Fuel Choices Summit

Tel Aviv, November 2-3, 2016

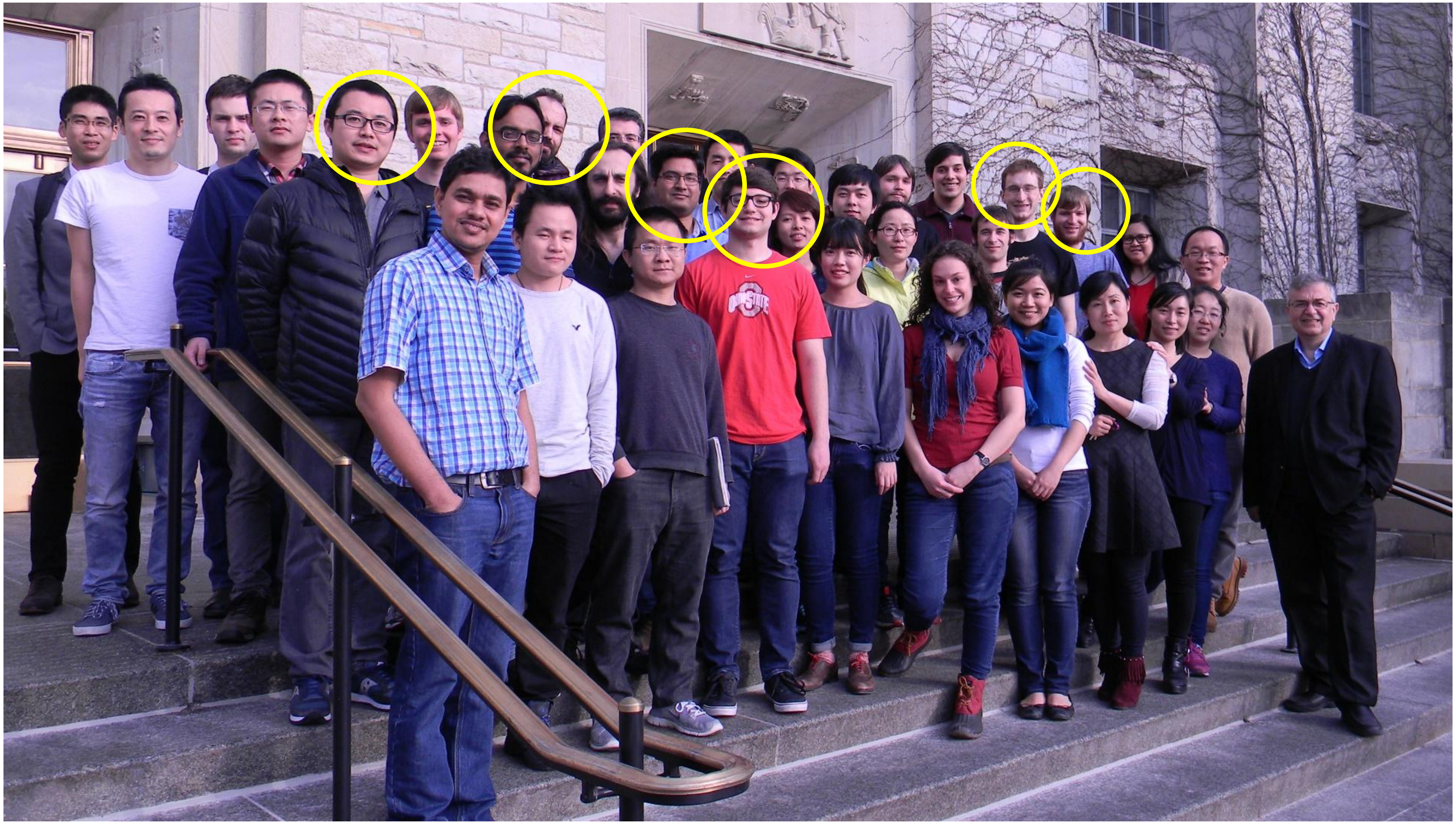
2016 Eric and Sheila Samson Prime Minister's Prize

Heat to Electricity with nano-Thermoelectrics

Mercouri Kanatzidis

Northwestern University, Evanston, IL, USA

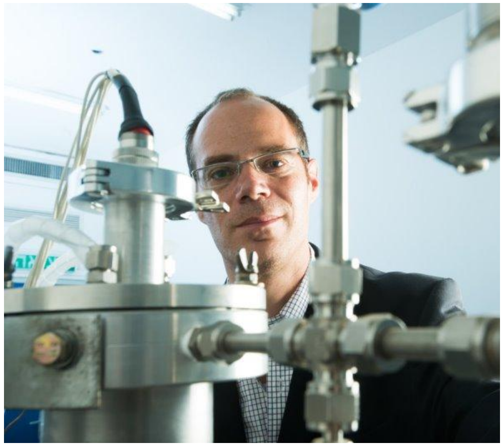
2016



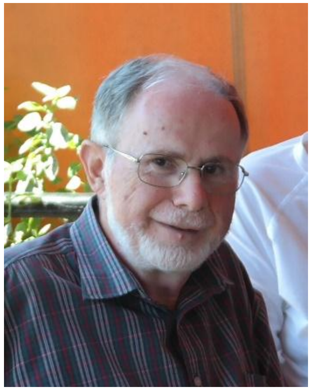
Collaborators

■Vinayak Dravid, NU

■Ctirad Uher, Michigan



■Yaniv Gelbstein, Ben Gurion, Israel



■Stathis Polychroniadis, Aristotle Univ, Greece

■Chris Wolverton, NU

■David Seidman, NU

Jiaqing He
SUST, Shenzhen, China

Students

Alyssa Hayens, PhD 2016
Jonathan Syrigos, PhD 2016
Nicholas Calta, PhD 2015
Rachel Korkosz, PhD 2015
Yurina Shim, PhD 2014
Ye Seul Lee, PhD 2014
Ronald Soriano, PhD 2014
Sandy Nguyen, PhD 2013
Collin Morris, PhD 2012
Youngtak Oh, PhD 2012
Myung-Gil Kim, PhD 2012
Melanie Francisco, PhD 2011
Steven Girard, PhD 2011
Joshua Mertz, PhD 2011
Tarun Bera, PhD 2010
Joseph Sootsman, PhD 2009,
Santanu Bag, PhD 2009
Maria Chondroudi, PhD
Aurélie Guéguen, PhD 2008
Nan Ding, PhD 2007
Jun Ho Kim, PhD 2006
Xiu-Ni Wu, PhD 2006
Ratnasabapathy G. Iyer, PhD 2004
James Salvador, PhD 2004

Sumahan Misra, MS 2004
Marina Zhuravleva, PhD 2003
Bradley Sieve, PhD 2002
Jenifer Aitken, PhD 2001
Lykourgos Iordanidis, PhD 2000
Stephane DeNardis, MS 2000
Kyoung-Shin Choi, PhD 2000,
Jean D Breshears, PhD 2000,
Joy M Heising, PhD 1999,
Lei Wang, PhD 1999
Rhonda Patschke, PhD 1999
Jason Hanko, PhD 1998
Konstantinos Chondroudis, PhD 1997
Andy Enos Axtell III, PhD 1995
Chenggang Wang, PhD 1995
Kang Woo Kim, PhD 1995,
Anthony Sutoric, PhD 1994
Tim McCarthy, PhD 1994
Yu Ju Liu, PhD 1994
Hsiou Ju Liao, PhD 1993
Song ping Huang, PhD 1993
Sandeep Dingra, PhD 1992,
Chun-Guey Wu, PhD 1992,
Yonbong Park, PhD 1992,
Jun-Hong Chou (Richard), PhD,

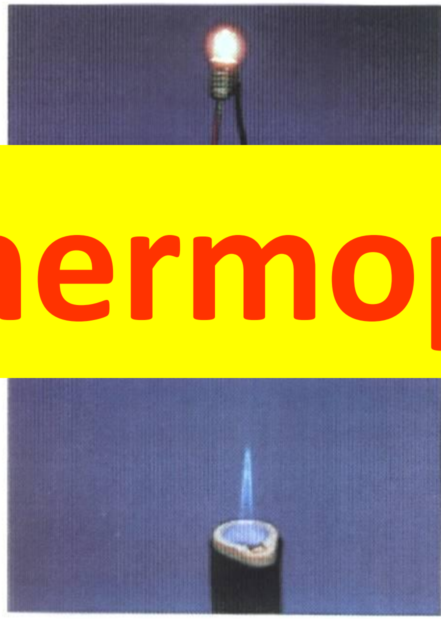
Postdocs and Research Associates

- Abhishek Banerjee, PhD
  Peng Wang, PhD
  Hsueh-Chung (Stan) Liao, PhD
  Subrahmanyam (Subbu) Kota S, PhD
  Mihai Sturza, PhD
  Lei Fang, PhD
  Raj Cheriyedath, PhD
  Lidong Zhao, PhD
  Shichao Wang, PhD
  Arief Wibowo, PhD
  Daniel Shoemaker, PhD
  Zohreh H.Fard, PhD
  In Chung, PhD
  Alexandros Katsoulidis, PhD
  Kyriaki Polychronopoulou, PhD
  Ben Yuhas, PhD
  Jiaqing He, PhD
  Kanishka Biswas, PhD
  Ioannis Androulakis, PhD
  Simon Johnsen, PhD
  Sebastian Peter, PhD
  Alexander Rothenberger, PhD
  Maryam Shafaei Fallah, PhD
  Ilyia Todorov, PhD
  Christopher Stender, PhD
- Danielle Gray, PhD
  Gerasimos Armatas, PhD
  Mi-Kyung Han, PhD
  Hui-Lien Tsai, PhD
  Pierre Ferdinand Poudeu, PhD
  Hanna Lind, PhD
- Regina Pocha, PhD,
- Chia her Lin, PhD
- Kuei Fang Hsu, PhD
  John Androulakis, PhD
- Eric Quarez, PhD
- Pantelis Trikalitis, PhD
  Kasthuri Rangan, PhD
  Susan Latturner, PhD
- Junghwan Do PhD
  Theodora Kyratsi PhD
- Sandrine Sportouch, PhD
  Michael Wachhold, PhD (DFG-Fellow)
- Antje Mrotzek, PhD (DFG-Fellow)
- Hans O. Stephan PhD (DFG-Fellow)
- Seong-Ju Hwang PhD,
- Oleg Palchik PhD
- Tracy Kerr, PhD
  Servane Coste PhD
  Spyros Glenis, PhD
  Dr. Hui-Lien Tsai,
  Greg Marking, PhD,
- Xianchong Chen, PhD
  Xiang Zhang, PhD
  Debu Chakrabarty, PhD
  Wakgari Hirpo, PhD
  May Nyman, PhD
  Yoshikata Matsushita, PhD
- Santanu Banerjee, PhD
  Kyunghan Ahn, PhD
  Indika Arachchige, PhD
- Qichun Zhang, PhD
  Manolis Manos, PhD
- Guo-Fu Wang PhD (deceased)
  Francois Bonhomme PhD
  Birinchi Das PhD
- Kuei-Fang Hsu, PhD,
- K. Kasthuri Rangan, Ph.D.,
-

Funding

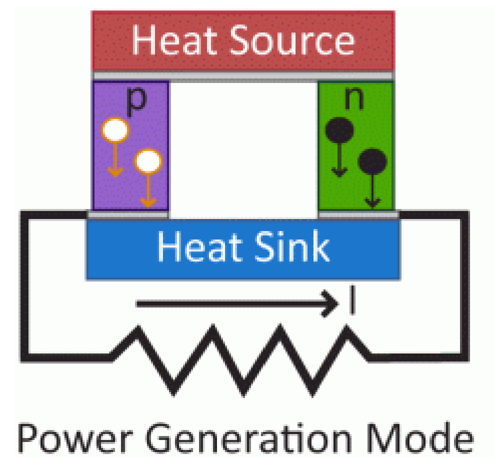
Heat to Electrical Energy Directly

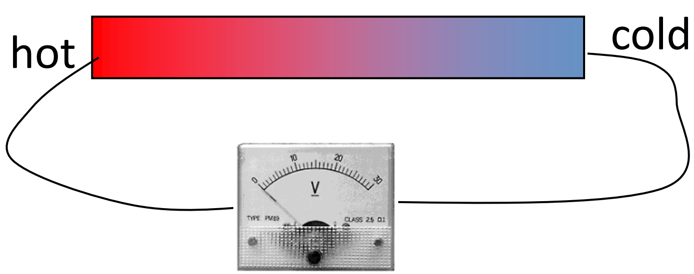
Up to 25% conversion efficiency with right materials



Electrical
Power Generation

Thermopower $S = \Delta V/\Delta T$

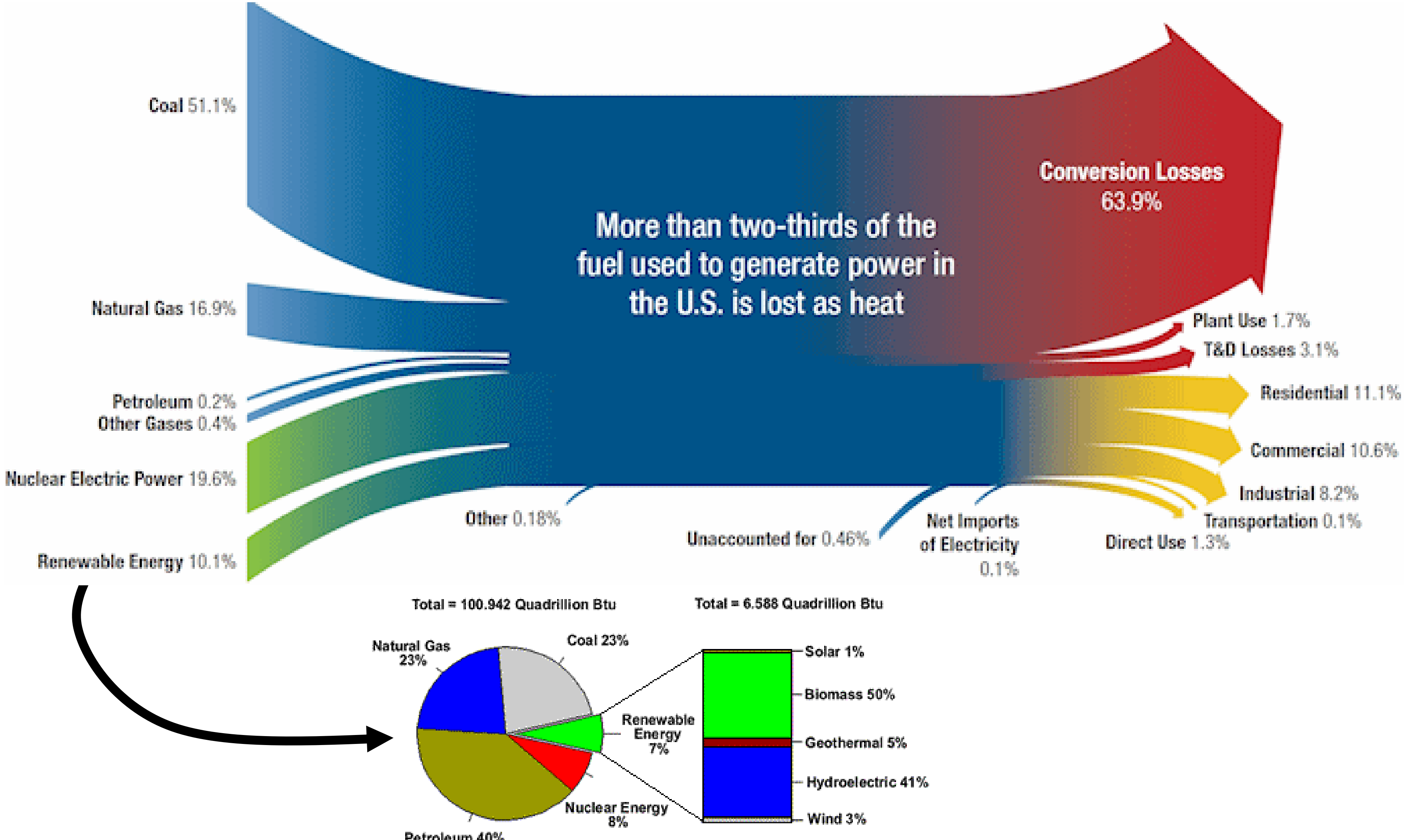




TE devices have <u>no moving parts, no noise, reliable</u>

Thermopower $S = \Delta V/\Delta T$

U.S. Energy Flow, 2015



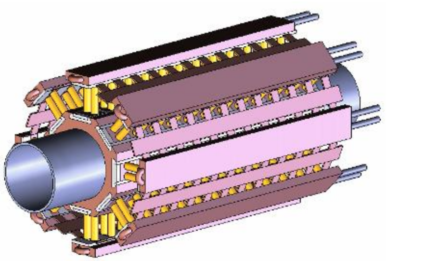
http://www.eia.doe.gov/emeu/aer/

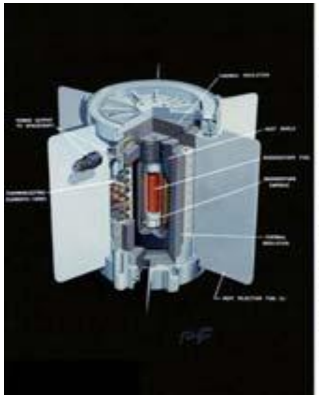
~65% of energy becomes waste heat,

~10% conversion to useful forms can have huge impact on overall energy utilization

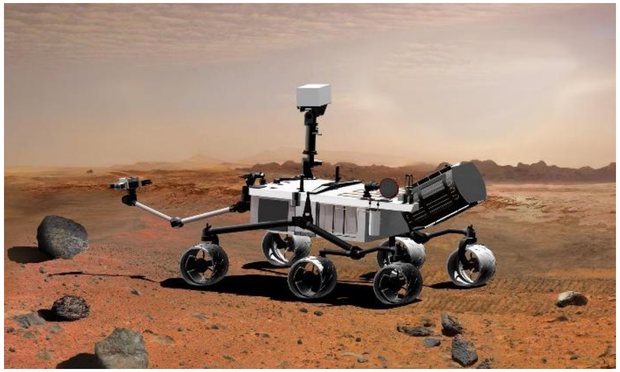
Thermoelectric applications

- Waste heat recovery
  - Automobiles
  - Over the road trucks
  - Marine
  - Utilities
  - Chemical plants
- Space power
- Remote Power Generation
- Solar energy
- Geothermal power generation
- Direct nuclear to electrical





PIONEER 10 and 11



Curiosity

TEG contribution to Future CAFE

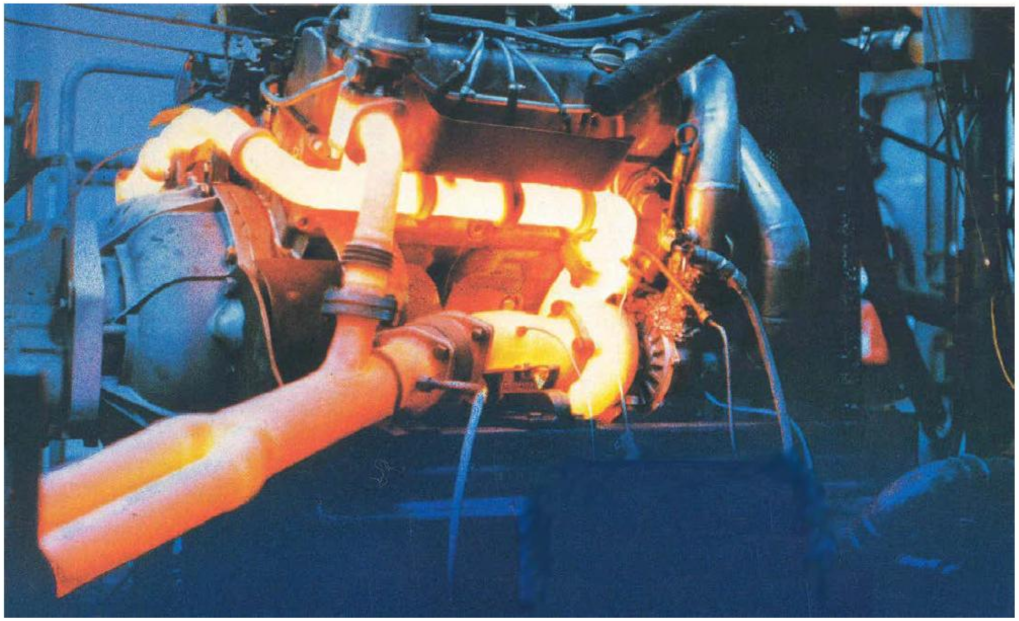
- White House announced an agreement with 13 major automakers to achieve 54.5 mpg by 2025

- Recovering engine exhaust waste heat using thermoelectric generators (TEGs) is consistent with this objective

- **Goal**: integrate vehicles with a technology that will improve fuel economy
- **Approach**: use thermoelectrics to convert energy in hot engine exhaust directly to electricity

Vehicular Engine Waste Heat Energy

Opportunity for improving fuel economy arises from **high temperature of vehicle exhaust systems**: converting heat to electricity reduces load on engine (electricity powers components; smaller alternator needed)



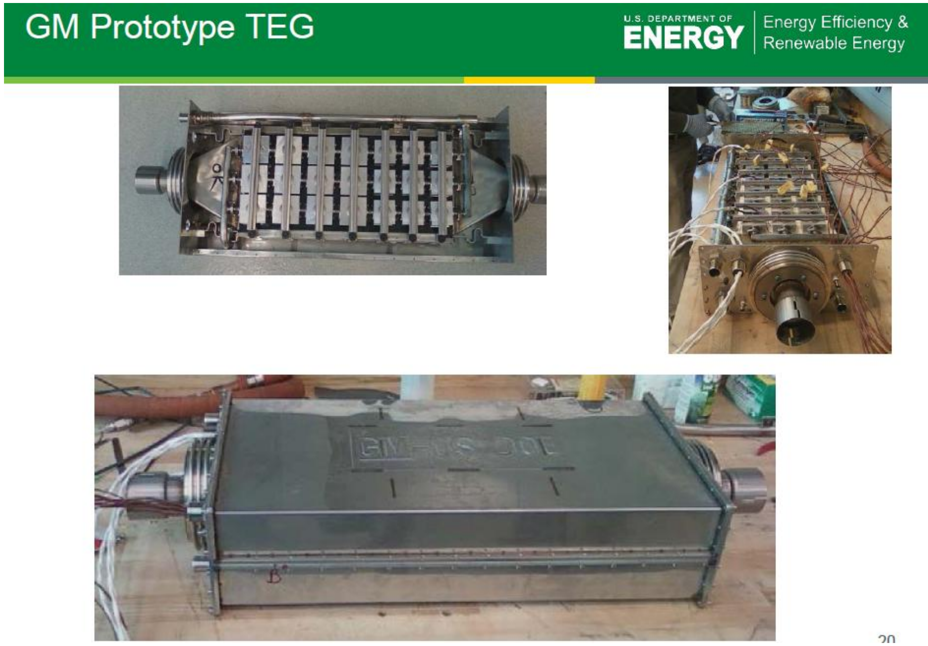
- **Target**: > 5% improvement in fuel economy; achieved by using output of TEG to power key electrical components

The power of increasing fuel economy by 1% and 5%

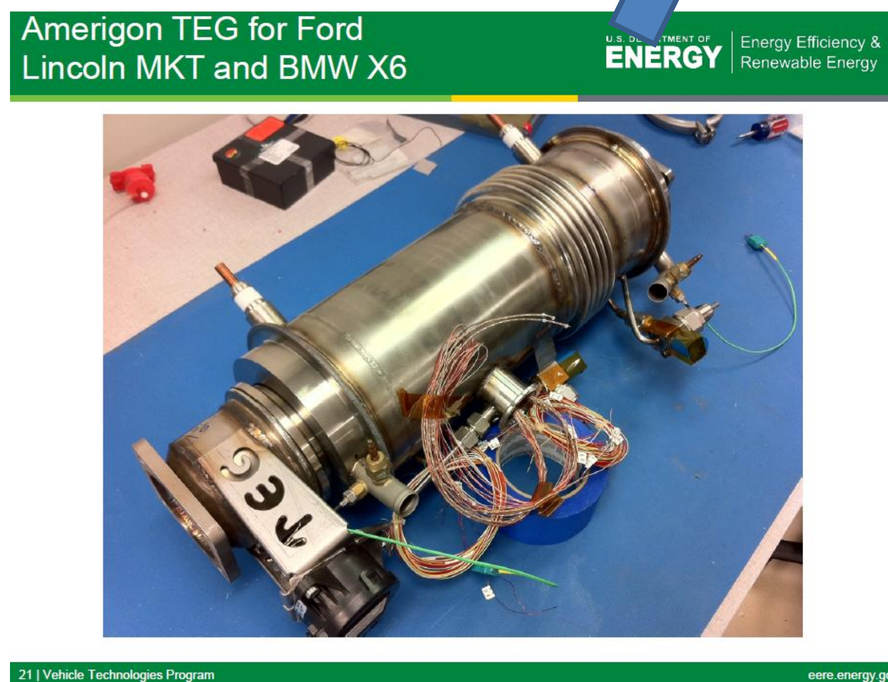
	Segment	Type of Savings	Estimated Fuel Savings over 1 Year (Billion nominal US Dollars)
Auto/Light-duty trucks	Personal	1% Fuel Savings	$5.0 B
Heavy-duty trucks	Commercial	1% Fuel Savings	$1.4 B
Auto/Light-duty trucks	Personal	5% Fuel Savings	$25 B
Heavy-duty trucks	Commercial	5% Fuel Savings	$6.9B

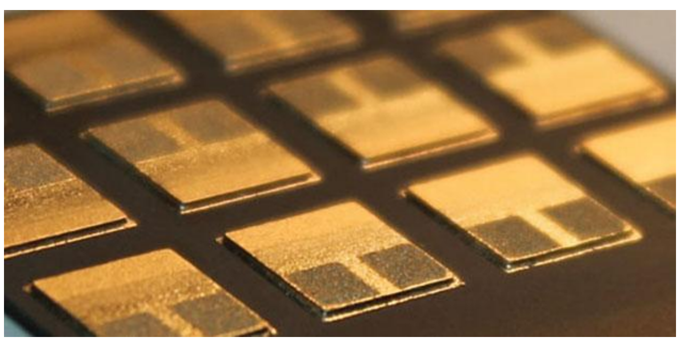
Reference: Davis (2012), Transportation Energy Data Book, Table 1.17. EIA (2013), "Gasoline and Diesel Fuel Update" (http://www.eia.gov/petroleum/gasdiesel/ accessed March 2013)

More efficient vehicle: Lower CO_2 emissions…



Gentherm

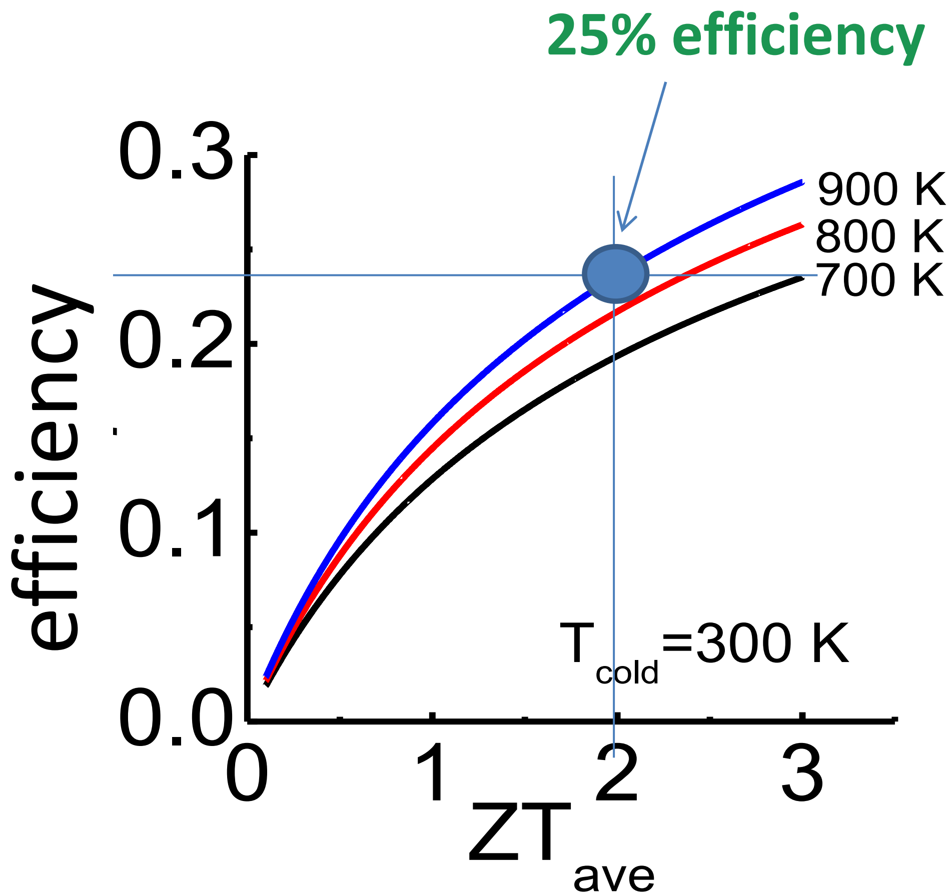




Alphabet Energy

TEG Installation in BMW X6

Figure of Merit and Conversion Efficiency



Thermopower

Electrical conductivity

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

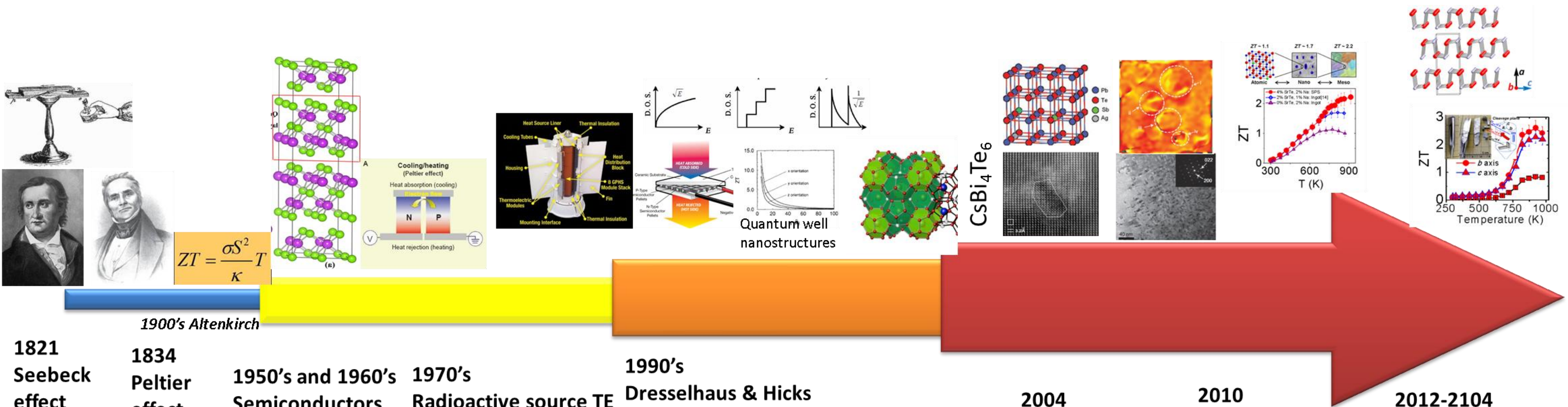
Temperature

Thermal conductivity

$$\eta = \left(\frac{T_H - T_C}{T_H}\right) \cdot \frac{\sqrt{1+ZT_{avg}} - 1}{\sqrt{1+ZT_{avg}} + (T_C / T_H)}$$

efficiency

A brief history



1821
Seebeck effect

1834
Peltier effect

1950's and 1960's
Semiconductors
Bi_2Te_3, ZT~1
ONR funds

1970's
Radioactive source TE
NASA, SiGe, PbTe
AgGeSbTe

1990's
Dresselhaus & Hicks
Nanoscale Bismuth
Glen Slack:: phonon glass electron crystal
Prediction of high ZT

2004
LAST material
ZT~1.5
Nanostructures discovered

2010
Endotaxial Nanostructures
ZT~1.7
DOE-EFRCs

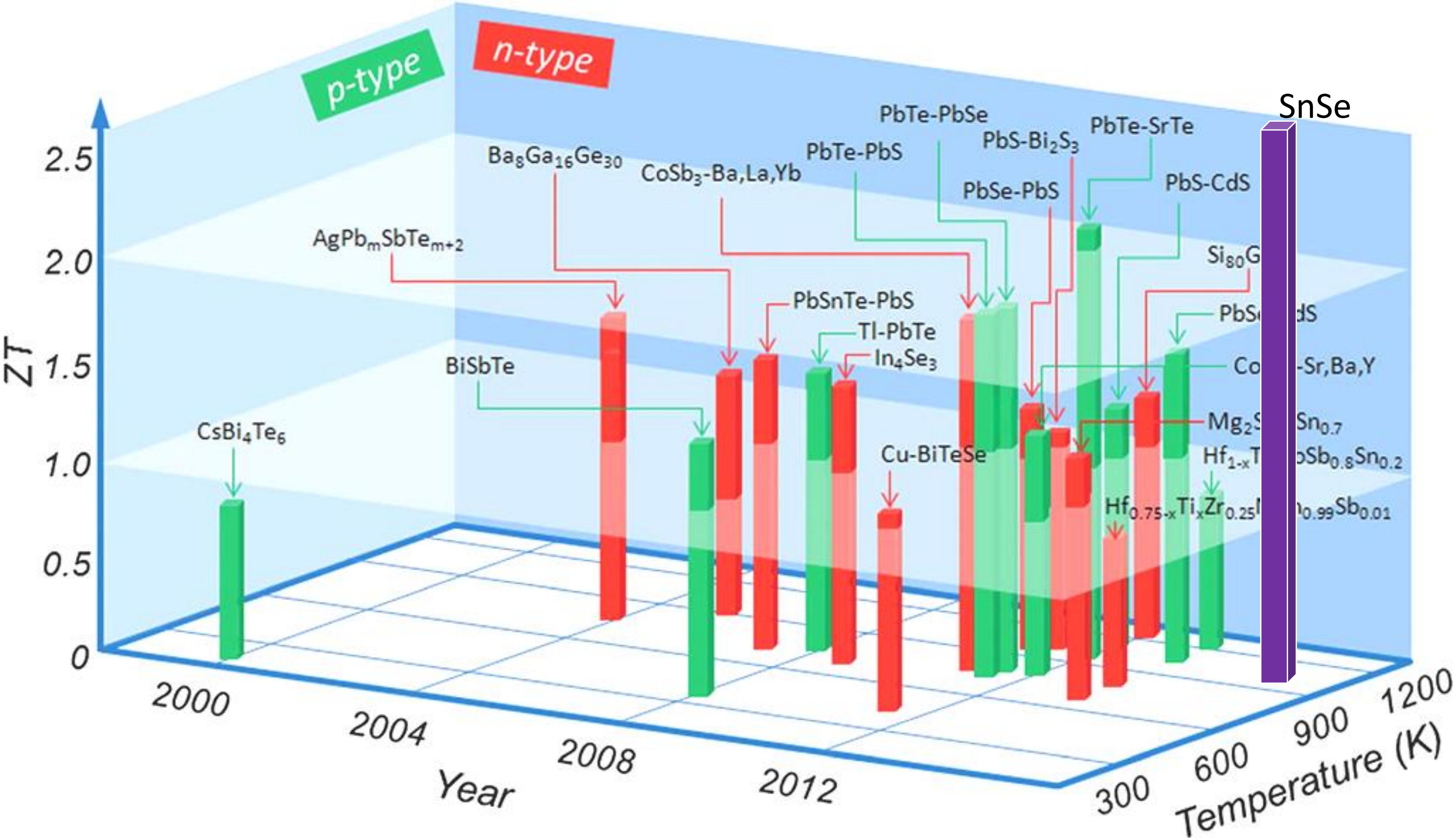
2012-2104
Panoscopic TE
ZT~2.2

SnSe ZT~2.6

1st paradigm of TE optimization developed

nanostructuring paradigm of TE optimization proposed

High ZT materials



Zhao LD, *et al* (review), ***EES*** 2014, 7, 251-268

ZT and Electronic Structure

Isotropic structure

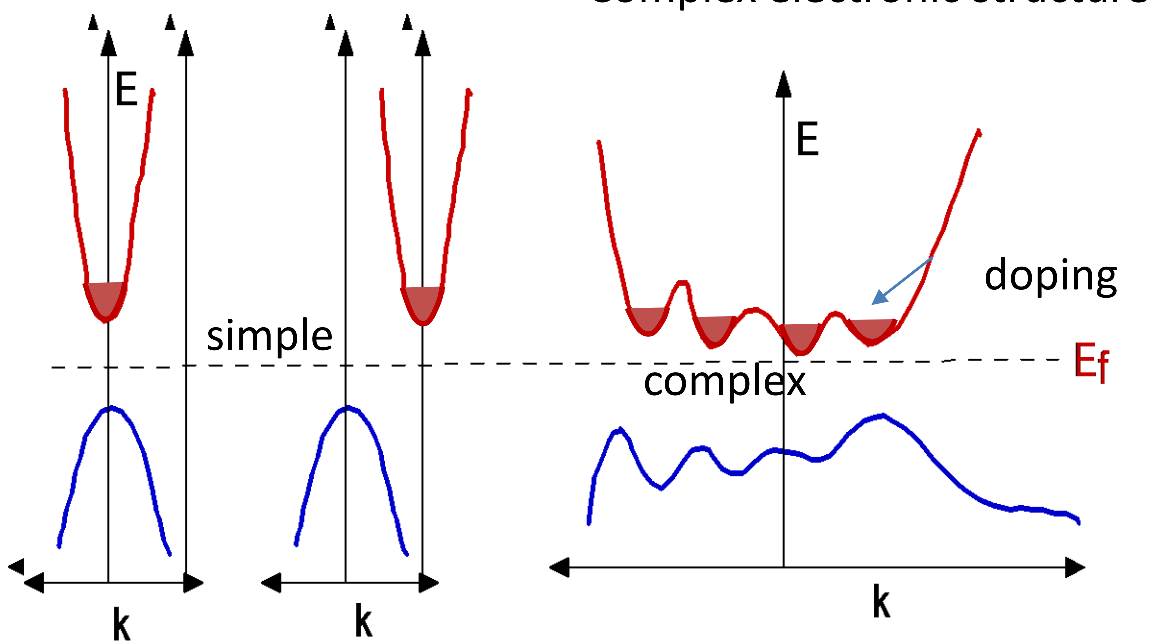
effective mass

$$Z_{max} \propto \gamma \frac{T^{3/2} t \sqrt{\frac{m_x m_y}{m_z}}}{k_{latt}} e^{(r+1/2)}$$

For acoustic phonon scattering
r=-1/2

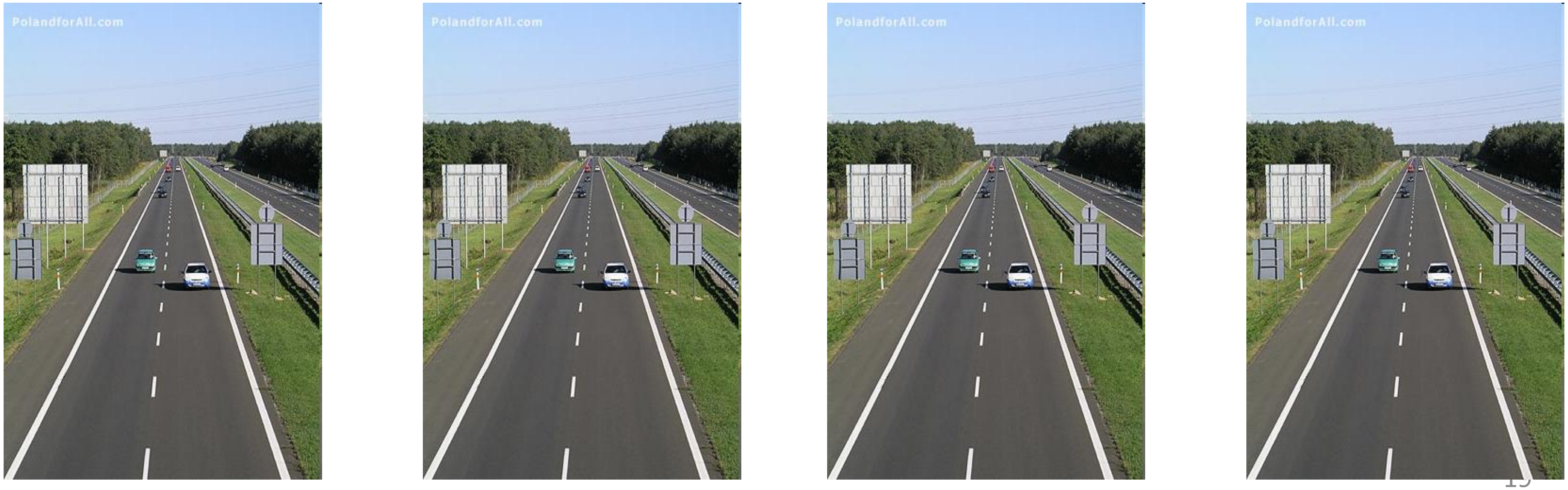
Complex electronic structure

t=scattering time
r= scattering parameter
κ_{latt}= lattice thermal conductivity
T = temperature
γ= band degeneracy



Large γ comes with
(a) high symmetry e.g. rhombohedral, cubic
(b) off-center band extrema

Multiple valleys….are better



What about thermal conductivity?

$$zT = \frac{S^2 \sigma}{\kappa_l + \kappa_e}$$

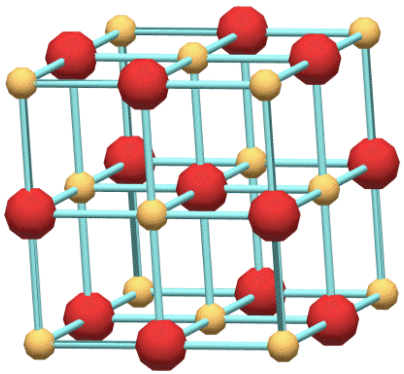
- **Diamond 1600 W/mK**

- **PbTe 2.2 W/mK**

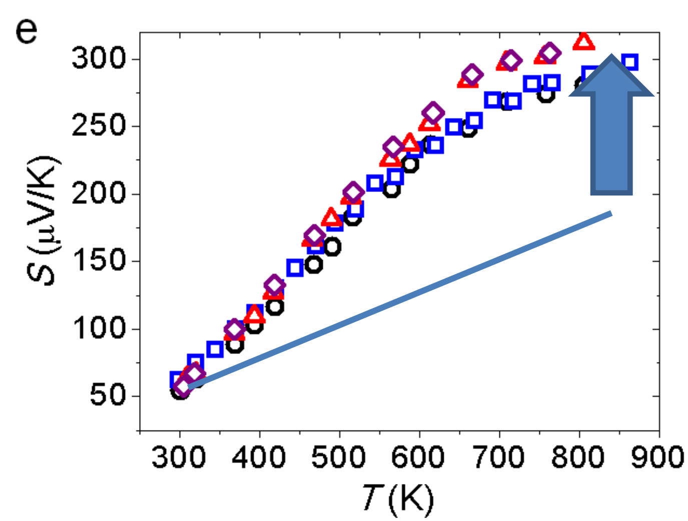
- **Cu 400 W/mK**

- **Wood 0.2 W/mK**

Marvelous electronic structure of PbTe

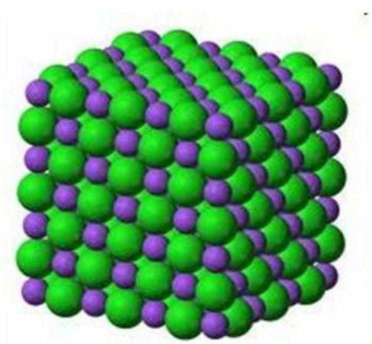


a≈6.45 Å (300K)

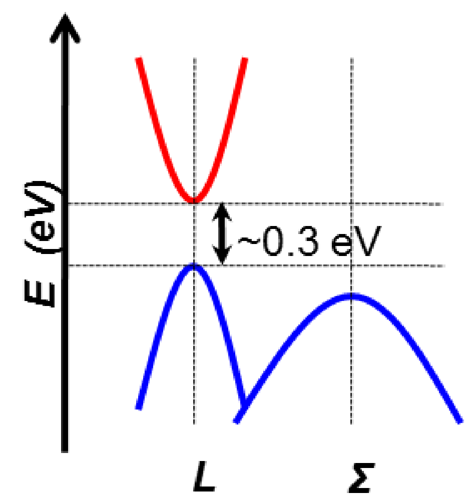


Introducing strain into PbTe

- SrTe: rock salt structure Fm-3m
- a = 6.660 Å
- PbTe: a = 6.460 Å



Solubility of SrTe unknown



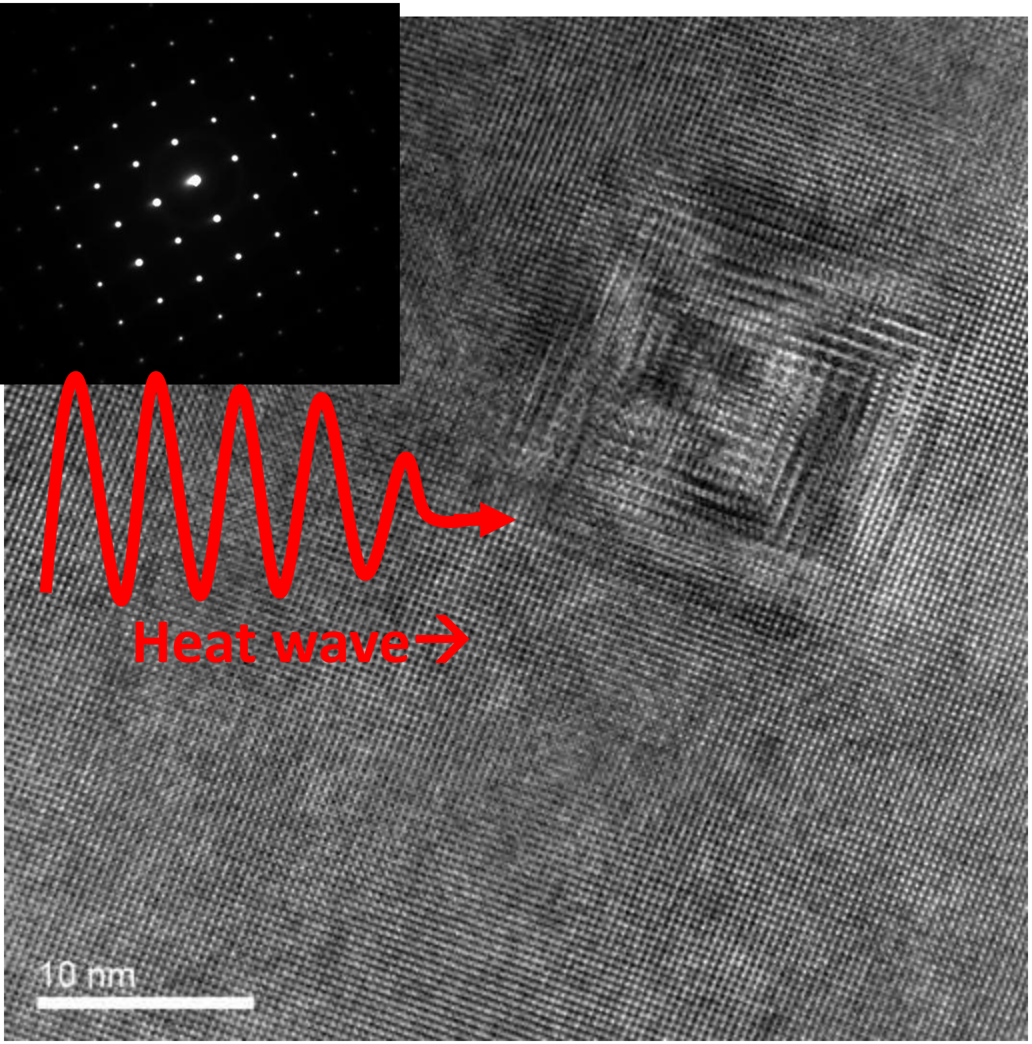
Valence band has two peaks

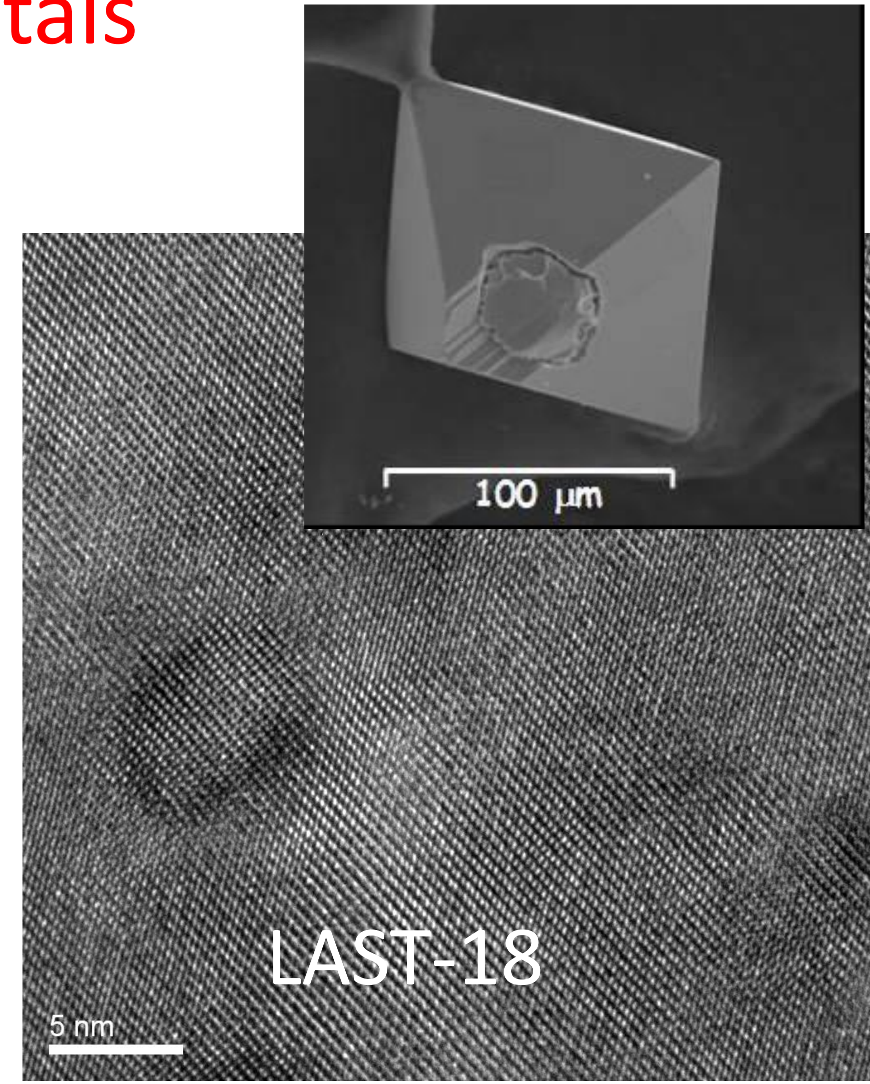
How do we lower thermal conductivity

without lowering electrical conductivity?

Breaking up (heat…) waves

Endotaxy: Coherently embedded nanocrystals

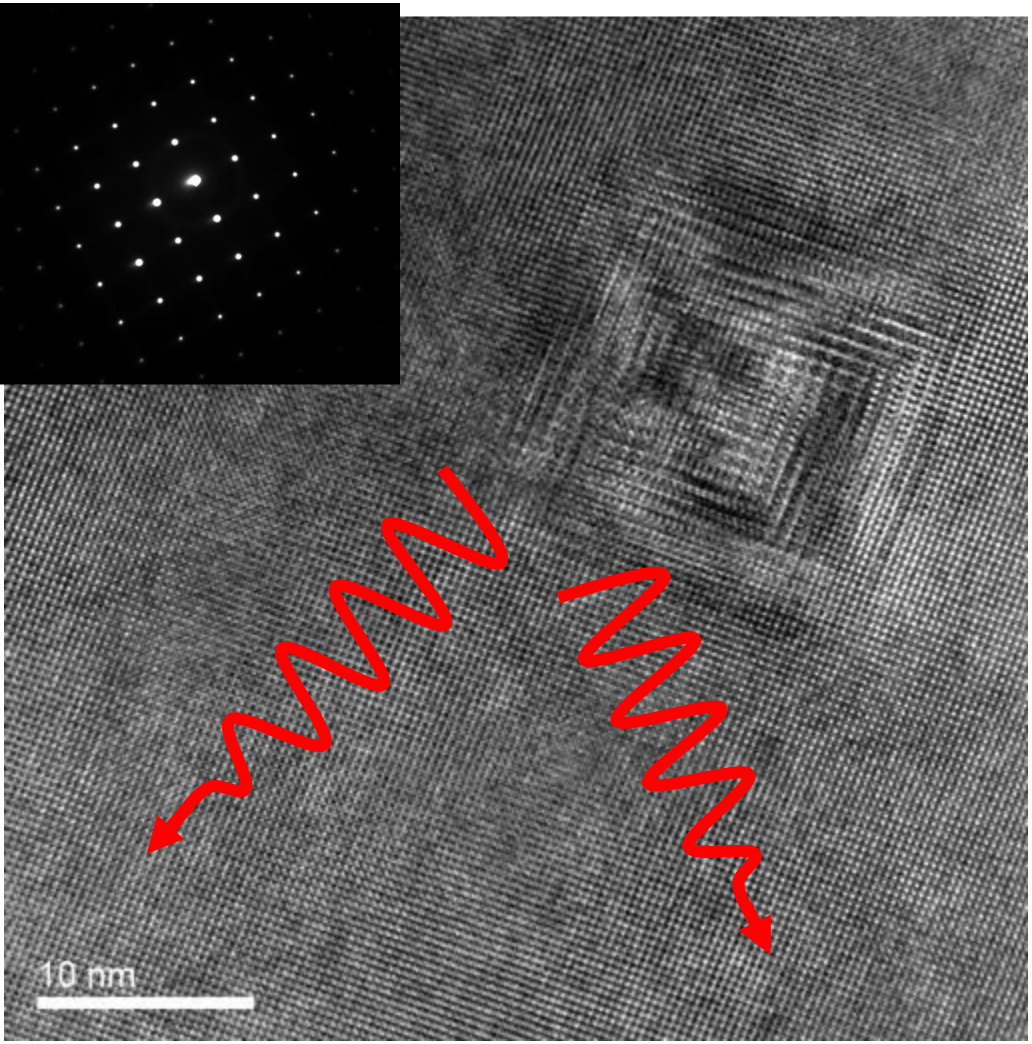


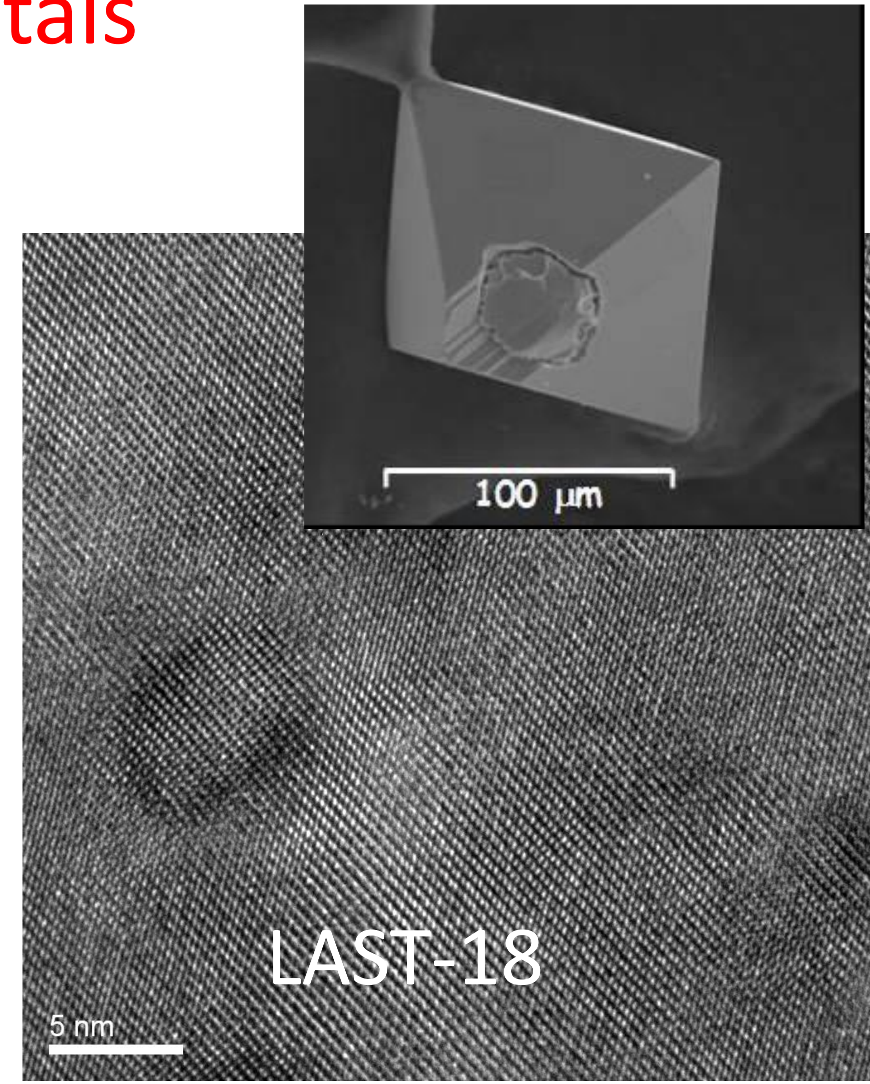


LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

He, Dravid, Pcionek, Polychroniadis, Frangis

Endotaxy: Coherently embedded nanocrystals

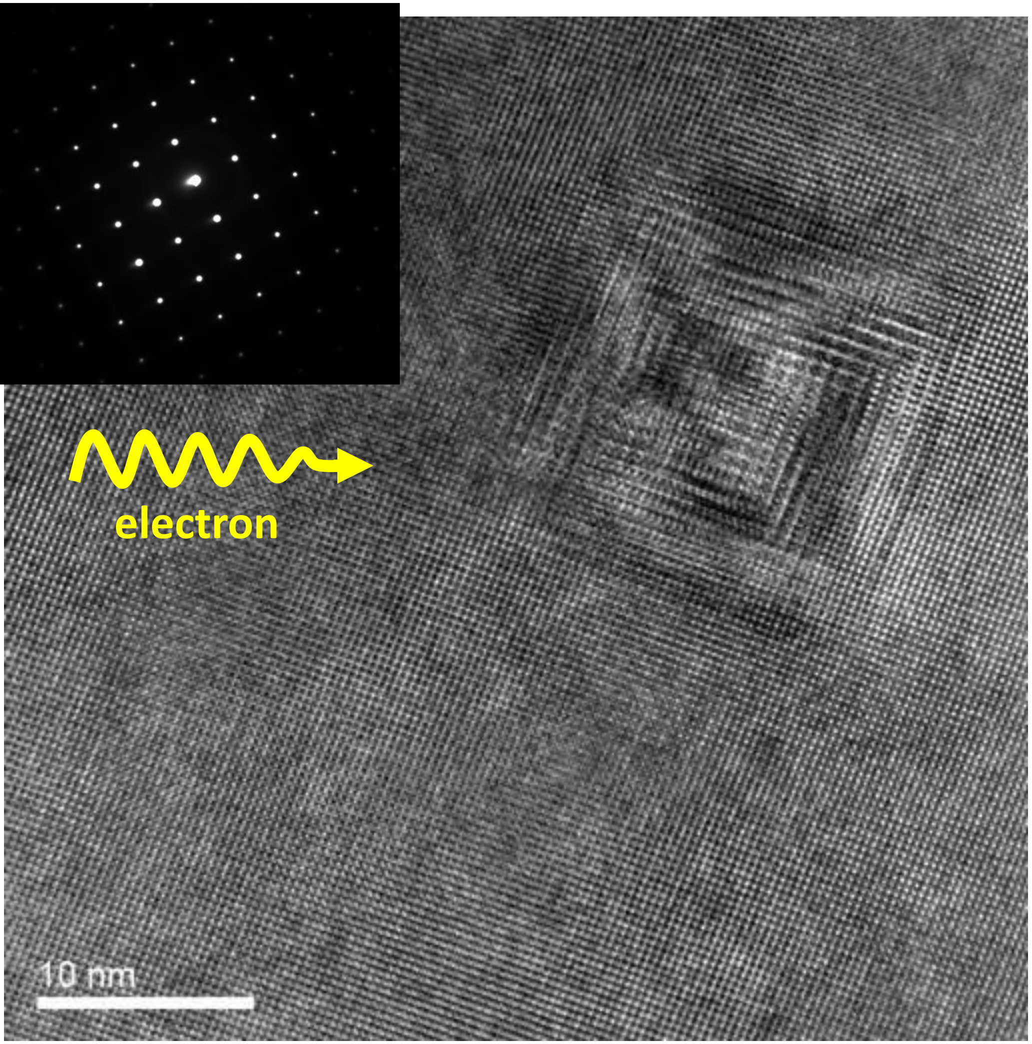


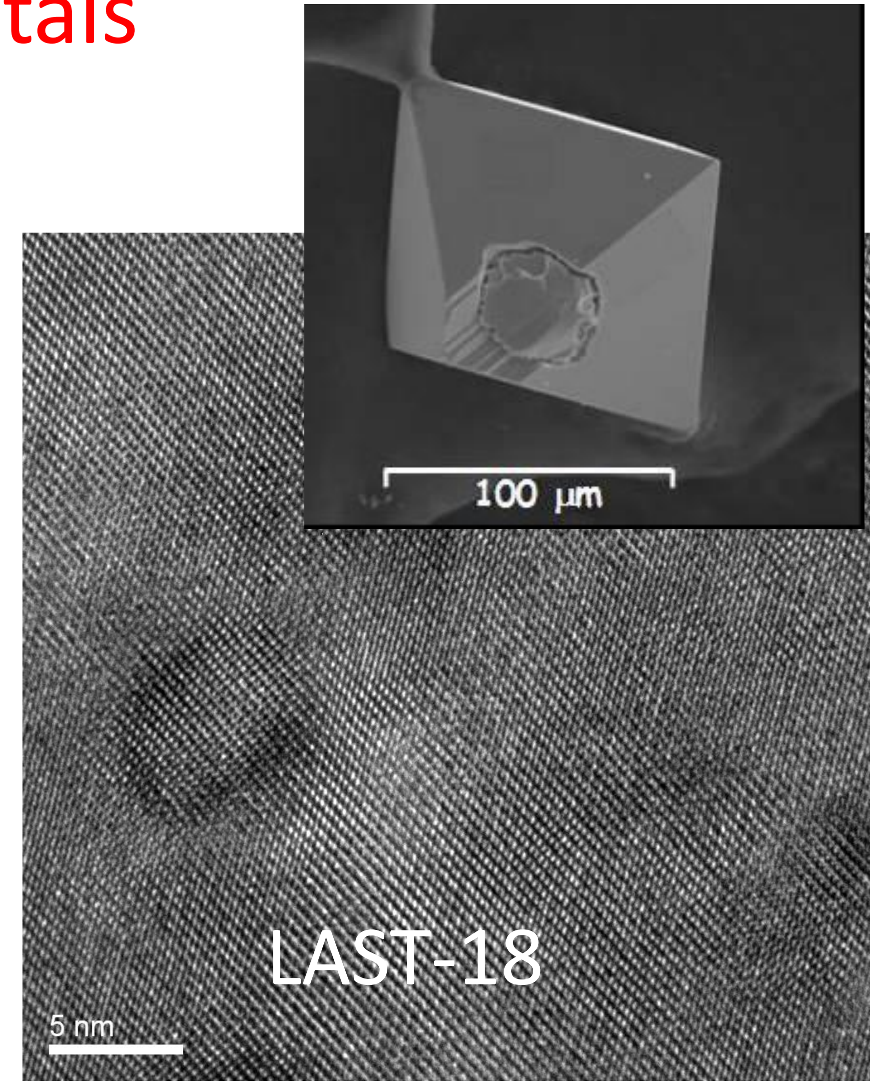


He, Dravid, Pcionek, Polychroniadis, Frangis

LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

Endotaxy: Coherently embedded nanocrystals

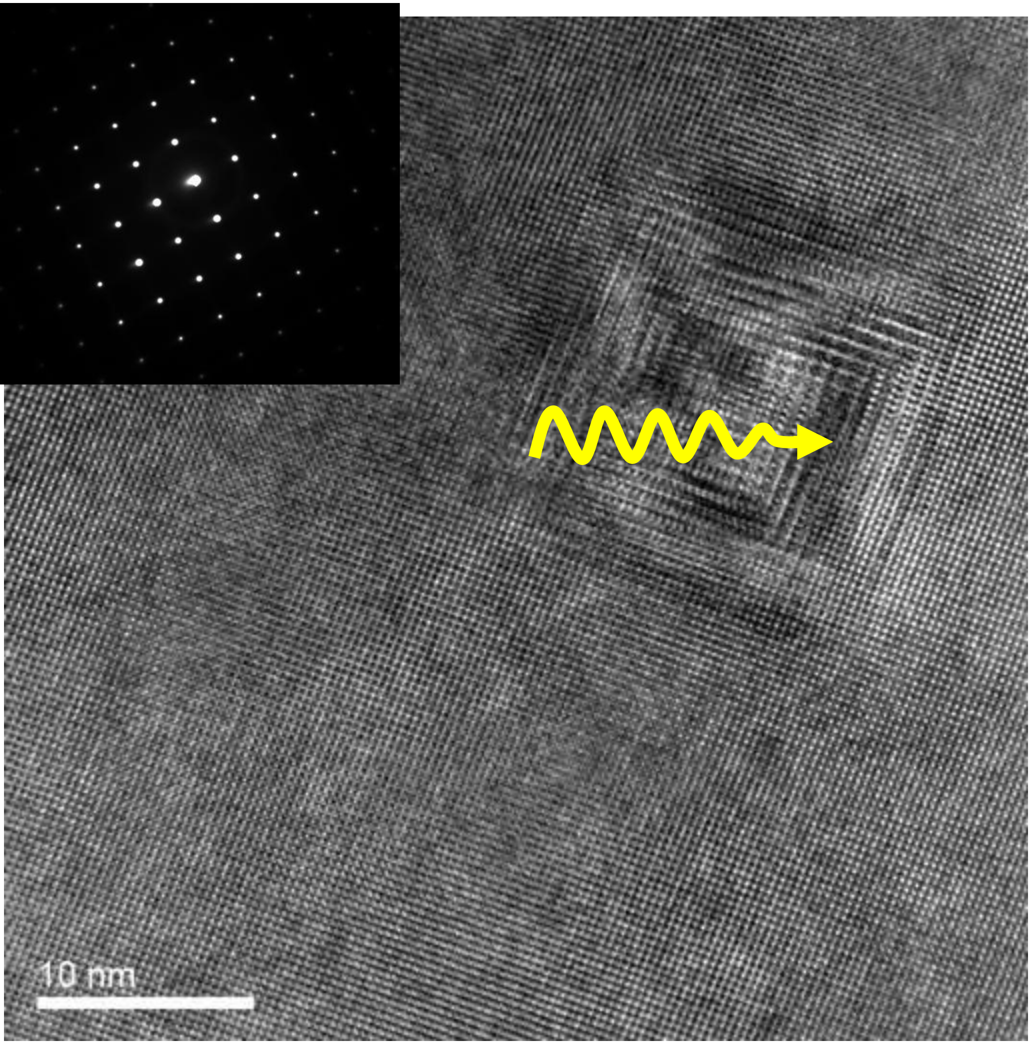


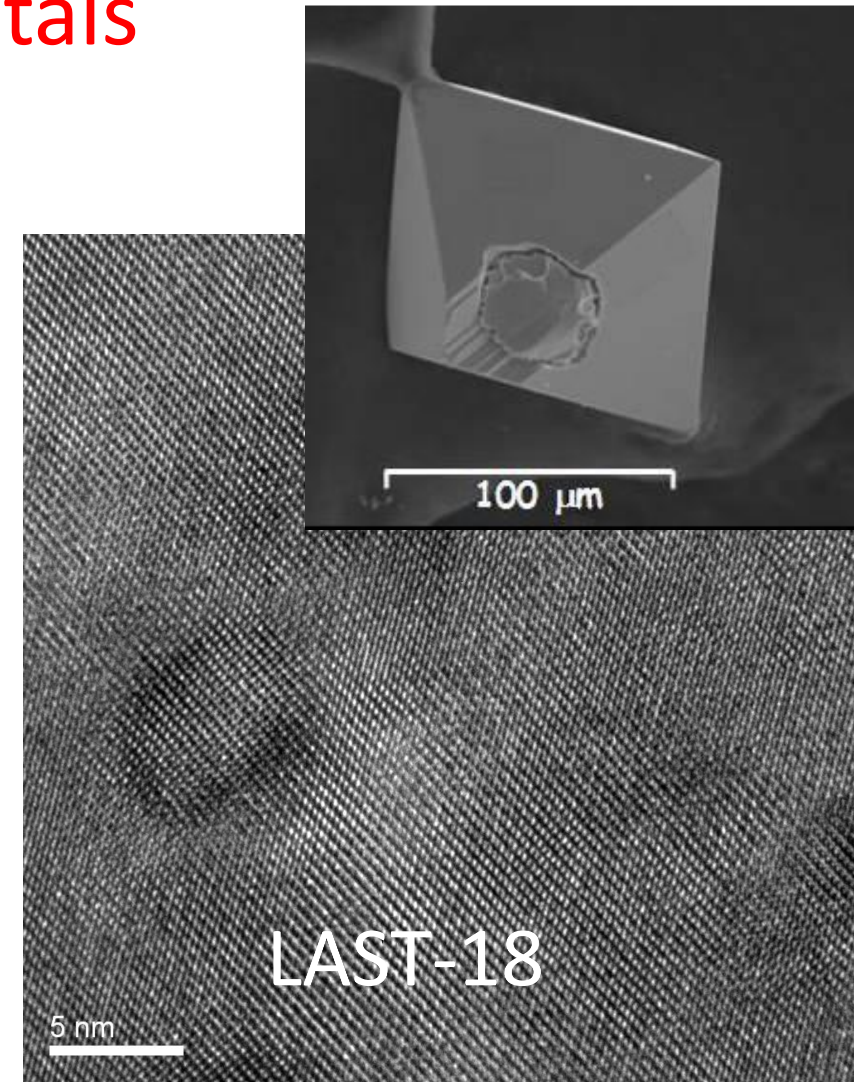


LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

He, Dravid, Pcionek, Polychroniadis, Frangis

Endotaxy: Coherently embedded nanocrystals

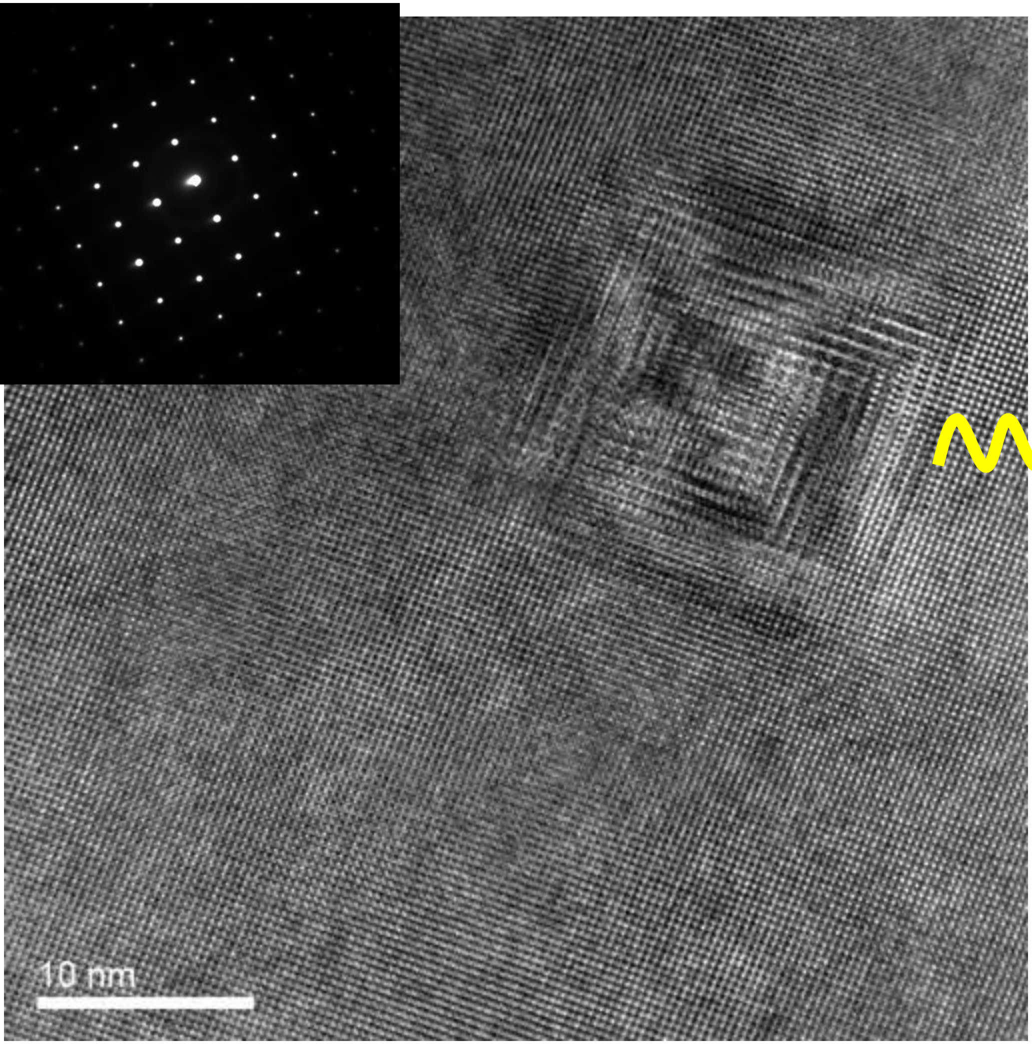


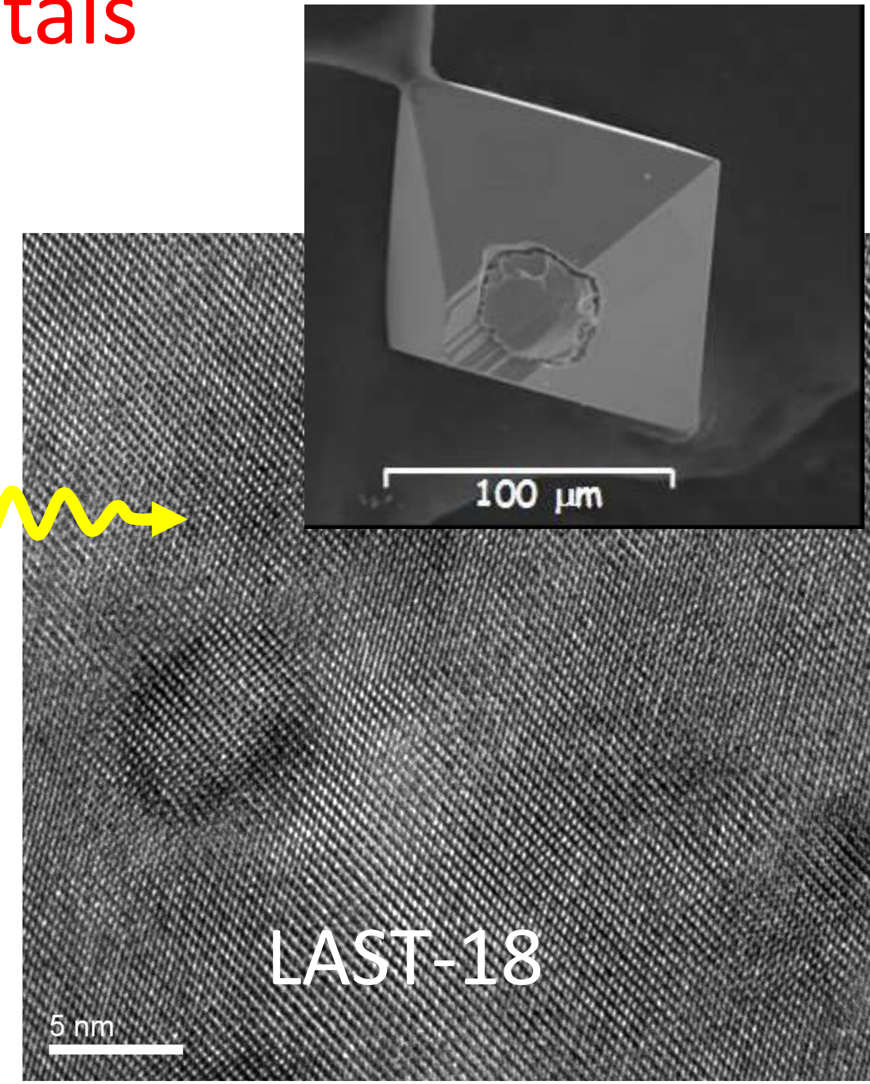


LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

He, Dravid, Pcionek, Polychroniadis, Frangis

Endotaxy: Coherently embedded nanocrystals



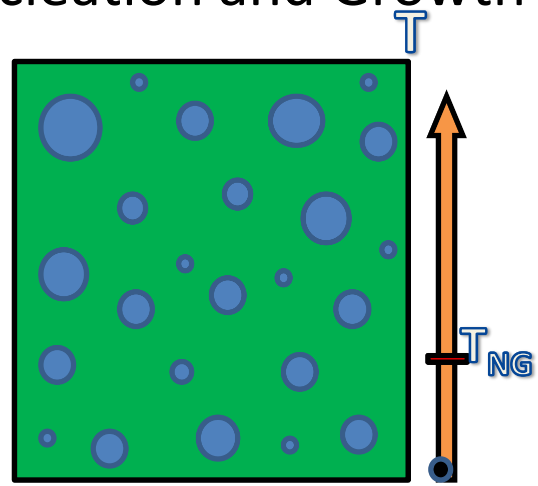


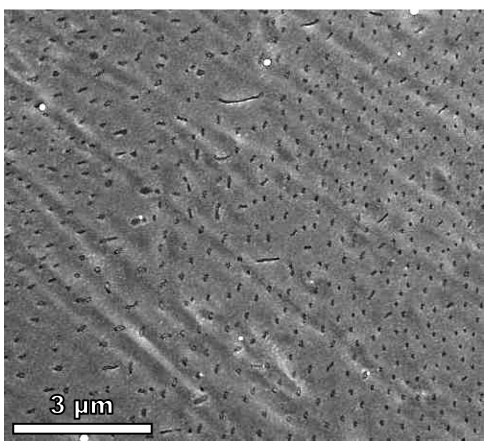
LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

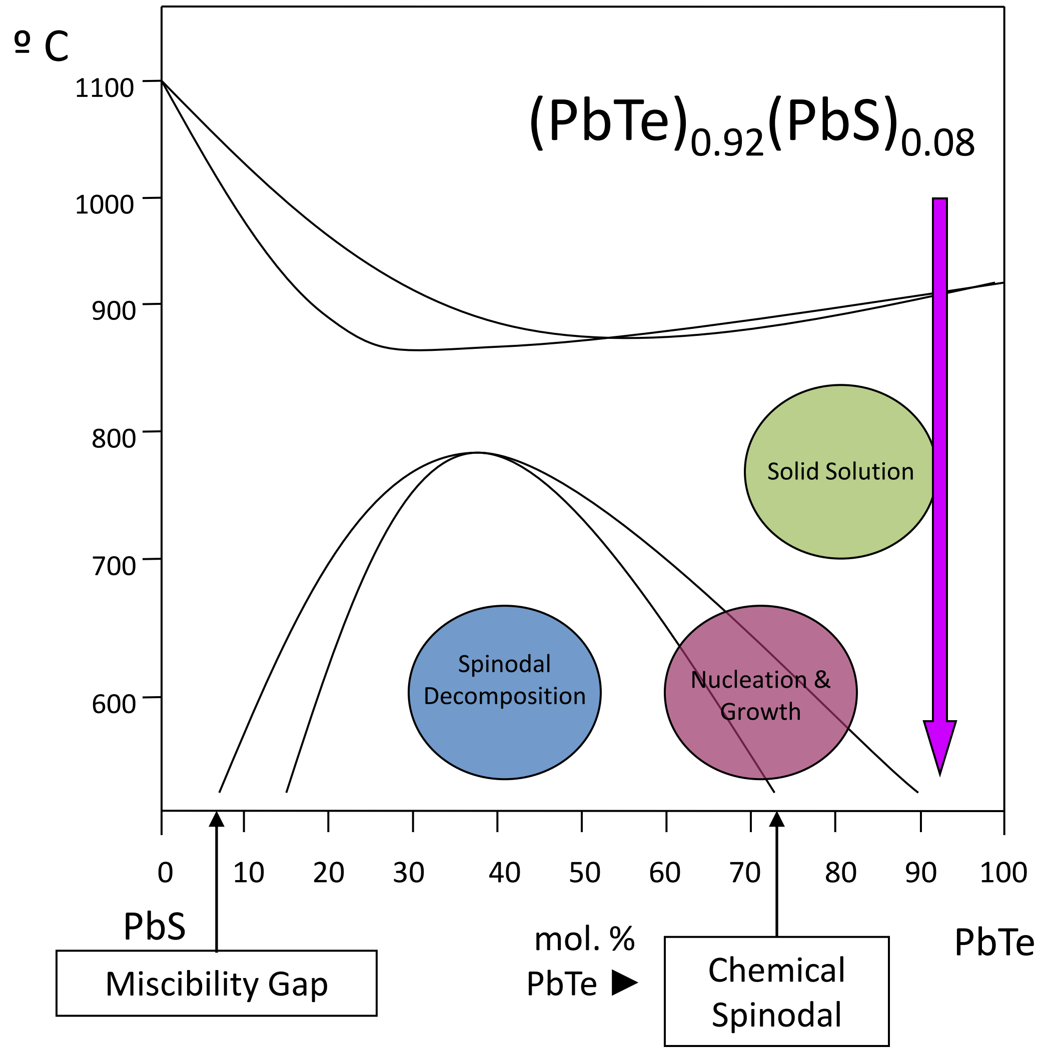
He, Dravid, Pcionek, Polychroniadis, Frangis

Model PbTe – PbS system for nanostructured TEs

Nucleation and Growth

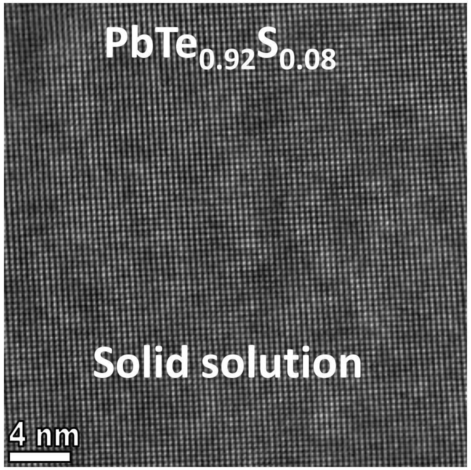






John Androulakis

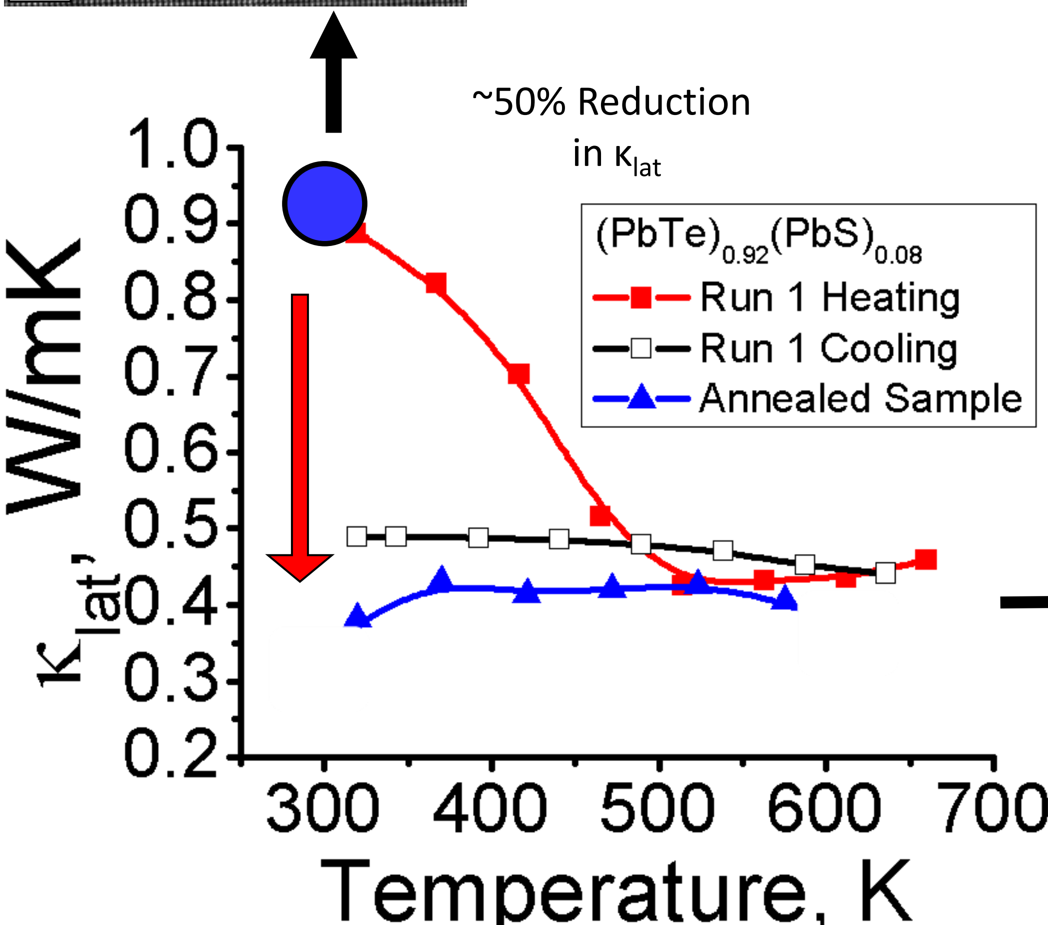
Steven Girard



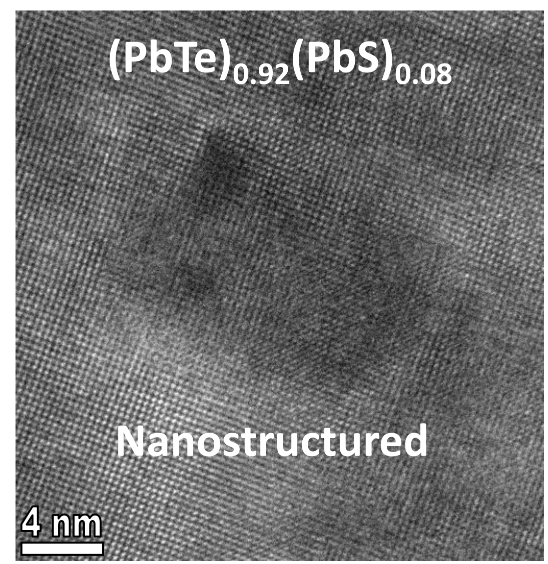
in situ nanoscale precipitation of PbS reduces lattice thermal conductivity.

$$PbTe_{0.92}S_{0.08} \xrightarrow{\text{heat}} (PbTe)_{0.92}(PbS)_{0.08}$$

Solid solution → Nanostructured

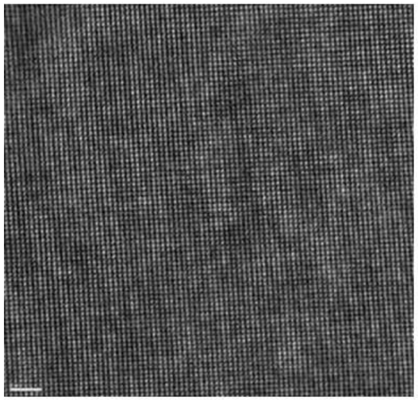


Girard

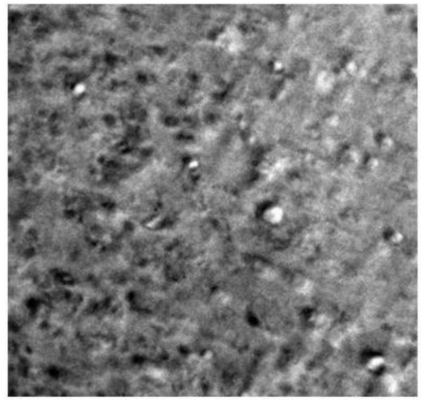


Band alignment is important

Through band alignment



Pristine matrix

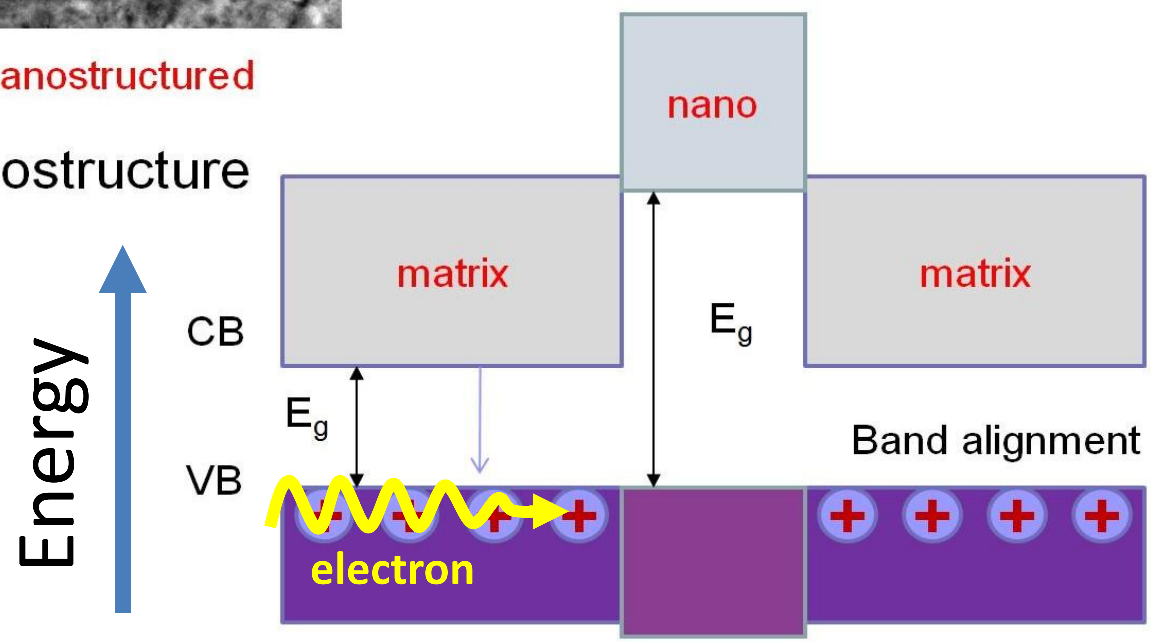


nanostructured

$\kappa_{pristine} >> \kappa_{nanostructure}$

Comparable mobilities

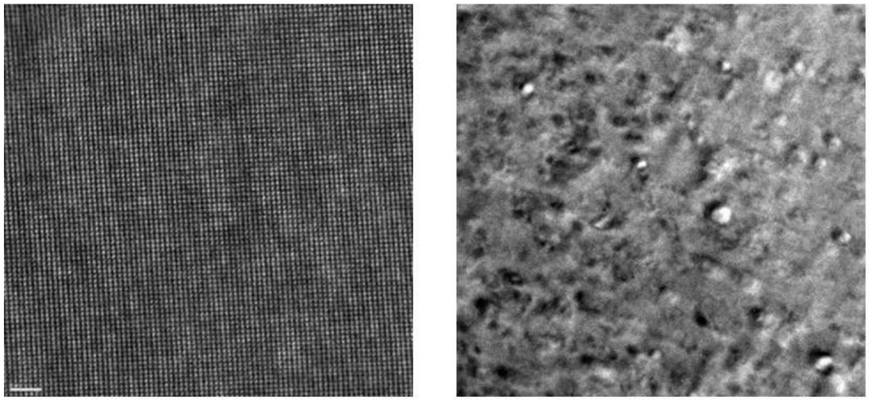
$\mu_{pristine} \sim \mu_{nanostructure}$



K. Biswas et al Nature Chemistry **2011**, 3, 160–166

Band alignment is important

Through band alignment

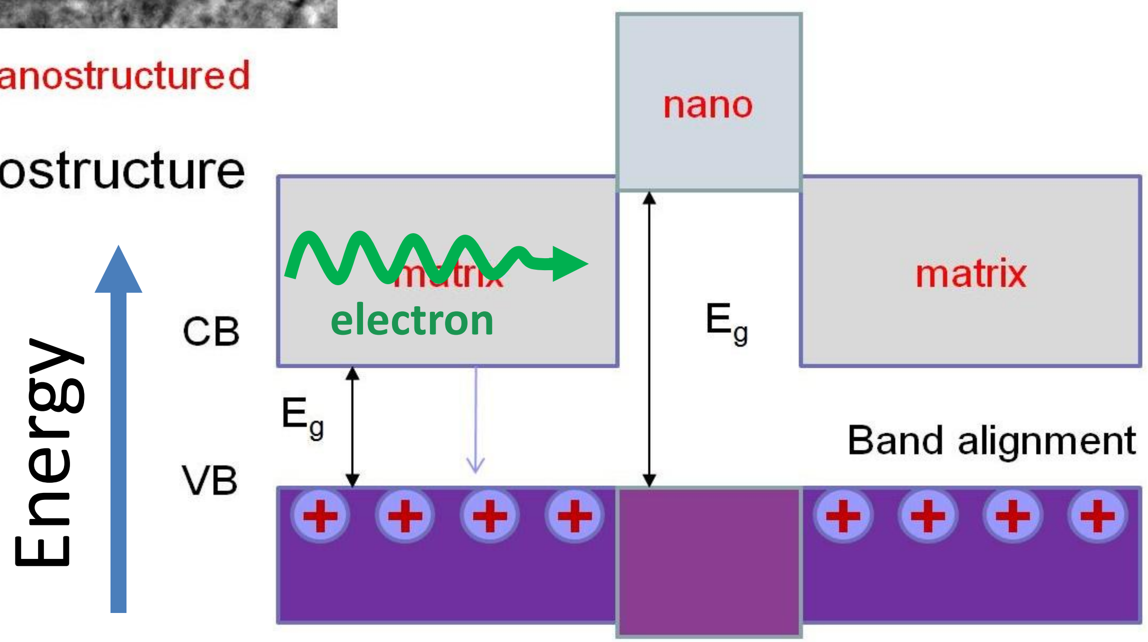


Pristine matrix   nanostructured

$$\kappa_{pristine} >> \kappa_{nanostructure}$$

Comparable mobilities

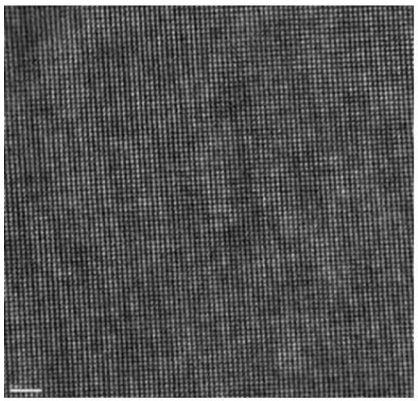
$$\mu_{pristine} \sim \mu_{nanostructure}$$



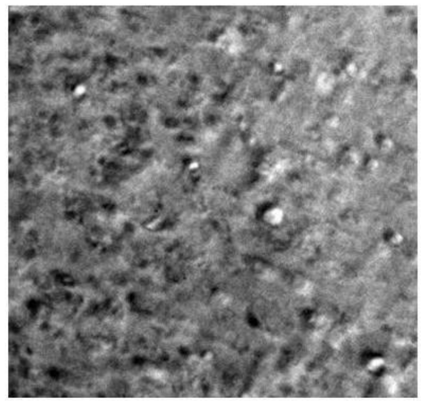
K. Biswas et al Nature Chemistry **2011**, 3, 160–166

Band alignment is important

Through band alignment



Pristine matrix

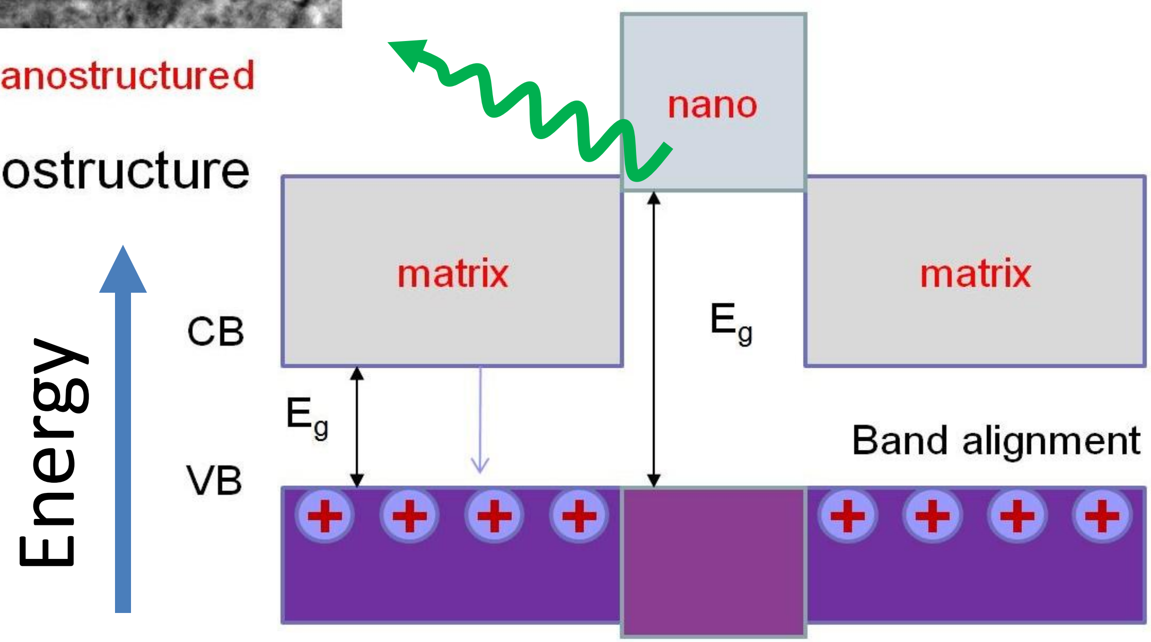


nanostructured

Comparable mobilities

$$\mu_{pristine} \sim \mu_{nanostructure}$$

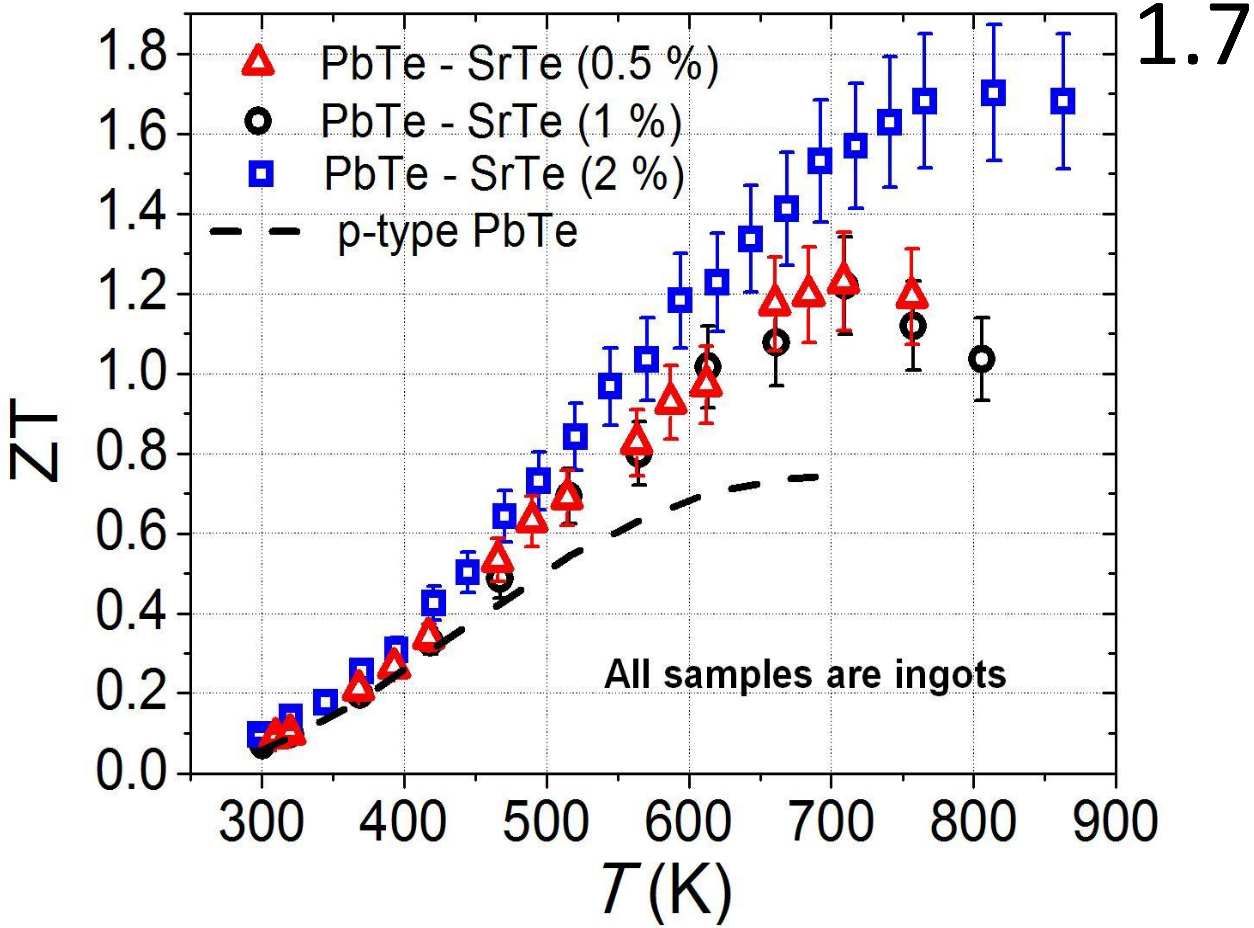
$$\kappa_{pristine} >> \kappa_{nanostructure}$$



K. Biswas et al Nature Chemistry **2011**, 3, 160–166

Ingot crystal

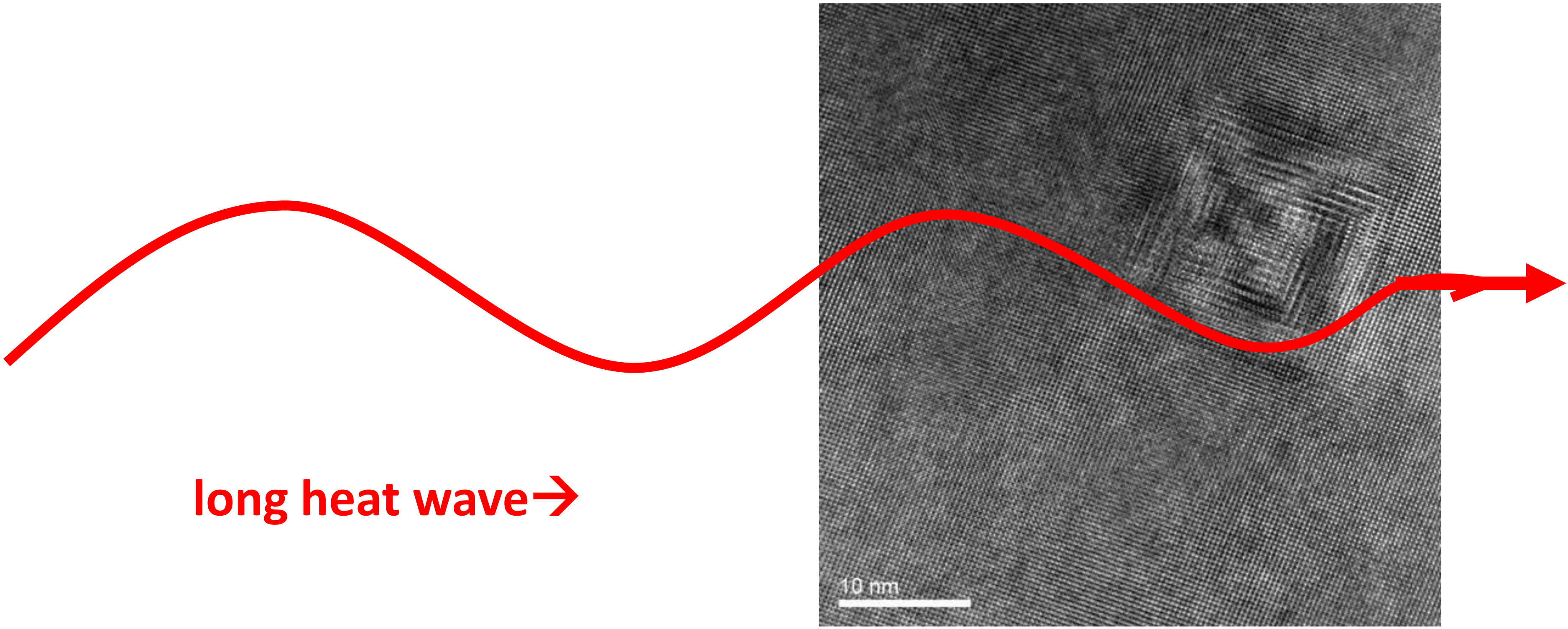
Figure of merit, ZT



K. Biswas et al Nature Chemistry **2011**, 3, 160–166

K. Biswas et al Nature Chemistry **2011**, 3, 160–166

What about long waves?

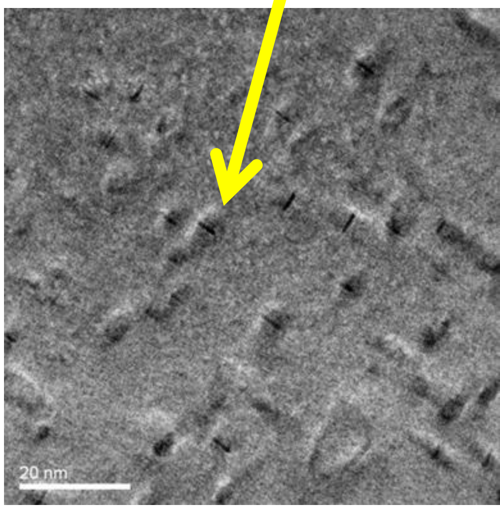


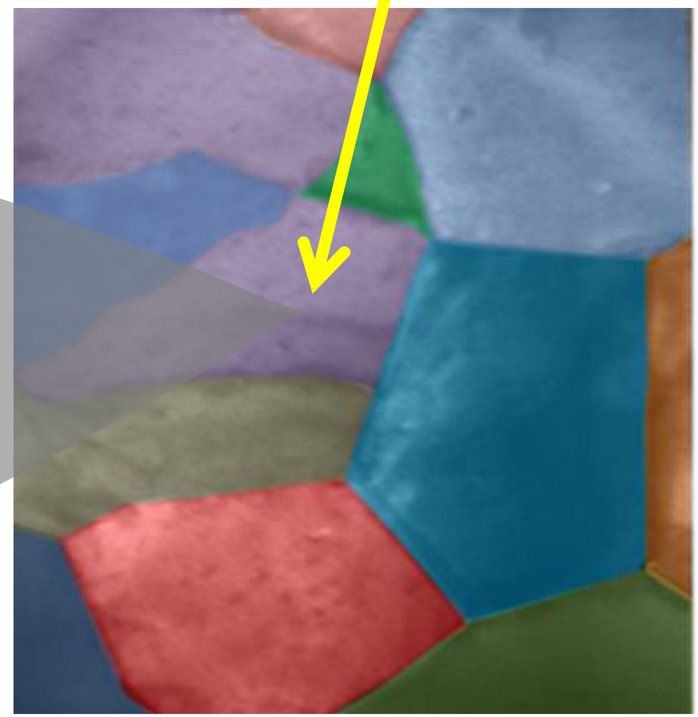
Nano-scale, meso-scale

Submicron grains

nanostructures

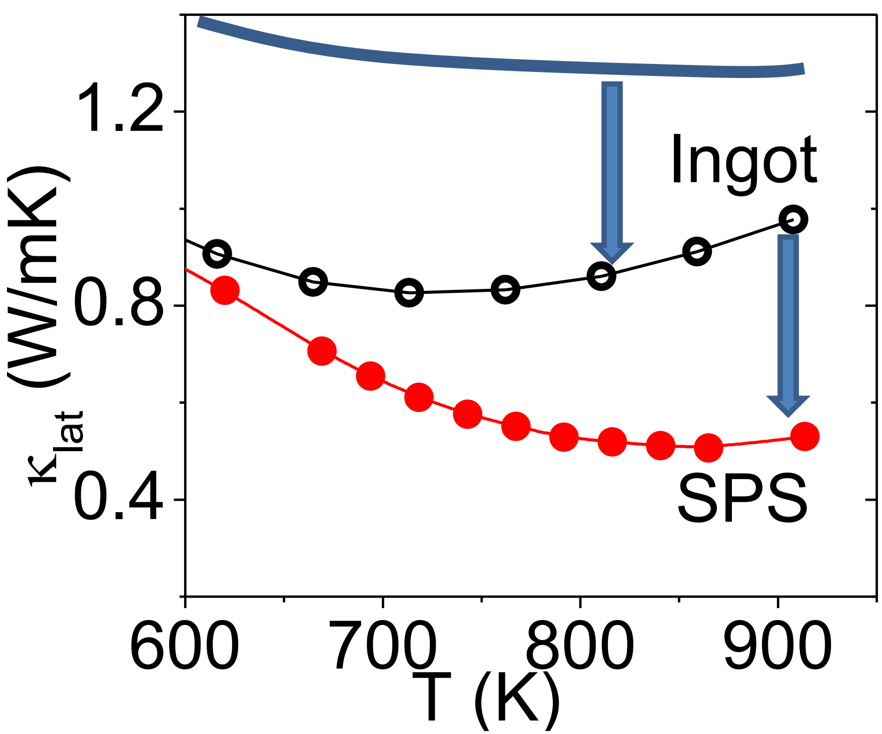
mesostructures





Spark Plasma Sintering

Thermal conductivity PbTe-x%SrTe



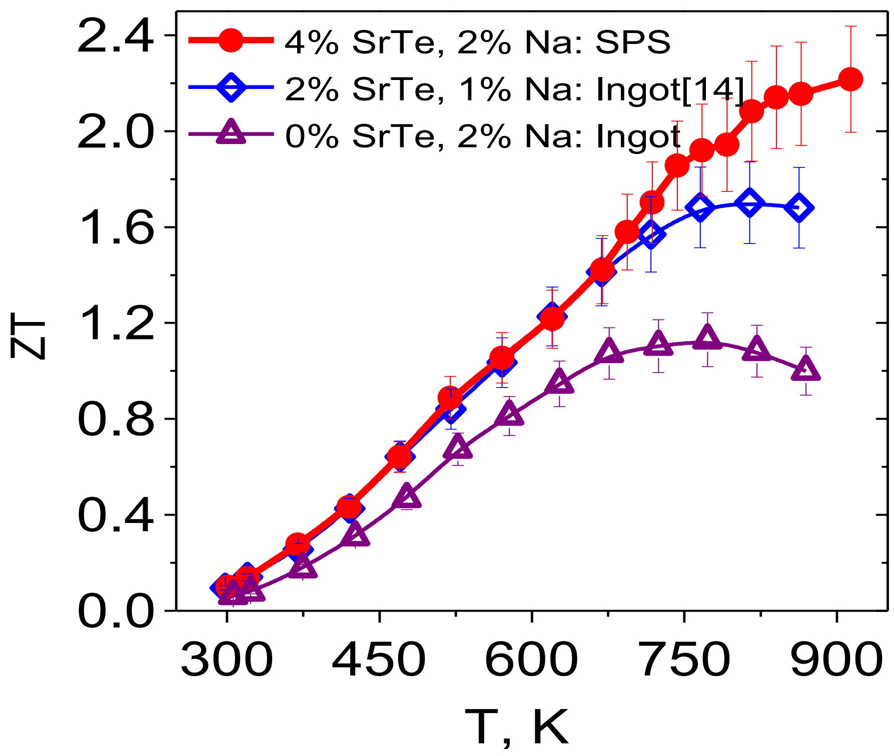
PbTe: No nanostructures

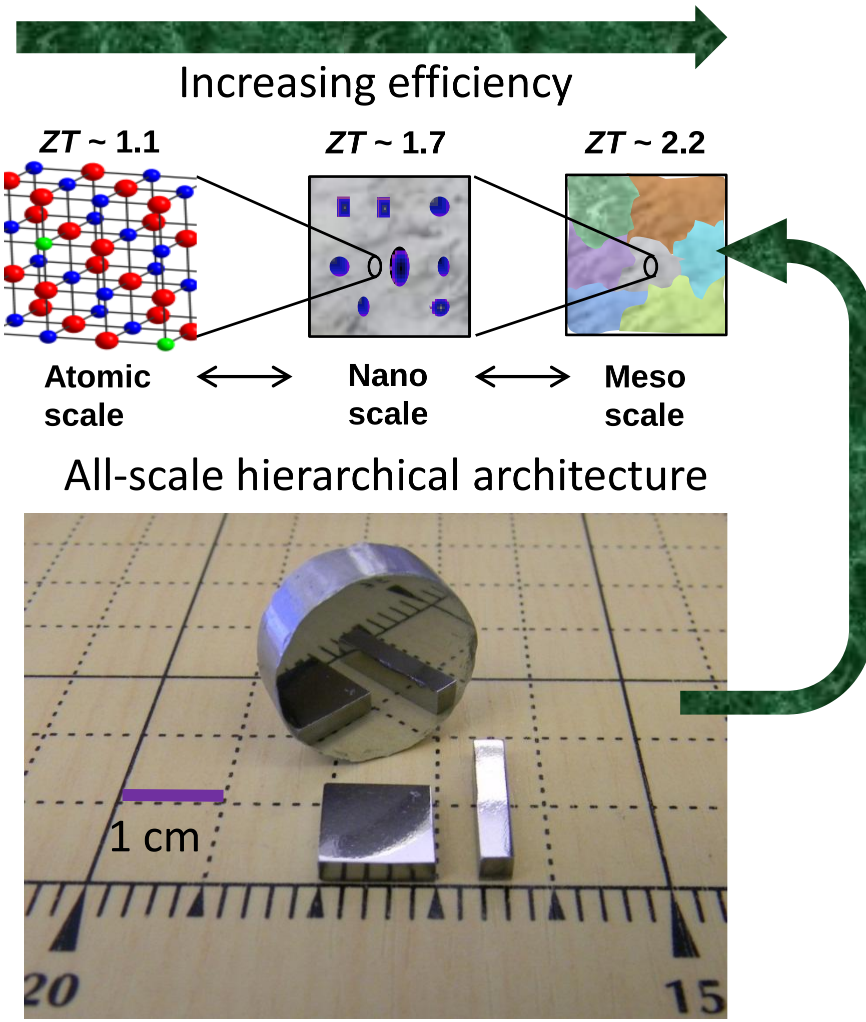
Nanostructures only

Nanostructures and mesoscale

K. Biswas, Jiaqing He, I. D. Blum, C-I Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid & M. G. Kanatzidis *Nature* **2012**, 489, 414–418

All length scales: record high ZT



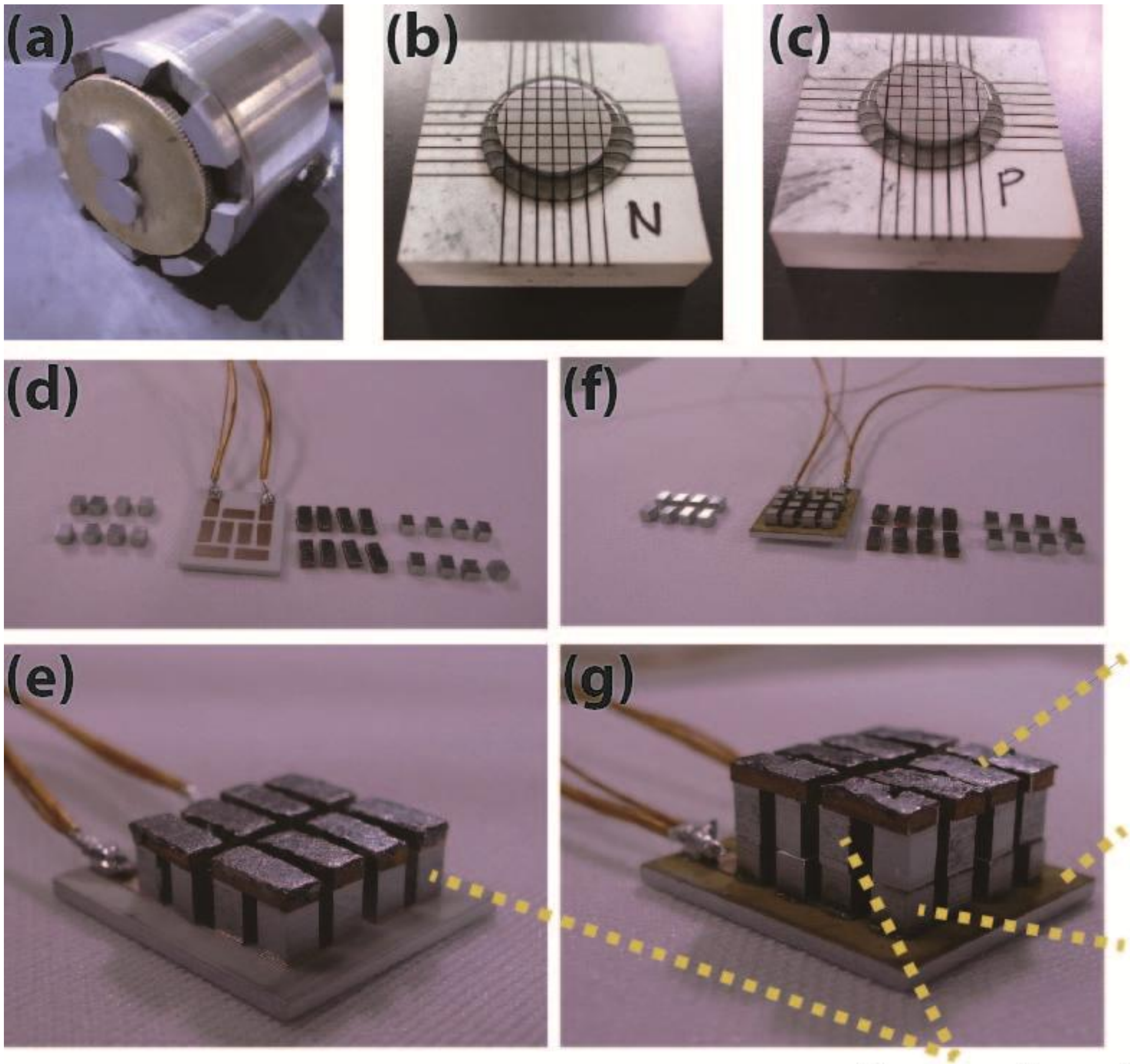


K. Biswas, Jiaqing He, I. D. Blum, C-I Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid & M. G. Kanatzidis *Nature* **2012**, 489, 414–418

NORTHWESTERN
UNIVERSITY

Thermoelectric device

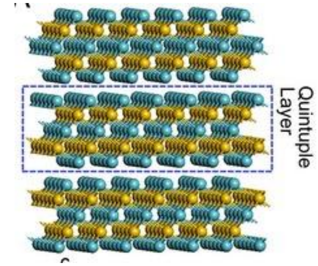
Collaboration with Dr Michihiro Ohta, AIST, Japan

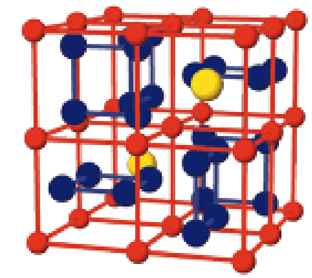


>12% efficiency

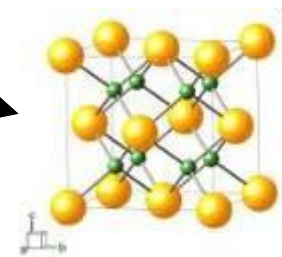
ΔT~500 °C

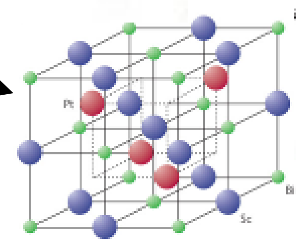
Leading thermoelectric materials

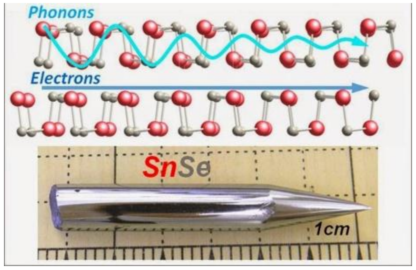


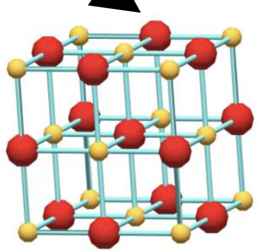


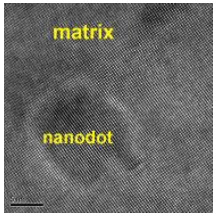
- Bi_2Te_3-Sb_2Te_3 (ZT~1) (300K)
- Filled Skutterudites (*Ca,Yb*)Fe_4Sb_{12} (ZT~1.5, 900K, n-type)
- Mg_2(Si,Sn) (ZT~1.4, 1000 K)
- Half-Heusler alloys (ZT~0.8, 900K)
- MgAgSb (ZT~1.2 400K)
- GeTe/PbTe (ZT~2, 800K)
- SnSe (ZT~2.6, 930K)
- Nanostructured PbTe, SnTe, (ZT~2.2)











Please attend Symposium CC for more