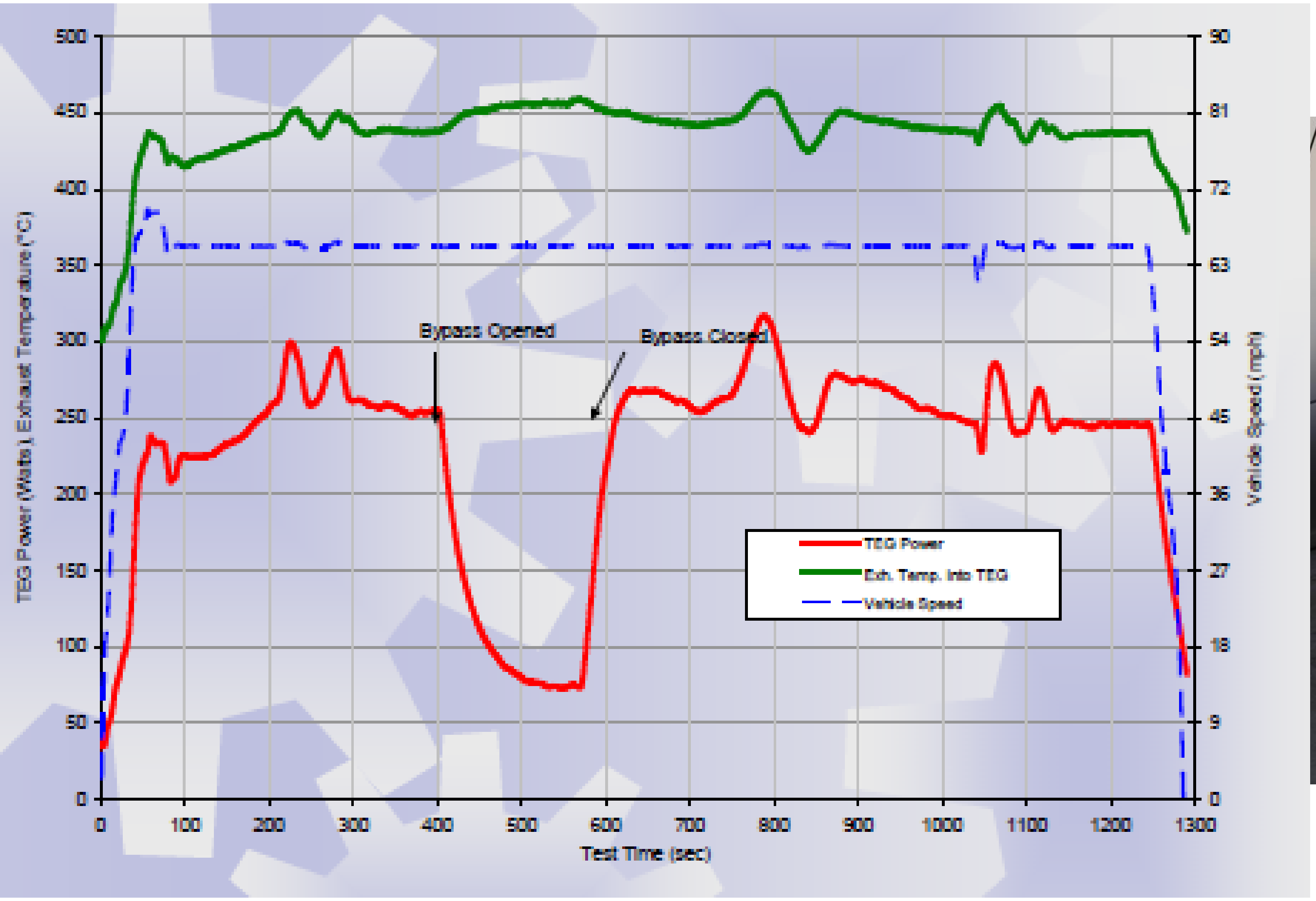
II. Power generation from energy harvesting

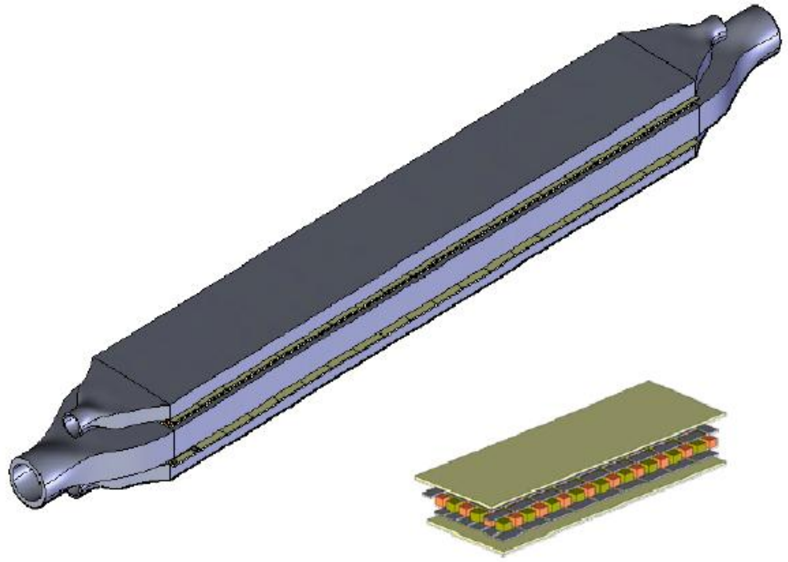
Radioisotope thermoelectric generator



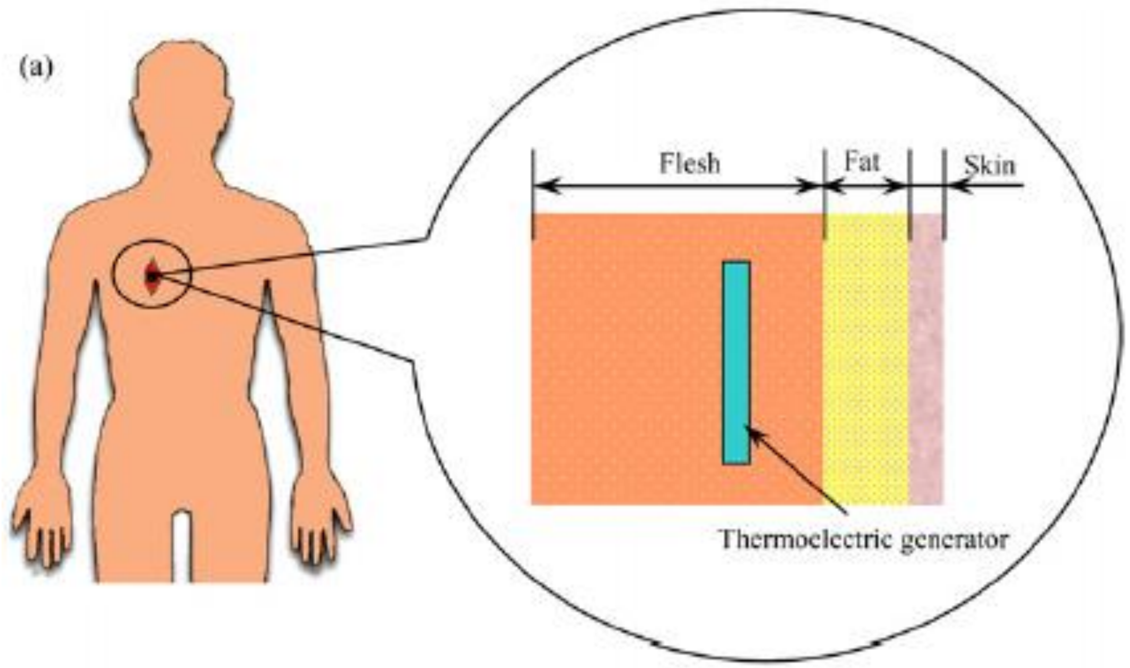
$^{238}PuO_2$

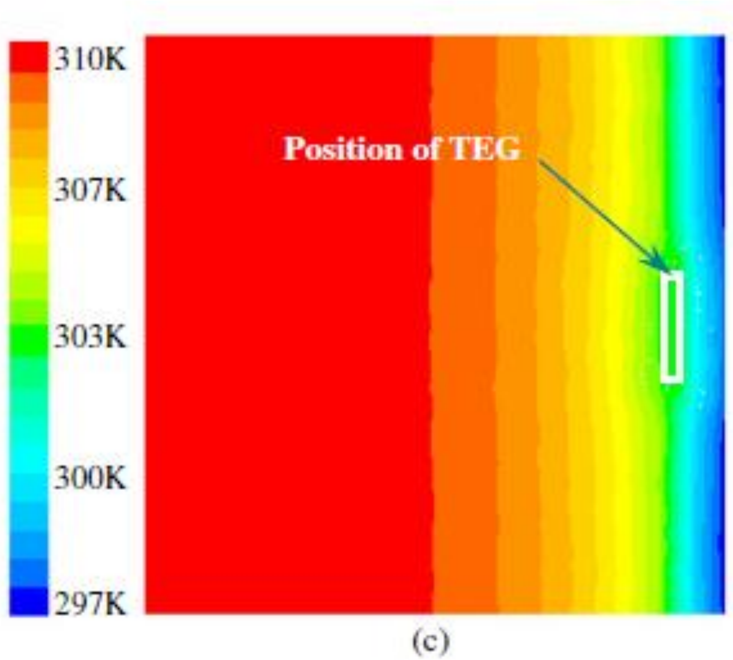
II. Power generation from energy harvesting

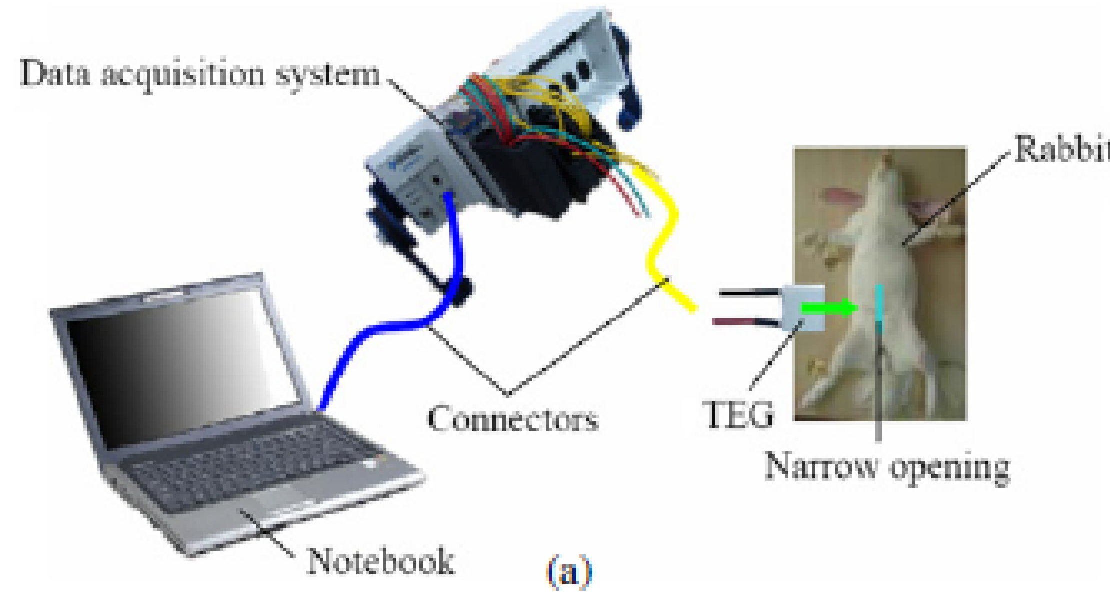


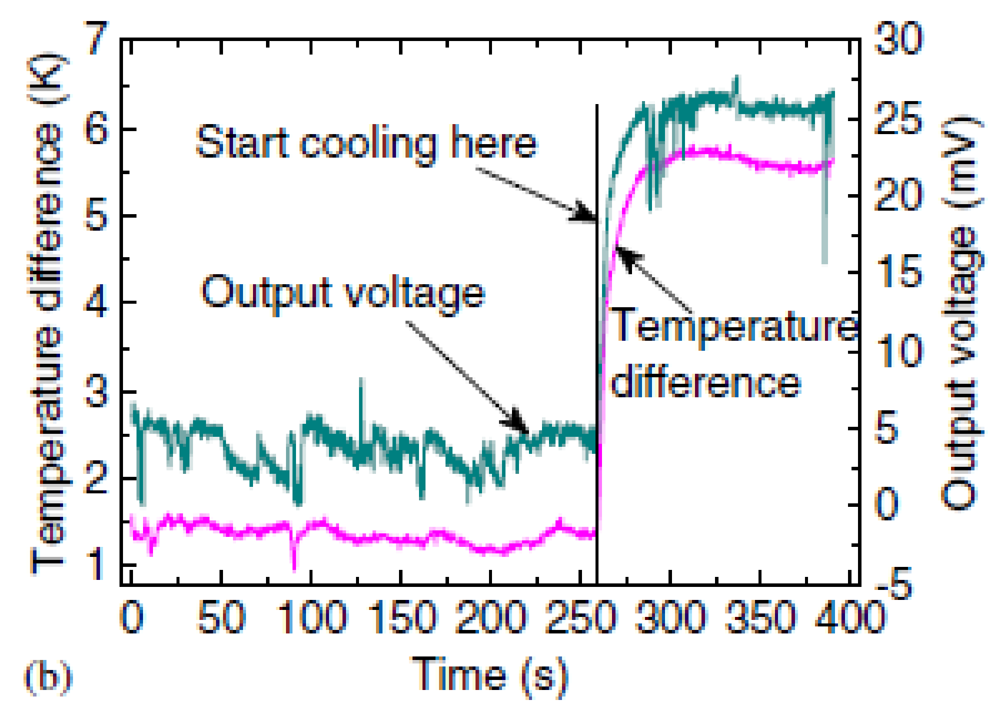


II. Biomedical applications



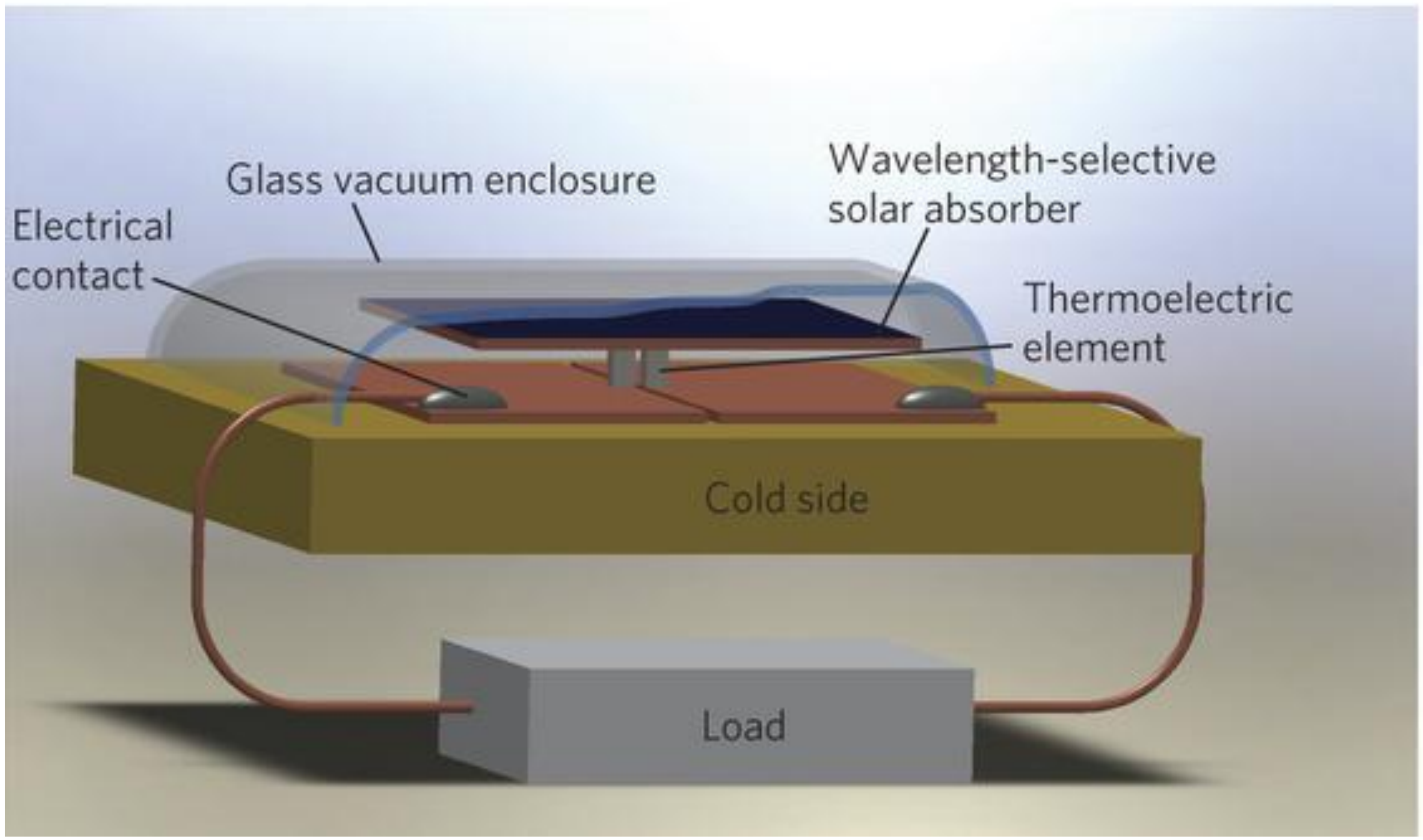


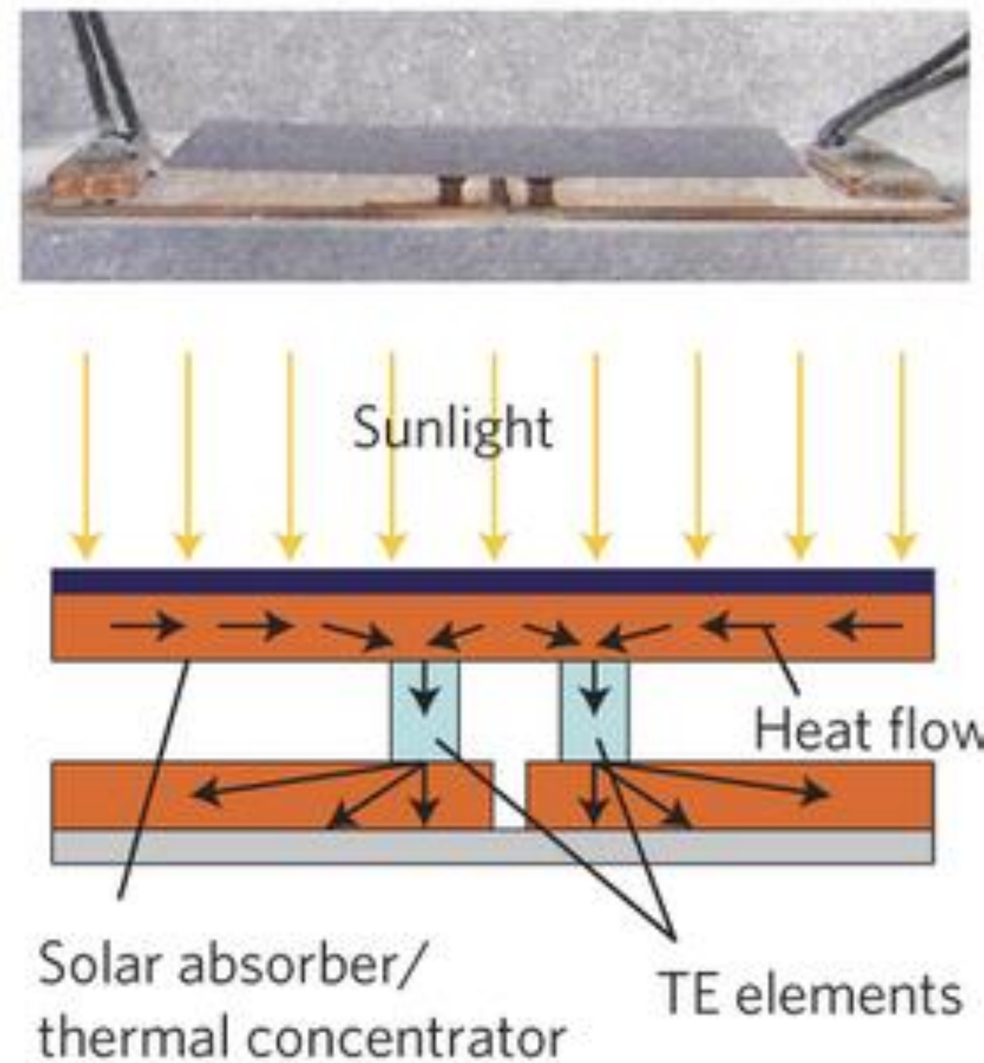




Y. Yang et al., J. Phys. D: Appl. Phys. **40**, 5790 (2007)

II. Increasing efficiency in hybrid devices





D. Kraemer et al., Nature Materials **10**, 532 (2011)

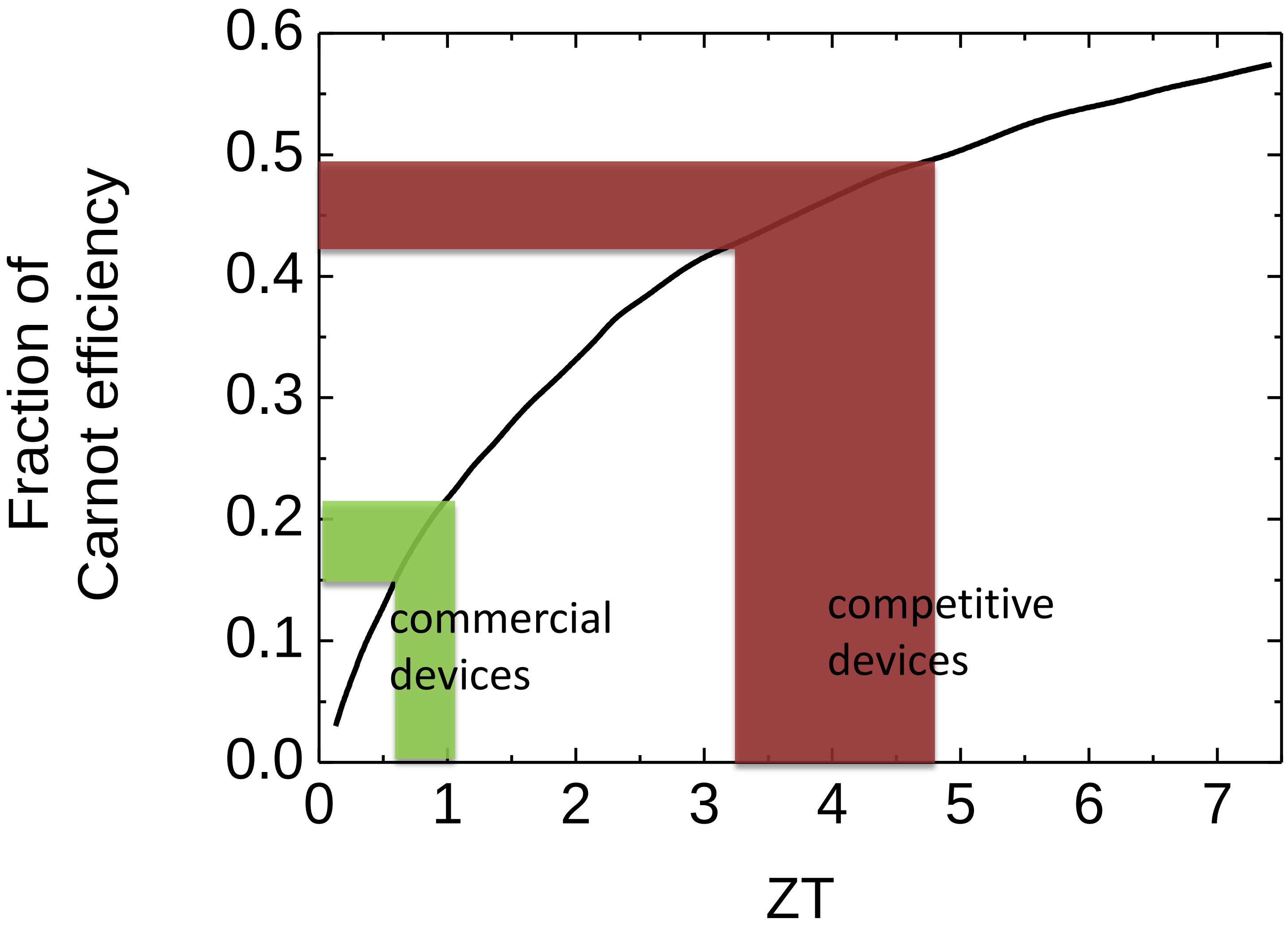
II. Power generation from energy harvesting

"heat sources" are everywhere!

The objective:

- ❑ To reach ZT = 3-4

$$Z = \frac{S^2\sigma}{\kappa}$$



- ❑ How?: reducing thermal conductivity without degrading electrical conductivity

III. Basic transport theory of TE phenomena

Derivation of the transport coefficients

$$J = \sigma E - S\sigma\nabla T$$

$$U = S\sigma T E - k\nabla T$$

$$\tau(E) = \tau_0 E^r$$

$$S = -\frac{k}{e}\left(\eta - \frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)}\right), \qquad \eta = \frac{\mu}{kT}$$

J. M. Ziman, *Electrons and Phonons* (1960)

III. Basic transport theory of TE phenomena

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η>>1 (metals and degenerate semiconductors)

$$S = -\frac{\pi^2 kT}{3e}\left(\frac{8m^*}{h^2}\right)\left(\frac{\pi}{3n}\right)^{2/3}\left(\frac{3}{2}+r\right)$$

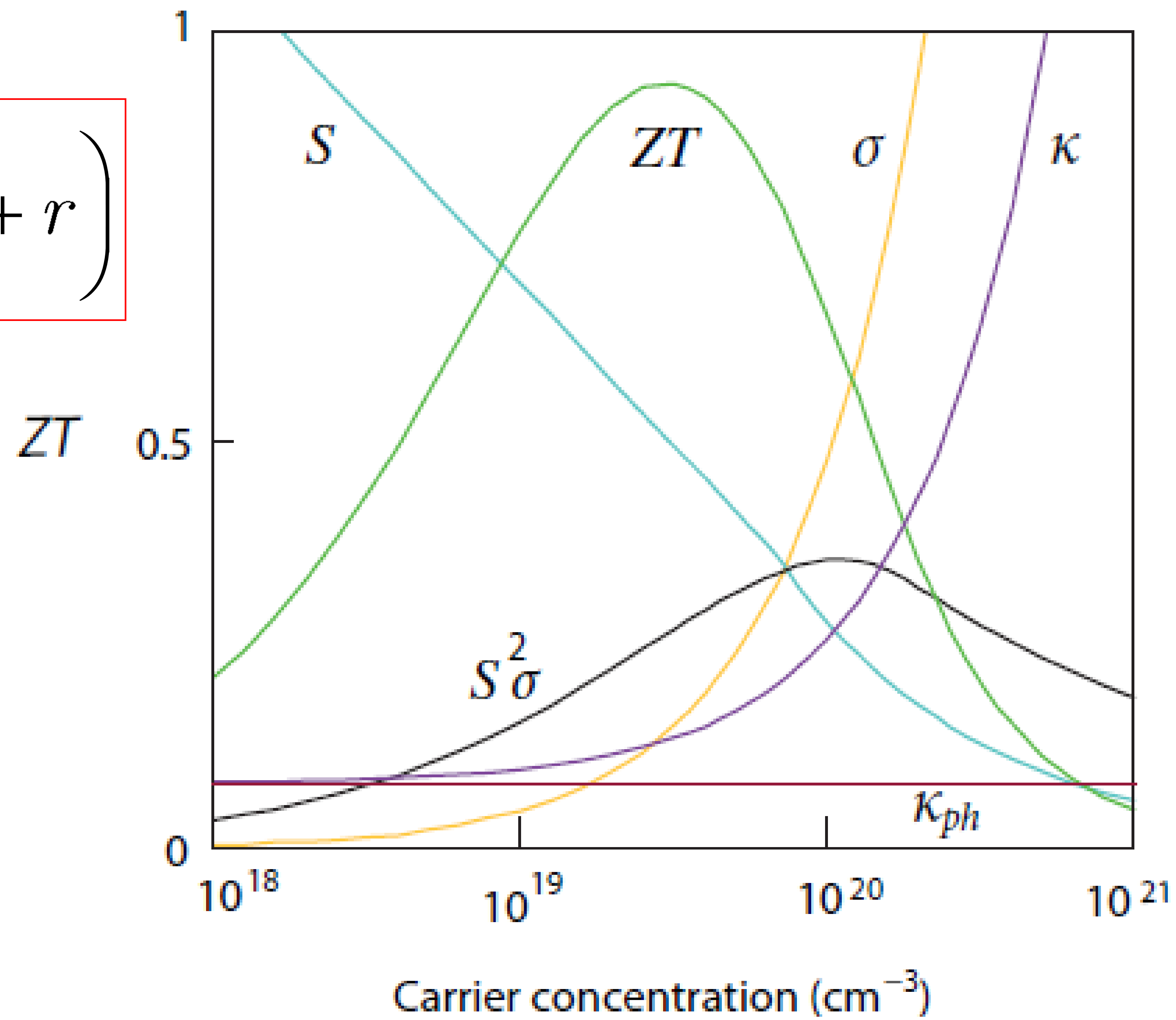
m* and n are the factors we can tune to increase S

III. Basic transport theory of TE phenomena

η>>1 (metals and degenerate semiconductors)

$$S = -\frac{\pi^2 k T}{3e}\left(\frac{8m^*}{h^2}\right)\left(\frac{\pi}{3n}\right)^{2/3}\left(\frac{3}{2}+r\right)$$

$$\sigma = -\frac{e^2 n \tau}{m^*}$$



TE power factor:

$$\mathrm{PF} = \mathrm{S}^2\sigma$$

III. Basic transport theory of TE phenomena

Classical semiconductors

for electrons

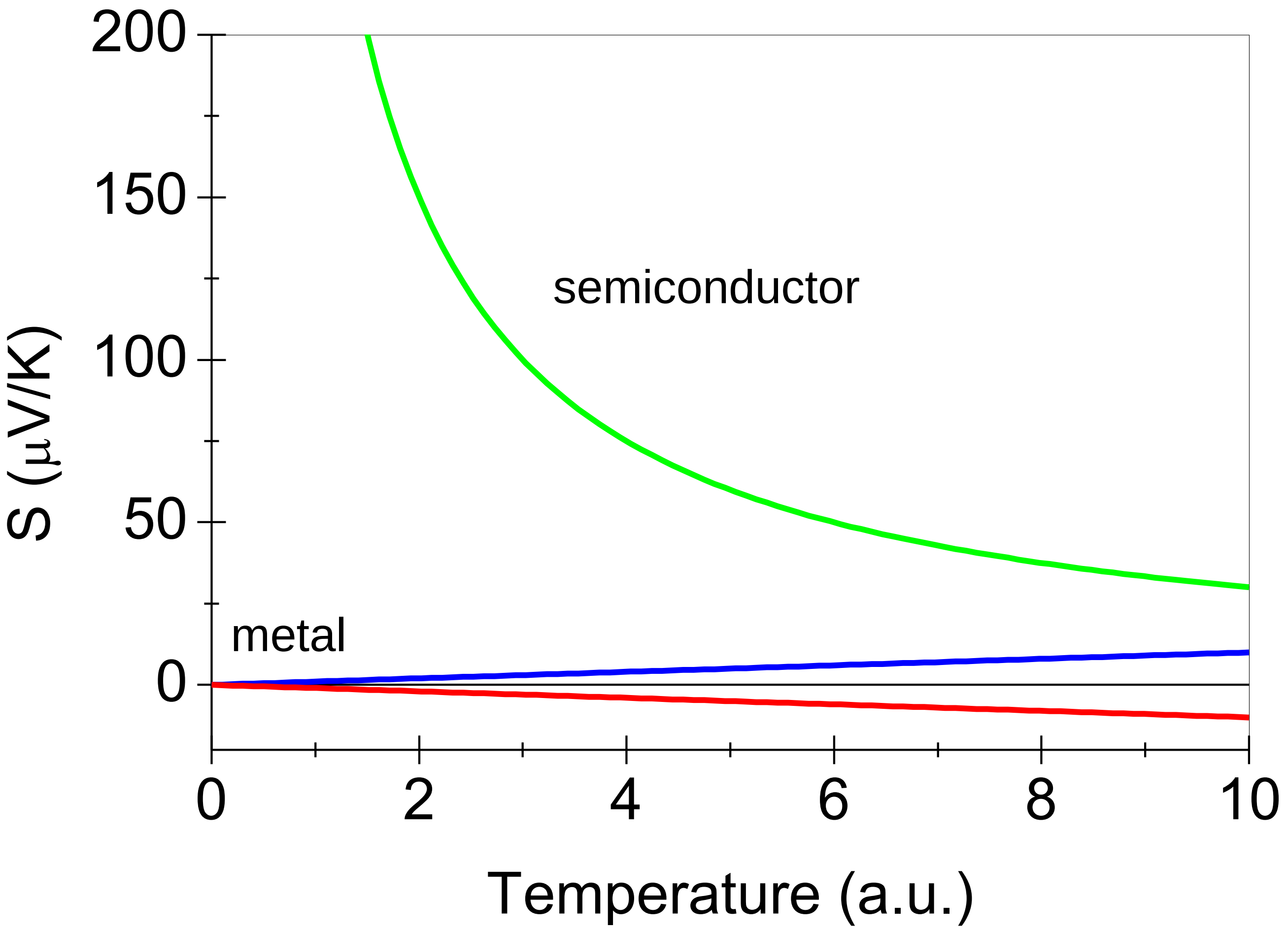
$$S = -\frac{k}{e}\left(\frac{E_c - \mu}{kT} + r + \frac{5}{2}\right)$$

for holes

$$S = \frac{k}{e}\left(\frac{\mu - E_v}{kT} + r + \frac{5}{2}\right)$$

for two-band conductors

$$S = \frac{\sigma_e S_e + \sigma_h S_h}{\sigma_e + \sigma_h}$$



J. M. Ziman, *Electrons and Phonons* (1960)

III. Basic transport theory of TE phenomena

The high temperature limit of the Boltzmann equation (Heikes formula)

$$S(T \to \infty) = -\frac{k}{e}\left(\frac{\mu}{kT}\right)$$

$$\frac{\mu}{T} = -\left(\frac{\partial \Xi}{\partial N}\right) = -k_B\left(\frac{\partial \ln \Omega}{\partial N}\right)$$

If no two particles can occupy the same site

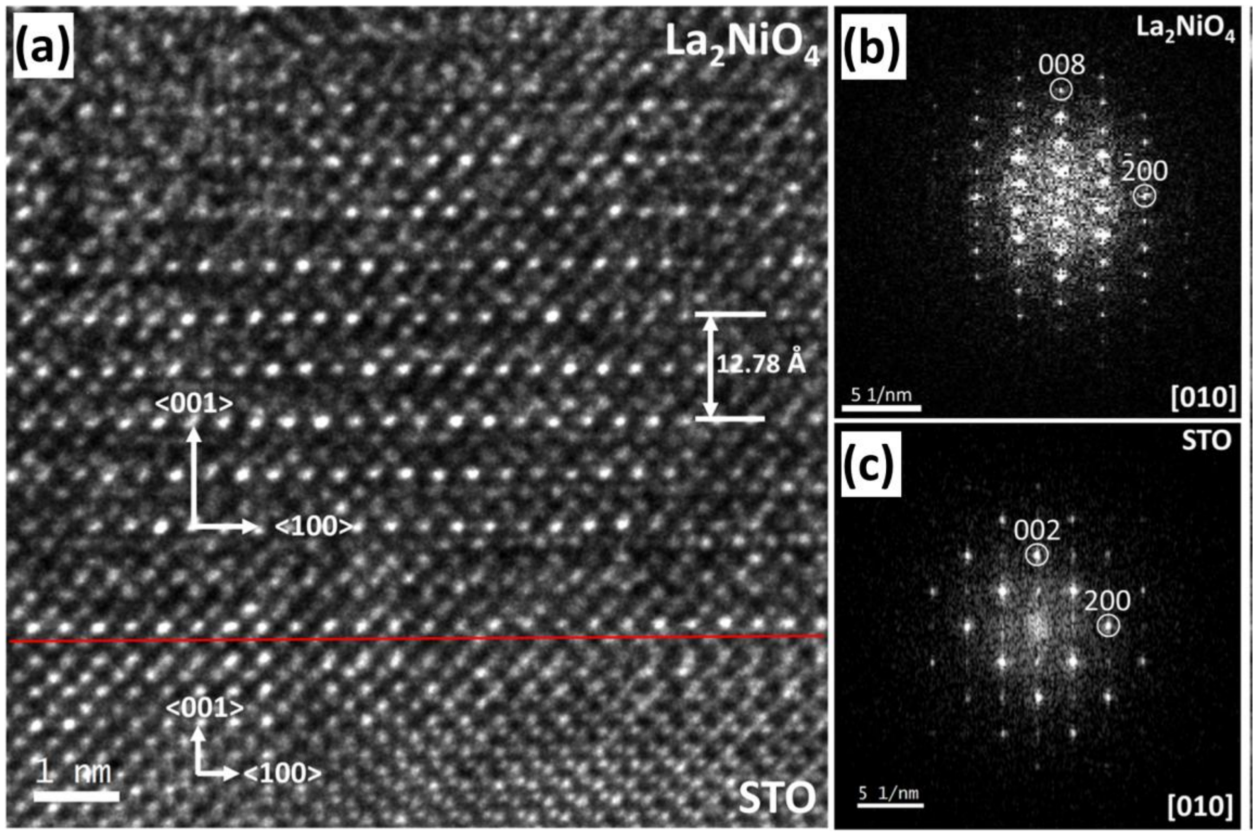
$$S = -\frac{k}{e}\ln\left(\frac{1-\alpha}{\alpha}\right)$$

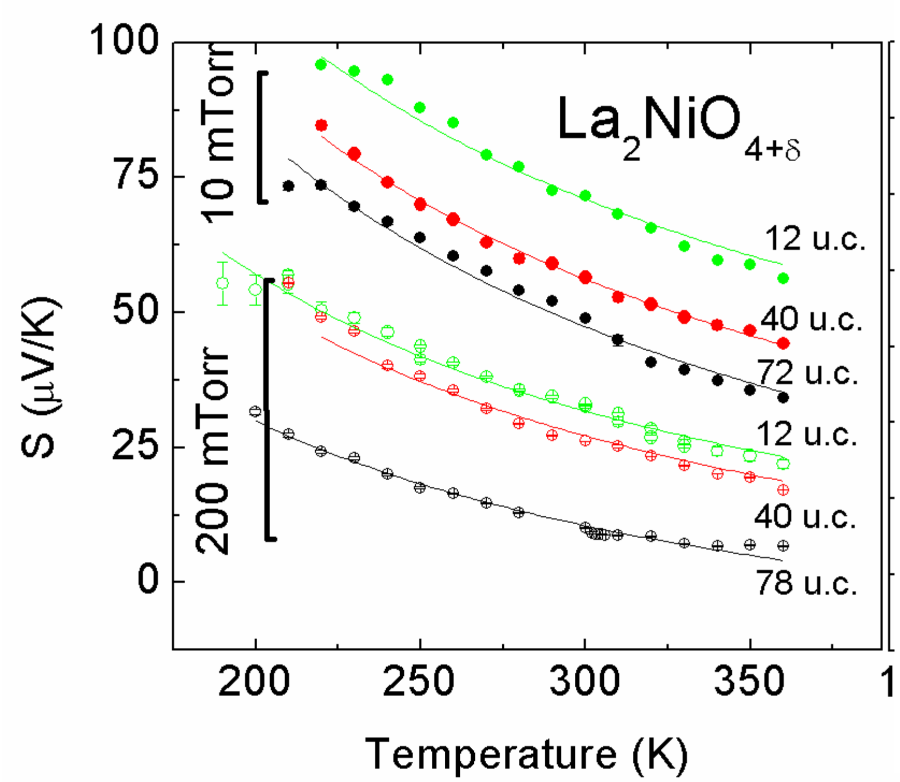
Correlations modify the statistical distribution of charge-carriers and therfeore S

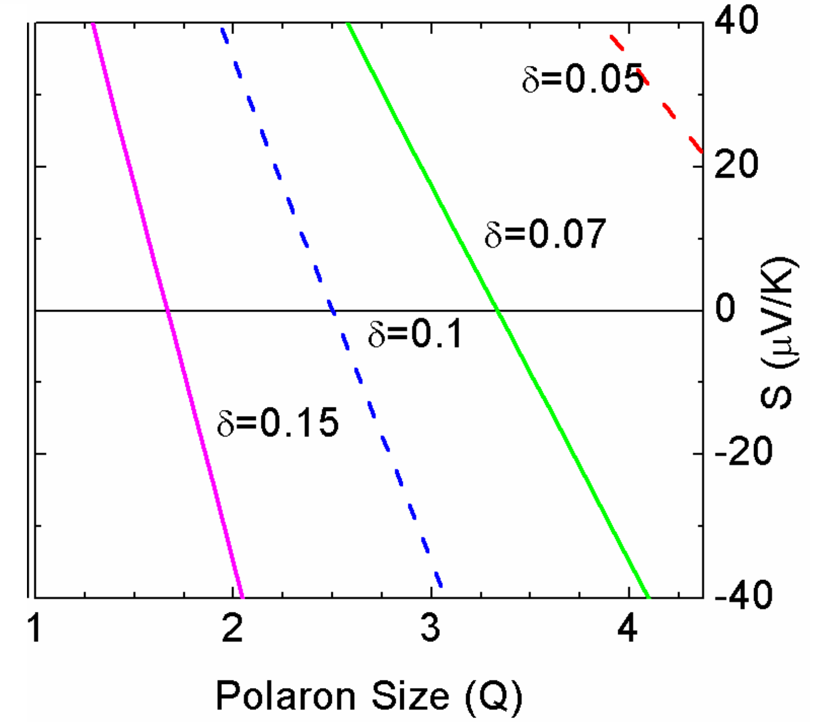
Heikes and Beni Phys. Rev. B **13**, 647 (1976)

An example of a polaronic conductor:

$La_2NiO_{4+\delta}$





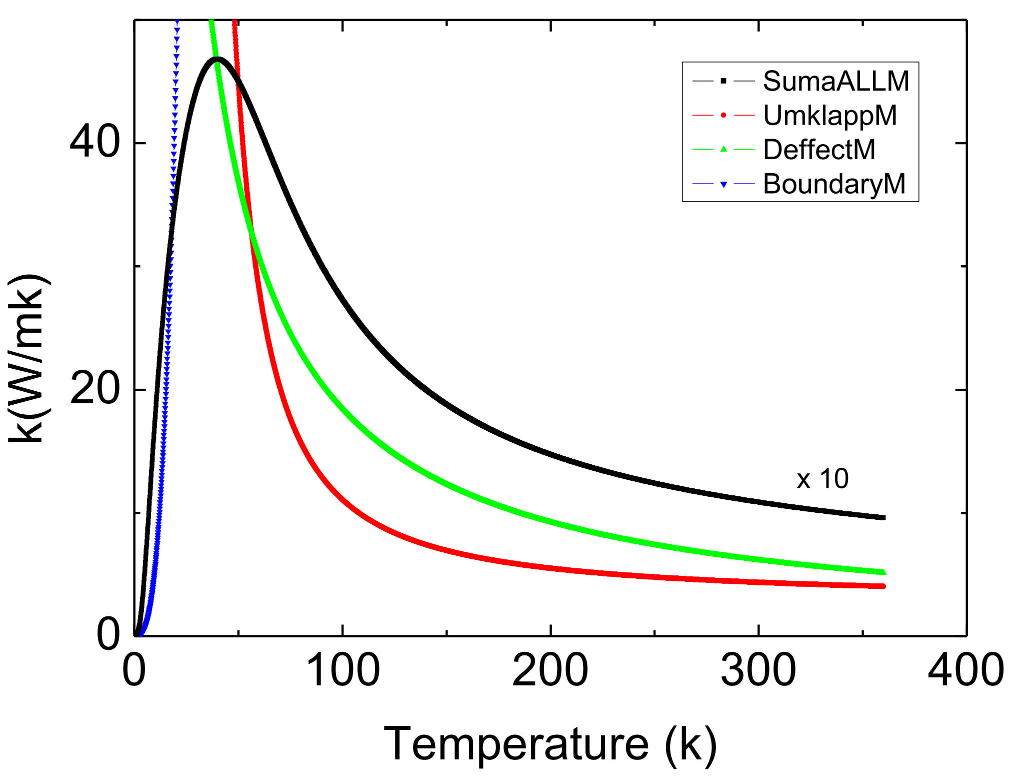


Paul Bach & F. Rivadulla, APL Materials (2013)

The Debye model for thermal conductivity

$$\kappa(T) = \frac{1}{2\pi^2 v_s} \int_0^{\omega_D} \tau(\omega) \frac{\hbar\omega^4}{k_B T^2} \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} d\omega$$

$$\tau^{-1}(\omega) = \frac{v_s}{1.8d} + \frac{\hbar\gamma^2\omega^2}{M v_s^2 \Theta} T e^{\frac{-\Theta}{\alpha T}} + \frac{V_0}{4\pi v_s^3} \sum_i x_i S_i^2$$



Boundary scattering Umklapp point deffect

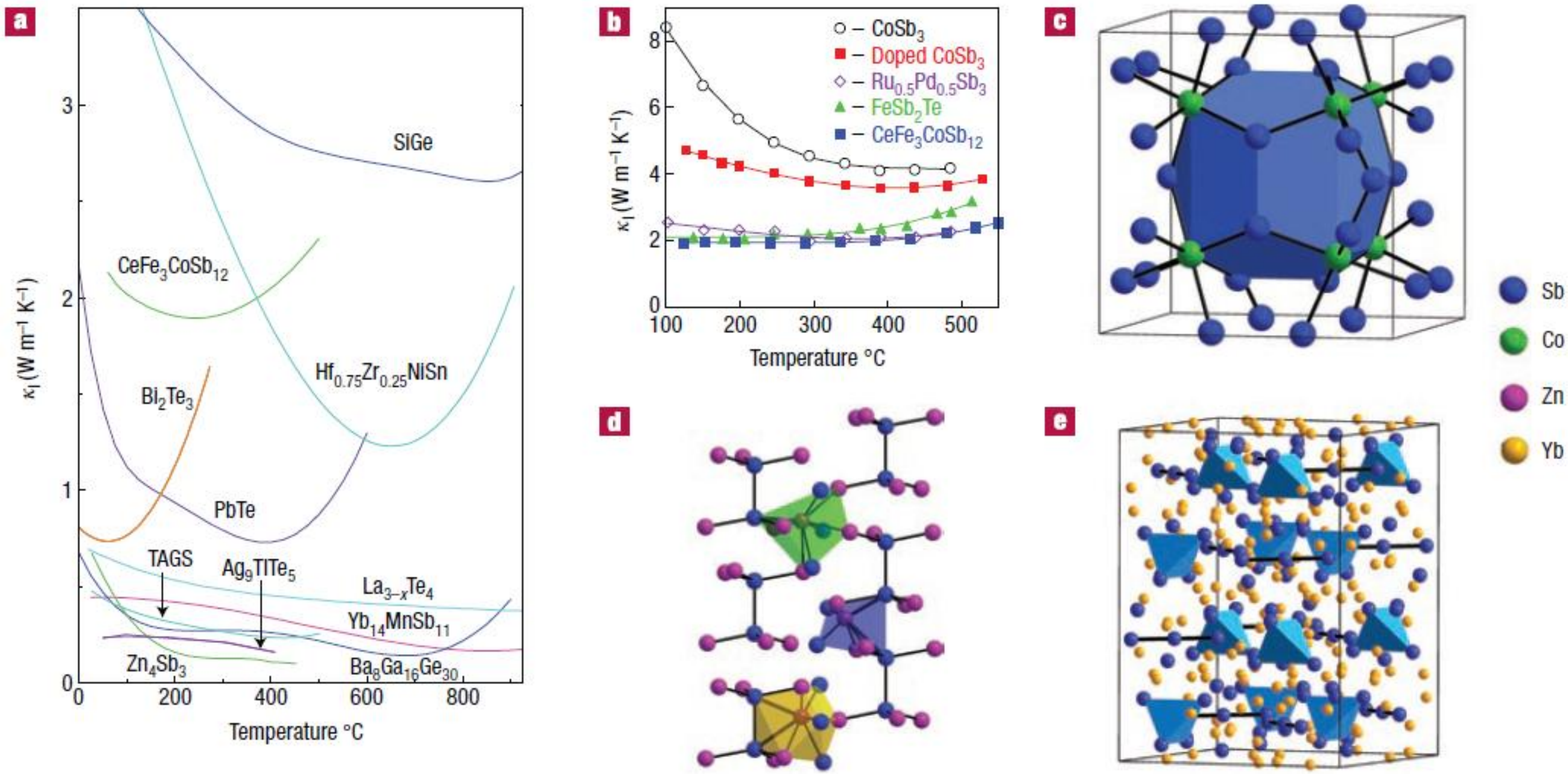
IV. Rule of thumb for TE (Disalvo rule's)

- Being a semiconductor.
- Being dopable up to carrier densities of about 10^{19} carrier/cm^3.
- Having a high symmetry crystal structure with a large number of heavy elements per unit cell.
- Being an alloy or having "rattling" sites to further reduce the lattice thermal conductivity.
- Have a small electronegativity differences between the compounds

F. J. DiSalvo, Science 285, 703 (1999).

IV. Lowering thermal conductivity: (the ideal compromise) Phonon-glass/electron crystal

skutterudites

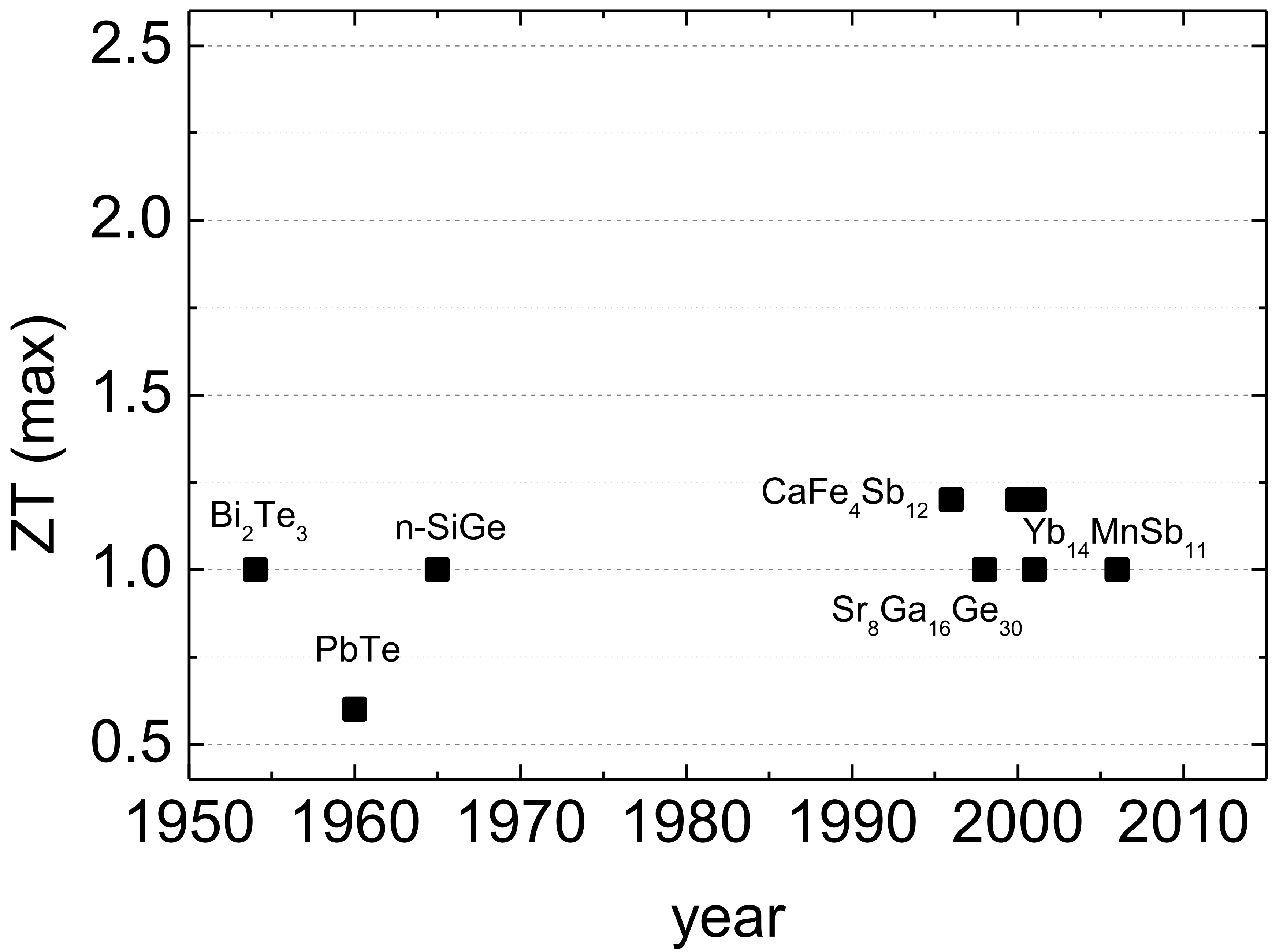


Heusler alloys

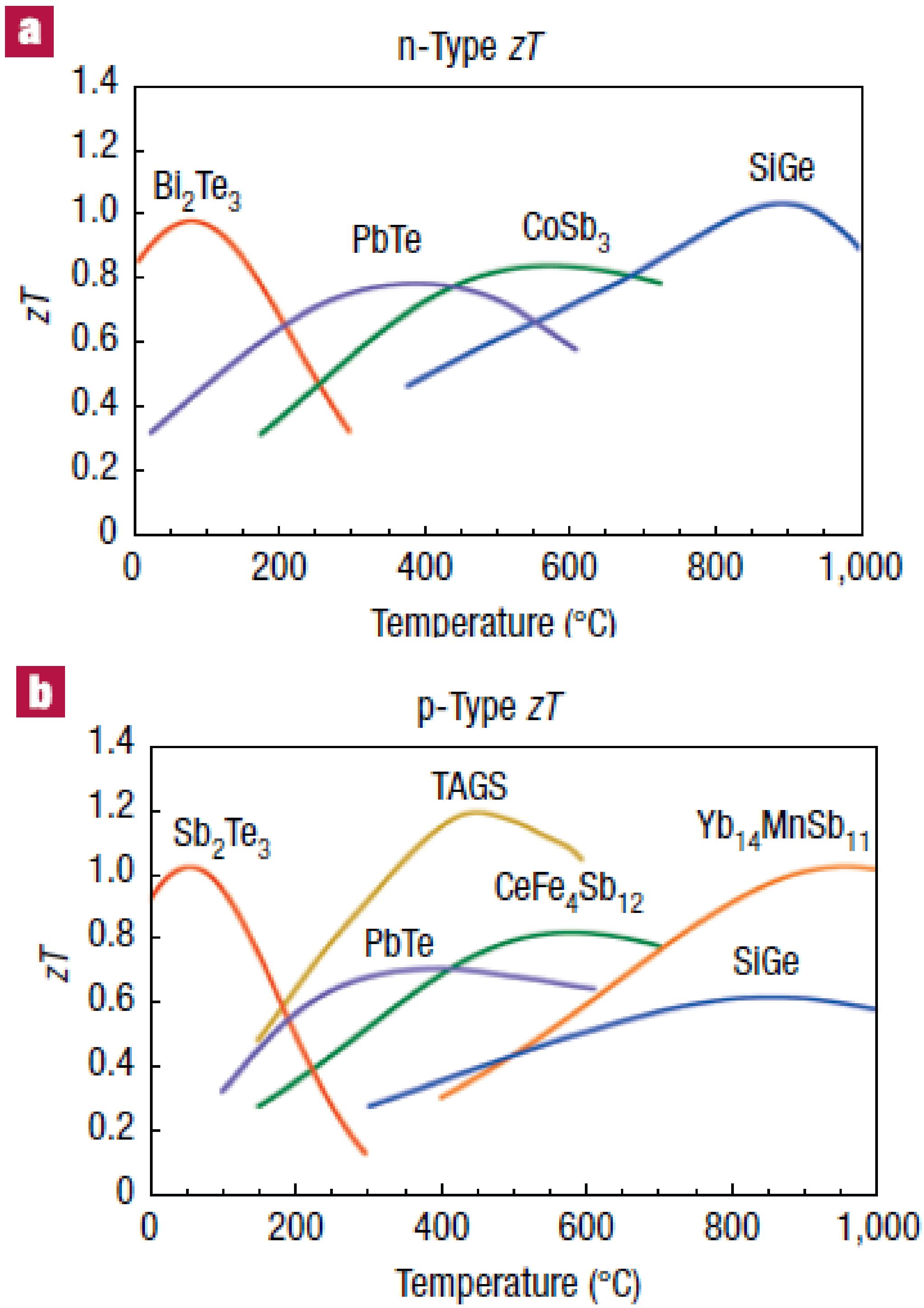
Zintl Phases

Snyder & Toberer, Nat. Mat. (2008)

IV. Rule of thumb for TE (Disalvo rule's)



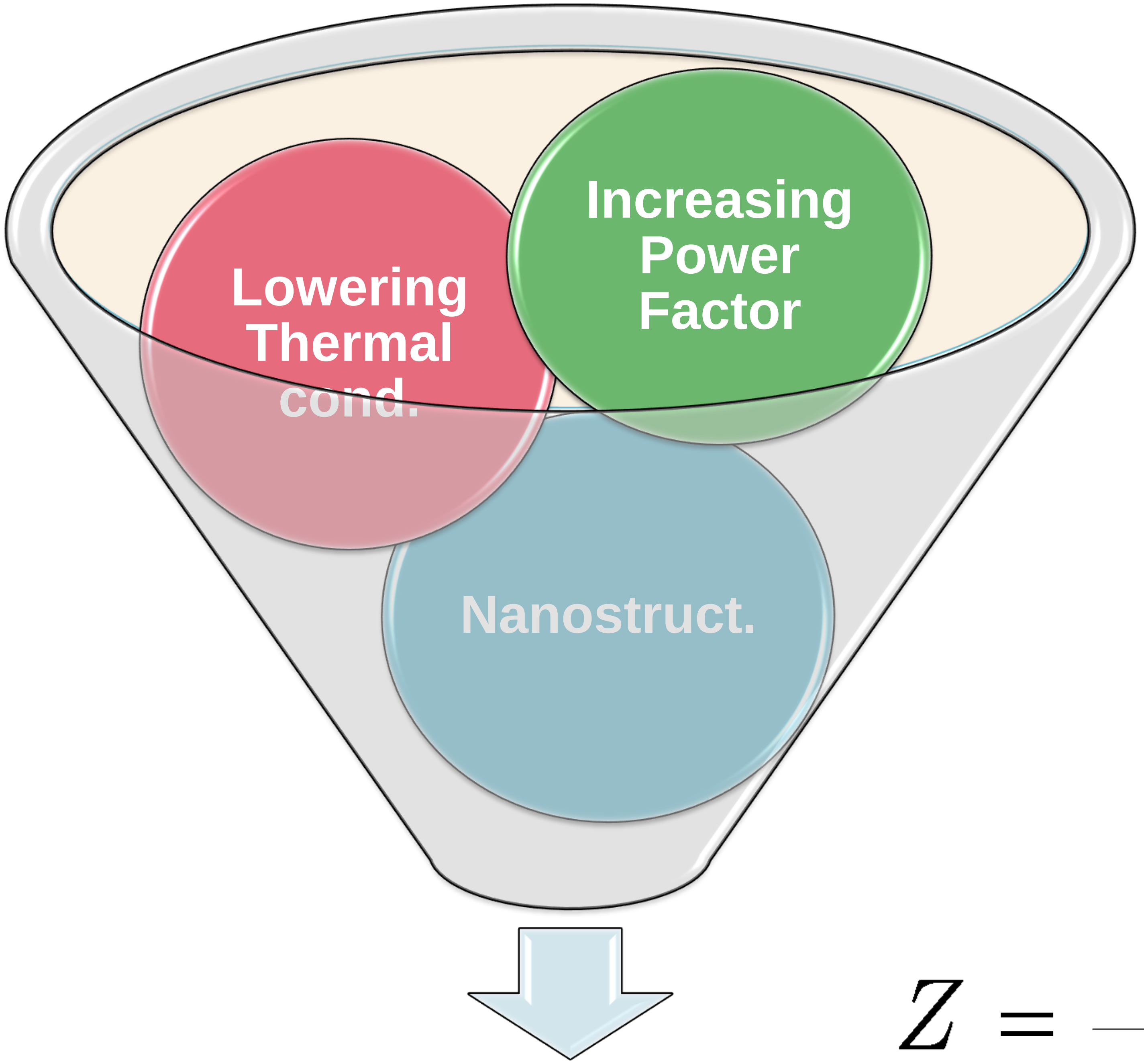
IV. Rule of thumb for TE (Disalvo rule's)



- Toxicity
- Bi_2Te_3 T(melt)=585ºC
- Shortfall of Te by 2025

$$s = \frac{\sqrt{1+zT} \pm 1}{\alpha T}$$

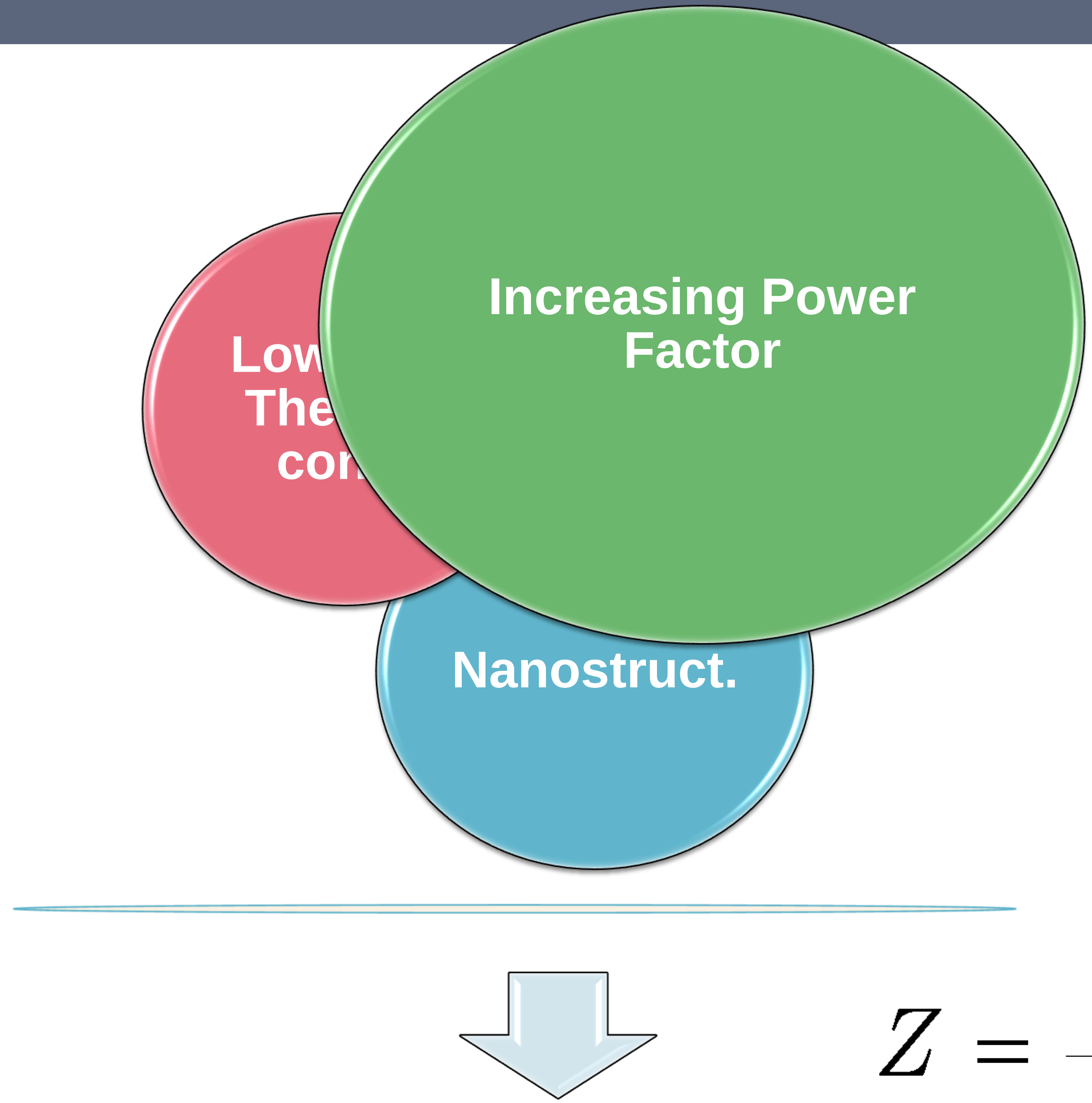
V. Current strategies for optimizing TE figure of merit



Increase ZT

$$Z = \frac{S^2\sigma}{\kappa_{el} + \kappa_{ph}}$$

V. Current strategies for optimizing TE figure of merit

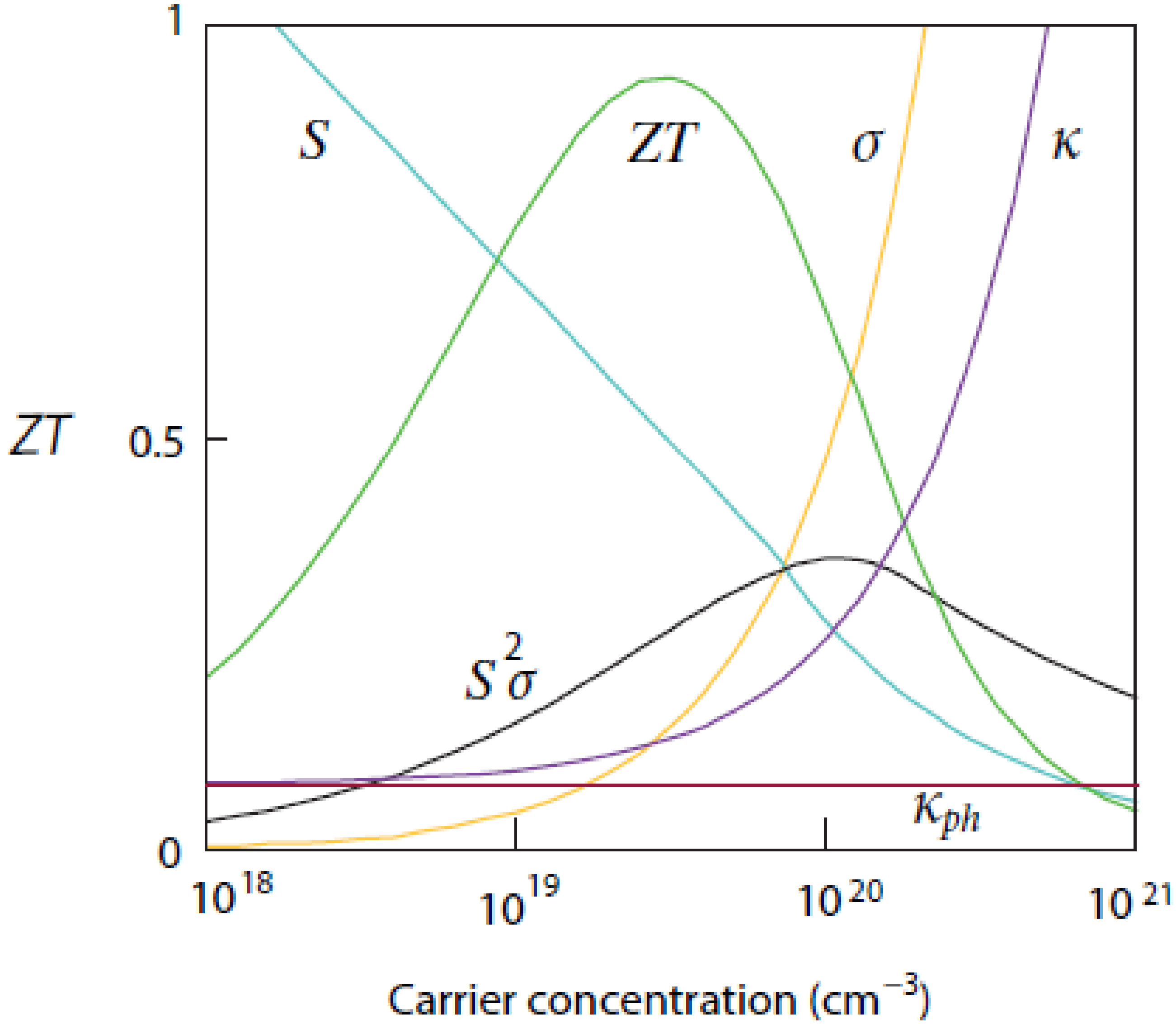


Increase ZT

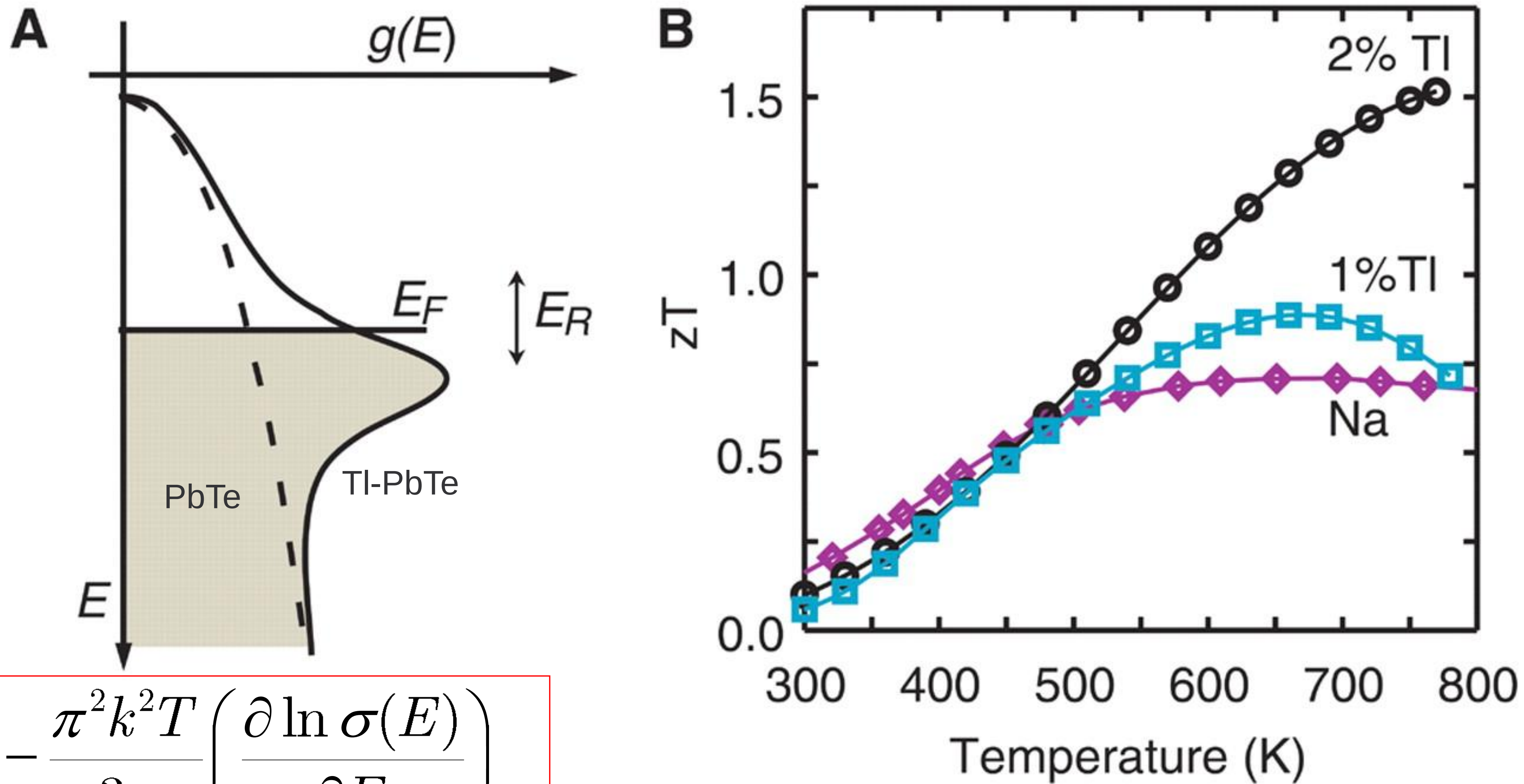
$$Z = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{ph}}$$

V(I). Increasing power factor: optimizing n and m*

$$PF = S^2\sigma \qquad \sigma = \frac{ne^2\tau}{m^*}$$



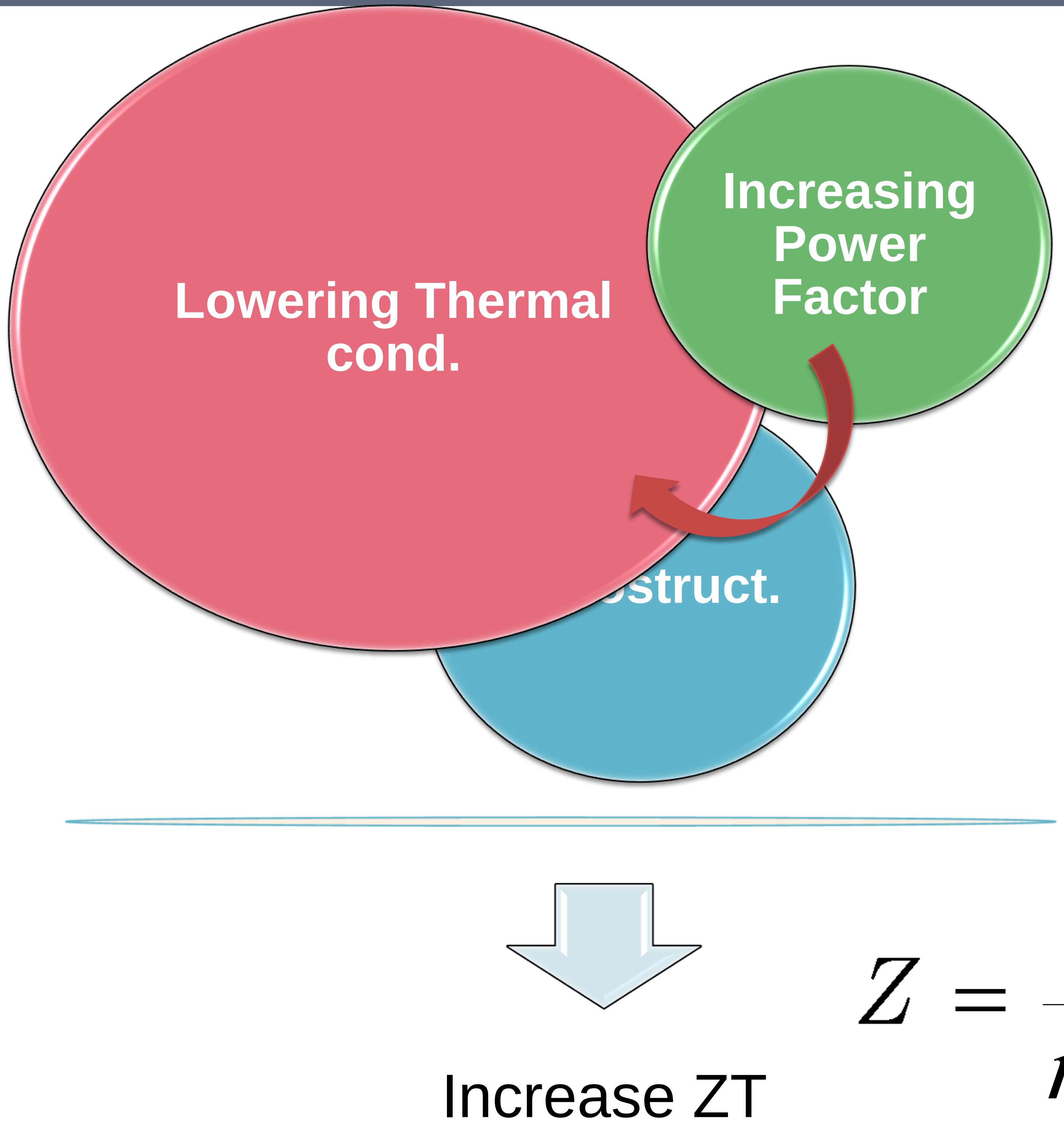
V(I). Increasing power factor: band engineering



$$S = -\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln \sigma(E)}{\partial E}\right)_{E_F}$$

J P Heremans et al. Science (2008)

V. Current strategies for optimizing TE figure of merit



$$Z = \frac{S^2\sigma}{\kappa_{el} + \kappa_{ph}}$$

V(II). Lowering thermal conductivity

$$\kappa = \kappa_{el} + \kappa_{ph}$$

10-100 nm

$$\kappa_{ph} = \frac{1}{3} C v \lambda$$

$$\frac{\kappa_{el}}{\sigma} = LT = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

$L=2.44\times10^{-8}\ W\Omega/K^{-2}$

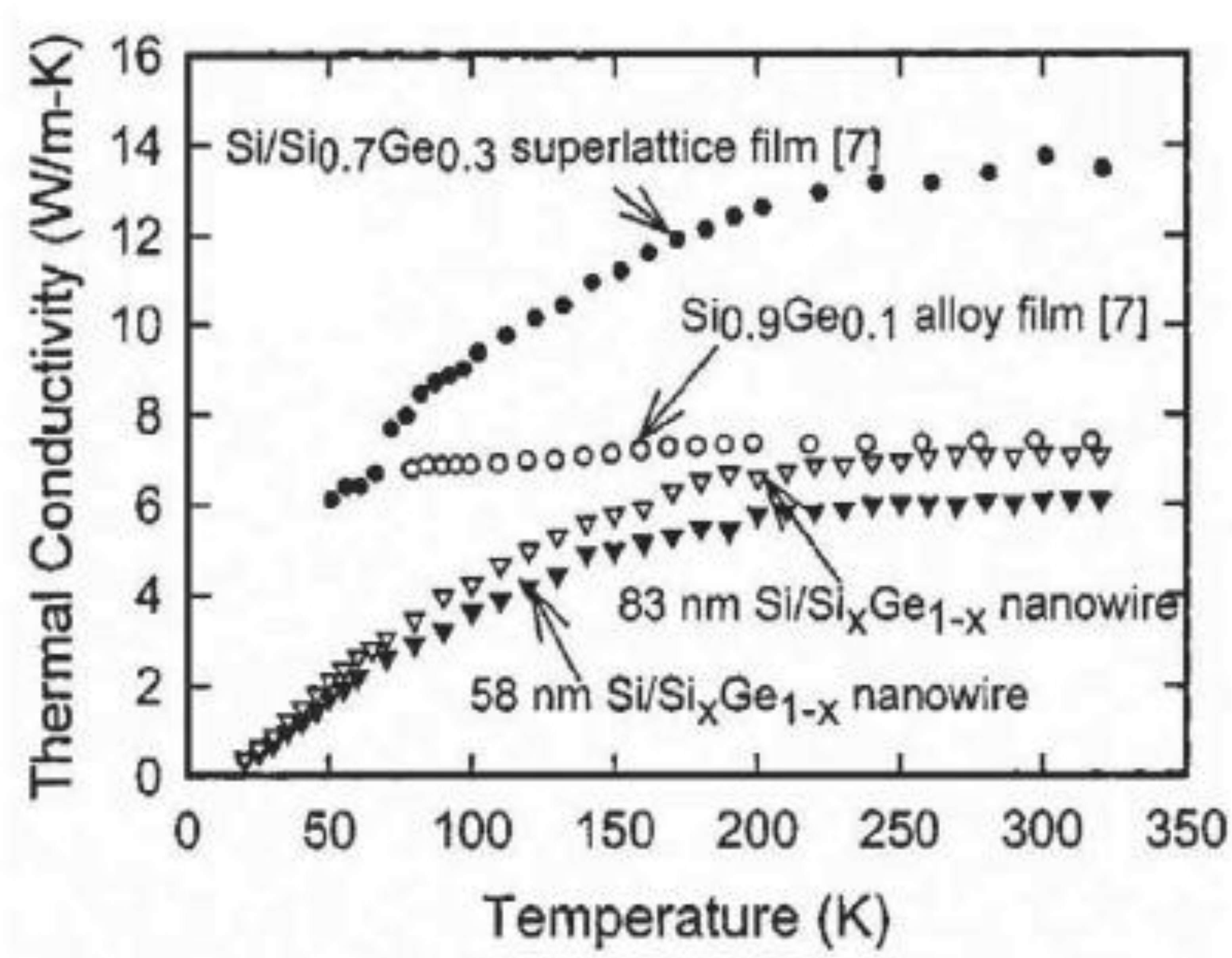
Alloys:

$\kappa \approx$ 5-10 W/mK

Amorphous:

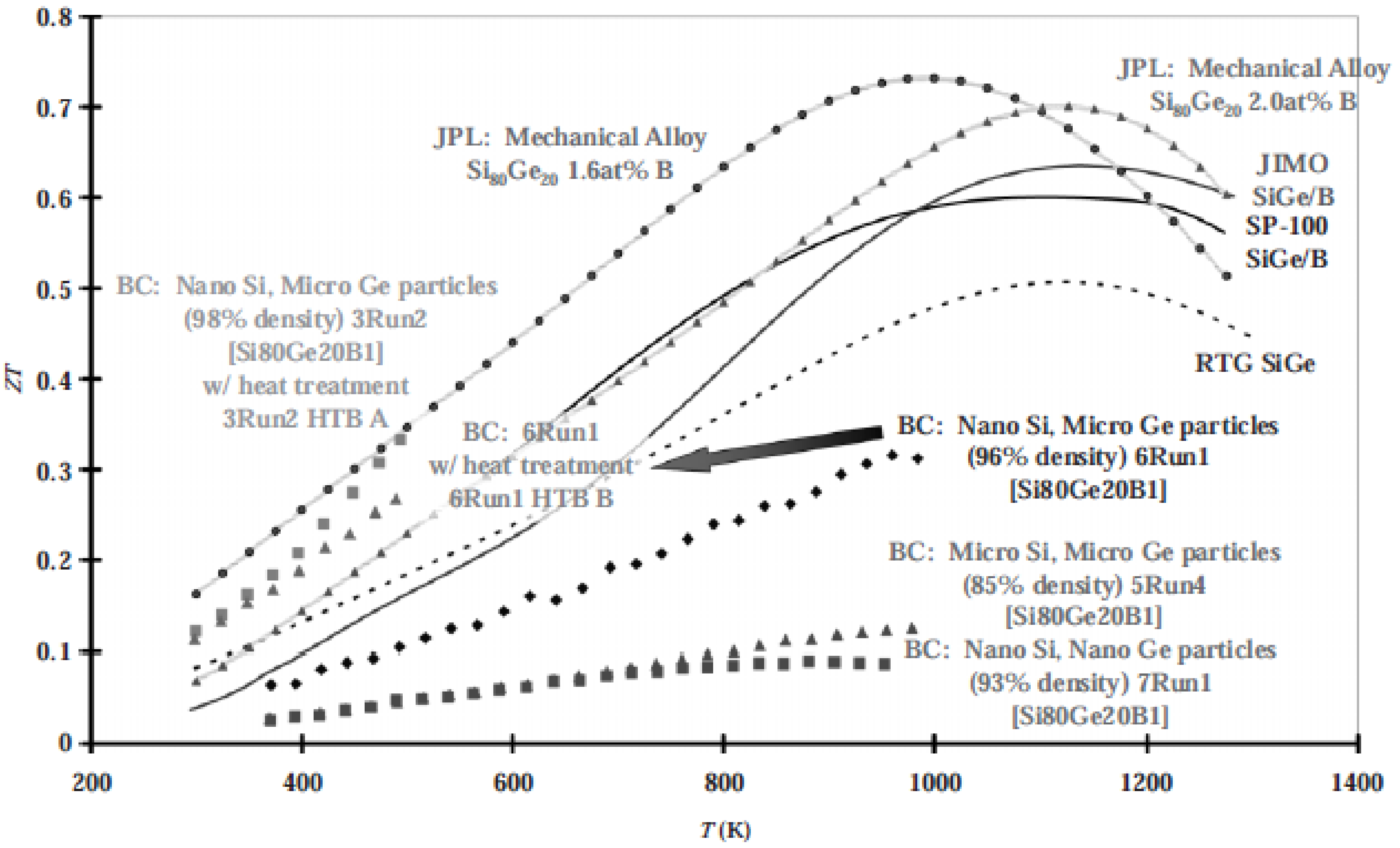
$\kappa \approx$ 1-3 W/mK

V(II). Lowering thermal conductivity: beating the alloy limit (5 W/mK < κ < 10 W/mK)

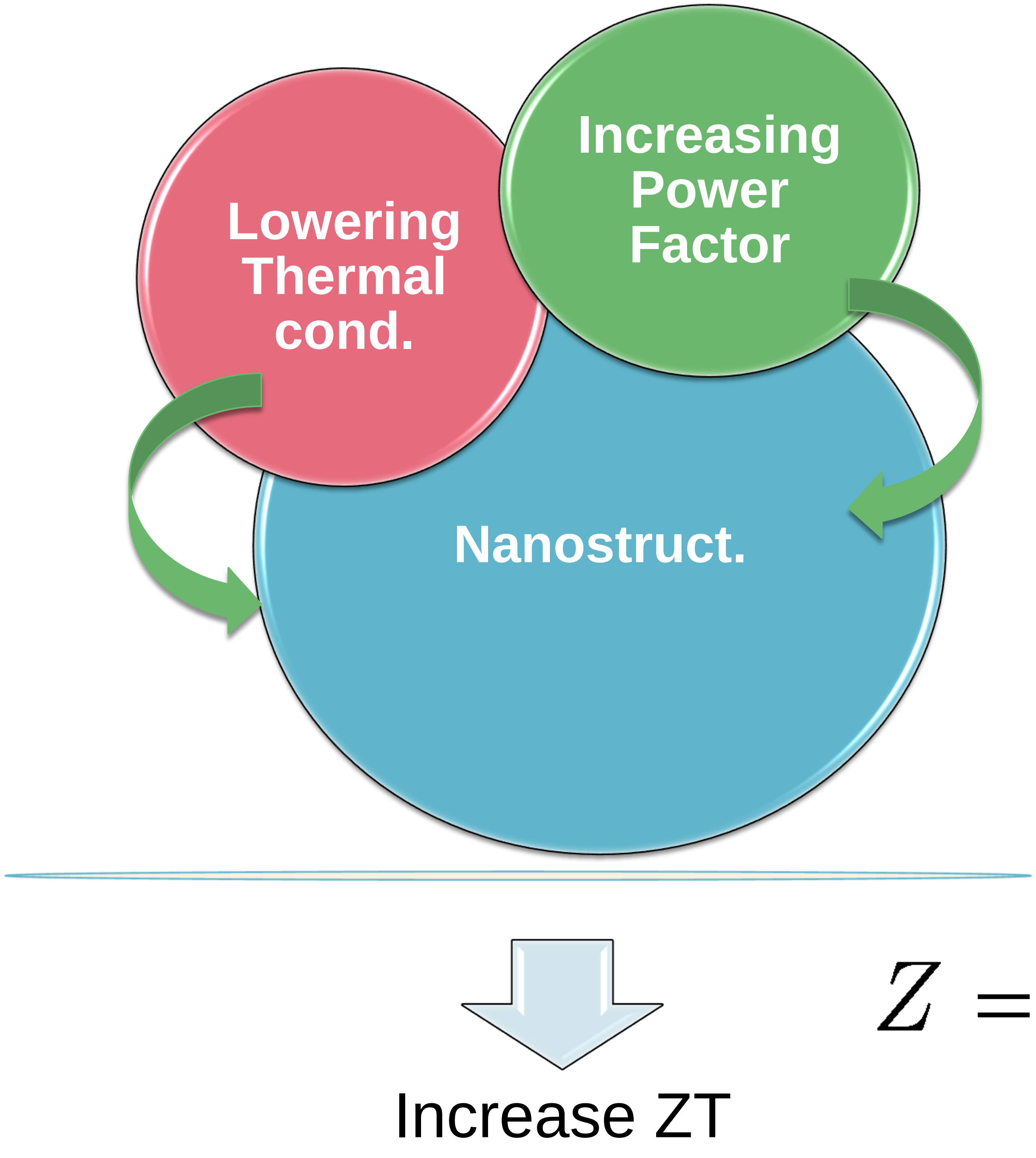


Li et al. Appl. Phys. Lett. (2003)

V(II). Lowering thermal conductivity: beating the amorphous limit (1.3 W/mK < κ < 3 W/mK)



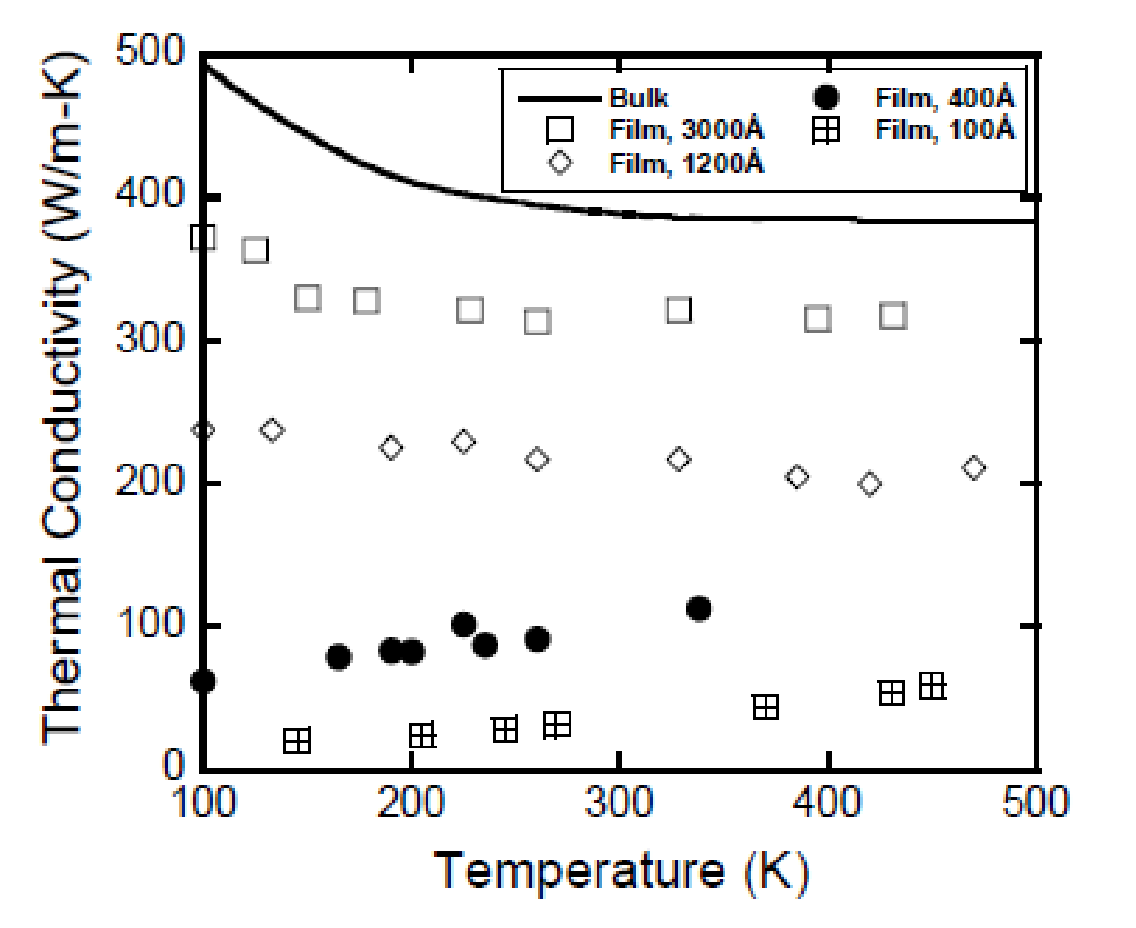
V. Current strategies for optimizing TE figure of merit



$$Z = \frac{S^2\sigma}{\kappa_{el} + \kappa_{ph}}$$

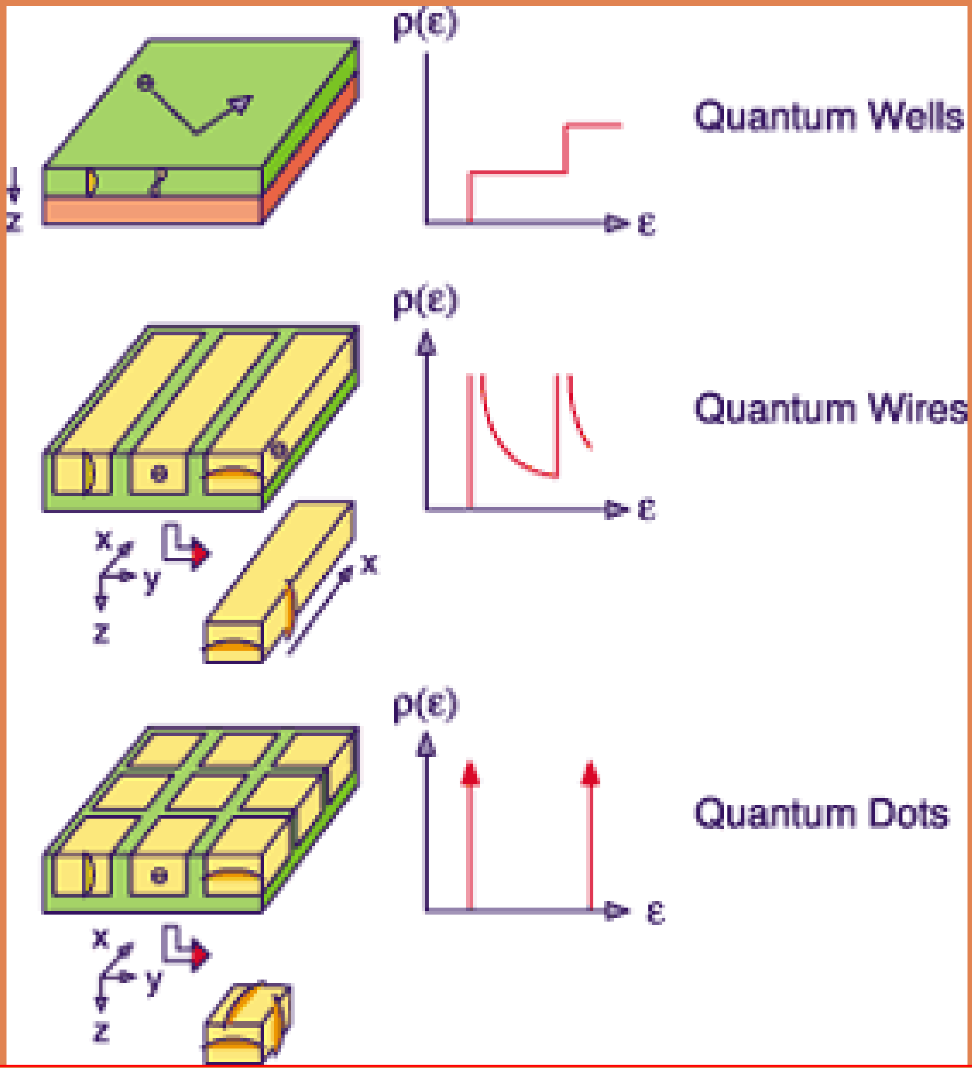
V(III). Nanostructuring

III a): Reducing thermal conductivity



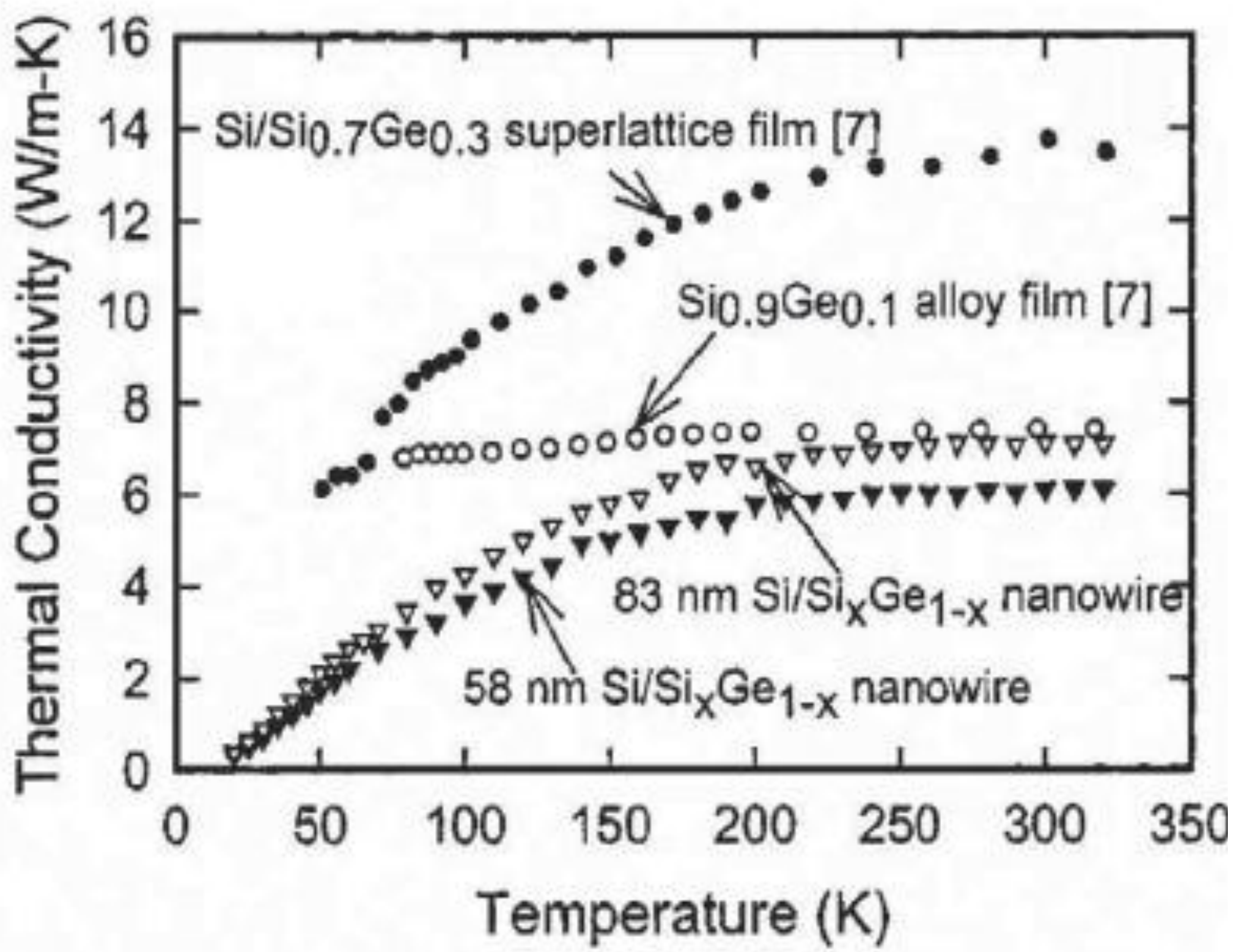
B. Yang and G. Chen
"Thermal conductivity: Theory and Applications"
Ed. By TM Tritt

III b): Enhancing thermopower

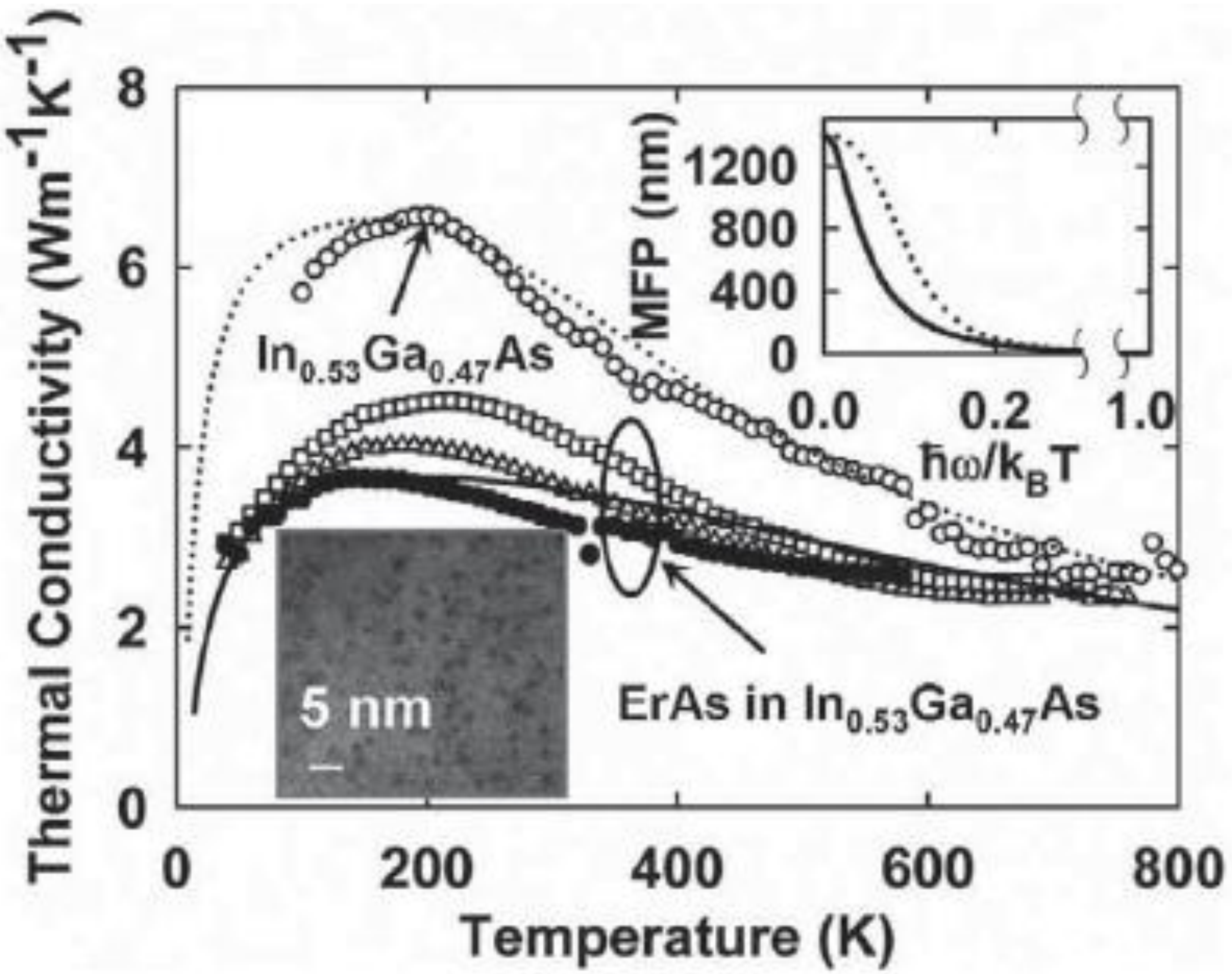


$$S = -\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln \sigma(E)}{\partial E}\right)_{E_F}$$

V(III). Lowering thermal conductivity: beating the alloy limit (5 W/mK < κ < 10 W/mK)

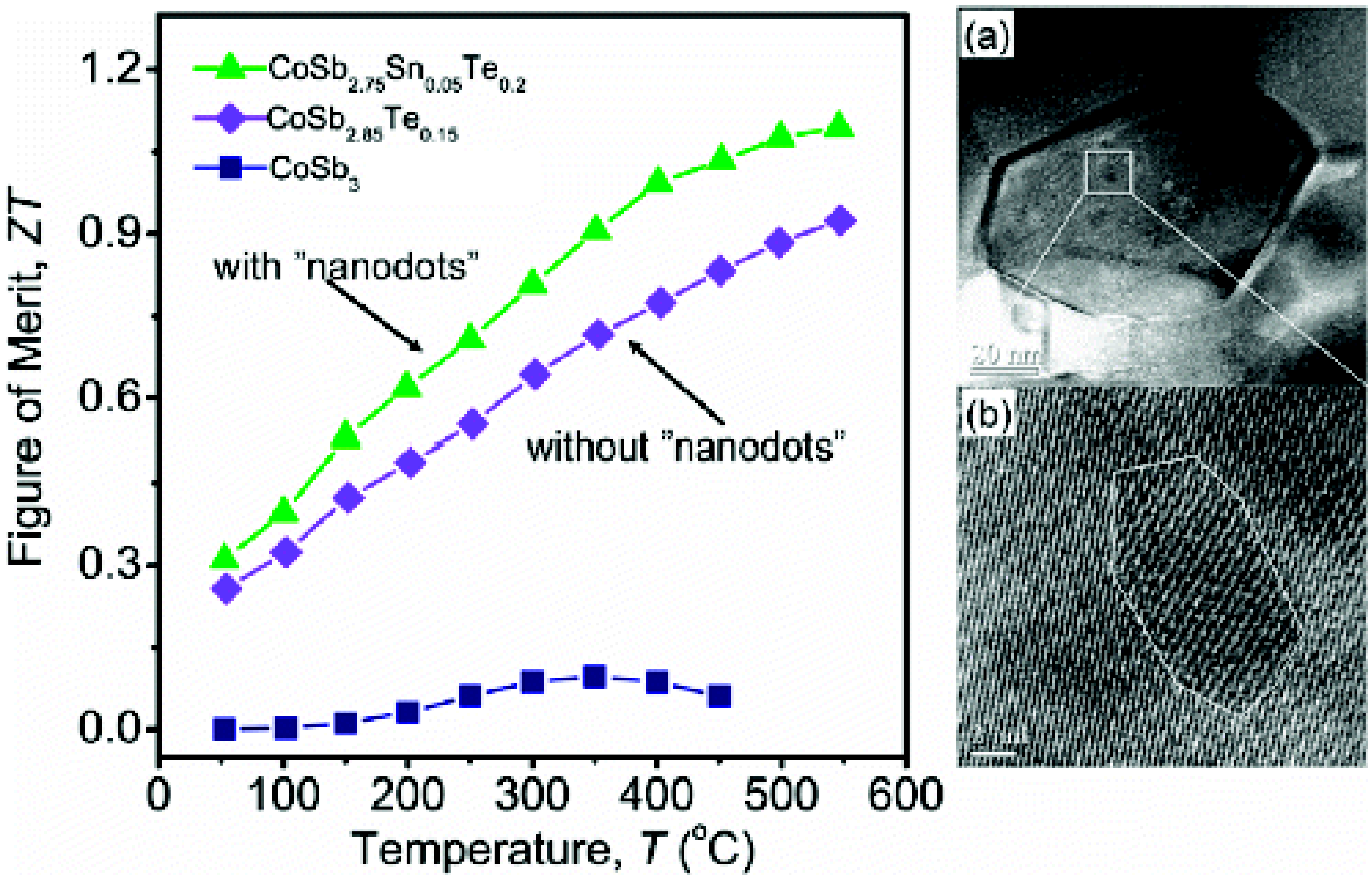


Li et al. Appl. Phys. Lett. (2003)



Kim et al. Phys. Rev. Lett. (2006)

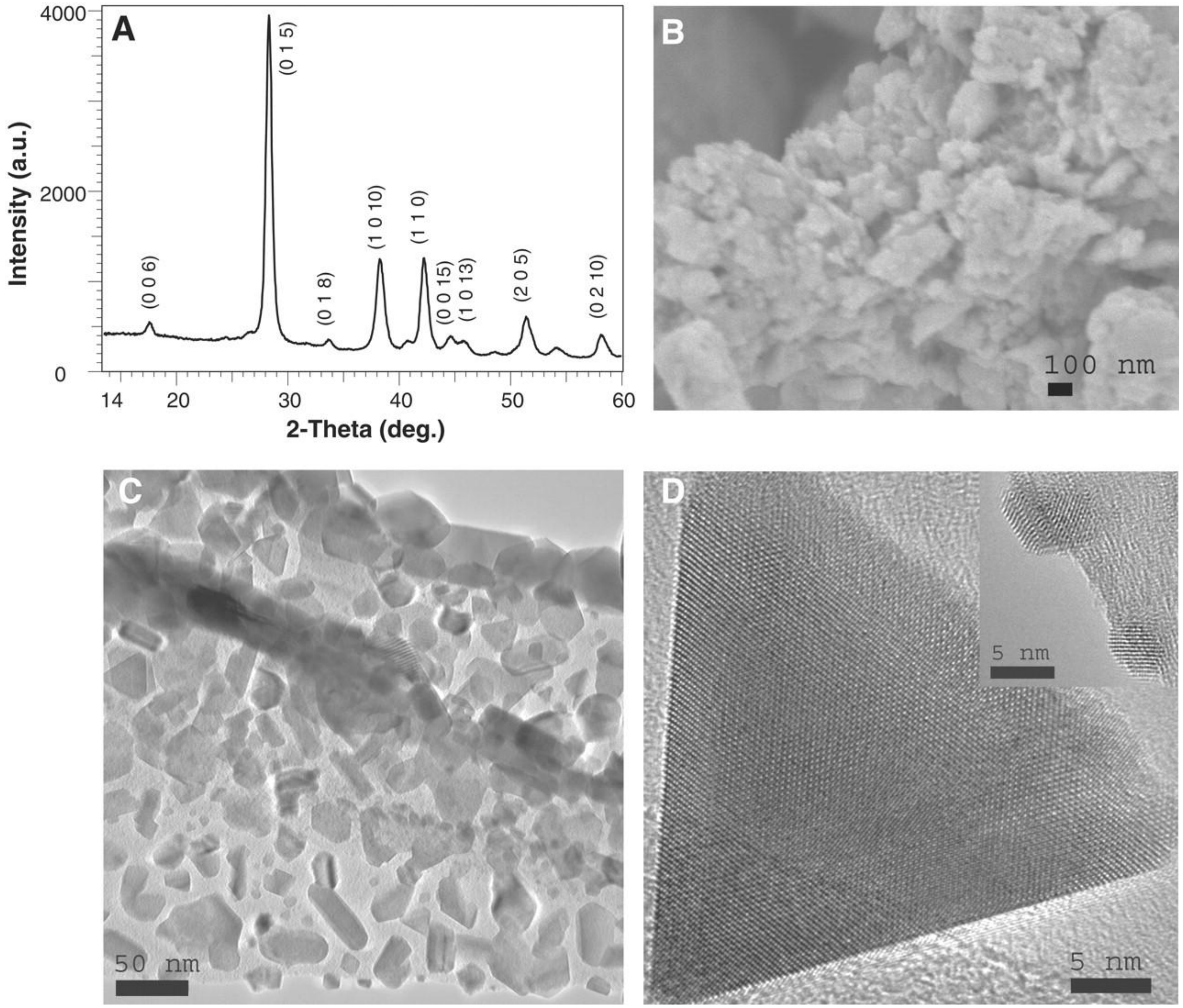
V(III). Nanostructuring: intrinsic nanostructures



Angew. Chem. Int. Ed. 2008, 47, 8618 –8622

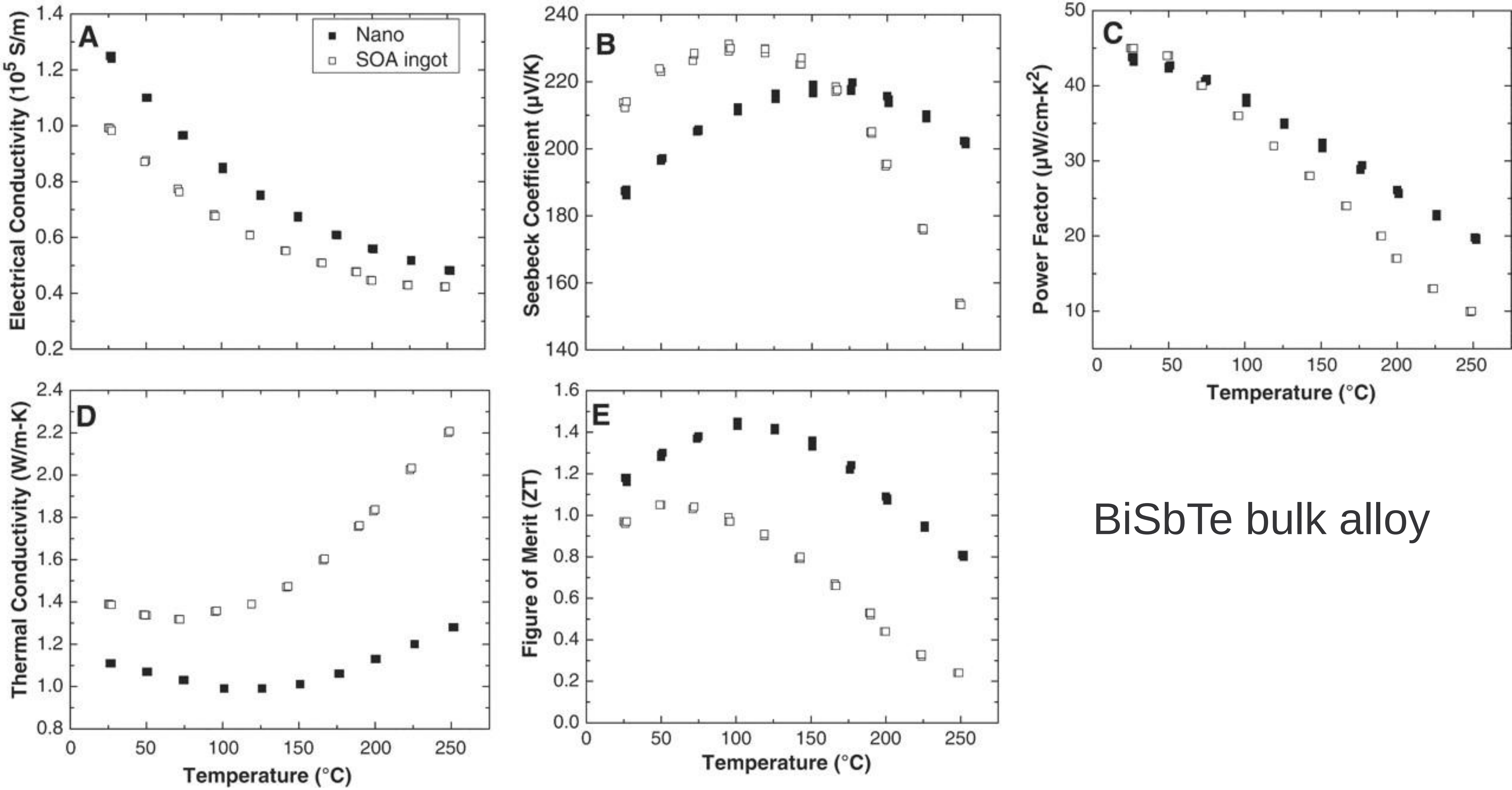
V(III). Nanostructuring: intrinsic nanostructures

BiSbTe bulk alloy



Poudel et al. Science (2008)

V(III). Nanostructuring: intrinsic nanostructures

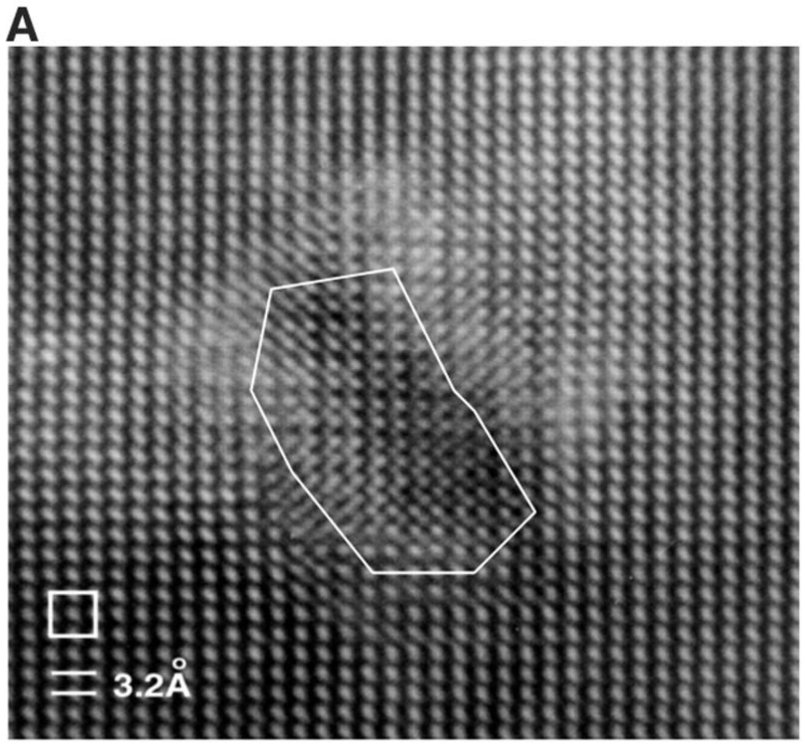


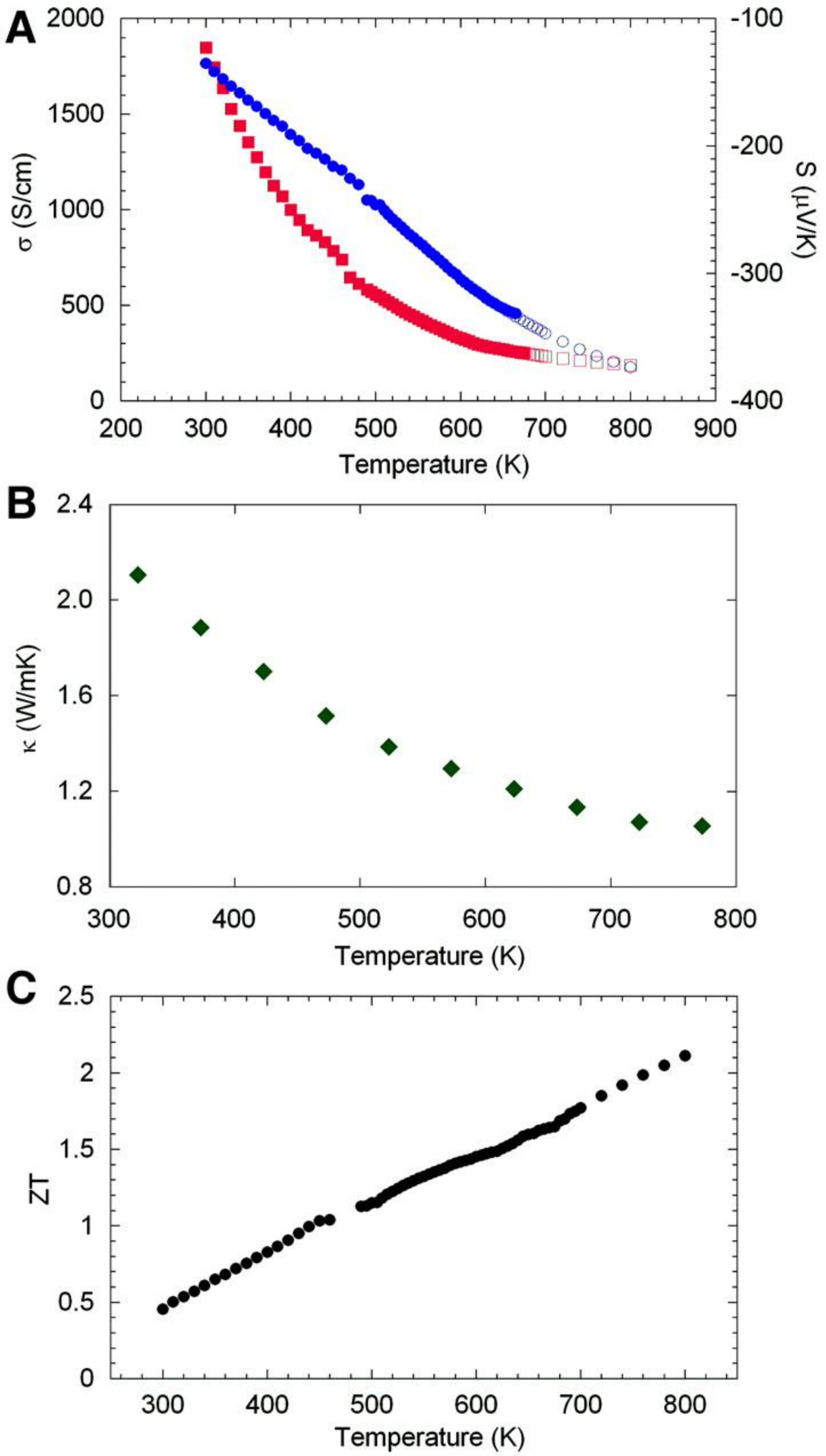
BiSbTe bulk alloy

Poudel et al. Science (2008)

V(III). Nanostructuring: intrinsic nanostructures

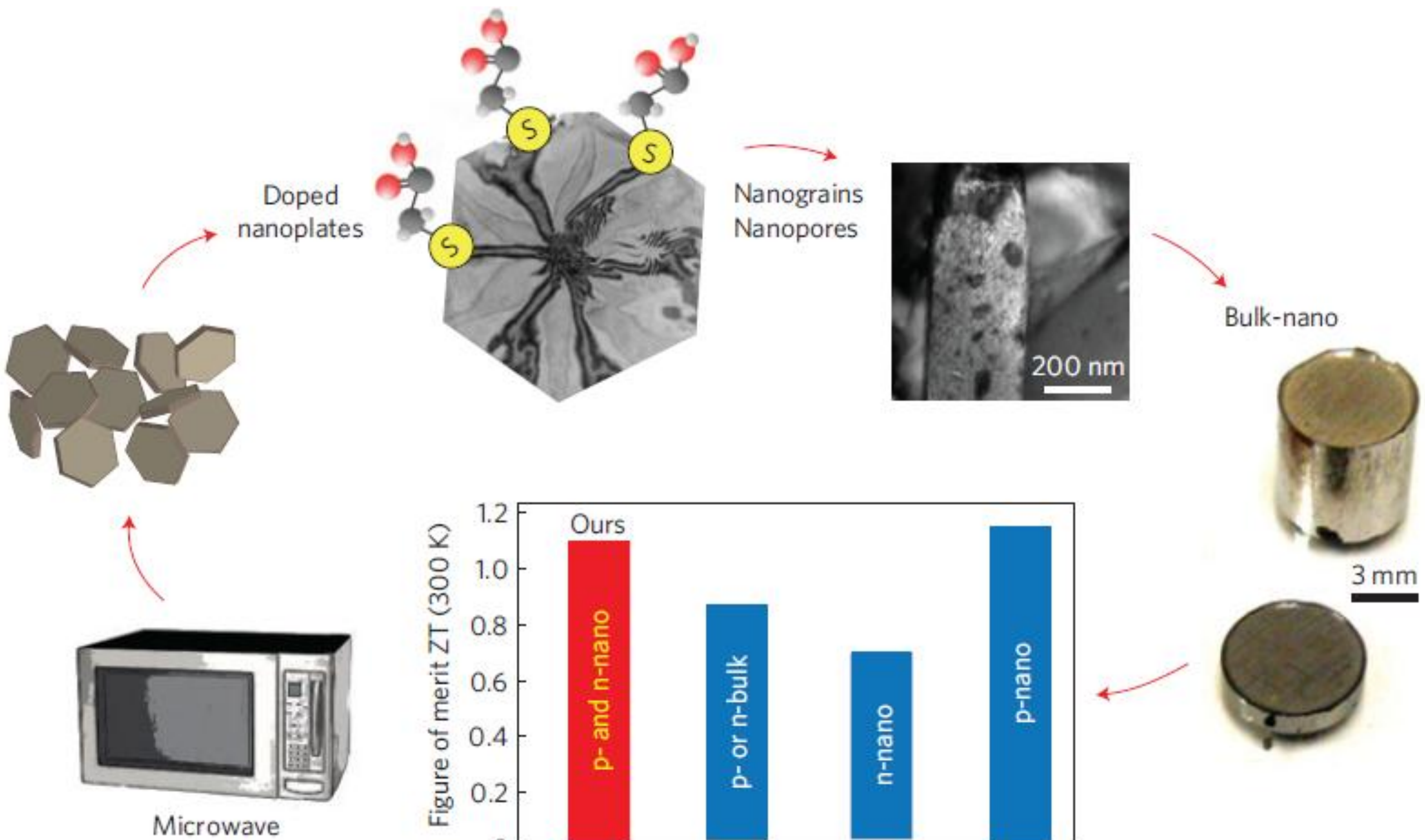
$AgPb_{18}SbTe_{20}$

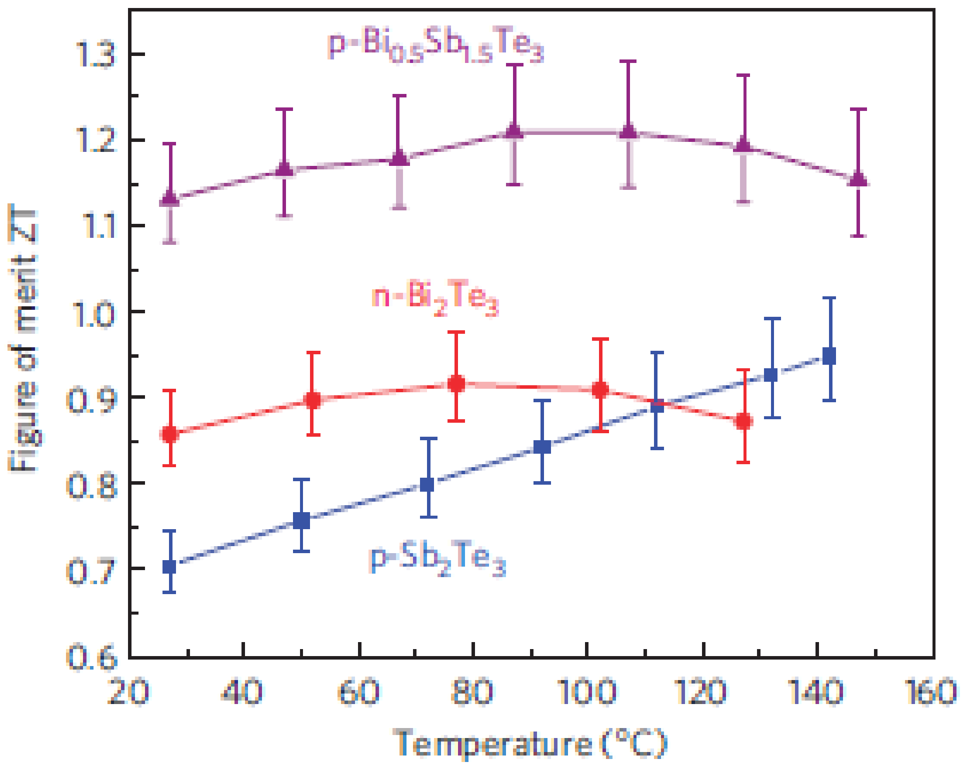




K F Hsu et al. Science (2004)

V(III). Nanostructuring: composites

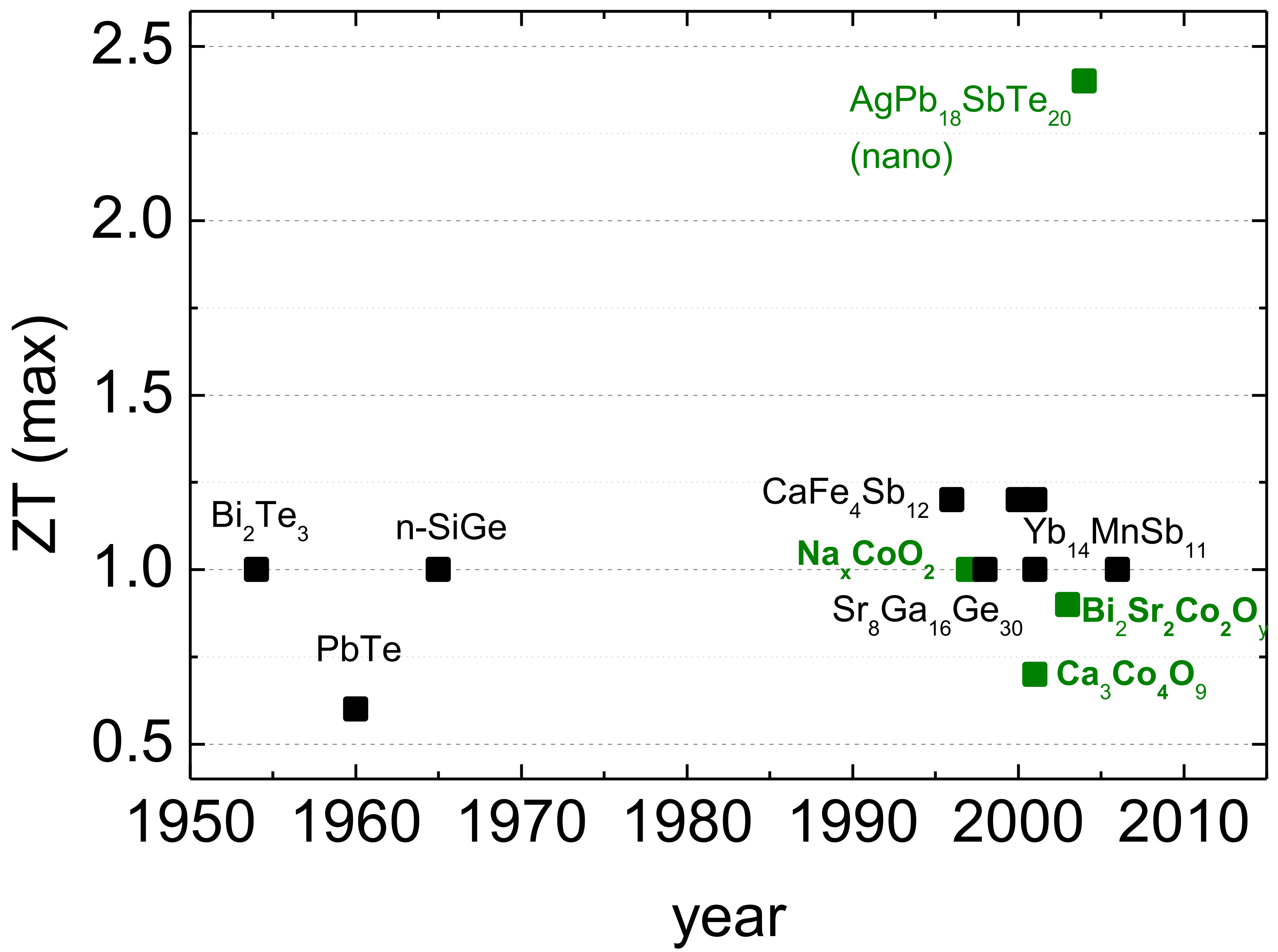




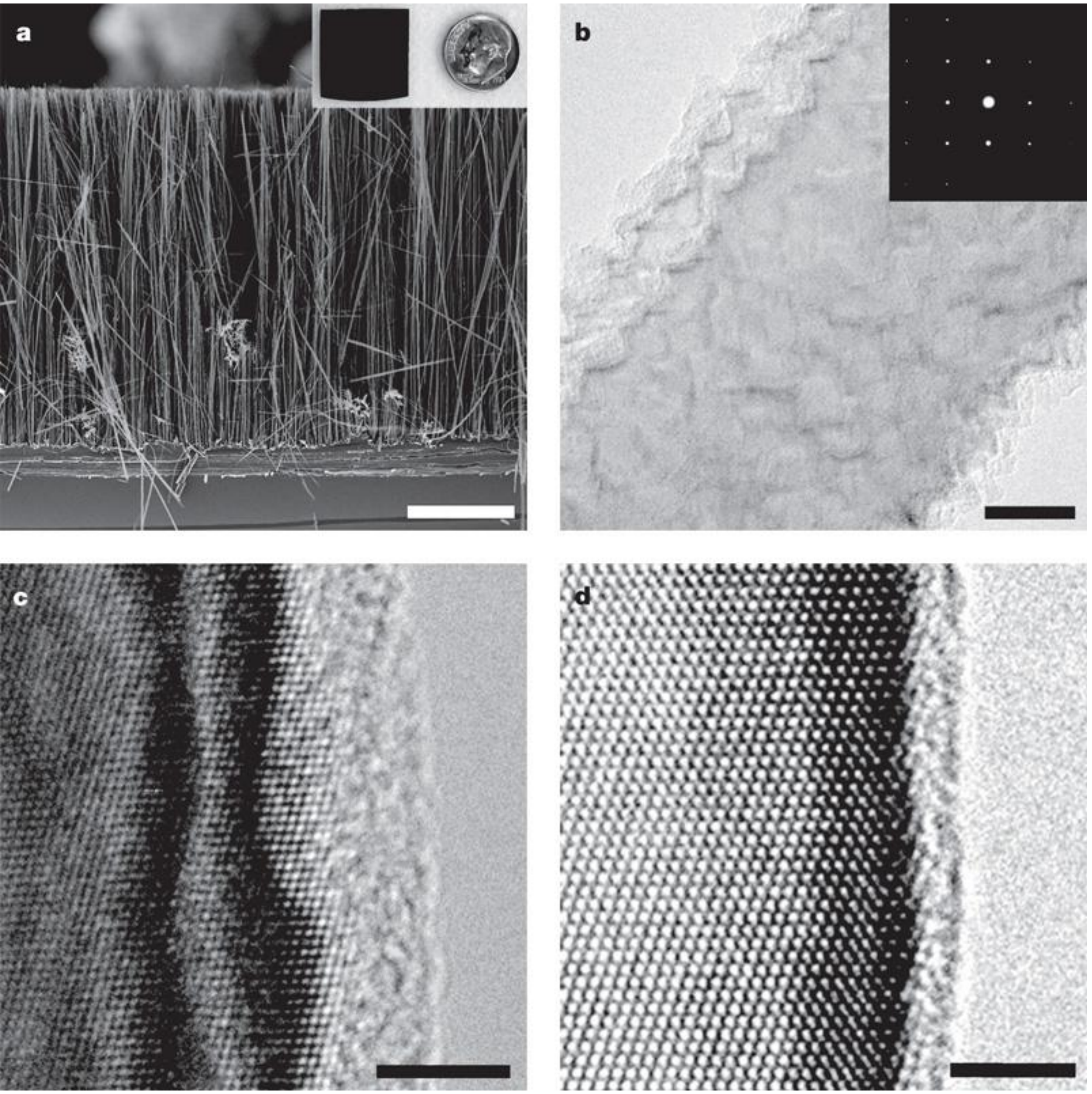
Mehta et al. Nat. Mat. (2012)

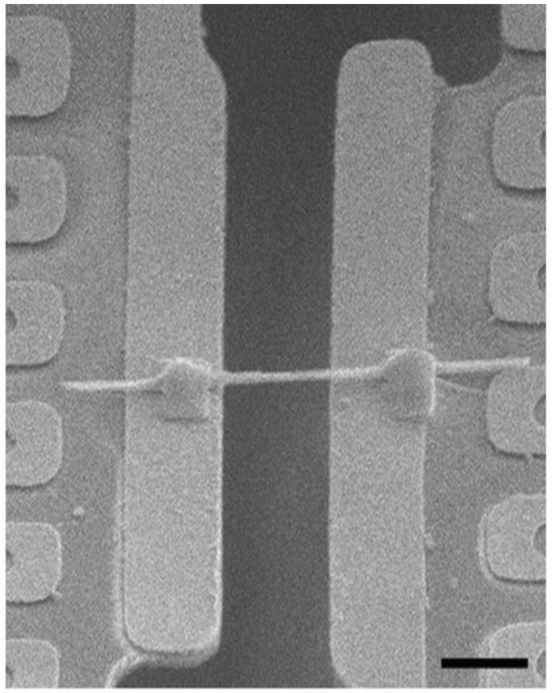
V(III). Nanostructuring: new materials beyond Disalvo rule's

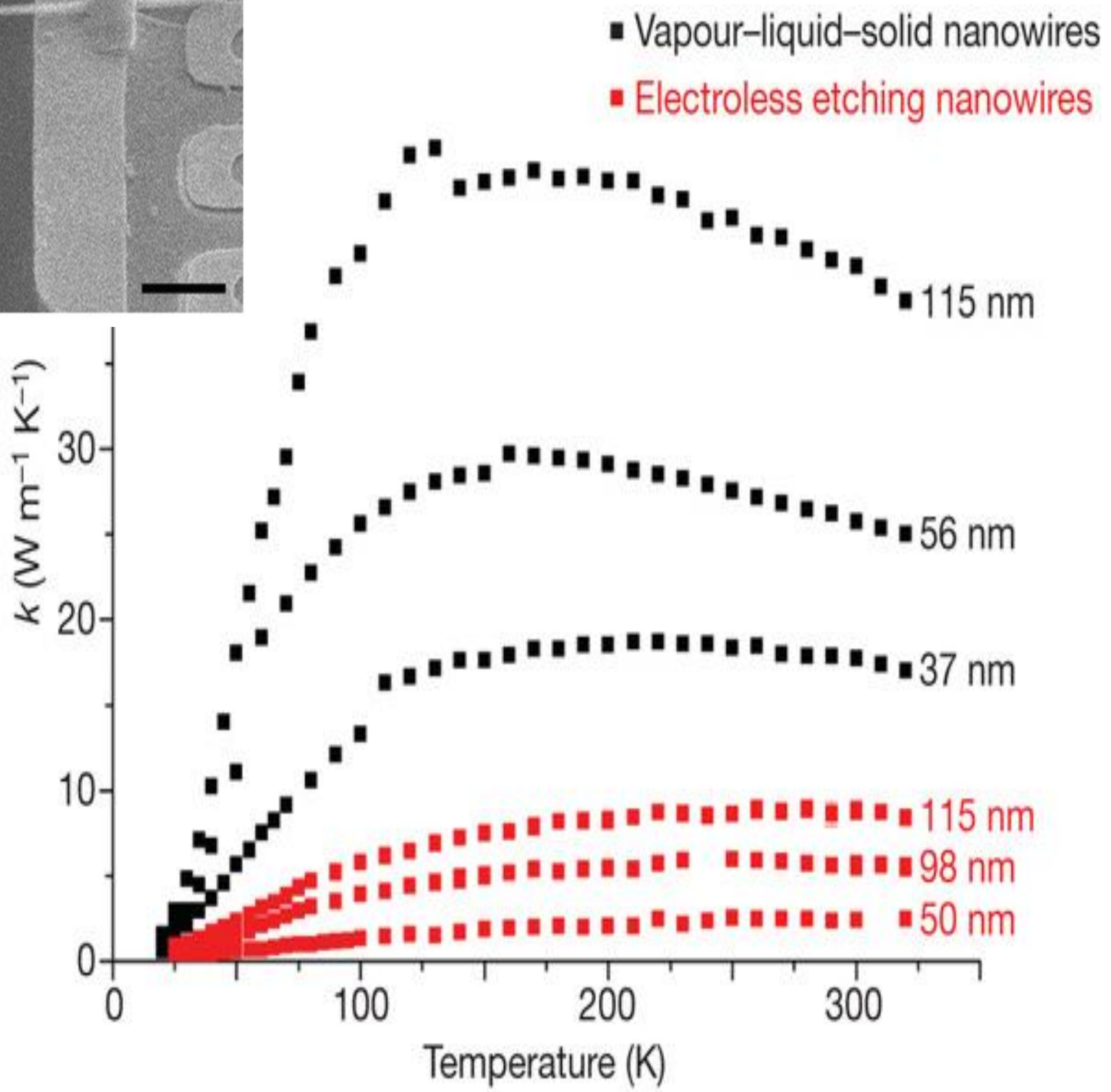
- extrinsic strategies to increase thermal conductivity (nanostructuring)



V(III). Nanostructuring: articial nanostructures



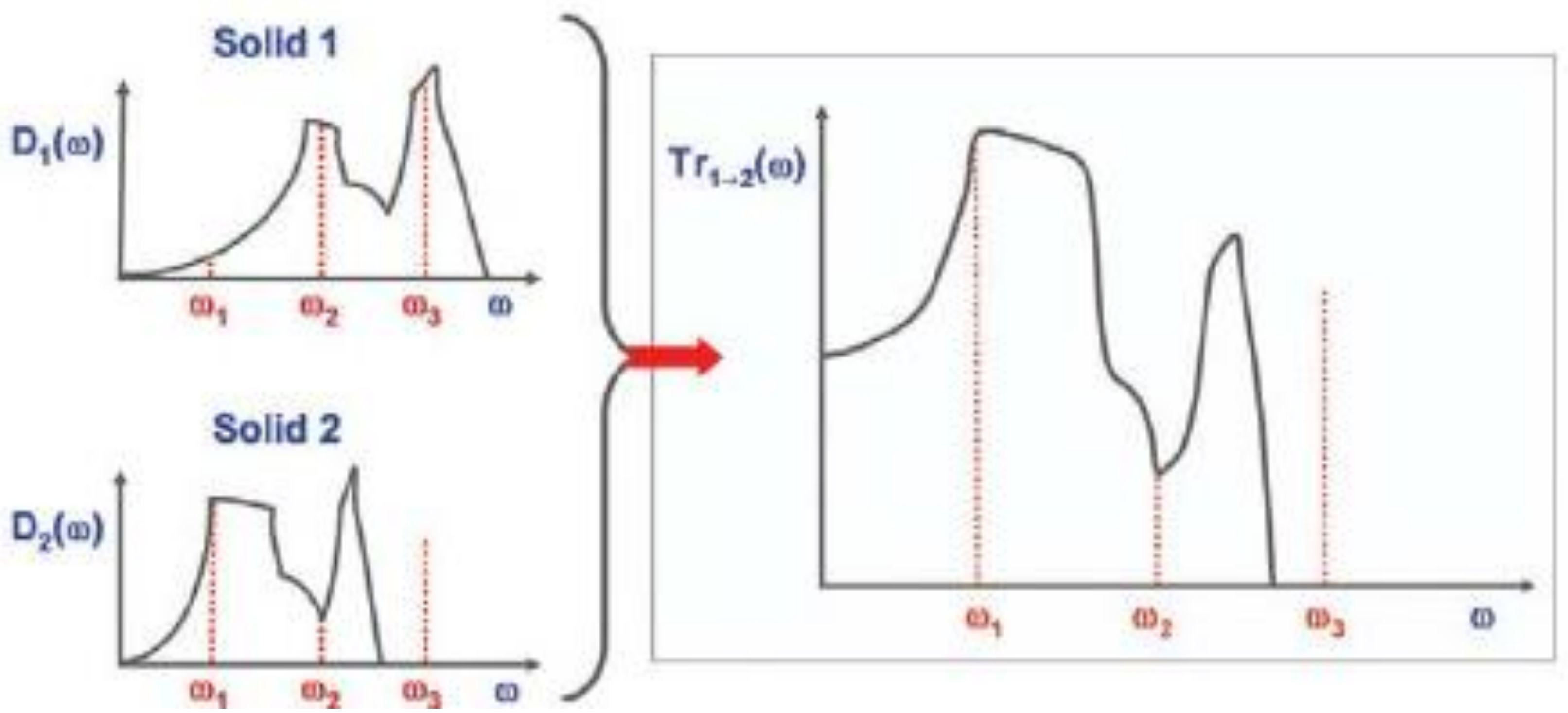


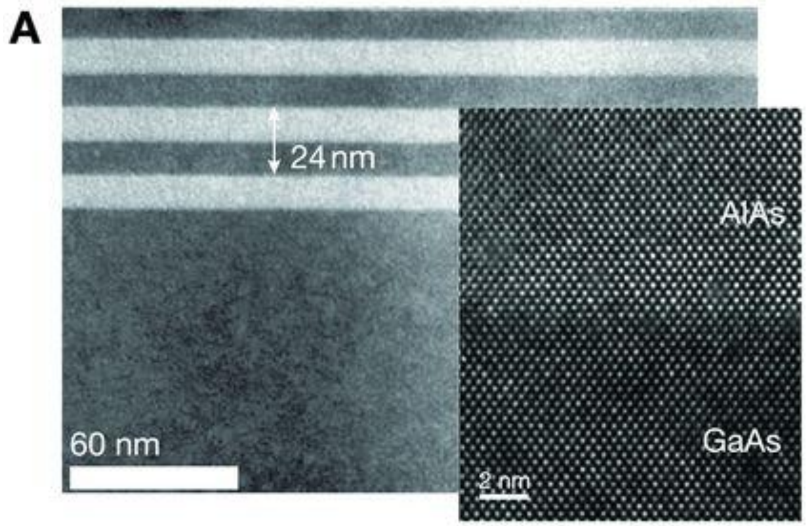


A. I. Hochbaum et al. Nature 451, 163 (2008)

V(III). Nanostructuring: phonon filtering

Inteface thermal conductance (flux normal to the interface under a thermal gradient) ≈ 10-200 MW/m^2K

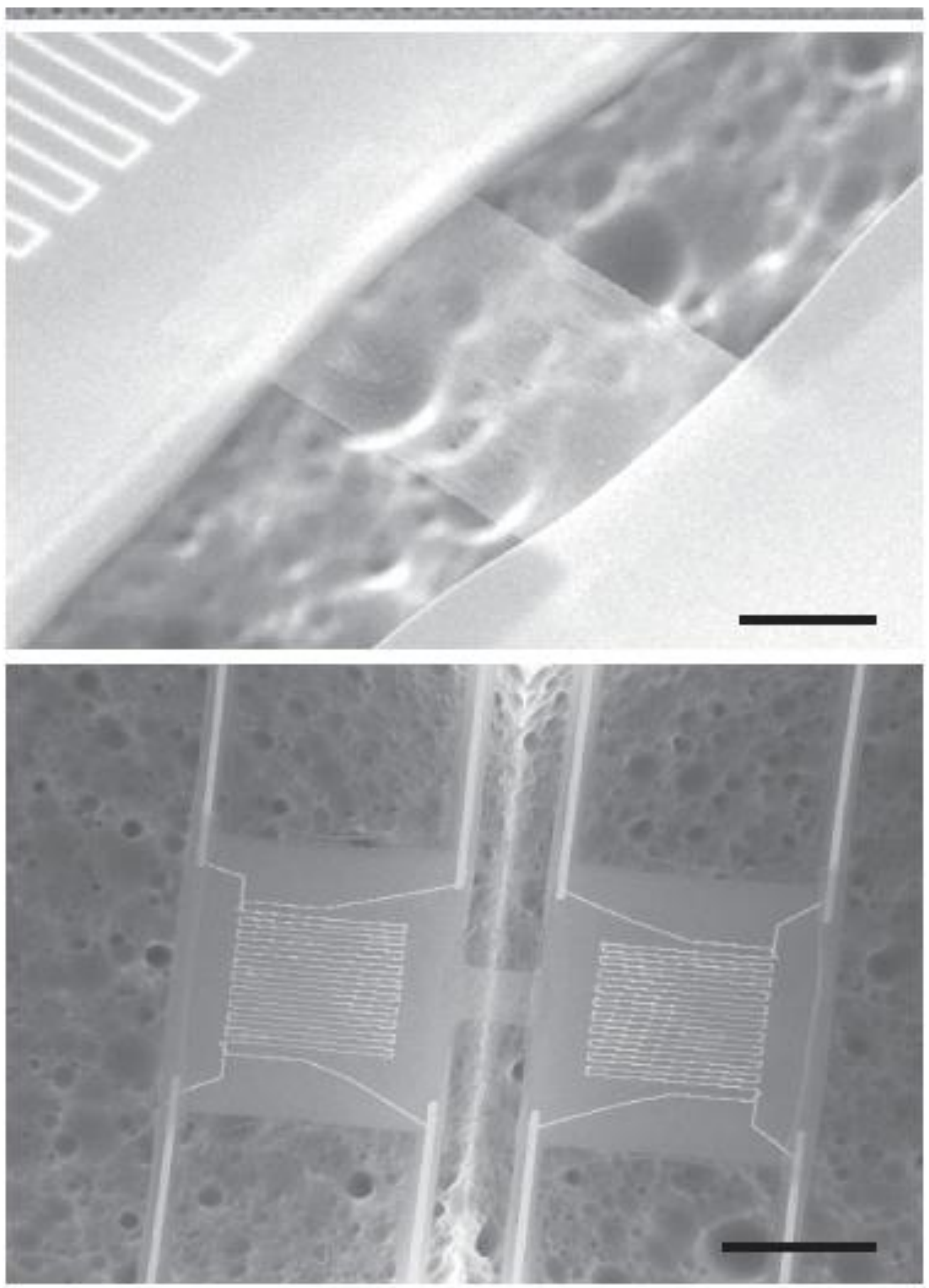


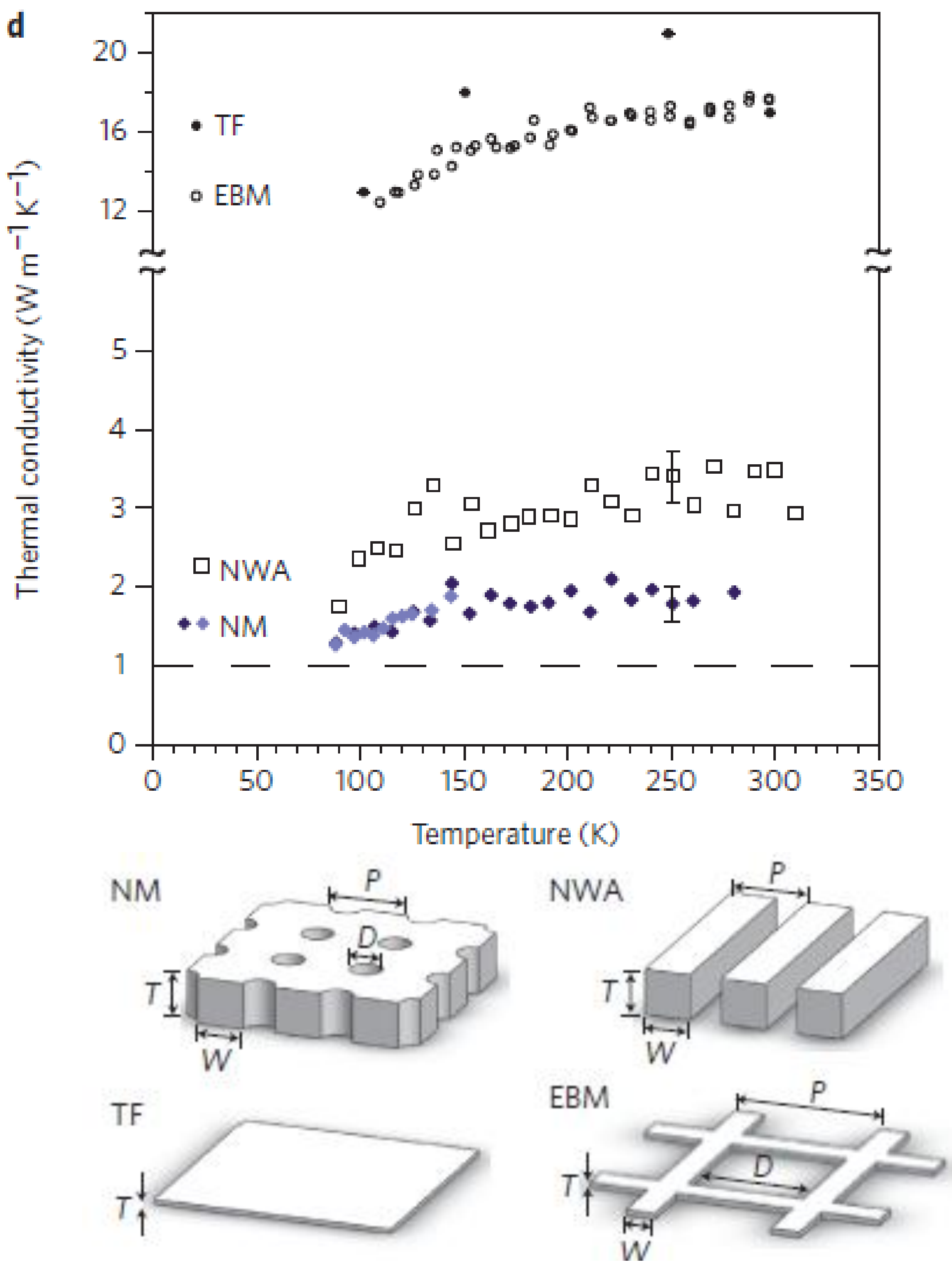


Artificial multilayers (GaAs/AlGaAs) ≈ 8-30 MW/m^2K

Selective phonon filtering

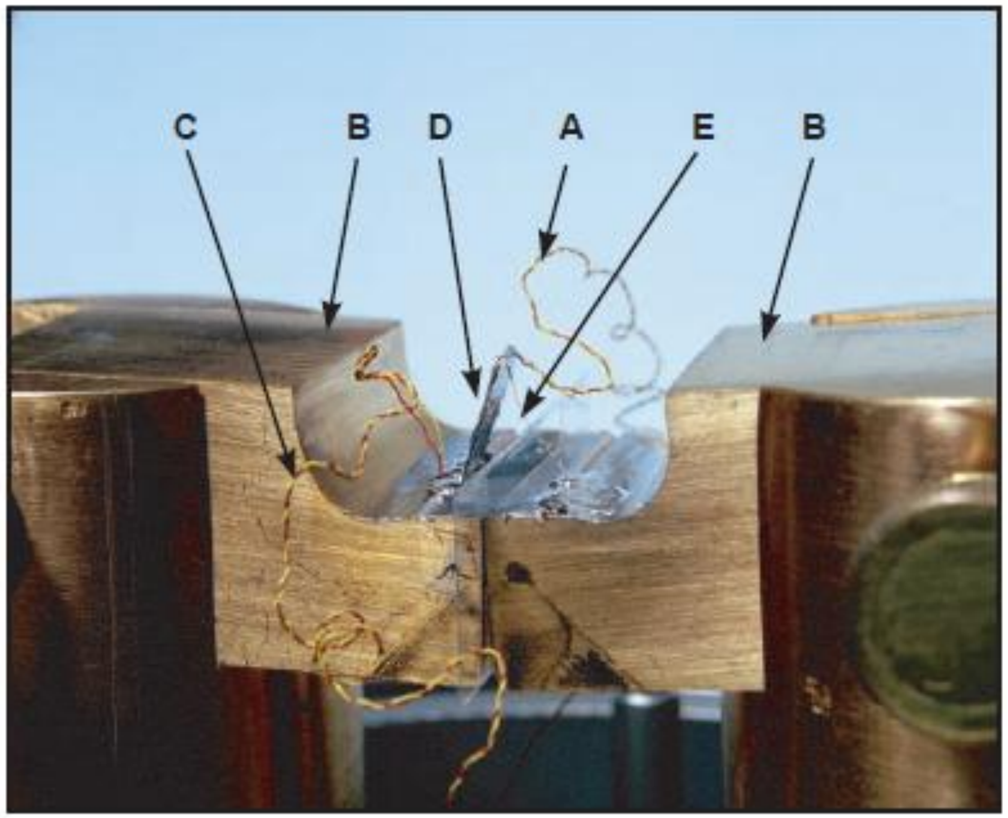
V(III). Nanostructuring: articial phononic crystals

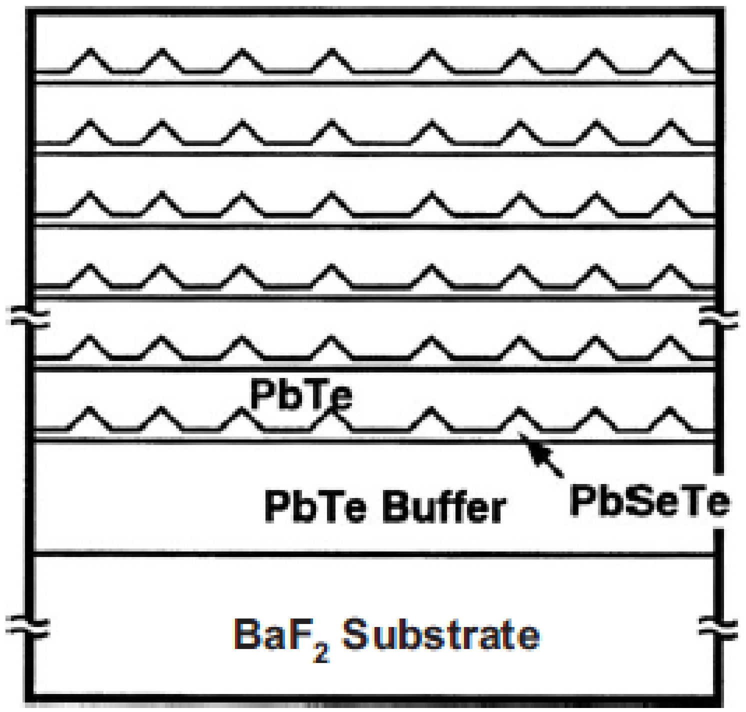


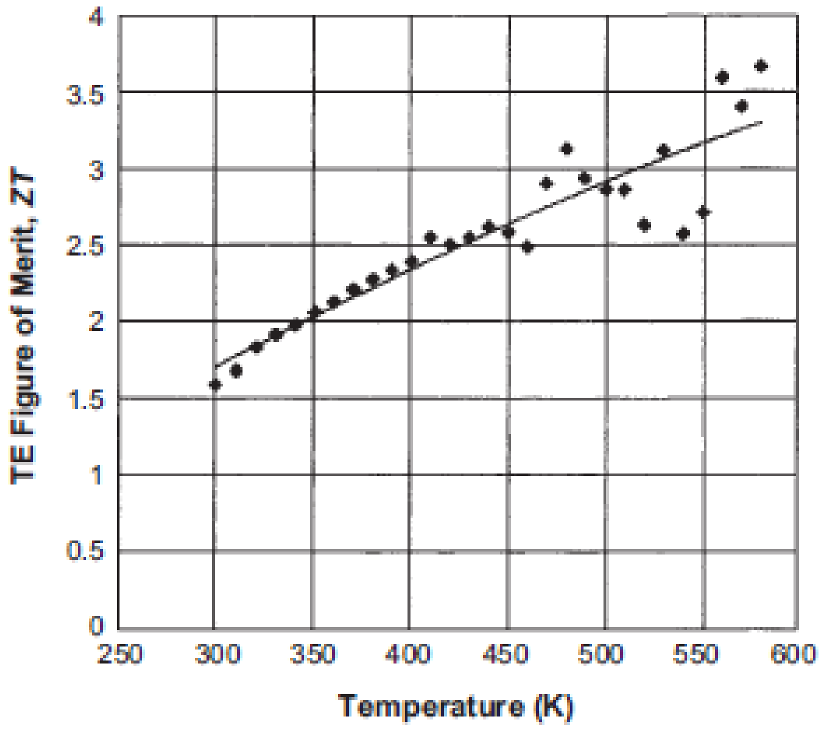


J. Yu et al. Nat. Nanotech. (2010)

V(III). Nanostructuring: articial phononic crystals







Sample	S(μV/K)	ZT	Carrier conc. (cm^{-3})	Carrier mobility (cm^2/V-s)
n-QDSL A	−219	1.6*	1.2×10^{19}	370
n-QDSL B	−208	1.3*	1.1×10^{19}	300
n-BiSbSeTe A	−228	0.9**	4.6×10^{19}	110

Harman et al. Science (2002)

V(III). Nanostructuring: articial nanostructures

PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Effect of quantum-well structures on the thermoelectric figure of merit

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(Received 3 December 1992)

Currently the materials with the highest thermoelectric figure of merit Z are Bi_2Te_3 alloys. Therefore these compounds are the best thermoelectric refrigeration elements. However, since the 1960s only slow progress has been made in enhancing Z, either in Bi_2Te_3 alloys or in other thermoelectric materials. So far, the materials used in applications have all been in bulk form. In this paper, it is proposed that it may be possible to increase Z of certain materials by preparing them in quantum-well superlattice structures. Calculations have been done to investigate the potential for such an approach, and also to evaluate the effect of anisotropy on the figure of merit. The calculations show that layering has the potential to increase significantly the figure of merit of a highly anisotropic material such as Bi_2Te_3, provided that the superlattice multilayers are made in a particular orientation. This result opens the possibility of using quantum-well superlattice structures to enhance the performance of thermoelectric coolers.

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 24 15 JUNE 1993-II

Thermoelectric figure of merit of a one-dimensional conductor

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We investigate the effect on the thermoelectric figure of merit of preparing materials in the form of one-dimensional conductors or quantum wires. Our calculations show that this approach has the potential to achieve a significant increase in the figure of merit over both the bulk value and the calculated two-dimensional superlattice values.

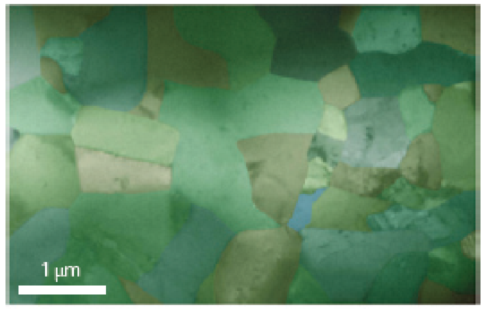
> 1500 citations

editorial

Reflections on thermoelectrics

On the twentieth anniversary of two influential papers we consider past developments and future opportunities for thermoelectric materials.

In May and June of 1993, Lyndon Hicks and Mildred Dresselhaus published two theoretical papers that showed reducing the dimensionality of thermoelectric materials could dramatically improve their performance[1,2]. In this issue, we publish a Commentary by Joseph P. Heremans, Mildred S. Dresselhaus, Lon E. Bell and Donald T. Morelli on the history and legacy of this work[3]. The authors explain that the two papers emerged from a need to provide



be possible, however, is the development of functionalities and applications that are unique to these materials. As in the case of the Curiosity rover, it is possible to imagine other self-powered controls or sensors. Alternatively, as in the case of the Climate Control Seat, it is possible to picture other compact devices for on-demand thermal management in home and commercial furnishings.

Twenty years ago, the work of Hicks

V(III). Nanostructuring: articial nanostructures

PHYSICAL REVIEW B **77**, 245118 (2008)

Aspects of metallic low-temperature transport in Mott-insulator/band-insulator superlattices: Optical conductivity and thermoelectricity

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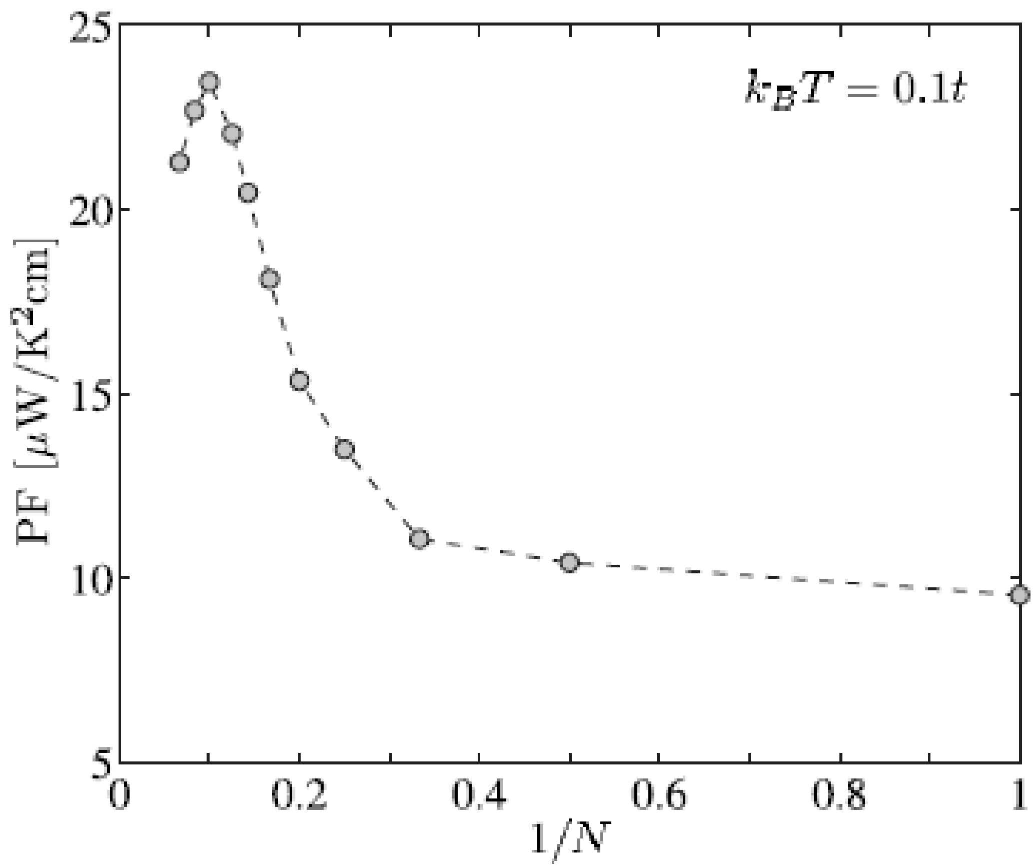
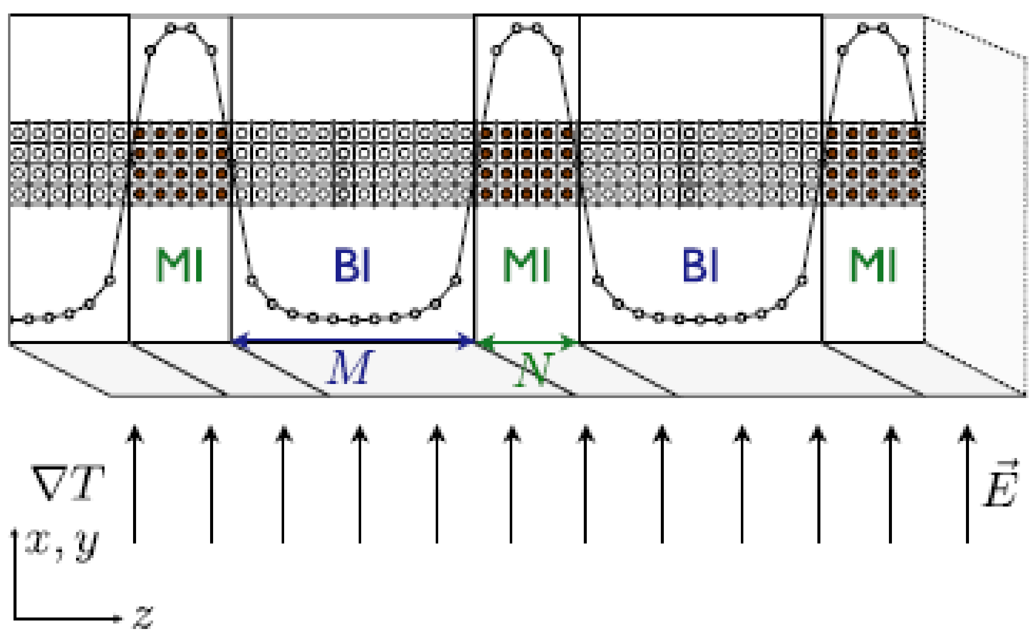
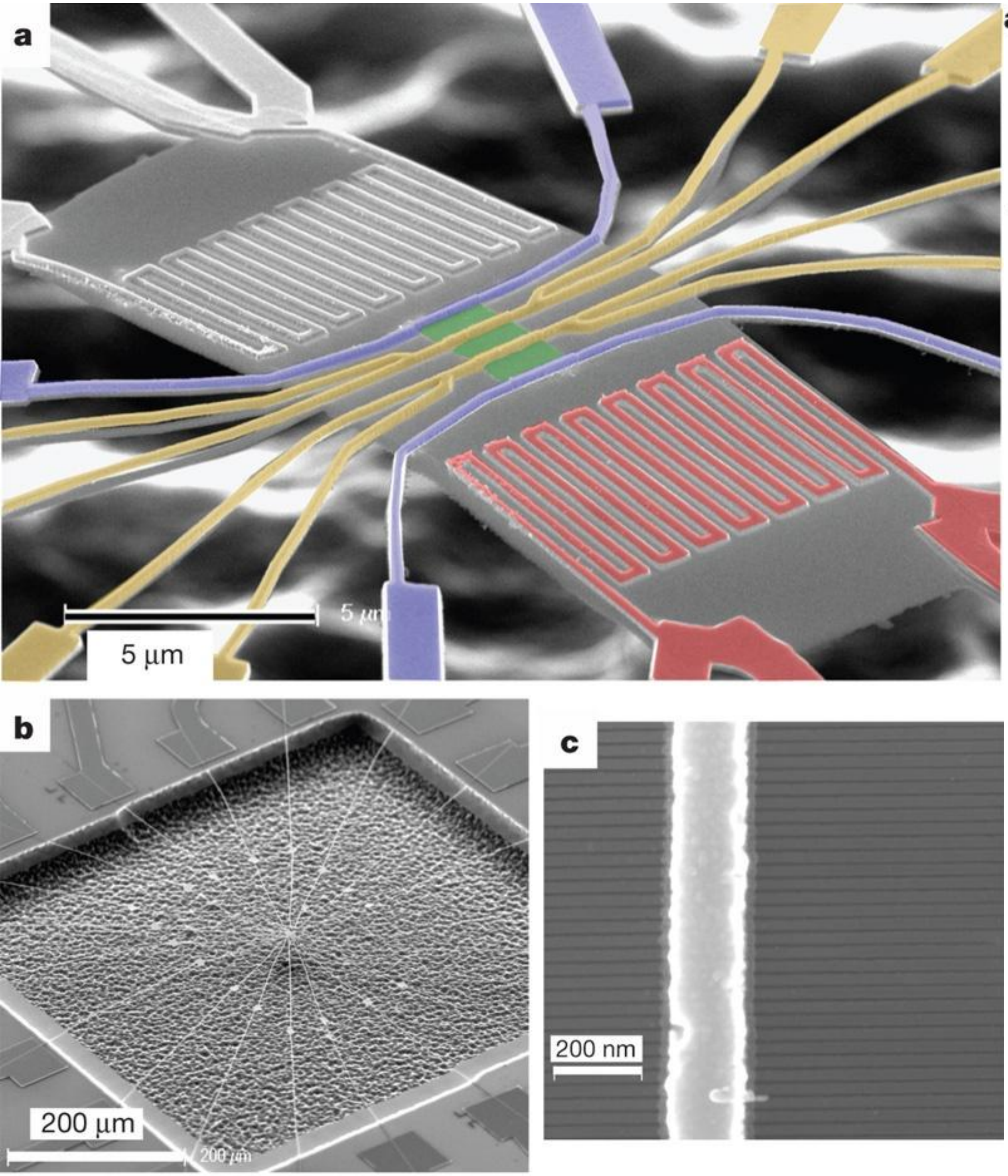
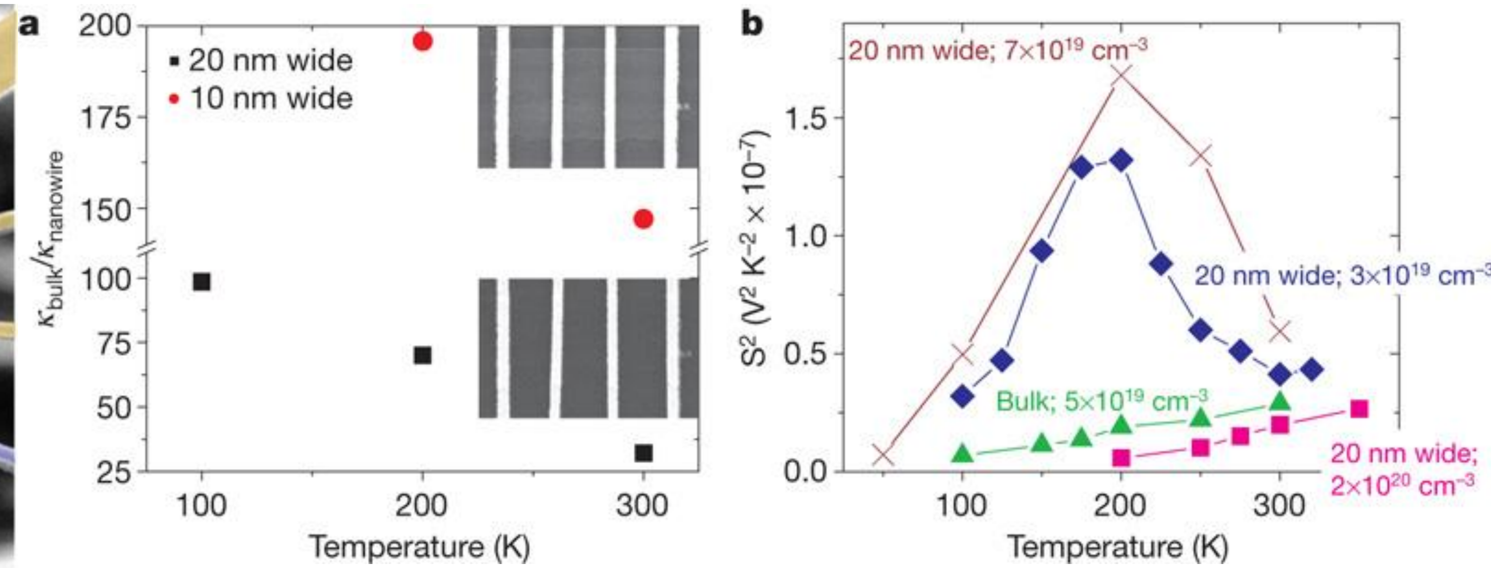
Theoretische Physik, ETH Zürich, CH-8093 Zürich, Switzerland
(Received 28 March 2008; revised manuscript received 23 May 2008; published 18 June 2008)

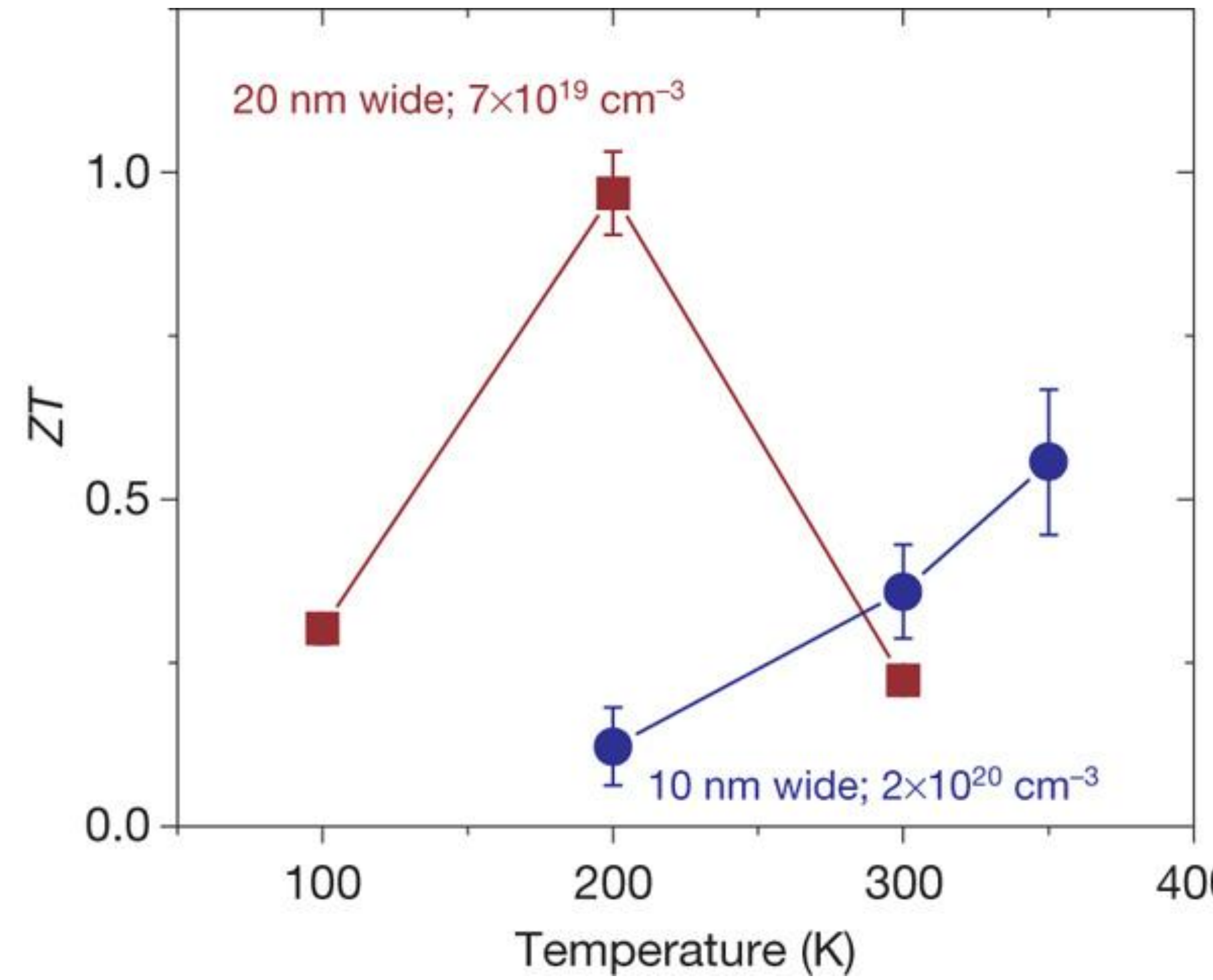




V(III). Nanostructuring: articial nanostructures

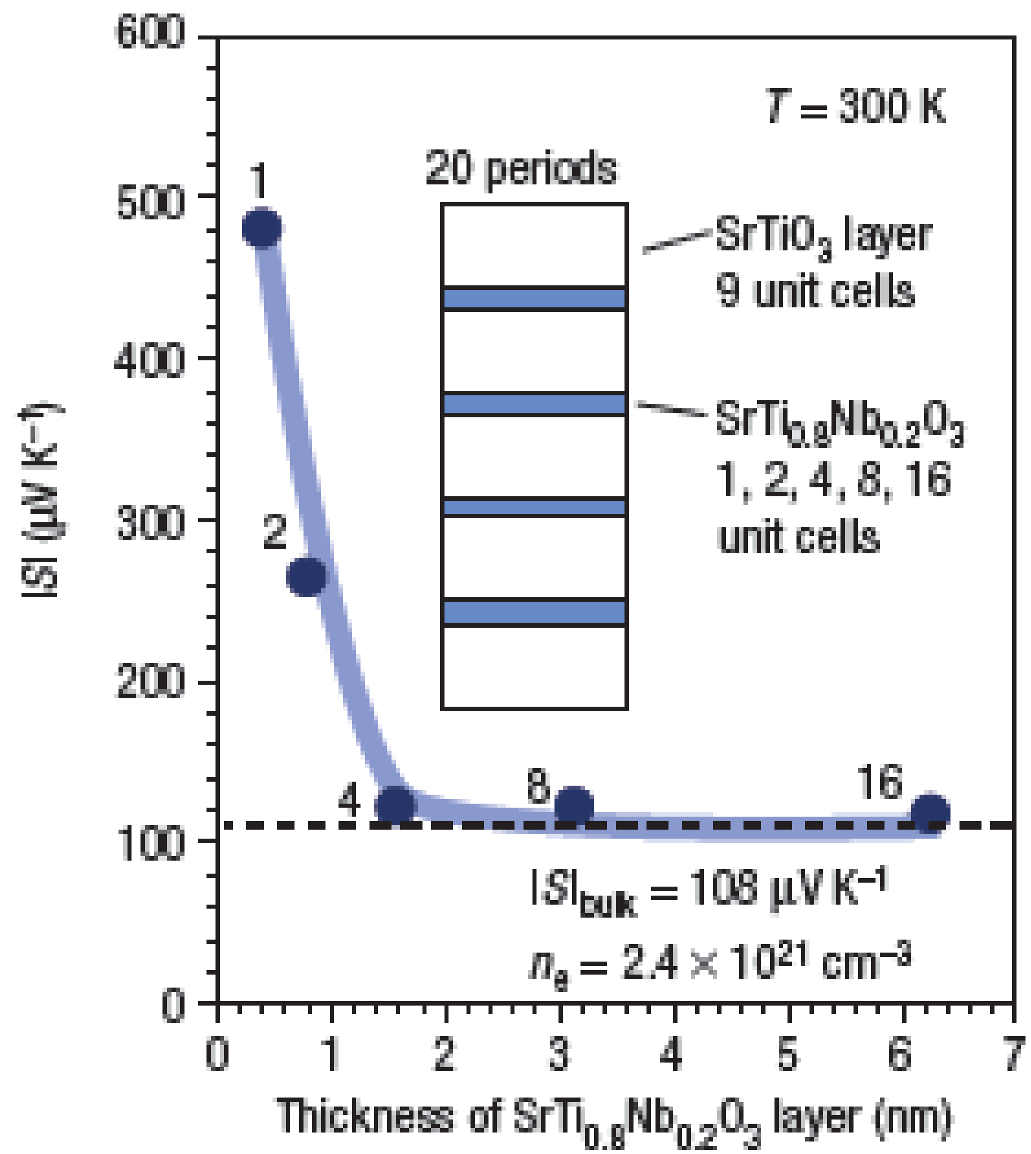


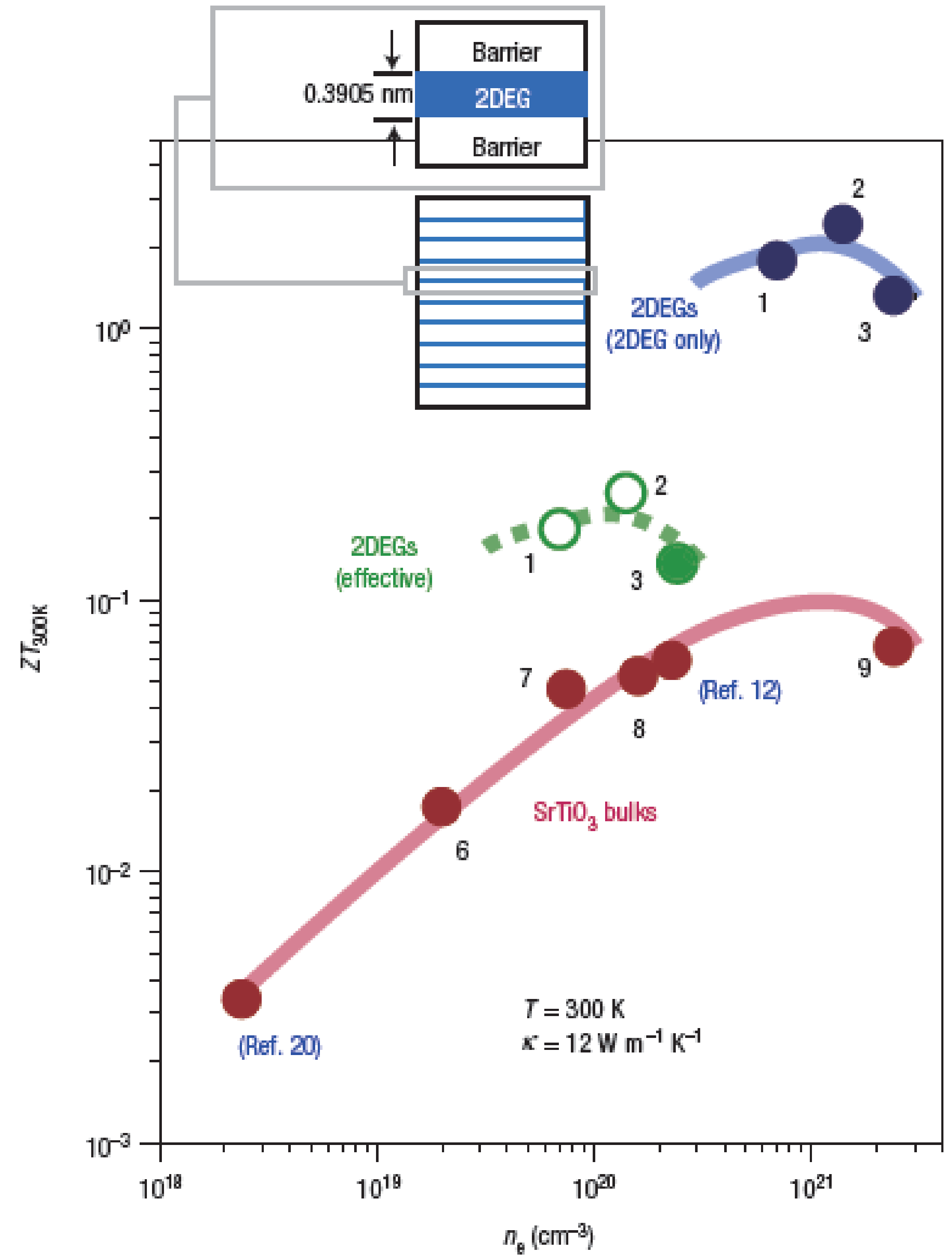




Boukai et al. Nature 451, 168 (2008)

V(III). Nanostructuring: effect of quantum confinement in articial nanostructures



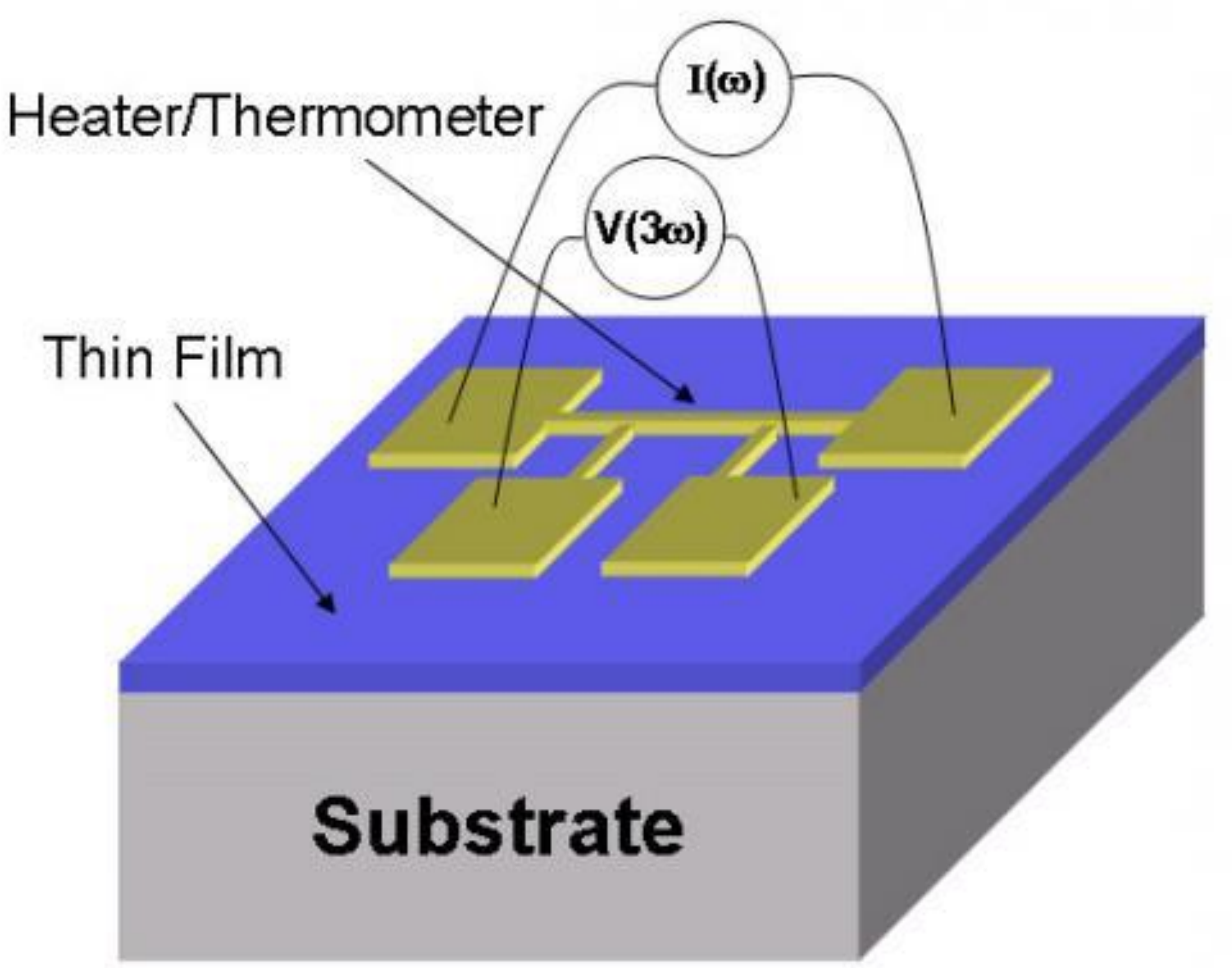


H. Ohta et al. Nat. Mat. (2007)

VI. Challenges the characterization of nanoTE systems

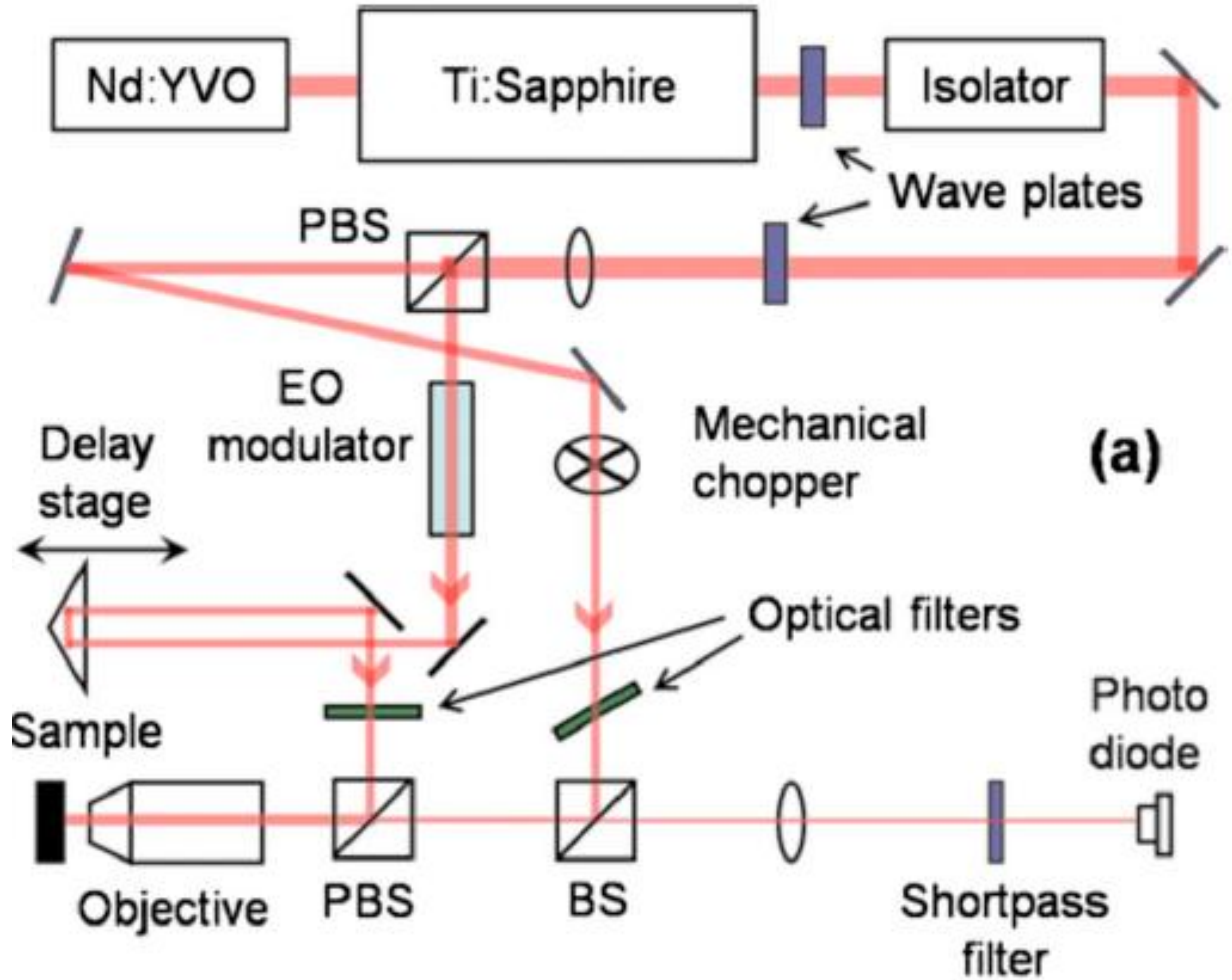
<u>The 3ω method :</u>

Measuring the thermal conductiivyt in thin-films



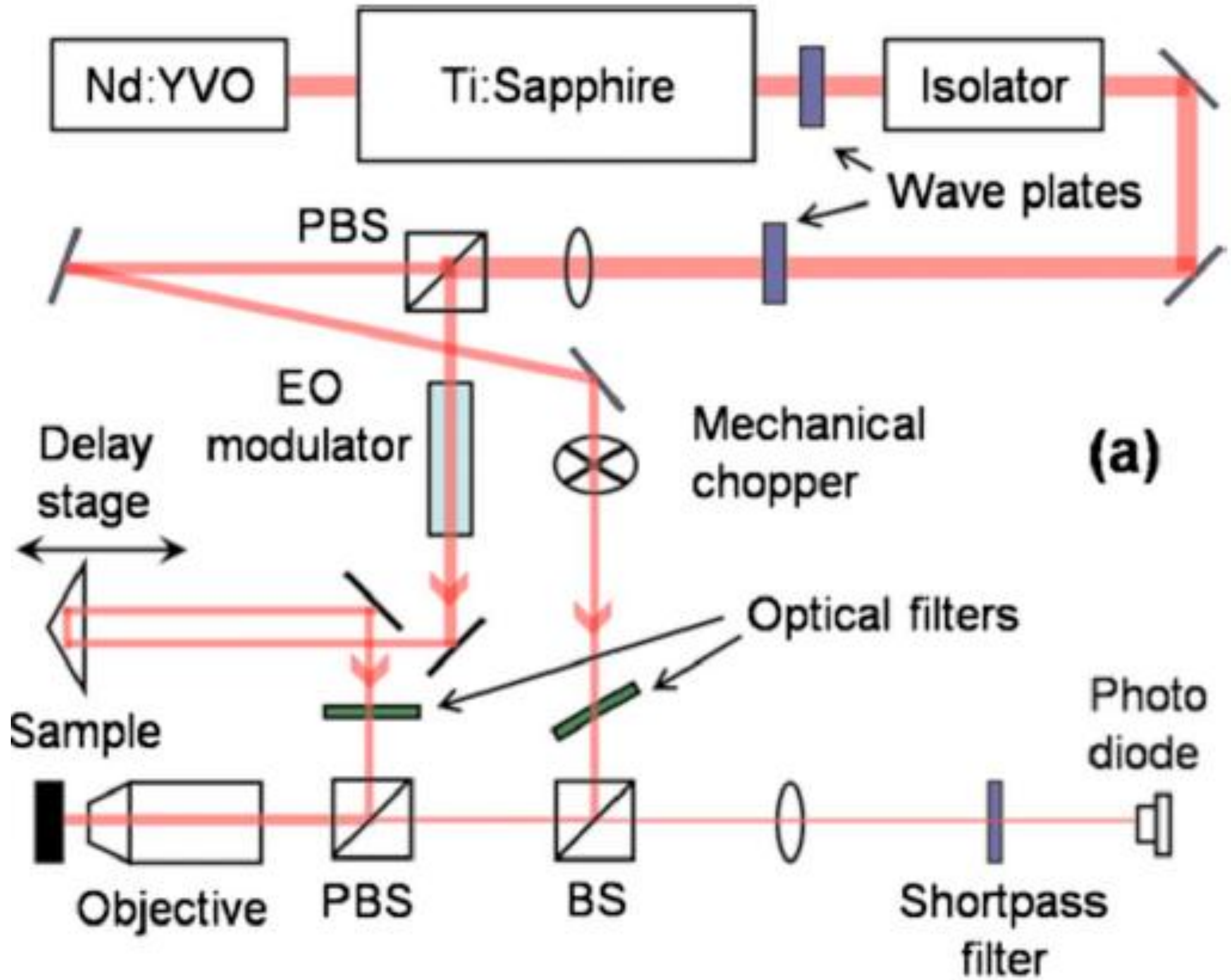
VI. Challenges the characterization of nanoTE systems

Time-domain thermoreflectance:



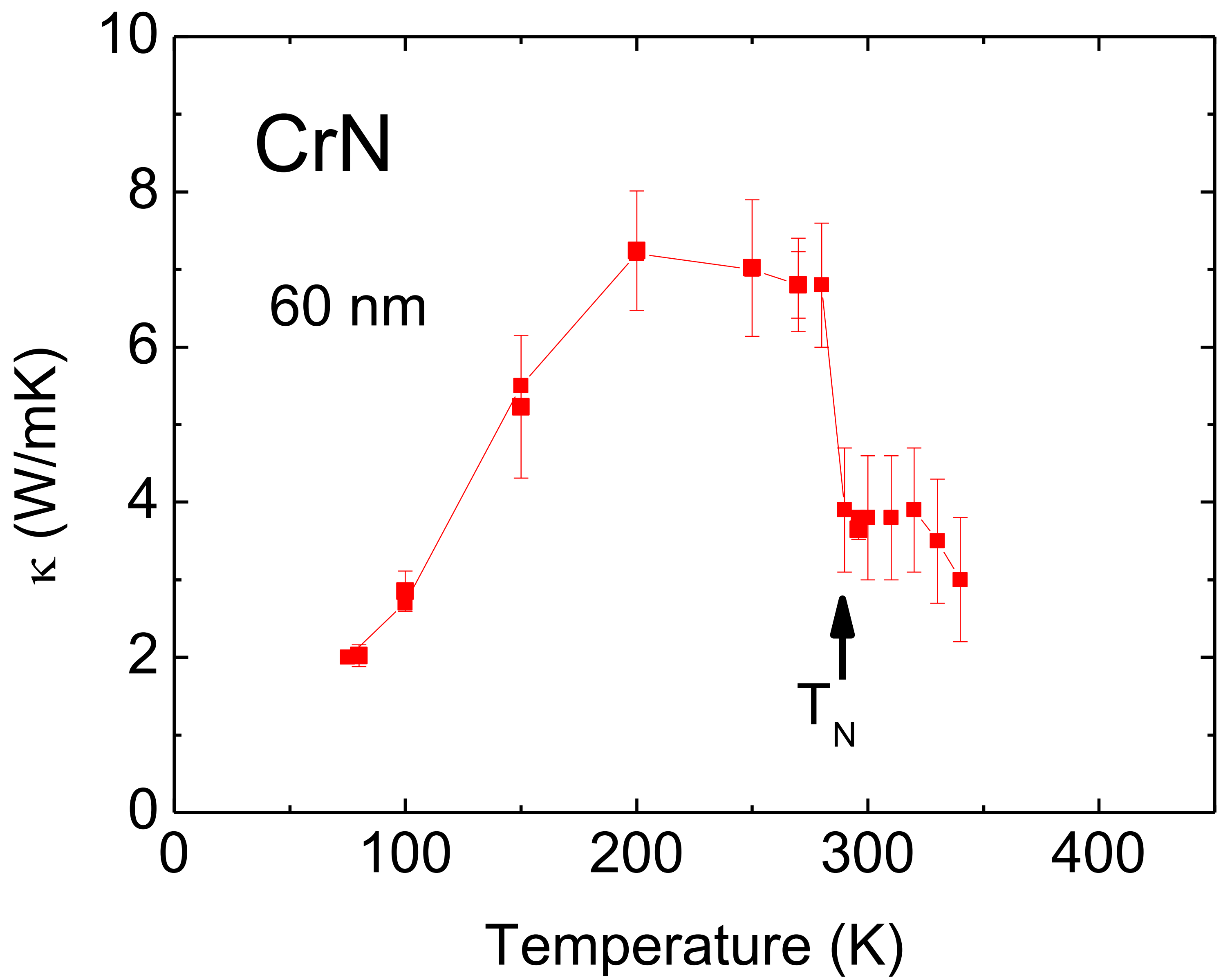
VI. Challenges the characterization of nanoTE systems

Time-domain thermoreflectance:

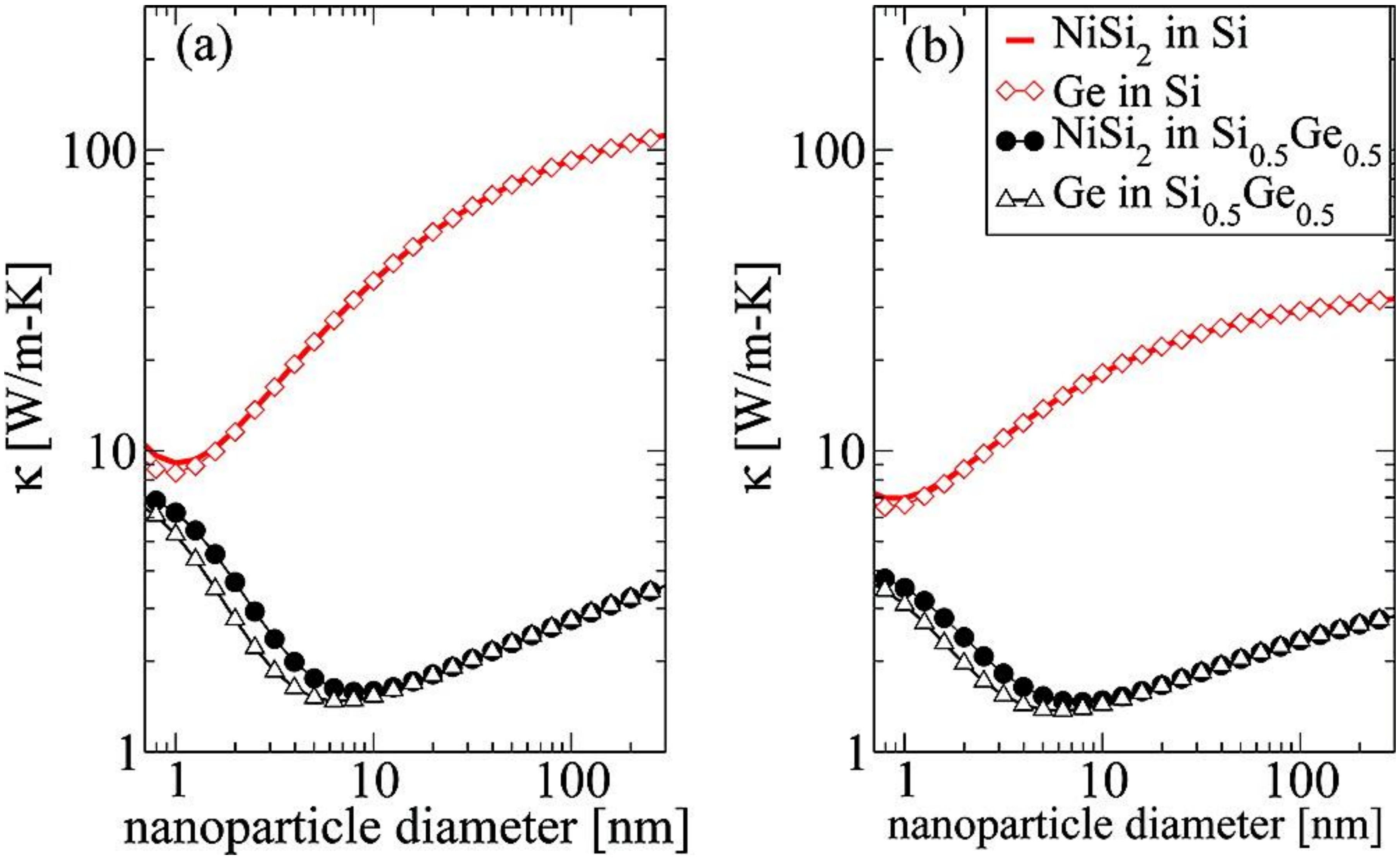


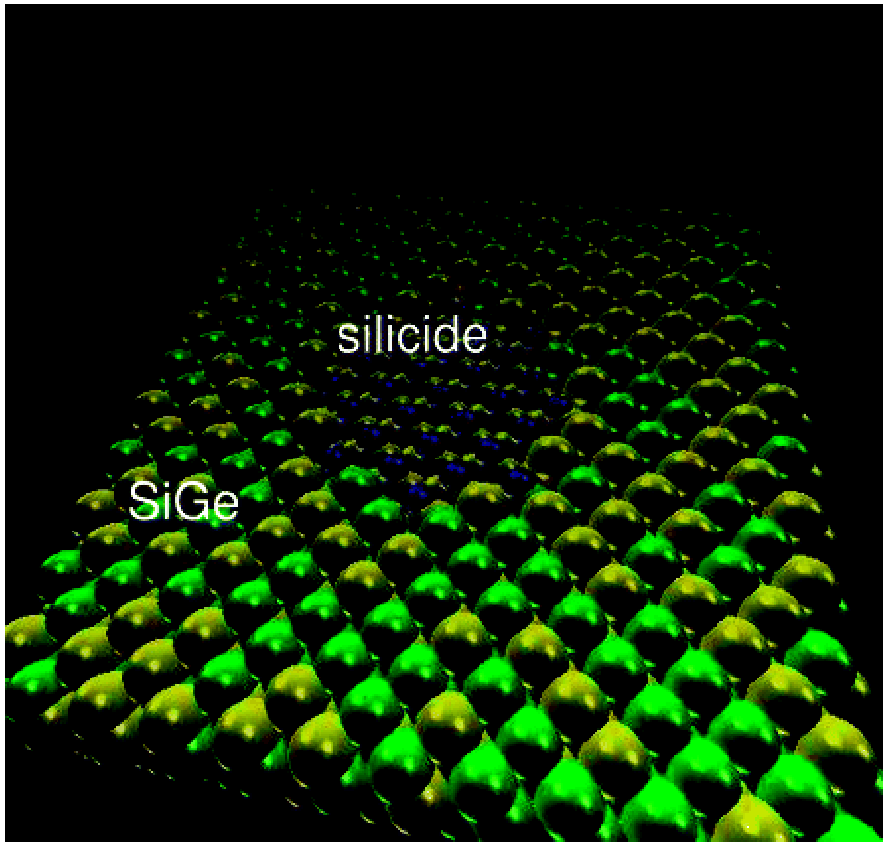
VI. Challenges the characterization of nanoTE systems

Time-domain thermoreflectance:



Challenges the characterization of nanoTE systems





N. Mingo et al. Nano Lett. (2009)

Conclusions

Nanostructuring is the future for TE technology