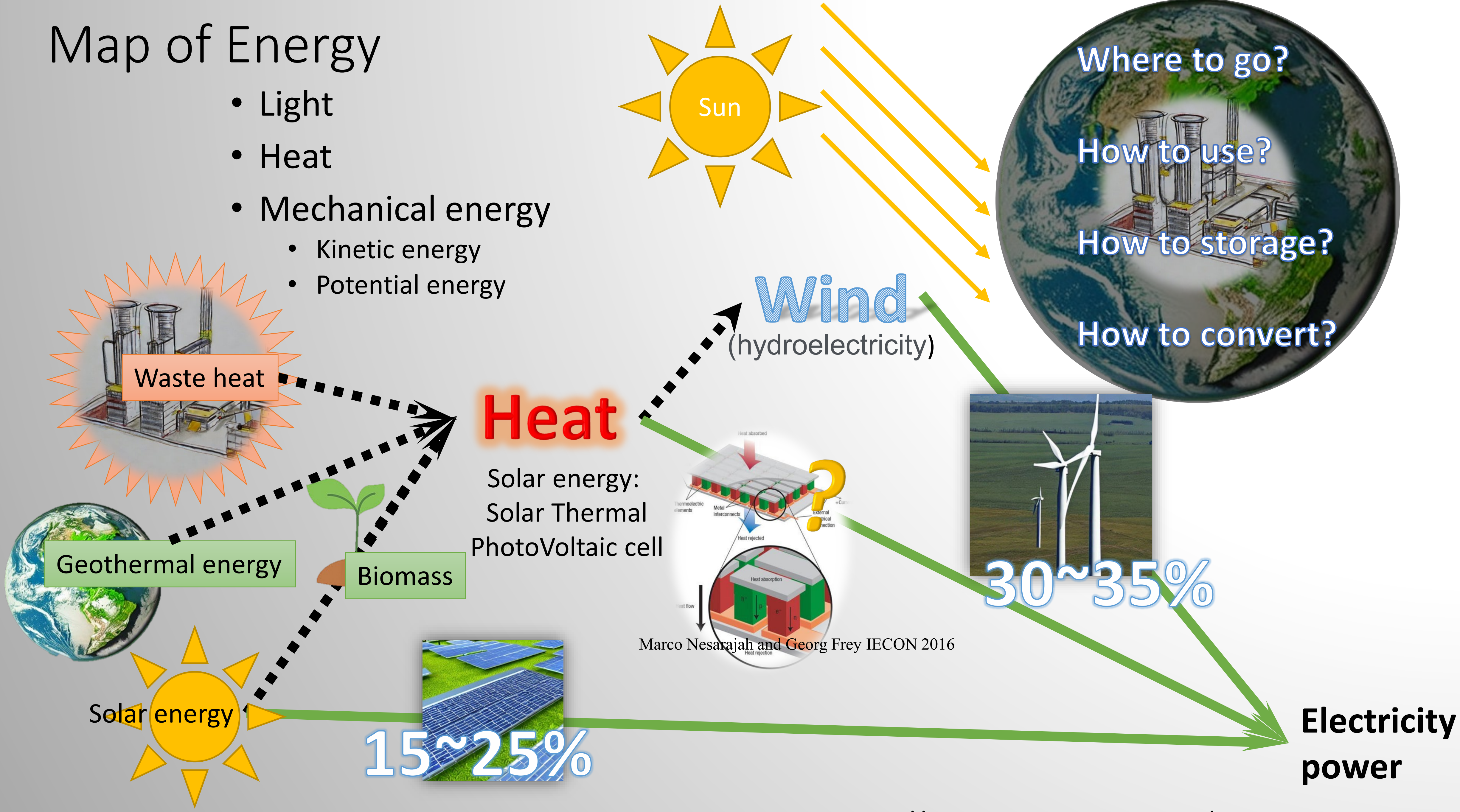
# Introduction to Thermoelectric

Institute of Physics, Academia Sinica

Min-Nan Ou

# Map of Energy

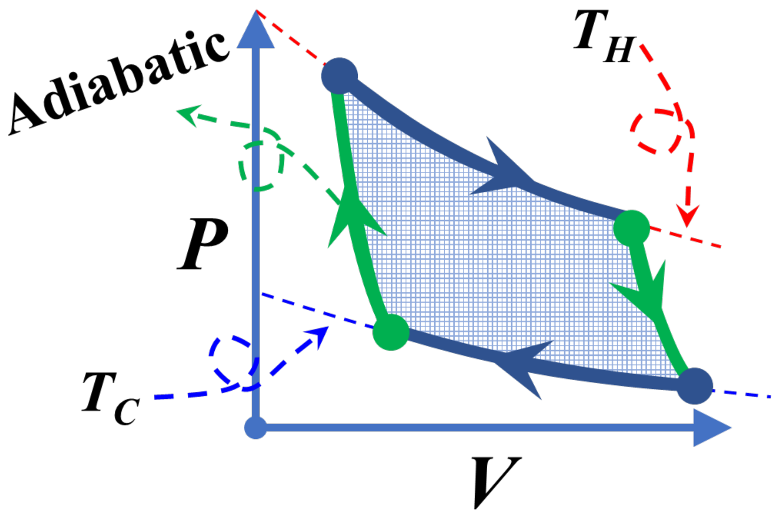
- Light
- Heat
- Mechanical energy
  - Kinetic energy
  - Potential energy

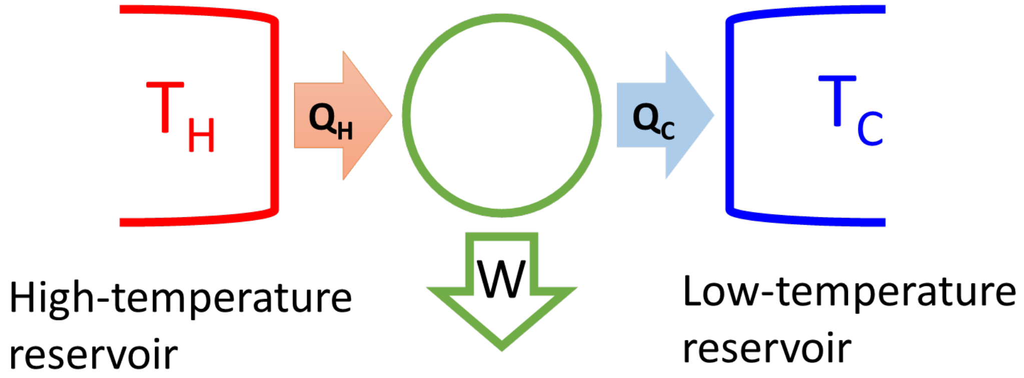



Drawing are made by https://stablediffusionweb.com/Drawings

# Waste energy from thermal engines:

- According to 2nd law of thermodynamics, the maximum efficiency of heat transformed to work would be the Carnot cycle as follow,




(關鍵評論)https://www.thenewslens.com/article/164239

- Efficiency of Carnot cycle: $\eta_C = \frac{T_H - T_C}{T_H}$
- Example:
  - $T_H$ = 1000 K (~727 ℃), $T_C$ = 600 K (~327 ℃) ⇨ $\eta_C = 0.4$

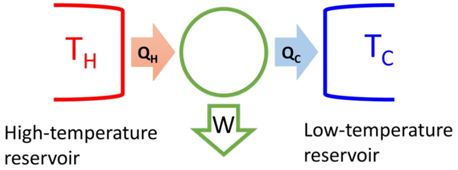
# Review

Abram F. Ioffe

$$\eta = \left\{\frac{(T_H - T_C)}{T_H}\right\}\left\{\frac{(1+ZT)^{0.5}}{T_C/T_H + (1+ZT)^{0.5}}\right\},$$

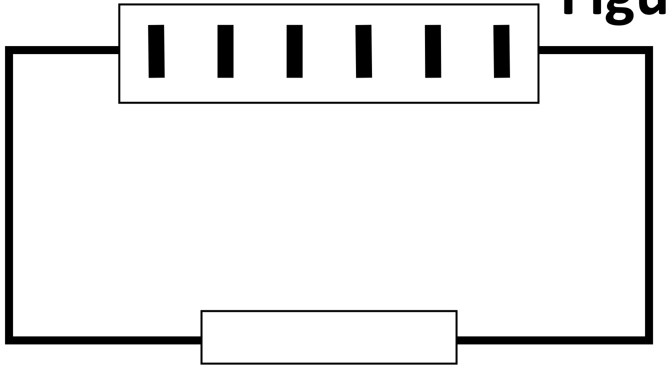
Carnot cycle

Material factor




## Ioffe (1957)

**Figure of merit**



Loading

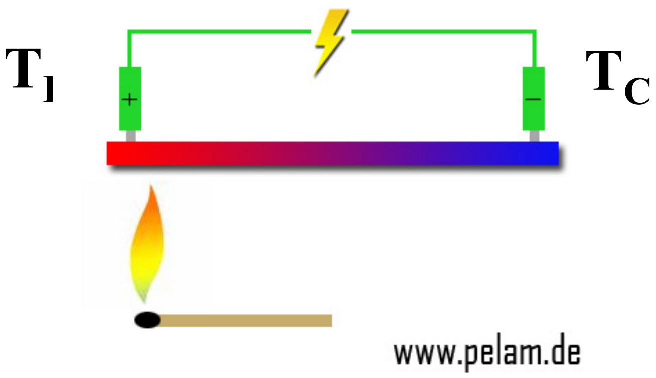
$$ZT = \frac{S^2\sigma}{\kappa}T$$

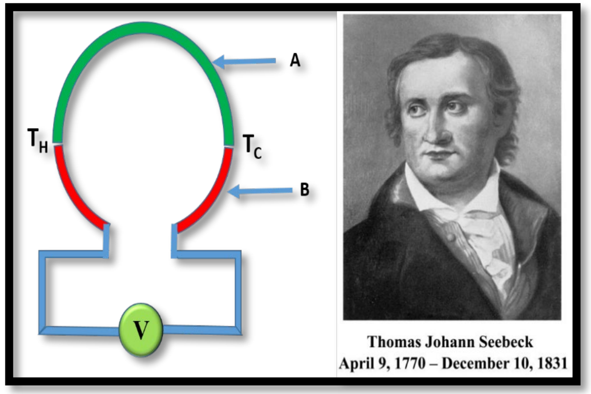
$$\kappa = \kappa_e + \kappa_{ph}$$

# The Seebeck Effect

## Heat → Electricity

| | | |
|---|---|---|
| 1821 | T . J . Seebeck<br>Seebeck effect: | Temperature gradient generates electrical potential<br>$V = \alpha_{AB} . \Delta T$ |

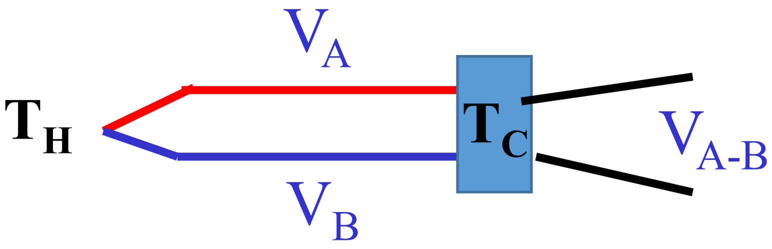



S= Seebeck Coefficient (V/K)

$\Delta V = S \times \Delta T$

# Practical Applications: Thermocouple




If A is P type, B is N type

$$V_{A\text{-}B}=(S_A-S_B)x(T_H-T_c)$$

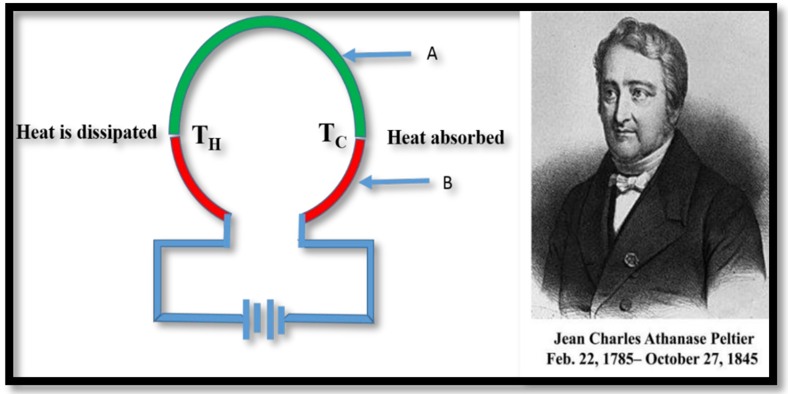
For example:
K type includes
P type Chromel ( 90% Ni+ 10 % Cr ) +21.7 μV/K
N type Alumel (95% Ni+2% Mn+2% Al+1% Si) -17.3 μ V/K

40 uV /K output

# Peltier Effects

**Electricity → Temperature Gradient**

| | | |
|---|---|---|
| 1834 | J . C . A Peltier<br>Peltier effect: | Applied voltage creates Temperature gradient $\pi_{AB} = \frac{Q}{I}$ |



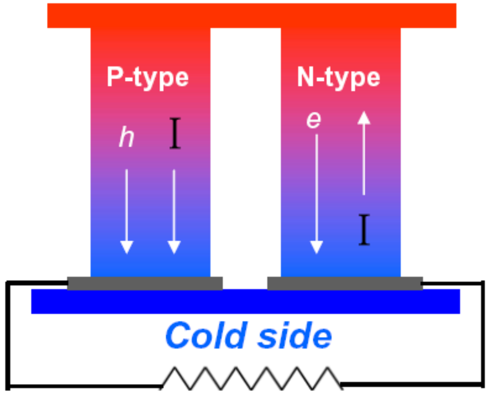

Jean Charles Athanase Peltier
Feb. 22, 1785– October 27, 1845

# Thomson Effects

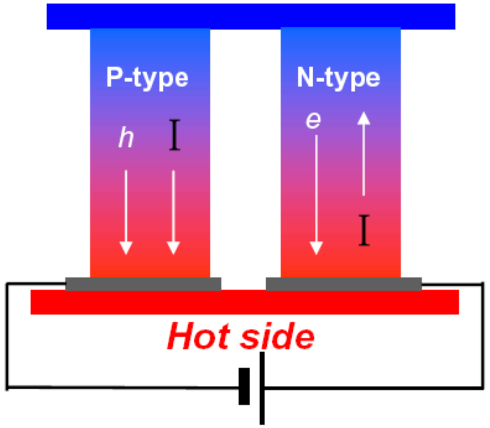
**Heat ⇆ electricity**

| | | |
|---|---|---|
| 1821 | T . J . Seebeck<br>Seebeck effect: | Temperature gradient generates electrical potential<br>$V = \alpha_{AB} . \Delta T$ |
| 1834 | J . C . A Peltier<br>Peltier effect: | Applied voltage creates Temperature gradient $\pi_{AB} = \frac{Q}{I}$ |
| 1855 | 湯姆森效應<br>Thomson effect | $\Pi_{AB} = T\, \alpha_{AB}$ |

# Working Principle



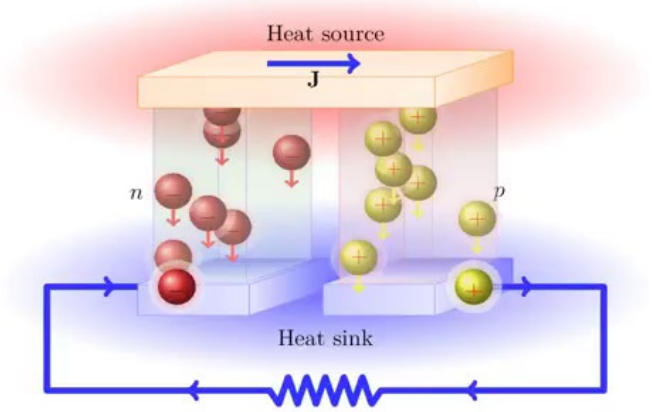

(a)

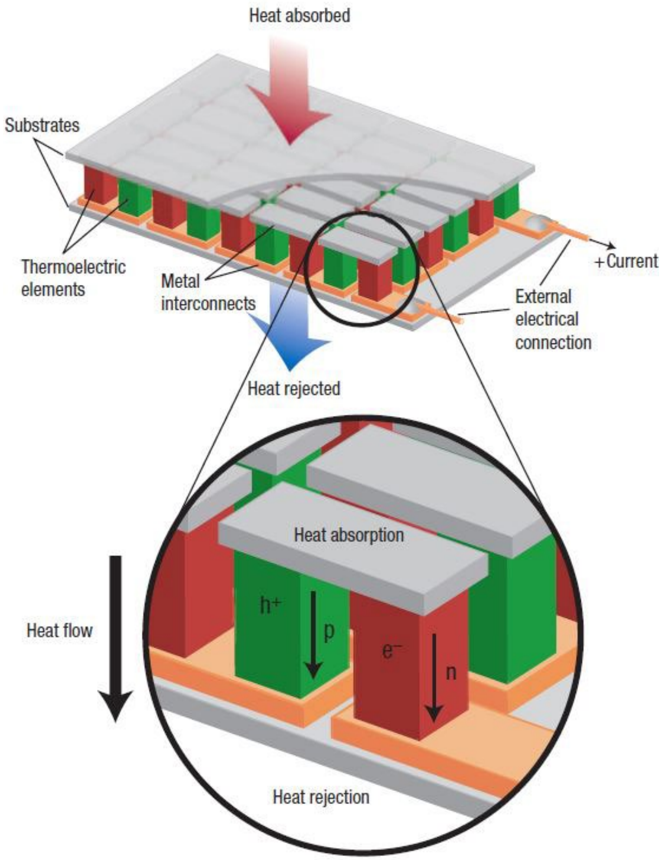



(b)

**Electrical Generator**

**Cooler**



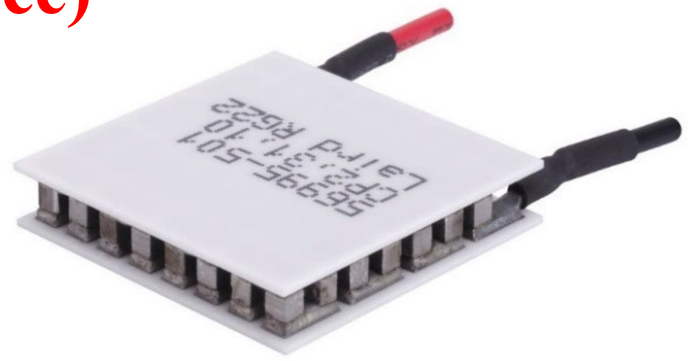

***P-N* Pairs**

Marco Nesarajah and Georg Frey IECON 2016

https://www.youtube.com/watch?v=21EC0lZ0imw

# The Advantages of Thermoelectric Devices

- ✓No moving parts (Low-noise operation)
- ✓Solid-state elements (Less maintenance)
- ✓High Scalability
- ✓High reliability: long lifetimes
- ✓Reversable operation: Easy switching from cooling to heating mode

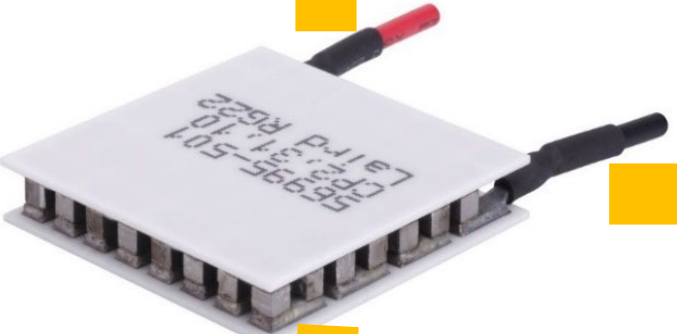


# TE Applications

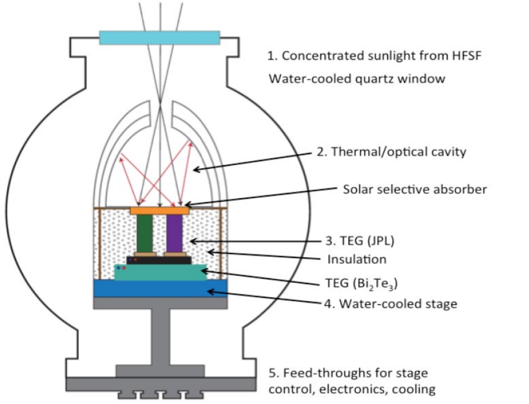
# Thermoelectric Generators

Vehicle exhaust BMW-BSST

## Industrial Waste-Heat



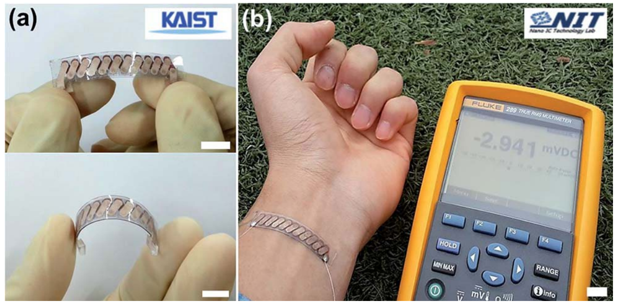
Wrist watch SEIKO




David Ginley *et al*. NREL, JPL

**Solar Thermoelectric Generators**

## Wearable TEG



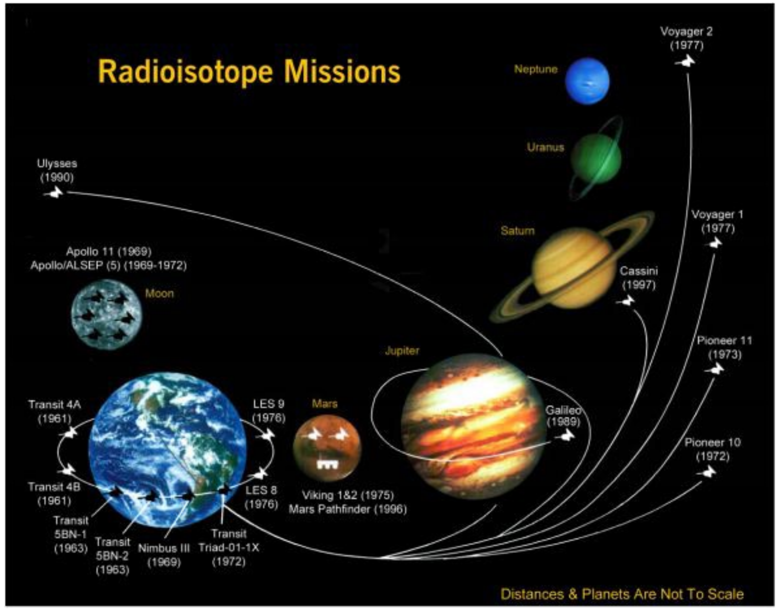


**Hybrid Solar Thermal System/GMZ**

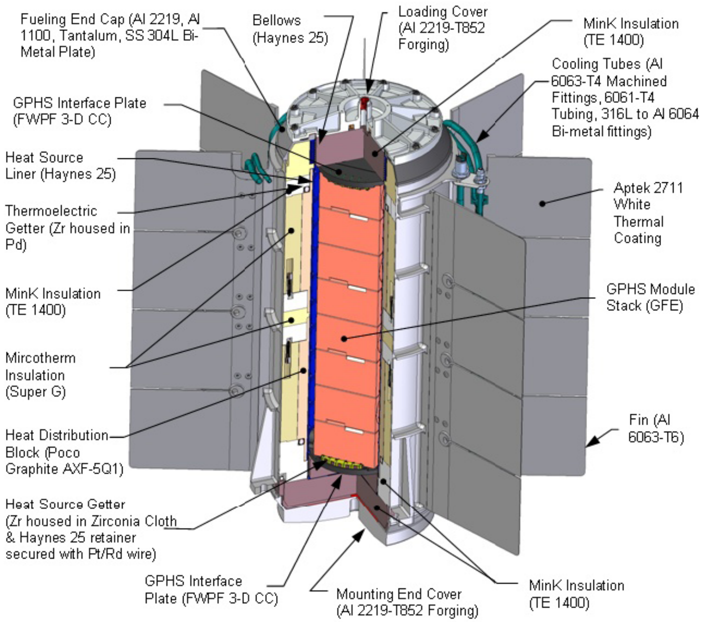
# Application 1: Thermoelectric Generators for Space - Radioisotope Thermoelectric Generators (RTG)

For Space Exploration missions, the electrical power is provided by converting the heat from a **Pu238 (Plutonium)** instead of sunlight have been used by NASA in a variety of missions such as Apollo, Pioneer, Viking, Voyager, Galileo, and Cassini.

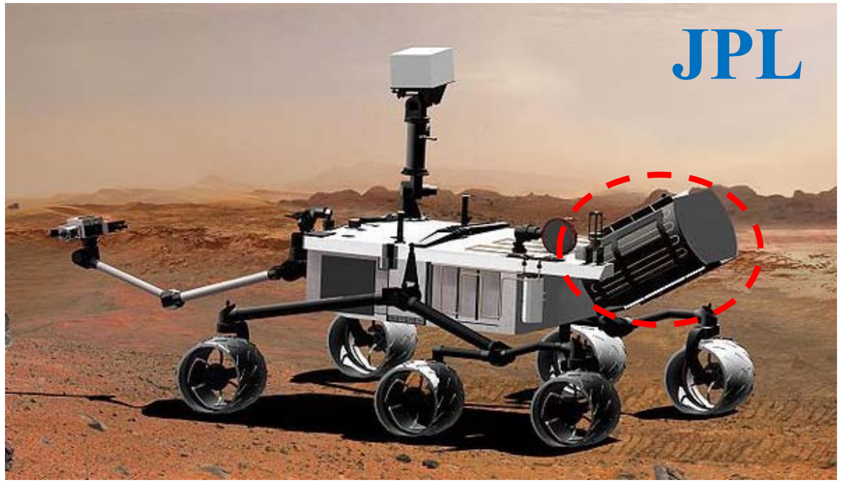
The power sources **for Voyager** are still operating, allowing the spacecraft to continue to make scientific discoveries after **over 35 years of operation**.




NASA Call for a new generation of RTG



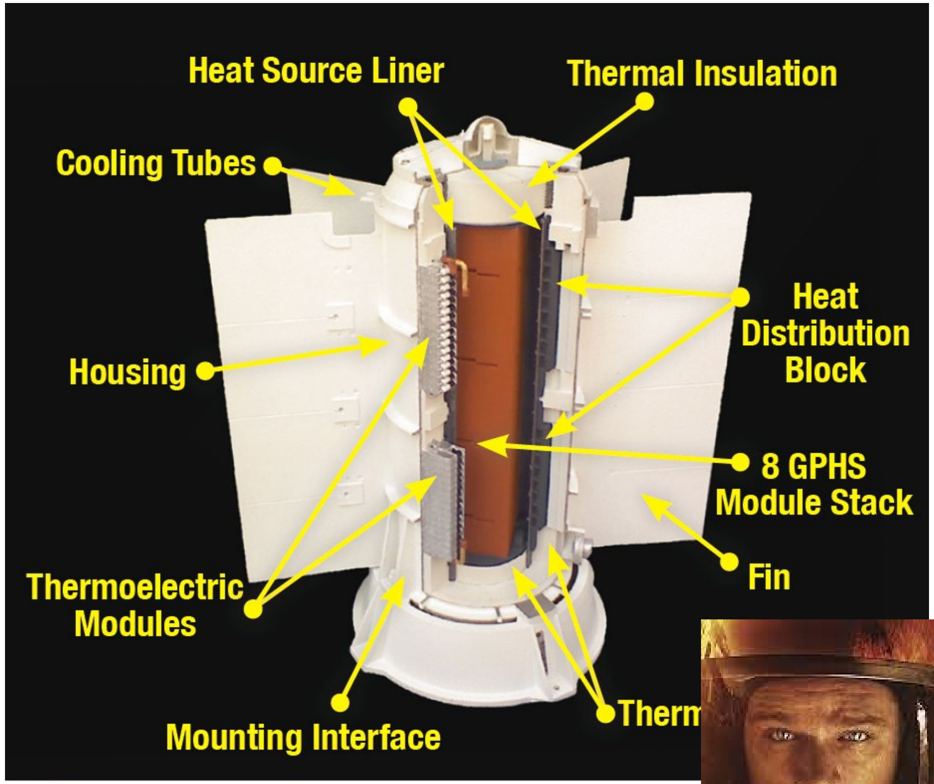
# Thermoelectric Generators




Mars Science Curiosity Rover

NASA/JPL


Radioisotope Thermometric Generator (RTG)

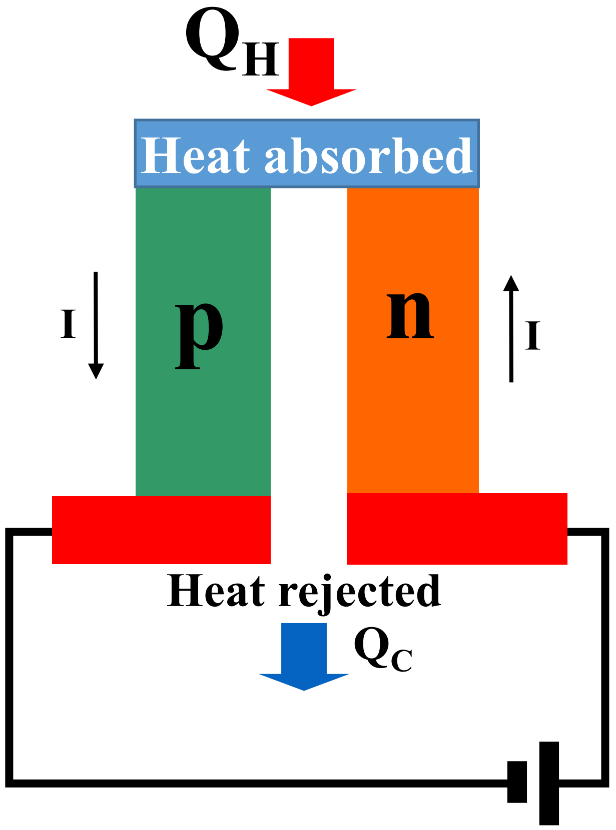




https://the-martian.fandom.com/wiki/RTG

# Cooler

Driven by an applied potential , electrons (holes) absorb heat from the lattice at the cold side, and reject heat to the lattice at the hot side (Refrigeration)



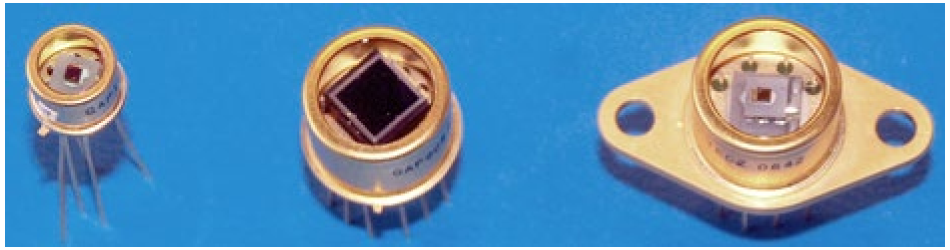

- ✓**No vibration**
- ✓**Less maintenance**
- ✓**Small size**
- ✓**High reliability**
- ✓**Heat manageable**

# TE Cooler: advantage over TEG with driving current I, ΔT > 40 K

**Local cooling on chip**

“GPD optoelectronics corp”

**InGaAs Thermoelectric Cooled IR Photodiodes**



**Medical-Grade Refrigerator**

“Phononic”
https://phononic.com


https://ibywind.com/

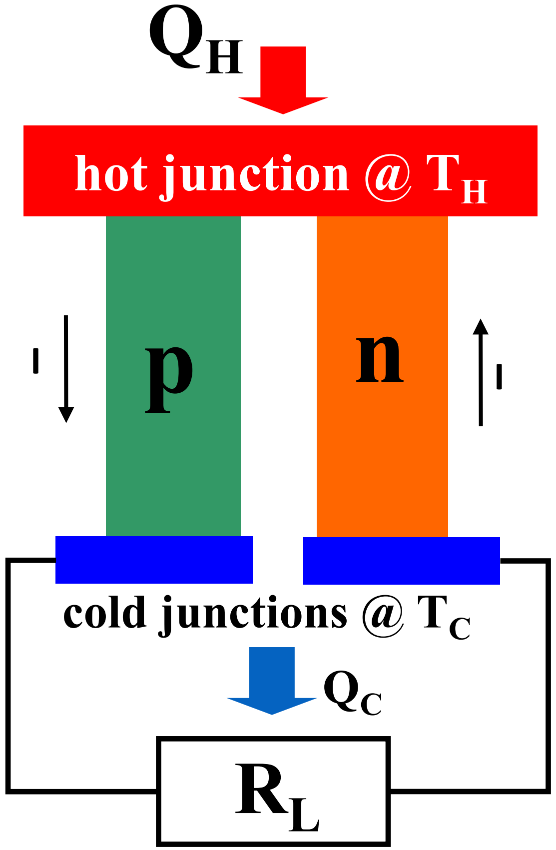
# TE development in history

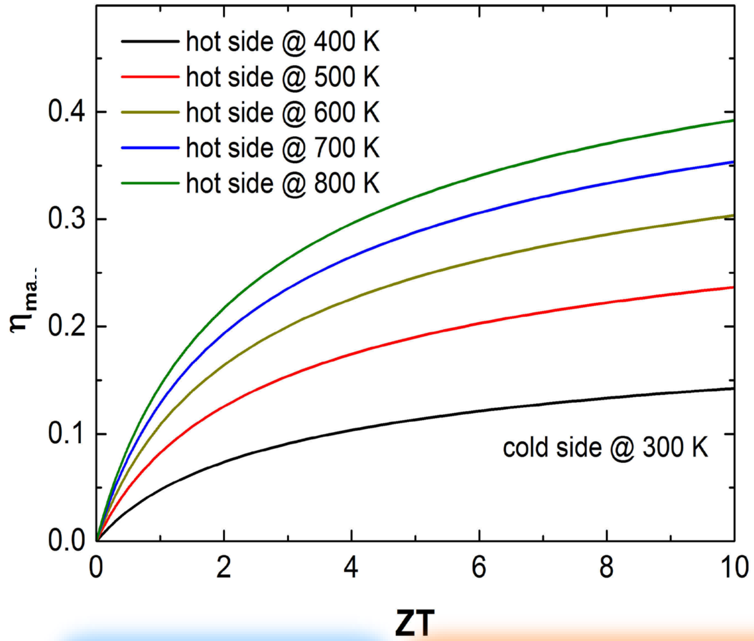
| Year | Alloy | ZT | Authors |
|---|---|---|---|
| | | P-type N-type | |
| **1955-1960** | $Bi_2Te_3$ | 1.0, 0.7 | ~300 K |
| **1997** | $Zn_4Sb_3$ | 1.3 | 670 K, T.Caillat et al |
| **2003** | PbTe/PbSeTe | 1.6 | 300 K, Harman et al |
| **2001** | $Bi_2Te_3/Sb_2Te_3$ | 2.4 | Venkatasubramanian, Nature 413, 597 |
| **2012** | Na:PbTe 2%SrTe | 2.2 | Biswas et al |
| **2014** | SnSe crystal | 2.6 ? | Zhao et al |
| **2020** | **$Ge_{1-x}Bi_xTe$ crystal** | **1.9** | **Y. Y. Chen's group** |
| 2020 | $Ge_{1-x}Sb_xTe$ crystal | 2.2 | Y. Y. Chen's group |

# Efficiency vs. ZT

$$Q_H = \kappa \Delta T + S T_H I + \frac{I^2 R}{2}$$

$$W = I^2 R_L = \frac{S^2 \Delta T^2 R_L}{(R + R_L)^2}$$




Carnot Cycle

Material factor < 1

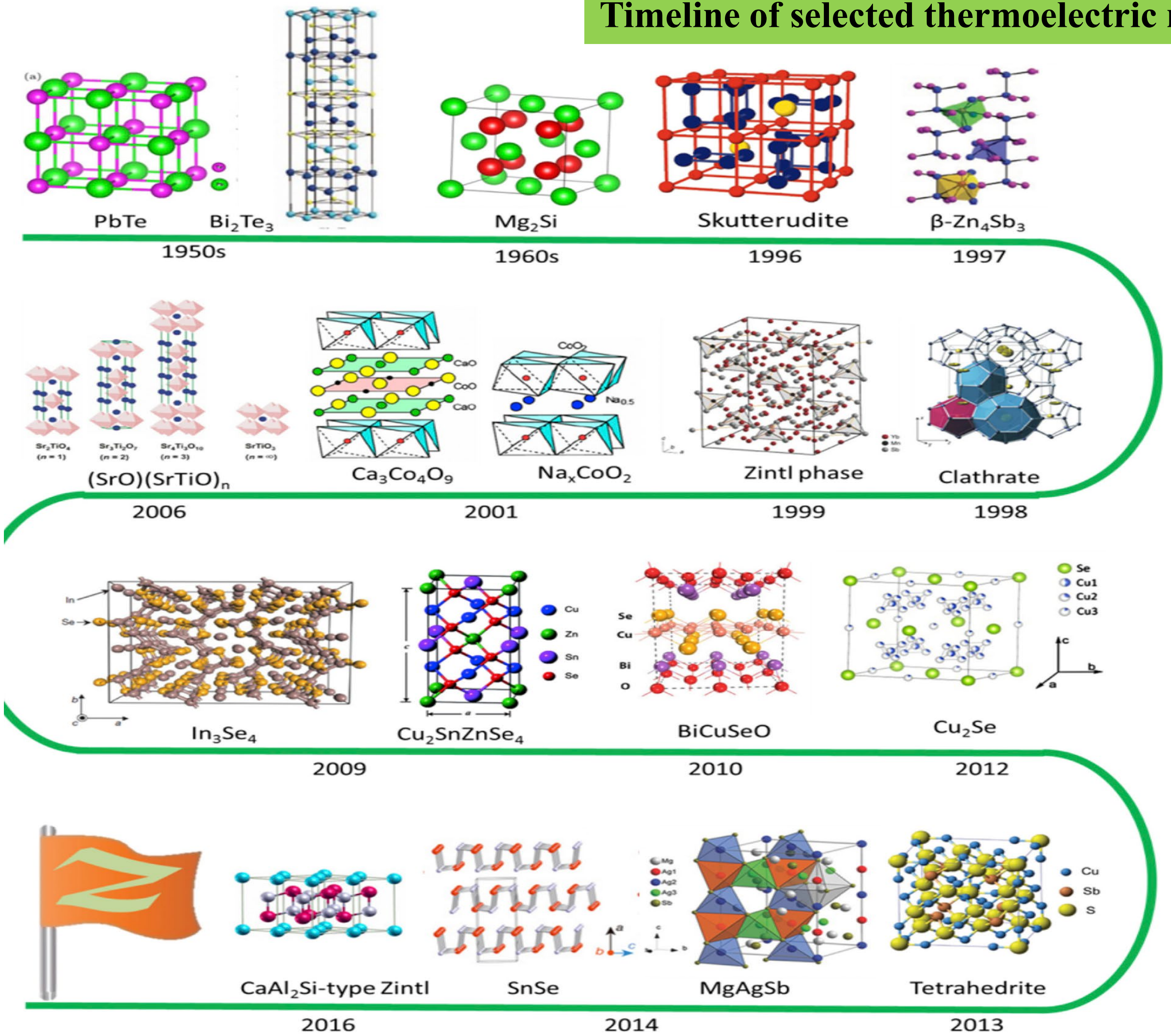
$$\eta = \frac{W}{Q_H} = \ldots = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C / T_H}$$

Real-world applications require
η > 0.1 (economically …)

# Seebeck Coefficient

| 材料 | 材料 | 導電率 (S/m) | 西貝克係數 (μV/K) |
|---|---|---|---|
| 金屬元素 | Au | $4.1 \times 10^7$ | 1.7 |
| | Cr | $7.9 \text{ X } 10^6$ | 18 |
| 半導體 | Si | 1000 | 400 |
| | Se | $8.3\text{x}10^6$ | 900 |
| 半導體化合物 | P-type $Bi_{1.5}Sb_{0.5}Te_3$ | $5\text{x}10^4$ | 185 |
| | N-type $Bi_2Te_{2.7}Se_{0.3}$ | $1\text{x}10^5$ | -230 |

# Timeline of selected thermoelectric materials



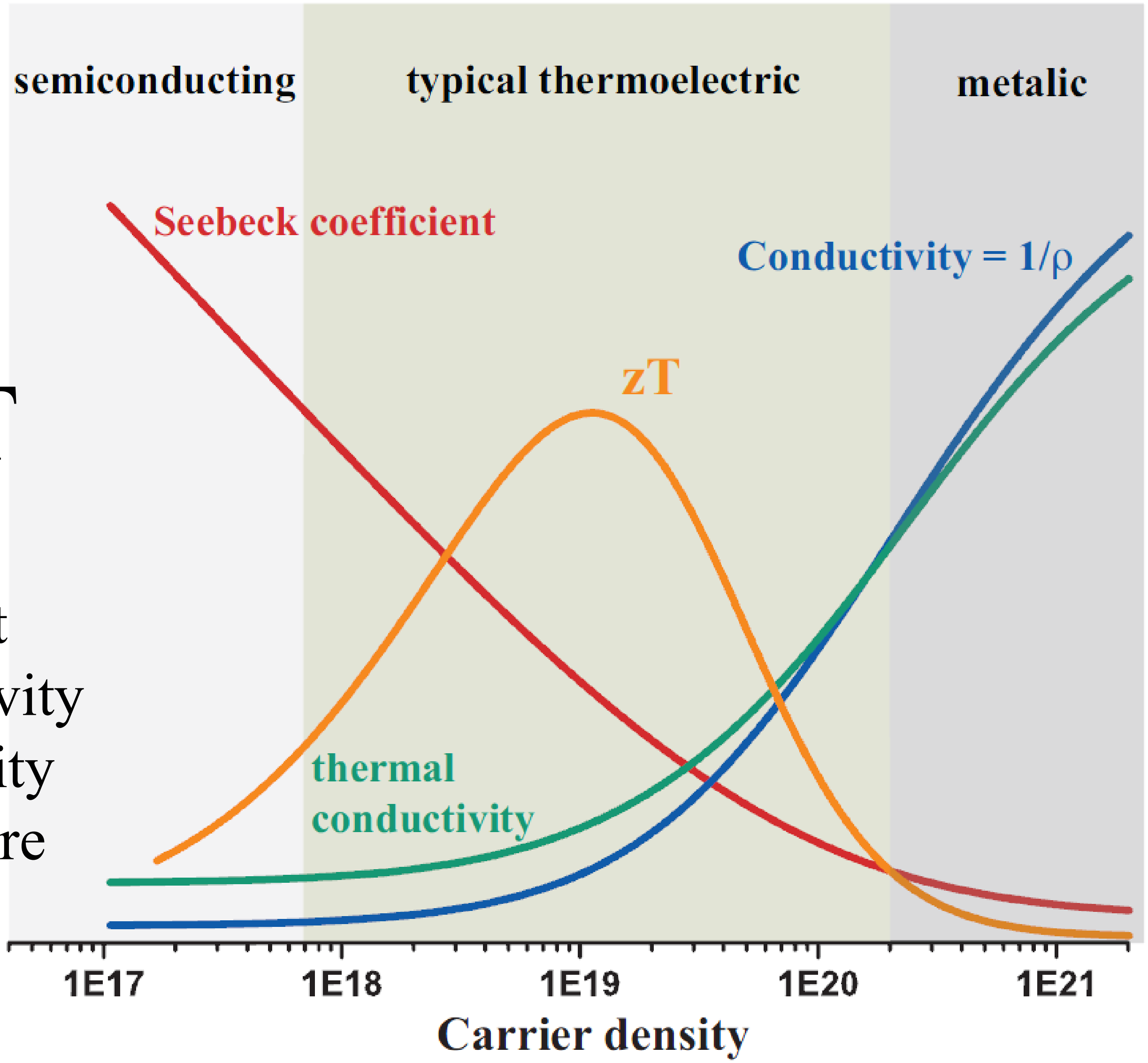



Source: *Materials Today Physics,* **1**, 50 (2017)

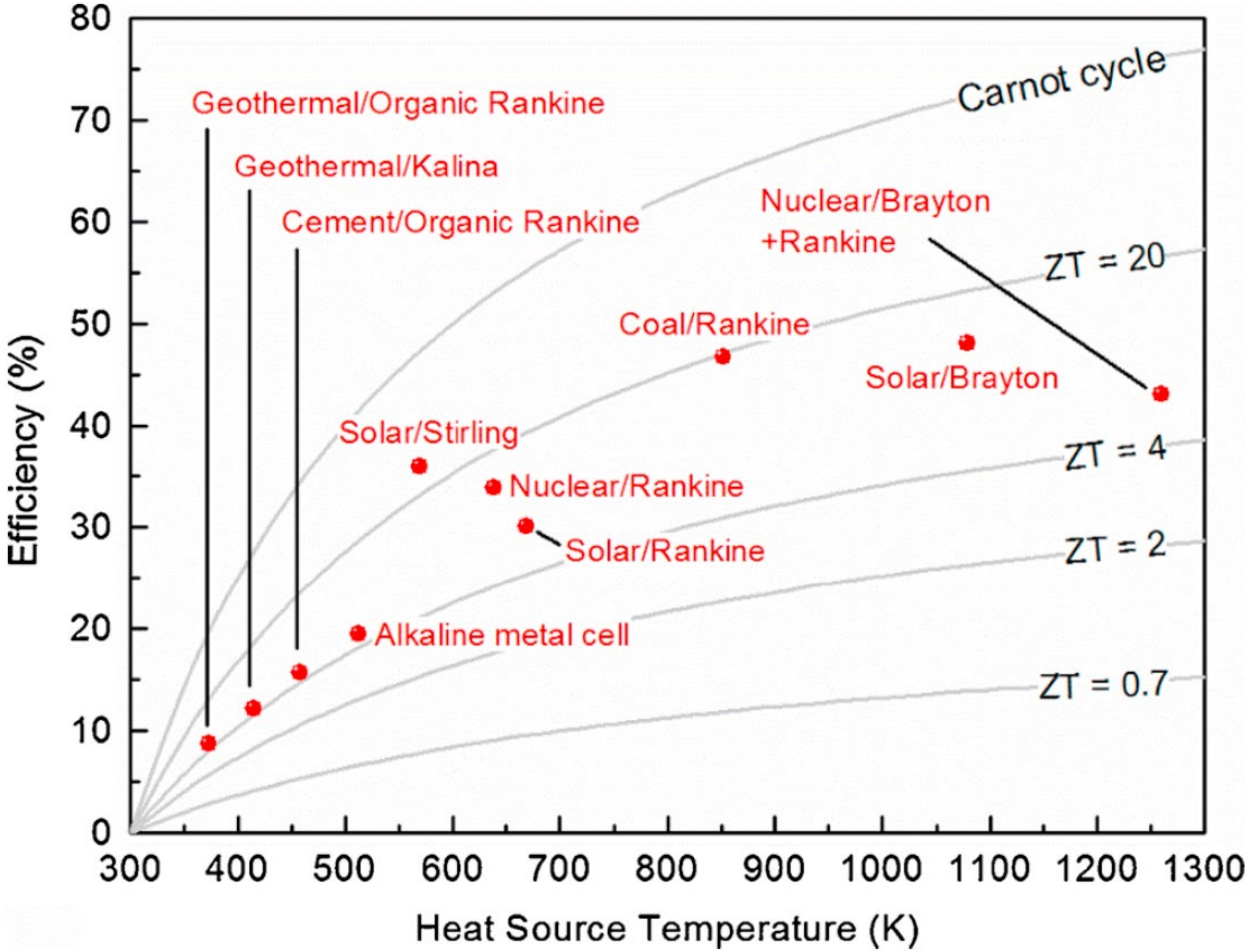
# Dimensionless figure-of-merit ZT

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

$S$ : Seebeck coefficient
σ : Electrical conductivity
κ : Thermal conductivity
T :Absolute temperature

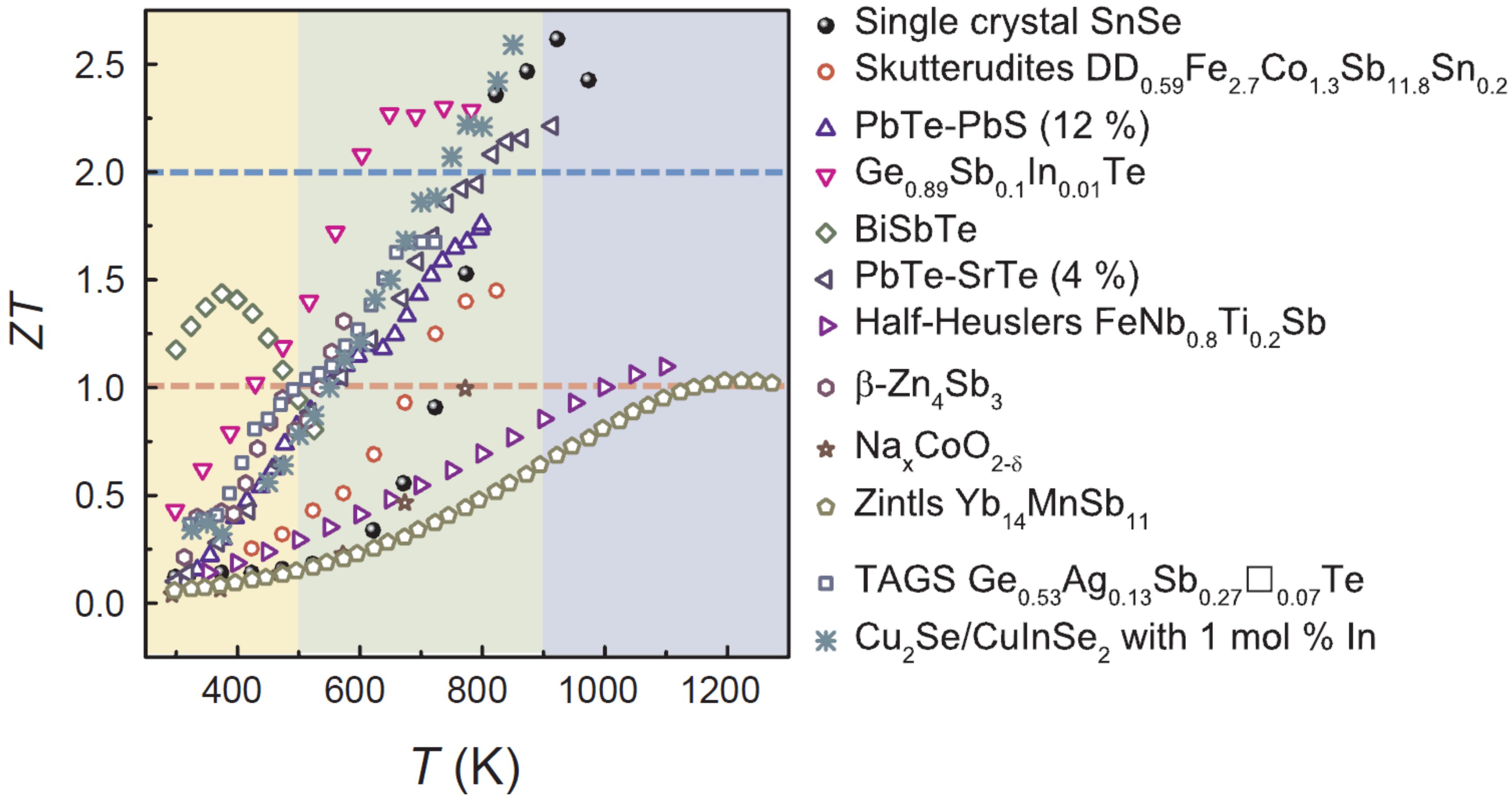


# TE generators vs. Conventional engines



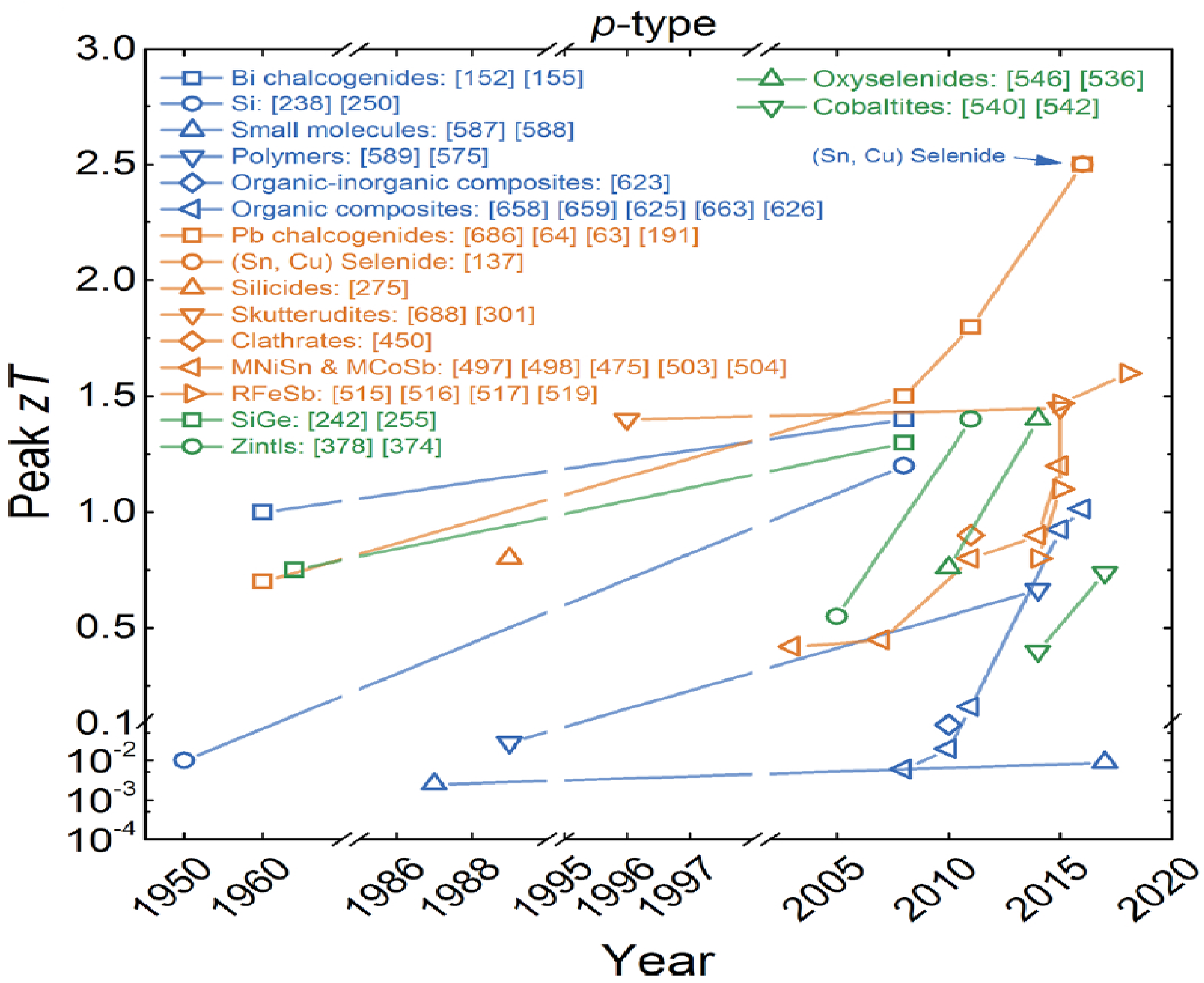

Data source: *Materials Science & Engineering* R (2019) : https://doi.org/10.1016/j.mser.2018.09.001

# *p*-type Thermoelectric Materials



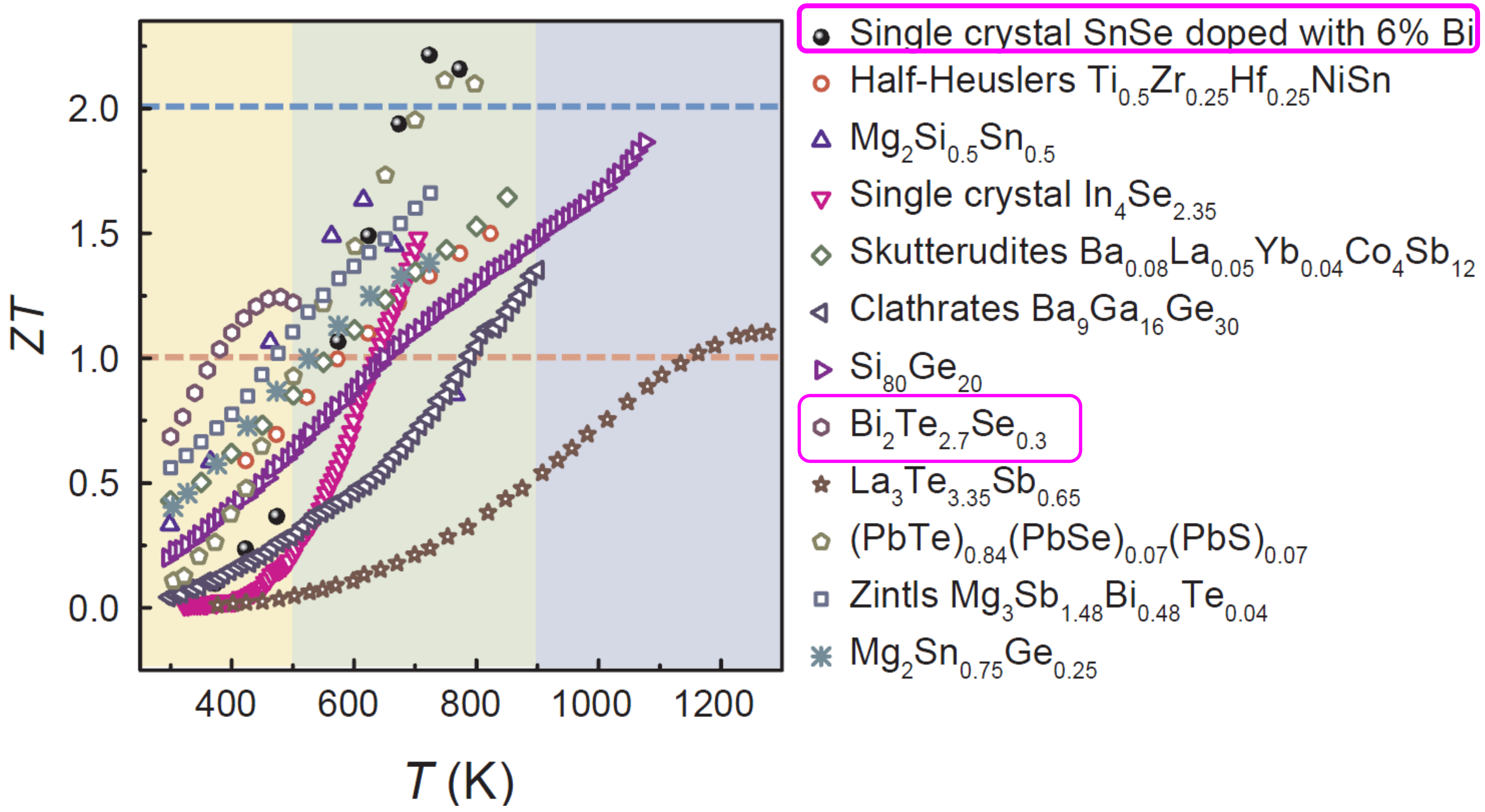



*Progress in Materials Science 97 (2018) 283*

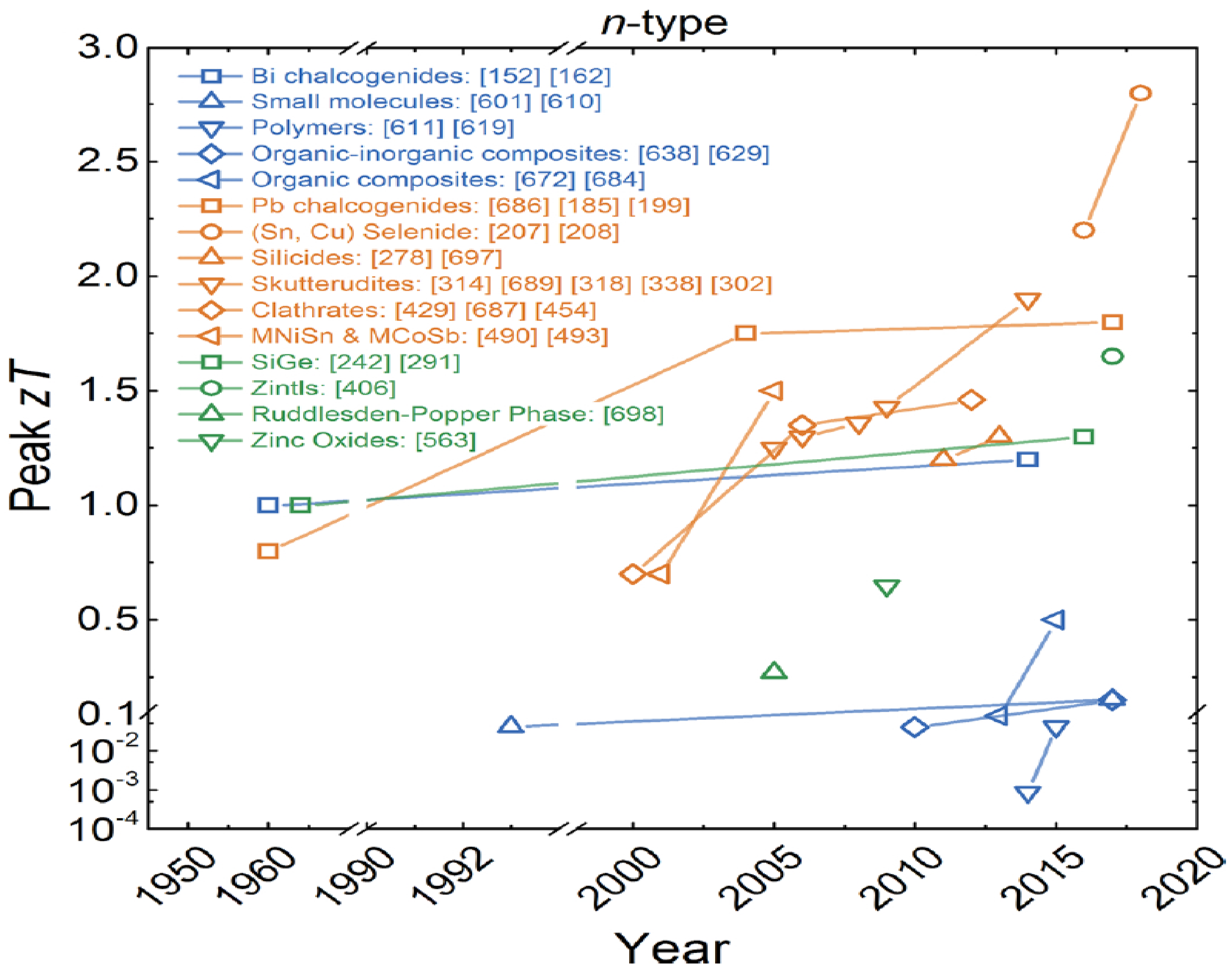



Data source: *Materials Science & Engineering* R (2019) : https://doi.org/10.1016/j.mser.2018.09.001

# *n*-type Thermoelectric Materials




*Progress in Materials Science 97 (2018) 283*




Data source: *Materials Science & Engineering* R (2019) : https://doi.org/10.1016/j.mser.2018.09.001

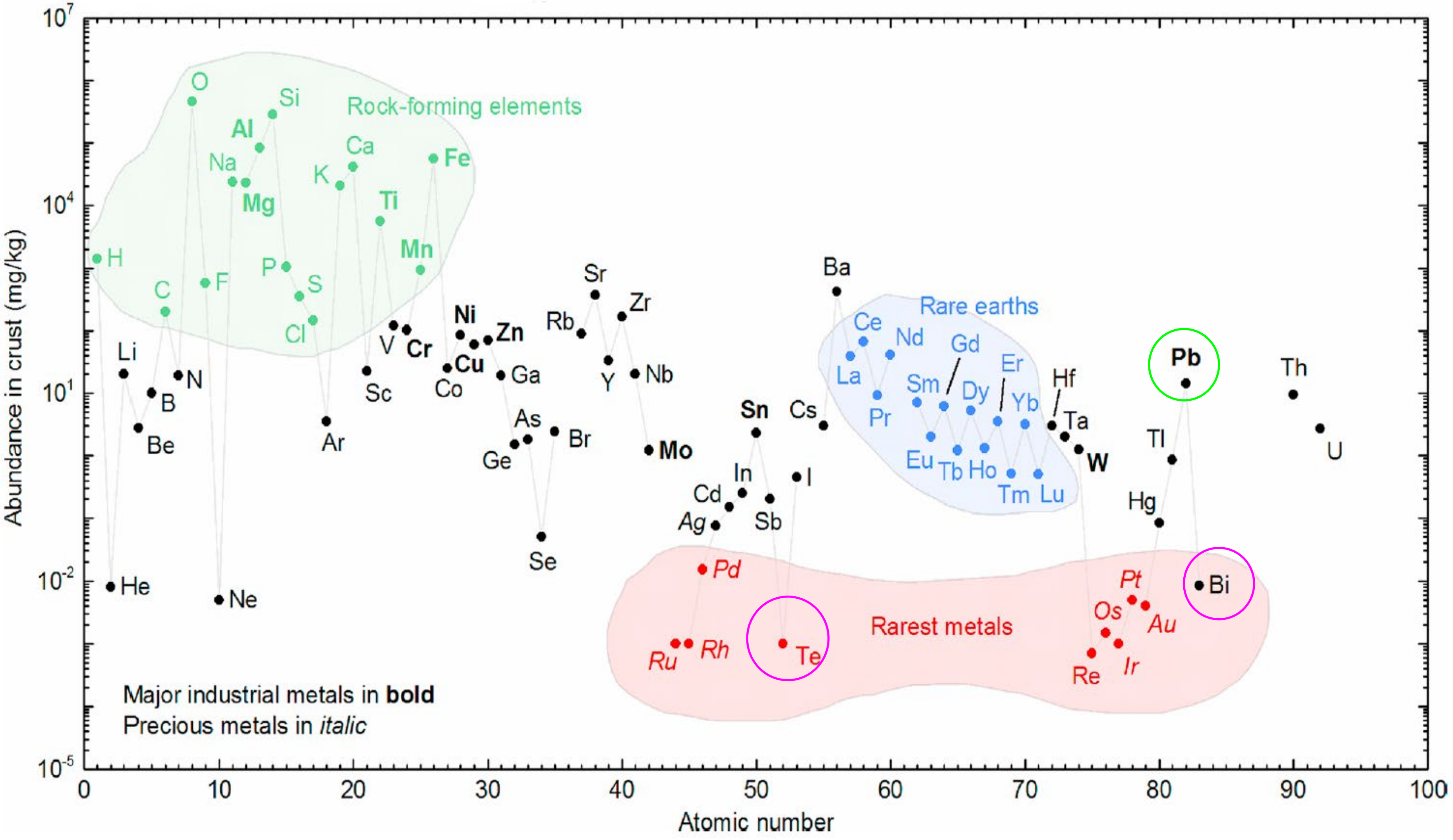
# Common characteristics of high-performance TE materials

1. An optimum band gap that is large enough to inhibit the excitation of minority carriers
   → narrow band gap, covalent bonding
2. Lower thermal conductivity
   → compounds formed between heavier elements
3. Materials with more symmetrical crystal structures tend to have better electronic properties than others with lower symmetry
4. The compound could be heavily doped.
5. Complex structures with many atoms in the unit cell
   → so the heat-carrying phonon is damped.

*ex*: $Bi_2Te_3$, PbTe, GeTe, SnSe, $Si_{1-x}Ge_x$

# Major challenge in thermoelectrics

" higher performance, non-toxic and sustainable "




Data source: *Materials Science & Engineering* R (2019) : https://doi.org/10.1016/j.mser.2018.09.001

# II. Stratagem of enhancing ZT

- ✓ **Electronic band structure**－band convergence $ZT = \frac{\sigma S^2}{\kappa} T$
- ✓ **Reduction in thermal conductivity** $ZT = \frac{\sigma S^2}{\kappa} T$

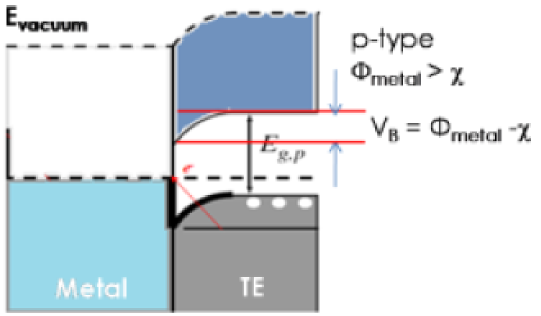
  Intrinsically low lattice κ , Defect Engineering
- ✓ **Synergistically manipulating charge and phonon transports** $ZT = \frac{\sigma S^2}{\kappa} T$
- ✓ **3D charge and 2D phonon transports** $ZT = \frac{\sigma S^2}{\kappa} T$

# Mechanisms for *S* enhancement in bulk

| Mechanism | Theory | Simulation | Material |
|---|---|---|---|
| **Carrier filtering** | **[1999]** Thermionic emission current in heterostructures | **[2008]** Band bending at PbTe/metal interfaces | **[2009]** Bulk(PbTe)<br>**[2010]** Bulk(skutterudite)<br>**[2011]** Bulk(TAGS)<br>**[2011]** Pt-$Sb_2Te_3$ |
| **Resonant State** | **[1956]** Virtual bound (resonant) state by doping<br>**[1996]** DOS engineering | **[2006]** Doped PbTe | **[2008]** Tl-doped PbTe<br>**[2009]** Sn-doped $Bi_2Te_3$ |

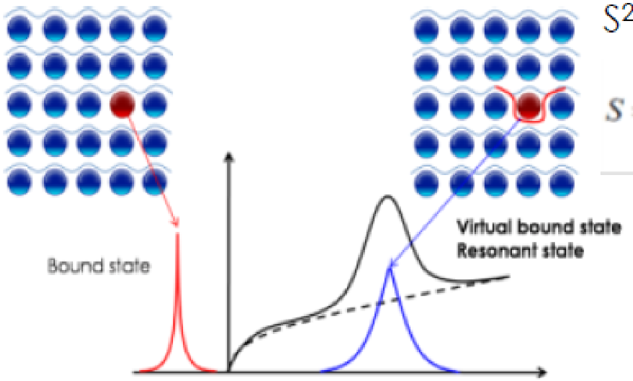
## Carrier filtering effect

$$\frac{\pi^2 k_b^2 T}{3q}\left(\frac{d\ln N(E)}{dE} + \frac{d\ln \tau(E) v(E)^2}{dE}\right)_{E=E_F}$$




S.V. Faleev, *Phys. Rev. B* 77, 214304 (2008)

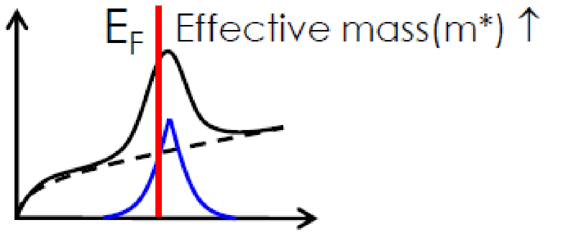
## Resonant state




J. Friedel, J. Physics, 1956

If $E_F$ is tuned to near a peak in DOS, $S^2\sigma$ would be sharply increased!

$$S = \frac{\pi^2}{3}\cdot\frac{k_B}{e}\cdot k_B T\left[\frac{g(E)}{n(E)} + \frac{1}{\mu(E)}\cdot\frac{\partial \mu(E)}{\partial E}\right]_{E=E_F}$$




ORNL, PNAS, 1996

# Stratagem of enhancing ZT

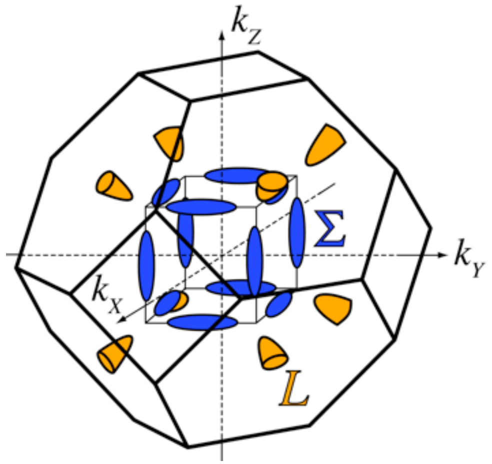
- ✓ **Electronic band structure**－band convergence
- ✓ **Reduction in thermal conductivity**

  Intrinsically low lattice κ , Defect Engineering
- ✓ **Synergistically manipulating charge and phonon transports**
- ✓ **3D charge and 2D phonon transports**

# Thermoelectric quality factor (*B*)

$\sigma = ne\mu$

$\mu \propto \frac{1}{m^*_{band}}$




$B \propto \frac{N_v}{m^*_{band}\kappa_L}$

$S \propto m^*_{DOS}$

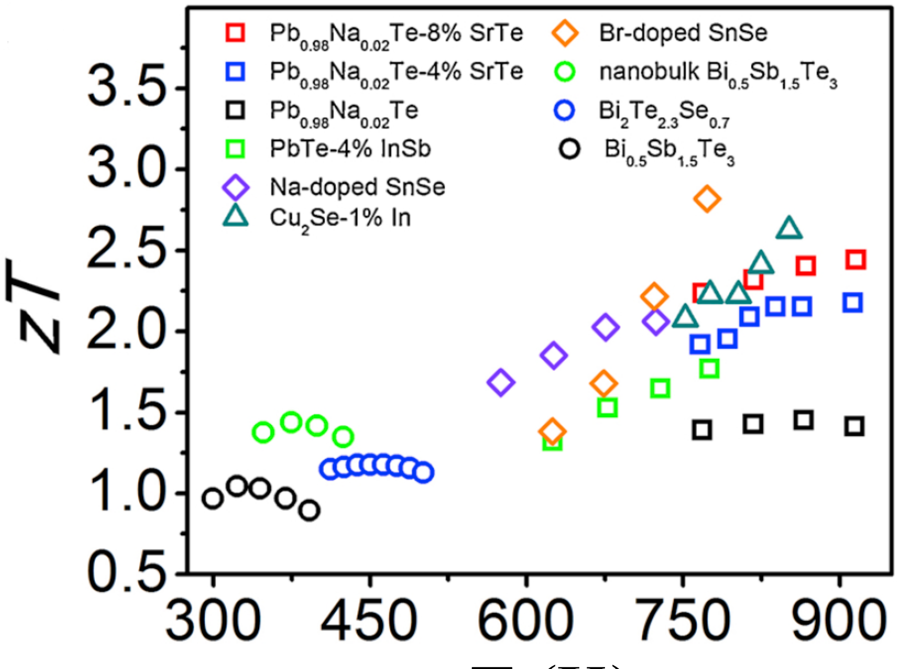
$m^*_{DOS} = N_v^{2/3} m^*_{band}$

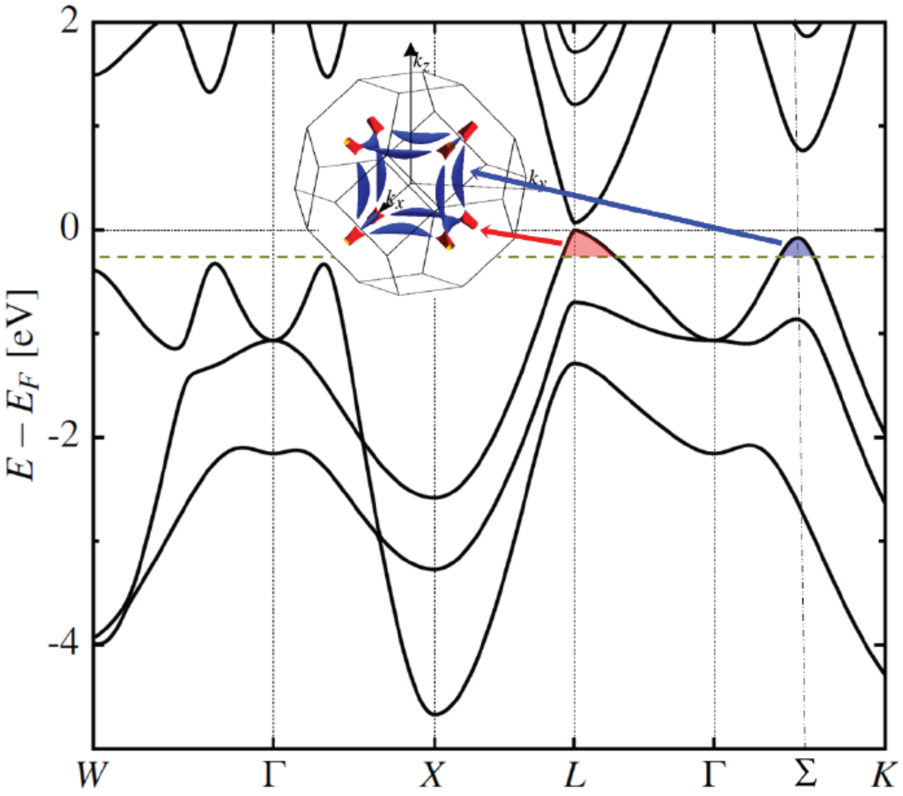
$S = \frac{8\pi^2 k_B^2}{3eh^2} m^*_{DOS} T \left(\frac{\pi}{3n}\right)^{2/3}$

$\mu$ : carrier mobility (in $cm^2\ V^{-1}s^{-1}$)
$m^*$: Density of states effective mass
$m_b^*$ : band effective mass
$N_v$ : the number of band valleys
$\kappa_L$ : latteice thermal conductivity

# Importance of band convergence

PbTe, PbSe, GeTe, SnSe, SnTe, $Mg_2Sn_{1-x}Ge_x$…….



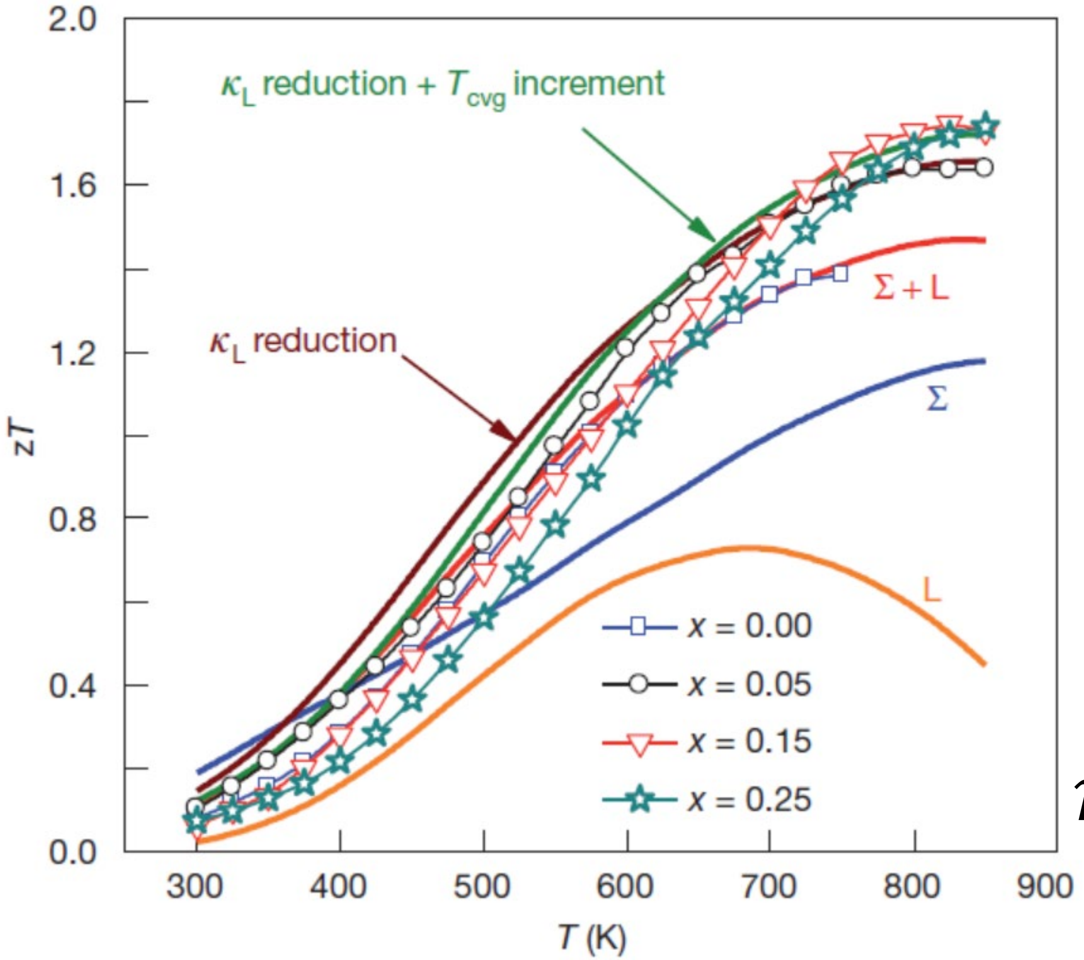

Fermi surface and band structure

Materials Project https://materialsproject.org

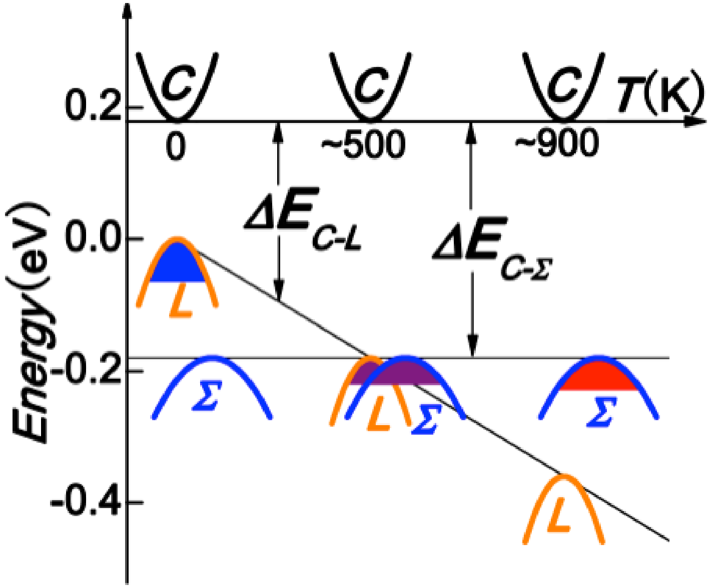
The schematic *L* (red) and *Σ* (blue) carrier pockets

# Convergence of electronic bands for PbTe

G. Jeffrey Snyder *et al*. Nature, 473, 66 (2011)




$PbTe_{1-x}Se_x$




$$m^*_{DOS} = N_v^{2/3} m^*_{band}$$

Valley degeneracy

# Heavy and Light holes in PbTe

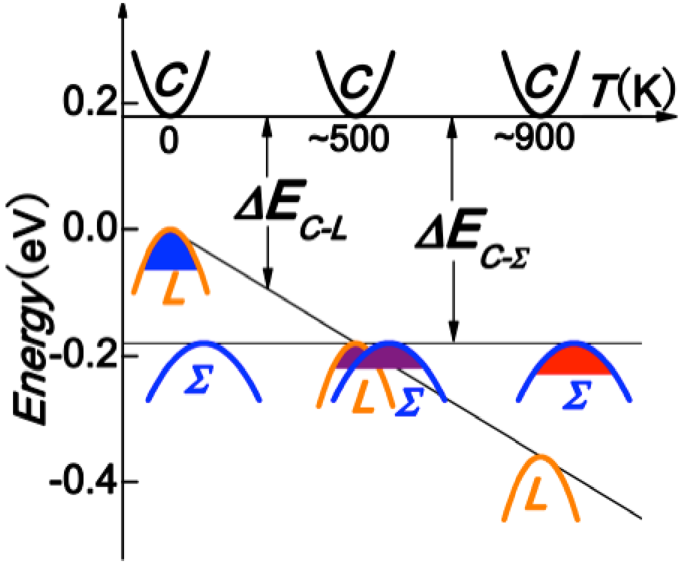
Valence Band Maximum is at *L* point

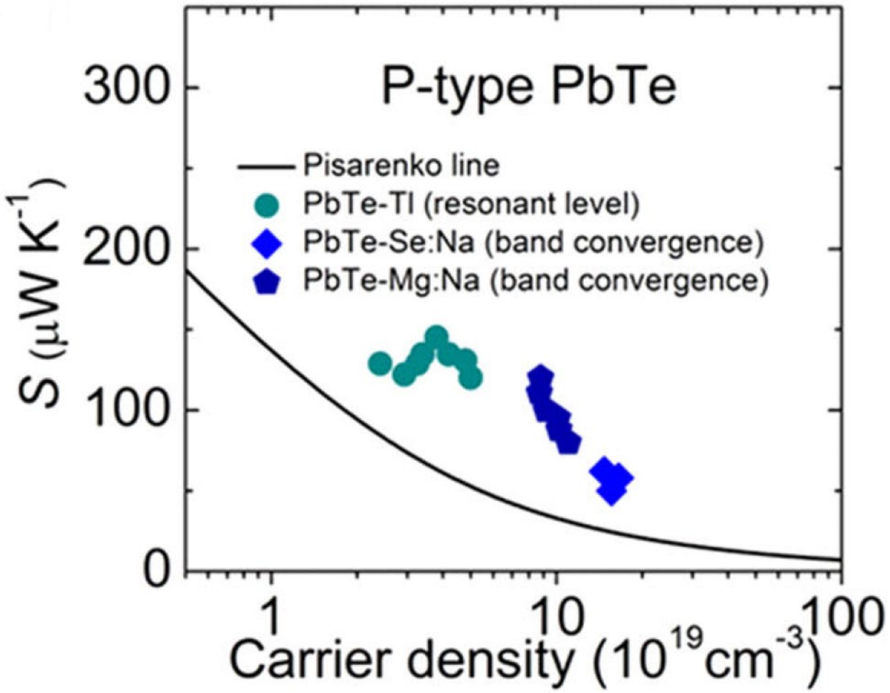
- "Light Band" $N_V = 4$, $m_b^* = 0.14\, m_e$

(8 half pockets at the L point lead to $N_v = 4$)

Second valence band occurs at $\Sigma$ line

- "Heavy Band" $N_V = 12$, $m_b^* = 0.28\, m_e$



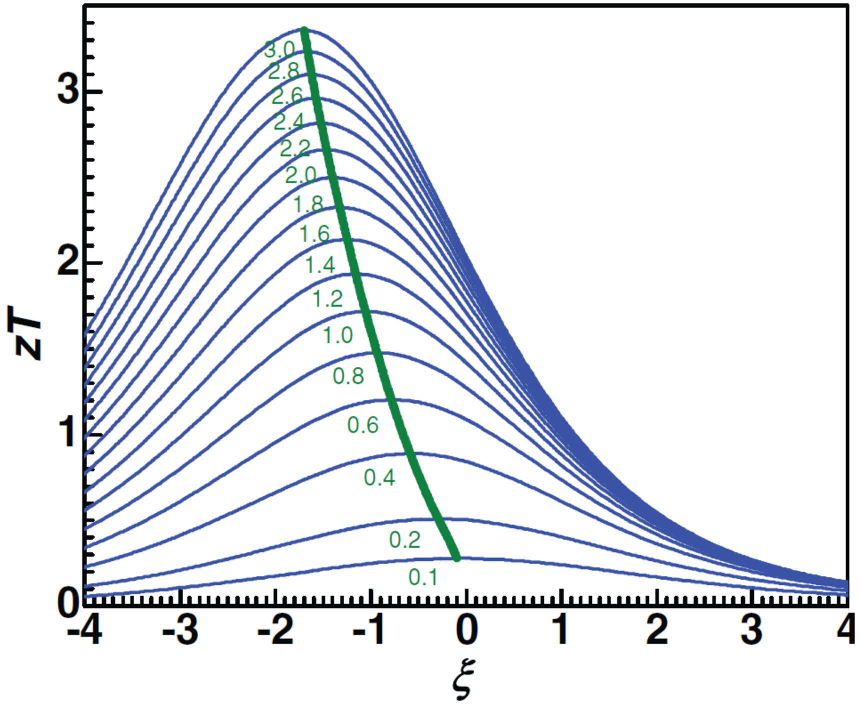



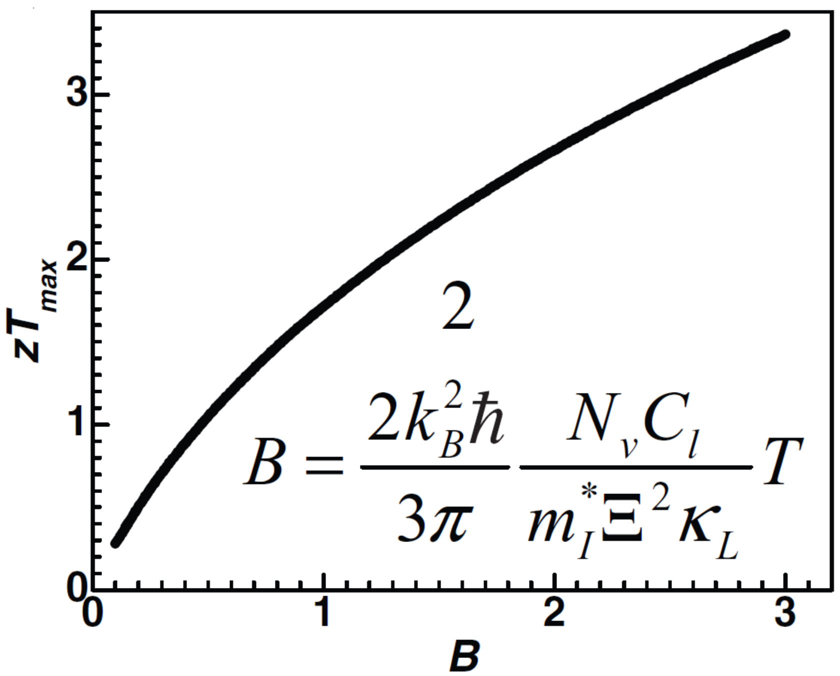

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m_{DOS}^* T\left(\frac{\pi}{3n}\right)^{2/3}$$

$$\sigma = ne\mu$$

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

# Tuning the reduced Fermi level by doping enables an optimization of $zT$




| | PbTe | PbTe | PbSe | PbSe | PbS | $Si_{0.7}Ge_{0.3}$ | Bulk Si |
|---|---|---|---|---|---|---|---|
| type | n | P(L) | n | P(L) | n | n | n |
| $T_{operate}$ | 800 | 800 | 850 | 850 | 900 | 1000 | 1000 |
| $\mu_0 m^{*3/2}$ | | | | | | | |
| $N_v$ | 4 | 4 | 4 | 4 | 4 | 6 | 6 |
| $C_l$ (GPa) | 71 | 71 | 91 | 91 | 111 | 150 | 180 |
| $m_I^*$ | 0.15 | 0.17 | 0.17 | 0.17 | 0.25 | 0.27 | 0.26 |
| $\Xi$ | 23 | 28 | 27 | 38 | 28 | 15 | 15 |
| $\kappa_L$ | 0.75 | 0.75 | 0.65 | 0.65 | 0.95 | 4 | 45 |
| $B$ | 0.7 | 0.4 | 0.67 | 0.33 | 0.39 | 0.68 | 0.07 |

$k_B$: Boltzmann constant
$h$: Planck constant
$N_v$: number of degenerated valleys
$C_l$: average longitudinal elastic moduli
$m_I$*: inertial effective mass
$\Xi$: deformation potential coefficient.

*Adv. Mater.* **24**, 6125 (2012)

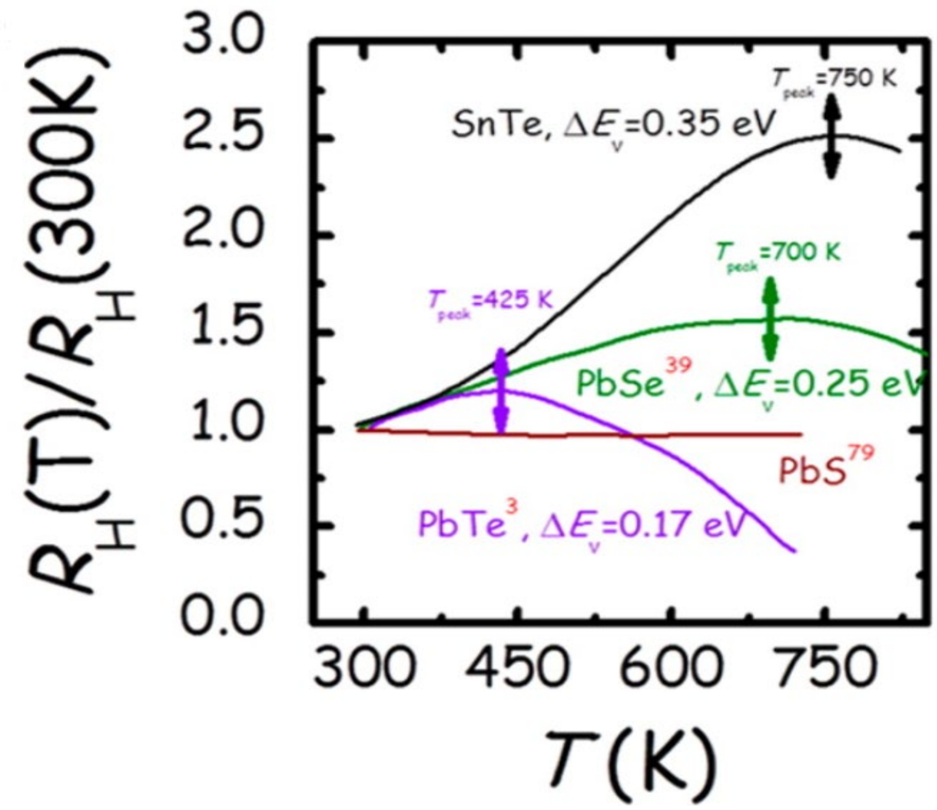
| | Bulk Ge | $Mg_2Si$ | $Mg_2Si_{0.6}Sn_{0.4}$ | SnTe | SnSe | $Cu_3SbSe_4$ | $Bi_2Te_3$ |
|---|---|---|---|---|---|---|---|
| type | n | n | n | p(L) | n | p | n (//c) |
| $T_{operate}$ | 1000 | 700 | 700 | 773 | 750 | 673 | 400 |
| $\mu_0 m^{*3/2}$ | | | | | | | |
| $N_v$ | 4 | 3 | 6 | 4 | 2 | 3 | 6 |
| $C_l$ | 160 | 120 | 100 | 58 | 58 | 80 | 71 |
| $m_I^*$ | 0.12 | 0.5 | 0.8 | 0.09 | 0.47 | 0.7 | 0.1 |
| $\Xi$ | 20 | 15 | 13 | 28 | 21 | 14 | 24 |
| $\kappa_L$ | 18 | 3 | 1.5 | 1.5 | 0.5 | 1 | 1.5 |
| $B$ | 0.14 | 0.15 | 0.38 | 0.3 | 0.15 | 0.22 | 0.26 |

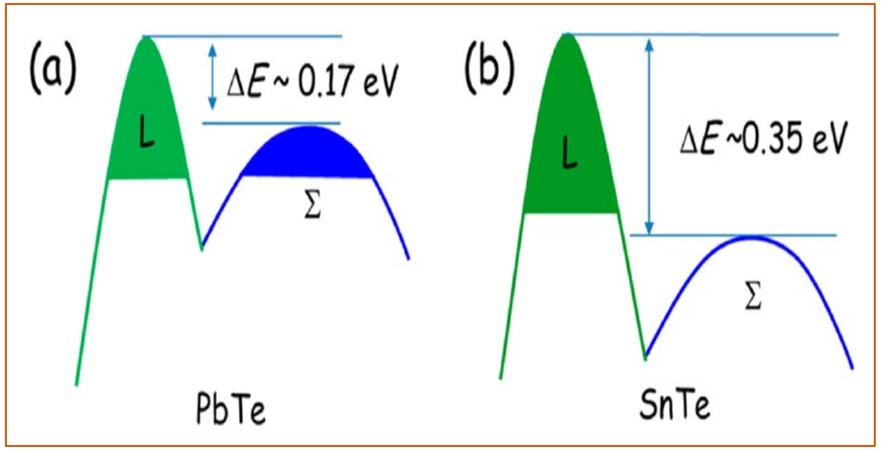
| | $Bi_{1-x}Sb_x$ | $CoSb_3$ | $La_3Te_4$ | $Bi_2Se_3$ | ZrNiSn |
|---|---|---|---|---|---|
| type | n | n | n | n | n |
| $T_{operate}$ | 150 | 850 | 1200 | 300 | 850 |
| $\mu_0 m^{*3/2}$ | 400 | | 10 | | 150 |
| $N_v$ | | 3 | | 1 | |
| $C_l$ | | 100 | | | 180 |
| $m_I^*$ | | 1.6 | | 0.15 | |
| $\Xi$ | | 10 | | | |
| $\kappa_L$ | 9 | 0.5 | 0.5 | 1.3 | 4.5 |
| $B$ | 0.03 | 0.6 | 0.56 | 0.03 | 0.4 |

*Adv. Mater.* **24**, 6125 (2012)

# Thermal effect on “the Energy Band Modification”

## Temperature-dependent Hall coefficient ($R_H$)




Hall coefficient ($R_H$, normalized relative to room-temperature value) for p-type SnTe, PbSe (39) and PbTe (3) show a strong temperature dependence indicative of a two-band conduction. The peaking temperature ($T_{peak}$) in the $R_H$-$T$ curves is related to the magnitude of the energy difference ($\Delta E_v$) between the two valence bands.

Ref: *J. Am. Chem. Soc.* **137**, 11507 (2015)

# II. Stratagem of enhancing ZT

- ✓ **Electronic band structure**－band convergence
- ✓ **Reduction in thermal conductivity**

  Intrinsically low lattice κ , Defect Engineering
- ✓ **Synergistically manipulating charge and phonon transports**
- ✓ **3D charge and 2D phonon transports**

# Intrinsically low $\kappa_L$

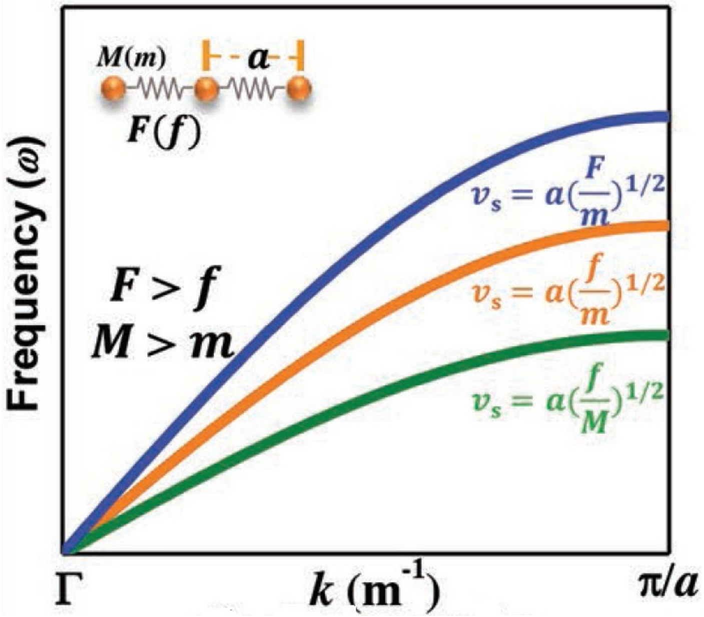
$$\kappa_{tot} = \kappa_L + \kappa_e$$

Intrinsic low thermal conductivity is of practical interest due to its robustness against grain size, temperature range and other structural variations.

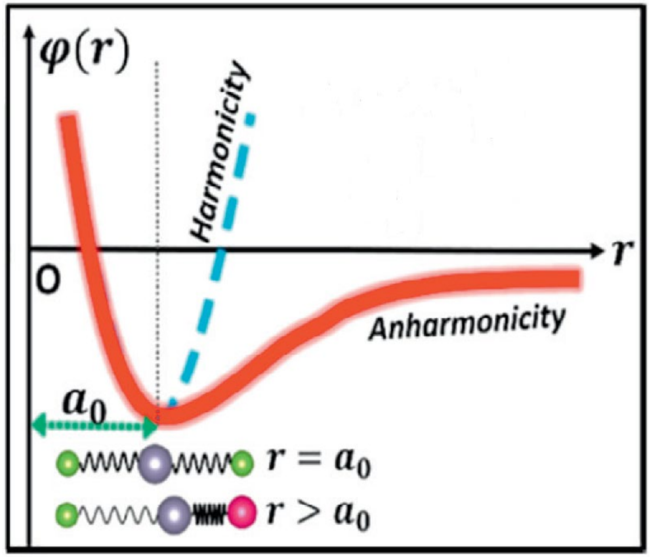
$$\kappa_L = \frac{1}{3} C_V v_g^2 \tau \qquad v_g = \frac{l}{\tau}$$

$C_v$ : specific heat
$\upsilon_g$ : group velocity
τ : phonon relaxation time

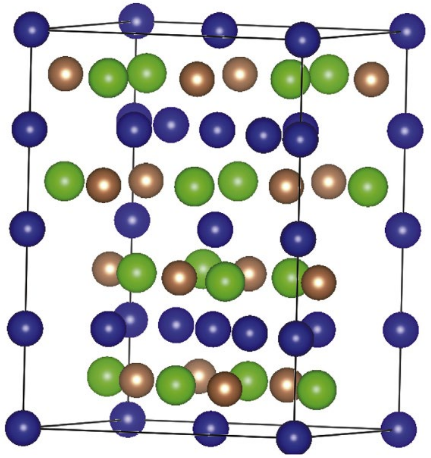
Low phonon group velocity




Large anharmonicity

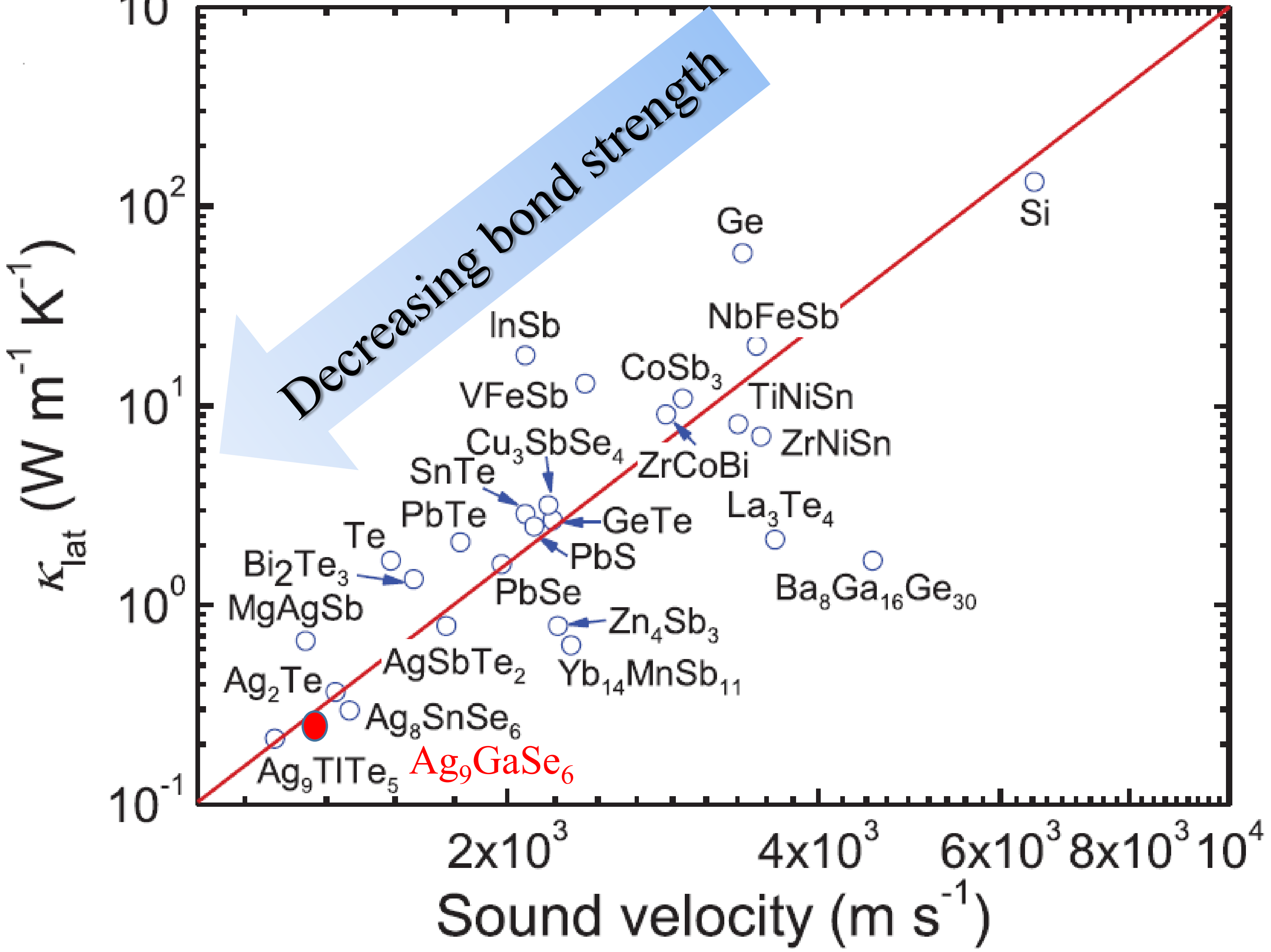



Structure complexity



**Phonon-glass**
**Electron-crystal**

$$\kappa_L = \frac{1}{3} C_V v_g^2 \tau$$

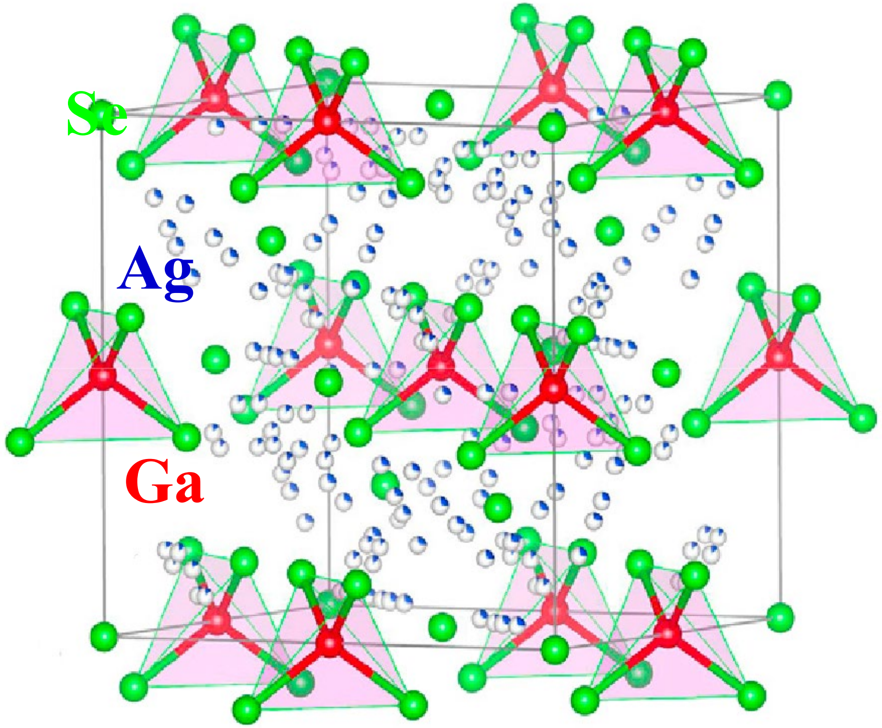


Ex:

# $Ag_9GaSe_6$

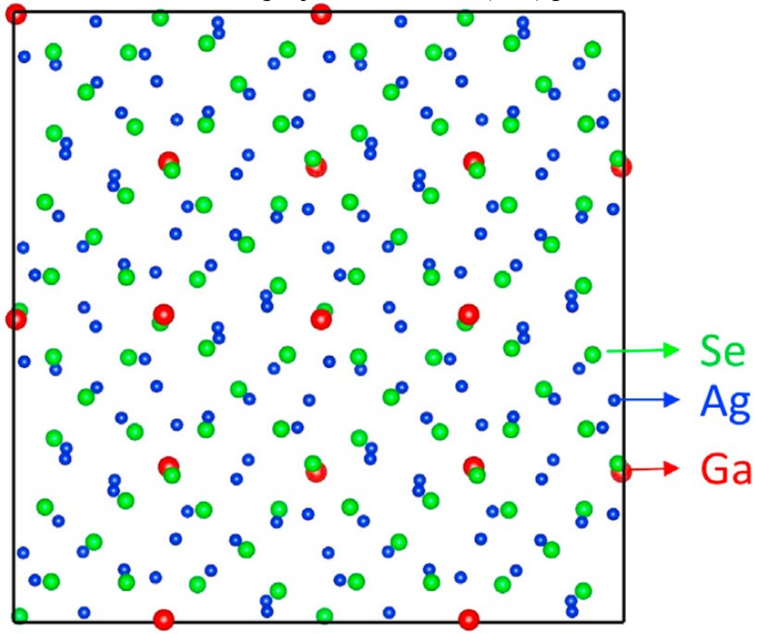
***"weakly bonded Ag"***

$\kappa_L \sim 0.15$ W/m-K

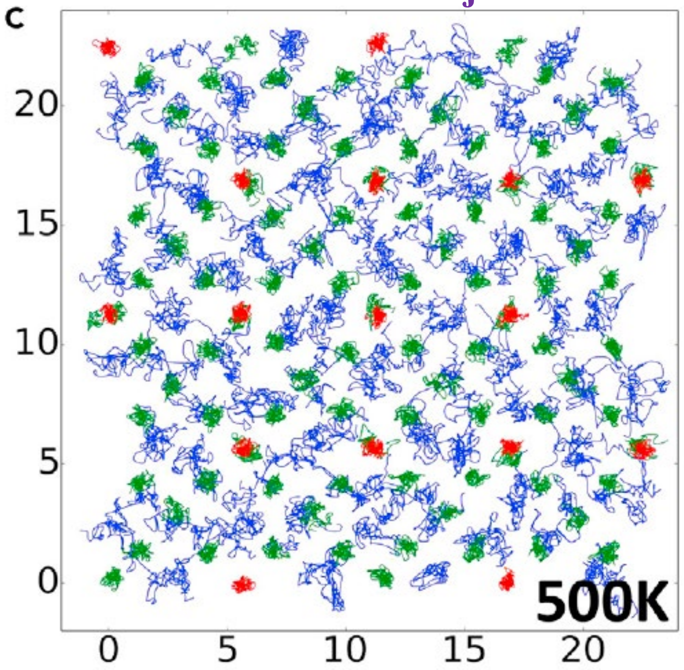



*Joule*, **1**, 816 (2017)

projected onto the (100) plane

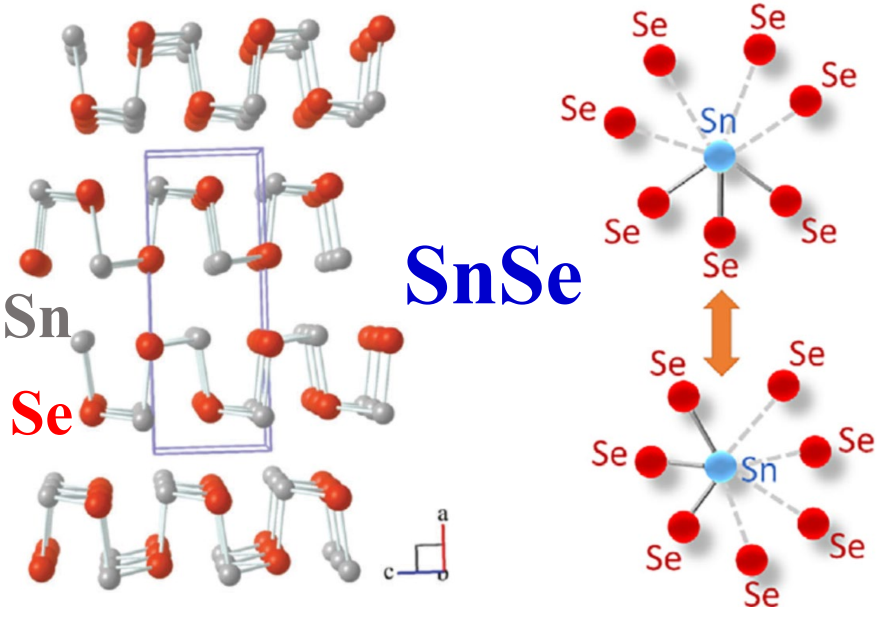



**atomic trajectories**

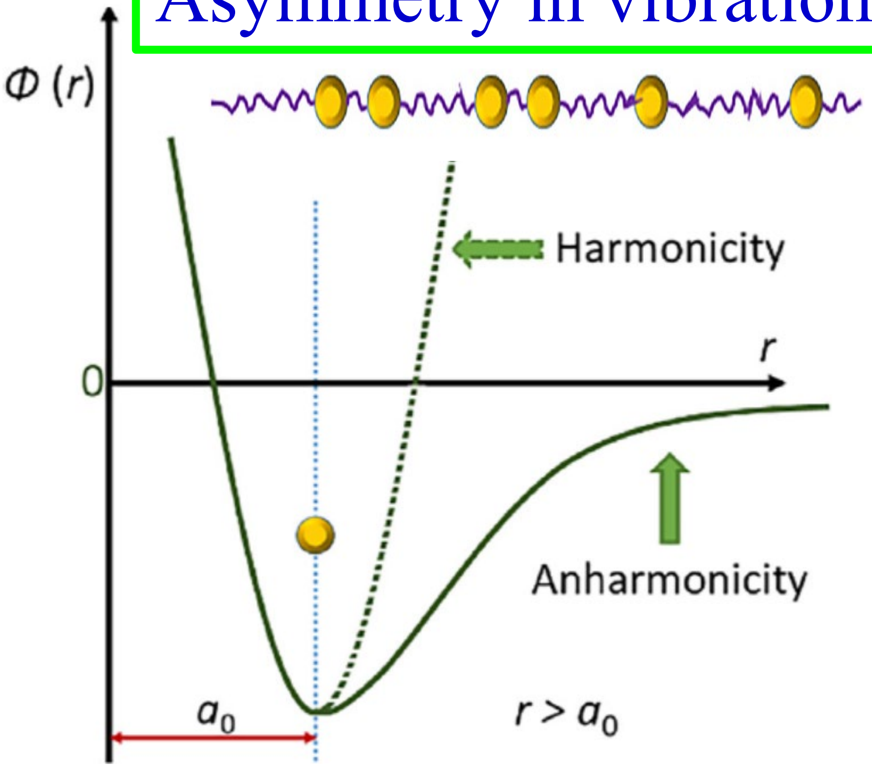


# Anharmonicity

Although all bonding in real materials is anharmonic, the degree of anharmonicity varies strongly from material to materi[al]



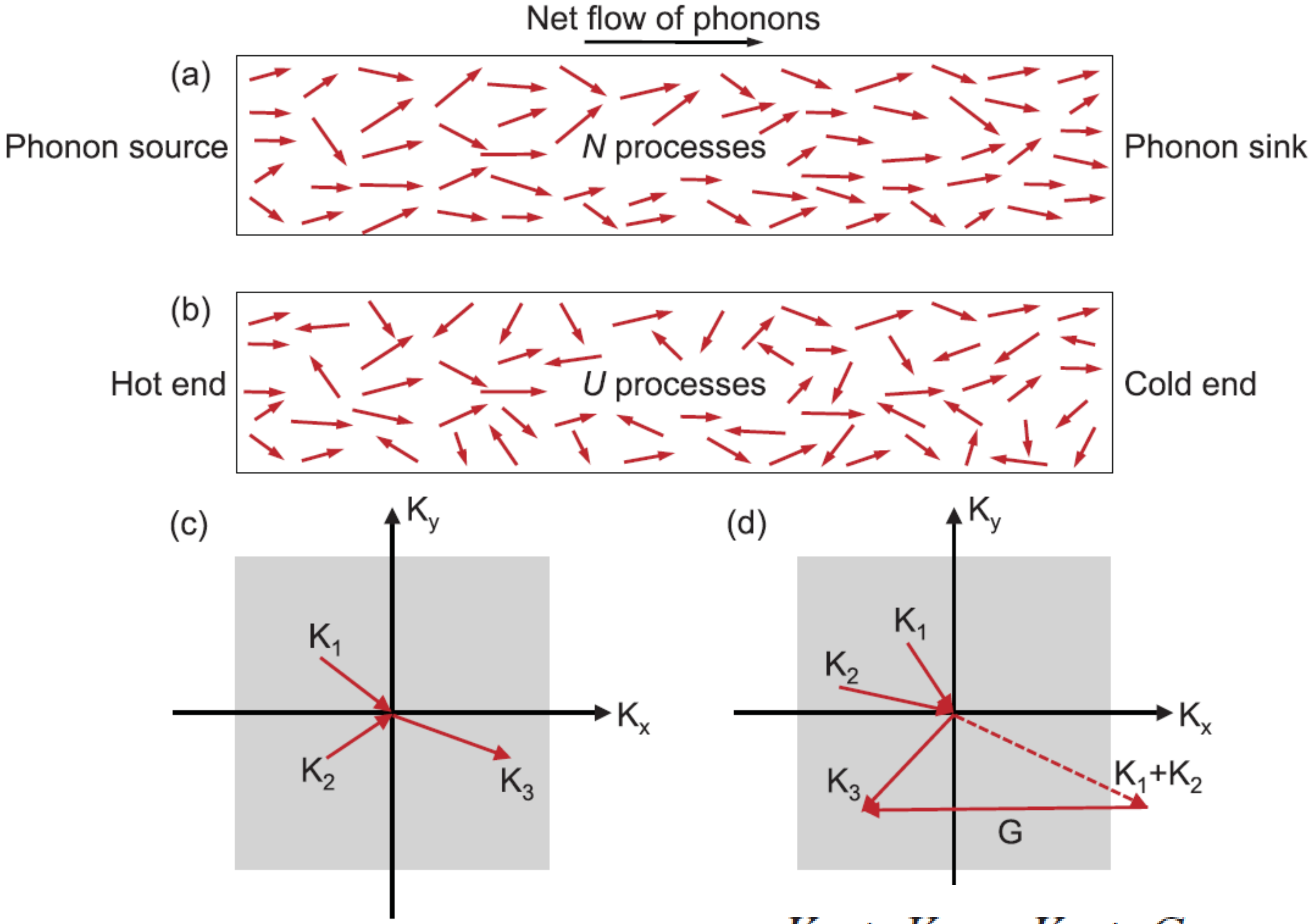

Asymmetry in vibration




$$\kappa_L = \frac{1}{3} C_V v_g^2 \tau$$

Minimize τ by intensifying the scattering rate of phonons

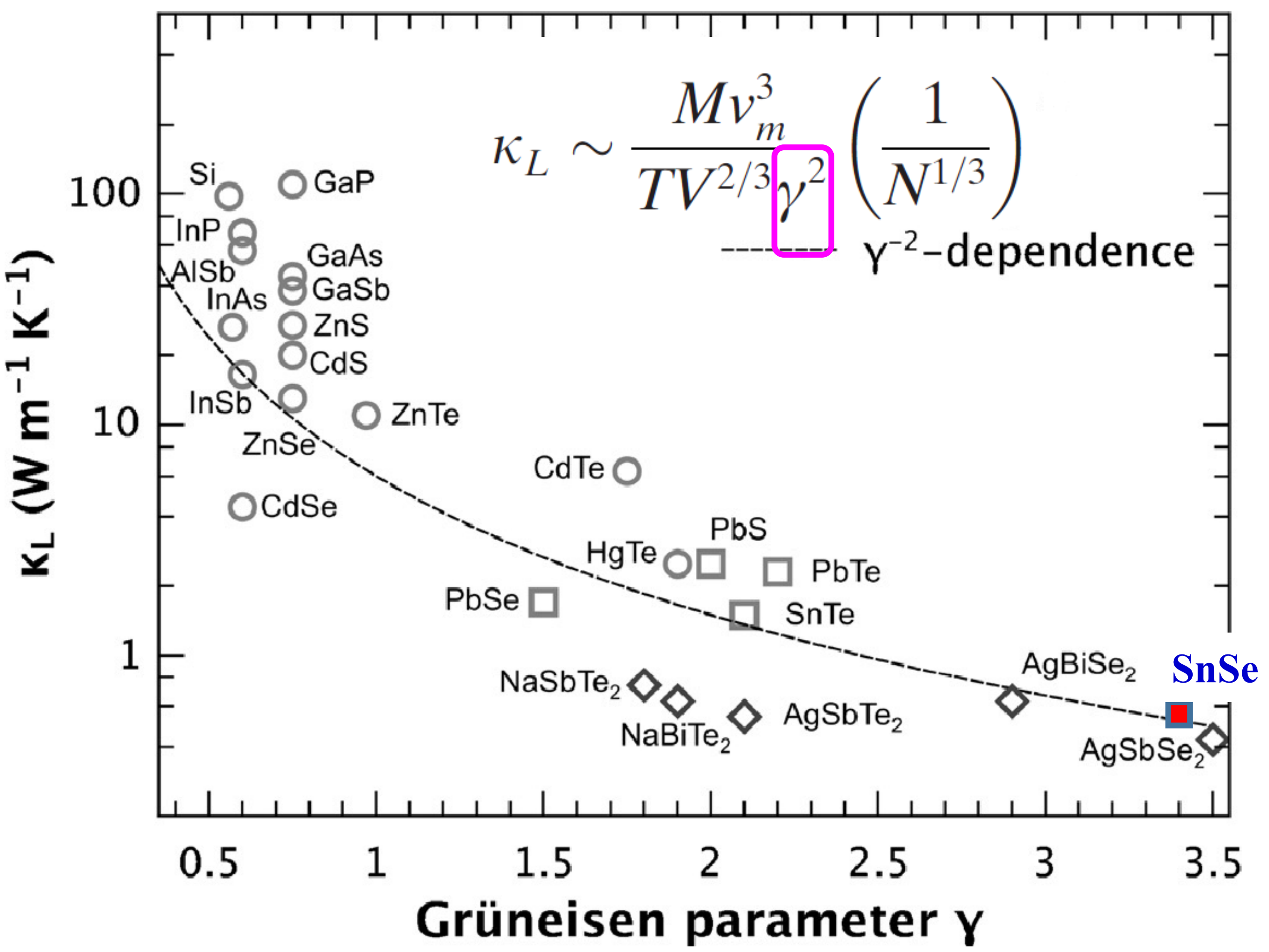
# Phonon – Phonon Umklapp scattering




$$K_1 + K_2 = K_3$$

$$K_1 + K_2 = K_3 + G,$$

$$\kappa_{lat} \sim T^{-1}$$




$$\gamma = -\frac{d\ ln\omega_i}{d\ lnV} = \frac{3\beta B V_m}{C_V}$$

**Grüneisen parameter ( γ ):**

- ✓ The rate of change of the vibrational frequency of a given mode with volume.
- ✓ To measure the strength of anharmonicity.



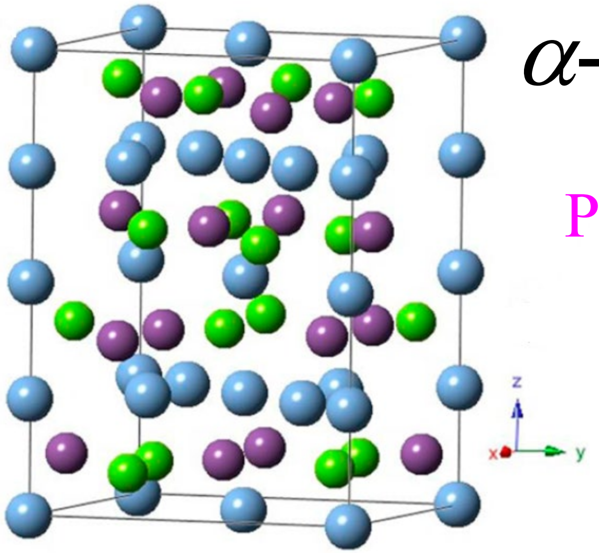
*Angew. Chem. Int. Ed.* **55**, 6826 (2016)

# Complex crystal structure $\kappa_L = \frac{1}{3} C_V v_g^2 \tau$

Compounds with a large number of atoms ($N$) in the primitive unit cell will exhibit low $\kappa_L$ due to the large quantities of optical branches ($3N$-$3$).

Only a fraction of the heat can be transported by the limited acoustic branches: $C_V^a = C_V / N$

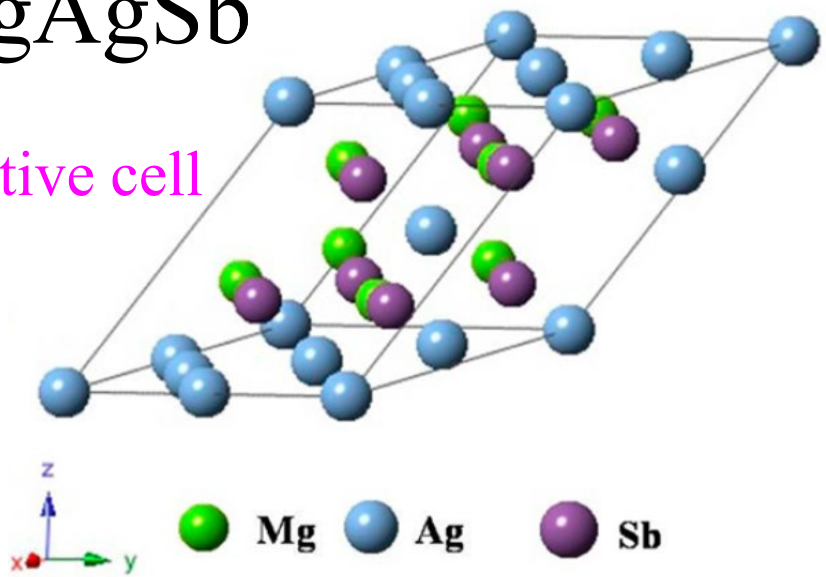
$\alpha$-MgAgSb




body-centered tetragonal (I-4c2)

24 atoms

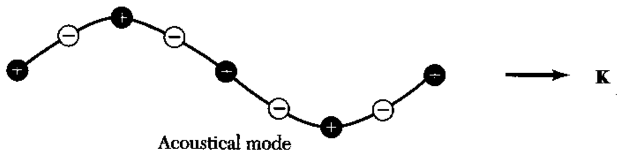
Primitive cell

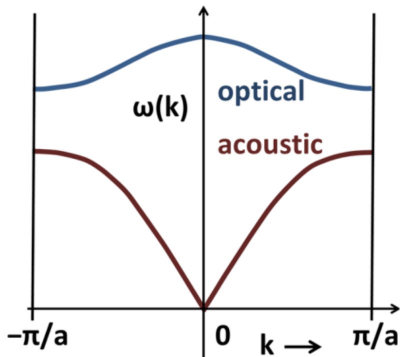


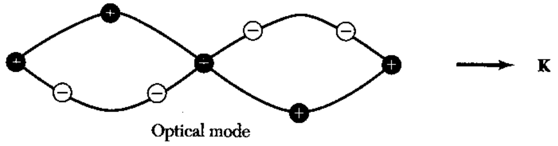
# Acoustic Phonon v.s. Optical Phonon

- High Group velocity
- Only 3 modes per primitive cell
- Conduct most of heat

- Low Group velocity
- Have (3N-3) modes per primitive cell (large cells have many optical modes)
- Conduct less heat



# Complex crystal structure

$$\kappa_L = \frac{1}{3} C_V v_g^2 \tau$$

**$\alpha$-MgAgSb**

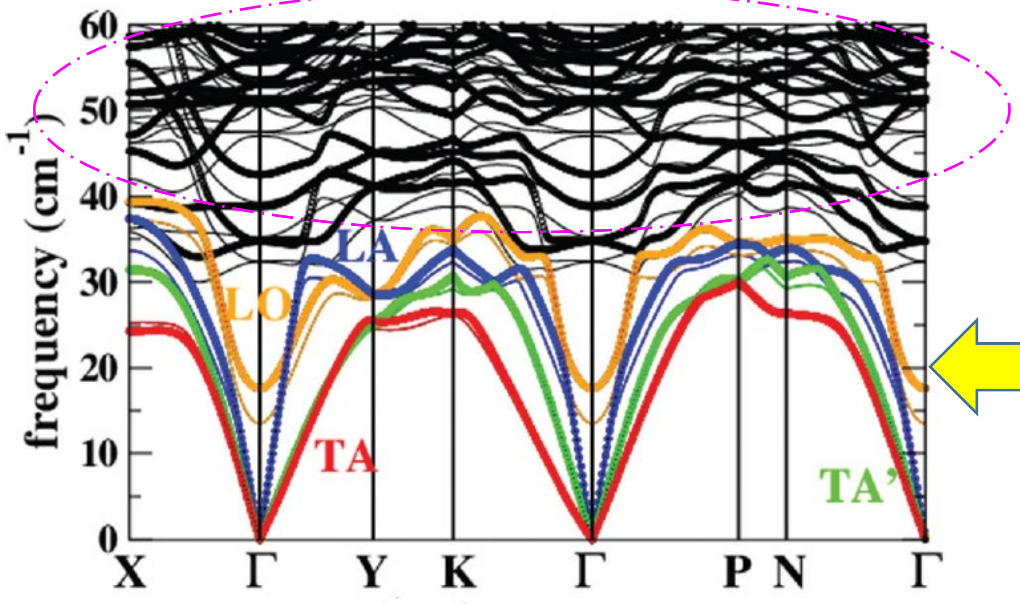
$N$=24 → Acoustic branches: 3
Optical branches : 69

$\kappa_L$: 0.6 W/m-K

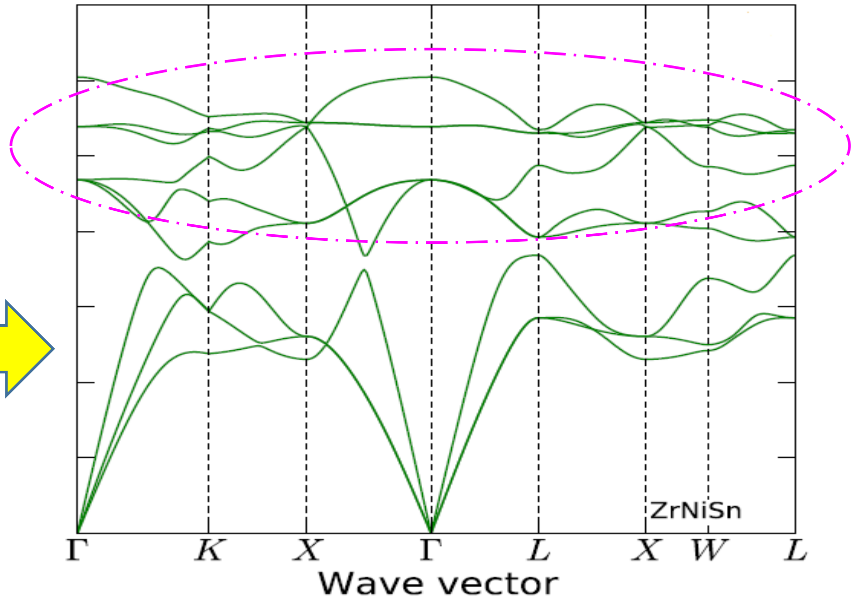
**ZrNiSn**

$N$=3 → Acoustic branches: 3
Optical branches : 6

$\kappa_L$:12 W/m-K

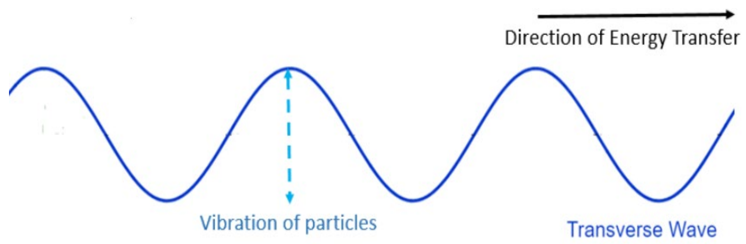



*Energy Environ. Sci.*, **11**, 23 (2018)




*PRB*, **95**, 045202 (2017)

# Phonon modes : Acoustic & Optical



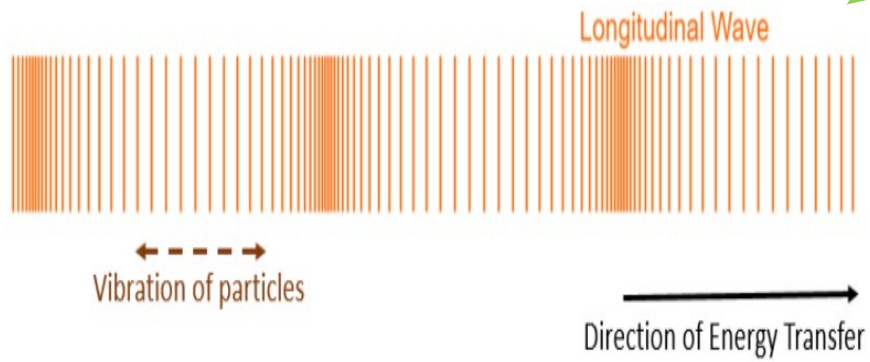

Transverse

- **Transverse Acoustic (TA)**
- **Transverse Optical (TO)**

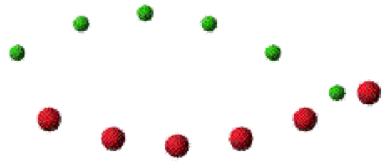
Waves

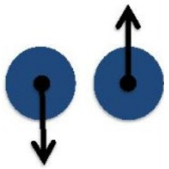
Longitudinal

- **Longitudinal Acoustic (LA)**
- **Longitudinal Optical (LO)**

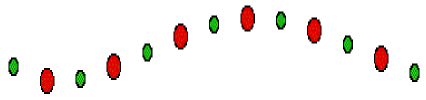


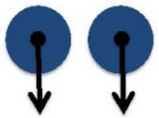
**Transverse Optical (TO)**



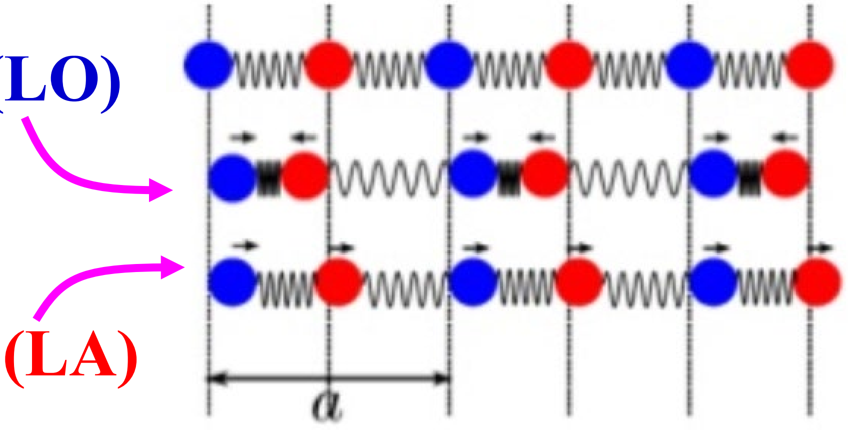


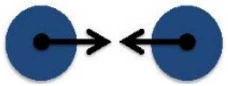
**Transverse Acoustic (TA)**



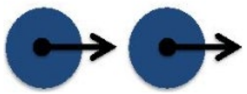


**Longitudinal Optical (LO)**



**Longitudinal Acoustic (LA)**

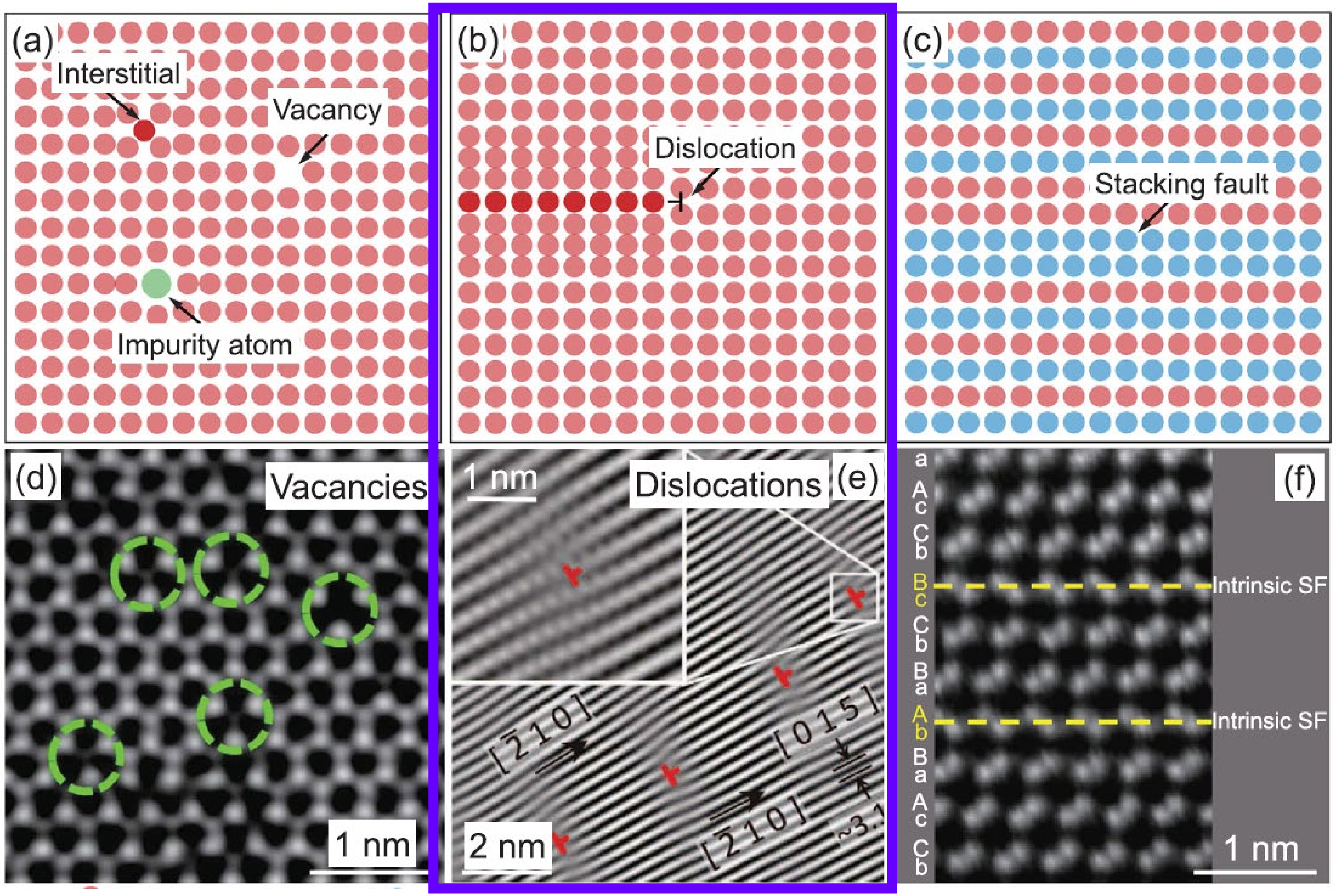


Images and movies from: Dr. *Taras Kolodiaynyi* & Dr. *Burak Himmetoglu*

# Defect engineering

$$\kappa_L = \frac{1}{3} C_V v_g^2 \tau$$

Phonon scattering by microstructural defects




Ref: *Advances in Physics*, **67**, 69-147 (2018)

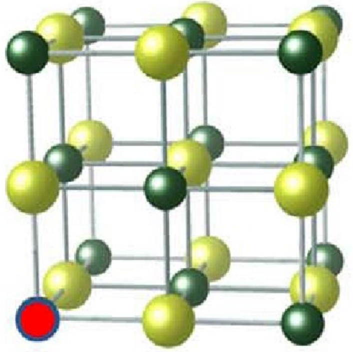
# II. Stratagem of enhancing ZT

- ✓ **Electronic band structure**－band convergence
- ✓ **Reduction in thermal conductivity**

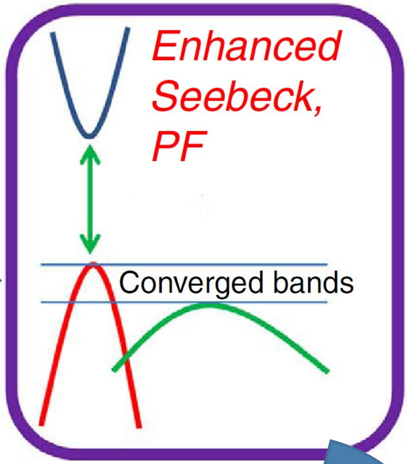
  Intrinsically low lattice κ , Defect Engineering
- ✓ **Synergistically manipulating charge and phonon transports**
- ✓ **3D charge and 2D phonon transports**

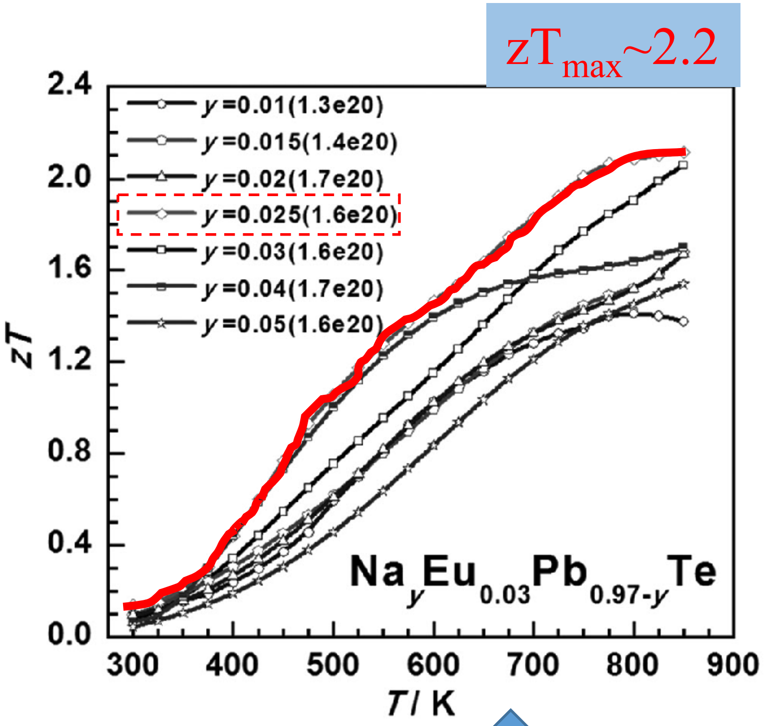
# Synergistically manipulating charge and phonon transports

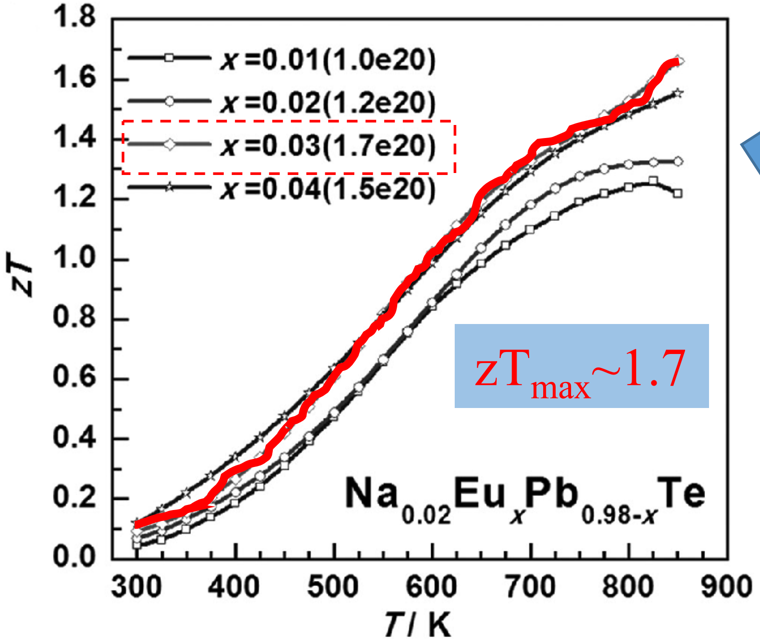
PbTe

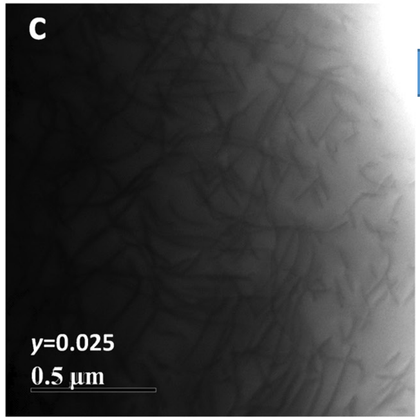


**EuTe doping**




higher density dislocations

*Adv. Mater.* **29**, 1606768 (2017)

# II. Stratagem of enhancing ZT

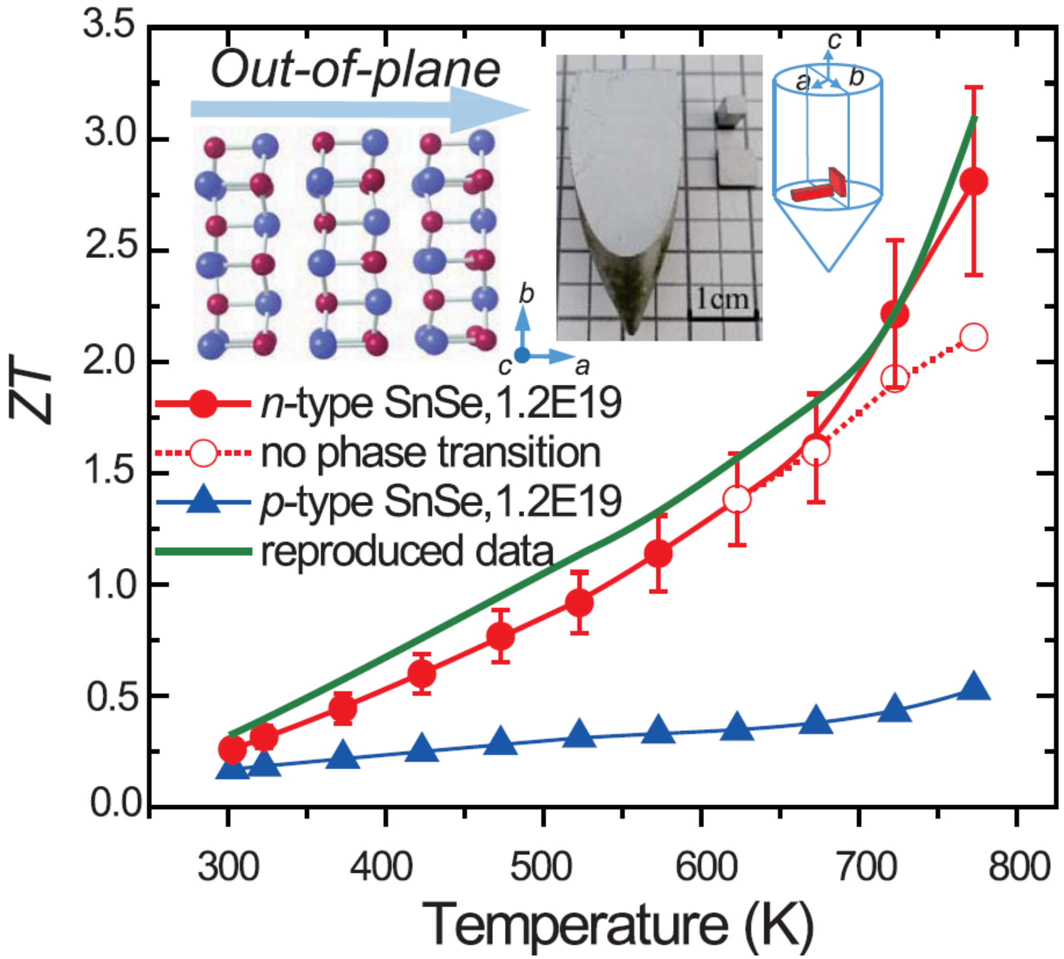
- ✓ **Electronic band structure**－band convergence
- ✓ **Reduction in thermal conductivity**

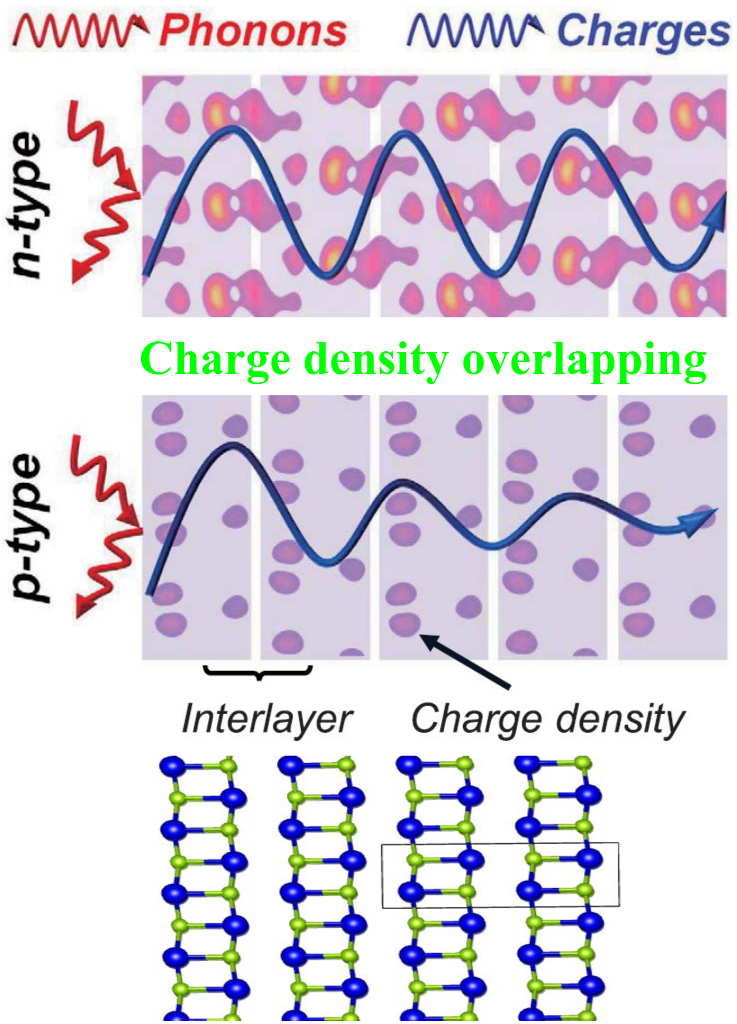
  Intrinsically low lattice κ , Defect Engineering
- ✓ **Synergistically manipulating charge and phonon transports**
- ✓ **3D charge and 2D phonon transports**

# 3D charge and 2D phonon transports

*Science* **360**, 778–783 (2018)

## *n*-type SnSe crystals



# Outline

- I. Introduction to thermoelectrics
- II. Stratagem of enhancing ZT
- III. Sample Fabrication
- IV. ZT Measurements and characterization techniques
- V. Future works

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

# Sample Fabrication

- 1.  Bulk Ingot, Polycrystal
- 2  Single crystal: Bridgmen method
- 3. Film :  by deposition.

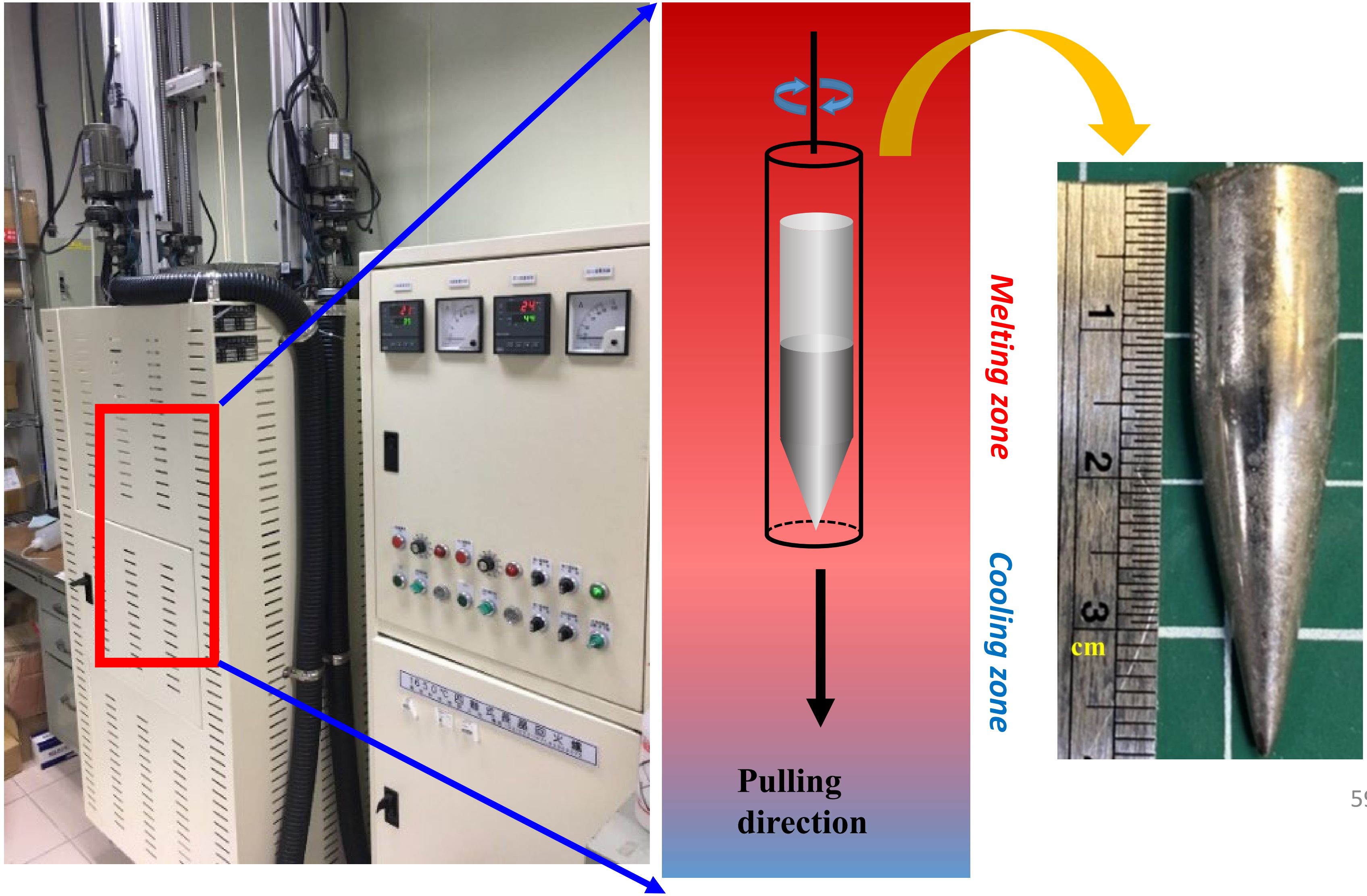
# Categories: Sample Fabrication

1. Equilibrium processes :
   Crystal growth, melting & slow cooling,
   melting + long-time annealing,
   multi-step solid state reactions

2. Non-equilibrium processes :
   quench, mechanical alloying
   hot deformation, melt spinning
   self-propagating high-temperature synthesis

3. Spark plasma sintering (SPS)

# Crystal growth of GeTe : Bridgman method



# 4. High Thermoelectric zT in GeTe Single Crystal with Sb Dopants

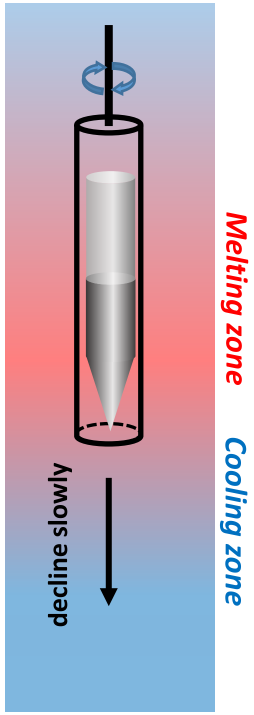
## Synthesizing of $Ge_{1-x}Sb_xTe$ crystals

- The **$Ge_{1-x}Sb_xTe$** crystals grown by Bridgman method that followed by a 2-step process.

- **1st step: pre-melting at high temperature**
    - Ge, Sb and Te are mixed by the stoichiometric ratio of high purity elements (99.999%)
    - Mixture sealed in the evacuated quartz ampoule under a vacuum of that better than $3 \times 10^{-5}$ Torr.
    - The sealed mixture is pre-melted at high temperature for 48 hours
- **2nd step: Bridgman crystalizing**
    - Sealed in the sharp evacuated quartz ampoule under a vacuum of that better than $3 \times 10^{-5}$ Torr.
    - Re-melting at melting zone.
    - Decline slowly at a rate of that <10 mm/hr into cooling zone.

(a)

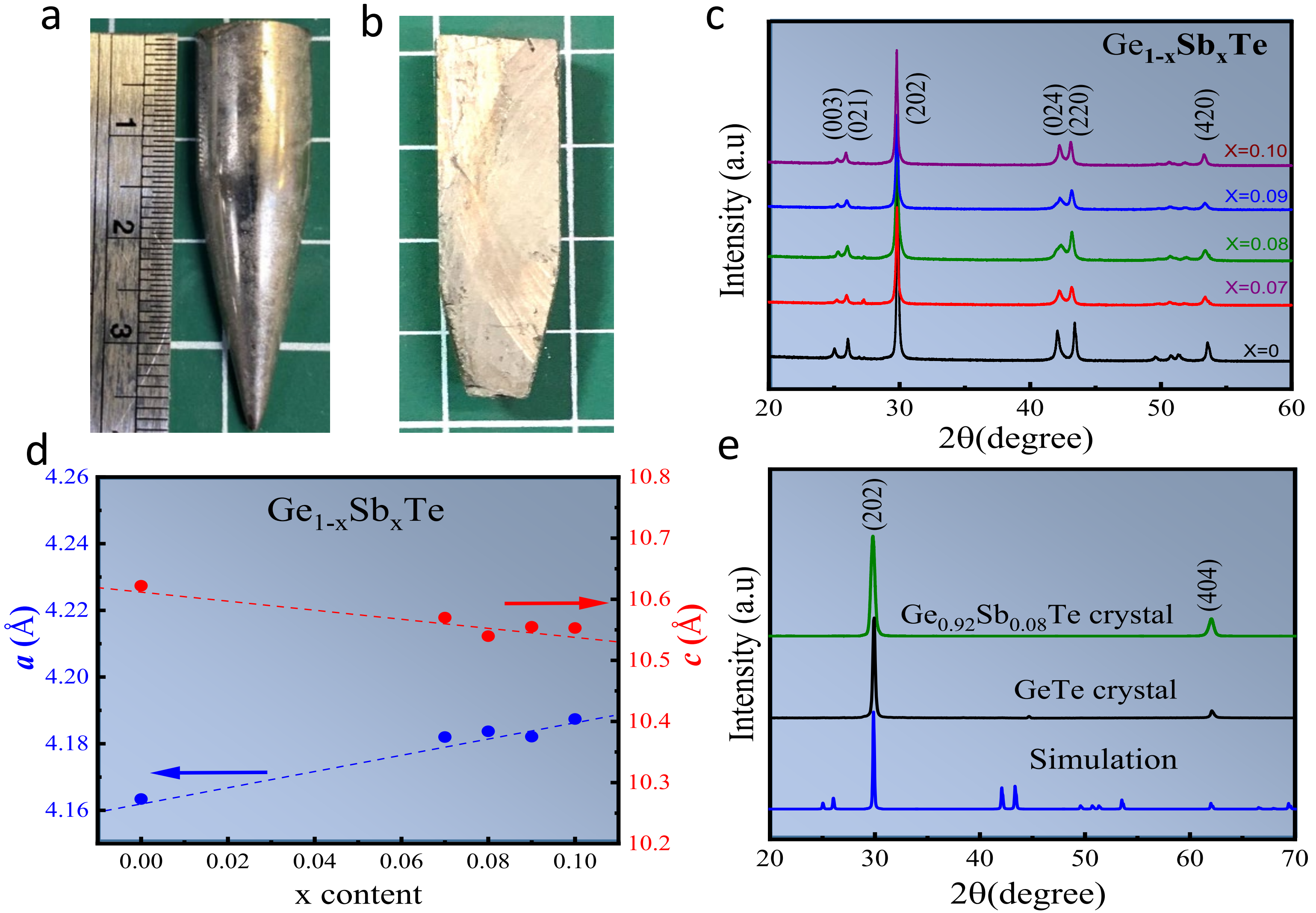
(b)



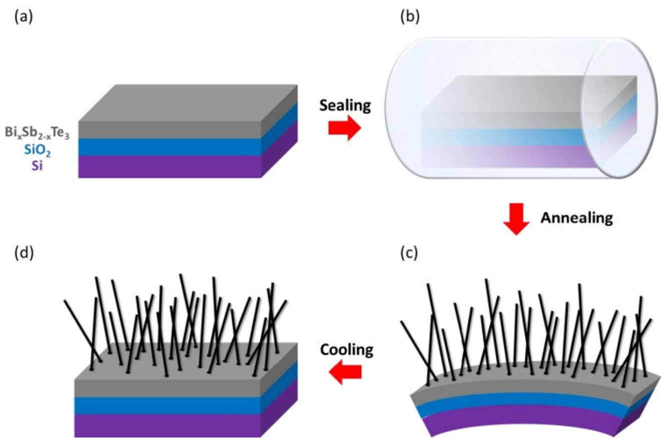

- The well known Bridgman method is employed to synthesize the antimony doped GeTe crystals.
    (a) The High temperature Bridgman furnace, right side the bulk material of a $Ge_{0.92}Sb_{0.08}Te$ crystal.
    (b) The interior temperature gradient of the vertical Bridgman furnace

# $Ge_{1-x}Sb_xTe$

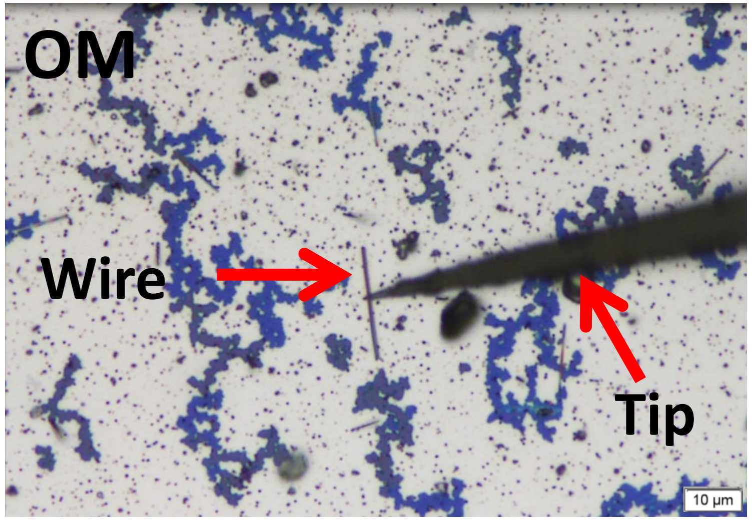
Fig.1



# Growth of $Bi_xSb_{2-x}Te_3$ nanowires




*Nano Lett., Vol. 9, No. 1, **2009***





$Bi_{1.5}Sb_{0.5}Te_3$ thin film after annealing at 490℃ for 5 days

# IV ZT Measurements and Characterization

## Thermoelectric transport parameters

1. Seebeck coefficient
2. Thermal conductivity
3. Electrical resistivity

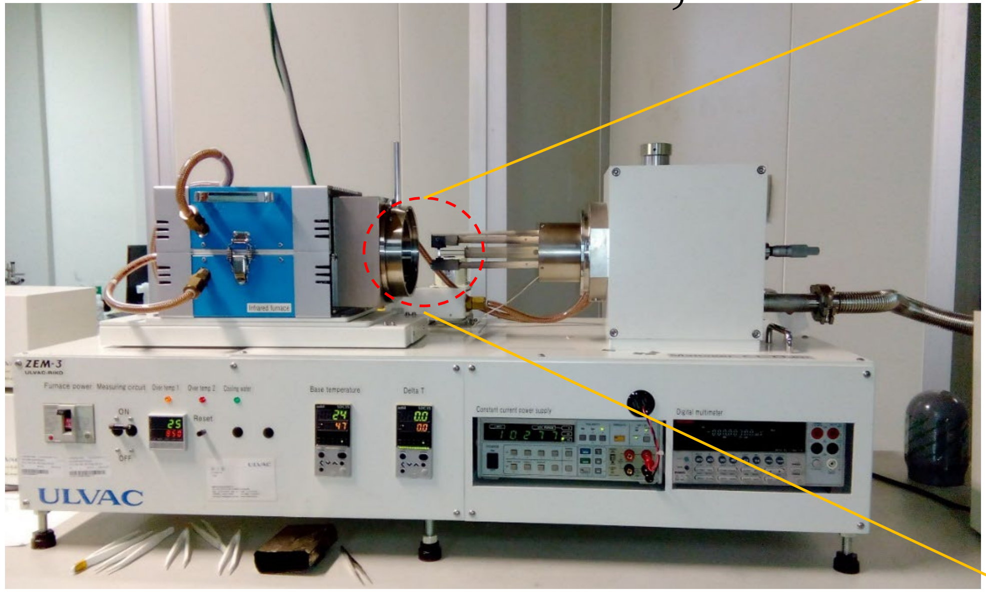
Measure uncertainty in $ZT$ :

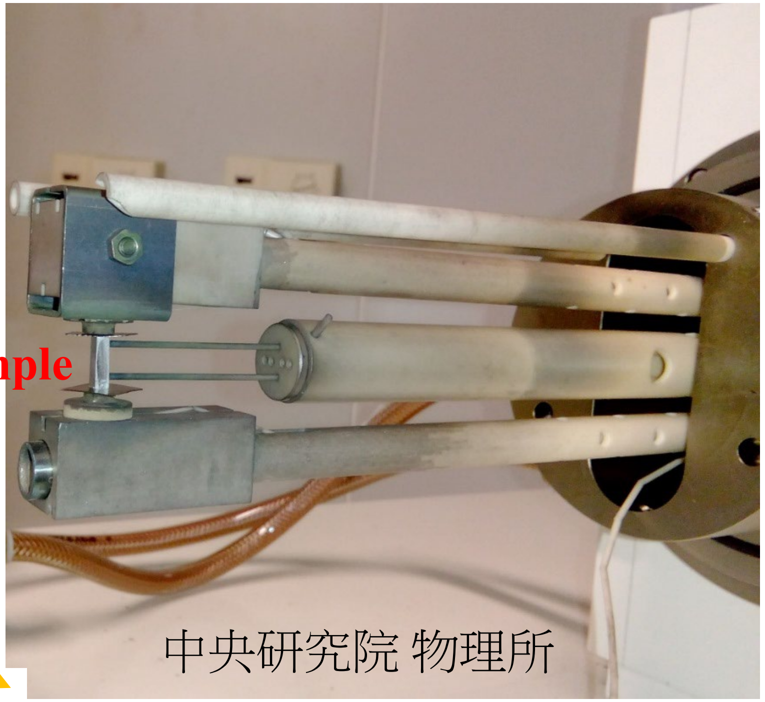
$$\frac{\Delta Z}{Z} = 2\frac{\Delta S}{S} + \frac{\Delta \sigma}{\sigma} + \frac{\Delta C_p}{C_p} + \frac{\Delta \lambda}{\lambda}$$

$$ZT = \frac{\sigma S^2}{\kappa}\mathrm{T} \quad \kappa = \lambda\rho C_p$$

# 1. Seebeck coefficient ( $\frac{\Delta V}{\Delta T}$ ) and electrical conductivity

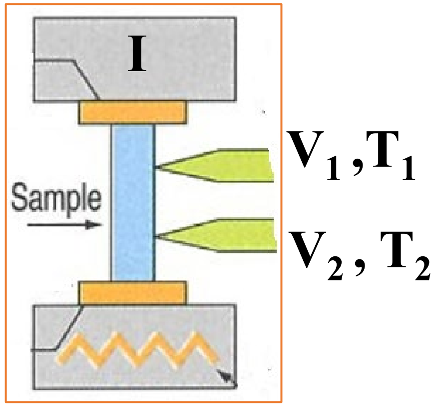
**ZEM-3** Bulk, film



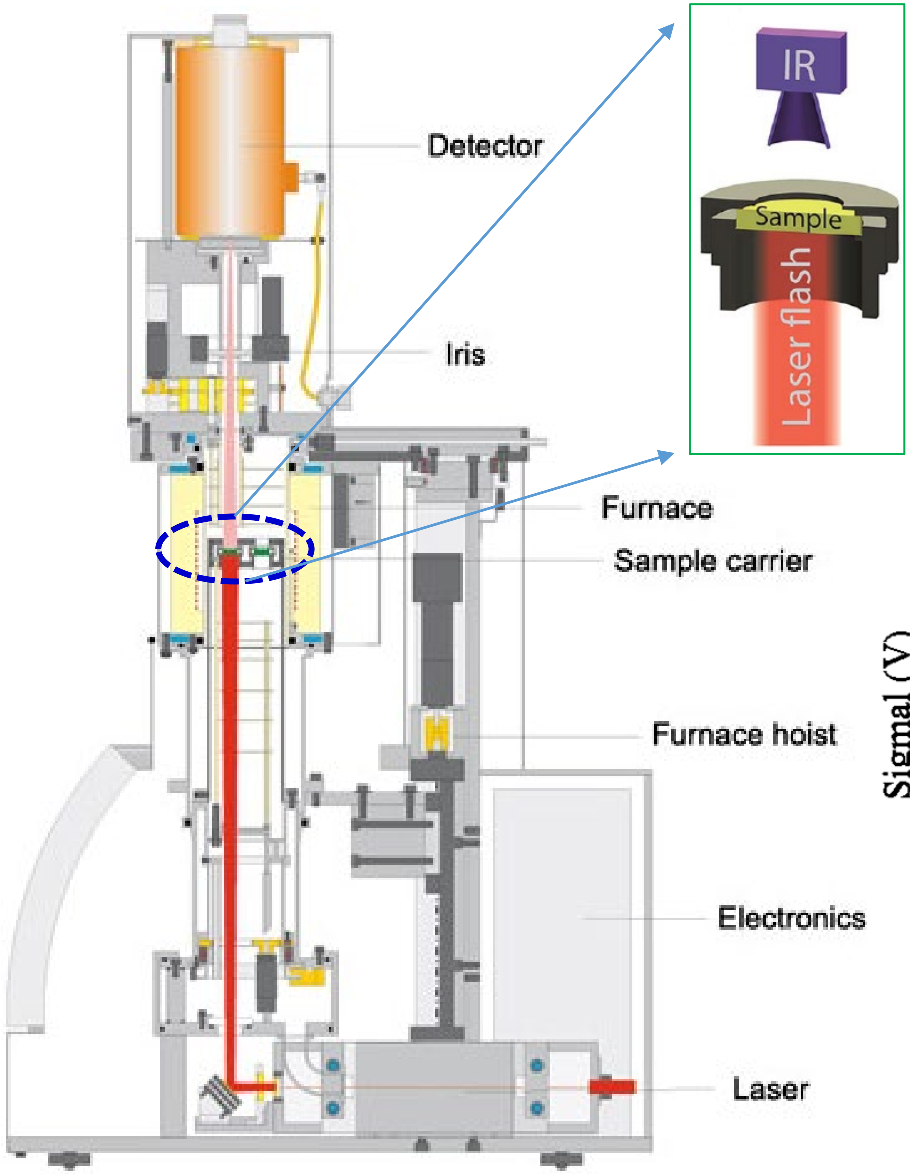




## Specifications

| | |
|---|---|
| **Measurement method** | Seebeck coefficient : Static dc method<br>Electric resistance : Four-probe method |
| **Temperature range** | 27 °C ～ 800 °C |
| **Number of measured temperature steps** | Maximum 125 |
| **Sample size** | 2 ~ 4 mm in square (diameter);<br>5 ~ 22 mm in length |
| **Lead interval** | 3, 6, 8 mm |




# Thermal conductivity measurement




**LFA 457, NETZSCH**

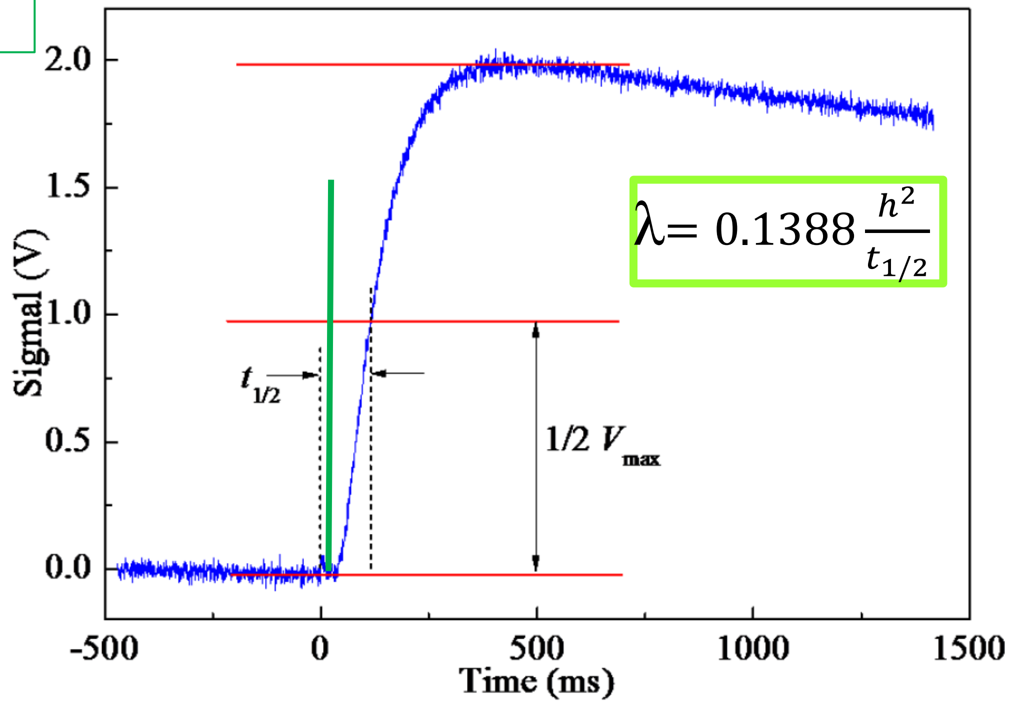
$$\kappa = \lambda \rho C_p$$

Diffusivity

Heat capacity

Thermal conductivity

Density



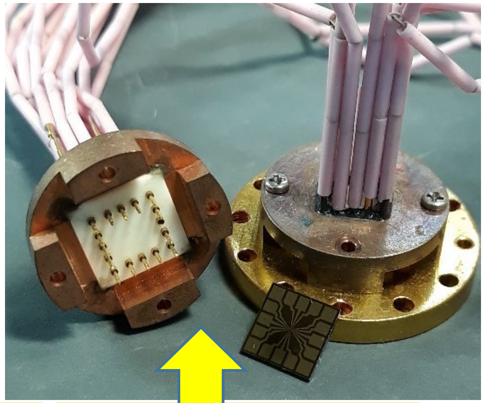

*Transient state method*

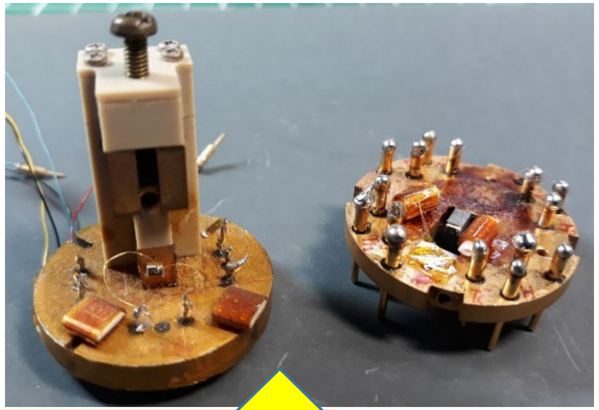
# Sample Size

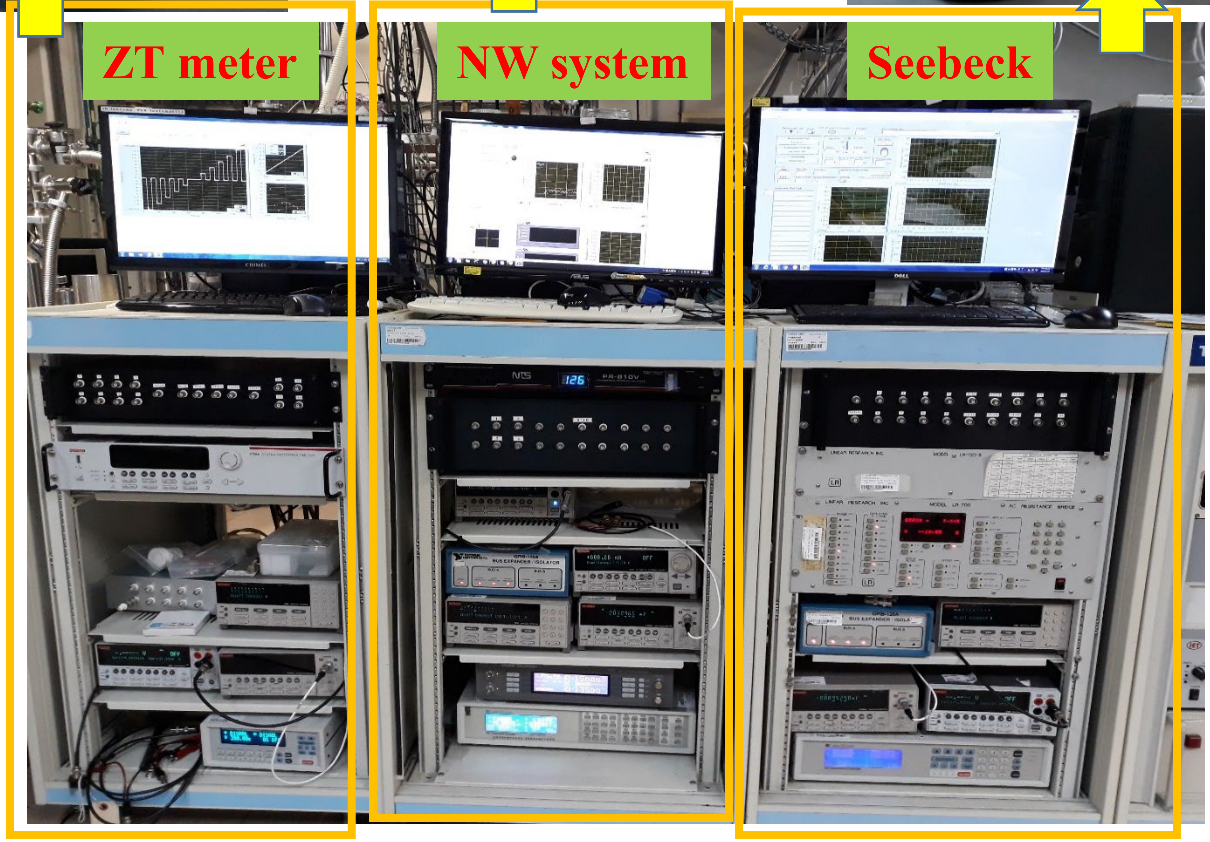

Sample Diameter (mm): 12.7, 10, 6

| Thermal Diffusivity range | Possible sample thickness |
|---|---|
| Low diffusivity e.g. polymers ($0.01$-$1\ mm^2/s$) | 0.05 to 3 mm |
| Medium diffusivity e.g. ceramics ($1$-$50\ mm^2/s$) | 0.5 to 5 mm |
| High diffusivity e.g. copper ($50$-$1200\ mm^2/s$) | 1 to 5 mm |

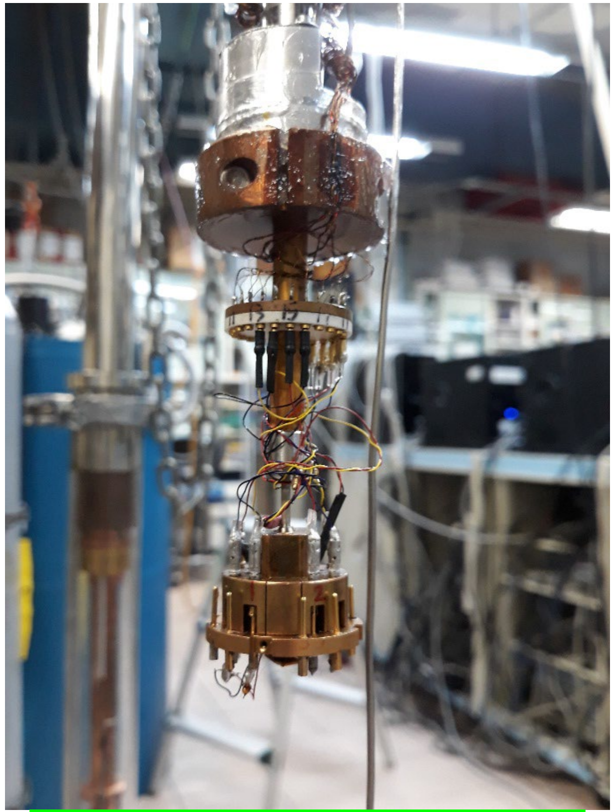
# Home-made thermoelectric measurement systems



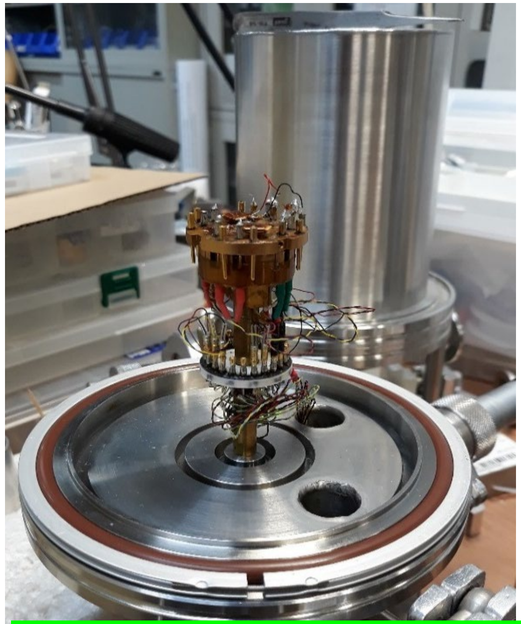




# Seebeck , electrical resistivity

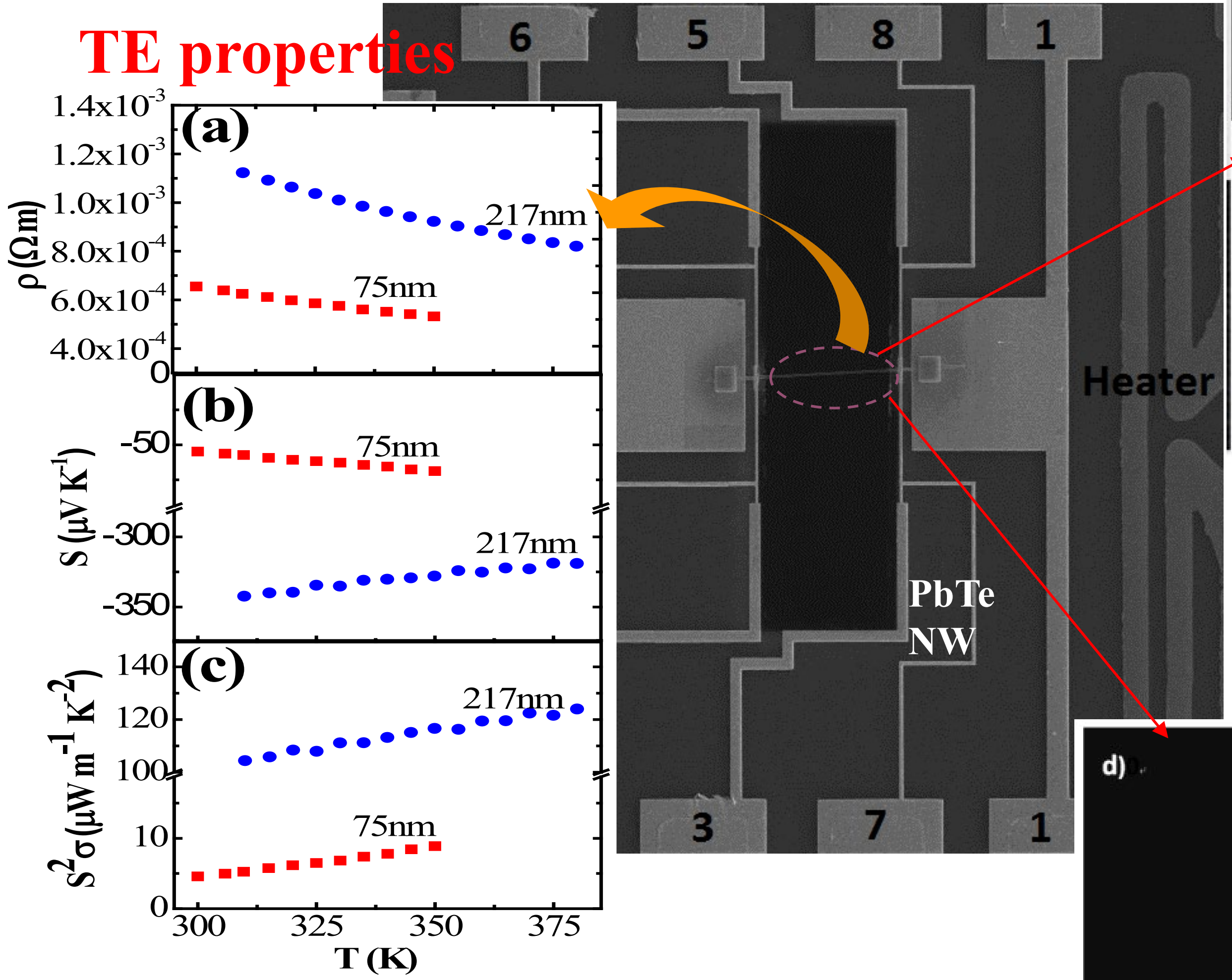
For -200 ºC ~27 ºC

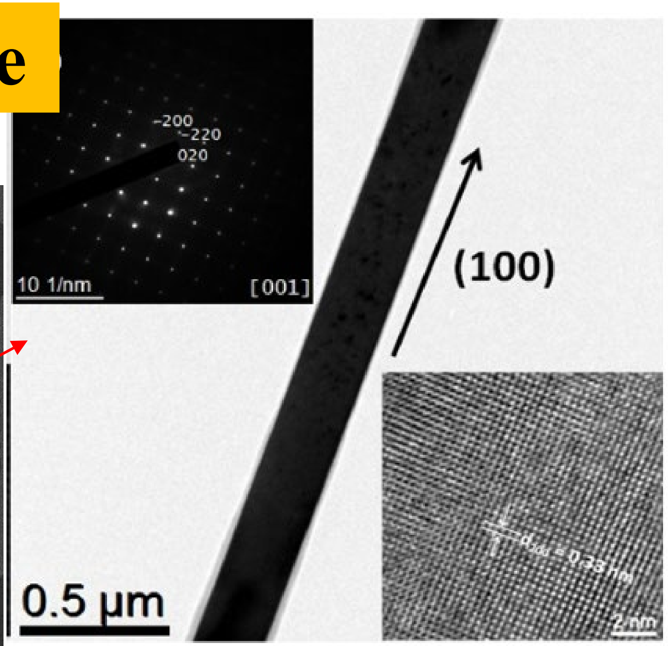


For 27 ºC ~100 ºC

For 27 ºC ~500 ºC

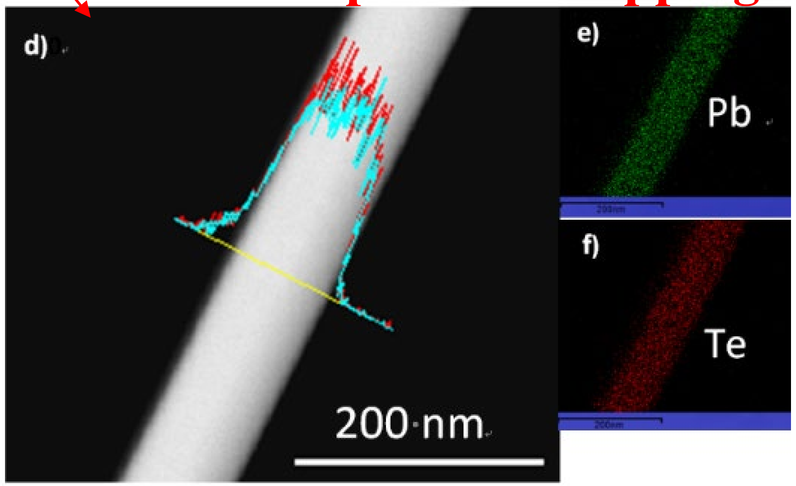
# III. ZT measure platform for Nanowire




## Structure

## Composition mapping

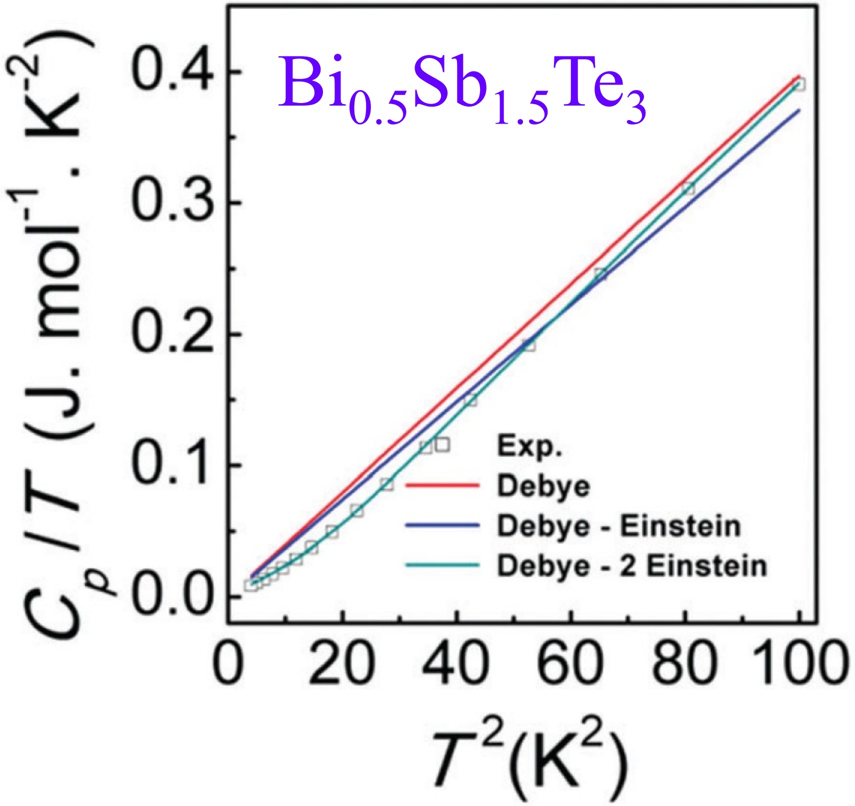



"Stress-induced growth of single -crystalline lead telluride nanowires and their thermoelectric transport properties", *Appl. Phys. Lett.* **103**, 023115 (2013)

# ZT Measurements, Specific Heat and Inelastic Neutron scattering

**Low-Temperature heat capacity measurement (0.5 ~300 K)**


Reduction of lattice thermal conductivity by low energy **multi-Einstein optic modes**

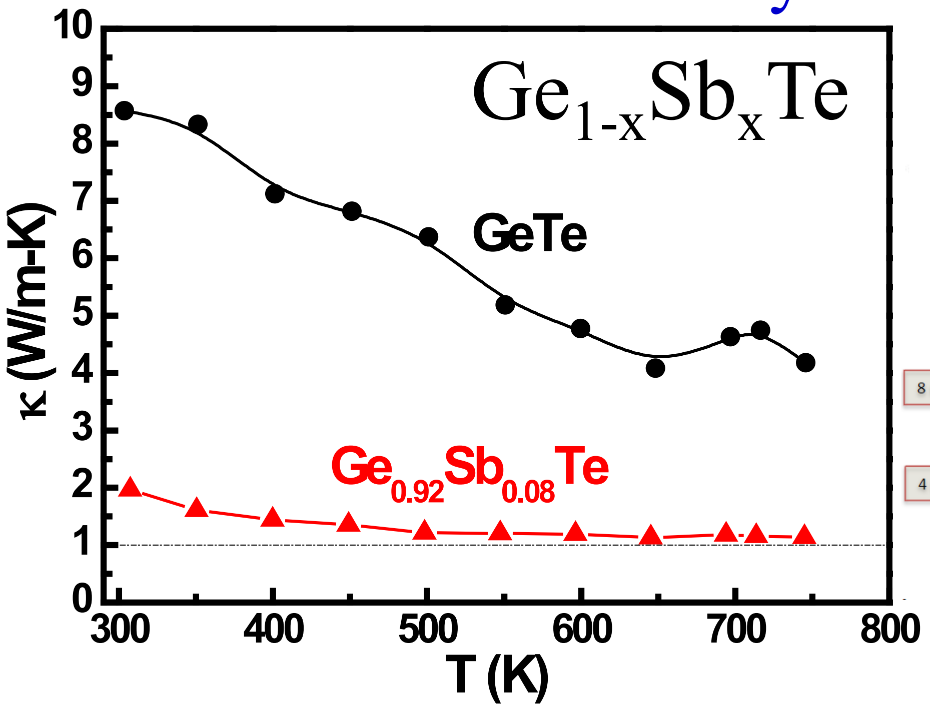



$$C_p/T = \gamma + \beta T^2 + \sum_{i=1}^{n} A_i(\Theta_{Ei})^2 (T^2)^{(-3/2)} \frac{e^{\Theta_{Ei}/T}}{(e^{\Theta_{Ei}/T}-1)^2}$$

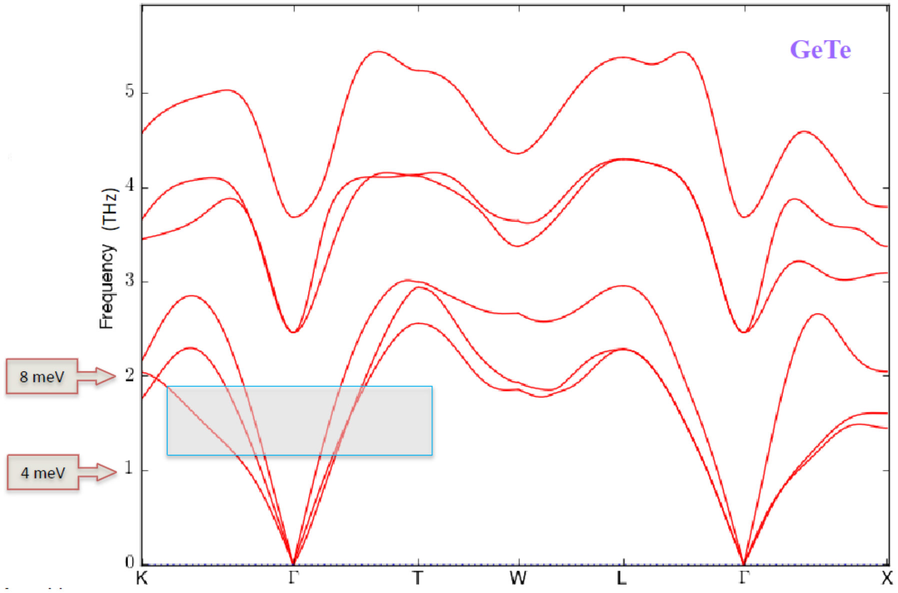
Two Einstein oscillators with oscillation frequencies of 0.73 THz (35 K) and 1.29 THz (62 K) in the Debye host. The presence of the **high frequency phonon modes** that freeze out at the suitably low temperature which couple with the long wavelength acoustic phonon modes, resulting in an intrinsically low thermal conductivity in BiSbTe alloys.

# ZT Measurements, Specific Heat and **Inelastic Neutron scattering**

## Thermal conductivity

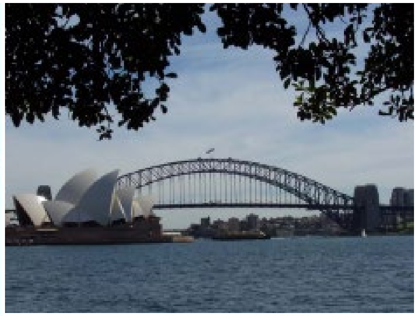


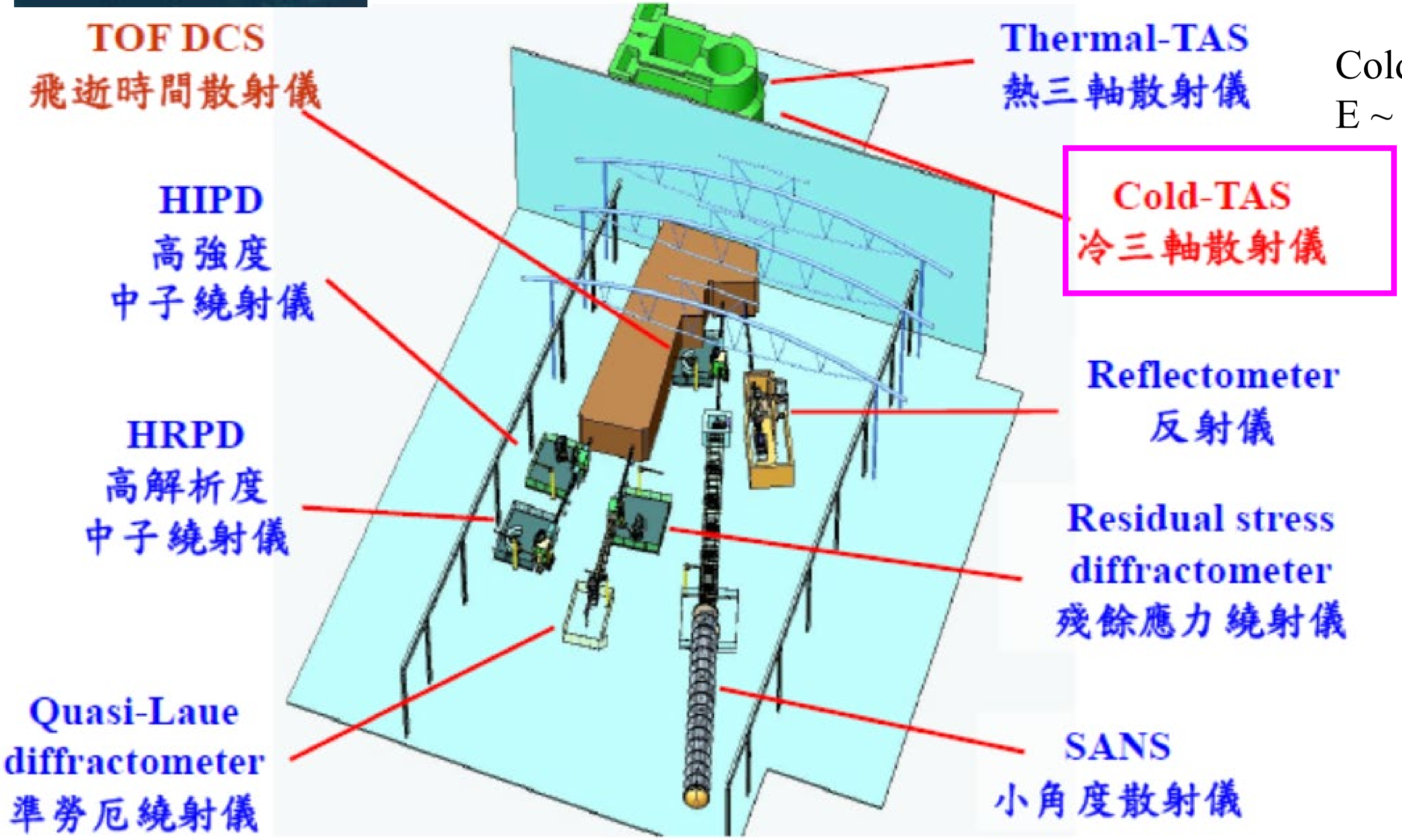

## Phonon dispersion




DFT calculation

# *Neutron instruments at ANSTO*






Cold neutron
E ~ 2 meV

# How to measure phonon dispersion curves ?

## Inelastic neutron scattering

If we can measure the energy lost by the neutron (by causing a vibration in the solid), and we can measure which direction you created the wave (wavevector, Q), then you can construct a phonon dispersion curve.

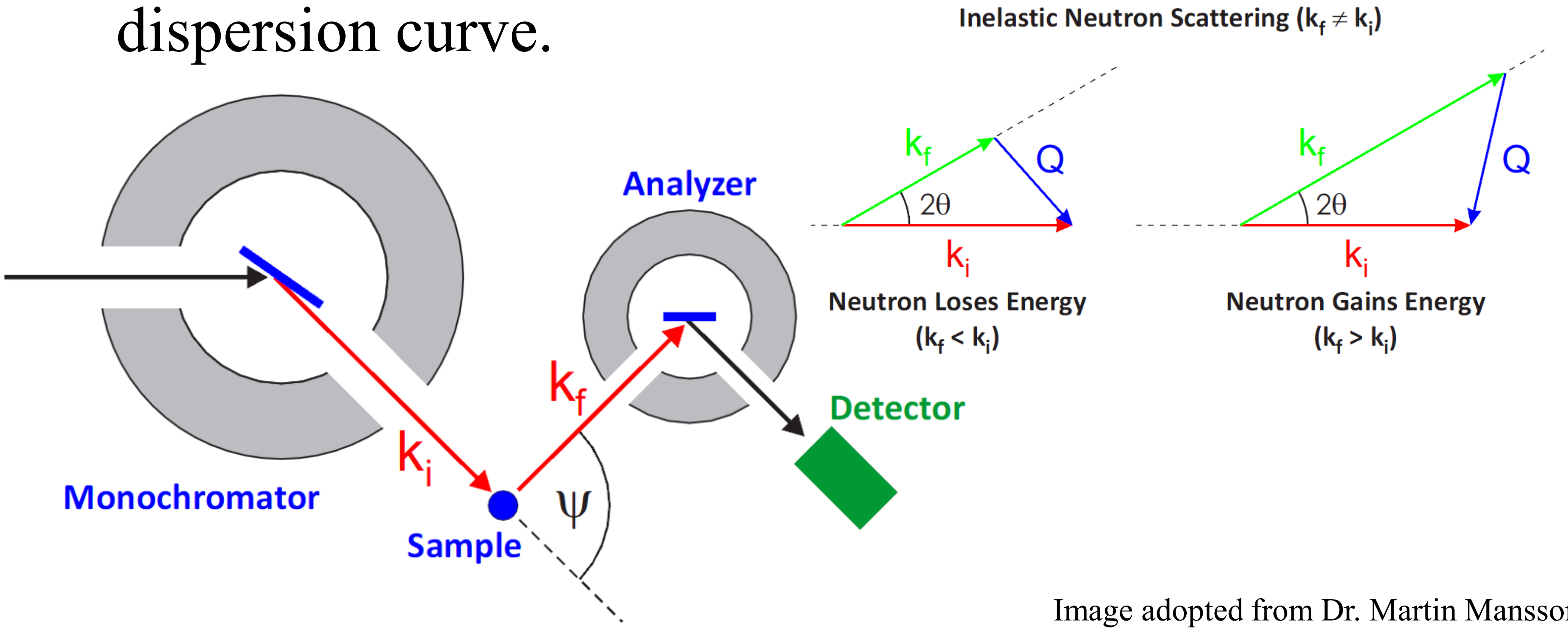


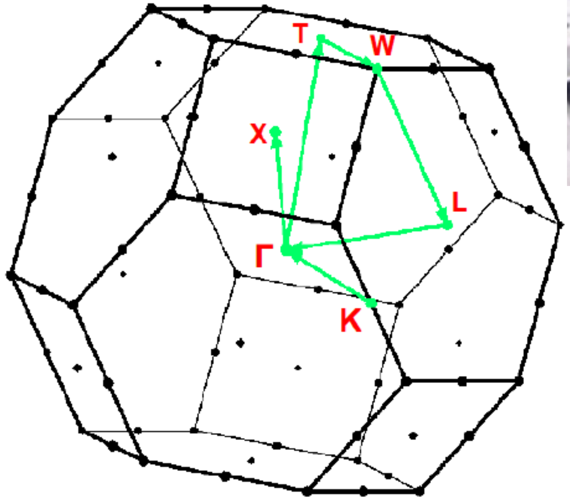

Image adopted from Dr. Martin Mansson
*Paul Scherrer Intitut*

# Scan Parameters

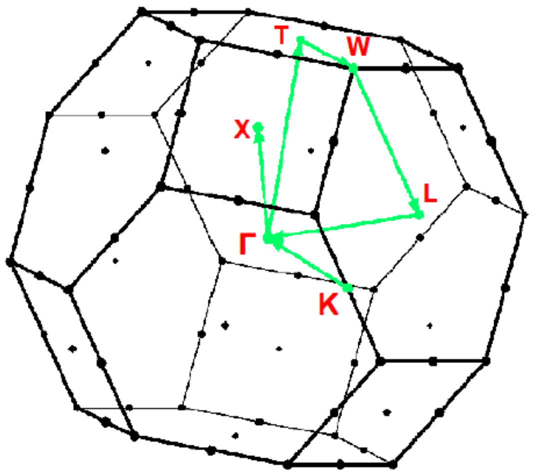
**SIKA - Cold Triple Axis neutron spectrometer**

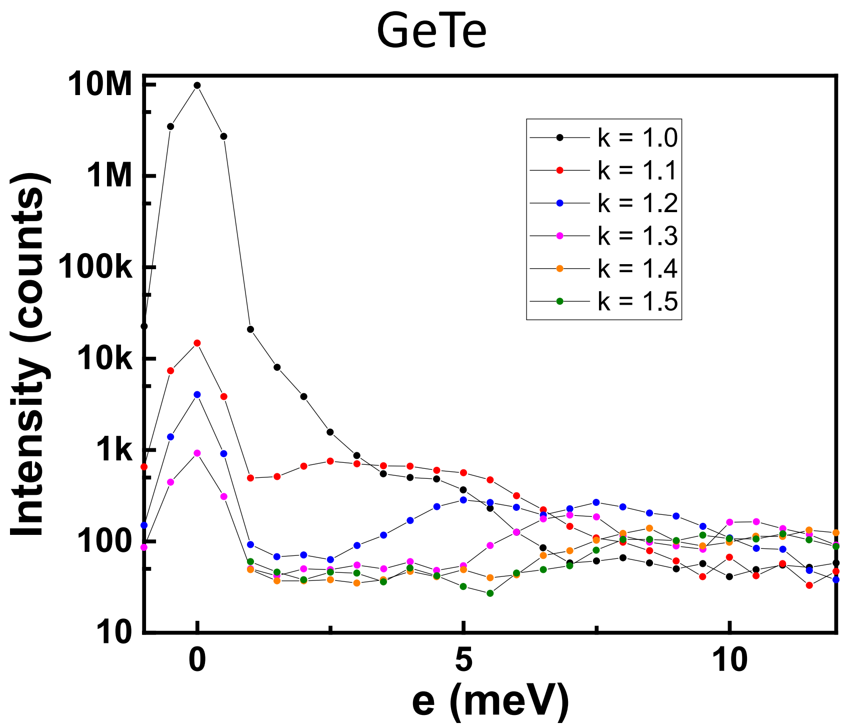
- GeTe
  - e = 0 ~ 12 meV
  - $\Gamma \rightarrow T$

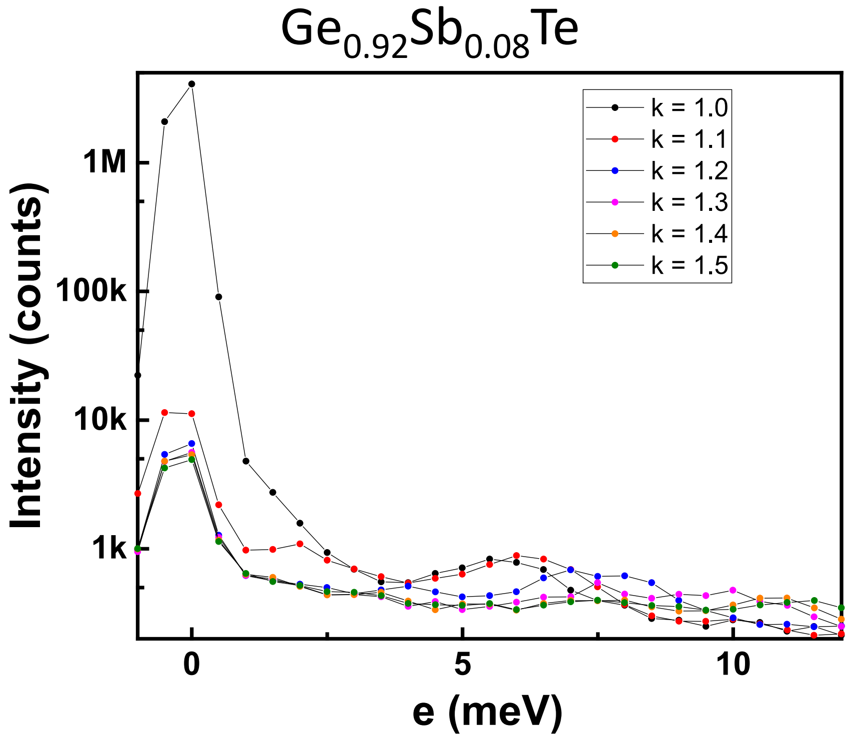
- $Ge_{0.92}Sb_{0.08}Te$
  - e = 0 ~ 12 meV
  - $\Gamma \rightarrow T$



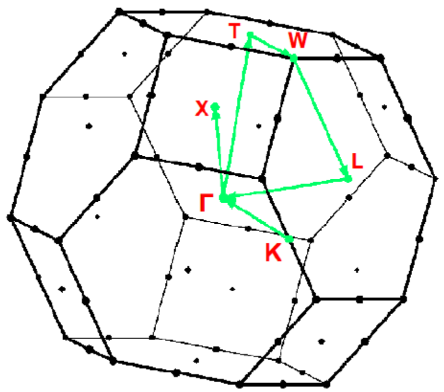
# Γ → T
# Q =1.0 ~ 1.5

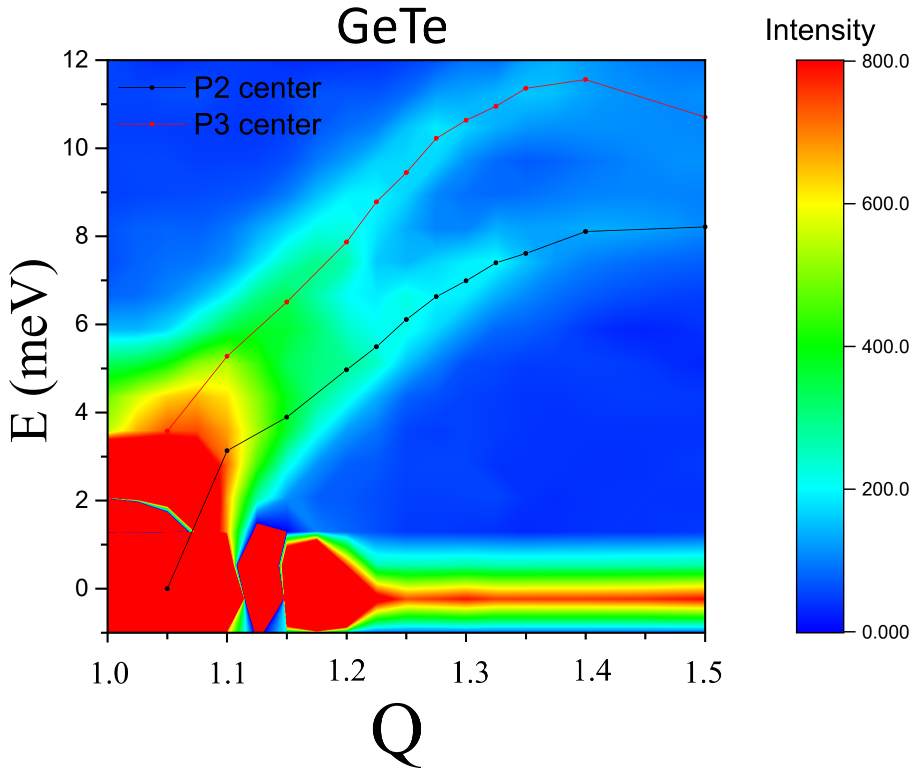

T
W
X
L
Γ
K

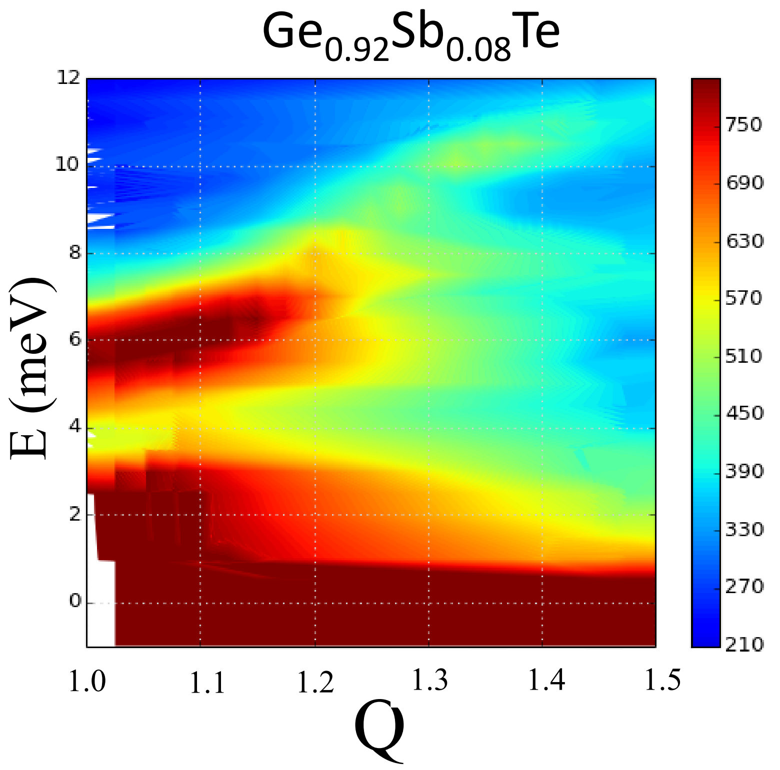

GeTe
Intensity (counts)
e (meV)
k = 1.0
k = 1.1
k = 1.2
k = 1.3
k = 1.4
k = 1.5
10M
1M
100k
10k
1k
100
10
0
5
10

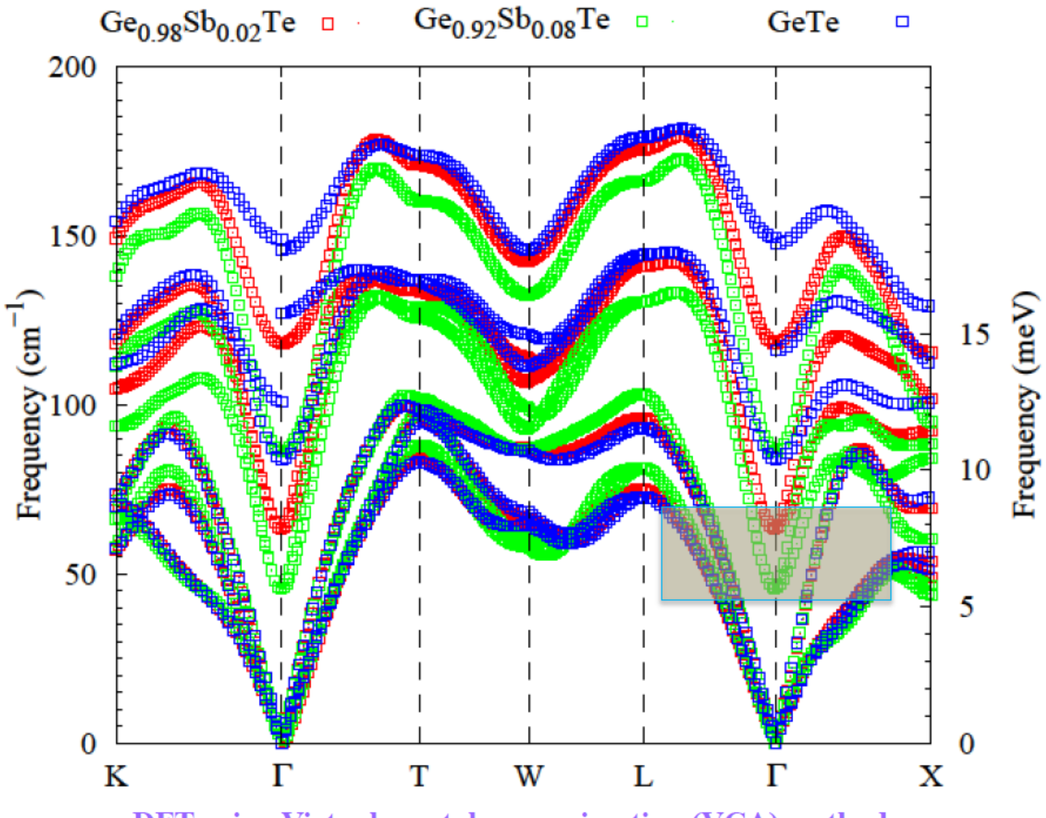

Ge0.92Sb0.08Te
Intensity (counts)
e (meV)
k = 1.0
k = 1.1
k = 1.2
k = 1.3
k = 1.4
k = 1.5
1M
100k
10k
1k
0
5
10

# $\Gamma \rightarrow T$
# $Q = 1.0 \sim 1.5$

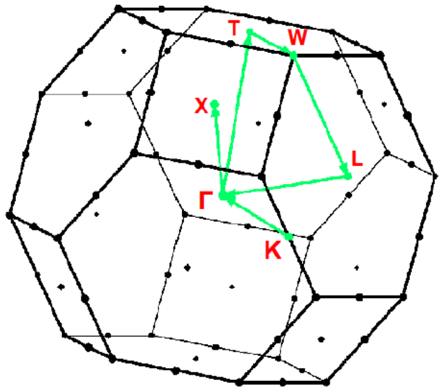


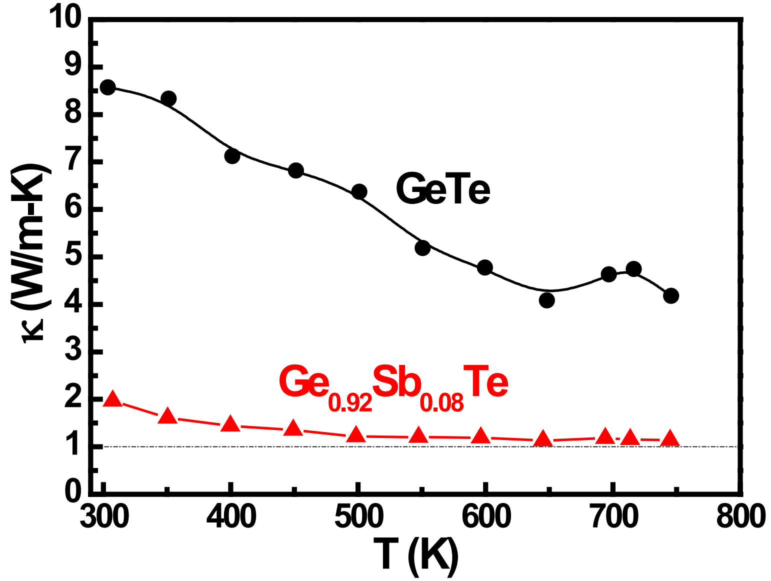






DFT using Virtual crystal approximation (VCA) methods



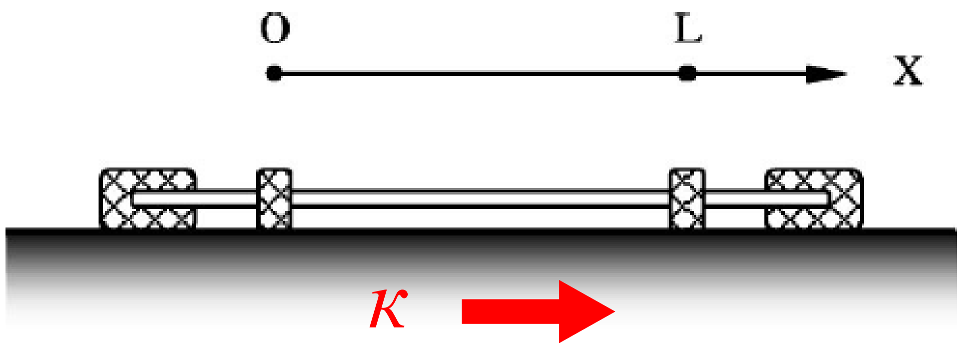



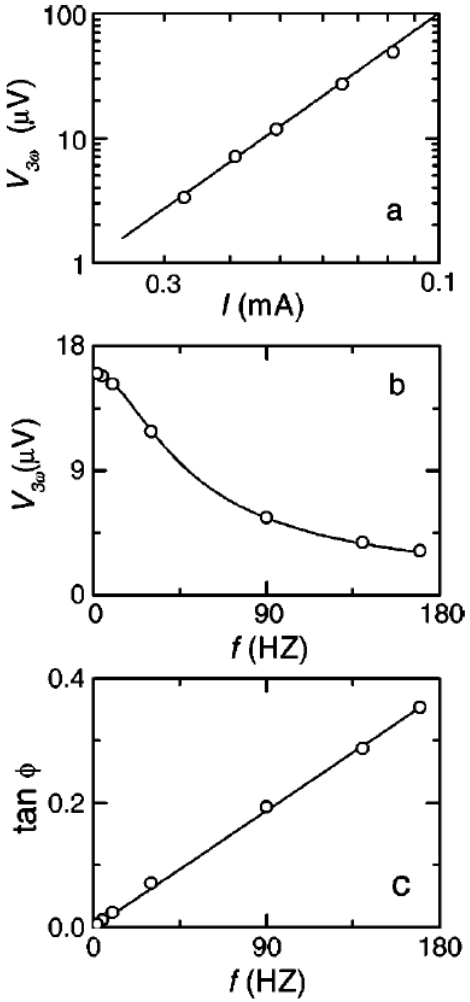

In the Γ point, $Ge_{0.92}Sb_{0.08}Te$ (green) have a phonon frequency around 6 meV (the shadow area) which cannot be seen from the pristine GeTe (blue) result. The overall phonon frequency got soften due to the Sb doping.

# *Thermal conductivity - 3ω method*

$$V_{3\omega} \approx \frac{4I^3LRR'}{\pi^4\kappa S\sqrt{1+(2\omega\gamma)^2}}$$

I: Root mean squar value of $I_0 \sin \omega t$
L: Length of the nanowire between voltage contact
R: Electric resistance at the substrate temperature $T_0$
$R'$: $(dR/dT)_{T_0}$
S: Cross section of the nanowire
γ: Thermal time constant



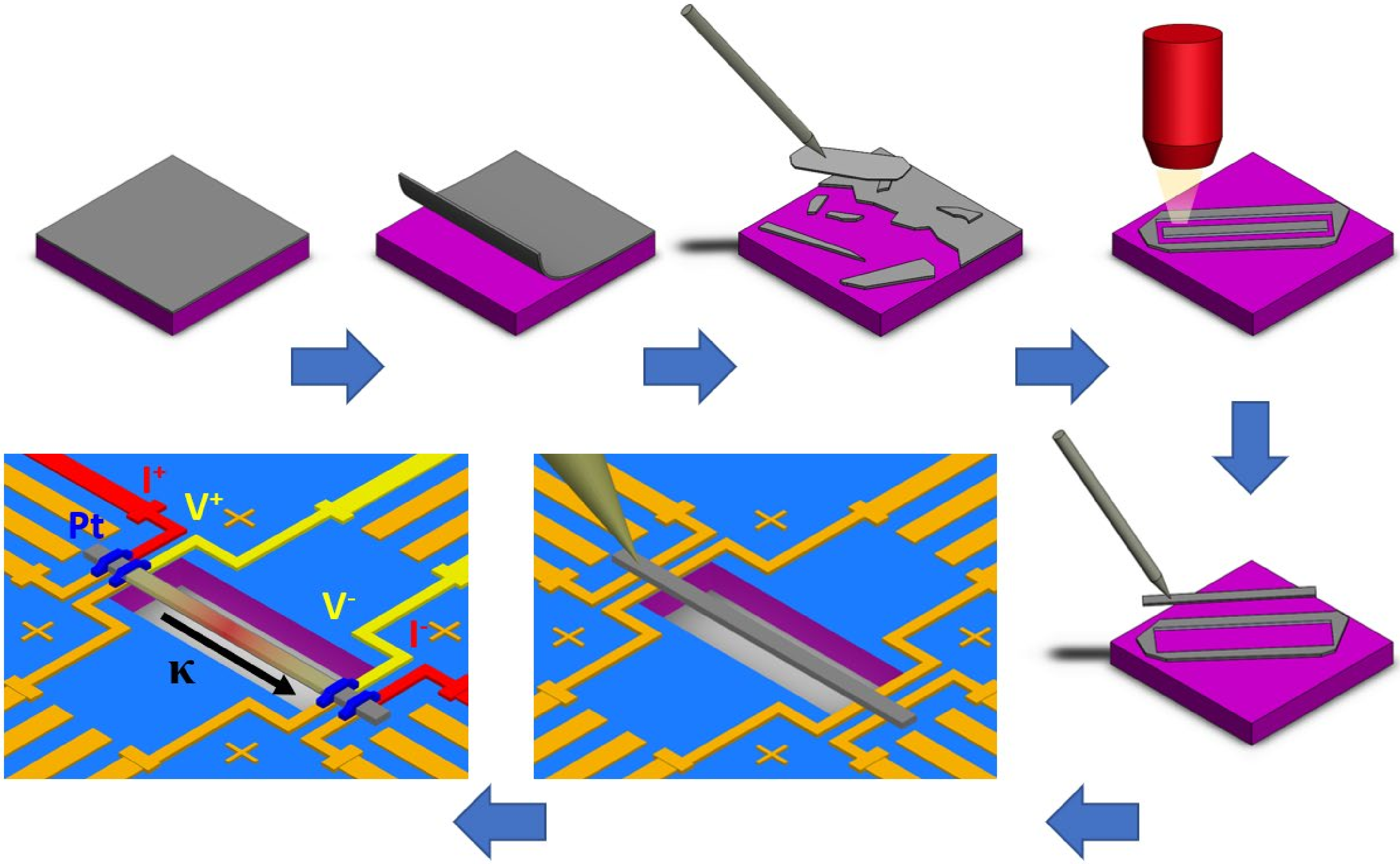

$$V_{3\omega} \propto I^3$$

$$V_{3\omega} \propto \frac{1}{\sqrt{1+(2\omega\gamma)^2}}$$

$$\tan\phi \propto \omega$$

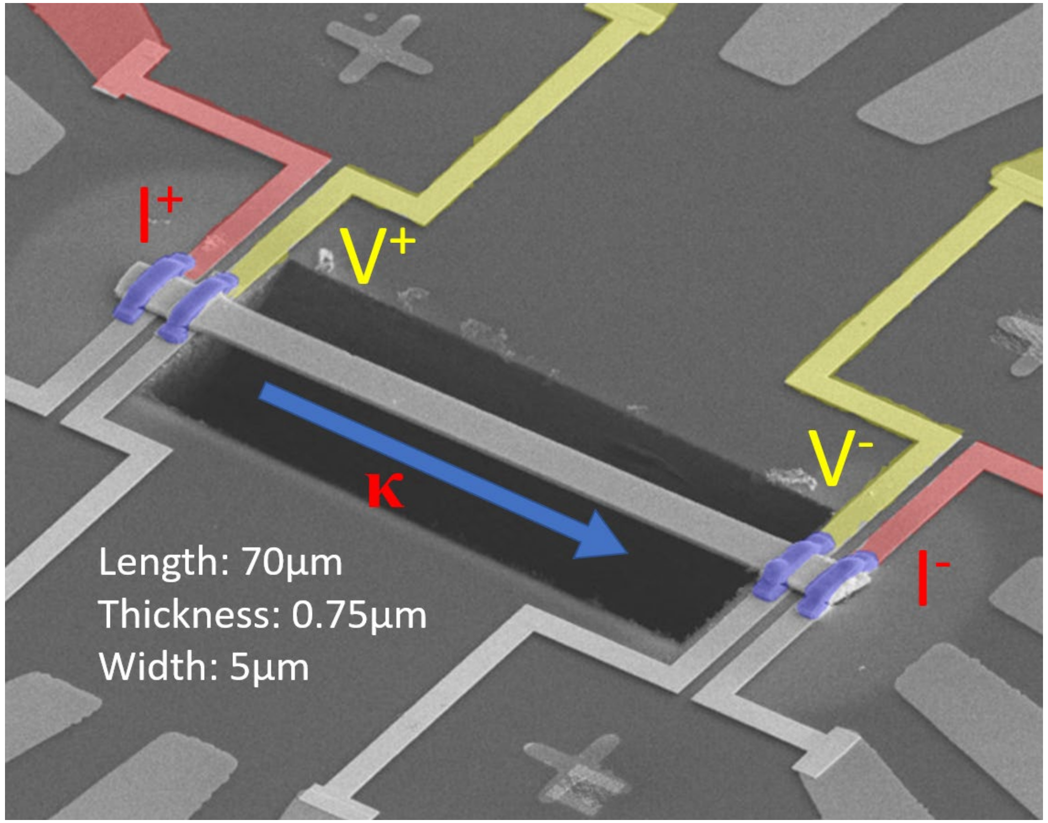
L. Lu, W. Yi, and D. L. Zhang, *3ω method for specific heat and thermal conductivity measurements*, Rev. Sci. Instrum., **Vol. 72**, No. 7 (2001)

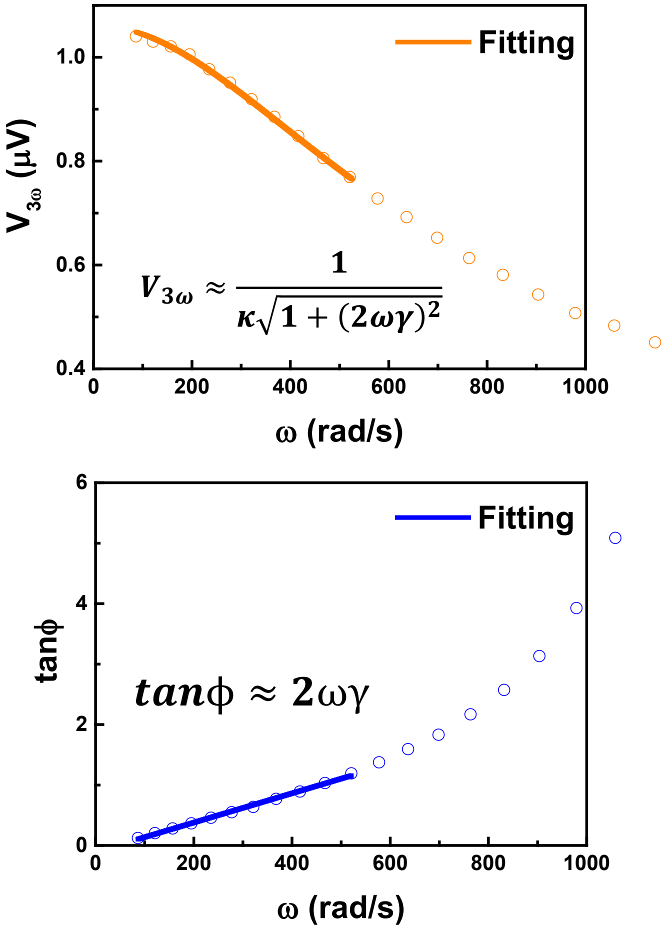
# *Thermal conductivity - 3ω method*



# *Thermal conductivity - 3ω method*

$$V_{3\omega} \approx \frac{4I^3LRR'}{\pi^4\kappa S\sqrt{1+(2\omega\gamma)^2}}$$



# Example 2

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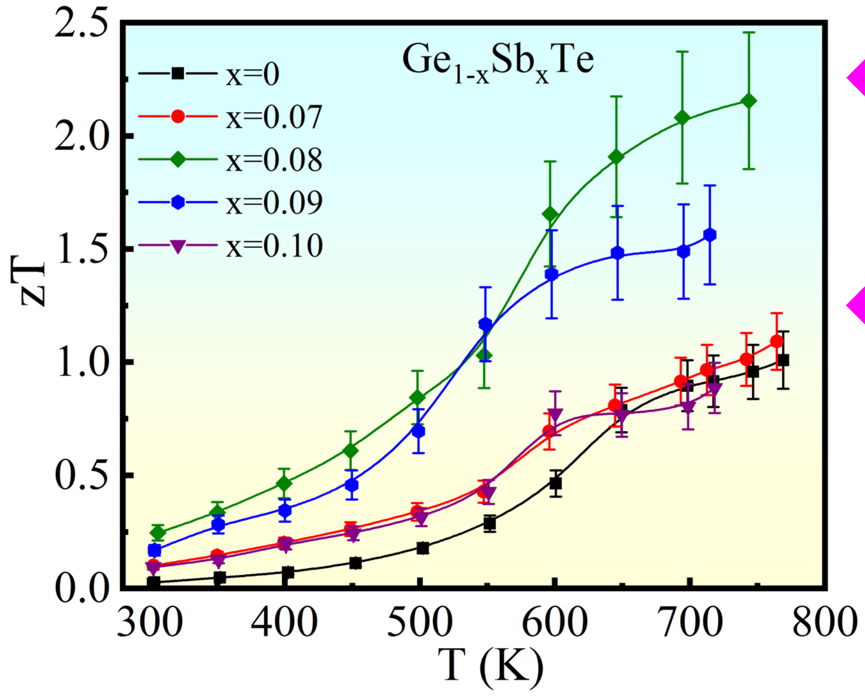
## High *zT* and Its Origin in Sb-doped GeTe Single Crystals

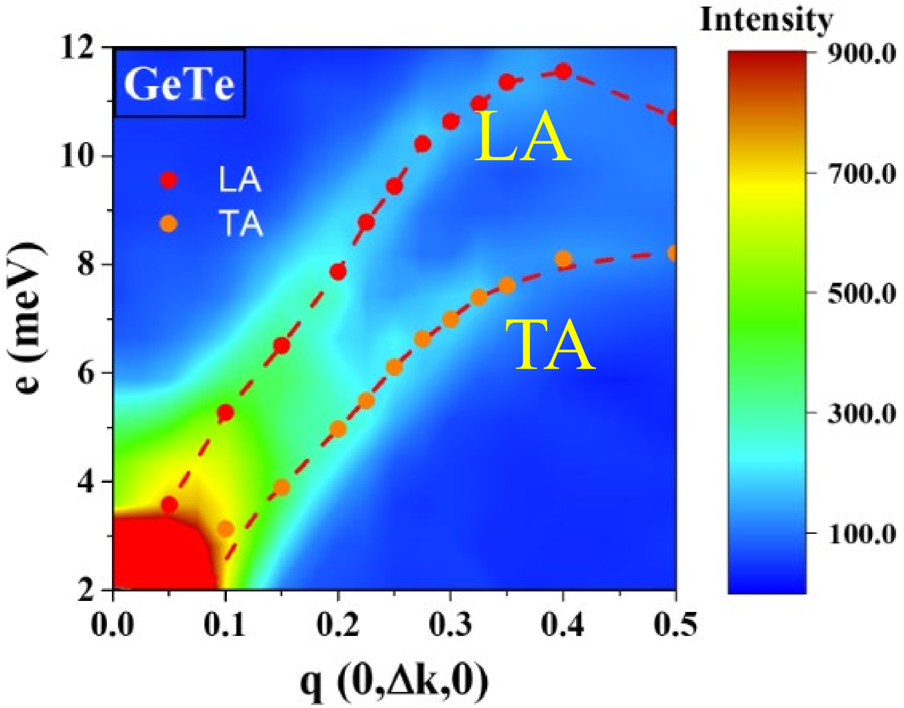
*Ranganayakulu K. Vankayala, Tian-Wey Lan, Prakash Parajuli, Fengjiao Liu, Rahul Rao, Shih Hsun Yu, Tsu-Lien Hung, Chih-Hao Lee, Shin-ichiro Yano, Cheng-Rong Hsing, Duc-Long Nguyen, Cheng-Lung Chen,* Sriparna Bhattacharya,* Kuei-Hsien Chen, Min-Nan Ou, Oliver Rancu, Apparao M. Rao, and Yang-Yuan Chen**

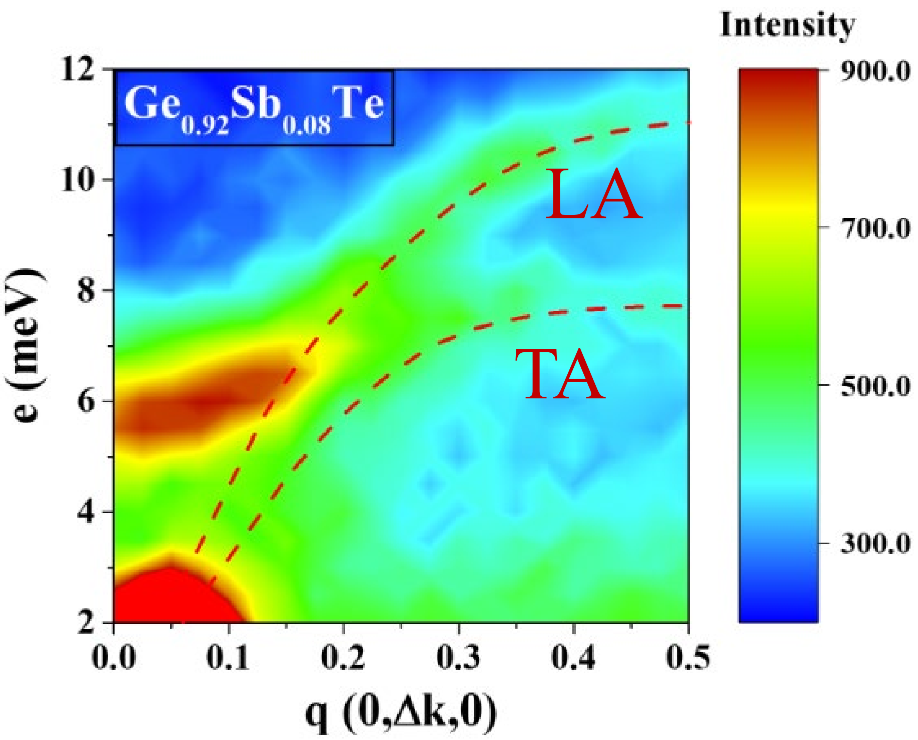
*Advanced Science*, Vol. 7, 2002494 (2020)




- A record high ***zT* of 2.2** at 740 K is reported in $Ge_{0.92}Sb_{0.08}Te$ crystals.
- Additional **phonon excitations** are discovered in $Ge_{0.92}Sb_{0.08}Te$ and help soften the phonon frequencies !

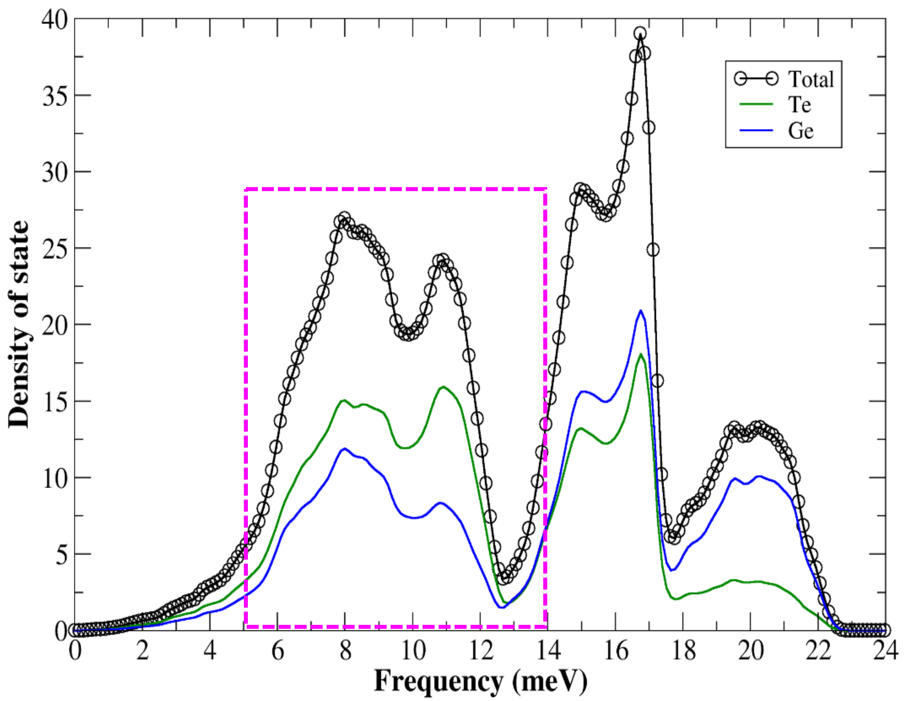
# Inelastic neutron scattering studies of GeTe and $Ge_{0.92}Sb_{0.08}Te$

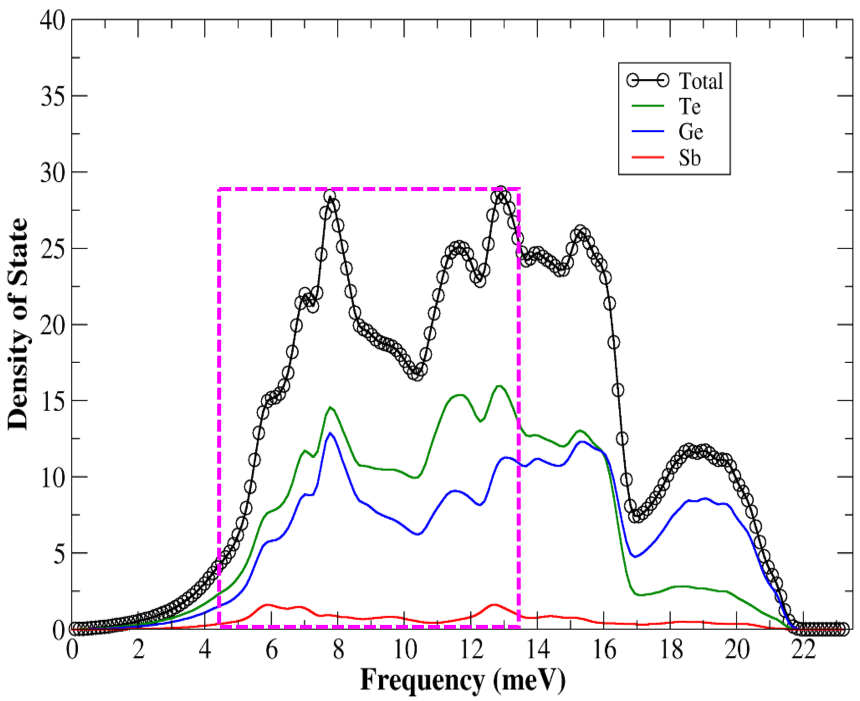



- Highlight the greater complexity of the phonon dispersion of Ge0.92Sb0.08Te compared to that of GeTe.
- An unexpected extra excitation between **5~7 meV** is observed in the $Ge_{0.92}Sb_{0.08}Te$ crystal.

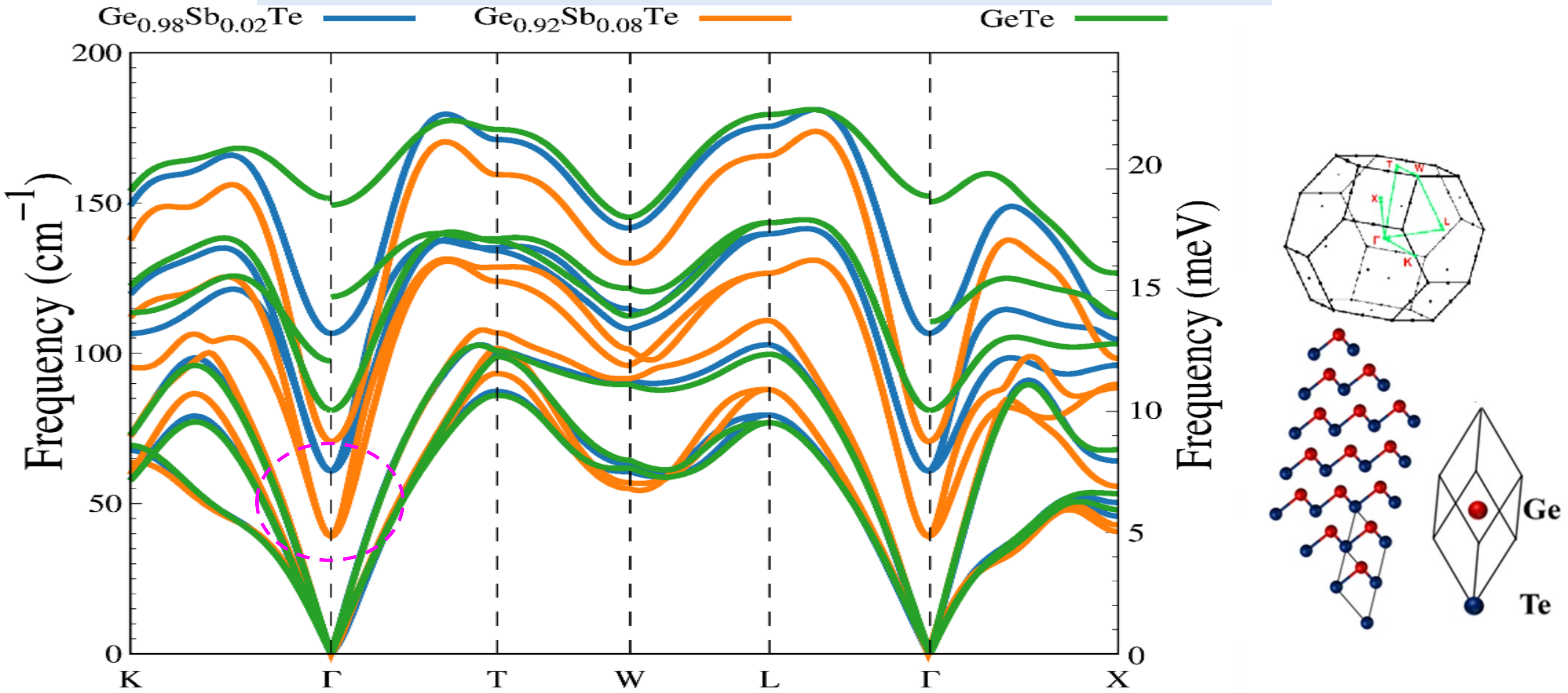
# Phonon density of state (PDOS)



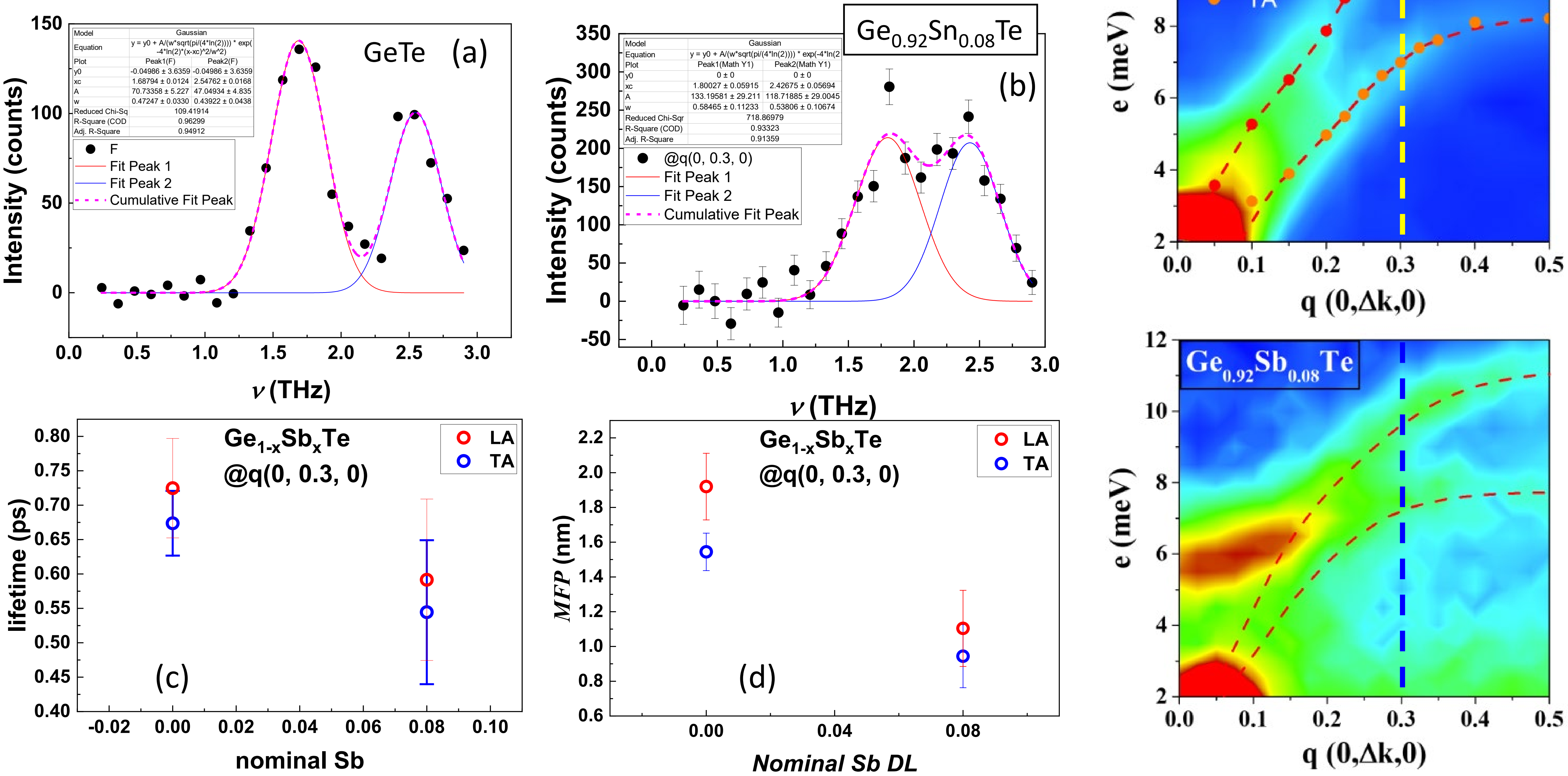

The results of PDOS show additional features between ≈ 5–7 and ≈12–13 meV for GST. We attribute these features to the presence of Sb dopants.

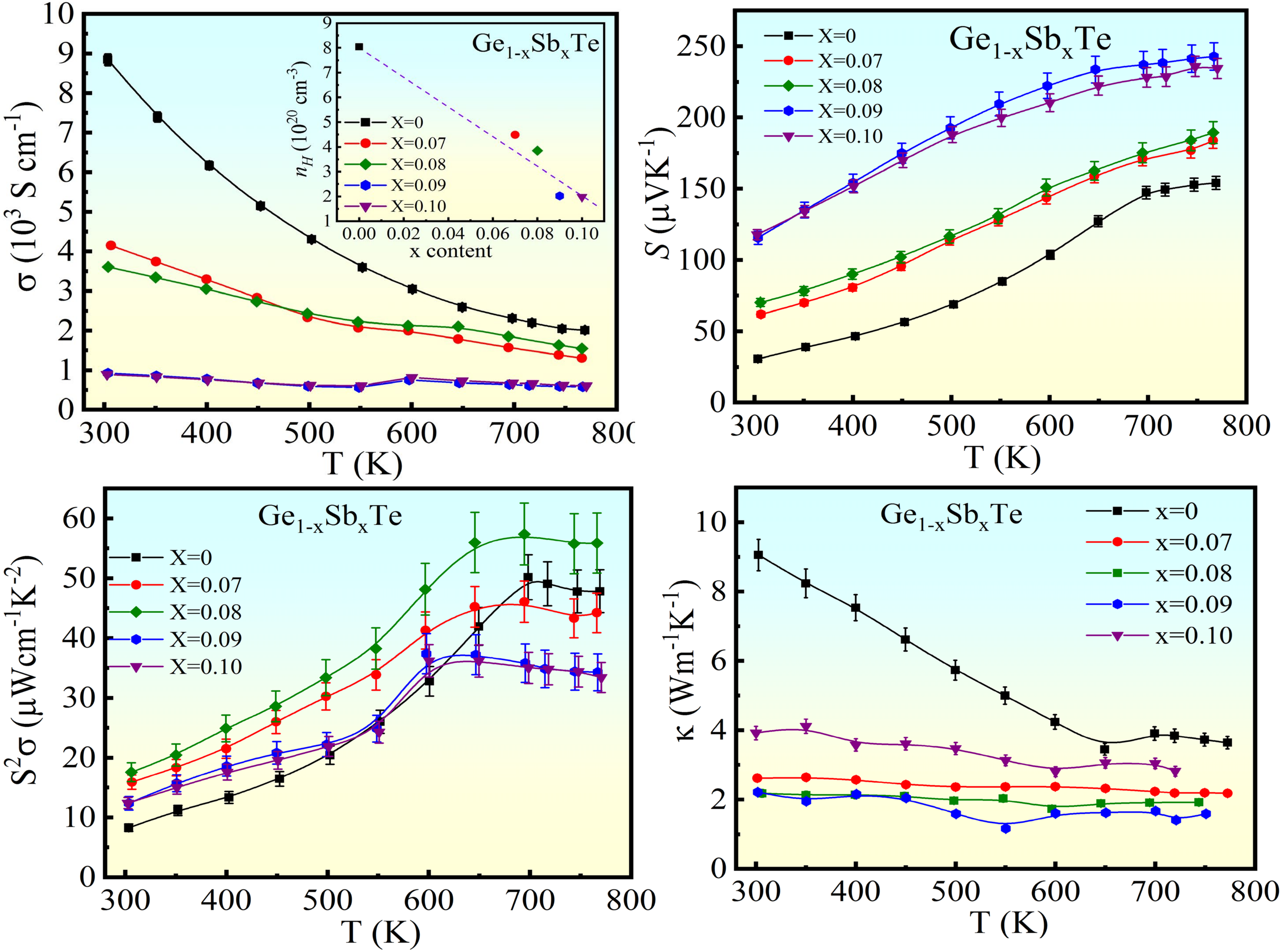
# Phonon density of state (PDOS)




- The overall phonon frequency got soften due to the Sb doping. For GeTe, in the Γ point, it cannot be found any phonon mode between 0~10 meV.
- The presence of a phonon ~ **5 meV** at the Γ point can clearly be seen in the dispersion of $Ge_{0.92}Sb_{0.08}Te$ (orange traces), which could provide extra decay channels for optical phonons, thereby increasing their scattering rate and lowering the thermal conductivity !

# Phonon transport





Ge1-xSbxTe
σ (10^3 S cm^-1)
T (K)
n_H (10^20 cm^-3)
x content
X=0
X=0.07
X=0.08
X=0.09
X=0.10
Ge1-xSbxTe
S (μVK^-1)
T (K)
X=0
X=0.07
X=0.08
X=0.09
X=0.10
Ge1-xSbxTe
S^2σ (μWcm^-1K^-2)
T (K)
X=0
X=0.07
X=0.08
X=0.09
X=0.10
Ge1-xSbxTe
κ (Wm^-1K^-1)
T (K)
x=0
x=0.07
x=0.08
x=0.09
x=0.10