2012 Thermoelectric Applications Workshop
Baltimore, MD

Nanostructures Thermoelectrics. The New paradigm

Mercouri Kanatzidis

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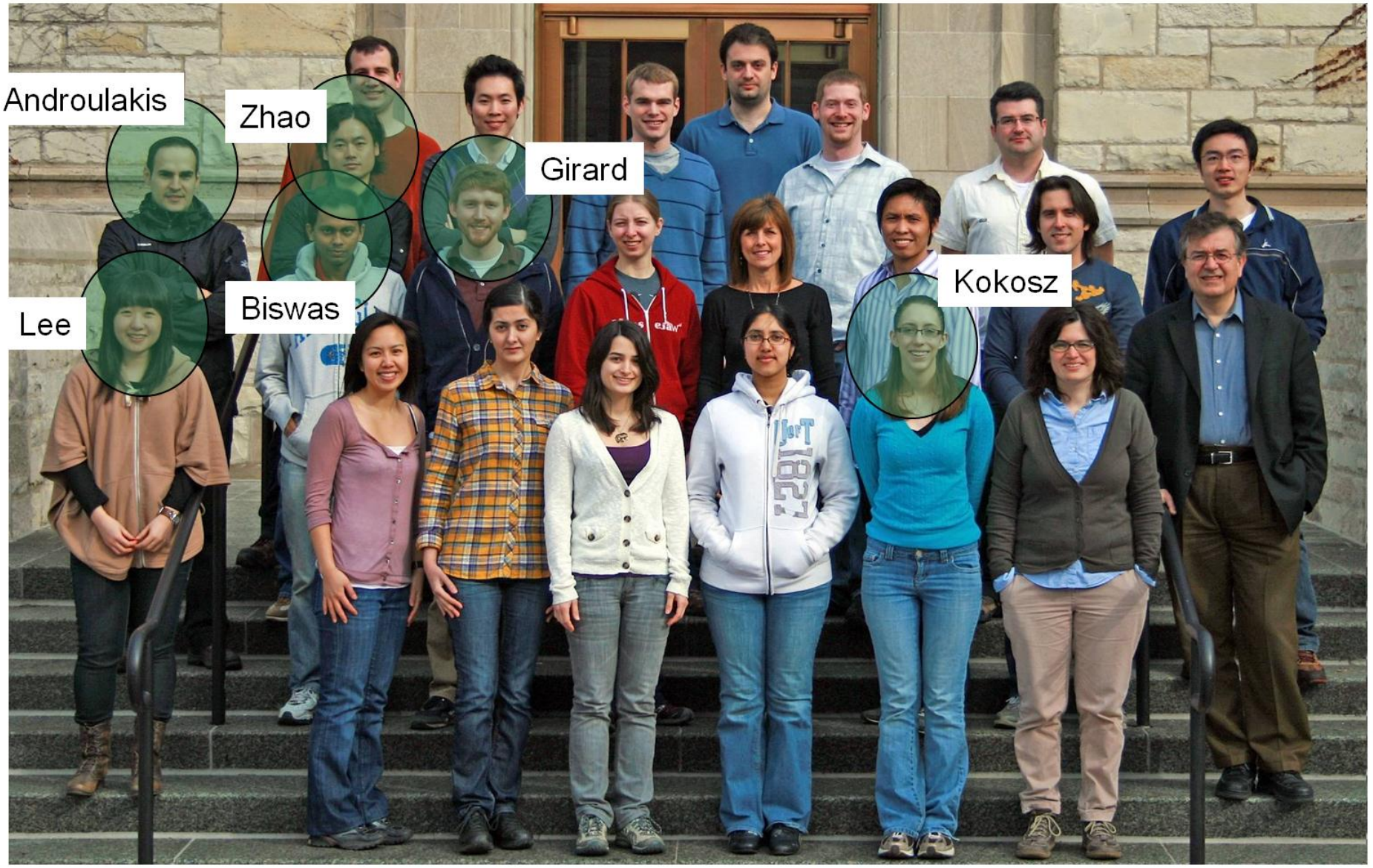
Androulakis
Zhao
Girard
Kokosz
Lee
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Collaborators

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- S. D. (Bhanu) Mahanti, MSU
- Ctirad Uher, Michigan
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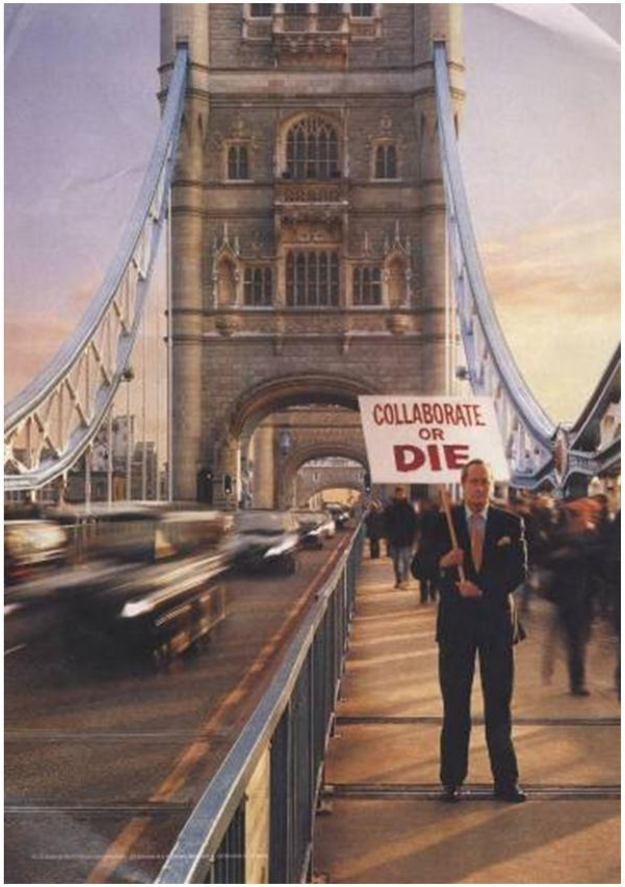
- Vinayak Dravid, NU
- David Seidman, NU
- SonBinh Nguyen, NU
- Chris Wolverton, NU
- Art Freeman, NU
- Ray Osborn, Argonne
- Stephane Rosenkranz, Argonne
- Duck Young Chung, Argonne

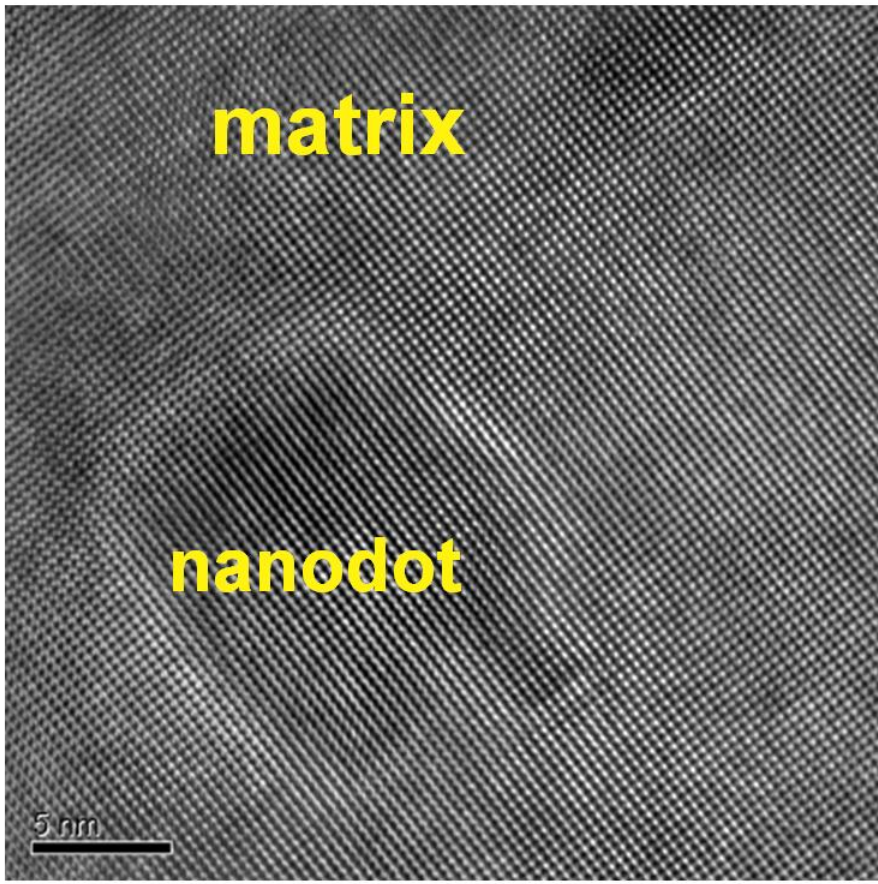


The nanostructure…

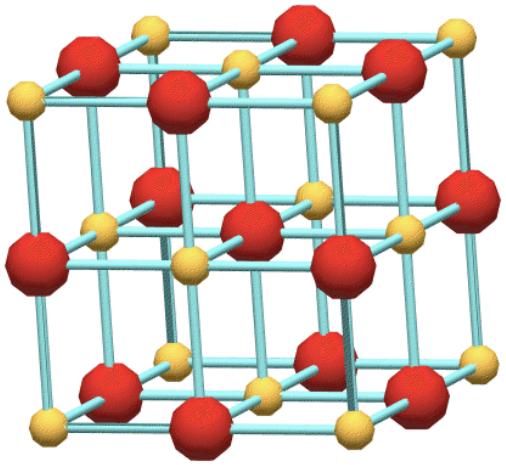
Endotaxy: lattice matched placement of one material inside another

Controlling nanostructuring

- New means of introducing nanostructures in bulk materials
  - Spinodal decomposition
  - Nucleation and growth
  - Liquid encapsulation



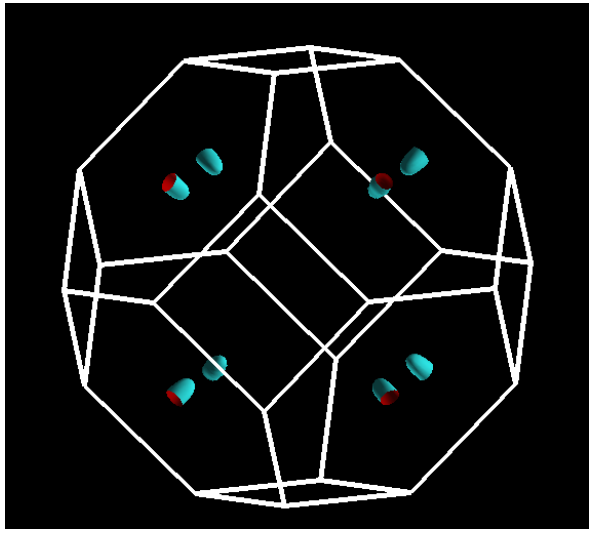
electronic band structure of PbTe

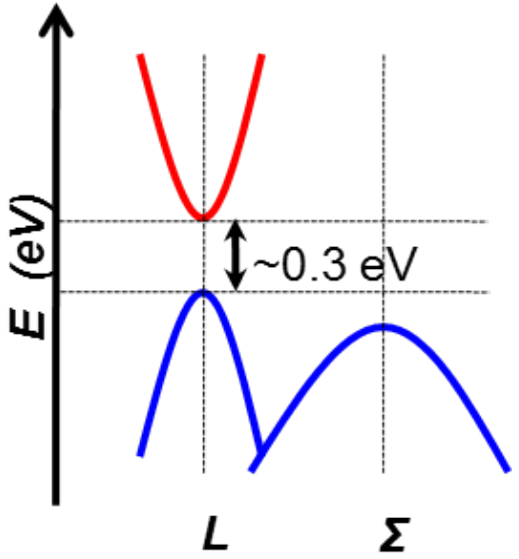


a≈6.45 Å (300K)

Valence band is multiple peaks

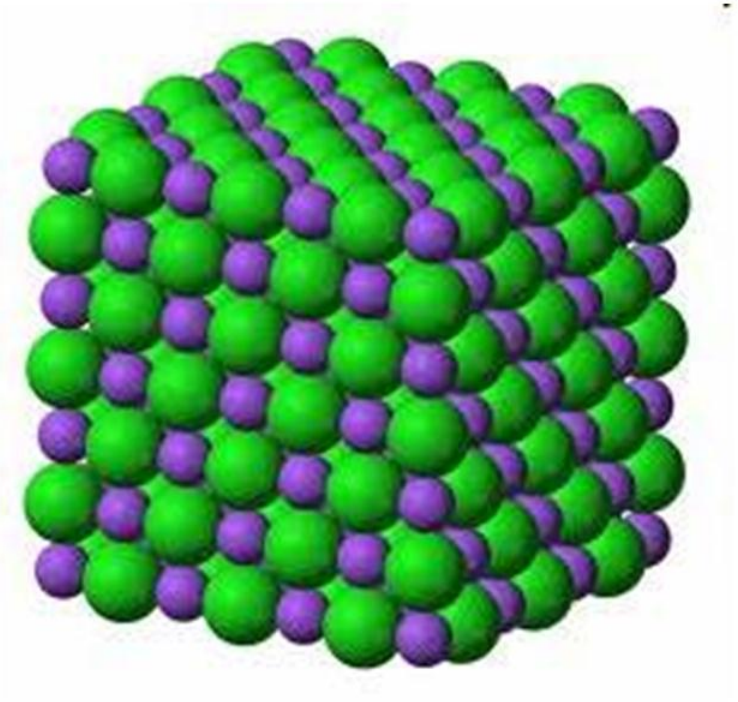
m^*_Σ (~$2m_0$) >> m^*_L(~$0.2m_0$)





Introducing strain into PbTe

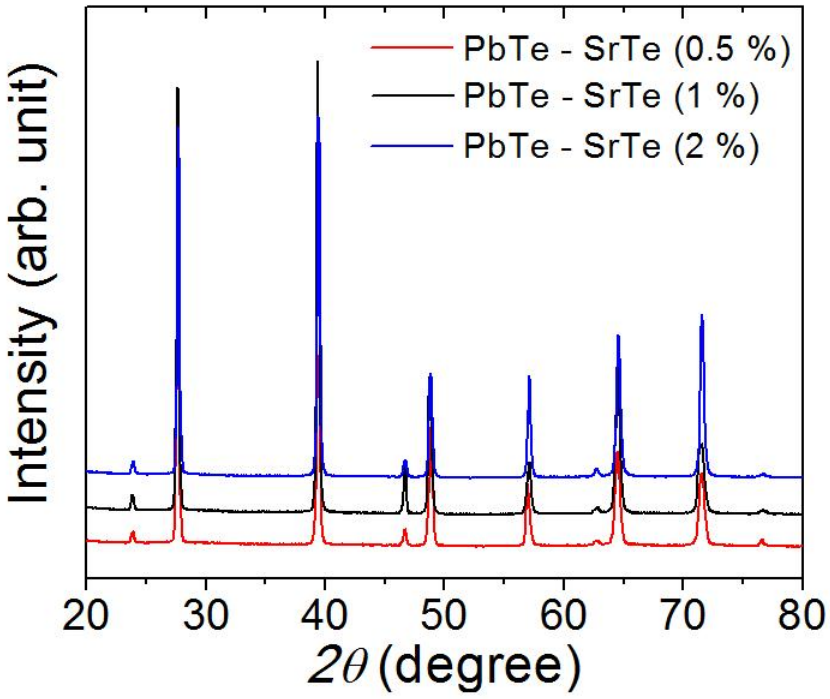
- SrTe: rock salt structure Fm-3m
- a = 6.660 Å
- PbTe: a = 6.460 Å

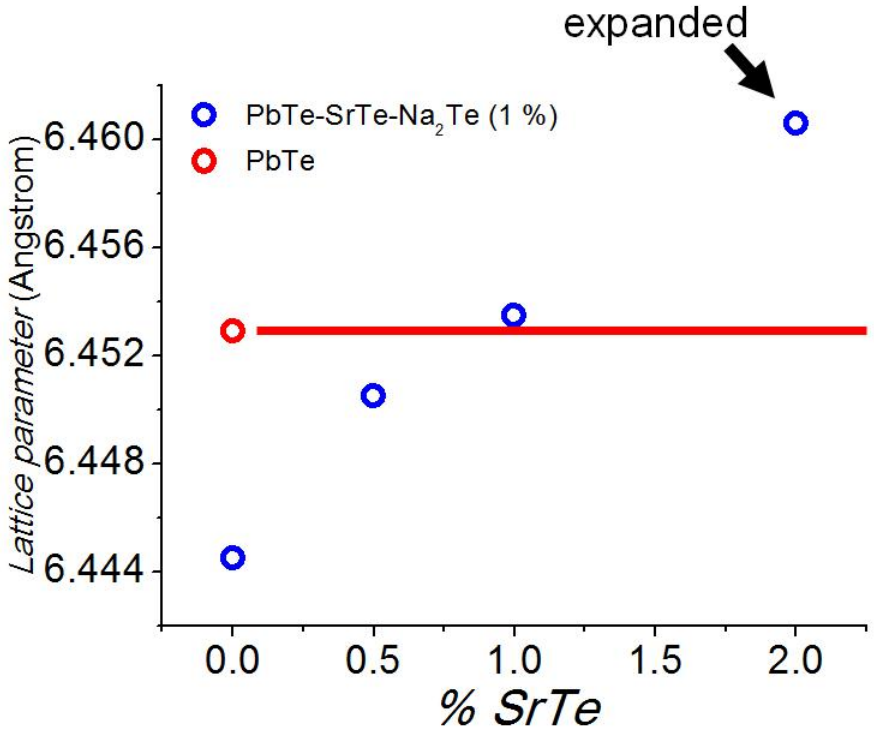


Solubility of SrTe unknown

MgTe, CaTe, BaTe

PbTe-SrTe : Powder X-ray diffraction



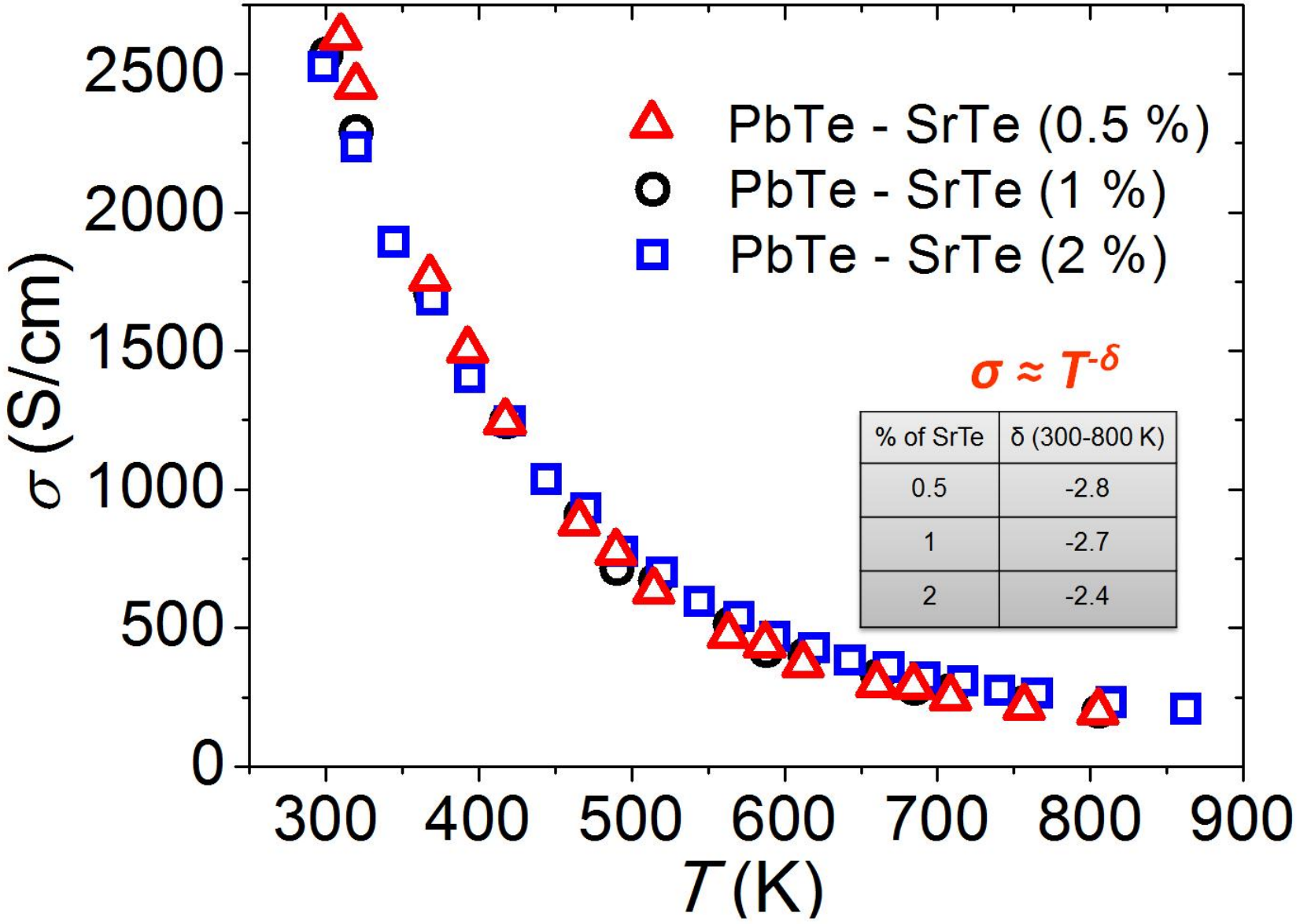


Indexed based on PbTe structure (space group $Fm\bar{3}m$)

No SrTe or other phase observed

TGA up to 900 K under N_2 atmosphere: Samples are stable without weight loss

Electrical conductivity



% of SrTe	δ (300-800 K)
0.5	-2.8
1	-2.7
2	-2.4

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Hall measurement

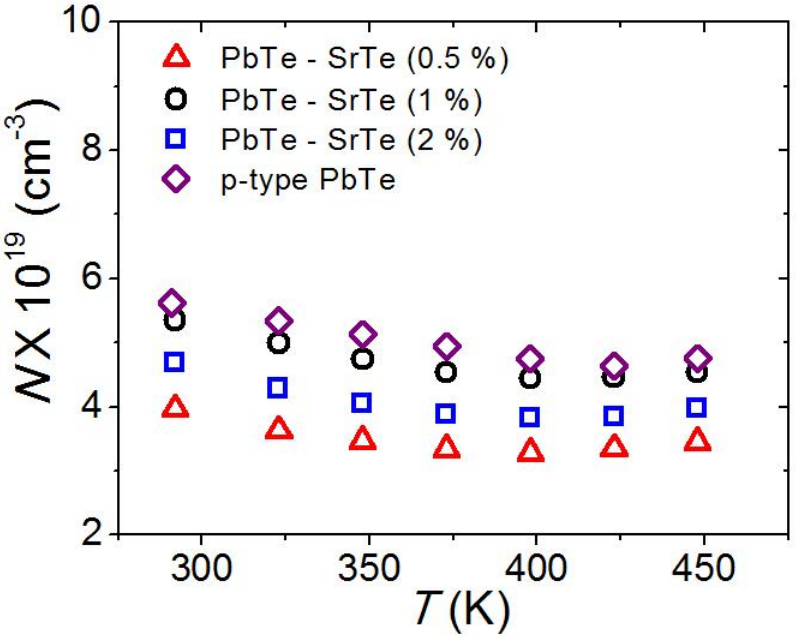
Two valance band: p-type PbTe

Light (h1) and heavy hole (h2)

Effective mass: $m_{h2} = 1.5m_{h1}$

$$\mu = \sigma/Ne$$

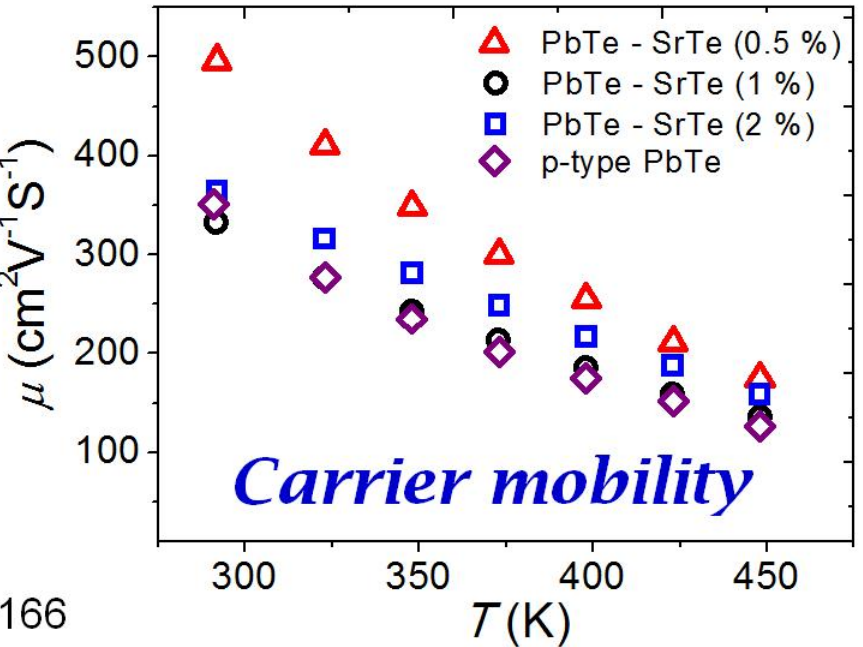
μ, mobility
σ, electrical conductivity
N, Carrier concentration



Assuming parabolic band and single band conduction

$$N=1/eR_H$$

N, carrier concentration
E, is the electronic charge
R_H is the Hall coefficient



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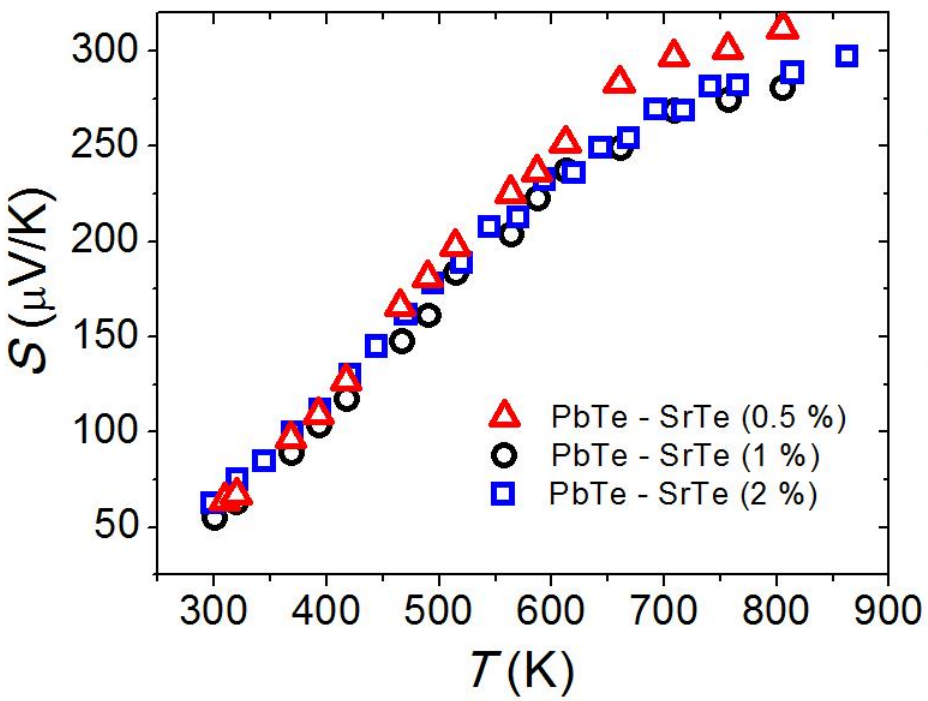
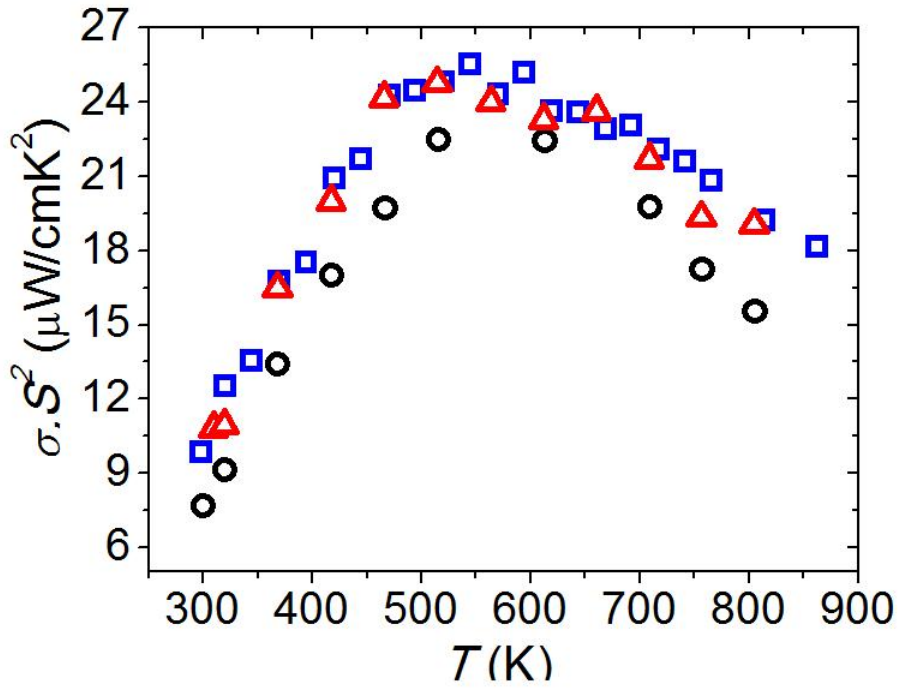
Seebeck coefficient and Power factor





$S = [S_{h1}\sigma_{h1} + S_{h2}\sigma_{h2}]/\sigma$

h1 = light hole
h2 = heavy hole

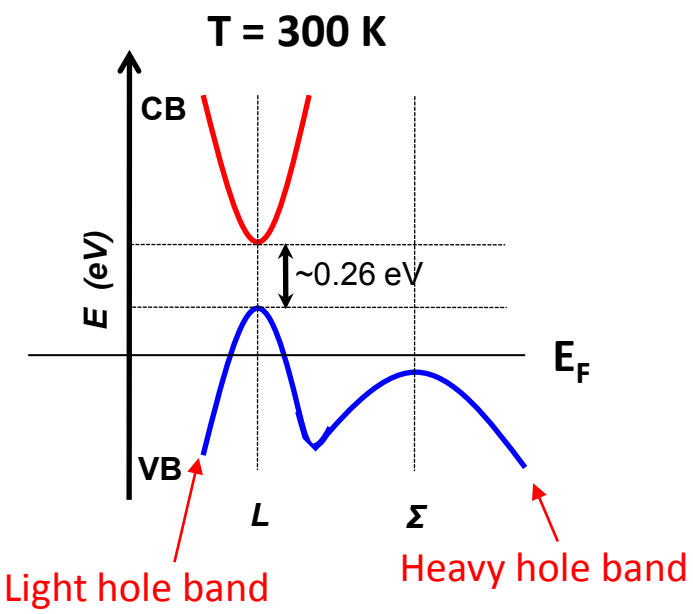
$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

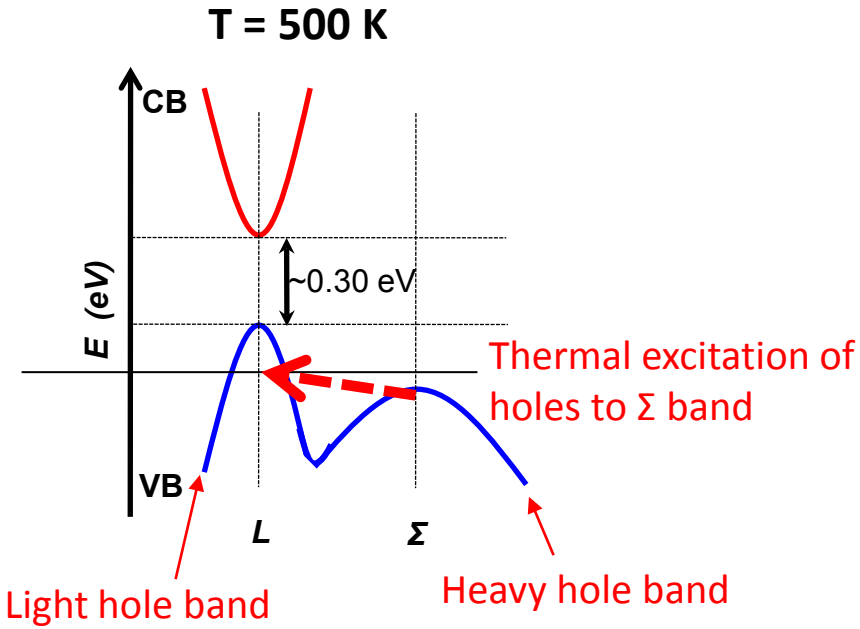
$m_{h2} = 1.5 m_{h1}$

Y. I. Ravich, B. A. Efimova, I. A. Smirnov, *Semiconducting Lead Chalcogenides* (Plenum, New York, vol 5, 1970).

J. G. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105-114 (2008).

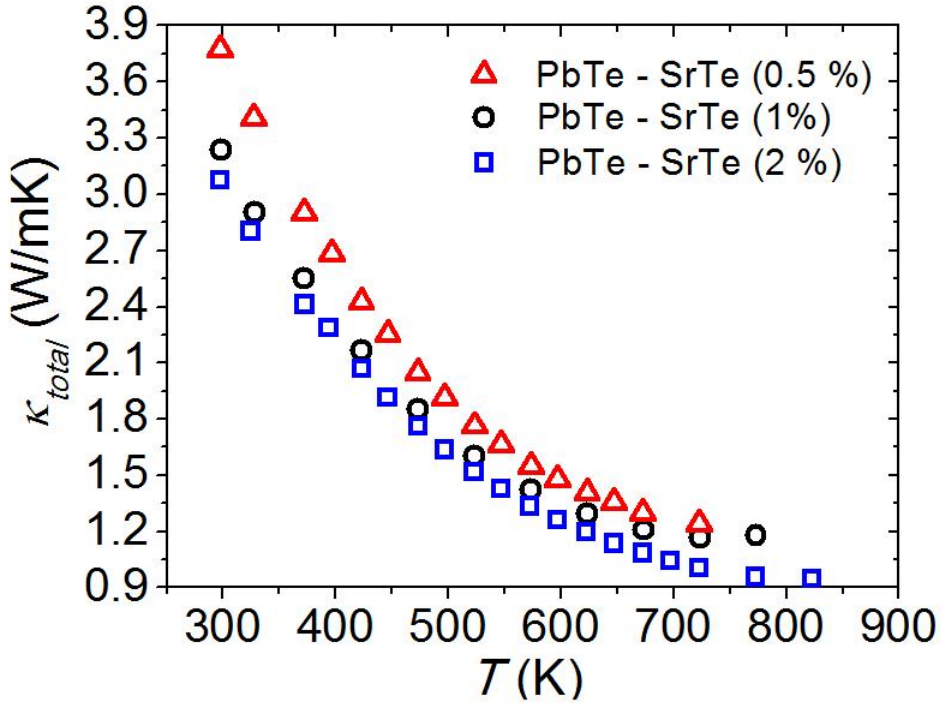
Valence bands of PbTe….

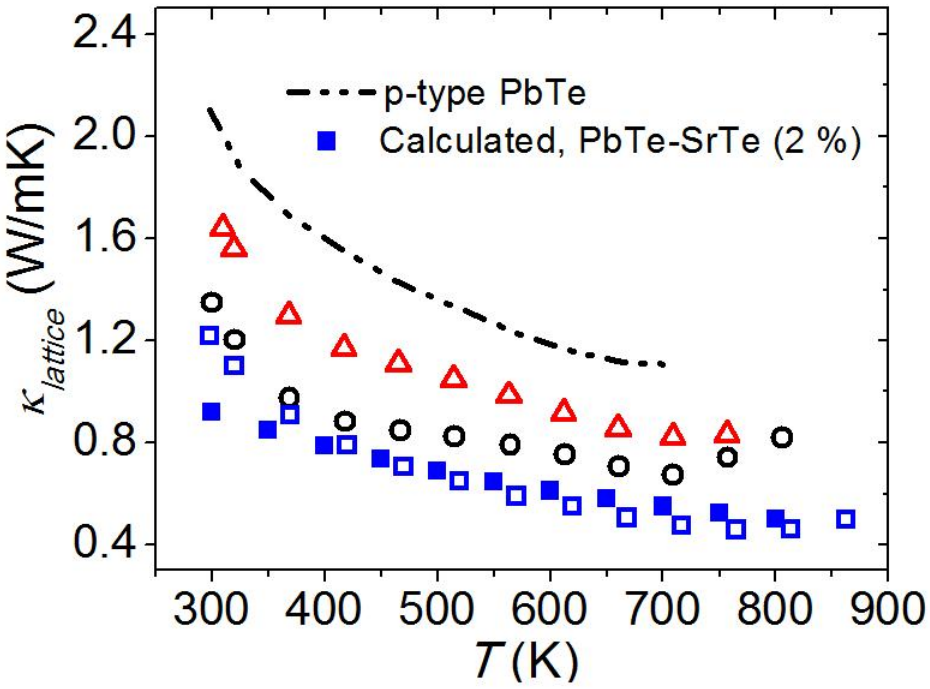




Rising temperature

Thermal conductivity





$\kappa_{total} = \kappa_{lattice} + \kappa_{electronic}$

$\kappa_e = L \cdot \sigma \cdot T$

$L_o = 2.44 \times 10^{-8}\ W\Omega K^{-2}$

All samples are ingots

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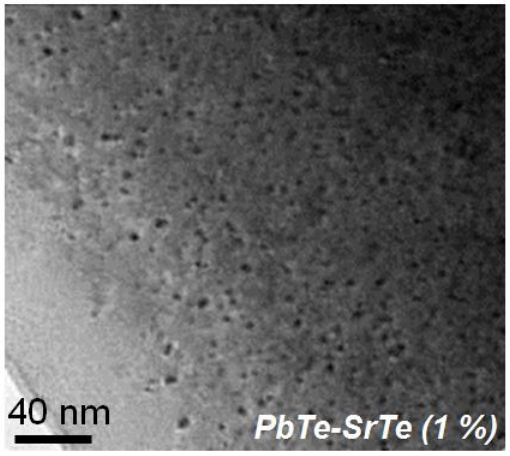
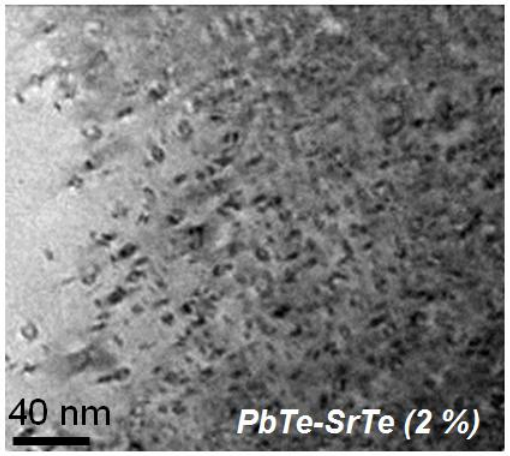
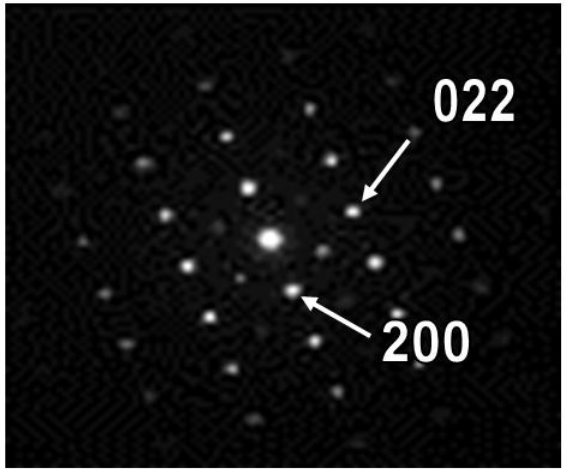
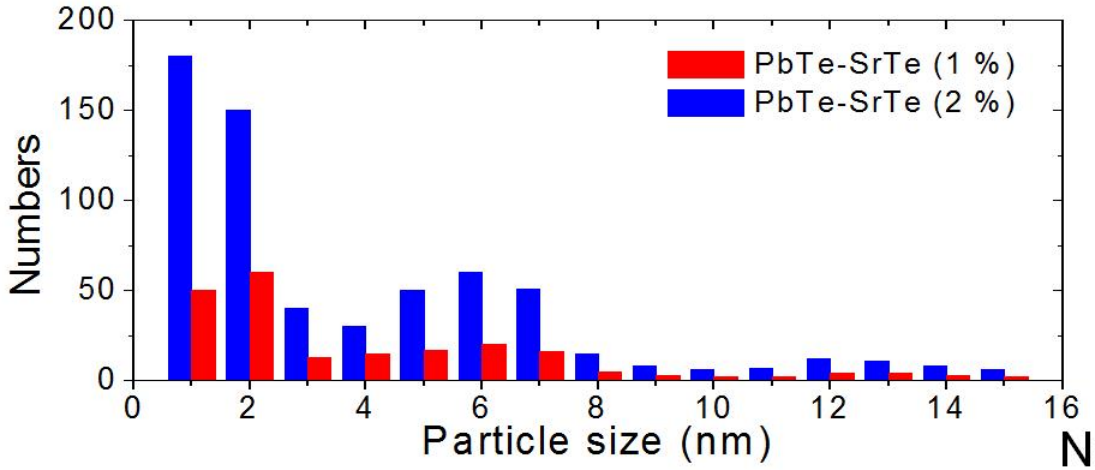
Transmission electron microscopy (TEM)









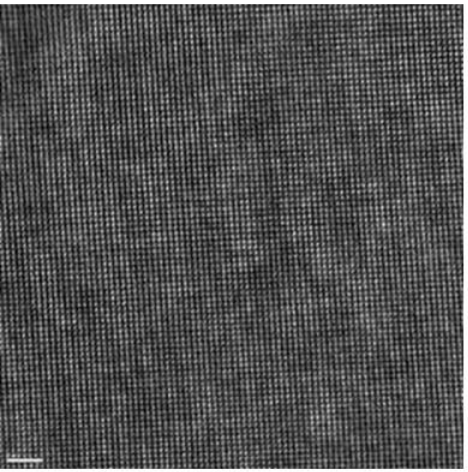
PbTe matrix and SrTe nanocrystals have similar symmetry, structure and lattice parameters, and corresponding crystallographic planes and directions are completely aligned in 3-D.

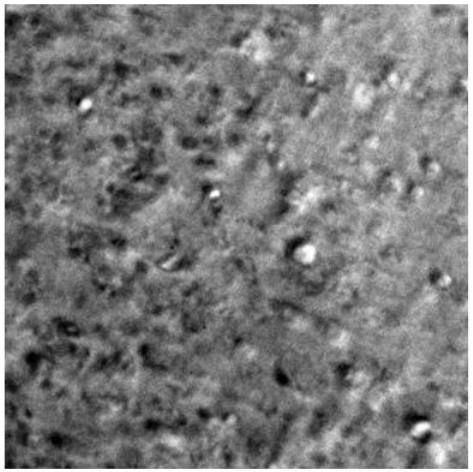
Nanoparticle Density $\approx 1.5 \times 10^{12}$ / cm^2

SrTe nanocrystals are endotaxially placed in the PbTe matrix

Nanocrystal density is greater in PbTe-SrTe(2%) than in PbTe-SrTe (1%)

Optimizing charge transport





Pristine matrix

nanostructured

$K_{pristine} >> K_{nanostructure}$

Comparable mobilities

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

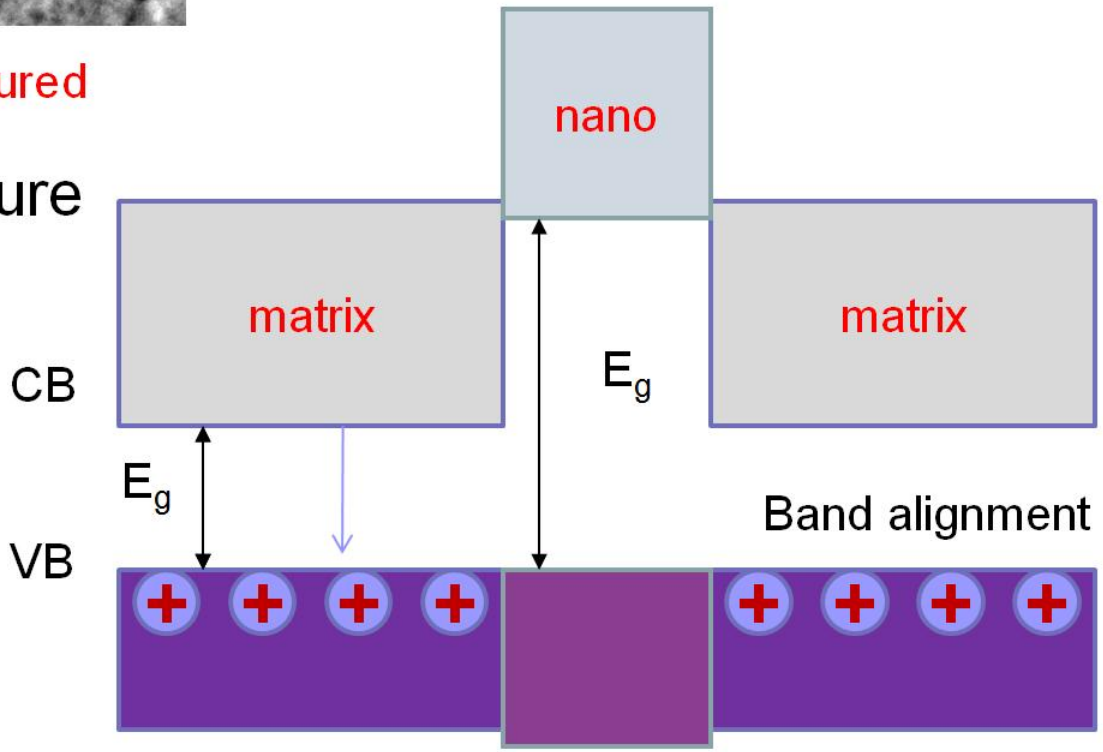
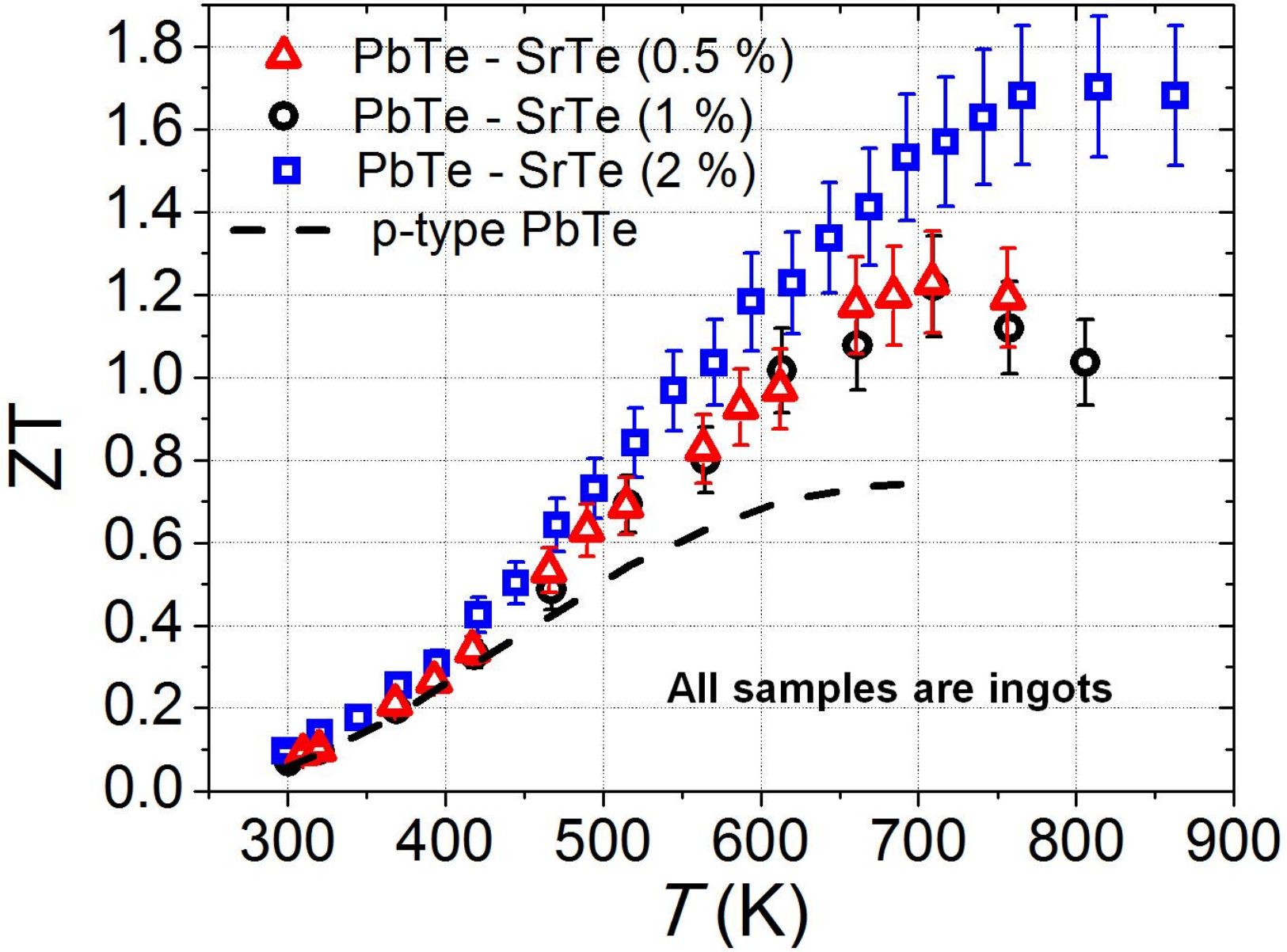


Figure of merit, ZT



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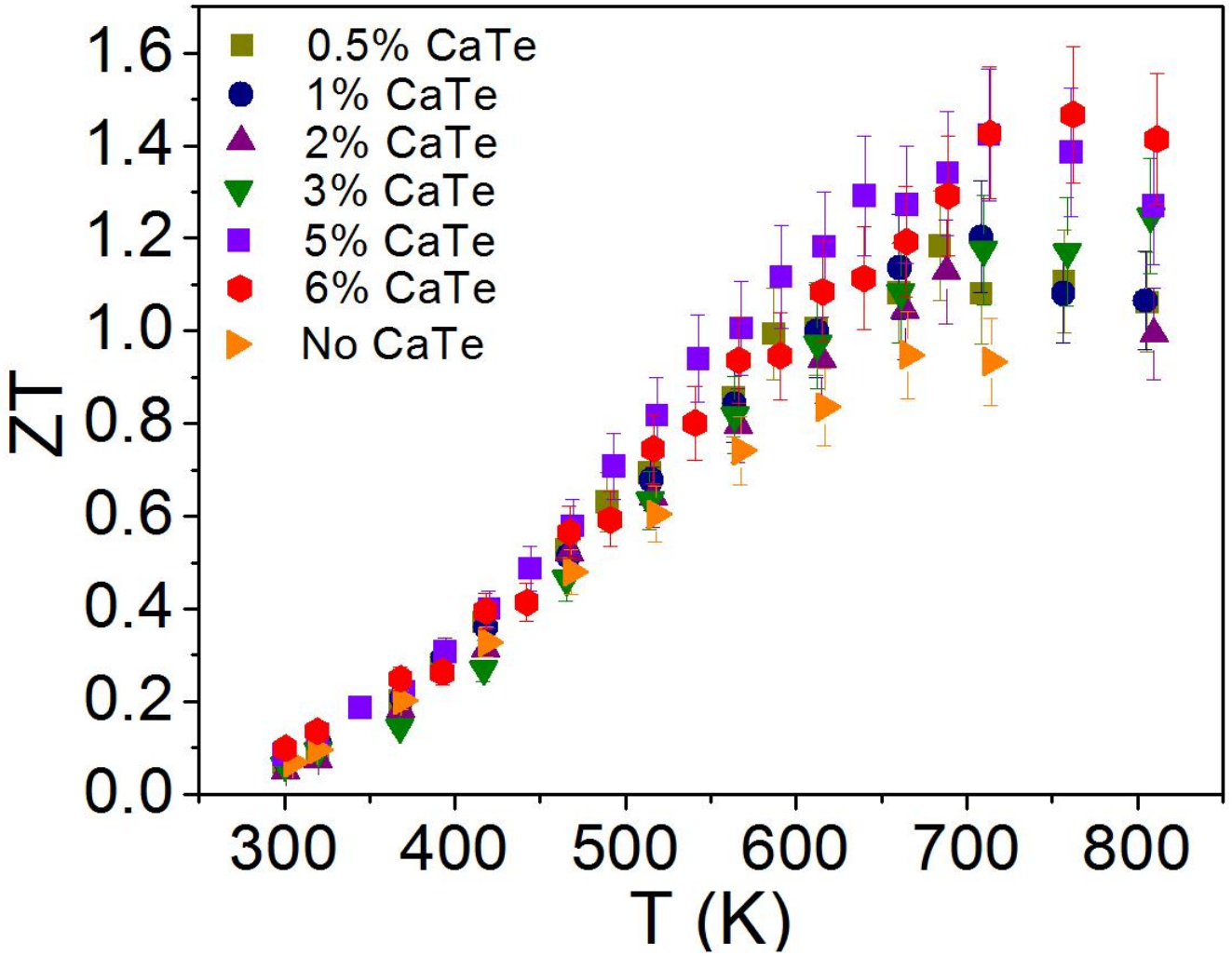
CaTe in PbTe

MgTe ZT~1.6
BaTe ZT~1.3



All samples are ingots

Earth abundant materials: Recent exciting results: thermal conductivity reduction

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Thermoelectrics from Abundant Chemical Elements: High-Performance Nanostructured PbSe–PbS

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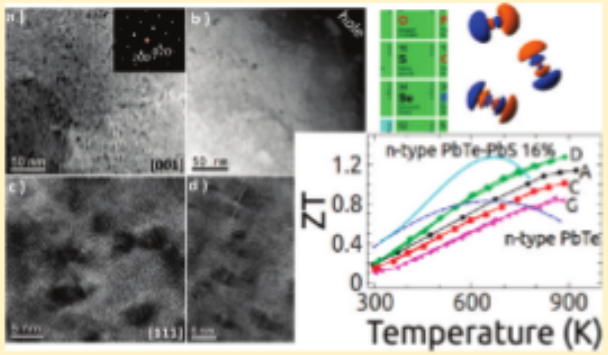
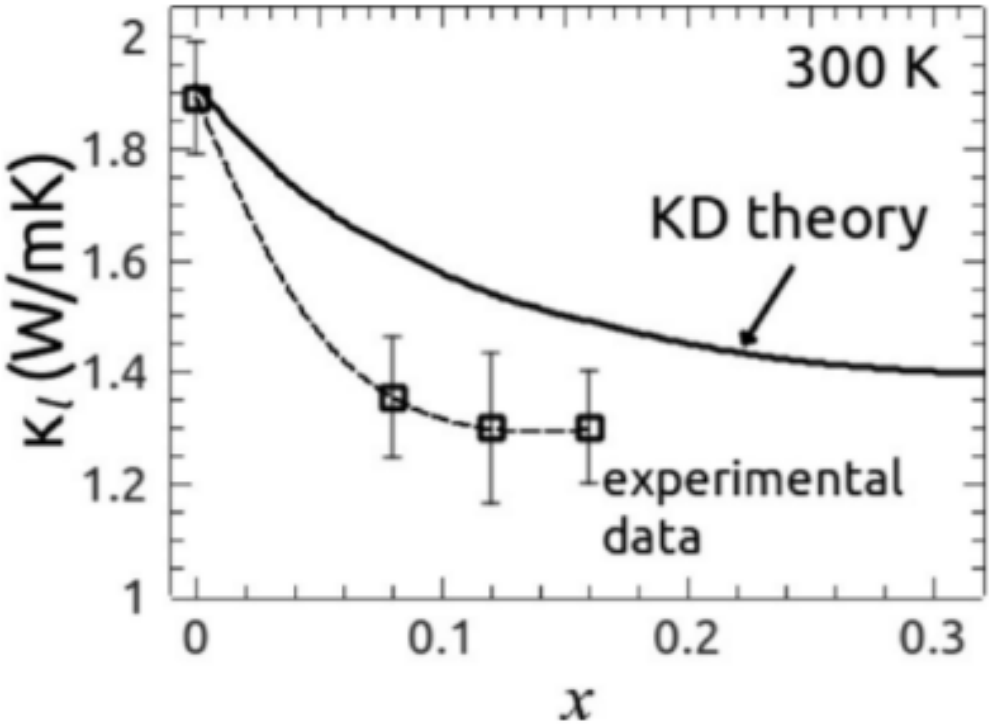
ABSTRACT: We report promising thermoelectric properties of the rock salt PbSe–PbS system which consists of chemical elements with high natural abundance. Doping with $PbCl_2$, excess Pb, and Bi gives n-type behavior without significantly perturbing the cation sublattice. Thus, despite the great extent of dissolution of PbS in PbSe, the transport properties in this system, such as carrier mobilities and power factors, are remarkably similar to those of pristine n-type PbSe in fractions as high as 16%. The unexpected finding is the presence of precipitates ~2–5 nm in size, revealed by transmission electron microscopy, that increase in density with increasing PbS concentration, in contrast to previous reports of the occurrence of a complete solid solution in this system. We report a marked impact of the observed nanostructuring on the lattice thermal conductivity, as highlighted by contrasting the experimental values (~1.3 W/mK) to those predicted by Klemens–Drabble theory at room temperature (~1.6 W/mK). Our thermal conductivity results show that, unlike in PbTe, optical phonon excitations in PbSe–PbS systems contribute to heat transport at all temperatures. We show that figures of merit reaching as high as ~1.2–1.3 at 900 K can be obtained, suggesting that large-scale applications with good conversion efficiencies are possible from systems based on abundant, inexpensive chemical elements.

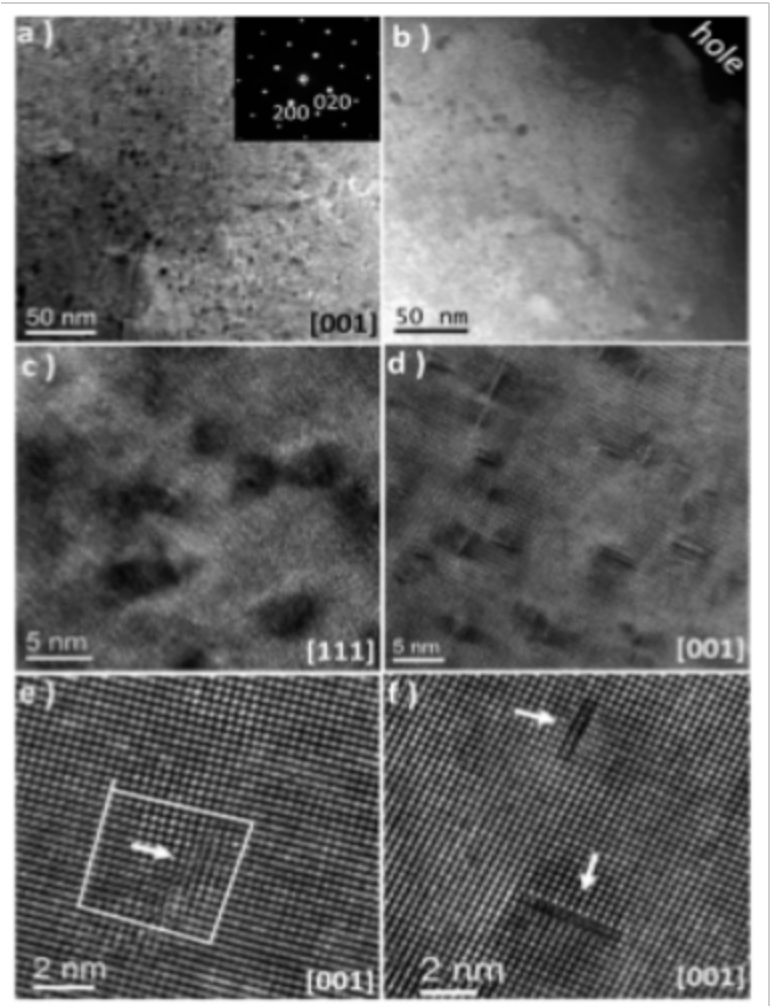


thermal conductivity reduction below alloy limit

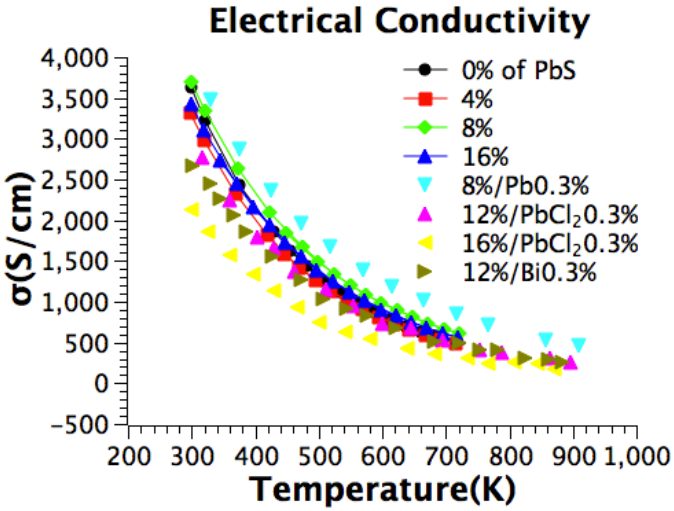


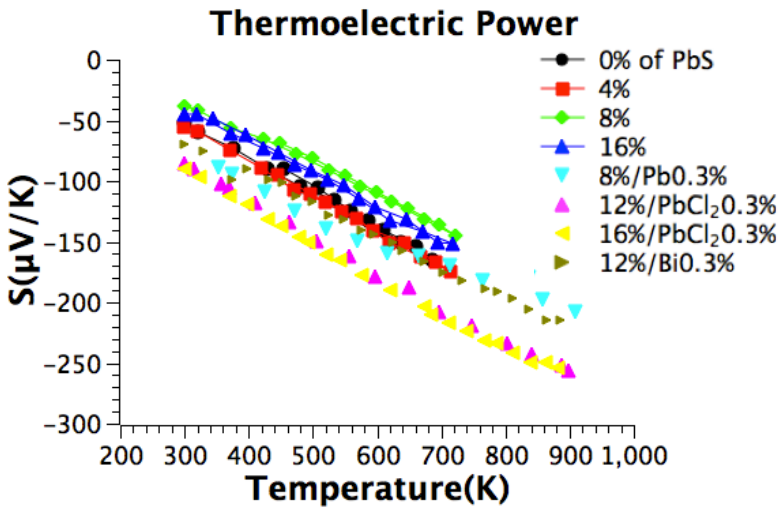
PbSe-PbS x%

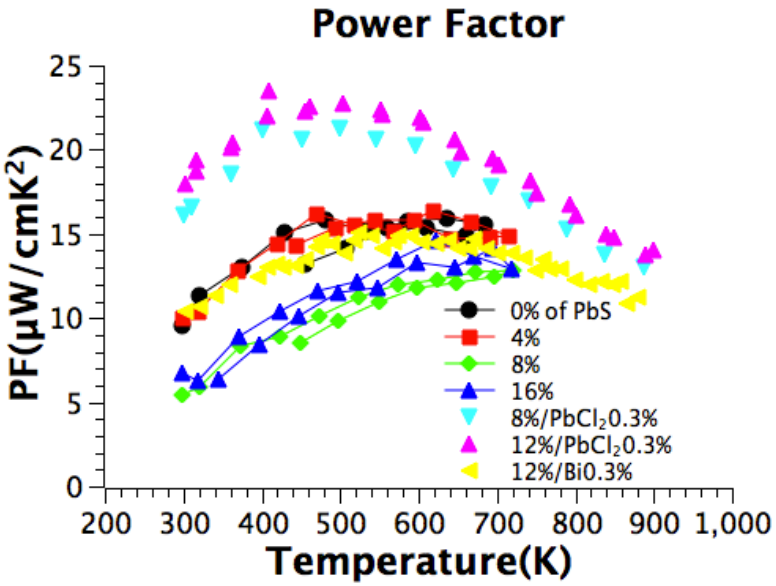
Density of precipitates increases with increasing x.

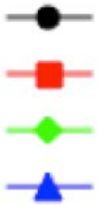


PbSe-x%PbS : doped with 0.3% of In
x = 0, 4, 8, and 16





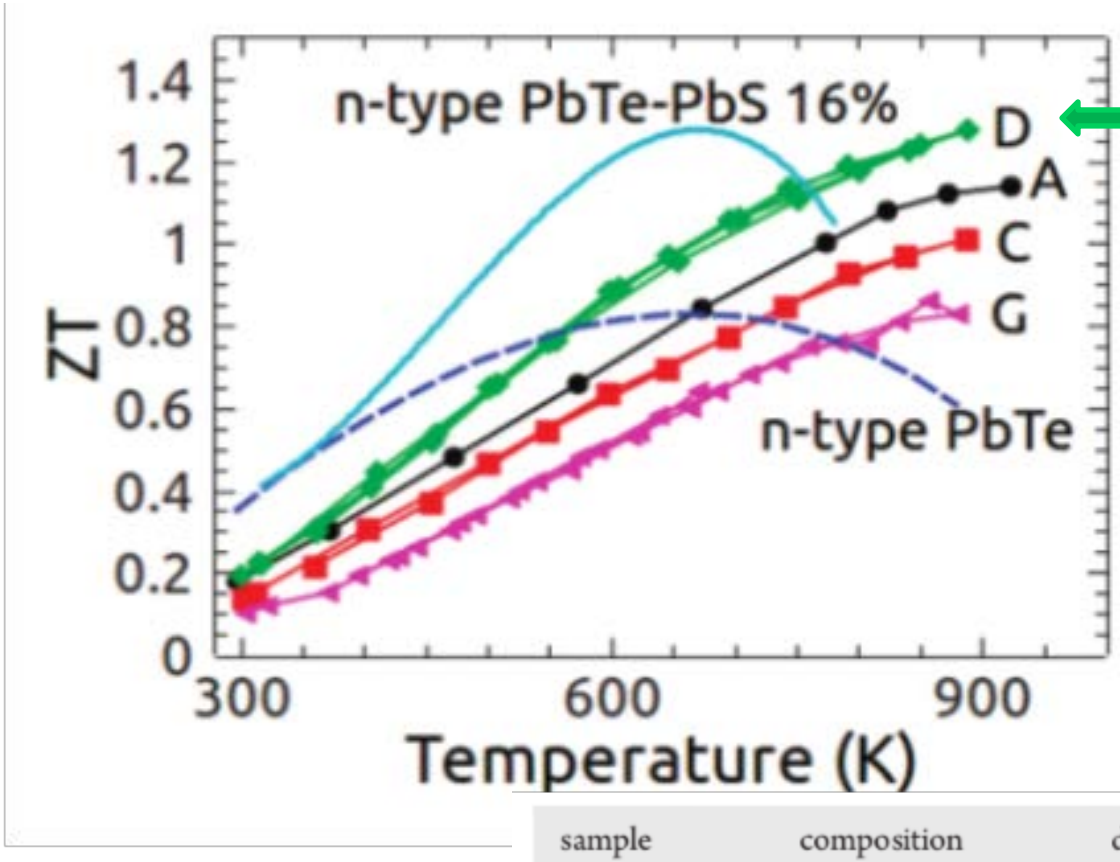




- 0% of PbS/0.3% of In : 3.04E19 cm^{-3}
- 4% of PbS/0.3% of In : 3.68E19 cm^{-3}
- 8% of PbS/0.3% of In : 5.58E19 cm^{-3}
- 12% of PbS/0.3% of In : 4.67E19 cm^{-3}
- 8% of PbS/0.3% of Pb* : 2.6E19 cm^{-3}
- 8% of PbS/0.3% of $PbCl_2$* : 2.8E19 cm^{-3}
- 12% of PbS/0.3% of $PbCl_2$* : 2.4E19 cm^{-3}
- 16% of PbS/0.3% of $PbCl_2$* : 2.2E19 cm^{-3}
- 12% of PbS/0.3% of Bi* : 3.2E19 cm^{-3}

Androulakis, J. ; Todorov, I. ; He, J. ; Chung, D. ; Dravid, V. ; Kanatzidis, M. ; *J. Am. Chem. Soc.* **2011**, 133, 10920

PbSe-PbS system: high ZT at 900K



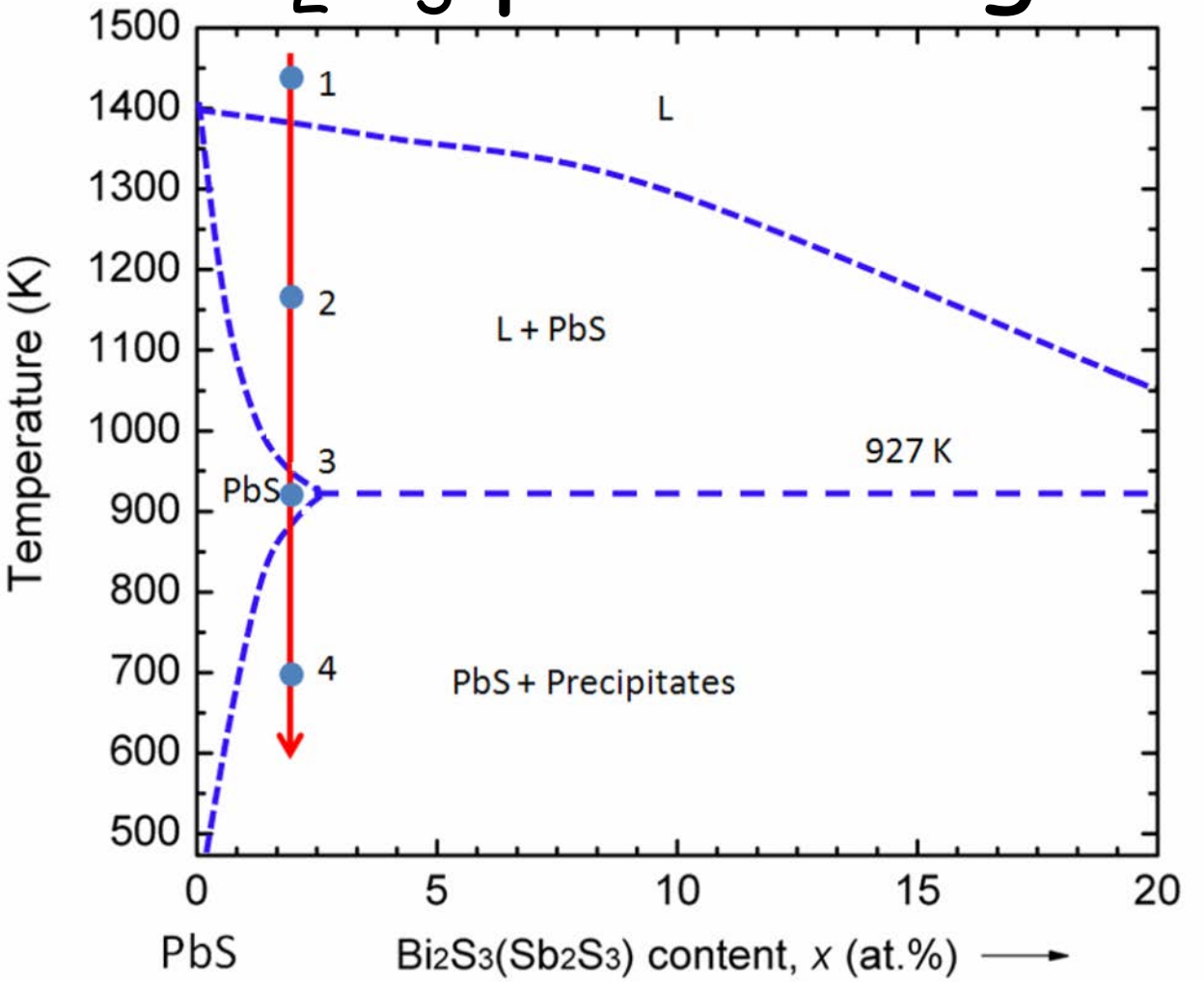
PbSe-PbS

sample	composition	dopant, mol %	n ($\times 10^{19}$ cm^{-3})
A	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.08$)	Pb, 0.30%	2.6
B	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.08$)	Pb, 0.35%	2.9
C	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.08$)	$PbCl_2$, 0.30%	2.8
D	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.12$)	$PbCl_2$, 0.30%	2.4
E	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.12$)	$PbCl_2$, 0.40%	4.5
F	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.16$)	$PbCl_2$, 0.30%	2.2
G	$(PbSe)_{1-x}(PbS)_x$ ($x = 0.12$)	Bi, 0.30%	3.2

Dopant plays strong role in the resulting ZT.

Thermoelectric Properties of n-type PbS

PbS-Bi_2S_3 phase diagram

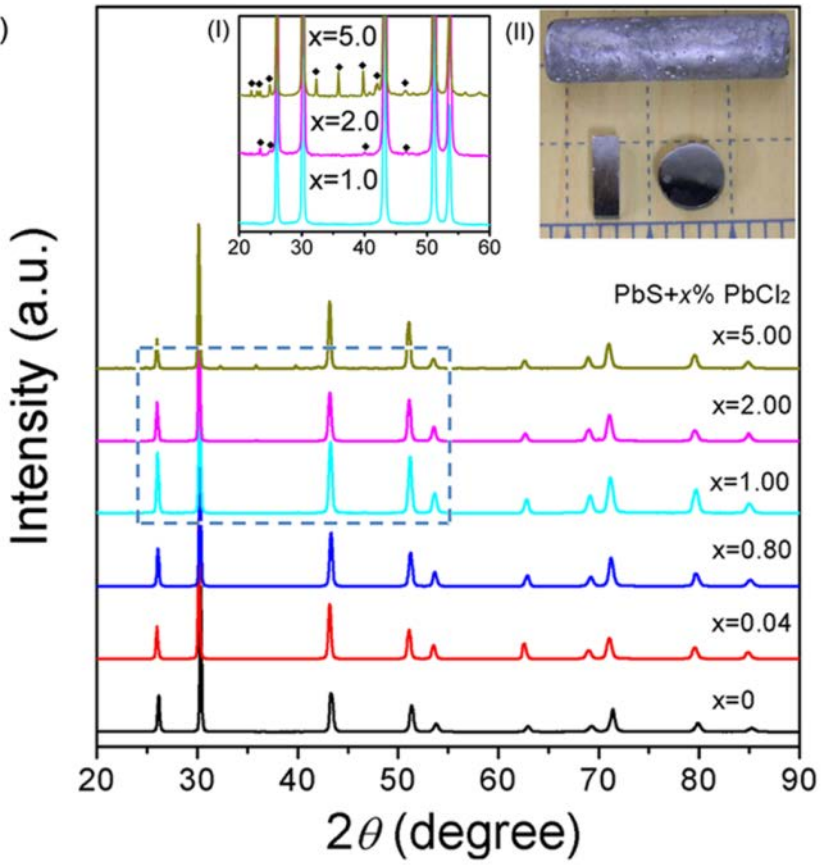


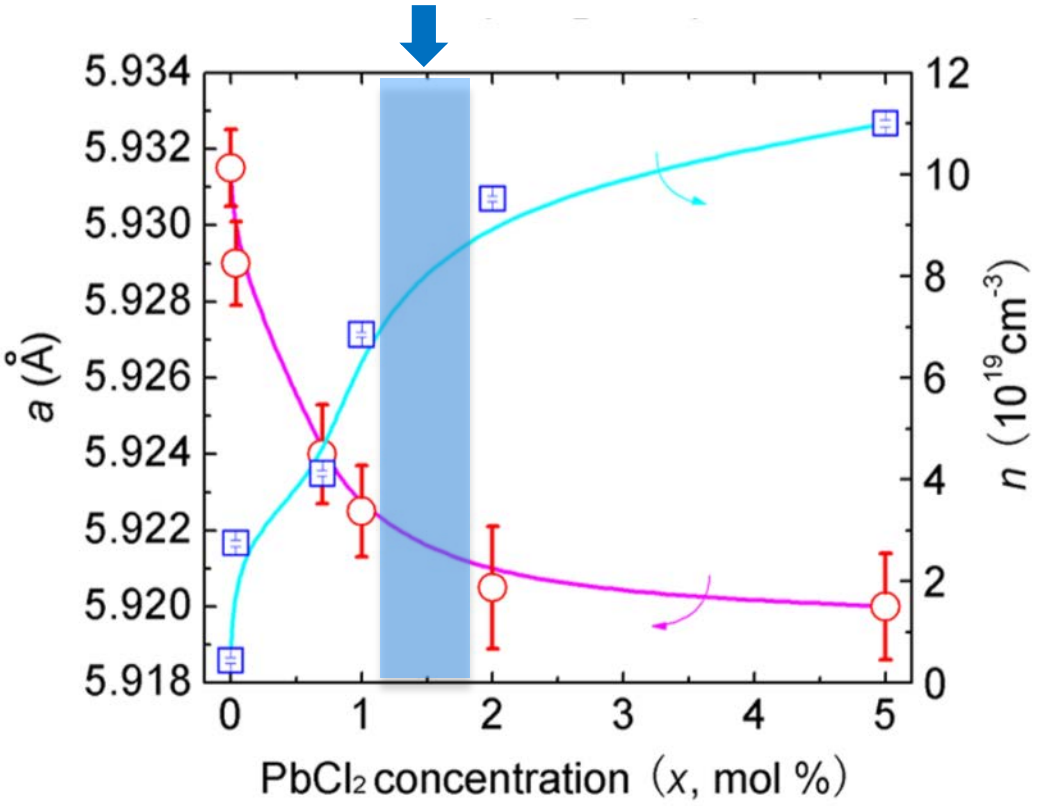
Binary phase diagram of PbS-$Bi_2S_3(Sb_2S_3)$

Garvin P. F., *Neues Jahrb. Mineral., Abh.*, **118**, 235(1973)

n-type PbS

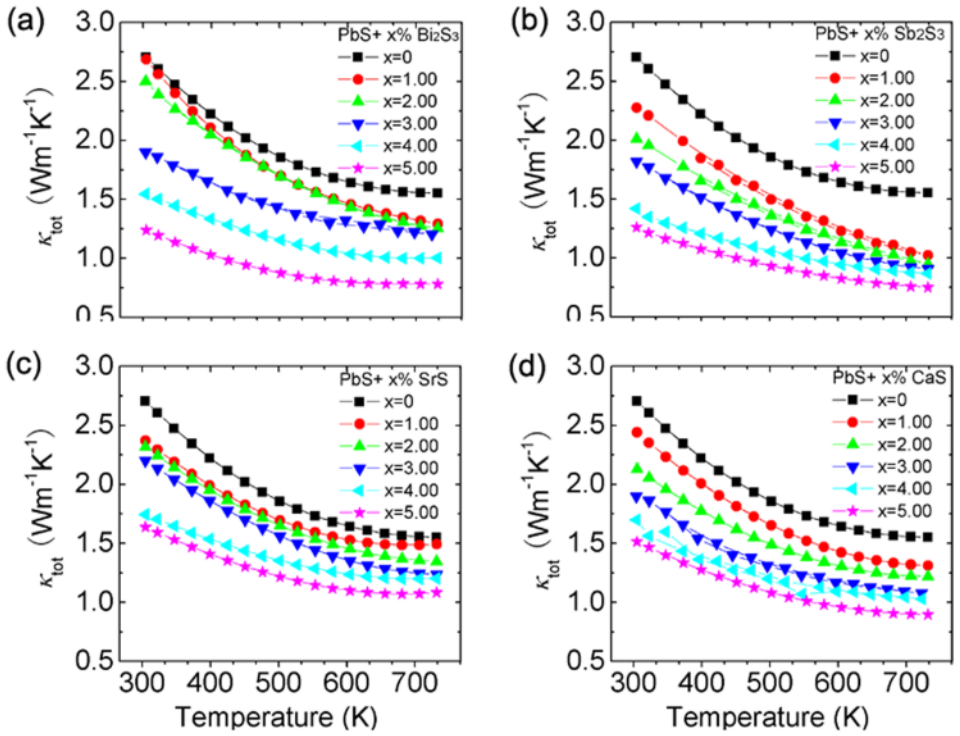
The solubility limit of $PbCl_2$ in PbS ranges between 1.0 and 2.0 mol %

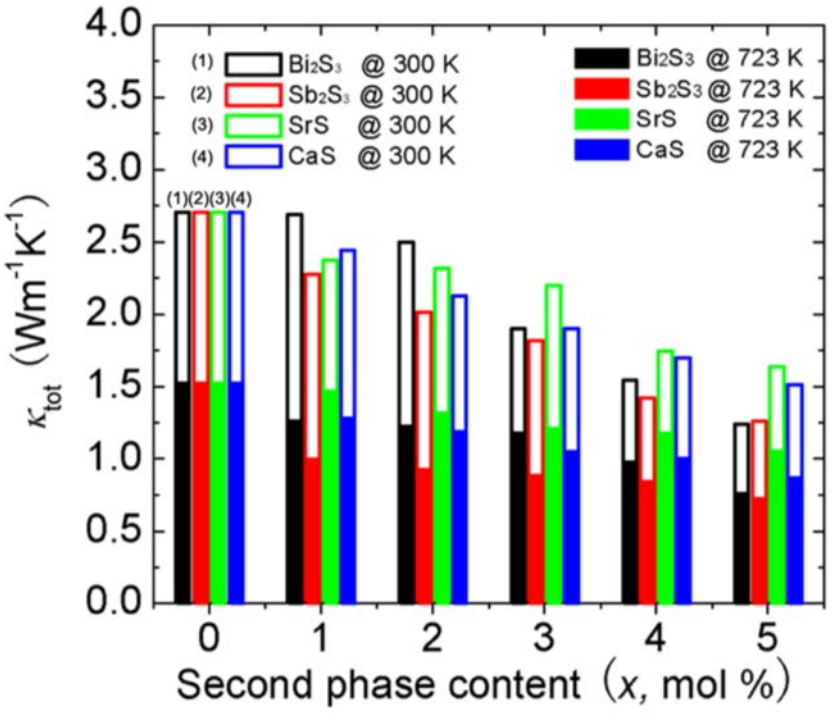




n-type PbS with second phases

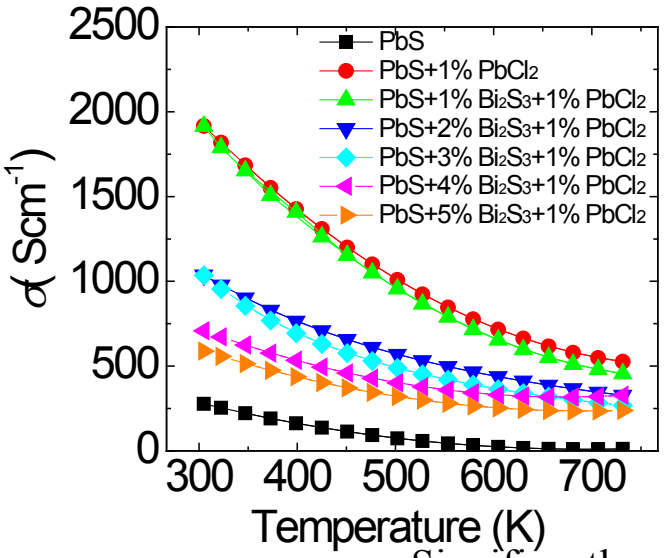
PbS with second phases without doping



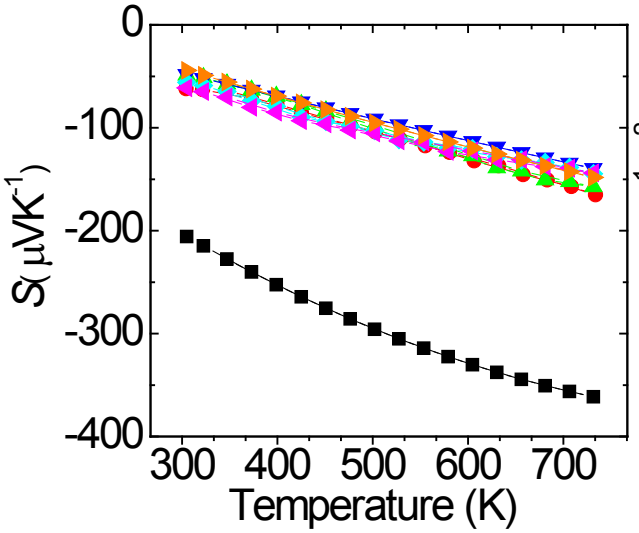


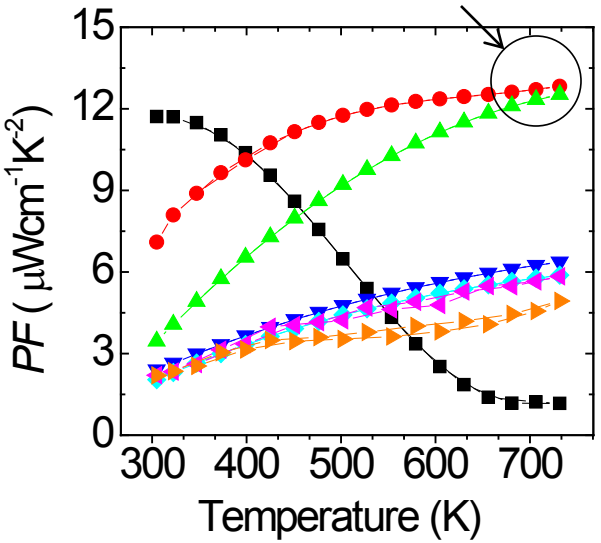
Second phases: Bi_2S_3, Sb_2S_3

n-type PbS with second phases

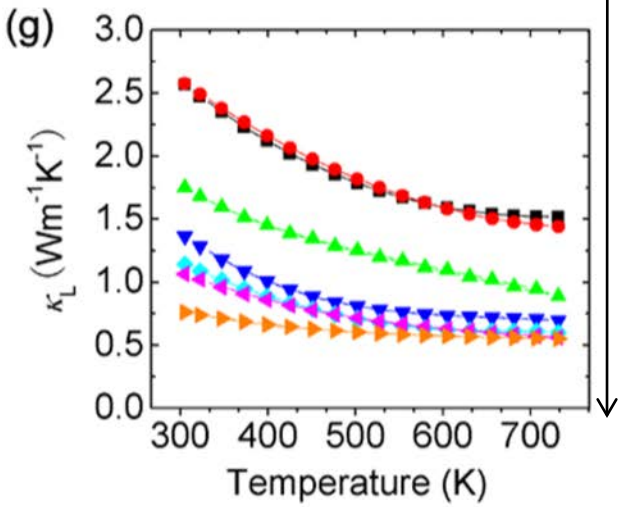


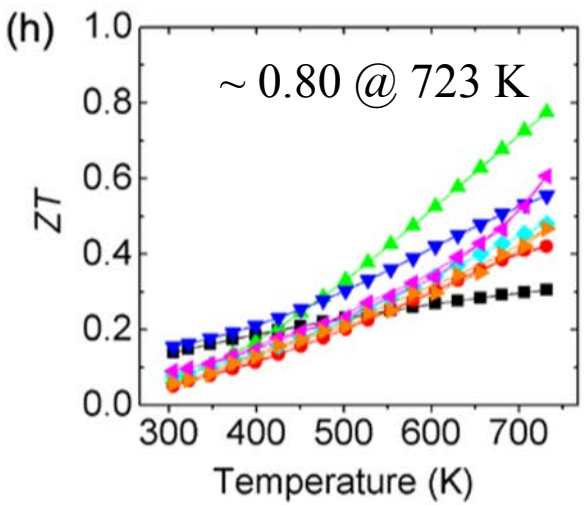
Seebeck independent on second phases



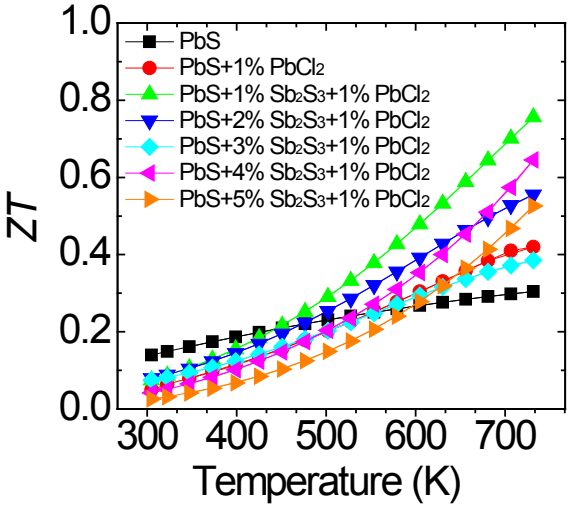


Significantly reduce

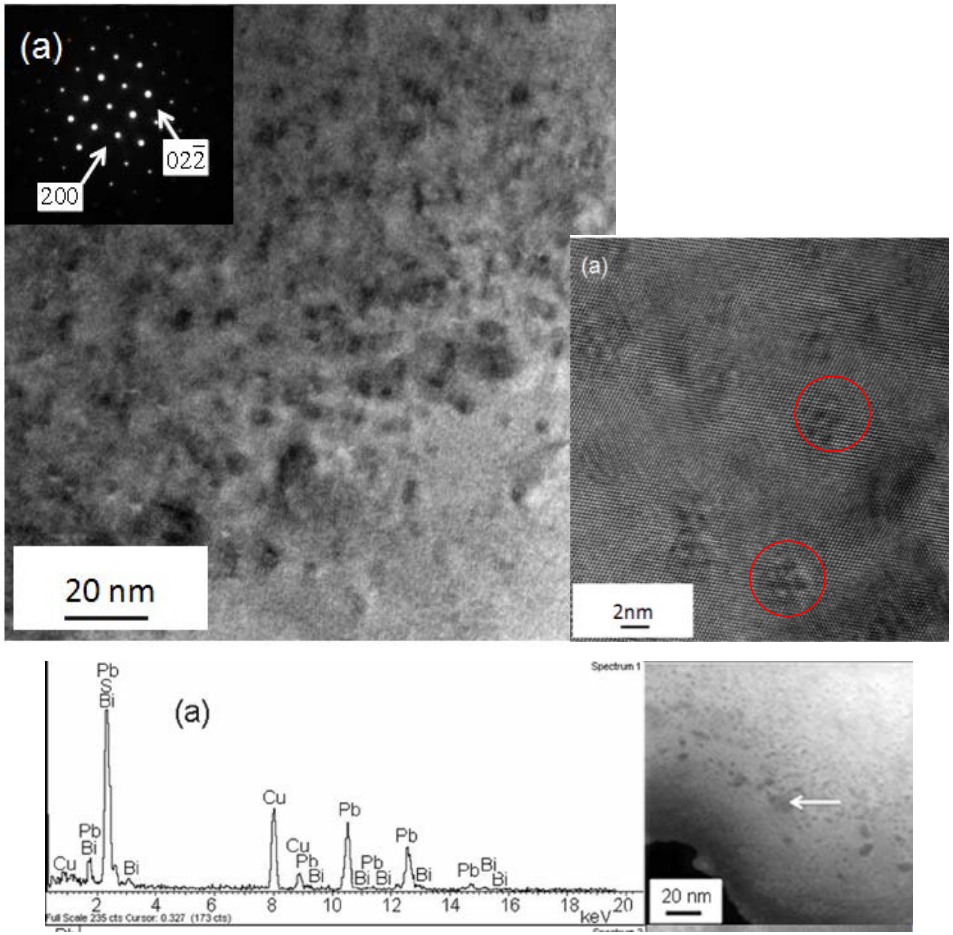


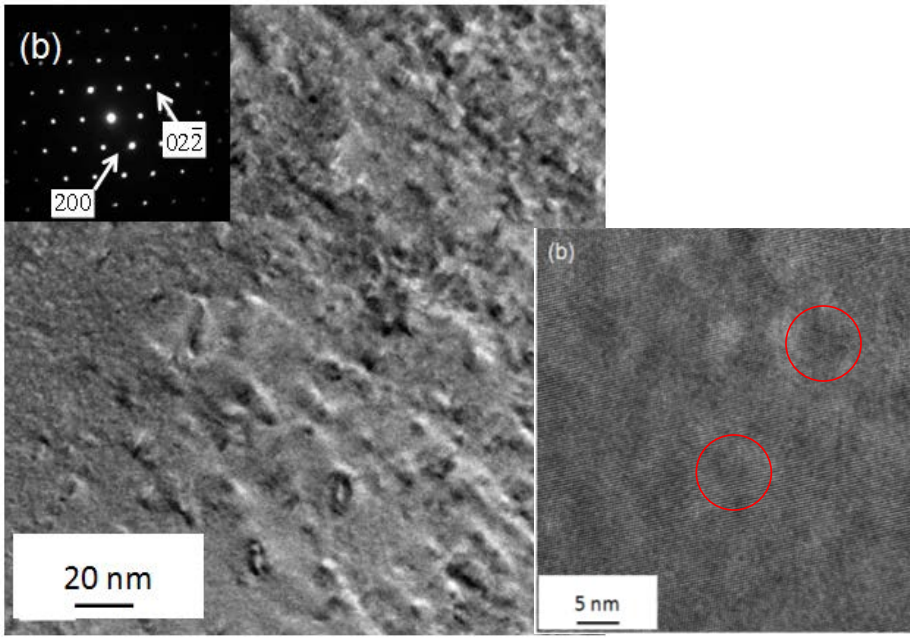


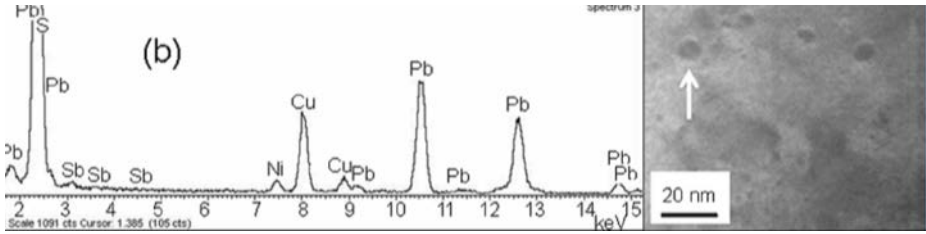
PbS with Sb_2S_3~ 0.78 @ 723 K



TEM: nanostructured PbS







PbS+1.0 at. % Bi_2S_3+1.0 at. % $PbCl_2$

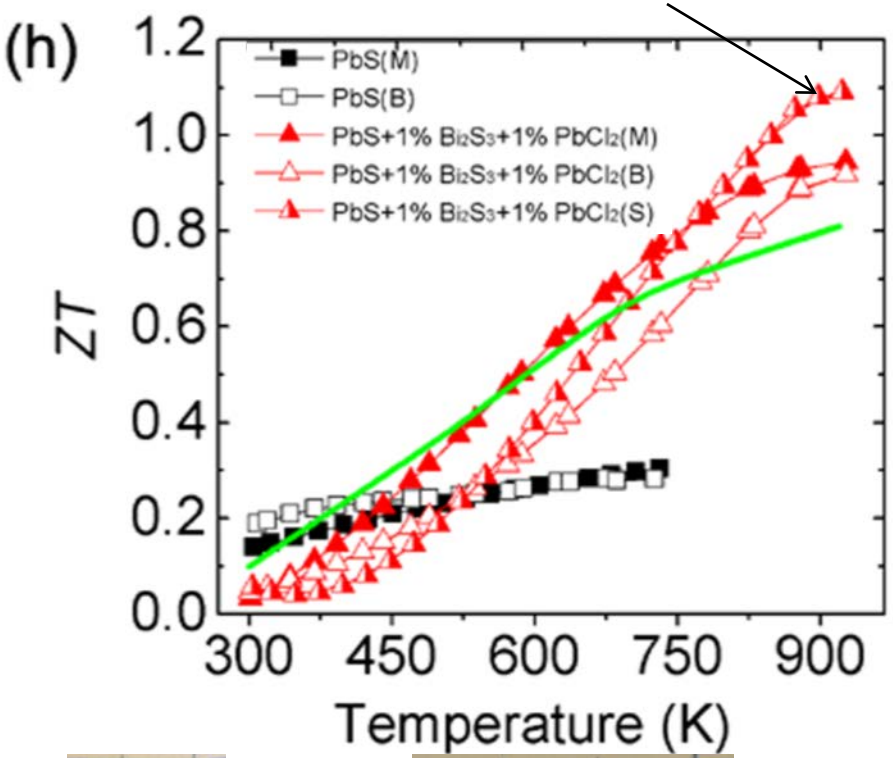
PbS + 1.0 at. % Sb_2S_3 + 1.0 at. % $PbCl_2$

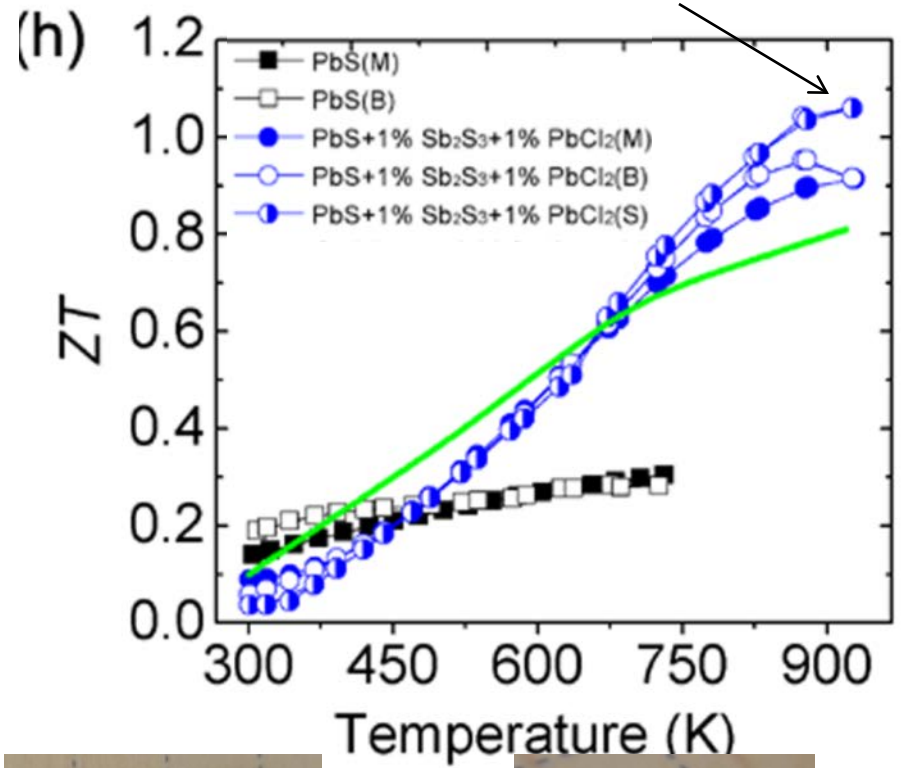
Nanostructures n-type PbS, ZT=1.1

ZT ~ 1.1 @ 923 K

Good repeatability !

ZT ~ 1.06 @ 923 K





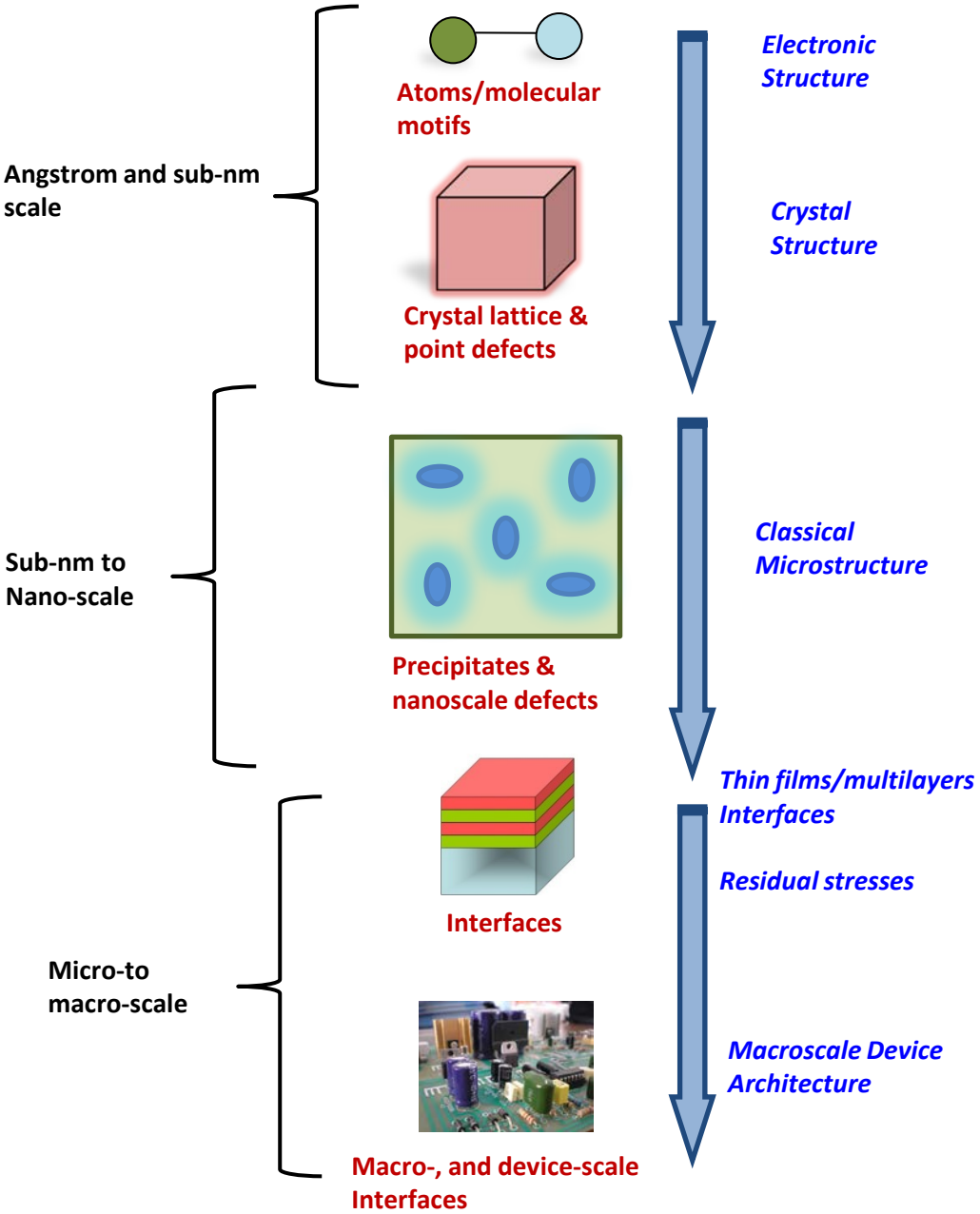
M: normal melting

B: Bridgman

S: SPS

BN coating

Panoscopic view of thermoelectrics



Hierarchical Length-scale Architecture:

Implications for "Nanostructured" Thermoelectrics

- ✓ Interactions along varied length-scales
- ✓ Identification of individual microstructure elements in electronic and phonon transport
- ✓ Tailoring and design of "microstructure"

Conclusions

- Strain at interfaces increases phonon scattering
- Small nanostructured (1-10 nm) are more likely to create strain
- Superior properties in p-type PbTe-SrTe achieved through endotaxial placement of nanoprecipitates
  - Nanostructures do not reduce the power factor and function exclusively as phonon scatterers
- Large power factor enhancements are need for continued ZT increases
- PbSe-PbS is nanostructured!
- PbSe-PbS n-type ZT~1.3 at 900K.
- High performance in PbS (ZT>1)