

1st Russian thermoelectric school

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ITMO University sport center “Yagodnoe”, Russia

Approaches for improving zT of thermoelectric materials

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What is the thermoelectric figure of merit?

In 1909, the German engineer Edmund Altenkirch showed that the efficiency of a thermoelectric material is proportional to the square of the Seebeck coefficient, and the most efficient are those materials whose electrical and thermal conductivity ratio does not obey the Wiedemann-Franz law. He suggested the following figure of merit:

$$z = \frac{\alpha^2 \sigma}{\kappa} = \frac{\alpha^2}{\kappa \rho}$$

here z is the figure of merit (K^{-1}), α is the Seebeck coefficient, σ is the electrical conductivity, ρ is the electrical resistivity, and κ is the total thermal conductivity, which represents the sum of the lattice and electronic contributions of the thermal conductivity $\kappa = \kappa_{lat} + \kappa_{el}$.

In 1949 Ioffe proposed zT instead of z as material's thermoelectric figure of merit:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T = \frac{\alpha^2}{\kappa \rho} T$$

What is the thermoelectric figure of merit?

It is important to distinguish the material's figure of merit zT and the device figure of merit ZT . For example, the maximum efficiency of the thermoelectric generator (device) can be expressed as

$$\eta = \frac{T_{hot} - T_{cold}}{T_{hot}} \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_{cold}/T_{hot}}$$

where η is the efficiency, T_{hot} and T_{cold} are the temperatures of the hot and cold junctions, respectively, \bar{T} is the average temperature between the cold and hot junctions. Here $Z = z$ only if temperature is assumed to be independent and thermoelectric properties of n - and p -type legs are matched, which is unrealistic approximation in majority of cases.

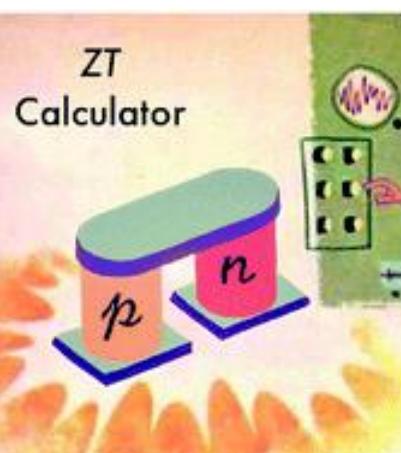
For thermocouple consisting of n - and p -type legs:

$$z\bar{T} = \frac{(z_p - z_n)^2 \bar{T}}{(\sqrt{\rho_n \kappa_n} + \sqrt{\rho_p \kappa_p})^2} \text{ while } Z\bar{T} = \left(\frac{T_{hot} - T_{cold}(1-\eta)}{T_{hot}(1-\eta) - T_{hot}} \right)^2 - 1$$

$$zT \neq ZT$$

ZT calculator

T (C)	Material	T (K)	Seebeck ($\mu\text{V/K}$)	resistivity ($10^{-3} \Omega \text{ cm}$)	thermal cond. (W/m K)	zT	max red eff	s (1/V)	u (1/V)	red eff	Φ	efficiency (V)	ZT
27	p-PbTe(Mg,Na)	300	106	0.71	2.52	0.19	4.3%	2.83	3.5000	4.1%	0.317		
52	p-PbTe(Mg,Na)	325	119	0.75	2.29	0.27	5.9%	3.26	3.5688	5.9%	0.319	0.4%	0.22
77	p-PbTe(Mg,Na)	350	131	0.81	2.09	0.36	7.6%	3.58	3.6430	7.6%	0.320	0.9%	0.26
102	p-PbTe(Mg,Na)	375	142	0.90	1.94	0.43	8.9%	3.70	3.7167	8.9%	0.322	1.5%	0.30
127	p-PbTe(Mg,Na)	400	154	1.01	1.79	0.52	10.4%	3.79	3.8061	10.4%	0.324	2.1%	0.34
152	p-PbTe(Mg,Na)	425	166	1.14	1.68	0.61	11.8%	3.81	3.9083	11.8%	0.326	2.7%	0.38
177	p-PbTe(Mg,Na)	450	178	1.28	1.57	0.71	13.3%	3.84	4.0218	13.3%	0.329	3.4%	0.42
202	p-PbTe(Mg,Na)	475	191	1.43	1.49	0.81	14.8%	3.83	4.1561	14.7%	0.331	4.2%	0.46
227	p-PbTe(Mg,Na)	500	205	1.59	1.40	0.95	16.5%	3.86	4.3206	16.4%	0.334	4.9%	0.50
252	p-PbTe(Mg,Na)	525	219	1.74	1.33	1.08	18.2%	3.87	4.5031	17.8%	0.337	5.7%	0.55
277	p-PbTe(Mg,Na)	550	229	1.90	1.26	1.21	19.6%	3.85	4.6827	19.0%	0.340	6.6%	0.59
302	p-PbTe(Mg,Na)	575	239	2.06	1.21	1.31	20.6%	3.79	4.8656	19.6%	0.343	7.4%	0.63
327	p-PbTe(Mg,Na)	600	247	2.22	1.16	1.42	21.7%	3.74	5.0637	20.2%	0.346	8.2%	0.67
352	p-PbTe(Mg,Na)	625	254	2.37	1.13	1.50	22.5%	3.66	5.2610	20.1%	0.349	8.9%	0.71
377	p-PbTe(Mg,Na)	650	258	2.52	1.09	1.58	23.2%	3.60	5.4512	20.0%	0.351	9.6%	0.74
402	p-PbTe(Mg,Na)	675	262	2.66	1.07	1.63	23.7%	3.51	5.6514	19.3%	0.354	10.3%	0.77
427	p-PbTe(Mg,Na)	700	266	2.80	1.04	1.70	24.3%	3.45	5.8775	18.6%	0.357	10.9%	0.79
452	p-PbTe(Mg,Na)	725	269	2.94	1.03	1.74	24.7%	3.35	6.1121	17.0%	0.359	11.5%	0.81
477	p-PbTe(Mg,Na)	750	269	3.08	1.02	1.73	24.6%	3.23	6.2871	14.9%	0.361	12.0%	0.82
502	p-PbTe(Mg,Na)	775	268	3.24	1.01	1.70	24.3%	3.10	6.4635	12.1%	0.362	12.4%	0.83
527	p-PbTe(Mg,Na)	800	268	3.42	1.01	1.67	24.1%	2.95	6.7206	8.0%	0.363	12.7%	0.82



ZT calculator: <http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/ztcalc.html>

G.J. Snyder, A.H. Snyder, Energy Environ. Sci. 10 (2017) 2280–2283.

TE module simulation from material's properties



Our website provides an easy way to compute the power and efficiency of thermoelectric generator modules from temperature-dependent thermoelectric properties. Since the simulator works on the client side, it does not collect any information.

Please follow the three steps below to complete a simulation.

Step 1: Input Thermoelectric Properties

You can directly edit the table or paste (Ctrl+V) spreadsheet (excel) data into the table. CLICK THE GRAY AREA of target table when you paste something. Be careful as PASTING WILL REPLACE the entire table.

Seebeck coefficient			Electrical resistivity			Thermal conductivity		
	Temp. [...] ▲	[v/K] ▲		Temp. [...] ▲	[Ω m] ▲		Temp. [...] ▲	[W/m/K] ▲
<input type="checkbox"/>	300	1.40e-4	<input type="checkbox"/>	350	4.00e-5	<input type="checkbox"/>	300	4.50
<input type="checkbox"/>	400	1.70e-4	<input type="checkbox"/>	400	5.00e-5	<input type="checkbox"/>	400	3.90
<input type="checkbox"/>	500	2.00e-4	<input type="checkbox"/>	500	6.67e-5	<input type="checkbox"/>	500	3.60
<input type="checkbox"/>	600	2.20e-4	<input type="checkbox"/>	600	8.00e-5	<input type="checkbox"/>	600	3.50
<input type="checkbox"/>	700	2.30e-4	<input type="checkbox"/>	700	8.00e-5	<input type="checkbox"/>	700	3.50
<input type="checkbox"/>	800	2.40e-4	<input type="checkbox"/>	800	6.67e-5	<input type="checkbox"/>	800	3.60
<input type="checkbox"/>	900	2.30e-4	<input type="checkbox"/>	900	5.00e-5	<input type="checkbox"/>	850	4.00

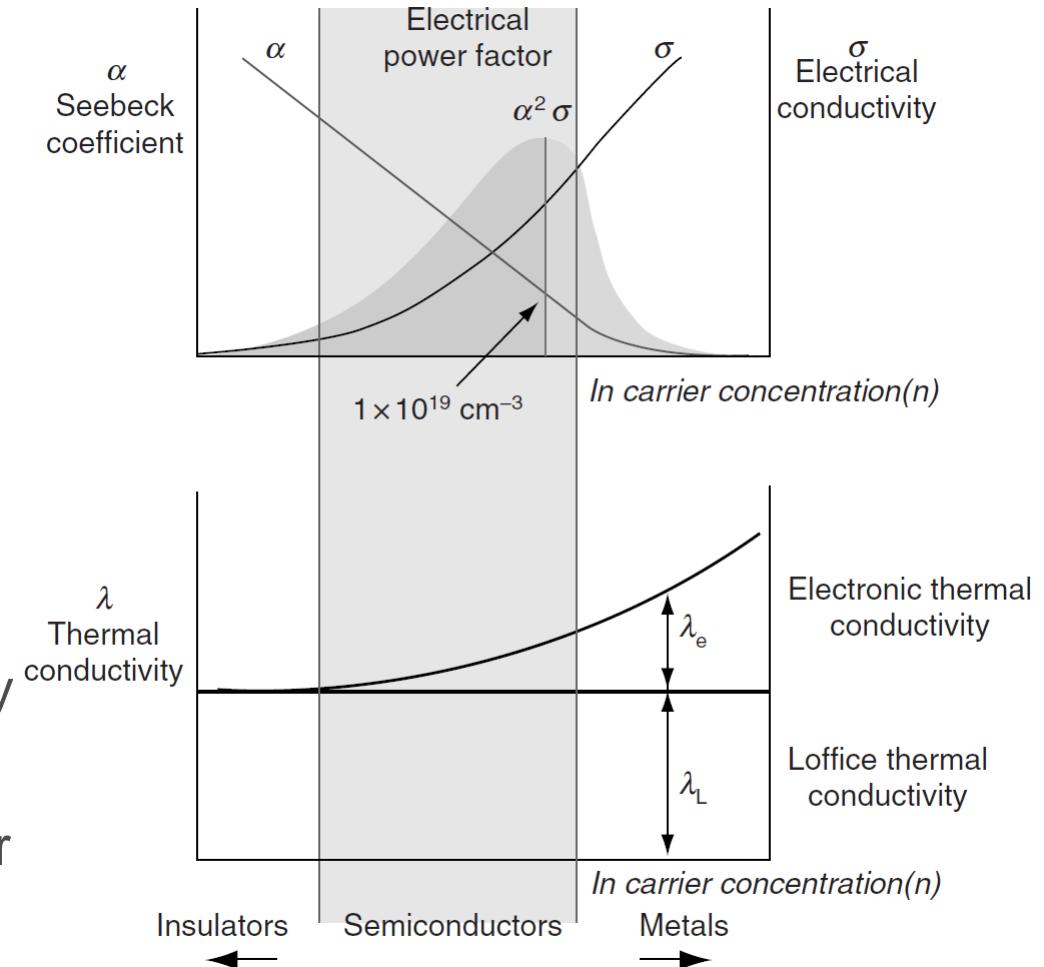
Strategies for the zT improvement

$$zT = \frac{\alpha^2 \sigma}{\kappa} T = \frac{\alpha^2 \sigma}{\sigma LT + \kappa_{lat}} T$$

There are two most intuitive strategies that comes to mind when you see the formula for the figure of merit:

- (1) maximization of the power factor $\alpha^2 \sigma$,
- (2) minimization of the lattice thermal conductivity κ_{lat} .

However, all the transport properties α , σ , and κ are strongly coupled and the main challenge is to tailor them in optimal way in order to develop thermoelectric material with superior performance.

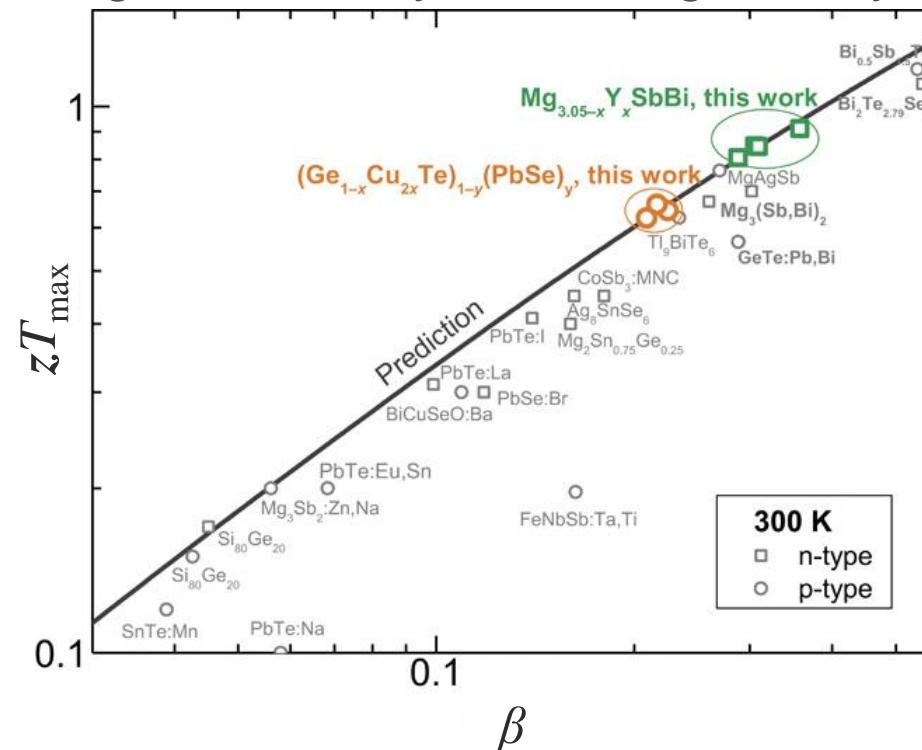


Quality factor

So-called quality factor B (or β) was firstly introduced in the late 50's and it determines the maximum attainable zT for a given material into its most fundamental material properties, assuming optimized carrier concentration:

$$B \propto \frac{\mu_w}{\kappa_{lat}} T^{5/2}$$

here $\mu_w = \mu_0 \left(\frac{m_d^*}{m_e} \right)^{3/2}$ is the weighted mobility, which is generally higher for multiband semiconductors.



Quality factor

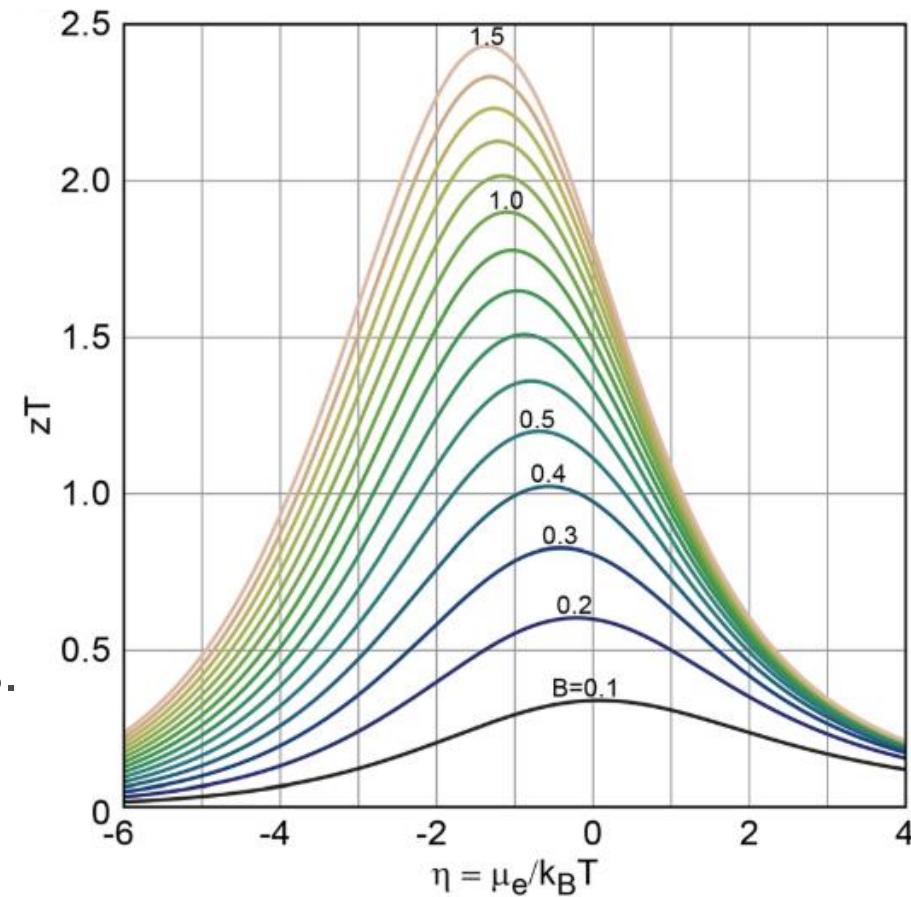
Many researchers using B as a metric for search of promising thermoelectric because B depends on temperature, but not doping, while giving an insight of the potential thermoelectric performance of material for a given chemical potential.

It also gives a valuable understanding on what kind of materials can potentially be effective as thermoelectric performance.

For example, in the framework of deformation potential

$$\tau_0 \propto 1/(m_b^*)^{3/2}, \mu_0 = e\tau_0/m_I^*, \text{ and } m_d^* = N_v^{2/3} m_b^*, \text{ thus,}$$
$$B \propto N_v/(m_I^* \kappa_l).$$

In this context, the most promising thermoelectrics should be among multiband semiconductors with low inertial effective mass.



Lattice thermal conductivity

Based on Leibfried and Schlömann model (lately corrected by Slack), the lattice thermal conductivity at high temperature $T > \theta_D$:

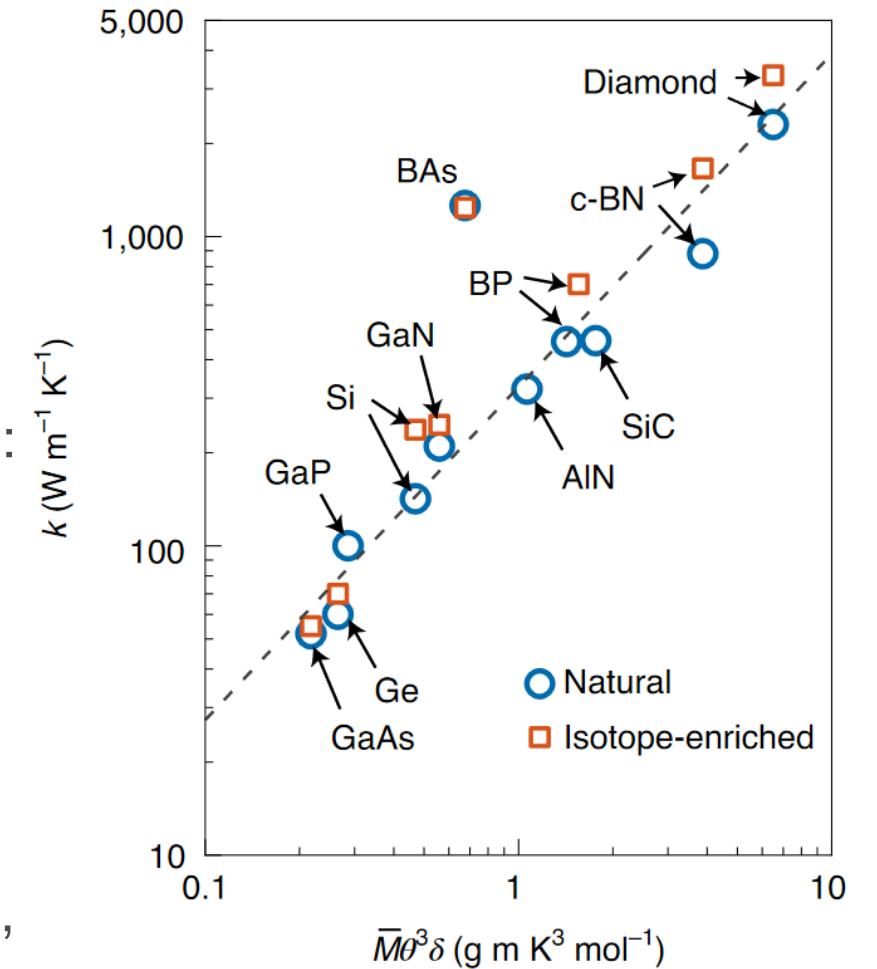
$$\kappa_{lat} = A \left(\frac{k_B \theta_D}{\hbar} \right)^3 \frac{\bar{M} \delta}{\gamma^2 N_{Av} n^{5/3} T}$$

where N_{Av} is the Avogadro constant, n is the number of atoms in the unit cell (molecule), $\delta^3 = V_{at}$, V_{at} is the average volume per atom, $A = f(\gamma)$.

Thus, several rules for low thermal conductivity can be formulated:

- (1) high mass of constituent atoms ($\bar{M} \delta \theta_D^3$ is maximized for light mass);
- (2) weak interatomic bonding;
- (3) complex crystal structure;
- (4) high anharmonicity.

Conditions (1) and (2) means a low θ_D , condition (3) means high n , and condition (4) means high γ .



J.R. Drabble, H.J. Goldsmid, Thermal Conduction in Semiconductors, Pergamon Press, (1963).

D.T. Morelli, G.A. Slack, in: S.L. Shindé, J.S. Goela (Eds.), High Therm. Conduct. Mater., Springer, New York, 2006, pp. 37–68.

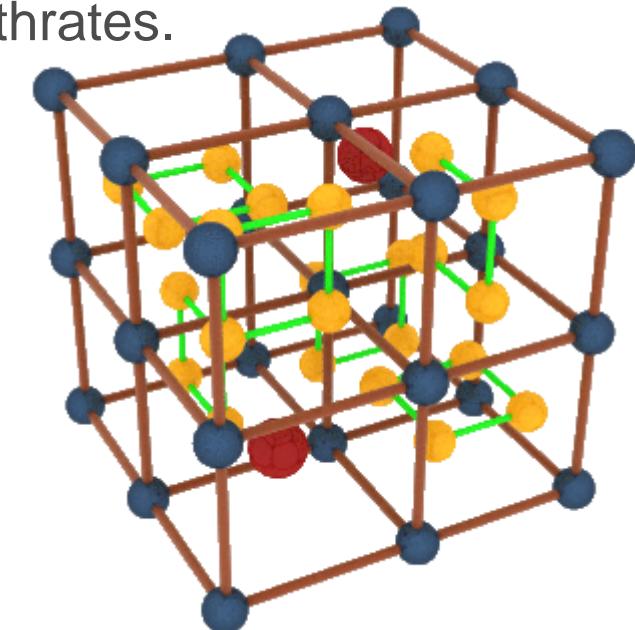
Fig. from X. Qian, J. Zhou, G. Chen, Nat. Mater. (2021)

G.A. Slack, J. Phys. Chem. Solids 34 (1973) 321–335.

Phonon glass electron crystal

In 1995 Glen A. Slack formulated the requirements for a thermoelectric materials in his concept of phonon glass electron crystal (PGEC) as follows: an effective thermoelectric material should conduct electricity effectively as a single crystal conductor and poorly conduct heat like glass. The most prominent representatives of this concept are skutterudites and clathrates.

In such systems, the guest atom can “rattle” around the center in the cage. This rattling motion is expected to scatter the low-energy acoustic phonons and, thus, decrease the thermal conductivity to values typically seen in glass. The electrons, on the other hand, can flow through the network of the cage as in a crystalline metal.



Crystal structure of
 $R\text{CoSb}_3$ skutterudite (R is
the rattling guest atom)



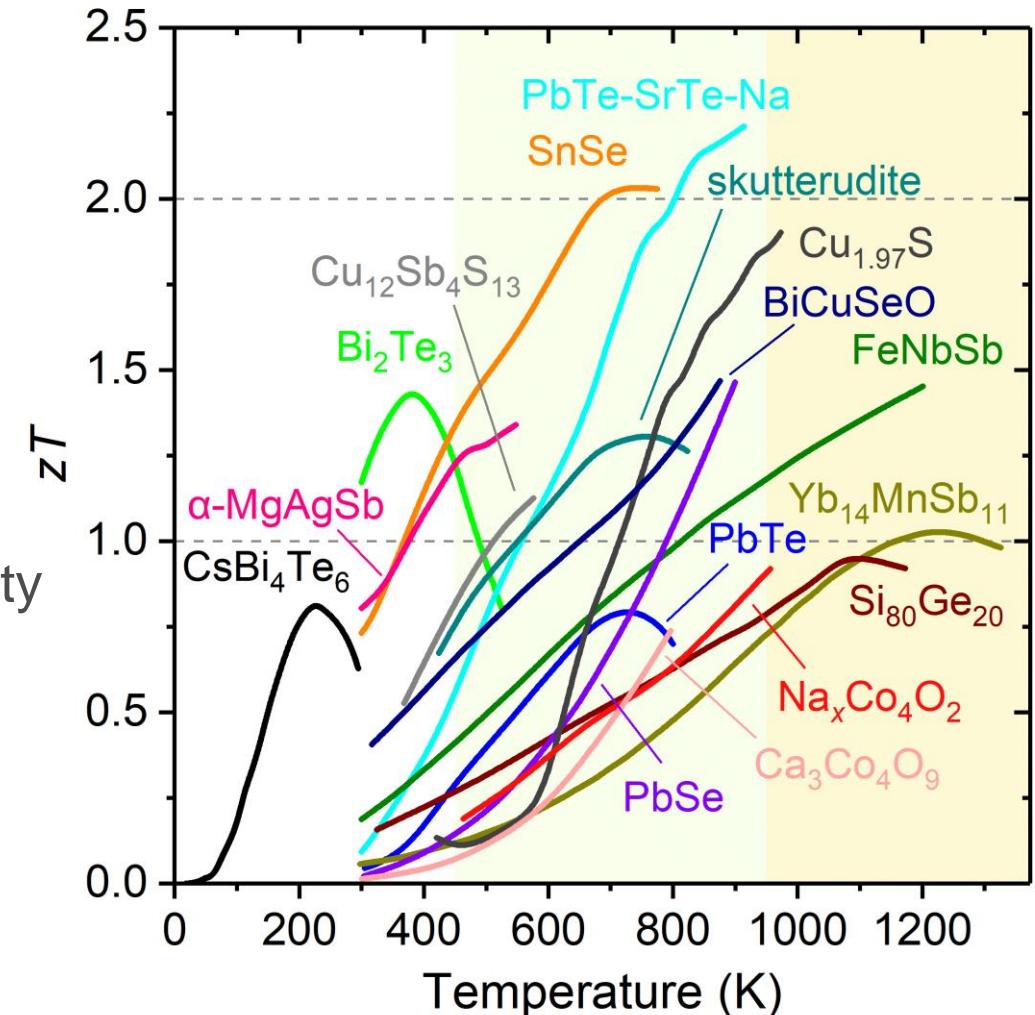
Summary

What are we looking for?

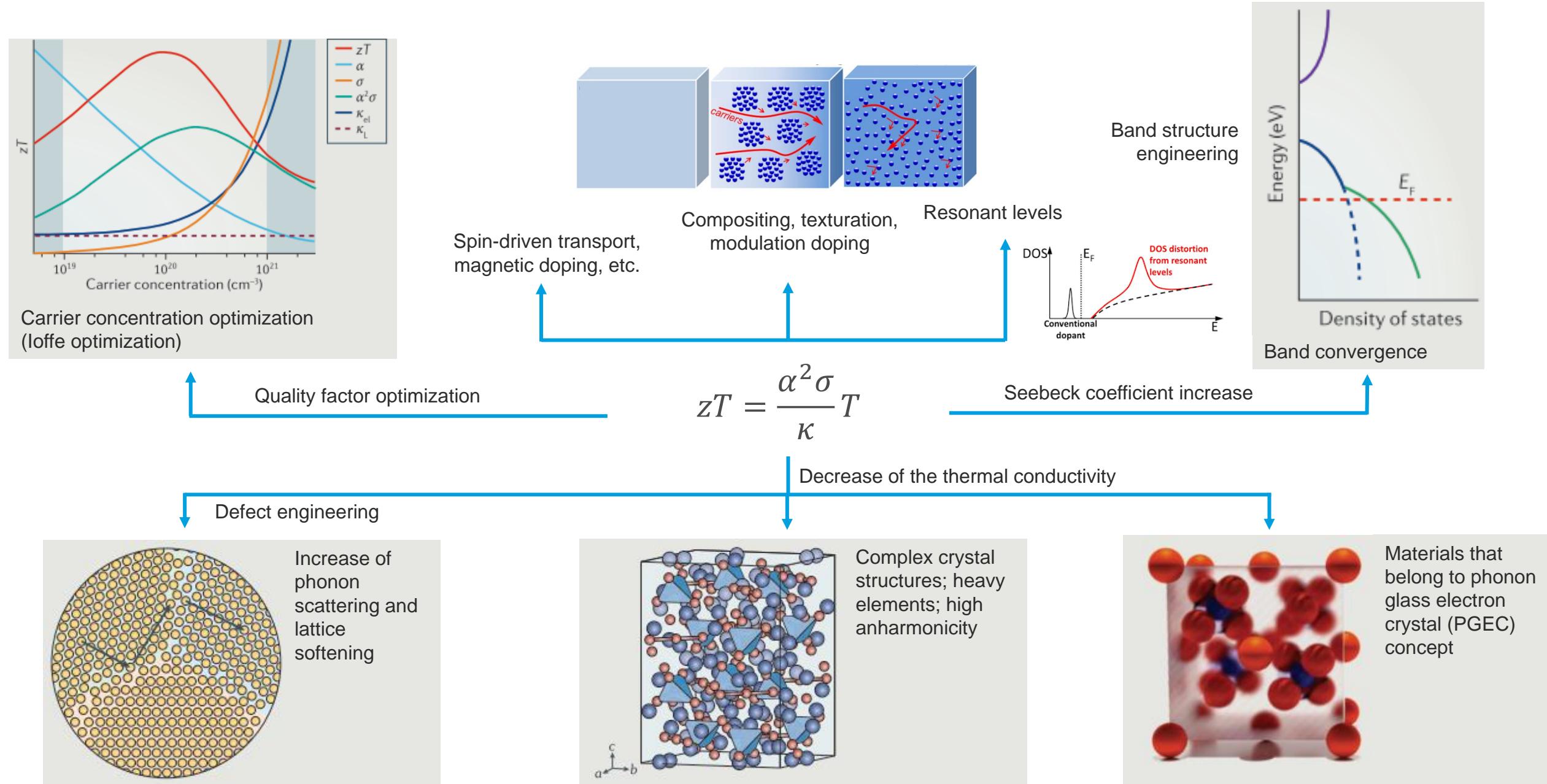
Doped (optimal n) multiband semiconductors (high μ_w) with complex crystal structure mainly composed of heavy elements (low κ_{lat}).

Along with that we also should remember that the following things are also important:

- The abundance of the constituent elements
- Chemical and thermal stability of material under working conditions
- Complexity of the synthesis technique and its scalability
- Ability to develop paired leg of another type of conductivity



Approaches for improving zT



Phonon scattering

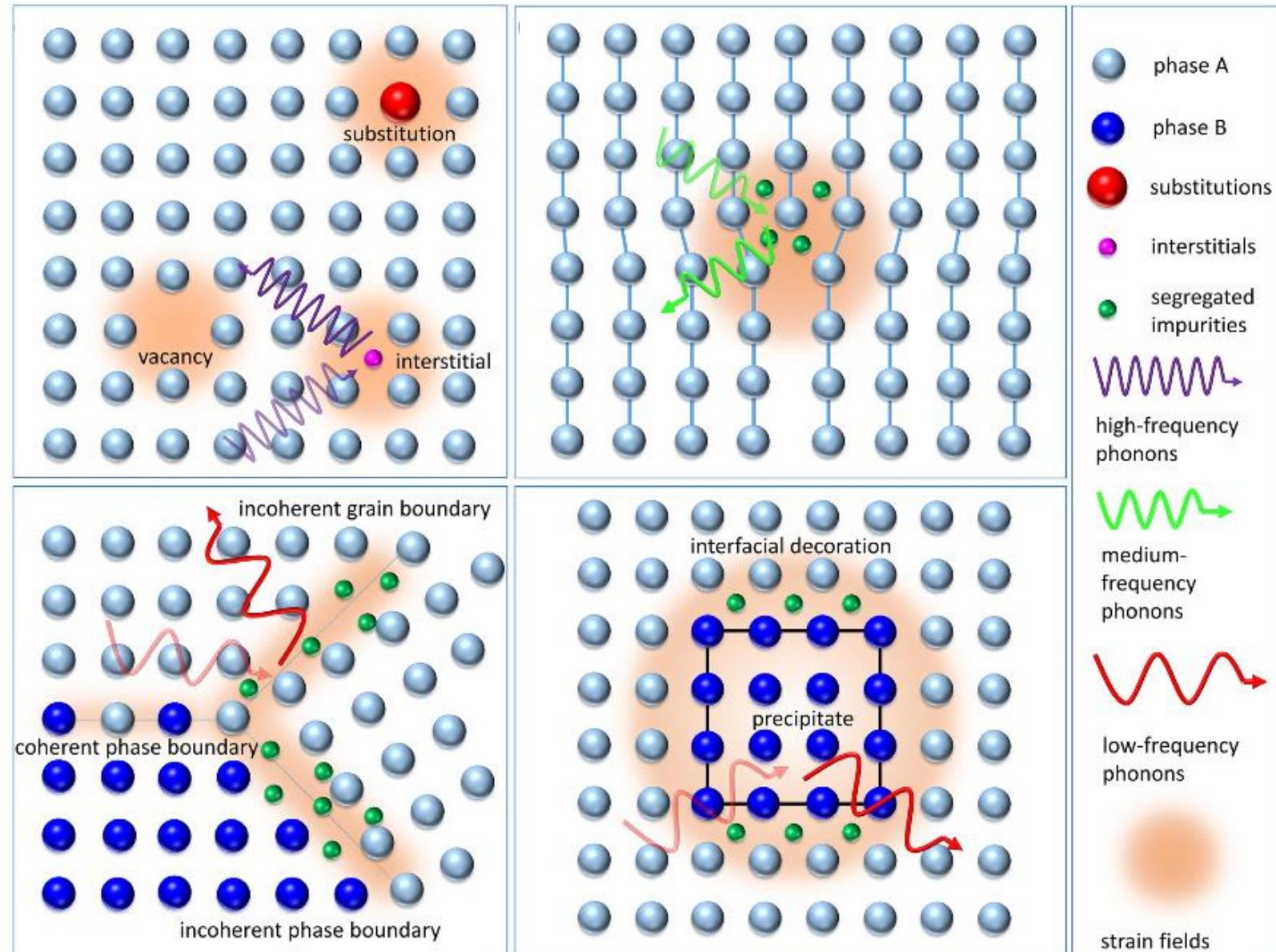
$$\kappa_{lat} = \frac{1}{3} \int C(\omega) v^2(\omega) \tau_c(\omega) d\omega$$

Debye model:

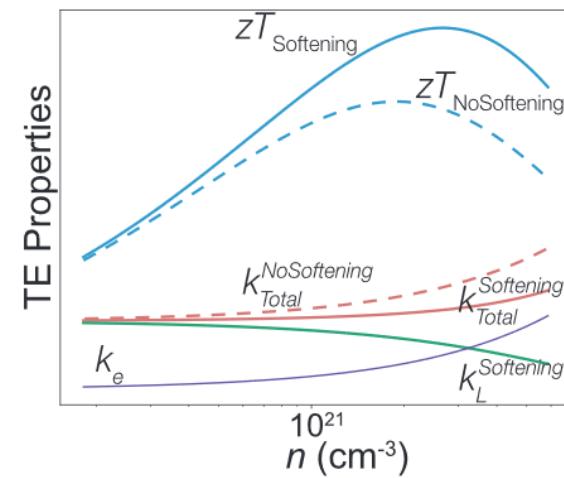
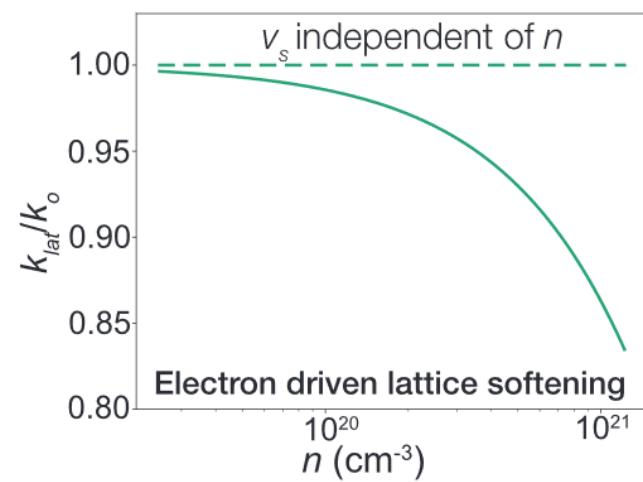
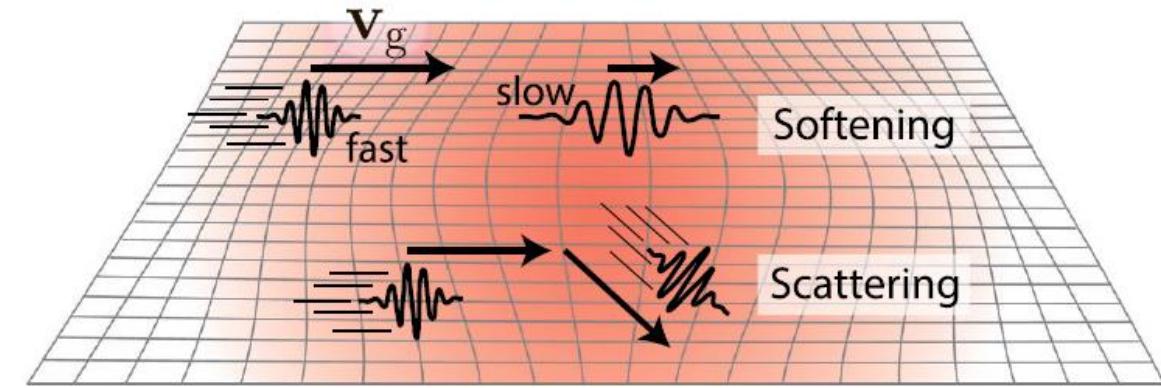
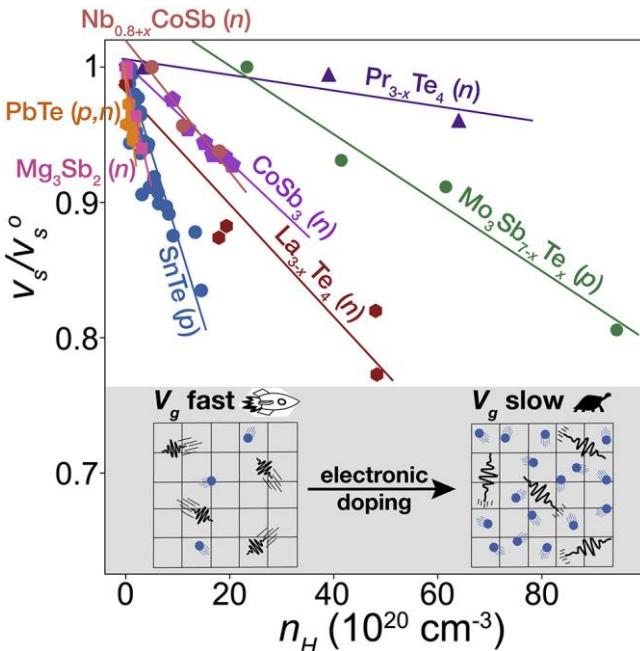
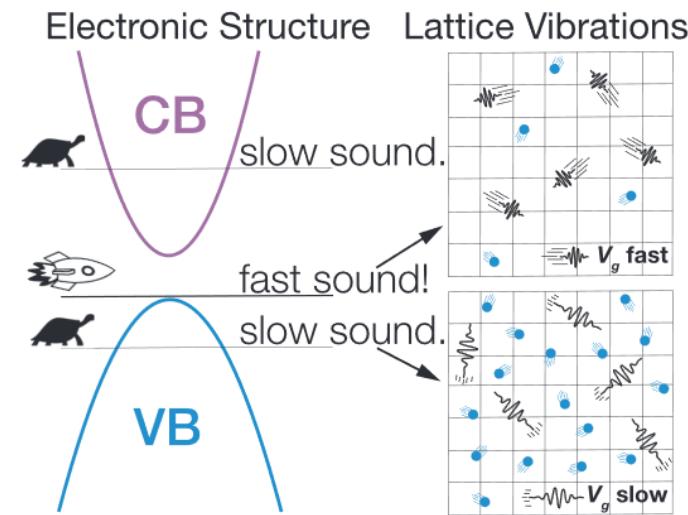
- phonon velocity is constant
- scattering channels are independent of each other

$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m} \left(\frac{k_B T}{\hbar} \right)^3 \cdot \int_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\frac{1}{\tau_c(x)} = \sum_i \frac{1}{\tau_i(x)}$$



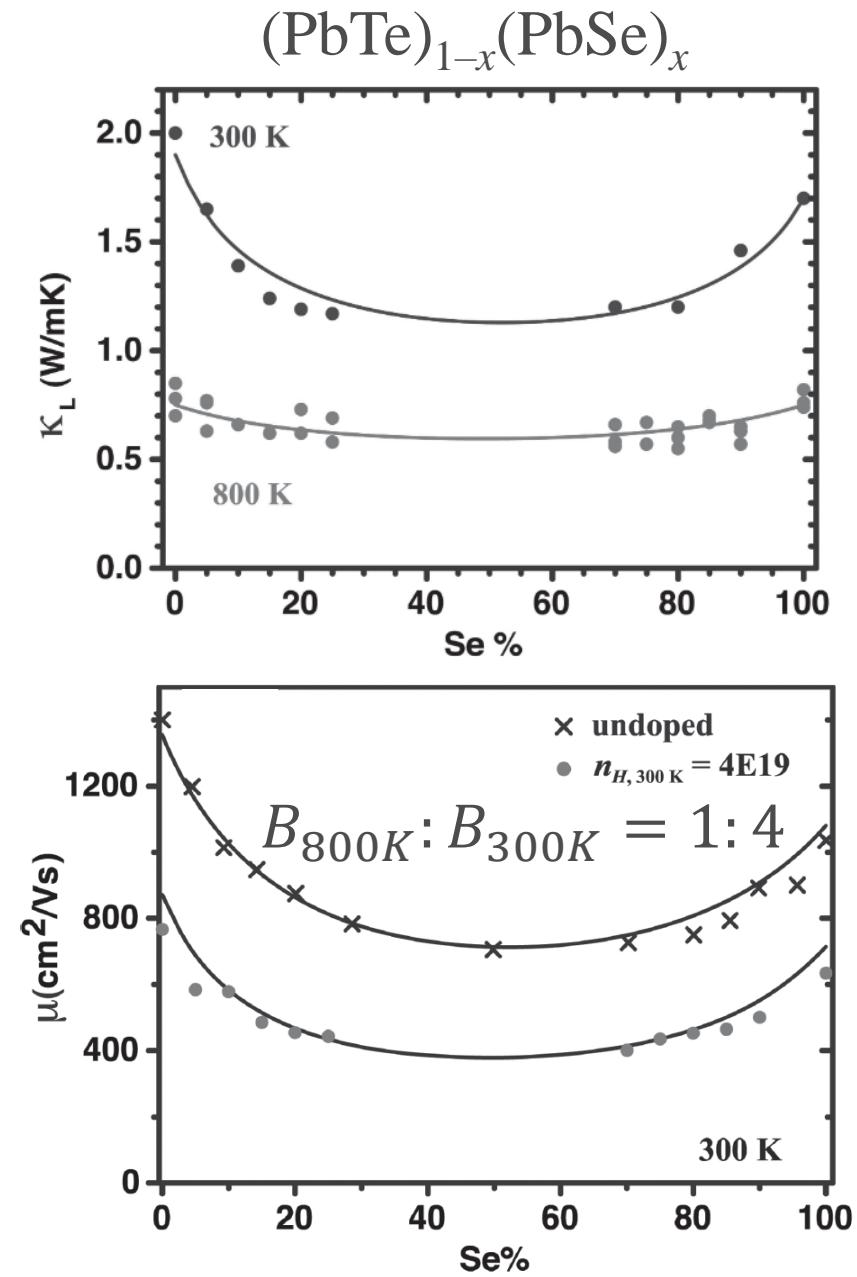
Lattice softening



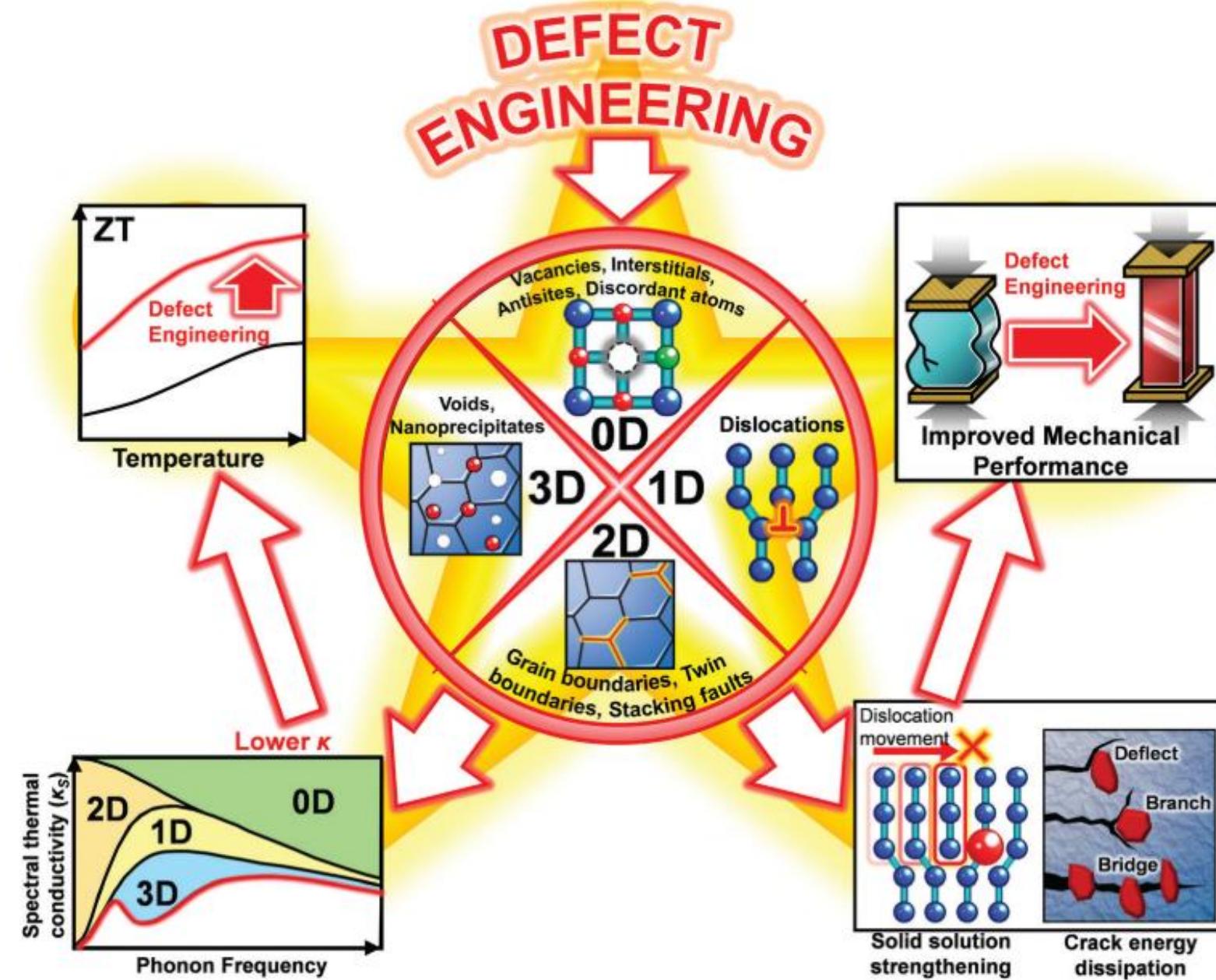
$$\kappa_{lat} = A \left(\frac{v_m^3}{T} \right)$$

Carrier concentration optimization

This approach is based on the theory of solid solutions proposed by A.F. Ioffe in 1956. Introduction of substitutional atoms leads to a distortion of the crystal lattice and thus to an increase in scattering of both phonons and charge carriers. This results in a decrease of the charge carrier mobility and the lattice thermal conductivity. However, their decrease is disproportional; accordingly, at some point in the chemical composition, a situation can be reached where the drop in the lattice thermal conductivity is much more significant than the drop in the mobility. In other words, it can be stated that this method is devoted to the optimization of the quality factor $B \propto \mu_w / \kappa_{lat}$ (see Figure).

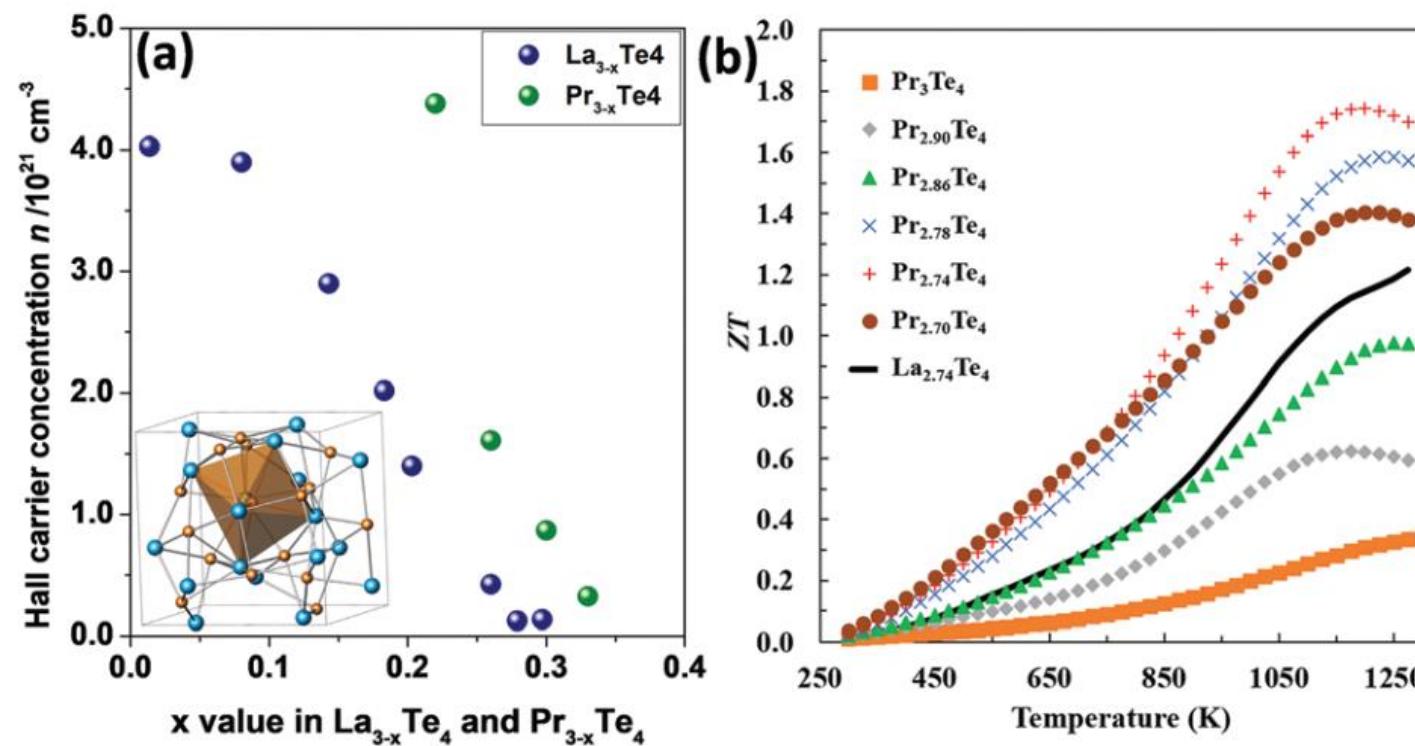


Defect engineering



Defect engineering. Point defects

- Dopants (charge carrier optimization)
- Vacancies
- Interstitial atoms
- Antisites
- Weak bonded guest atoms (rattlers)

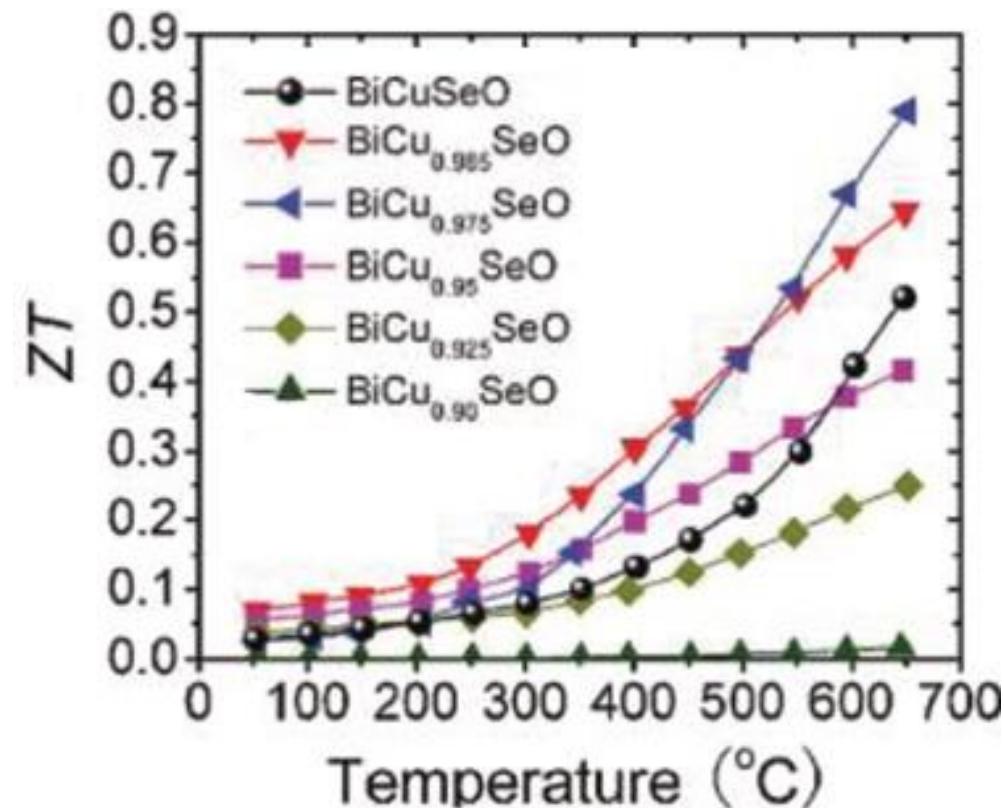


1e per formula unit in $R_3\text{Te}_4$
when xV_R is formed the number of
electrons is reduced by $(1-3x)$

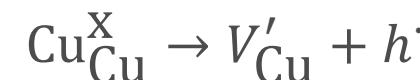
n-type

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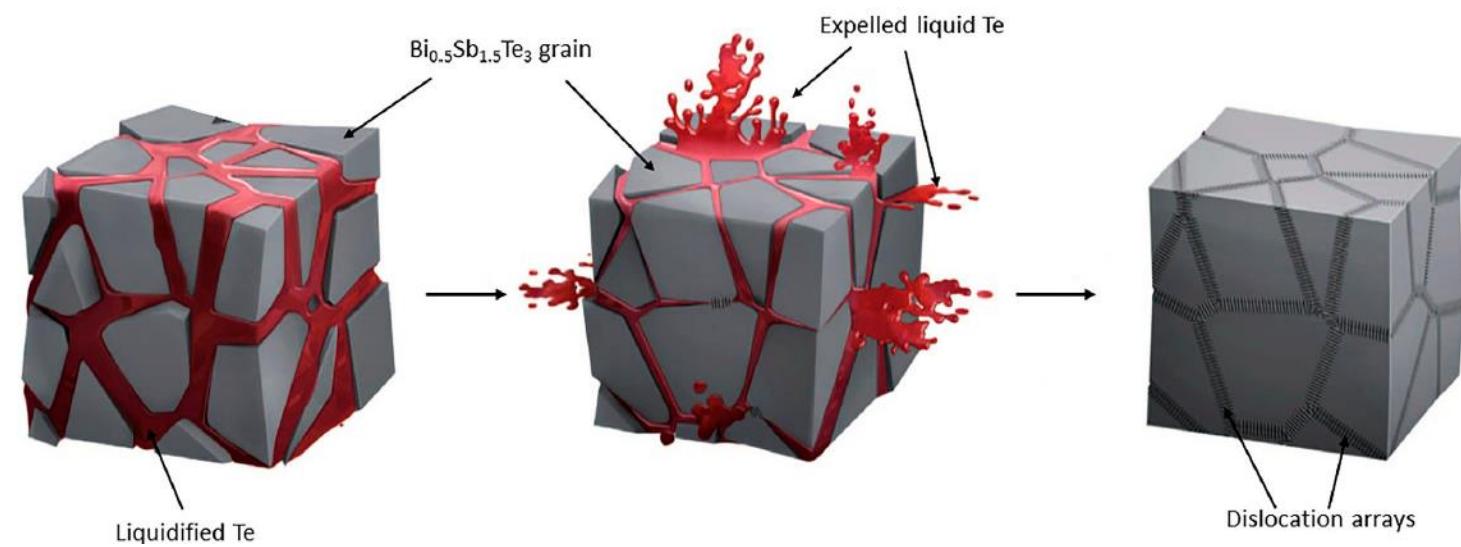


Stoichiometry control: vacancies at copper site leads to enhancement of the charge carriers concentration in BiCuSeO oxyselenides



p-type

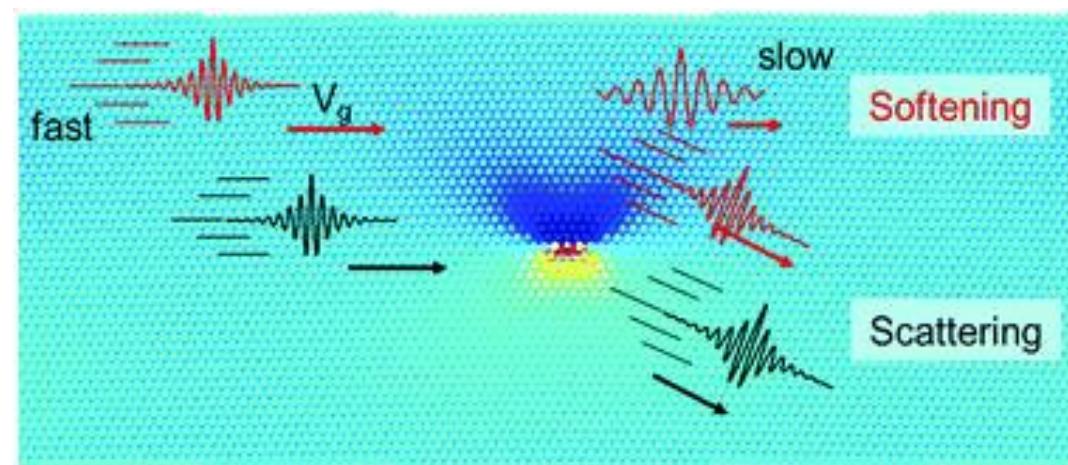
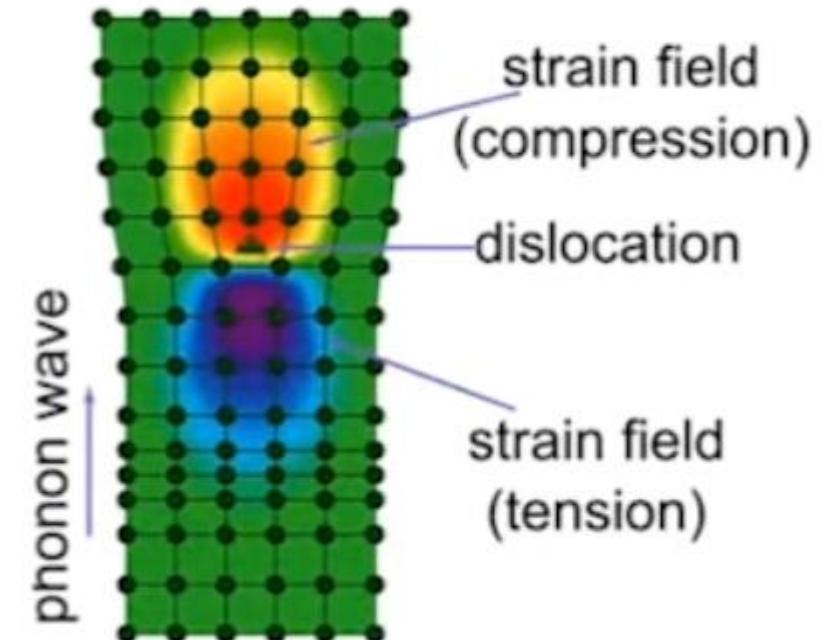
Defect engineering. Dislocations



THERMOELECTRICS

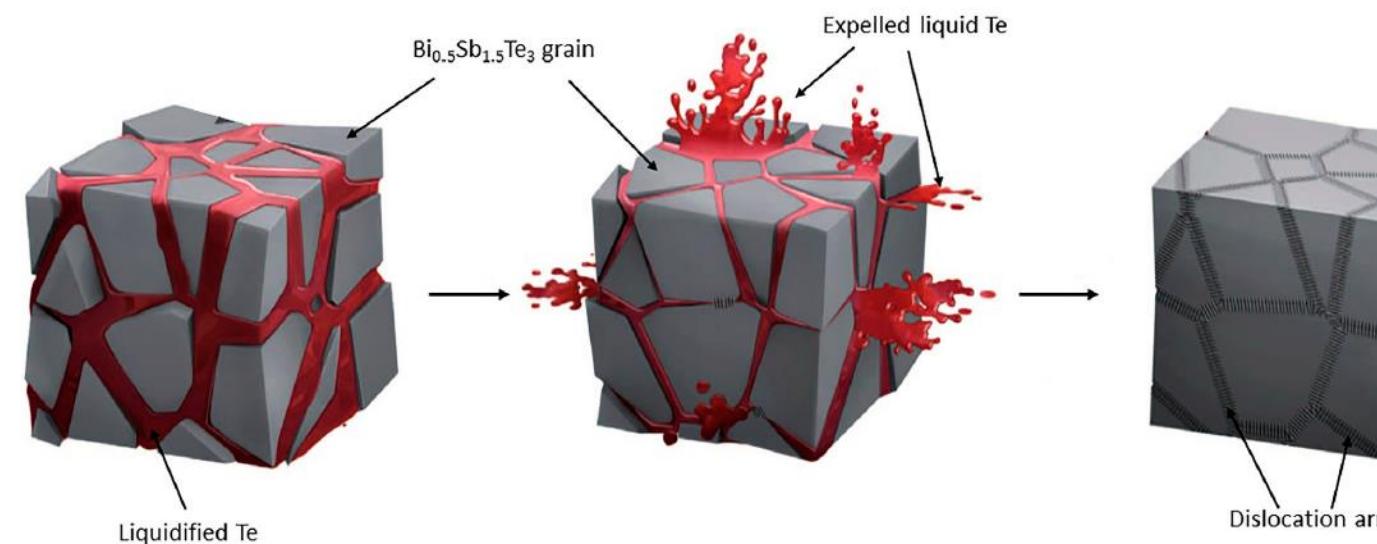
Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics

Sang Il Kim,^{1*}† Kyu Hyoung Lee,^{2*} Hyeon A Mun,^{3,4*} Hyun Sik Kim,^{1,5}
Sung Woo Hwang,¹ Jong Wook Roh,¹ Dae Jin Yang,¹ Weon Ho Shin,¹ Xiang Shu Li,¹
Young Hee Lee,^{3,4} G. Jeffrey Snyder,^{3,5} Sung Wng Kim^{3,4†}



S. Kim, et al., Science. 348 (2015) 109–114.
Y. Sun, et al., J. Mater. Chem. C 9 (2021) 8506–8514.
H.-S. Kim, et al., Mater. Horizons 3 (2016) 234–240.

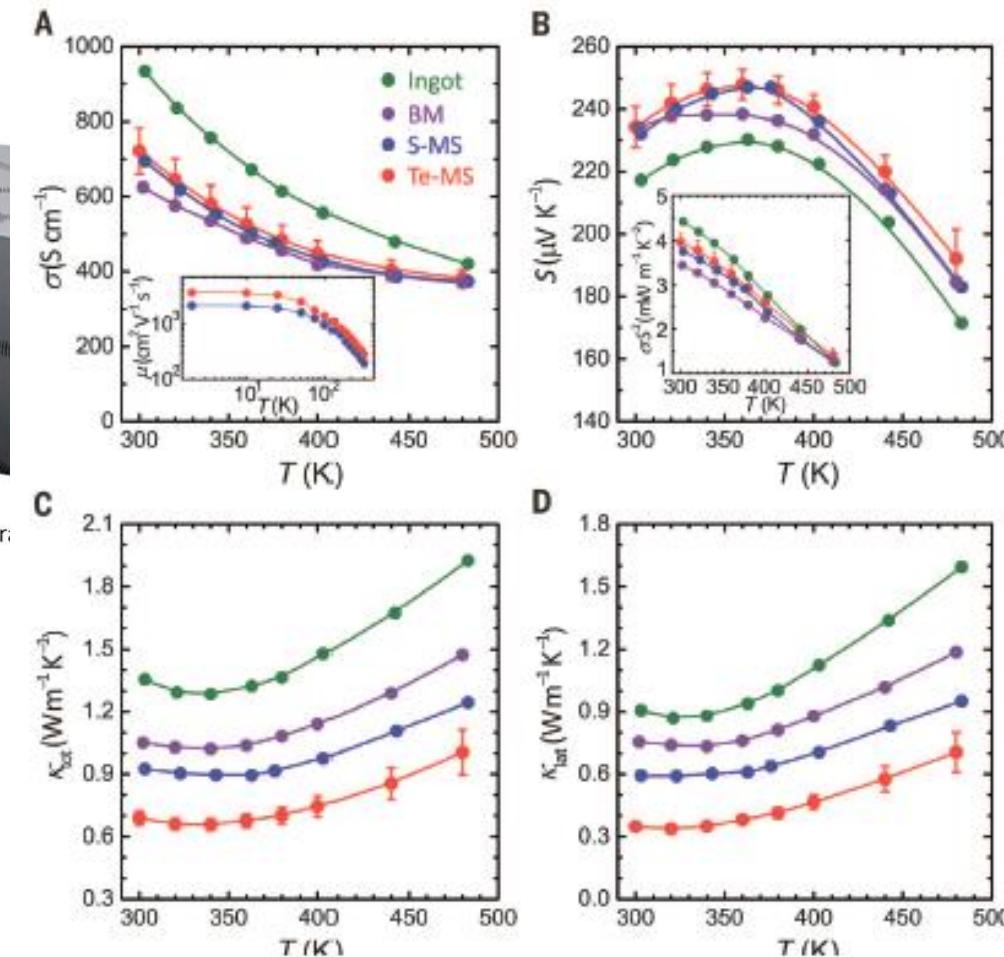
Defect engineering. Dislocations



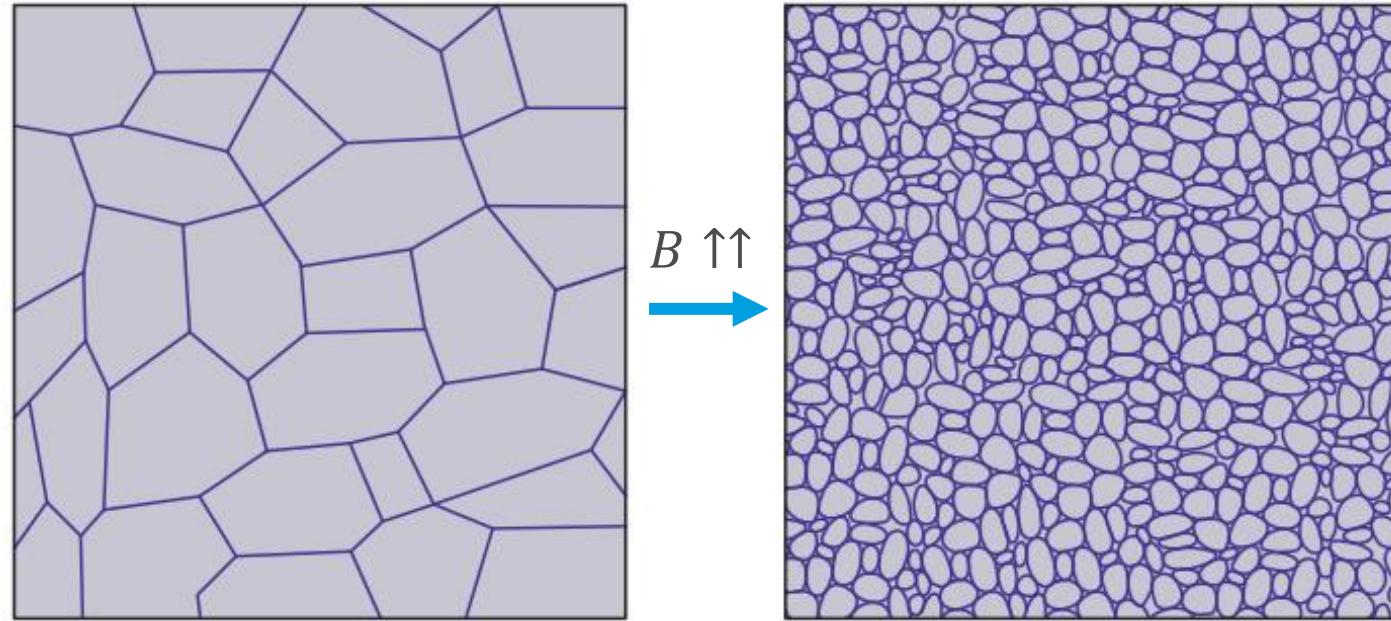
THERMOELECTRICS

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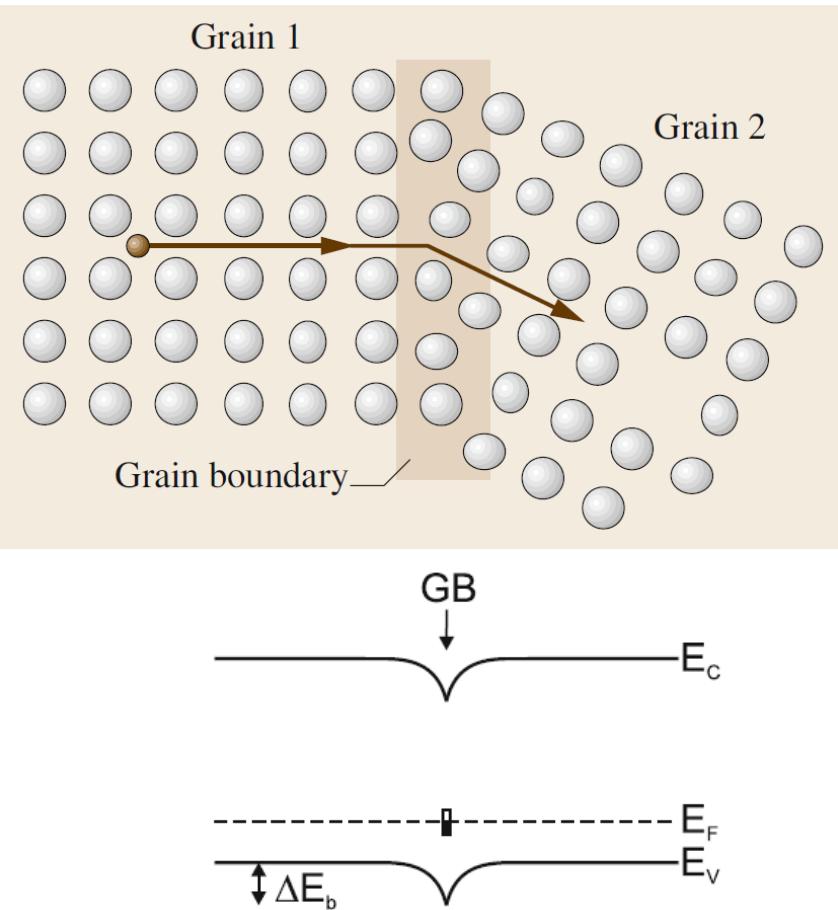
Defect engineering. Nanostructuring



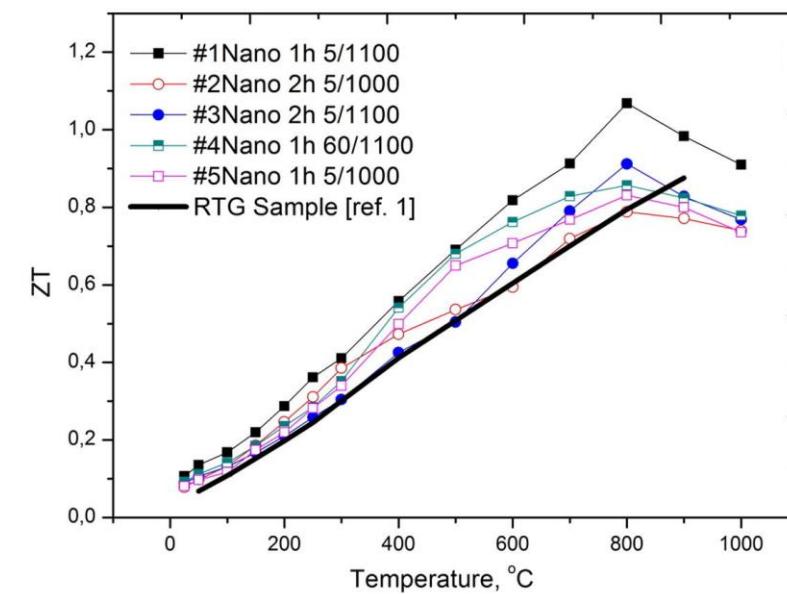
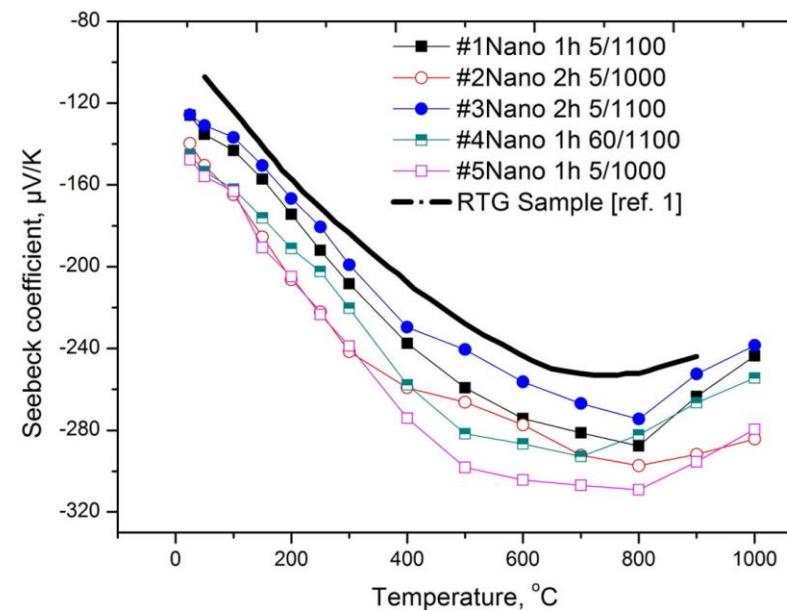
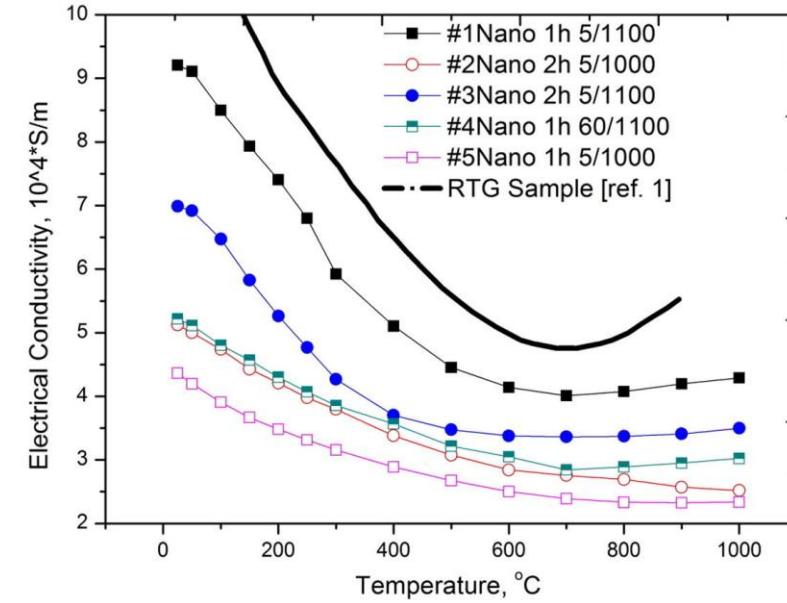
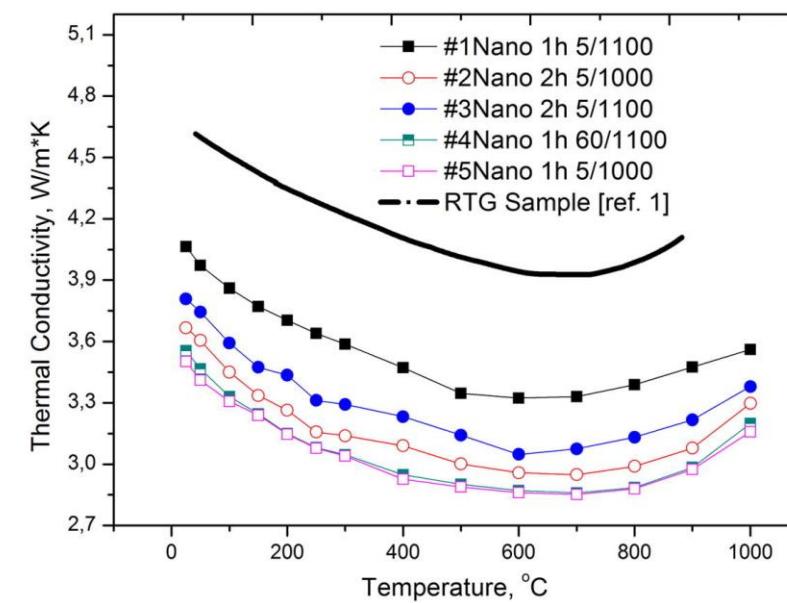
$$\kappa_{lat} = \frac{k_B}{2\pi^2 v_m} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\frac{1}{\tau_c(x)} = \frac{1}{\tau_{gb}(x)} = \frac{v_m}{L_G}$$

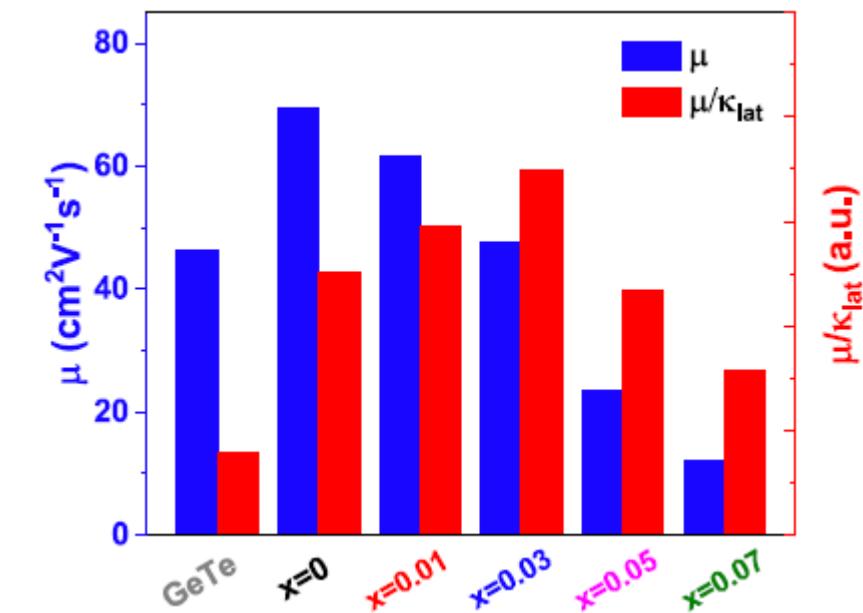
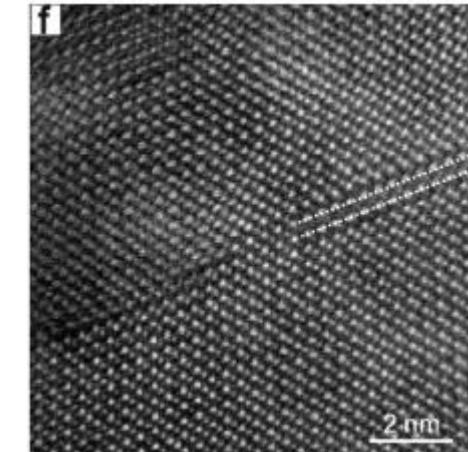
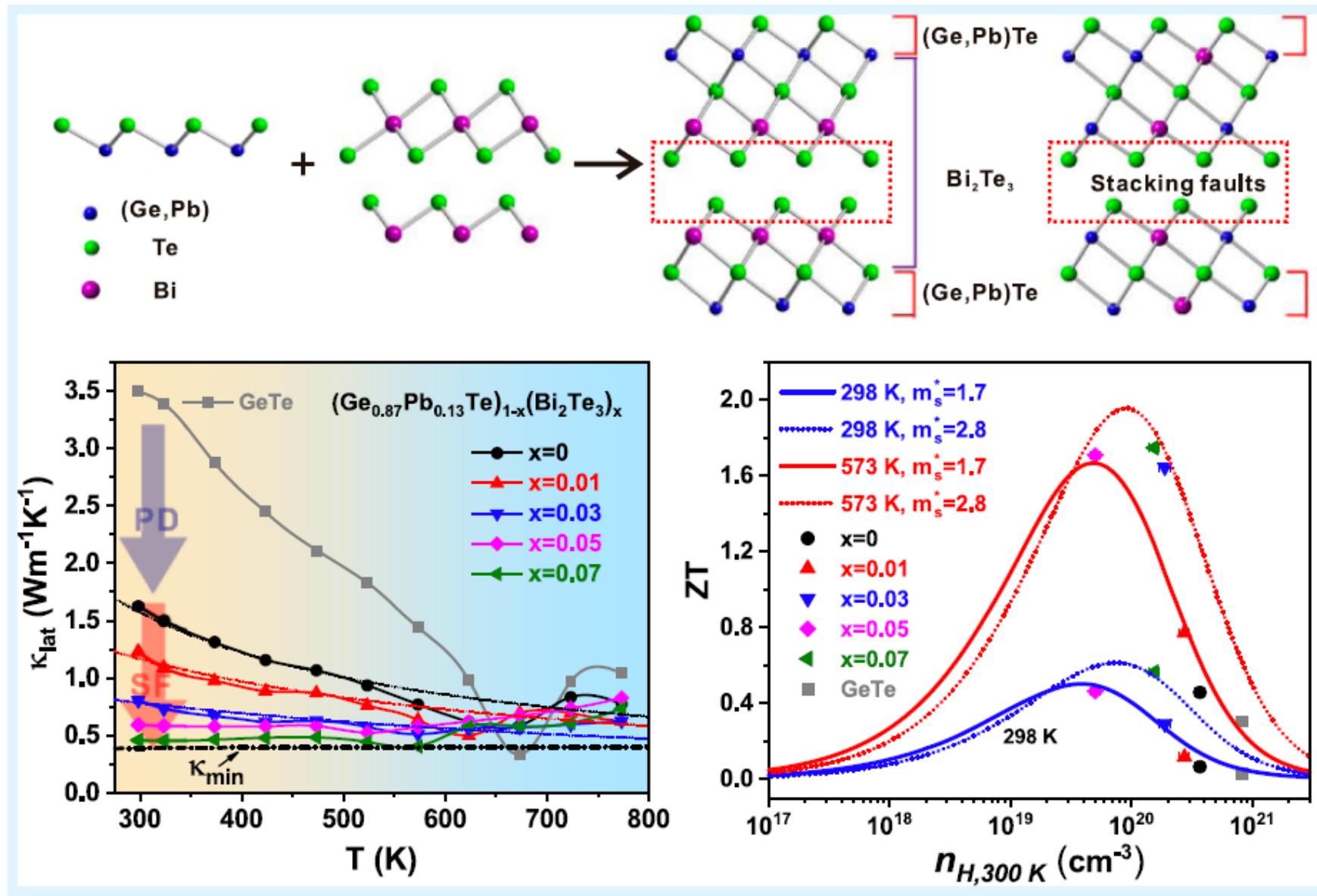
$$\mu_H \propto \frac{e L_G}{\sqrt{8m^* \pi k_B}} T^{-1/2} e^{-\Delta E_b/(k_B T)}$$



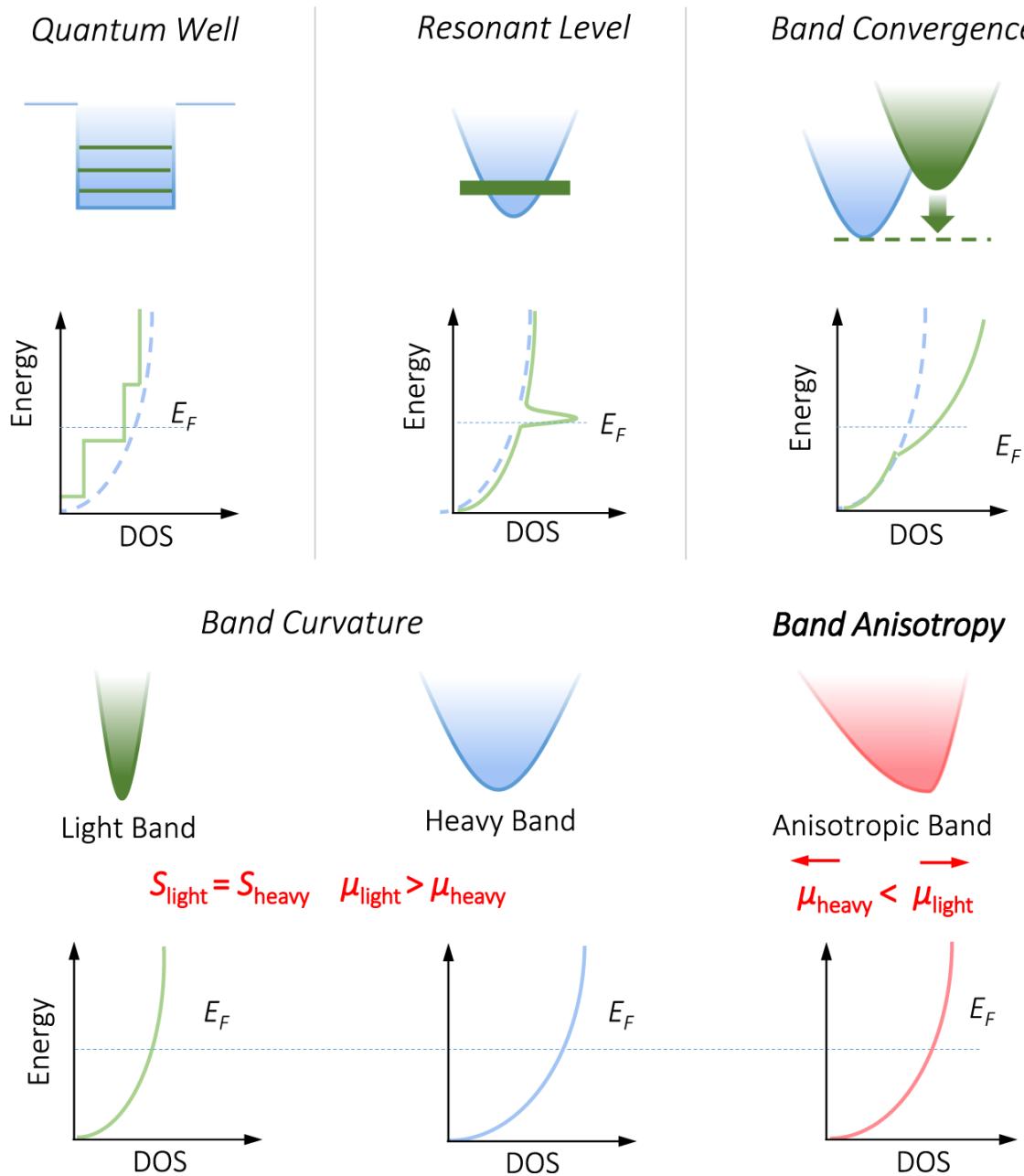
Defect engineering. Nanostructuring



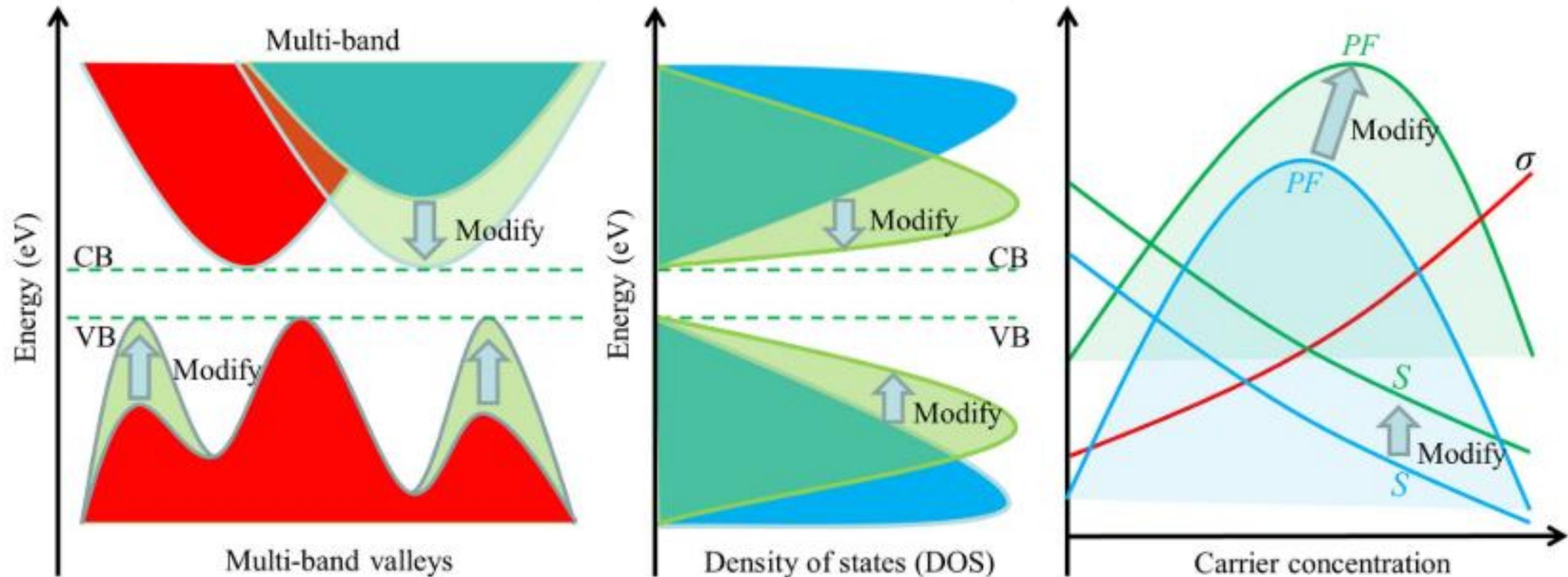
Defect engineering. Nanostructuring



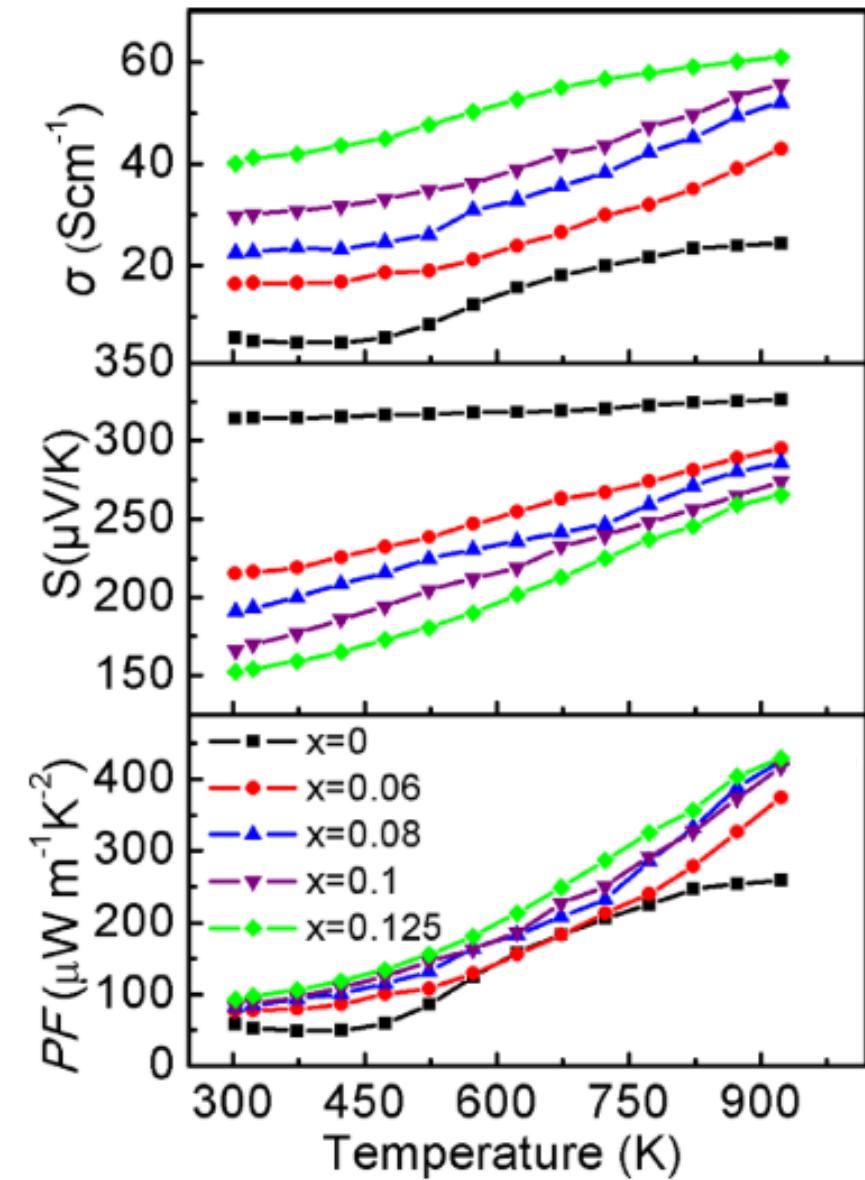
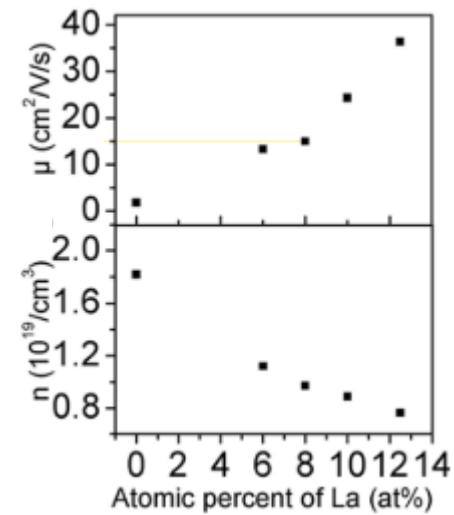
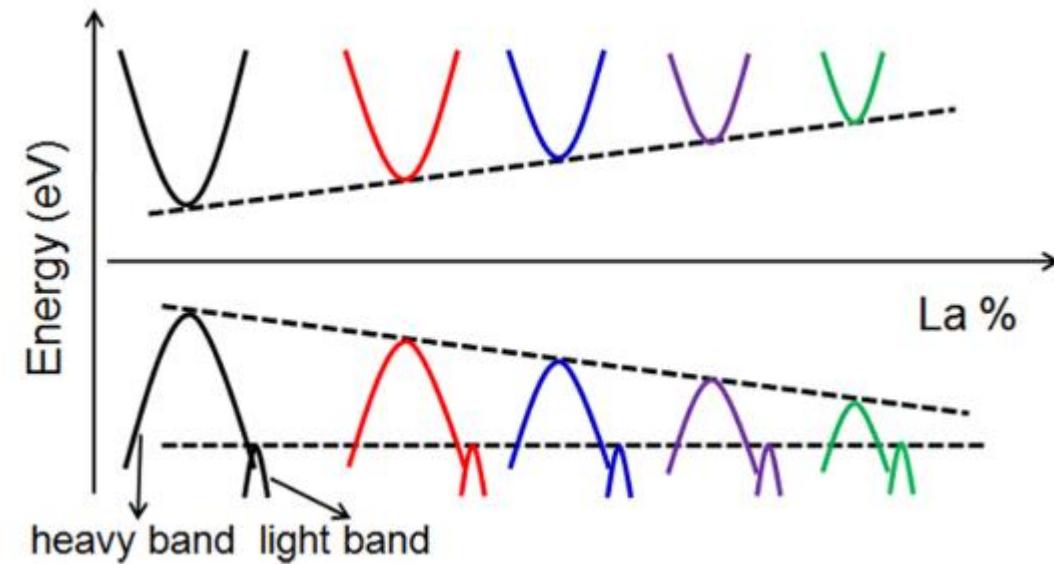
Band structure engineering



Band structure engineering



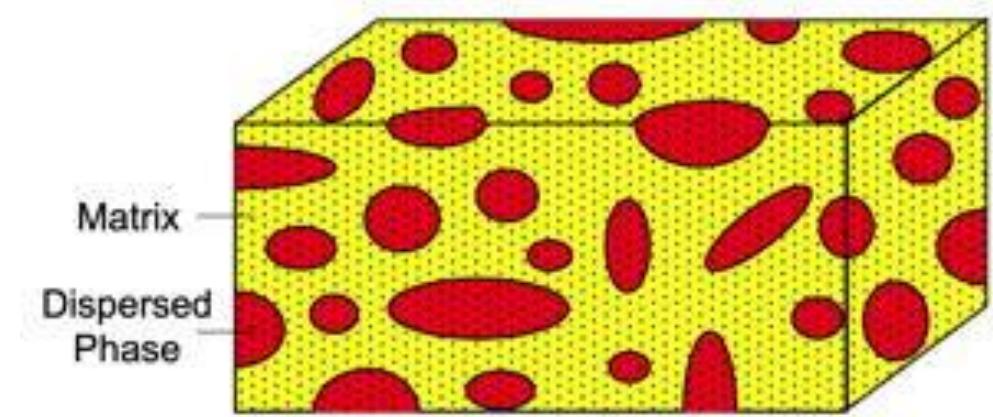
Band structure engineering



Composites

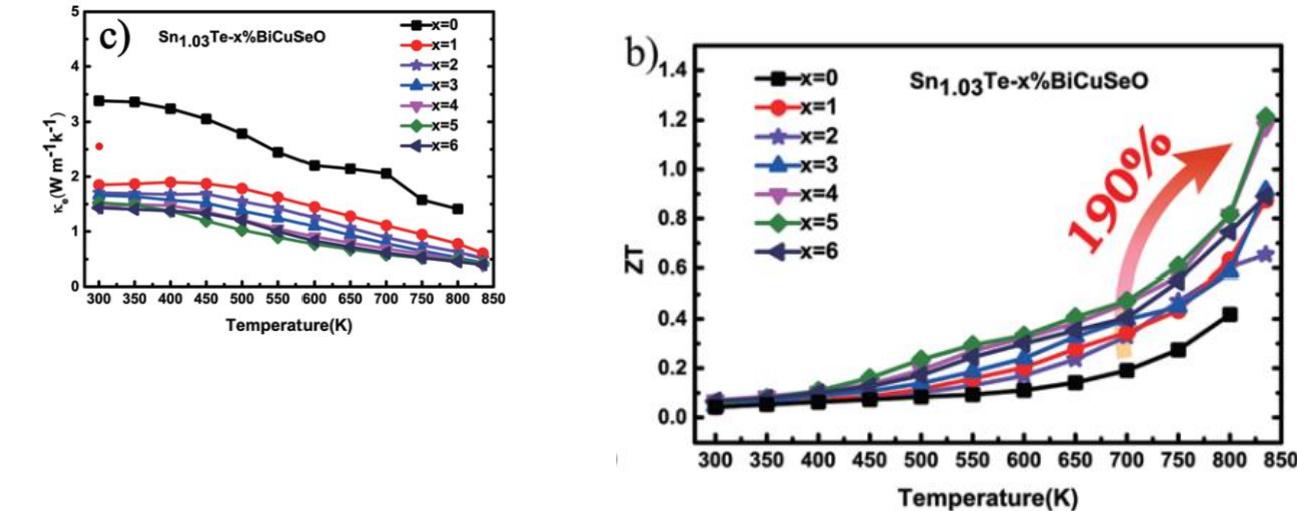
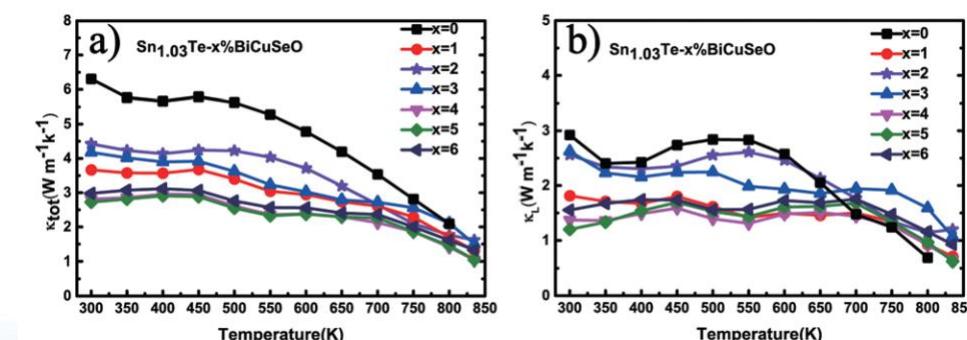
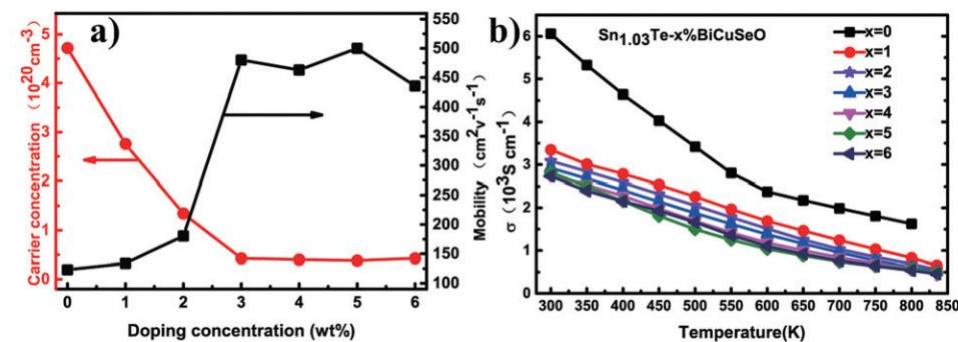
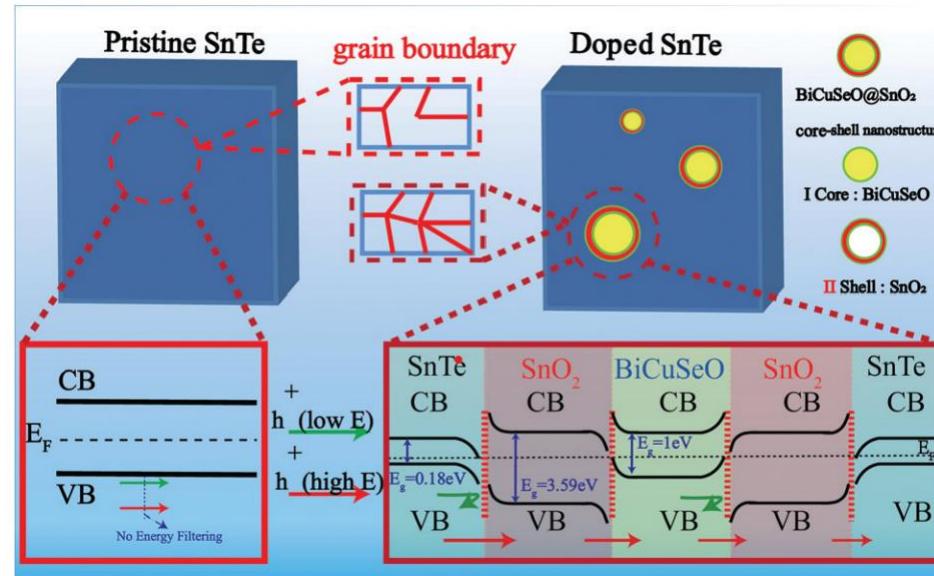
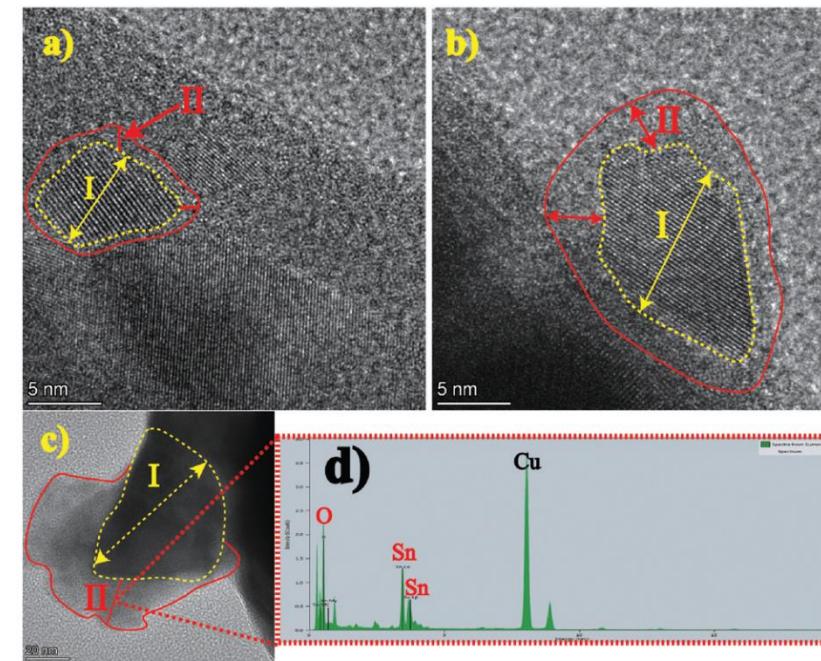
Filler type and properties:

- Particles size
 - Particles shape
 - Uniform or anisotropic filling
 - Dimensionality
 - Conductivity type, including metal/semiconductor/insulator
- ...

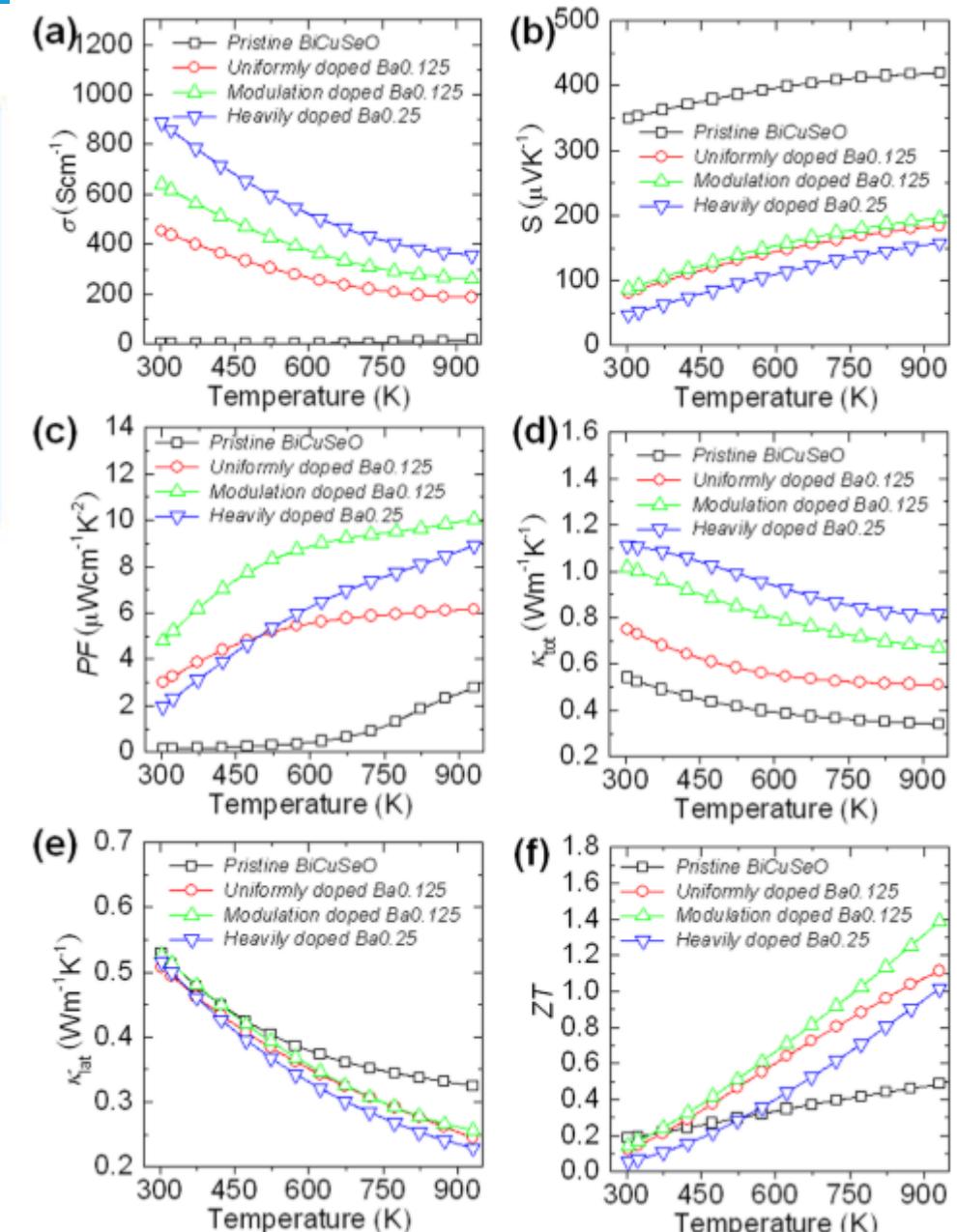
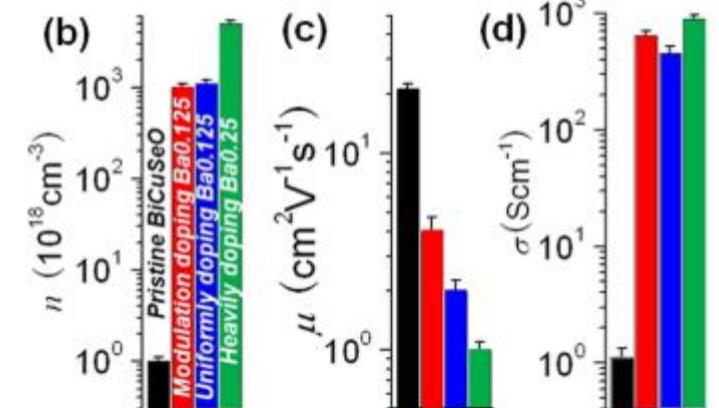
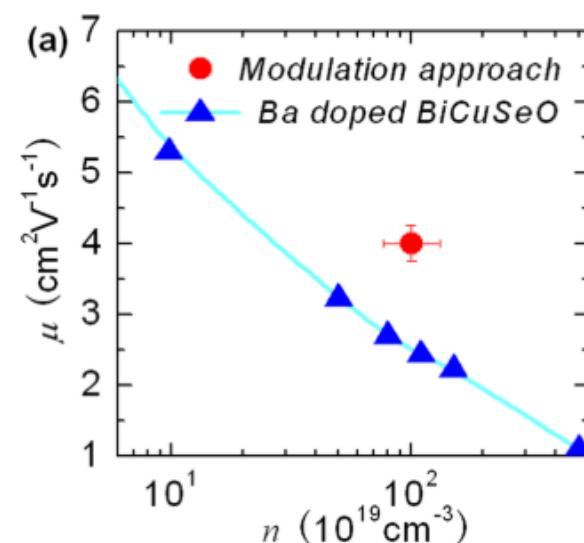
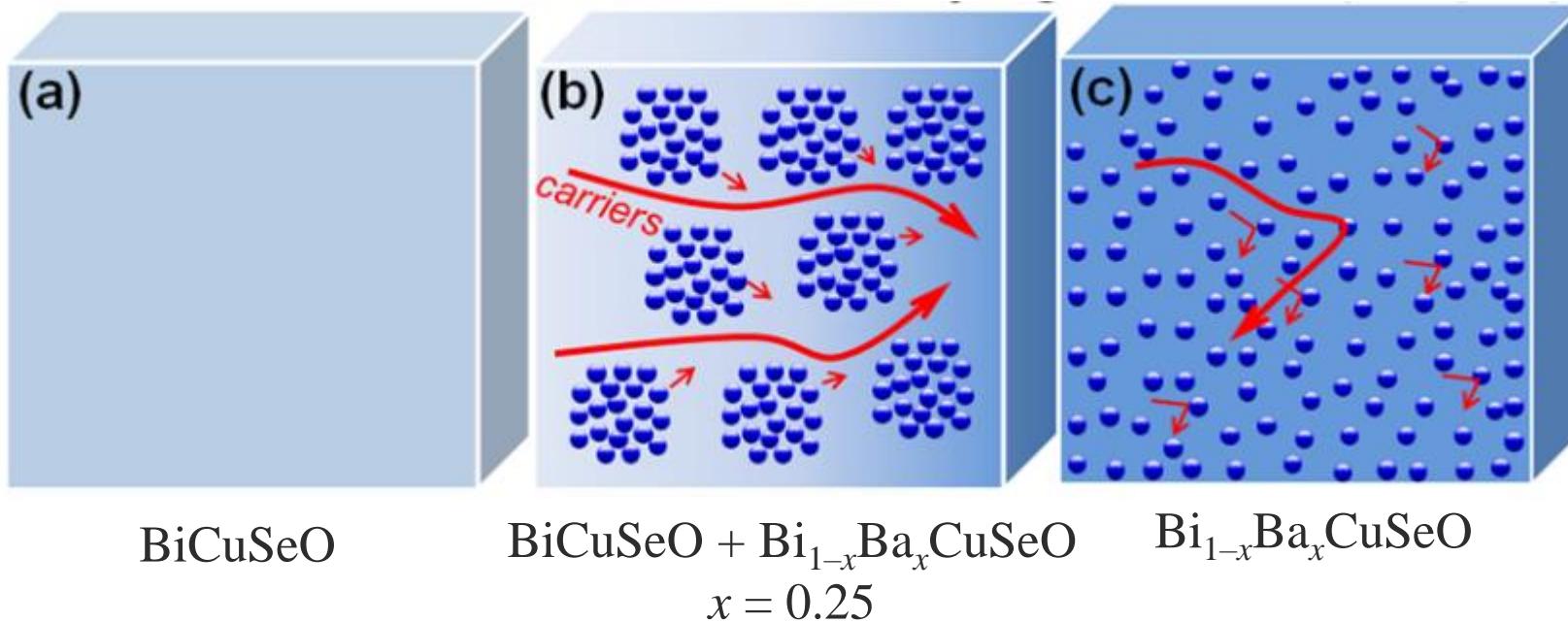


Endless number of possible combinations and effects such as the effect of energy filtering of charge carriers, modulation doping, superparamagnetism, etc.

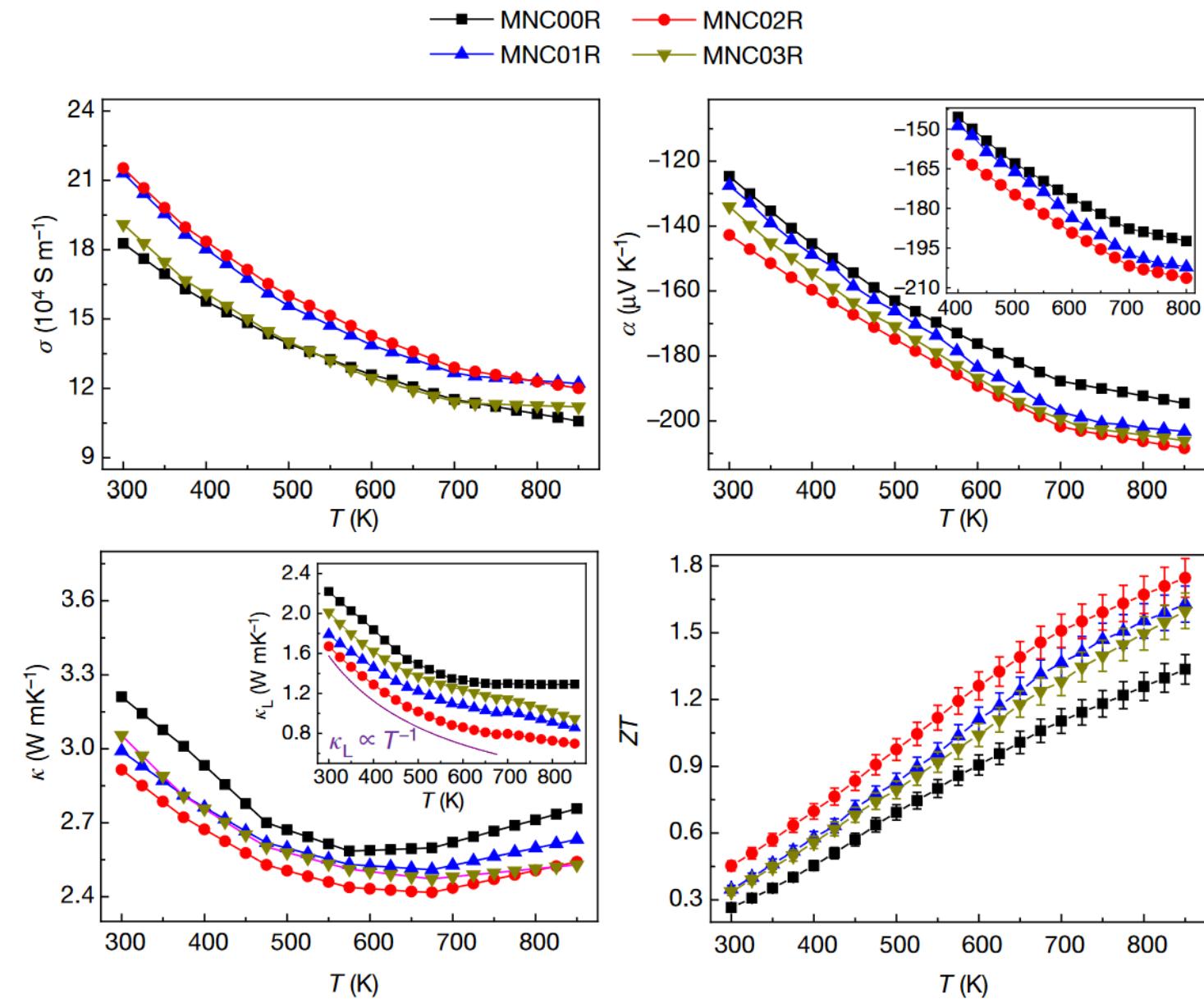
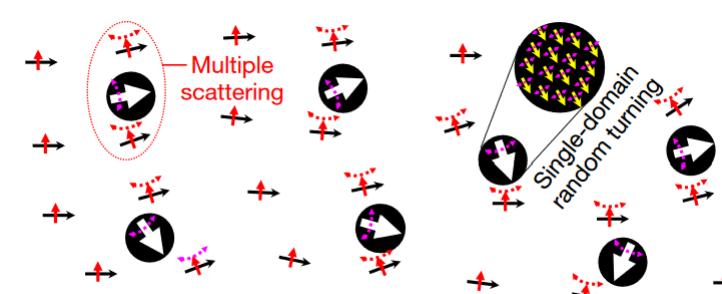
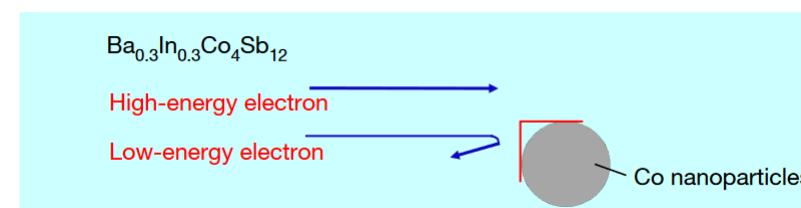
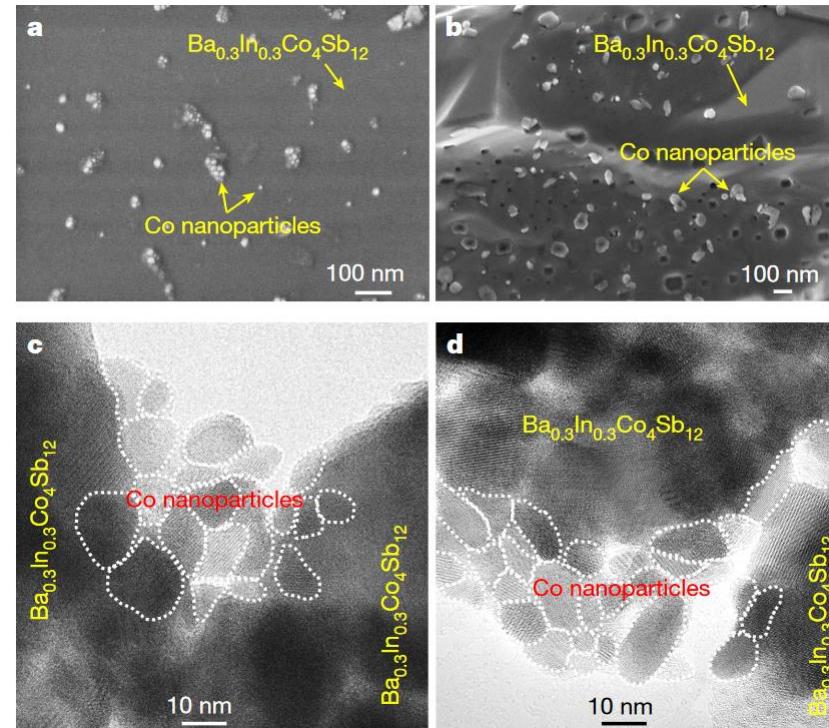
Energy filtering effect



Modulation doping



Superparamagnetism



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