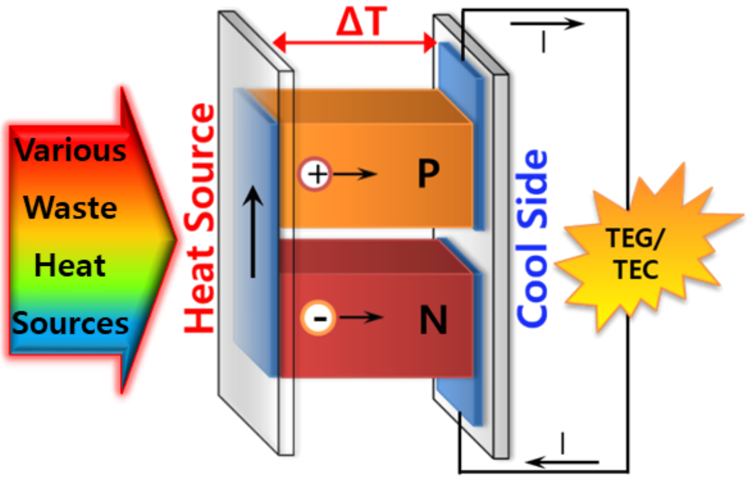
ACT2018, Oct. 7th, 2018, NTU, Taiwan

Introduction to Thermoelectrics



Soonil Lee

School of Materials Science and Engineering, Changwon National University, Korea

Outline

01 Introduction of Thermoelectric Effect

02 Introduction of Thermoelectric Materials

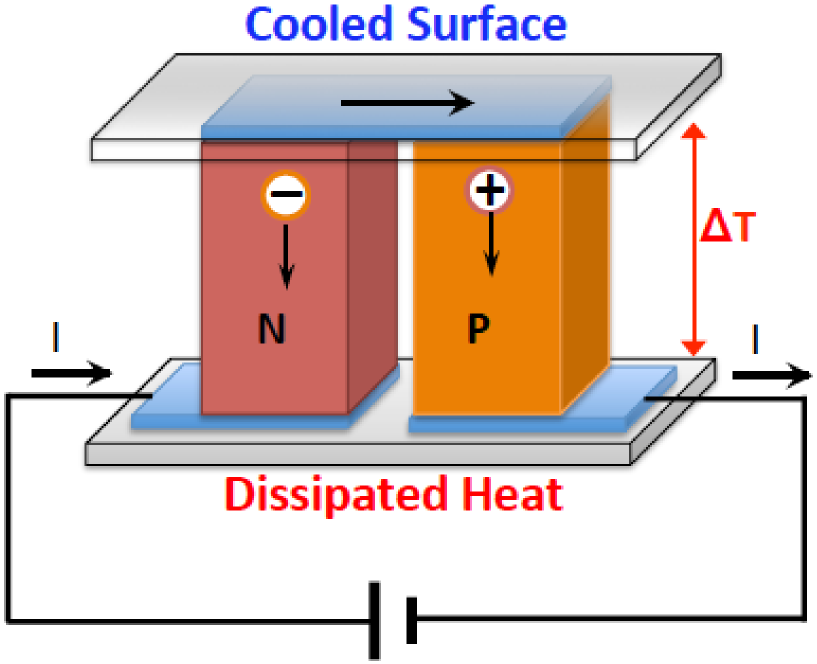
03 Thermoelectric Materials Engineering

04 Thermoelectric Modules Engineering

Thermoelectric Effect

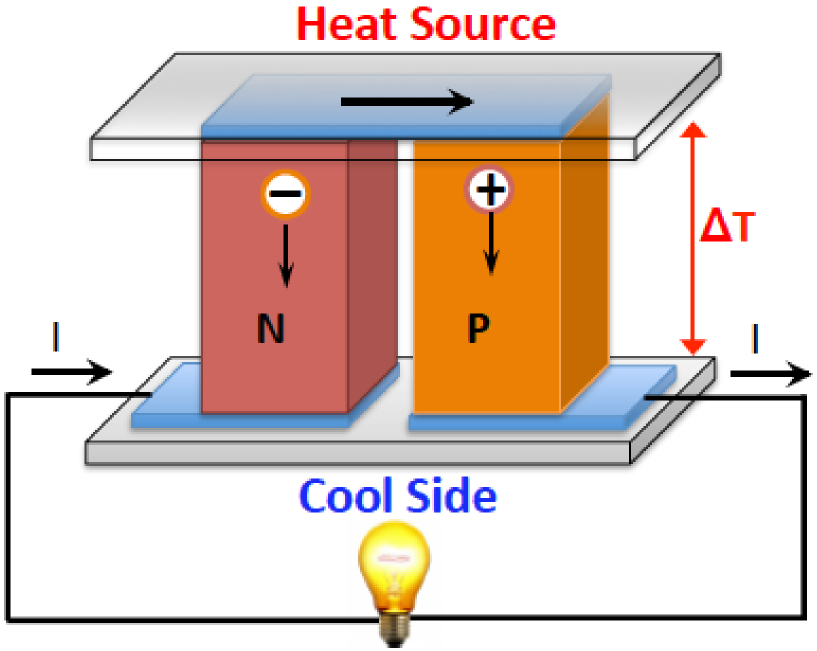
Thermoelectric Effect: direct conversion of temperature differences to electric voltage and vice versa (Seebeck effect, Peltier effect, Thomson effect)

The Peltier effect



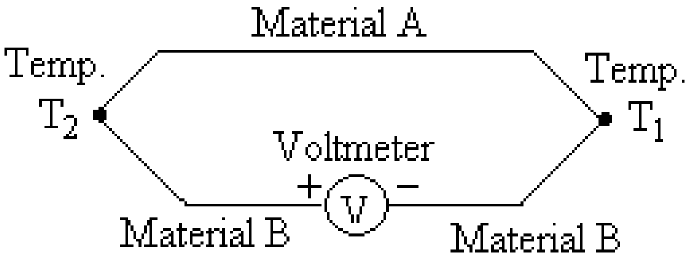
Thermoelectric Cooler

The Seebeck effect



Thermoelectric Power Generator

Thermoelectric Coefficients



1) Seebeck coefficient (Thermopower, thermoelectric power, thermal EMF coefficient):

$$S_{AB} = \frac{V}{\Delta T}$$

2) Peltier coefficient (π): how much heat is carried per unit charge

$$\pi_{AB} = \frac{q}{I}$$

q: rate of heating or cooling at each junction

Kelvin (Thomson) relation:

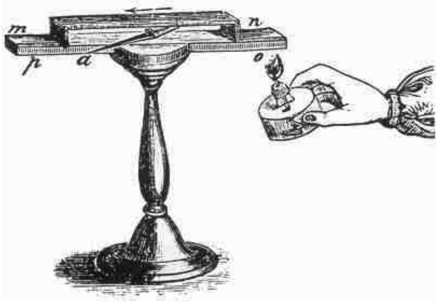
$$\pi_{AB} = S_{AB} T$$

3) Thomson coefficient (τ): a spatial gradient in temperature can result in a gradient in the Seebeck coefficient

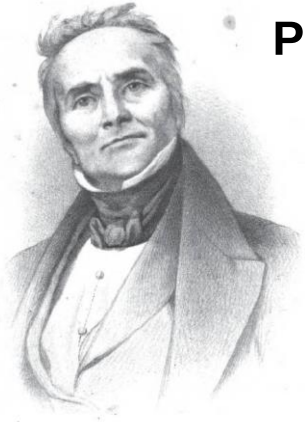
$$\tau_A - \tau_B = T \frac{dS_{AB}}{dT}$$

Brief History of Thermoelectrics

Seebeck Effect (1821-3)



Thomas Johann Seebeck



Peltier Effect (1834)

In 1834, Jean Charles Athanase Peltier found that an electrical current would produce heating or cooling at the junction of two dissimilar metals.

In 1851 Gustav Magnus discovered the Seebeck voltage does not depend on the distribution of temperature along the metals between the junctions an indication that the thermopower is a thermodynamic state function.

Gustav Magnus

Basis for thermocouple

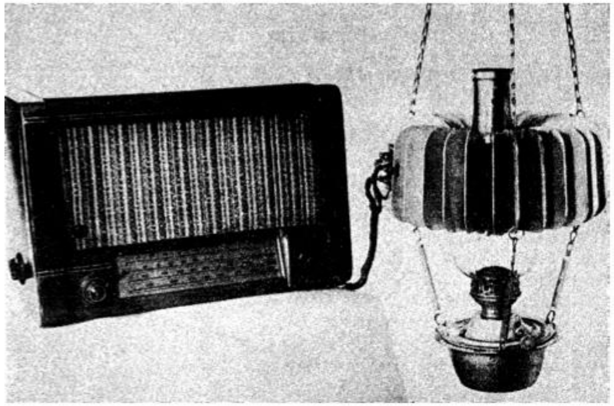
Thomson Effect (1851)

In 1851, William Thomson (later Lord Kelvin) issued a comprehensive explanation of the Seebeck and Peltier Effects and described their interrelationship (known as the Kelvin Relations).

http://www.thermoelectrics.caltech.edu/thermoelectrics/history.html

Brief History of Thermoelectrics

Figure of Merit, ZT (1949)



In 1949 Abram Fedorovich Ioffe developed the modern theory of thermoelectricity using the concept of the 'figure of merit' zT.

One of the first demonstrations of 0 C cooling was by H. Julian Goldsmid in 1954 using thermoelements based on Bi_2Te_3, and one of the first to utilize the thermoelectric quality factor, identifying the importance of high mobility and effective mass combination and low lattice thermal conductivity in semiconductors

In 1995, Glen Slack summarized the material requirements succinctly in the "phonon-glass electron-crystal" concept.

http://www.thermoelectrics.caltech.edu/thermoelectrics/history.html

Thermoelectric Refrigeration

Electric Voltage (Current) → Temperature Difference

Electric Current, ***I*** :

$$I = \frac{\sigma V A}{L}$$

Rate of Heat Flow, ***q*** :

$$q = -\frac{kA\Delta T}{L}$$

Cooling Power, q_1 :

$$q_1 = \left(S_p - S_n\right)IT_1 - (T_2 - T_1)\left(K_p + K_n\right) - I^2(R_p + R_n)/2$$

Coefficient of Performance, COP, ***Φ***:

$$\phi = \frac{\left(S_p - S_n\right)IT_1 - (T_2 - T_1)\left(K_p + K_n\right) - I^2(R_p + R_n)/2}{\left(S_p - S_n\right)I(T_2 - T_1) + I^2(R_p + R_n)}$$

Current for the maximum cooling power, I_q:

$$I_q = \left(S_p - S_n\right)T_1/(R_p + R_n) \quad \Rightarrow \quad \phi_q = \frac{ZT_1^2/2 - (T_2 - T_1)}{ZT_2T_1}$$

For maximum COP,

$$I_\phi = \frac{(S_p - S_n)(T_2 - T_1)}{(R_p + R_n)\{(1 + ZT_m)^{1/2} - 1\}} \qquad \phi_{max} = \frac{T_1\left\{(1 + ZT_m)^{1/2} - (\frac{T_2}{T_1})\right\}}{(T_2 + T_1)\{(1 + ZT_m)^{1/2} + 1\}}$$

Thermoelectric Refrigeration

Electric Voltage (Current) → Temperature Difference

Figure of Merit, *Z* :

$$\boldsymbol{Z = \frac{(S_p - S_n)^2}{(K_p + K_n)(R_p + R_n)}}$$ ⟹ This should be as small as possible.

So, the form factors satisfy the relation

$$\boldsymbol{\frac{L_n A_p}{L_p A_n} = \left(\frac{\rho_p k_n}{\rho_n k_p}\right)^{1/2}}$$

$$\boldsymbol{Z = \frac{(S_p - S_n)^2}{\left\{(k_p\rho_p)^{1/2} + (k_n\rho_n)^{1/2}\right\}^2}}$$

The maximum temperature depression, $\boldsymbol{\Delta T_{\mathrm{max}}}$, is reached when the cooling power and, thus, the COP fall to zero.

$$\boldsymbol{\Delta T_{max} = \frac{1}{2} Z T_1^2}$$

Thermoelectric Refrigeration

Electric Voltage (Current) → Temperature Difference

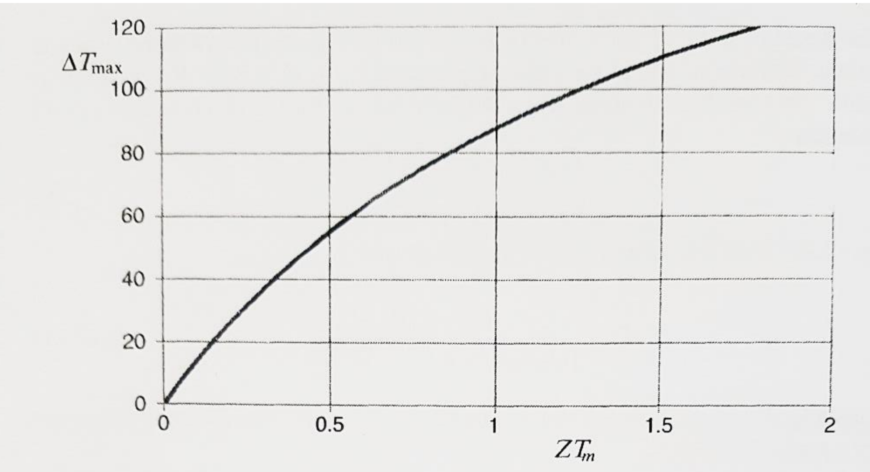


Fig. 2.3 Plot of maximum temperature depression against ZT_m for the heat sink at 300 K

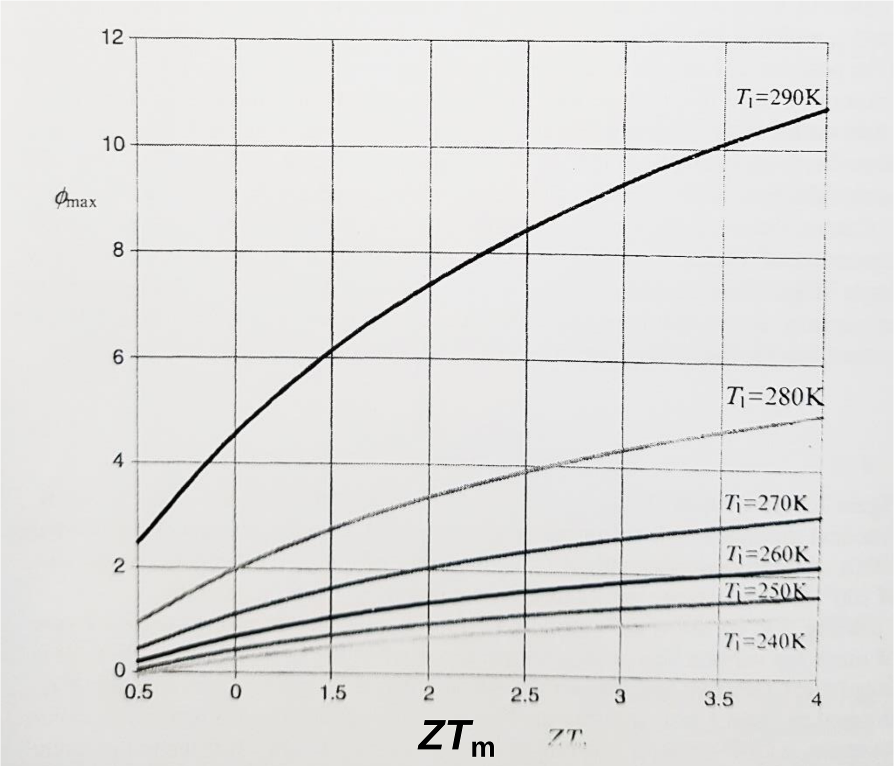


Fig. 2.4 Plot of optimum COP against ZT_m for the heat sink at 300 K

$$\phi_{max} = \frac{T_1\left\{(1+ZT_m)^{1/2} - \left(\frac{T_2}{T_1}\right)\right\}}{(T_2+T_1)\{(1+ZT_m)^{1/2}+1\}}$$

Julian H. Goldsmid, *Introduction to Thermoelectricity*, Springer (2010)

Thermoelectric Generation

Temperature Difference → Electric Voltage (Current)

Thermal EMF, E_{emf} :

$$E_{emf} = (S_p - S_n)(T_h - T_c)$$

Electric Current, I :

$$I = \frac{(S_p - S_n)(T_h - T_c)}{R_p + R_n + R_L}$$

Power delivered to the load, w :

$$w = I^2 R_L = \left(\frac{(S_p - S_n)(T_h - T_c)}{R_p + R_n + R_L} \right)^2 R_L$$

Total rate of **heat flow** from the source, q_1 :

$$q_1 = (S_p - S_n) I T_1 + (K_p + K_n)(T_h - T_c)$$

Efficiency, η:

$$\eta = w/q_1$$

*An increase in the load resistance reduces the power output but increases the efficiency.

For the maximum efficiency:

$$M = \frac{R_L}{R_p + R_n} = (1 + ZT_m)^{1/2}$$

Maximum Efficiency, η:

$$\eta = \frac{(T_h - T_c)(M - 1)}{T_h \left(M + \frac{T_c}{T_h} \right)}$$

*If ZT_m were much greater than unity, M would also be very large and the efficiency would approach $(T_h - T_c)/T_h$, which is the value for the **Carnot cycle**.

Thermoelectric Generation

Temperature Difference → Electric Voltage (Current)

$$\eta = \frac{(T_h - T_c)\left((1 + ZT_m)^{1/2} - 1\right)}{T_h\left((1 + ZT_m)^{1/2} + \frac{T_c}{T_h}\right)}$$

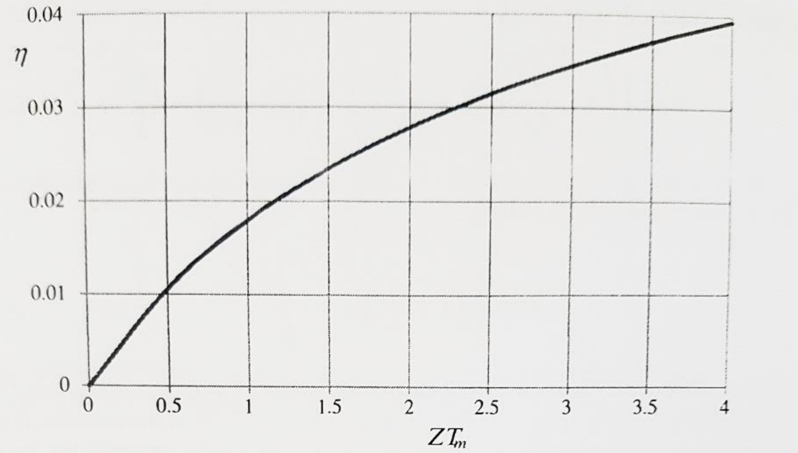
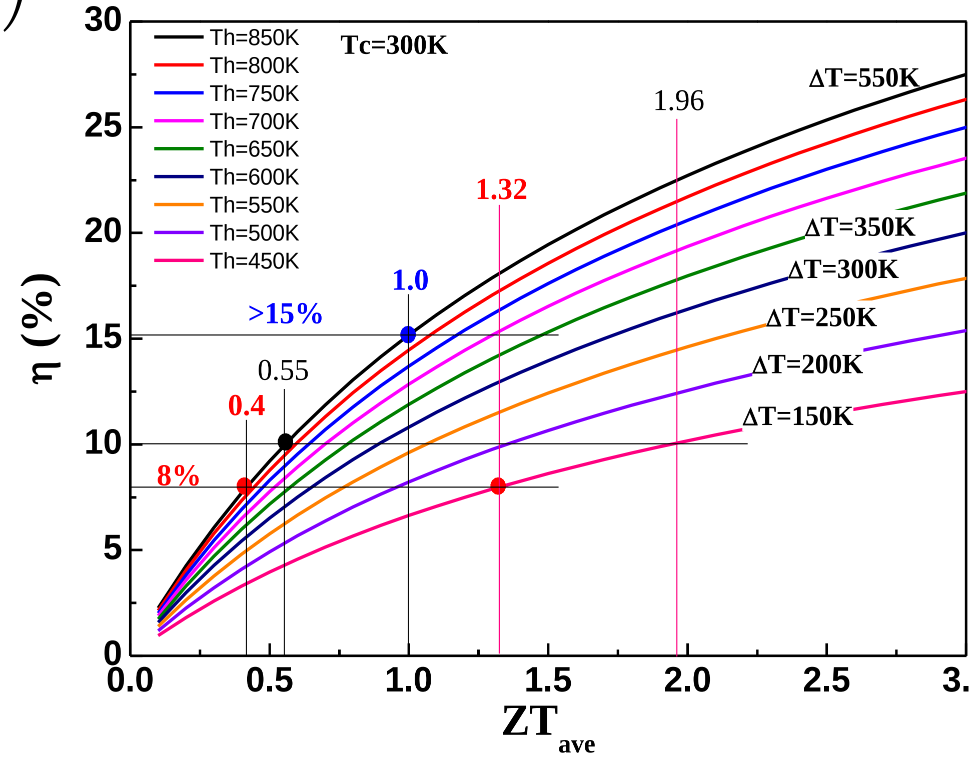


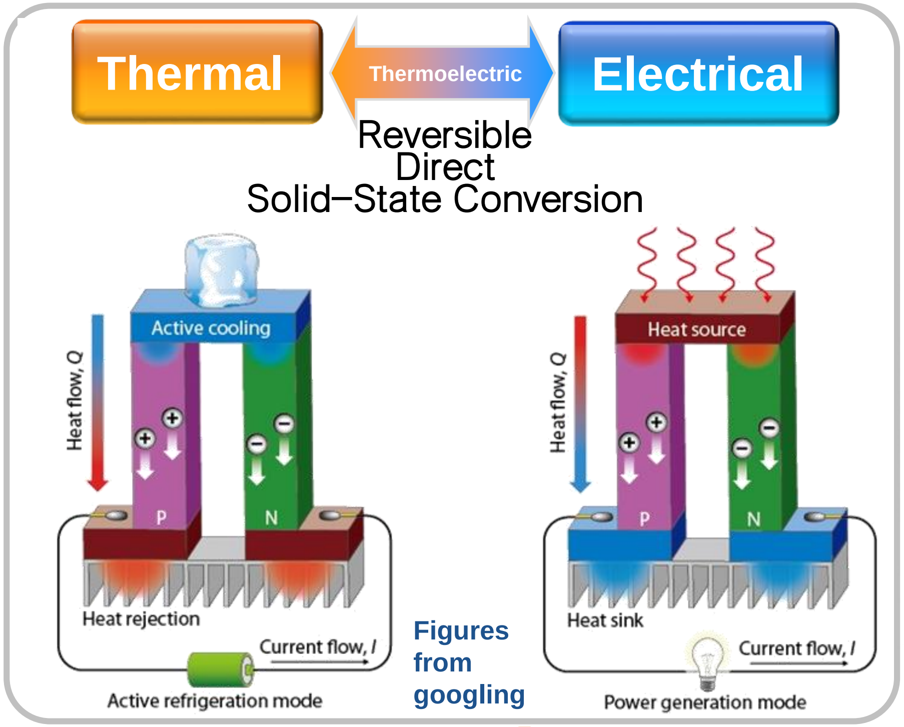
Fig. 2.6 Plot of efficiency against dimensionless figure of merit for the heat source at 400 K and the heat sink at 360 K

Julian H. Goldsmid, *Introduction to Thermoelectricity*, Springer (2010)



Thermoelectric Applications

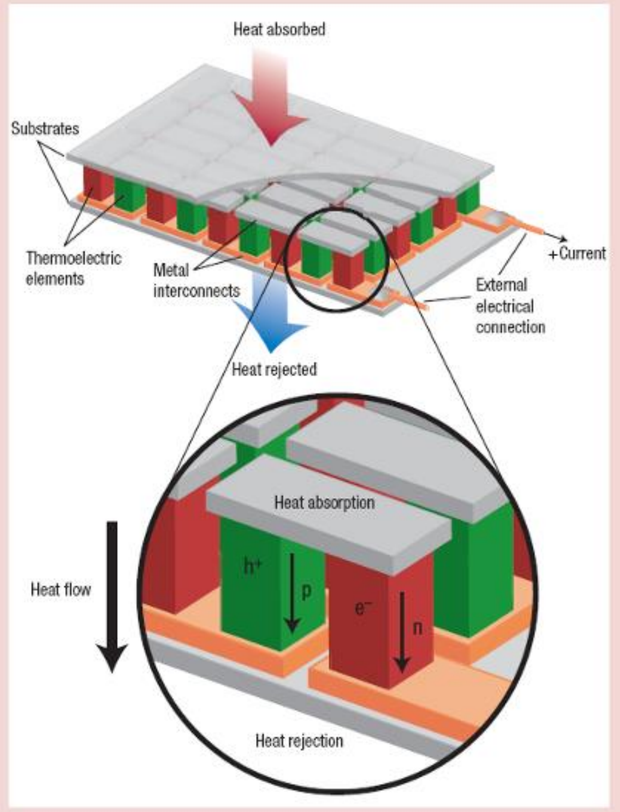
Thermoelectric : simple structure and high reliable



Thermal ⟷ Thermoelectric ⟷ **Electrical**

Reversible
Direct
Solid–State Conversion

Figures from googling



Snyder et al., *Nature* (2008)

Thermoelectric Cooling (Peltier Effect)

- Refrigerant–free cooling
- No–noise
- Precise temp. control
- Fast response
- Long life time
- Small local cooling

Thermoelectric Generation (Seebeck Effect)

- CO$_2$–free
- Recycle waste heat energy
- High reliability, No maintenance
- Stable output power (24h operation)
- DC/Micro/Independent power generation

TEC Applications

Development of Materials Technology

Common
Facilities
(Air Conditioner,
Refrigerator, etc.)

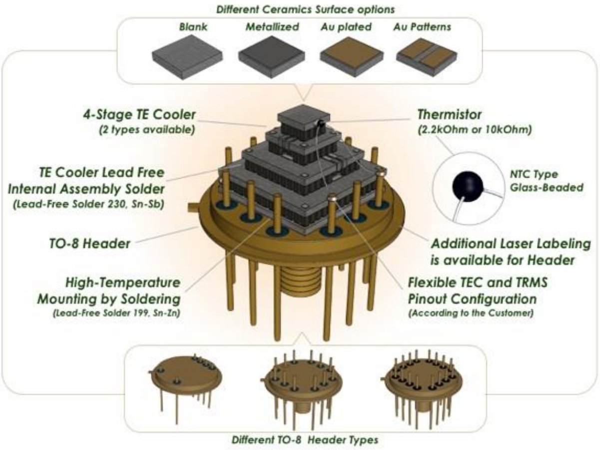
Conditioning
System,
Small Cooler

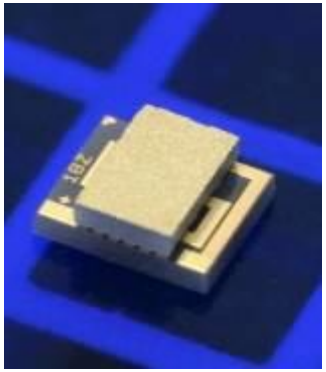
Chip cooling
Automobile,
Special cooling

(ZT)

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

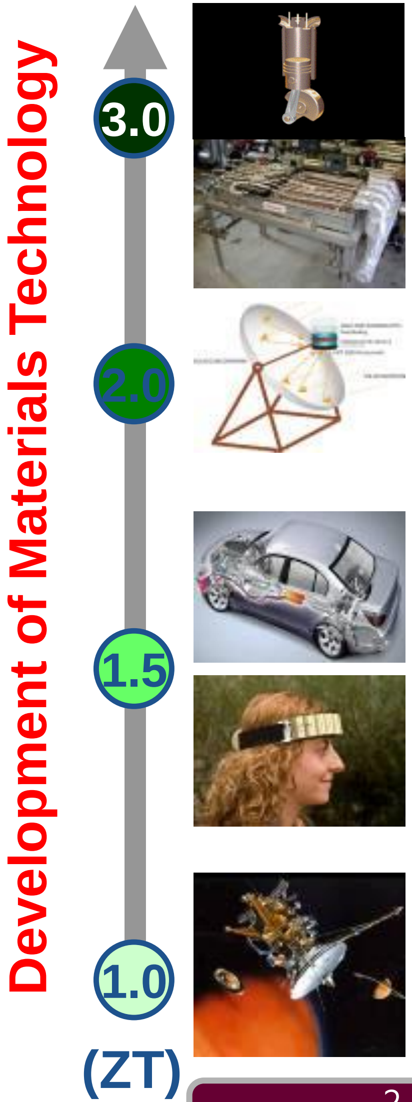
- Chip cooling





- Automobile/Special Cooling

TEG Applications Using Waste Heat



Replacement of Combustion Engine

Natural Heat
(Geothermal, Seawater, etc.)

Hybrid Gen.
(Solar-TEG)

Waste Heat
(Automobile, Plant)

Micro Power Source
(Body Heat)

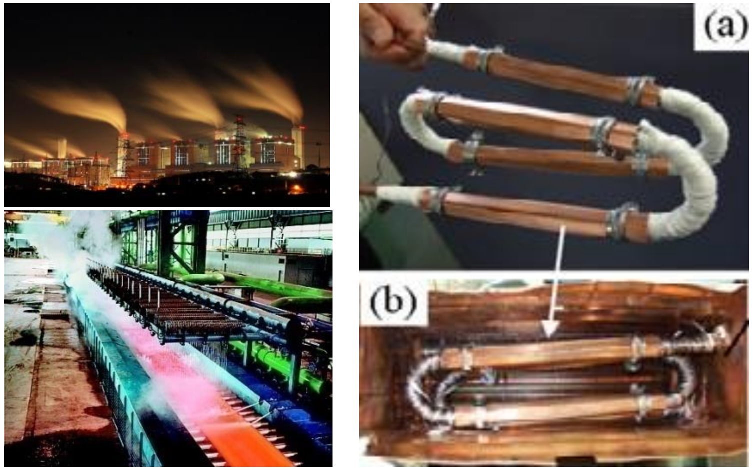
Aerospace
Radioisotope
Thermoelectric
Generation

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

Z : figure of merit
α : Seebeck coefficient
σ : electrical conductivity
κ : thermal conductivity

- Automobile TEG
  - BMW, GM, Volkswagen
  - 10% Fuel Efficiency Increase

- Industrial TEG
  - Incineration Plant
  - Industrial facilities



TEG Applications Using Waste Heat

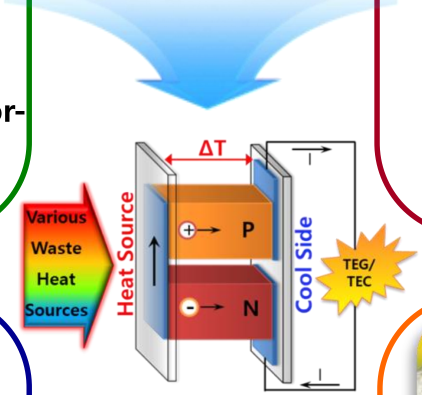
Industry Waste Heat


Plant WH-TEG


Power Plant-TEG


Incinerator-TEG

TEG



Transport Waste Heat


Automobile WH-TEG

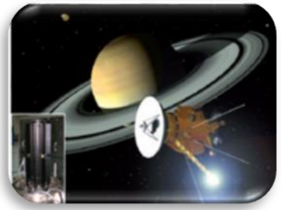

Ship WH-TEG

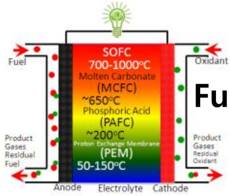

Aircraft WH-TEG

Natural WH / Convergence


Geothermal-TEG

Solar Heat-TEG

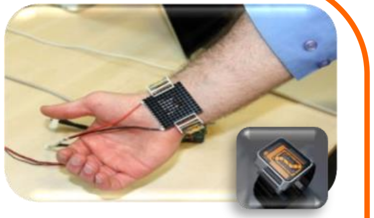

RTG



Fuel Cell-TEG

Body Heat / Micro Heat

Micro TEG



TEG Applications

Portable TEG for outdoor

Engineering Thermoelectric Materials

The maximum efficiency of a thermoelectric material for both power generation and cooling is determined by its figure of merit (*zT*):

Device: $$\eta_{\max} = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+T_c/T_h}$$

$$\frac{\Delta T}{T_h}$$: Carnot efficiency

Seebeck coefficient

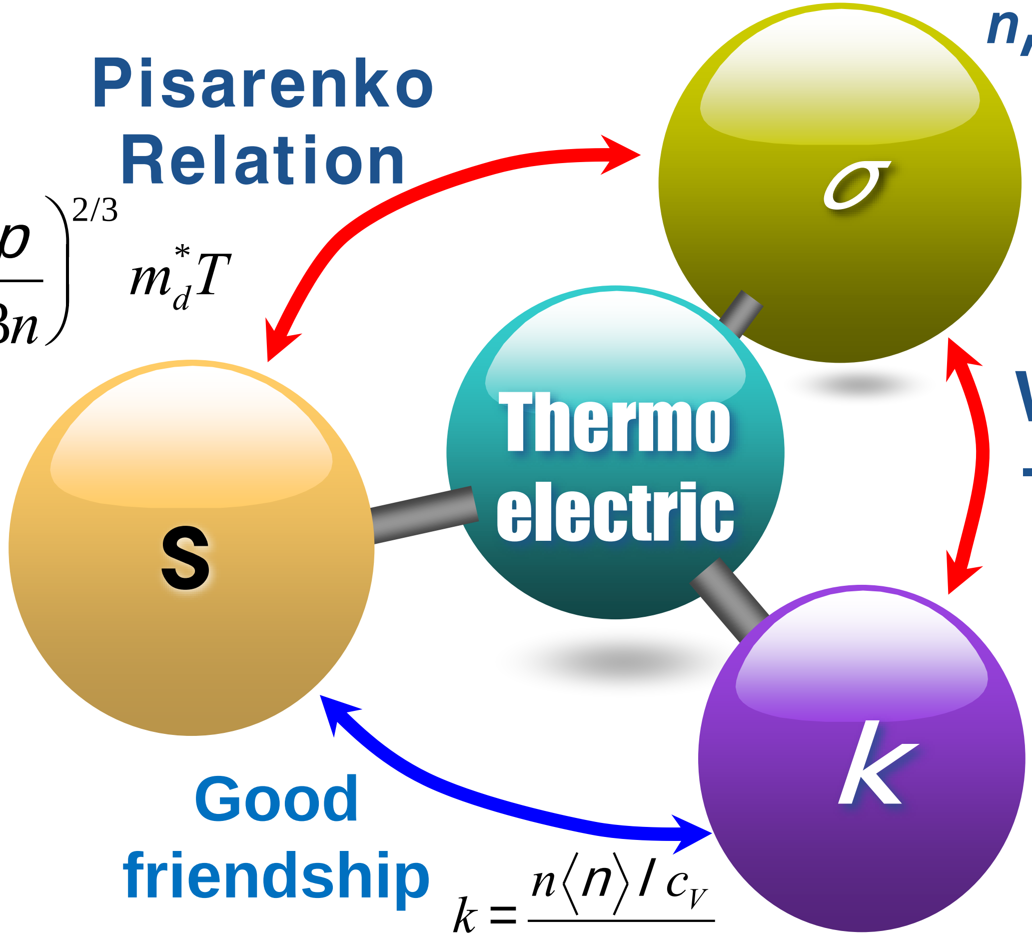
Electrical conductivity

Material: $$zT = \frac{S^2\sigma}{k}T$$

Thermal conductivity

Engineering Thermoelectric Materials

$$zT = \frac{S^2 s}{k} T = S^2 n_i \left(\frac{m_i}{k_e + k_l} \right) qT$$



n, *μ*

Pisarenko Relation

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

Wiedemann –Franz Law

$$\frac{k}{s} = LT$$

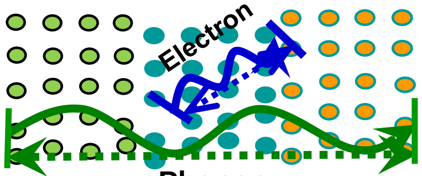
DOS
m*

Good friendship

$$k = \frac{n\langle n\rangle l\, c_V}{3N_A}$$

λ : mean free path

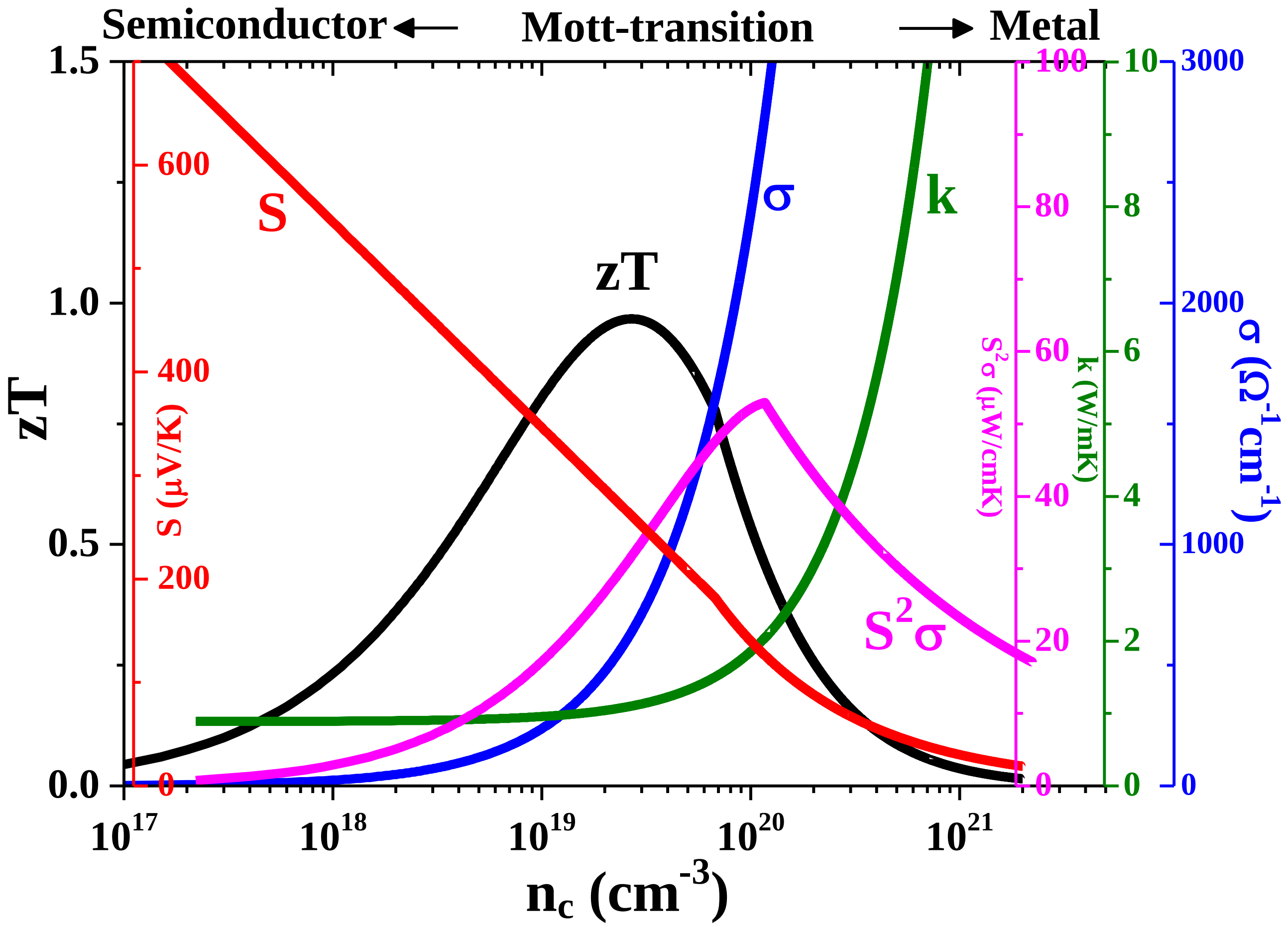
PGEC



Phonon

Engineering Thermoelectric Materials

$$zT = \frac{S^2\sigma}{k}T$$



S. Lee *et al.*, JECS 32 (2012)

Mott-criterion (metal-insulator transition):

$$n_e^{1/3}a_0 \sim 0.25$$

Engineering Thermoelectric Materials

Coupling

Pisarenko Relation

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

Wiedemann-Franz Law

$$\frac{k_e}{\sigma} = LT$$

Breaking the law

Decoupling

PGEC (Phonon-Glass Electron-Crystal)

Quantum Confinement

Carrier Filtering

Hierachical Structuring (defects)

PGEC without cages

……

Phonon Scattering

Engineering Thermoelectric Materials

$$zT = \frac{S^2 \sigma T}{k}$$

Higher Seebeck coefficient (S)
Higher electrical conductivity (σ)
Lower thermal conductivity (k)

Engineering Decoupling

Glasses have low lattice thermal conductivity but low Seebeck coefficient.
Crystals have high electrical conductivity but high thermal conductivity.

"Phonon-glass electron-crystal (PGEC)"

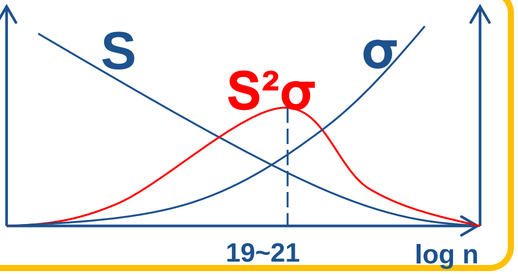
G. A. Slack, in CRC Handbook of Thermoelectrics (ed. Rowe, M.) 407-440 (CRC, Boca Ralon, 1995)

Original Paper:
A. F. Ioffe, S. V. Airapetiants, A. F. Ioffe,
N. V. Kolomoets and L. S. Stil'bans,
Dokl. Akad. Nauk. SSSR 106,981 (1956).

Engineering Thermoelectric Materials

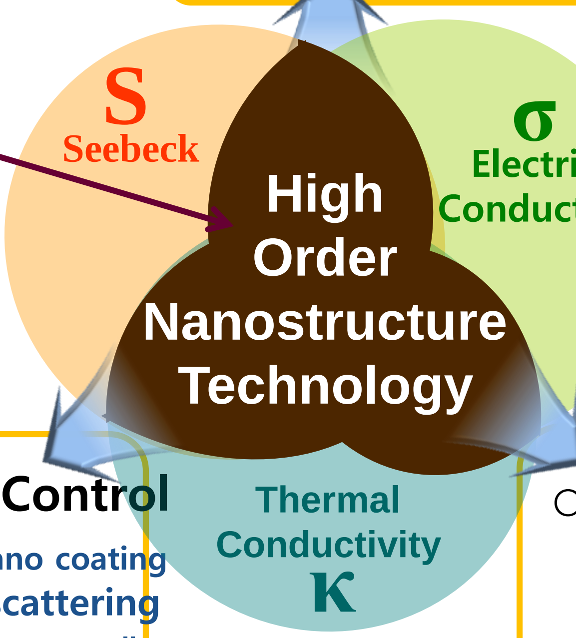
○ $S^2\sigma$ Concurrent Control

- ▷ carrier concentration
- ▷ Valence control
- ▷ $\alpha = -\,k/e \ln(N/C+A)$



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

Implementation Technology for Development



S Seebeck

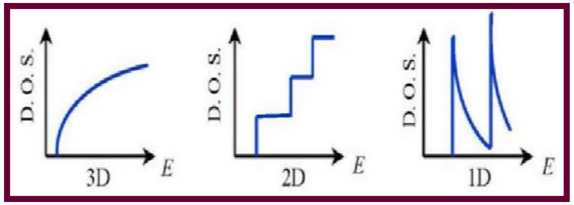
σ Electrical Conductivity

Thermal Conductivity κ

High Order Nanostructure Technology

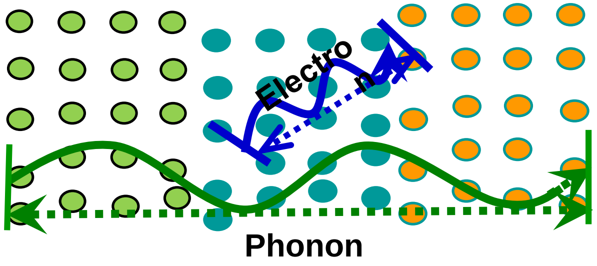
○ S/κ Concurrent Control

- ▷ Nano Block, Nano Wire, Nano coating
- ▷ DOS control, phonon scattering
- ▷ $DOS(E)=m^*/\pi h d_w$, d_w:quantum well



○ σ/κ Concurrent Control

- ▷ PGEC(Phonon Glass-Electron Crystal)



Engineering Thermoelectric Materials

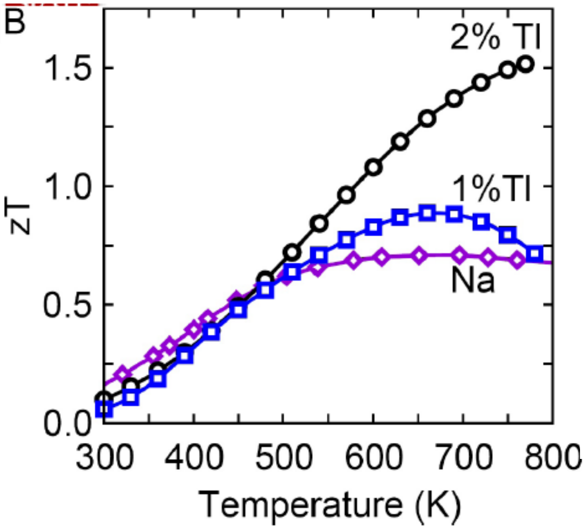
$$zT = \frac{S^2 \sigma T}{k}$$

- **Seebeck Coefficient**

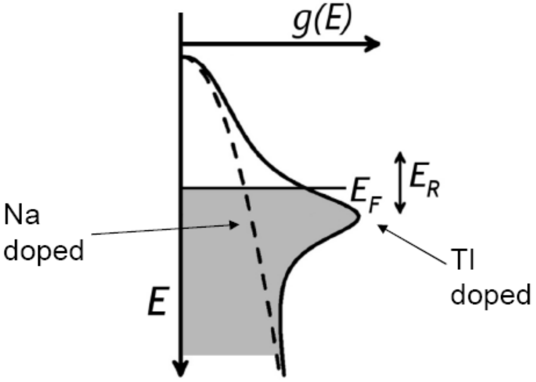
Mott relation for degenerate statistics,

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

$$S = \frac{8\pi^2 k_B T}{3qh^2}\cdot\boxed{m_d^*}\left(\frac{\pi}{3n}\right)^{2/3}$$



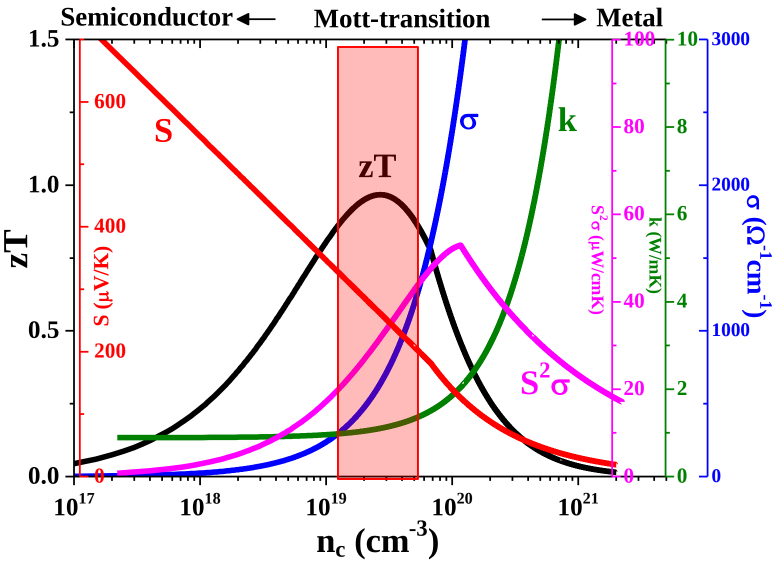
Na or Tl-doped PbTe



Heremans *et al*. Science 321, 554 (2008)

- **Electrical Conductivity**

$$\sigma = en\boxed{\mu}$$



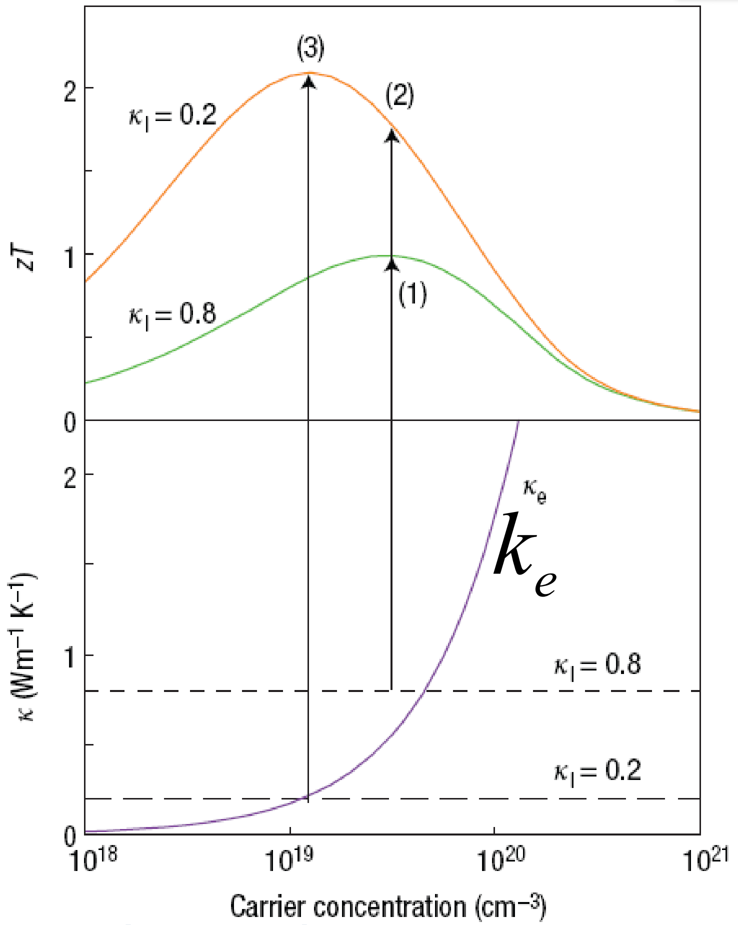
S. Lee *et al.*, JECS 32 (2012)

- Doping
- Nonstoichiometry
- Reduction
- Crystal Anisotropy
- Etc.

Engineering Thermoelectric Materials

- Thermal Conductivity

$$k = k_e + k_l$$



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

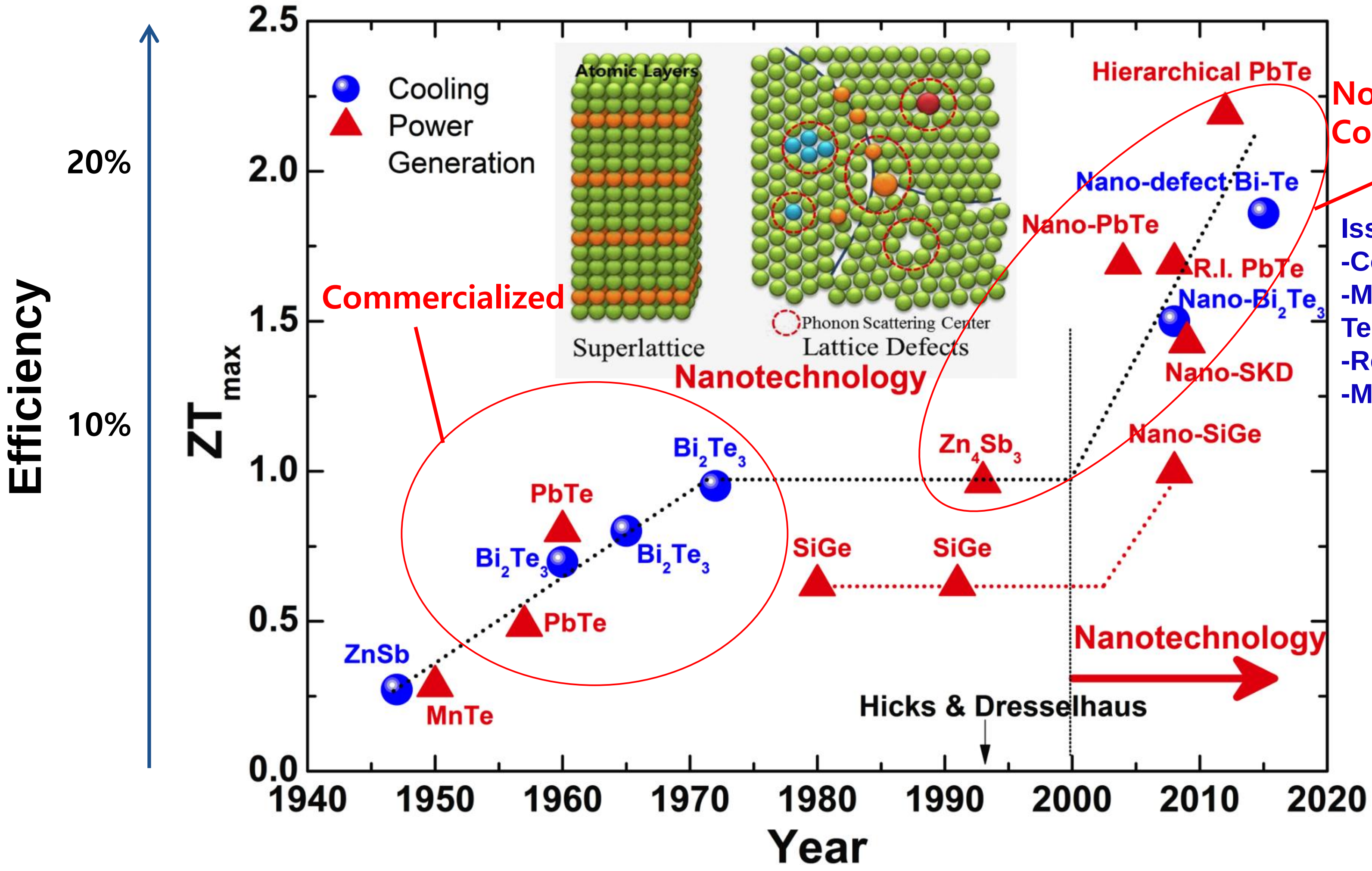
Phonon Scattering

$$zT = \frac{S^2 \sigma T}{k}$$

- Complex Structure Multiple Sites
- Large Unit Volume
- Heavy Atoms
- Random Vacancies
- Local Lattice Distortion
- Low Symmetry
- Complex Compositions (Alloying, Solid Solutions)
- Rattling Ions
- Segregation of Chemistry-Second Phases
- Nanostructures
- Intrinsic Localized Modes (ILM)
- Etc.

Need to control nanoscale

Engineering Thermoelectric Materials



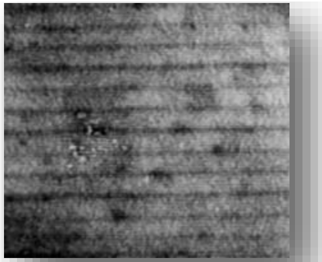
Issues:
- **-Cost**
- **-Mass production Technology**
- **-Reproducibility**
- **-Modularization**

Ref. : J. P. Heremans, et al. Nature Nanotechnology 8, 471–473 (2013)
Soonil Lee and W. S. Seo, Ceramist, 18[4] (2015)

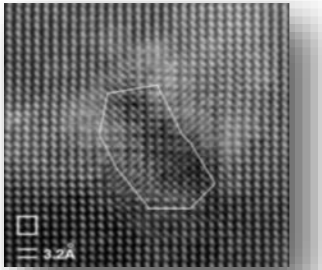
Engineering Thermoelectric Materials

Harman *et al.*,
Science **297**, 2229 (2002)
PbSeTe/PbTe Quantum dot superlattices

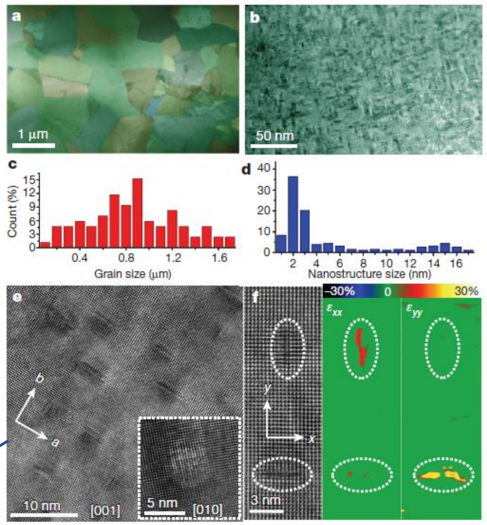
Venkatasubramanian *et al.*
Nature **413**, 597 (2001)
Bi2Te3/Sb2Te3

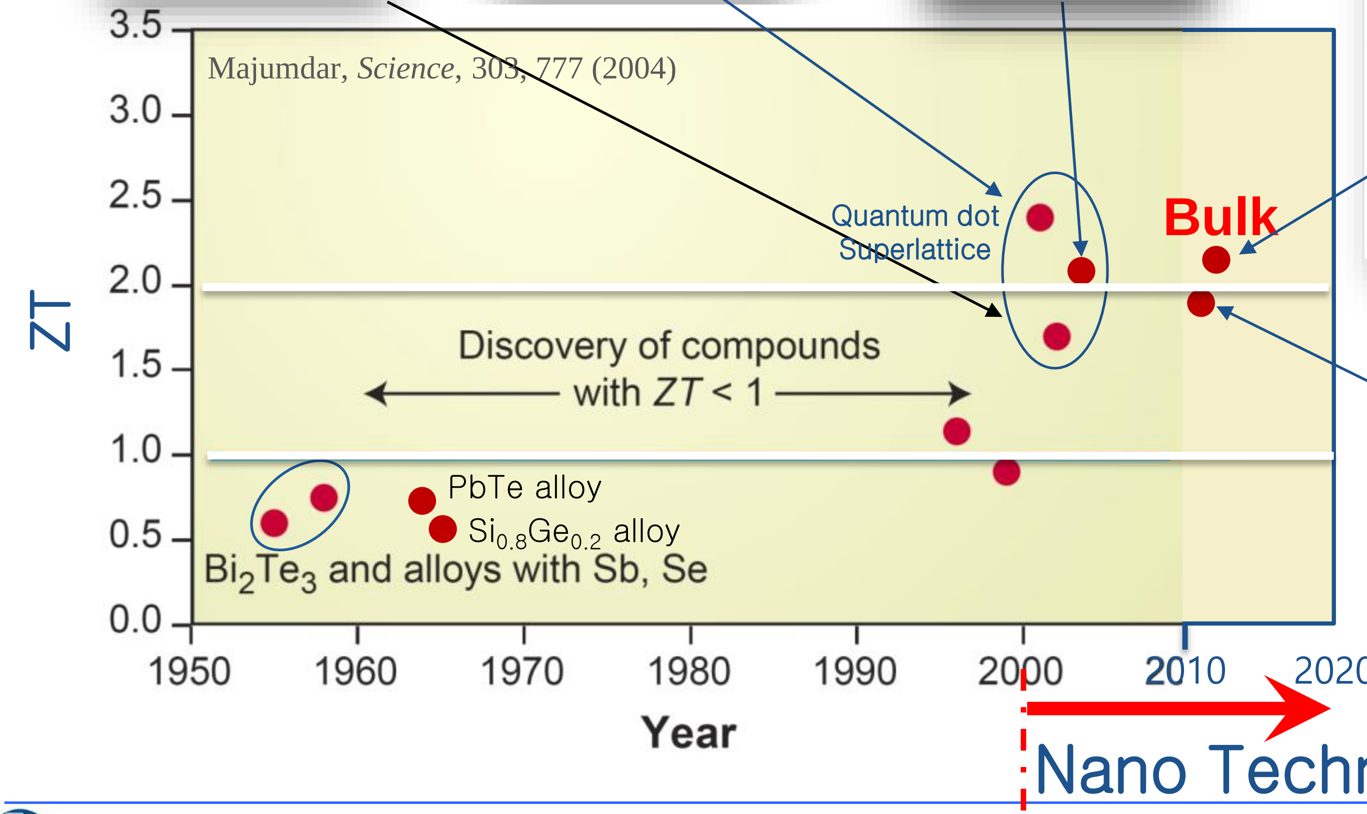


Kanatzidis *et al.*
Science **303**, 818 (2004)
$AgPb_mSbTe_{2+m}$



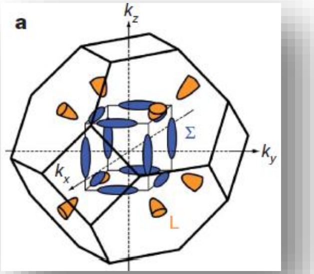
K. Biswas *et al.*
Nature **489**, 414 (2012)
PbTe+ 4 mol% SrTe + 2 mol% Na




Majumdar, *Science*, 303, 777 (2004)

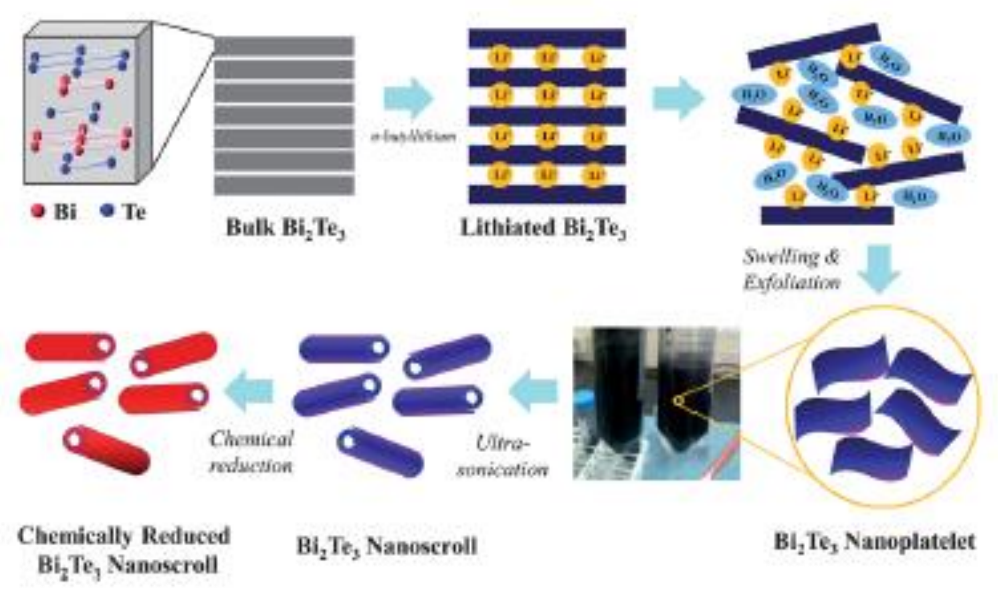
Nano Technology

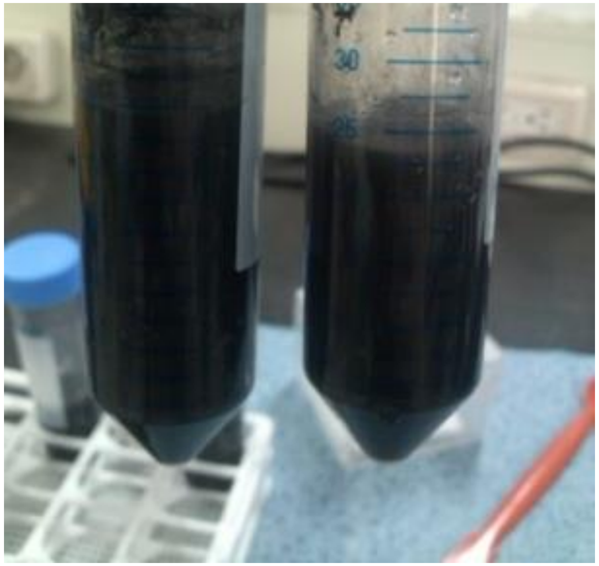
Y. Pei *et al.*
Nature **473**, 66 (2011)
$PbTe_{1-x}Se_x$ + 2 at.% Na



Chemical Exfoliation of Bi_2Te_3

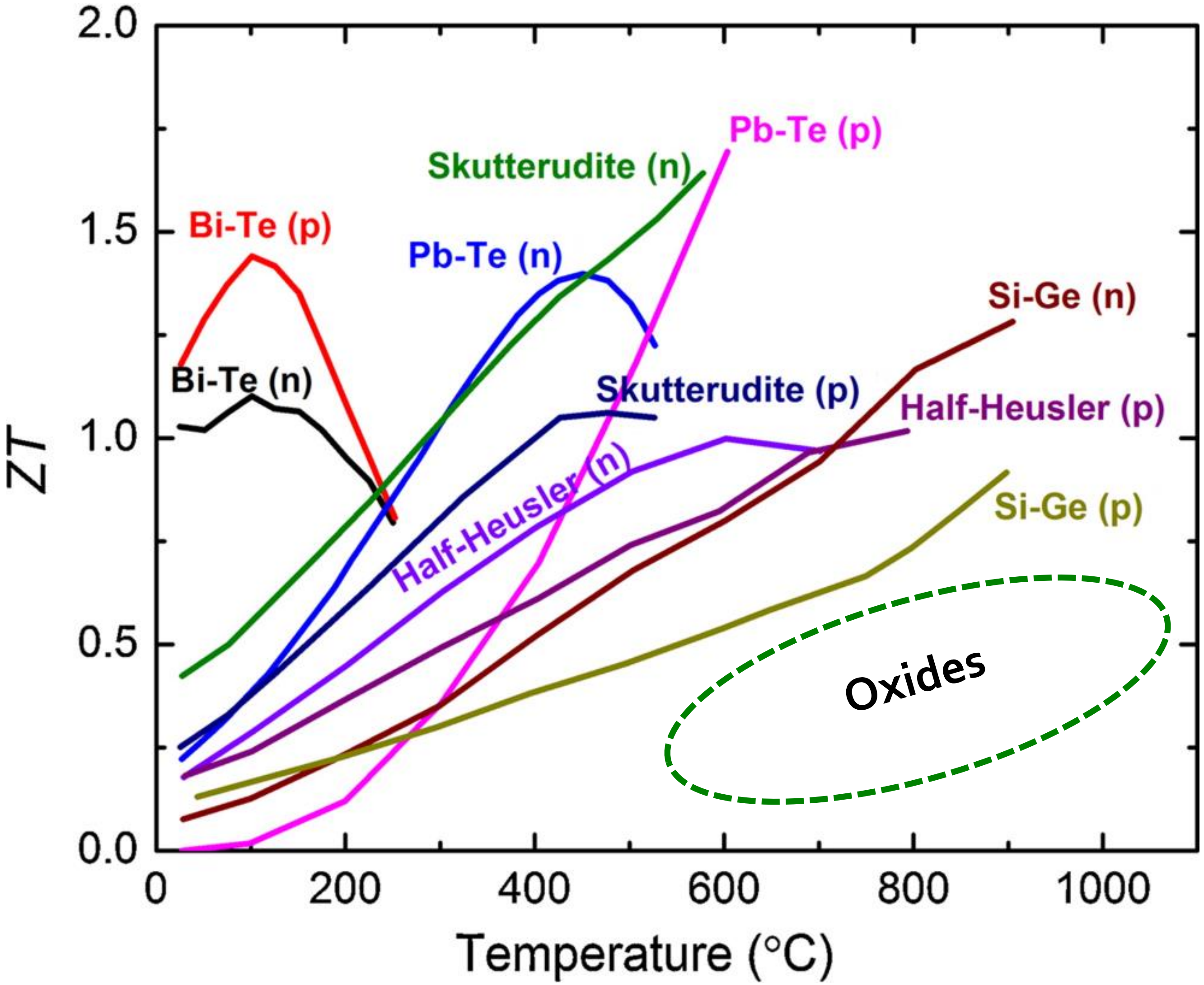
- **Lithium Intercalation: $Bi_2Te_3 + x\,(n\text{-}BuLi) \Rightarrow Li_xBi_2Te_3 + x/2\ \text{octane}$**
- **Exfoliation : $Li_xBi_2Te_3 + xH_2O \Rightarrow Bi_2Te_3\ (\text{exfoliated}) + xLiOH + x/2H_2 \uparrow$**





J. Y. Kim et al. ***J. Mater. Chem. A*** 2013

Thermoelectric Materials



Shuo Chen and Zhifeng Ren, Materials Today, 16[10], 387 (2013)

Mid-High Temp. Thermoelectrics:

Pb-Te,

Silicides,

Skutterudites,

Half-Heuslers

Si-Ge,

Oxides,

etc.

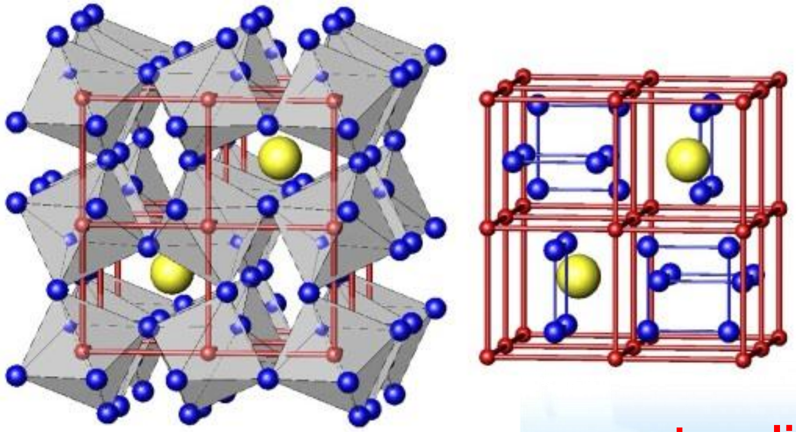
Development of Thermoelectric Materials

- **Thermal Conductivity (PGEC concept)**

$$k = k_e + k_l$$

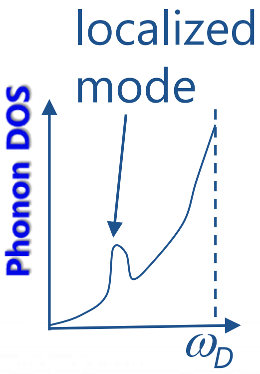
Phonon Scattering

$$zT = \frac{S^2 \sigma T}{k}$$

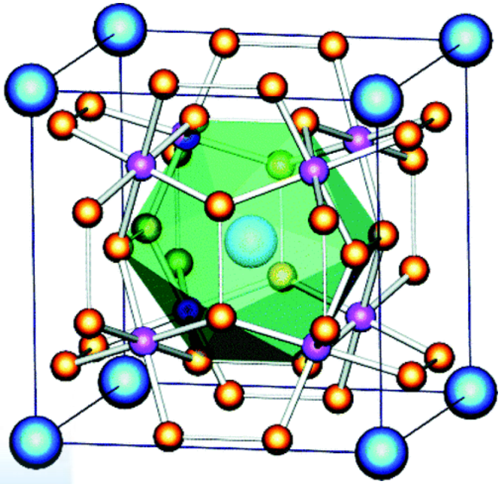


Filled Skutterudite

M.M. Koza *et al.*, PRB 81,174302 (2010)



Localized Vibration



Filled Skutterudite

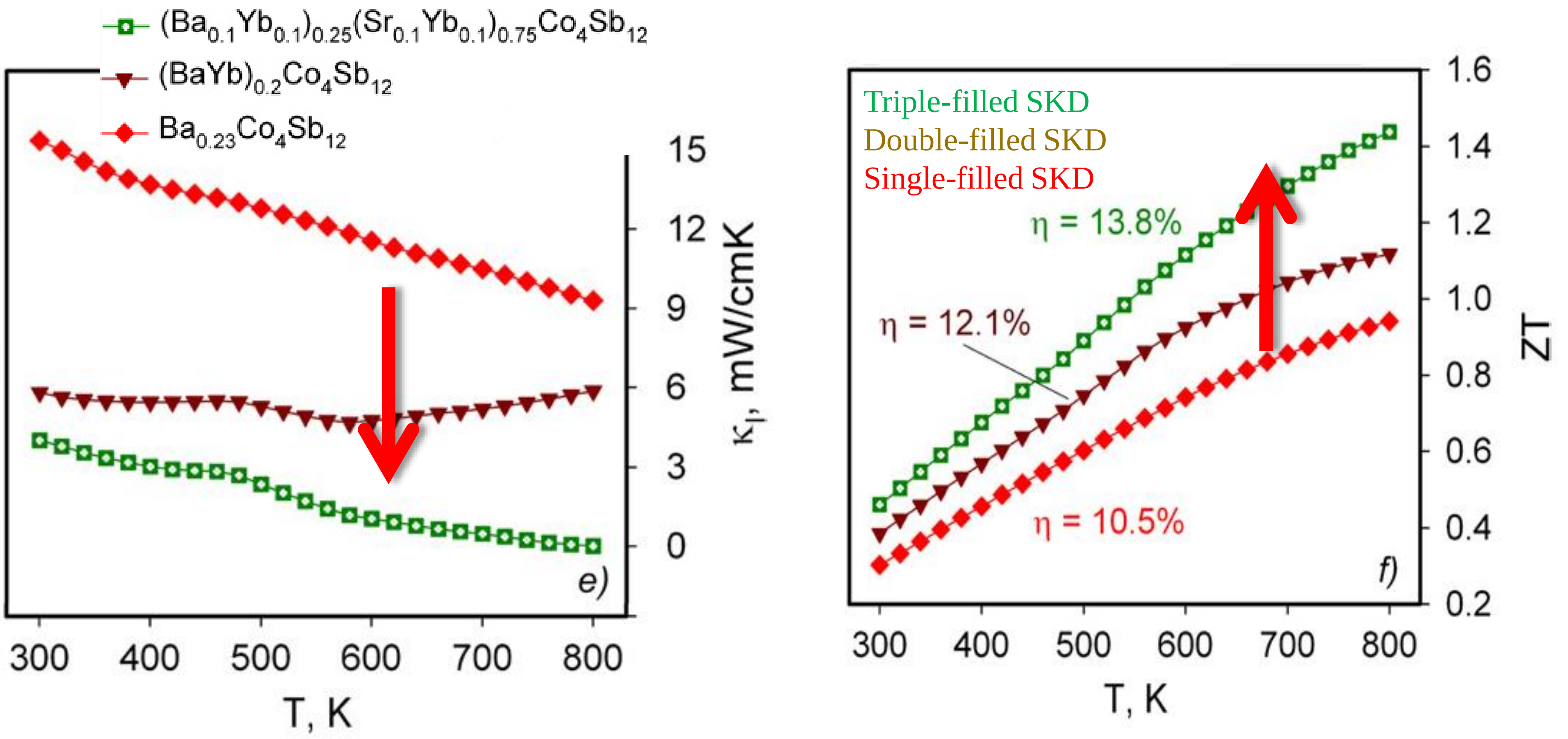
V. Pardo *et al.*, PRB 85, 214531 (2012)

Weak coupling of "Rattling filler" with the SKD.

Decoupling: High Electrical Conductivity and low Thermal Conductivity

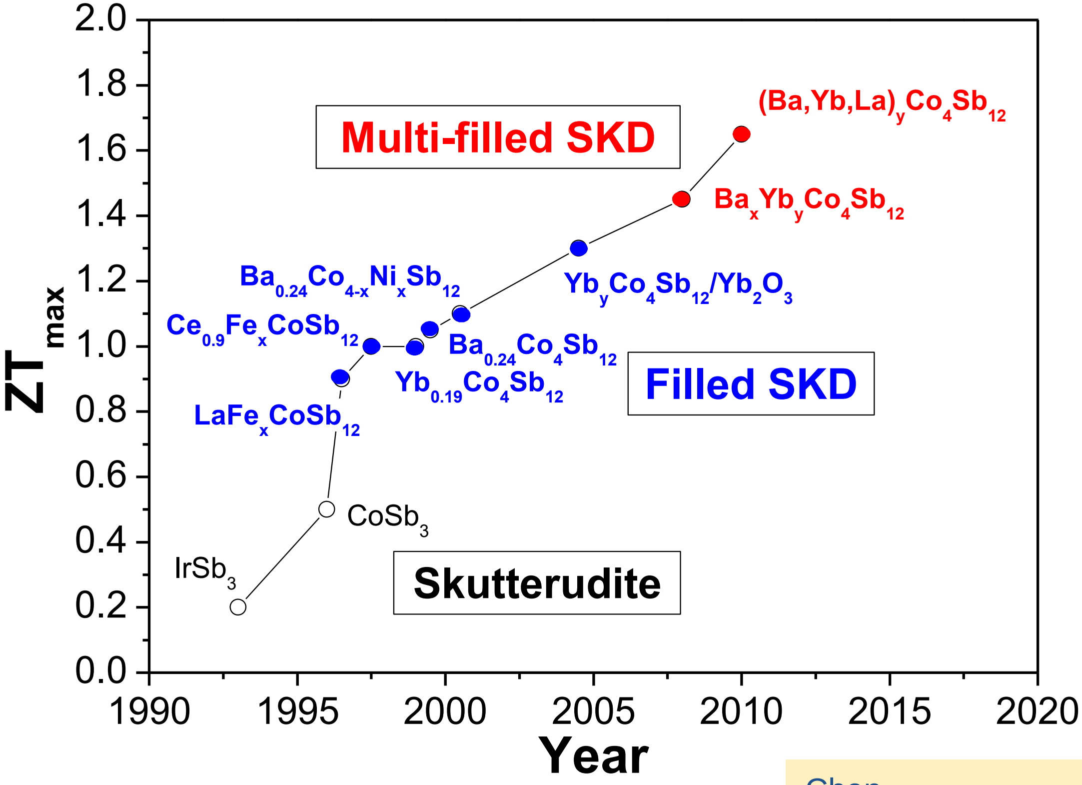
Development of Thermoelectric Materials

Filled Skutterudites



Xun Shi, et al., J. Am. Chem. Soc. 2011, 133, 7837–7846

Development of Thermoelectric Materials



*Ref.: ICT 2014

1994

Slack IrSb$_3$
ZT=0.2 (700K)

T. Caillat
ZT=0.5 (700K)

1996

Sales
LaFe$_3$CoSb$_{12}$
ZT=0.9 (800K)

1997

Sales
CeFe$_3$CoSb$_{12}$
ZT=1.0 (800K)

2000

Nolas
Yb$_y$Co$_4$Sb$_{12}$
ZT=1 (650K)

2001

Chen
Ba$_y$Co$_4$Sb$_{12}$
ZT=1.1 (850K)

2006

Zhao
Yb$_y$Co$_4$CoSb$_{12}$-Yb$_2$O$_3$
ZT=1.36 (850K)

2011

Shi
(Ba,Yb,La)Co$_4$Sb$_{12}$
ZT=1.7 (850K)

Development of Thermoelectric Materials

Broad Spectrum of Localized Modes

TABLE II. Spring constant k and resonance frequency ω_0 in the [111] and [100] directions of $R_{0.125}Co_4Sb_{12}$, where R = la, Ce, Eu, Yb, Ba, Sr, Na, and K.

		[111]		*[100]*	
R	Mass (10^{-26} Kg)	k (N/m)	ω_0 (cm^{-1})	k (N/m)	ω_0 (cm^{-1})
La	23.07	36.10	66	37.42	68
Ce	23.27	23.72	54	25.18	55
Eu	25.34	30.16	58	31.37	59
Yb	28.74	18.04	42	18.88	43
Ba	22.81	69.60	93	70.85	94
Sr	14.55	41.62	90	42.56	91
Na	3.819	16.87	112	17.18	113
K	6.495	46.04	141	46.70	142

1. J. Yang, W. Zhang, S. Q. Bai, Z. Mei, and L. Chen, Appl. Phys. Lett. **90**, 192111 (2007)

Development of Thermoelectric Materials

Electronegativity Rule for SKD Filler

$$\Delta\chi = \chi_{Sb} - \chi_i \geq 0.8$$

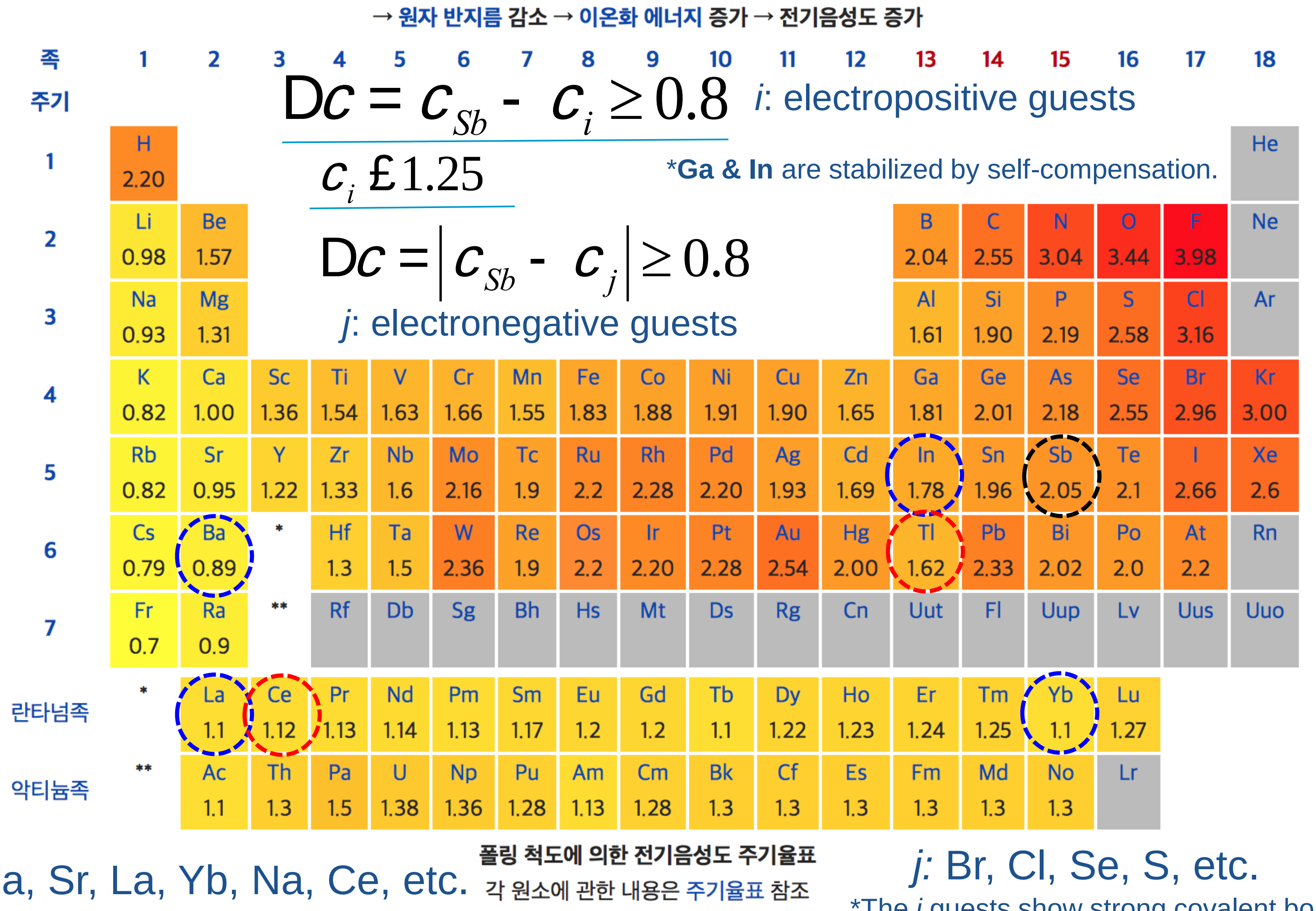
i: electropositive guests

$$\chi_i \leq 1.25$$

*__Ga & In__ are stabilized by self-compensation.

$$\Delta\chi = \left|\chi_{Sb} - \chi_j\right| \geq 0.8$$

j: electronegative guests



→ 원자 반지름 감소 → 이온화 에너지 증가 → 전기음성도 증가

족 주기	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
란타넘족	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
악티늄족	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr		

폴링 척도에 의한 전기음성도 주기율표

각 원소에 관한 내용은 주기율표 참조

i: K, Ba, Sr, La, Yb, Na, Ce, etc.

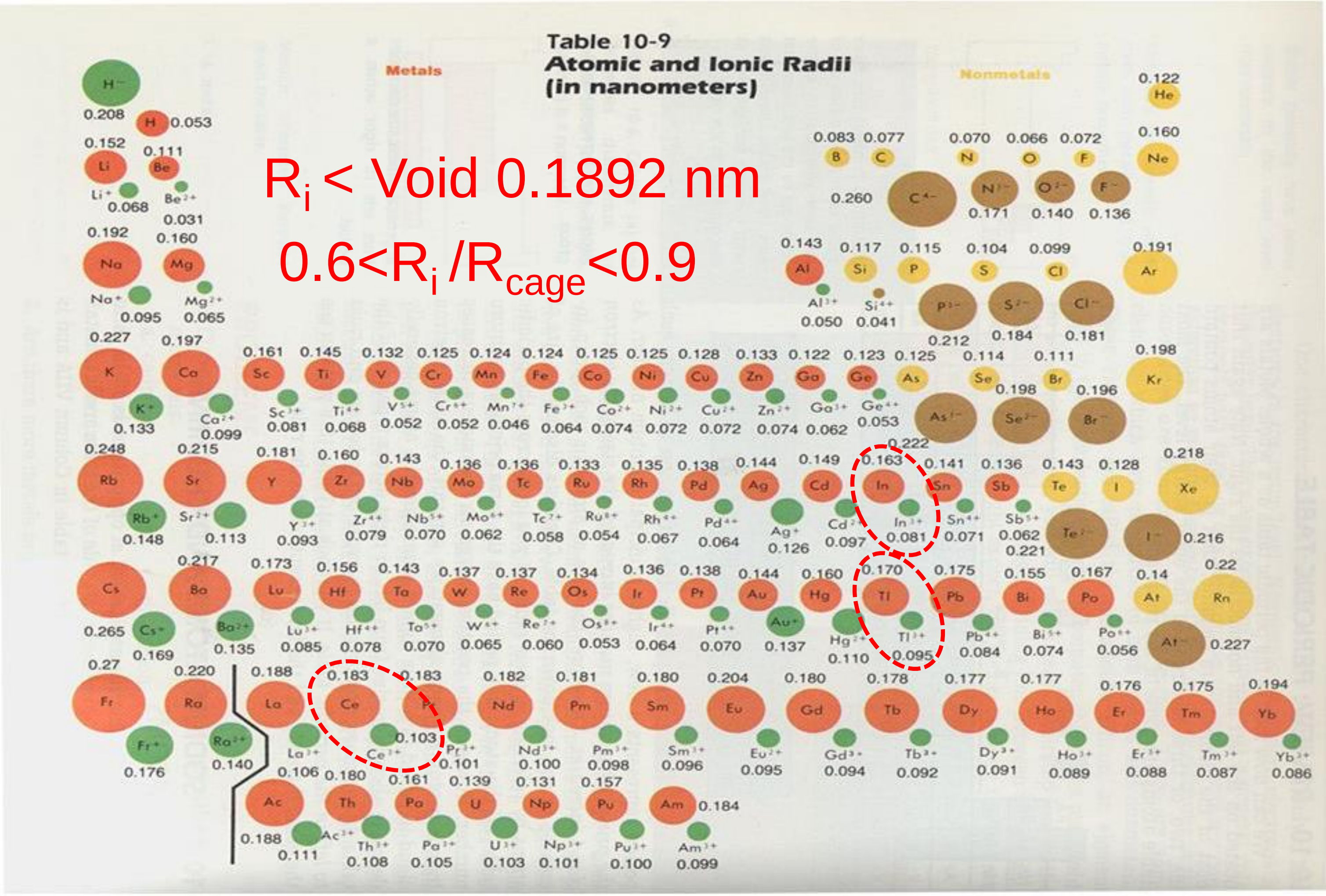
j: Br, Cl, Se, S, etc.

*The *j* guests show strong covalent bonding, leading to cluster vibration which decreases thermal conductivity

Development of Thermoelectric Materials

Ionic Size Rule for SKD Filler

Ionic Radii vs Atomic Radii

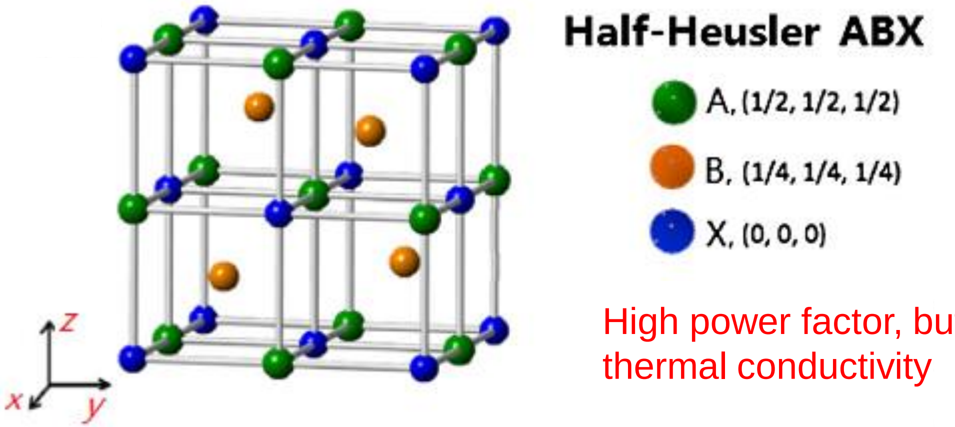


$R_i <$ Void 0.1892 nm

$0.6 < R_i / R_{cage} < 0.9$

Development of Thermoelectric Materials

Half-Heusler



Liu WS, Yan X, Chen G et al,. Nano Energy 1:42–56 (2012)

P-type : A = (Hf, Zr, Ti), **B = Co**, X= Sb

N-type: A = (Hf, Zr, Ti), B = Ni, X=Sn

High power factor, but high thermal conductivity

- ❖ Heavily alloy A site with large mass contrast (AA'NiSn)

  A: Ti → $Zr_xHf_yTi_{0.5}$

  κ: 9.3 W/mK → 3-6 W/mK

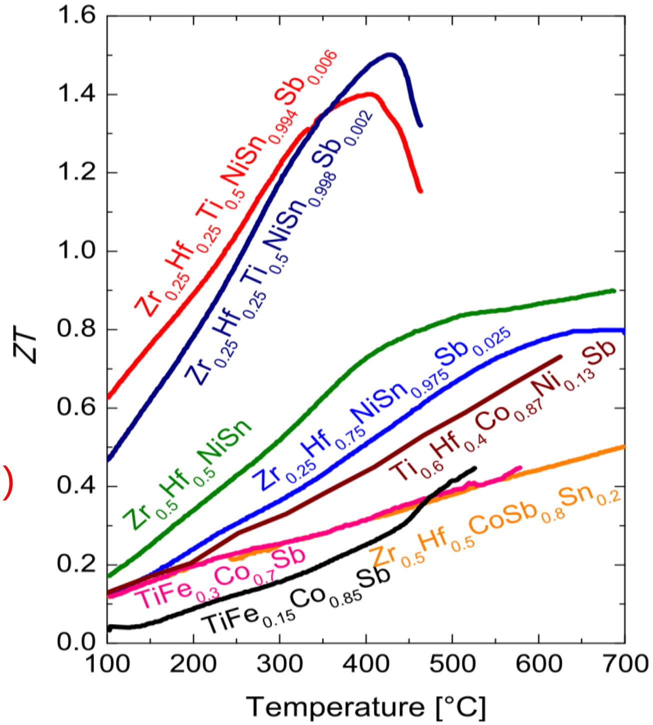
  By mass fluctuation (phonon-phonon scattering)

- ❖ Lightly dope on the X site to introduce carriers (AA'NiSn:Sb)

  X: Sn → $Sn_{1-\delta}Sb_\delta$

  σ: 100 S/cm → 1200 S/cm

Values from: H. Hohl et al, *J. Phys.: Condens. Matter* 11 (1999) 1697-1709.

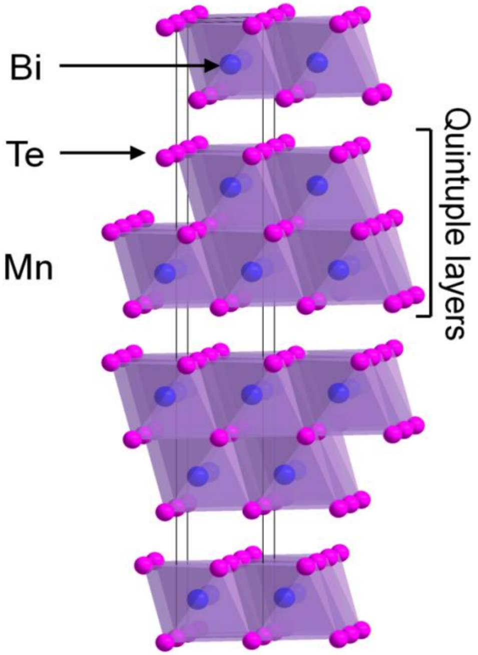


T.Graf et al, *Prog. Solid State Chem*. 39 (2011) 1-50

$(Hf_{0.5}Zr_{0.5})_{1-x}Ti_xNiSn_{0.998}Sb_{0.002}$

Development of Thermoelectric Materials

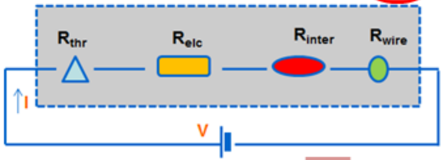
Charge Transport in Bi_2Te_3 System



- Bi_2Te_3 is a unique thermoelectric material which can be used around room temperature.
- It can be used for both cooling and power generation applications.
- But it has weak Van der Waals bonding. → need powder processing

Necessity of Charge Transport Study

$$Q_C = \alpha_{ab} T_c I \boxed{- \frac{1}{2} R I^2} - K \Delta T$$



* R_{thr} : R. of thermo element
* R_{elc} : R. of electrode
* R_{inter} : R. of joint material
* R_{wire} : R. of lead wire

To minimize Joule loss,
Over 1000 S/cm is required

$$\sigma(T) = q\, n(T)\, \mu(T)$$

Need to control the charge transport

- Carrier concentration control by **Sb substitution** (p-type)
- Carrier concentration control by **Cu doping** (n-type)
- Mobility enhancement by studying scattering centers

Development of Thermoelectric Materials

For non-degenerate semiconductor thermoelectrics

$$\boldsymbol{ZT = \frac{[\eta - (r + 5/2)]^2}{(\beta \exp(\eta))^{-1} + (r + 5/2)}}$$

$\boldsymbol{\eta}$: Fermi energy
r: scattering parameter
β: materials parameter

$\boldsymbol{\beta}$ was first introduced by Chasmar and Stratton,

$$\boldsymbol{\beta = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_0 T}{k_L}} \qquad \boldsymbol{\sigma_0 = 2e\mu \left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2}}$$

$$\boldsymbol{\beta \propto \left(\frac{\mu}{k_L}\right)\left(\frac{m^*}{m}\right)^{3/2}}$$

*Although ***ZT*** equation holds only for a non-degenerate semiconductor, the materials parameter, ***β***, remains useful when the material is partly or completely degenerated.

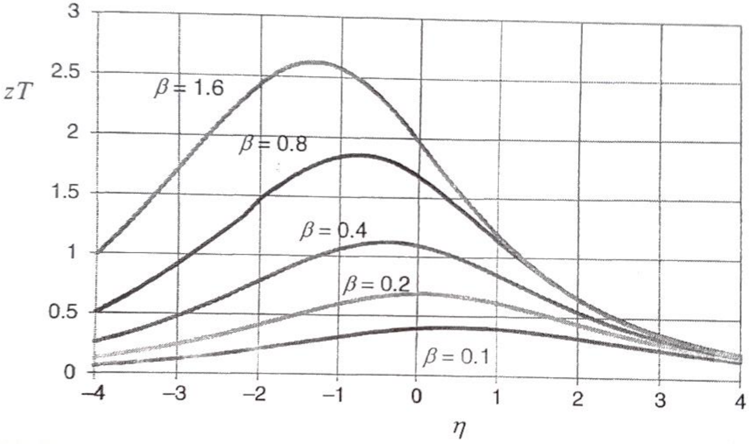
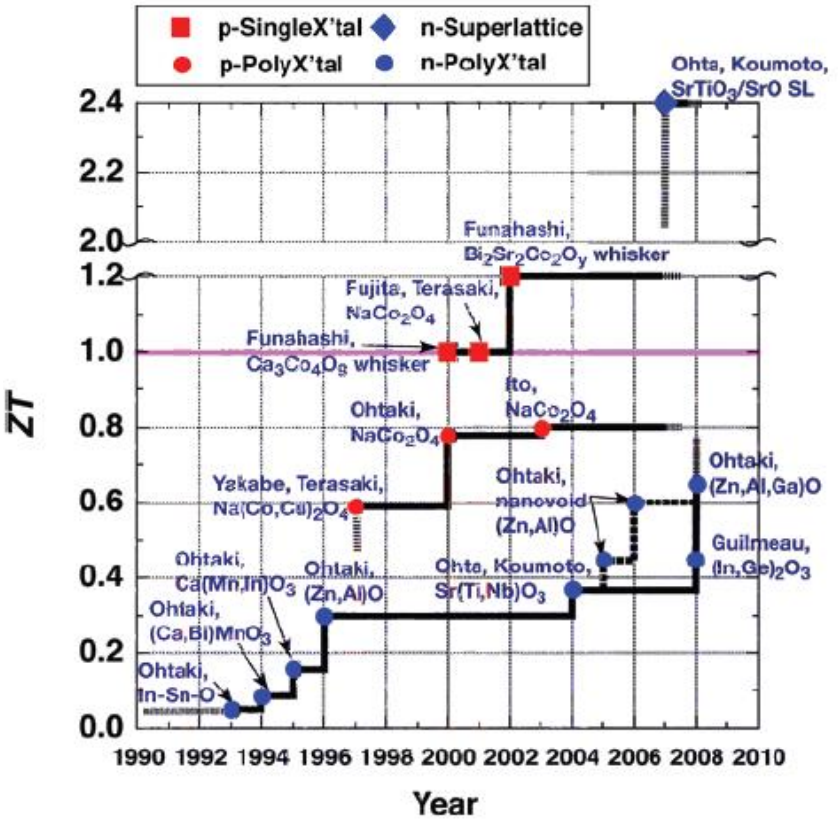


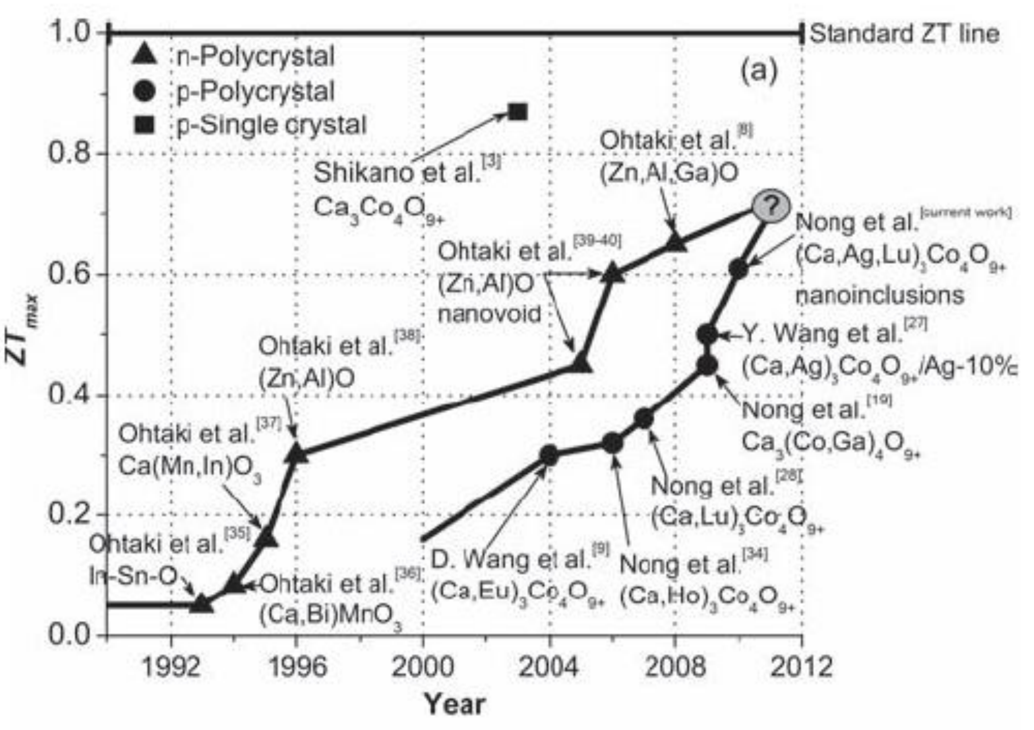
Fig. 4.2 The dimensionless figure of merit plotted against the reduced Fermi energy for different values of the parameter β. The scattering parameter $r = -1/2$

Julian H. Goldsmid, *Introduction to Thermoelectricity*, Springer (2010)

Development of Thermoelectric Materials

Oxide Thermoelectric Materials





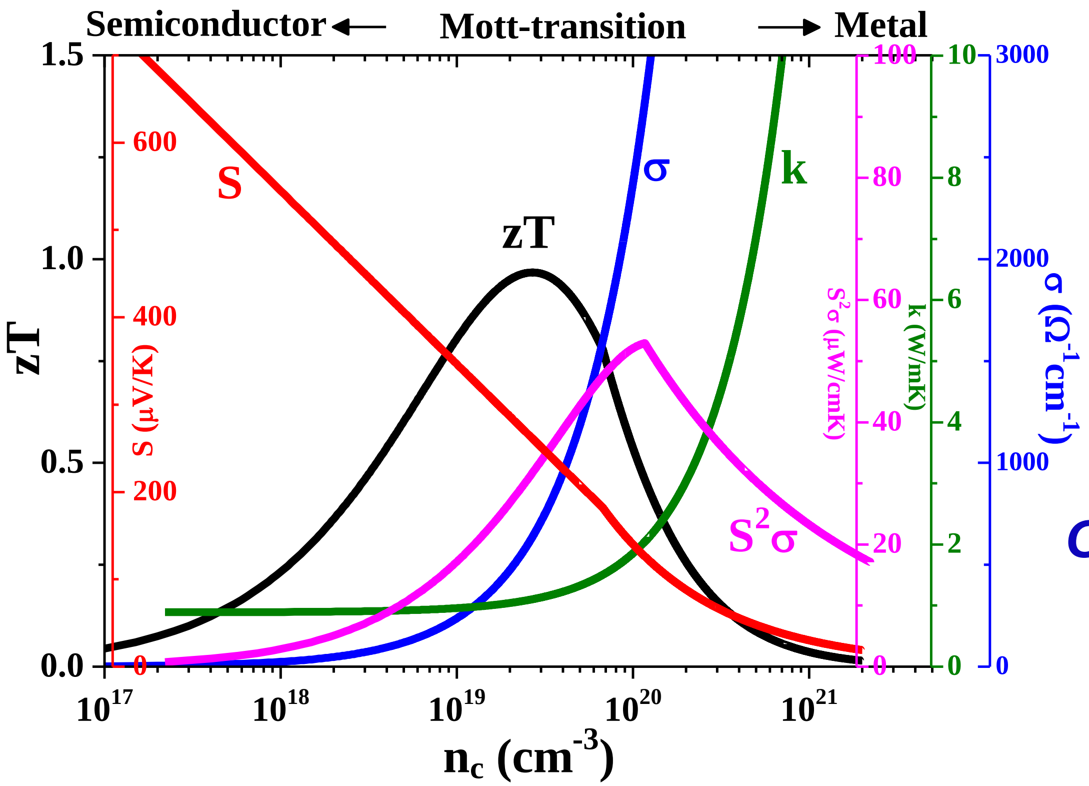
M. Ohtaki, Global COE Program Novel Carbon Resources Sciences Newsletter, 2010. 05.

N. V. Nong et al., Adv. Mater. 23, 2484 (2011)

Engineering Thermoelectric Materials

Oxide Thermoelectric Materials

How to create charge carriers in oxides?



Defect Engineering:

Oxide: Metal + Oxygen

$$M_{1-x-y}D_yO_{1-\delta}$$

***Cation* Vacancy** | **Donor dopant** | ***Oxygen* Vacancy**

***p*-type carrier** | ***n*-type carrier**

Mott-criterion

(metal-insulator transition): $n_e^{1/3} a_0 \sim 0.25$

$$D_2O_3 \rightarrow 2D_A^{\bullet} + 2e' + 3O_O^X$$

S. Lee *et al.*, JECS 32 (2012)

Oxide Thermoelectric Materials

How to generate the defects?

Equilibrium Concentration of Point Defects

Equilibrium Concentration varies with temperature and atmosphere:

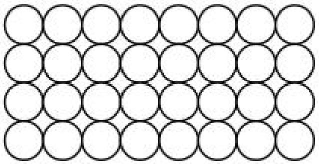
No. of defects

Activation energy (required for formation of vacancy)

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{k_B T}\right)$$

No. of potential defect sites

Temperature



Each lattice site is a potential vacancy site.

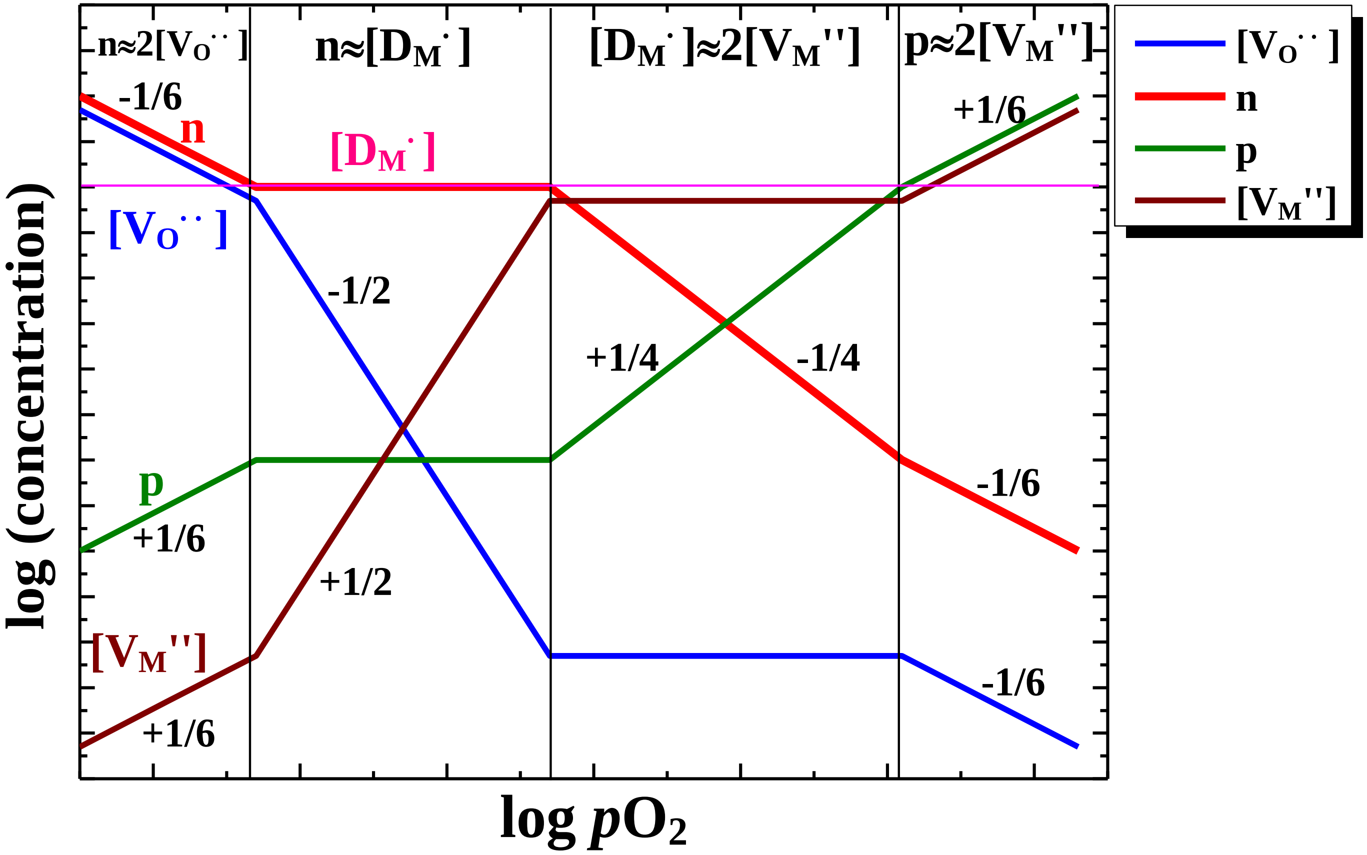
Engineering Thermoelectric Materials

Oxide Thermoelectric Materials

How to generate the charge carriers?

For *n*-type: Donor-doped MO / Reduced MO

$$D_2O_3 \rightarrow 2D_M^{\cdot} + 2e' + 3O_O^X \qquad O_O^X \rightarrow V_O^{\cdot\cdot} + 2e' + \frac{1}{2}O_2(g)$$

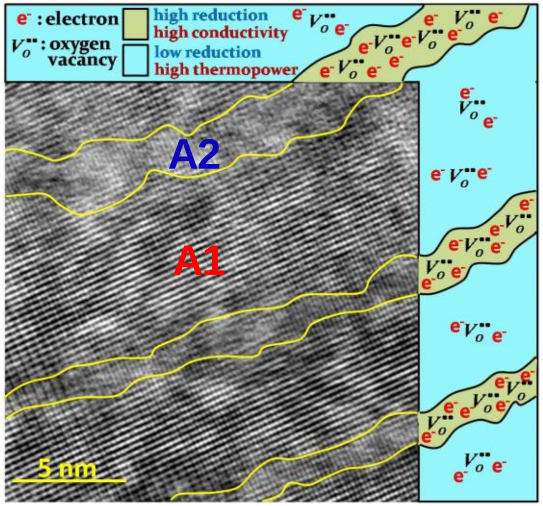


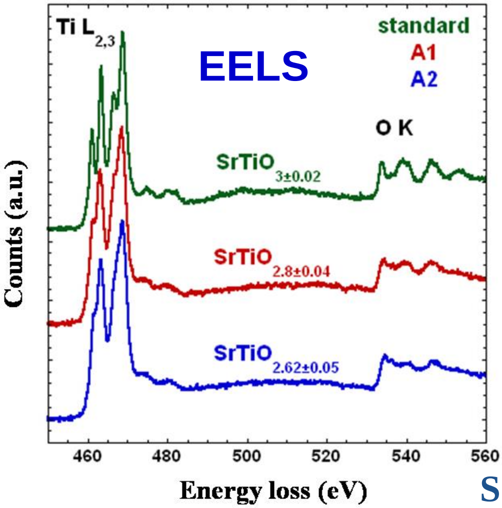
Development of Thermoelectric Materials

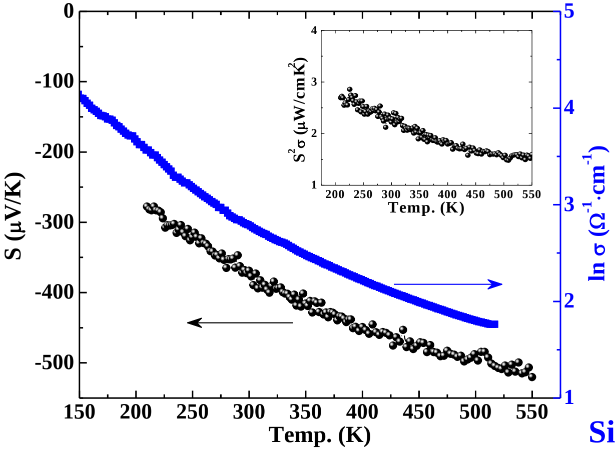
Oxide Thermoelectric Materials

Decoupling between σ and S

TEM image of Reduced $SrTiO_3$

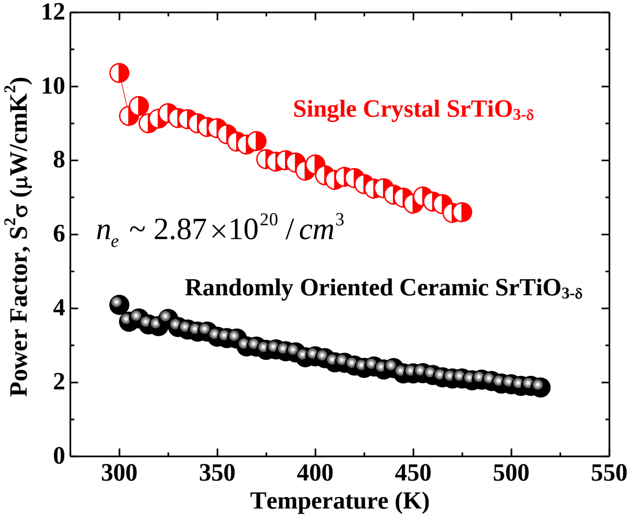






- Conductivity: metallic
- Thermopower: semiconducting

Single and Polycrystalline $SrTiO_{3-\delta}$

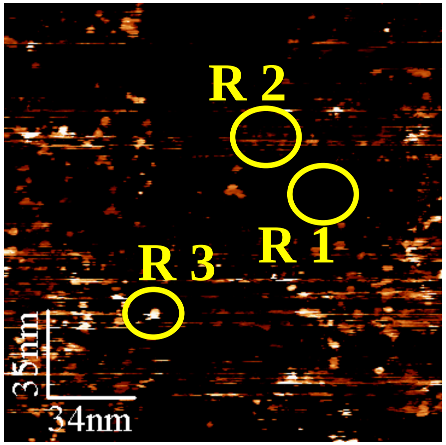


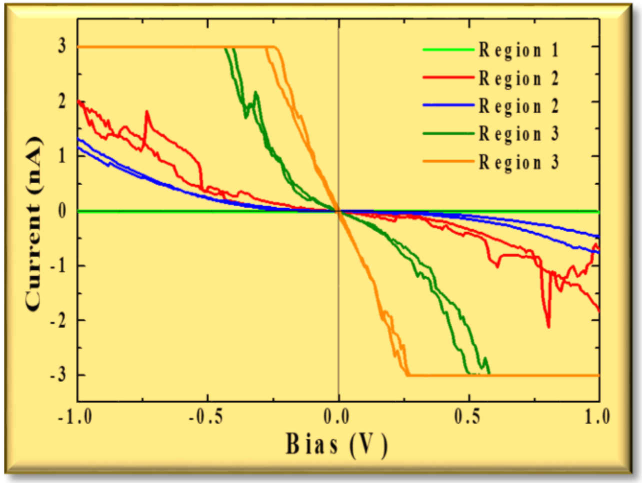
S. Lee *et al.*, Phys. Rev. B 79, 134110 (2009)

Development of Thermoelectric Materials

Oxide Thermoelectric Materials

- **Quantum Confinement Effect**

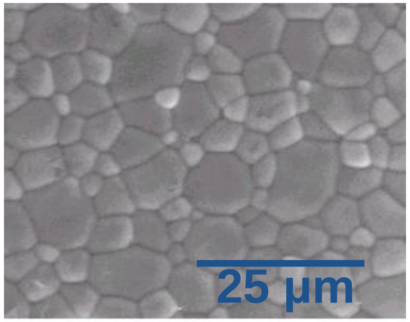




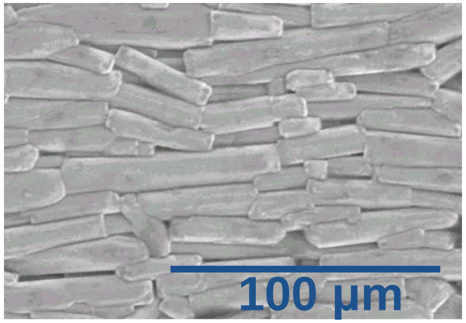
Conductive AFM

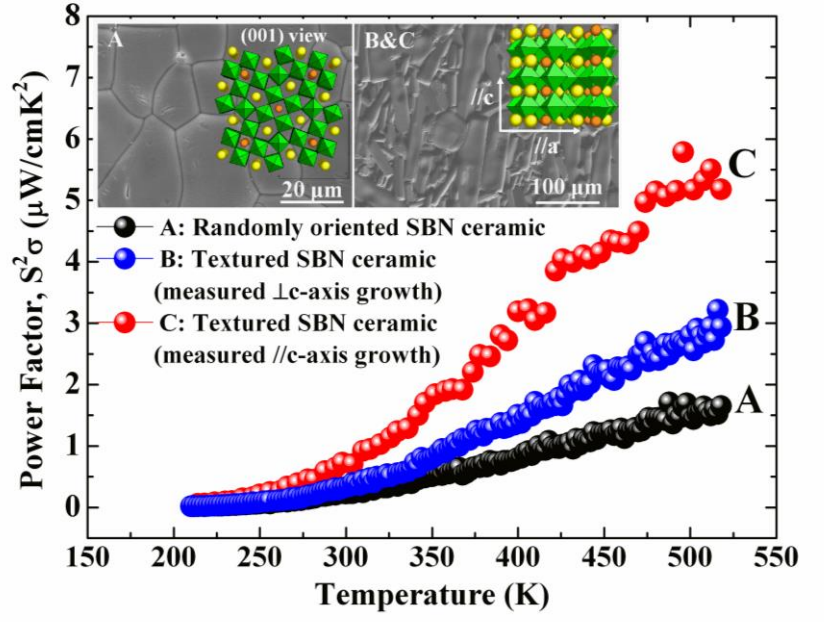
- **Textured Ceramic**

Randomly Oriented SBN



[001] Textured SBN

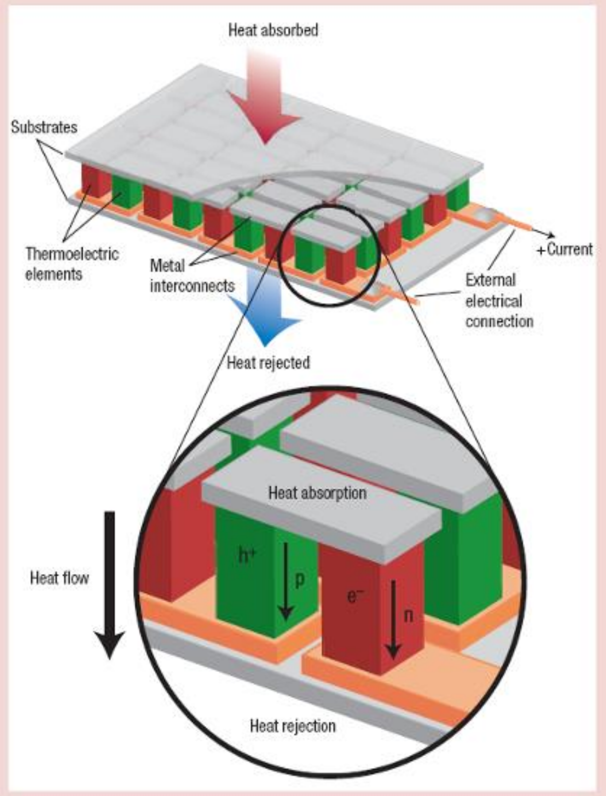




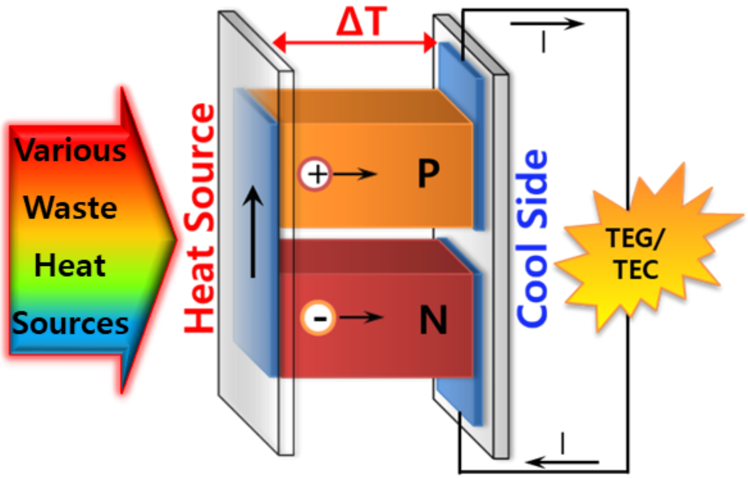
S. Lee *et al.*, JMR 26[1], 26-30 (2011)

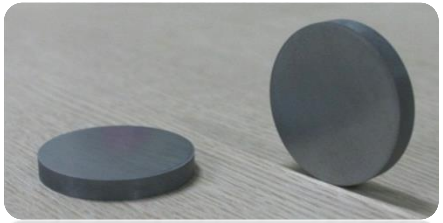
Thermoelectric Modules

Thermoelectric Module



Snyder et al., *Nature* (2008)





Engineering Thermoelectric Modules

High Efficiency (η) = Material Figure of Merit (ZT)
+ Modularization + System Design

Conversion Efficiency

$$\eta = \frac{T_h - T_c}{T_h}\cdot\frac{M-1}{M+(T_c/T_h)}$$

$$M = \sqrt{1+Z(T_h+T_c)/2}$$

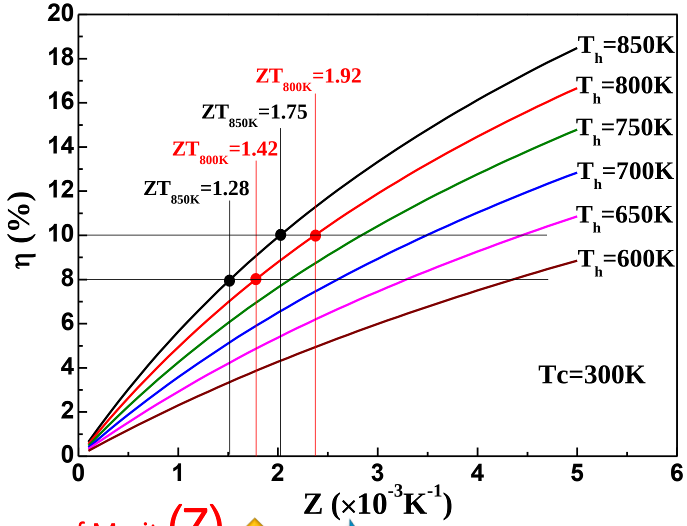


Figure of Merit (Z)
Temp. (T) ↑ ➡ Efficiency (η) ↑

Material ZT

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

Z : Figure of Merit
α : Seebeck Coeff.
σ : Electrical Cond.
κ : Thermal Cond.
T : Absolute Temp.

Module/System

$$P_{max} = \frac{1}{4}\frac{(\alpha_{pn}\Delta T)^2}{R_L}$$

$$(P_{max}@R_L = r_{pn})$$

P_{max}: Maximum Power
α_{pn}: pn Seebeck
ΔT: Temp. Difference
r_{pn} : Internal Resistance
R_L : External Resistance

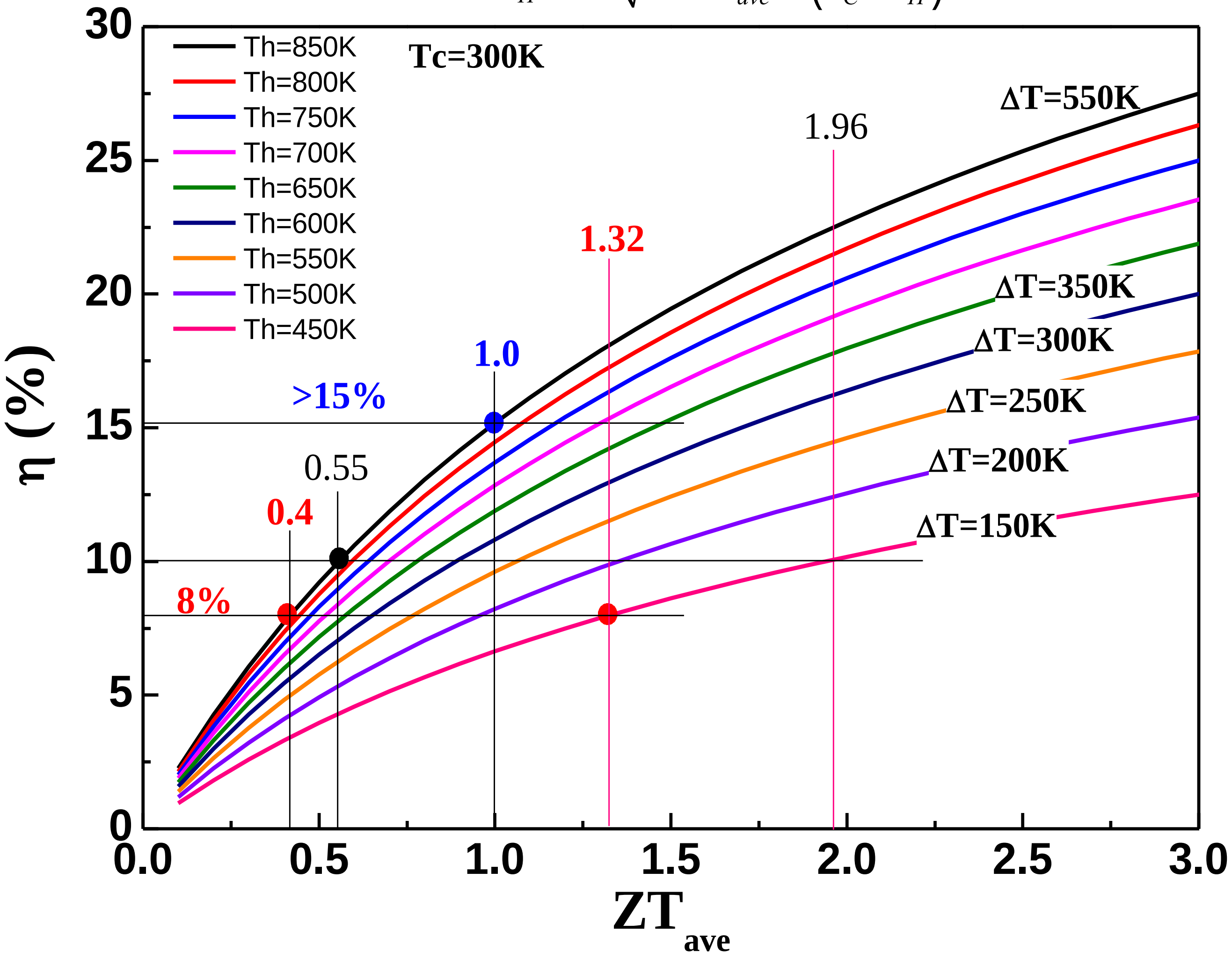
To commercialize

Z ↑, $R_{L\text{-}pn}$ ↓, ΔT ↑

Material Module System

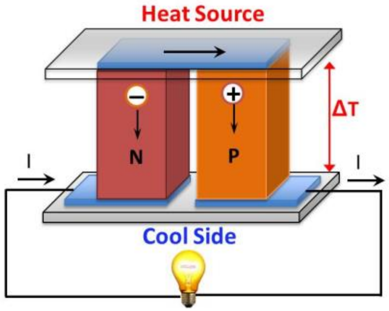
Engineering Thermoelectric Modules

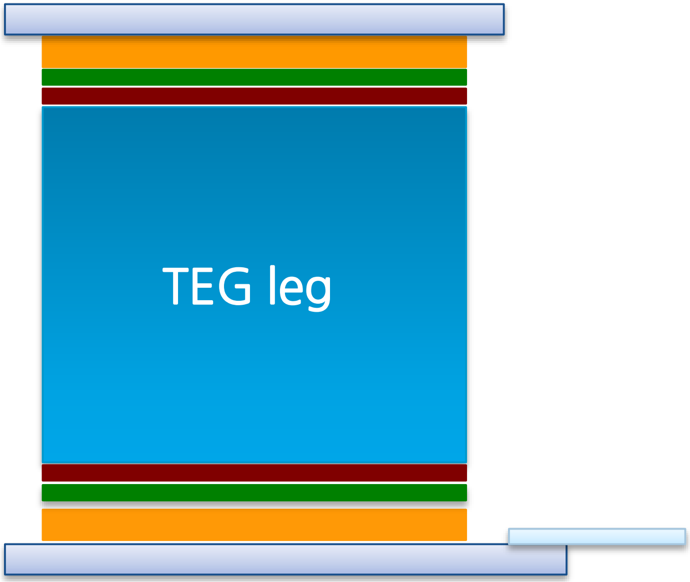
$$h = \frac{(T_H - T_C)}{T_H} \times \frac{\sqrt{1+ZT_{ave}} - 1}{\sqrt{1+ZT_{ave}} + (T_C / T_H)}$$



Engineering Thermoelectric Modules

Bottleneck of TEG Module for Mid-High Temperature Applications





Substrate	Thermal Cond., Thermal Expansion
Electrode	Electrical Cond., Thermal Expansion, Bonding Strength, Thermal Cond.
Brazing	Ohmic contact, Thermal Expansion, Bonding Strength/conditions, Durability
Diffusion Barrier	Ohmic contact, Thermal Expansion, Bonding Strength, forming conditions, Durability
TEG leg	ZT, High Temperature Stability, Mechanical Strength, Machinability,
Lead Wire	Ohmic contact, Electrical Conductivity

Development of Thermoelectric Modules

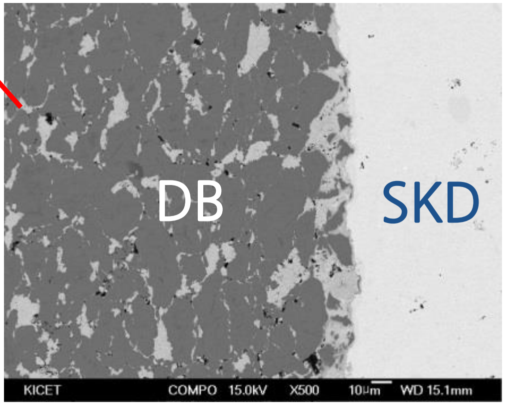
Diffusion Barrier Material and Process Design

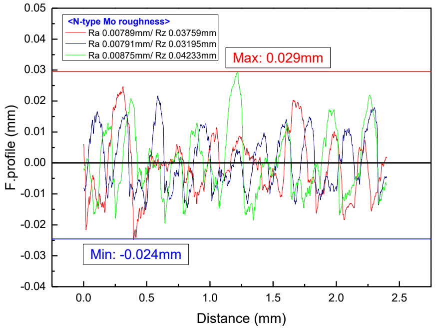
- Development of Diffusion Barrier (DB) Materials
- Development of DB Process

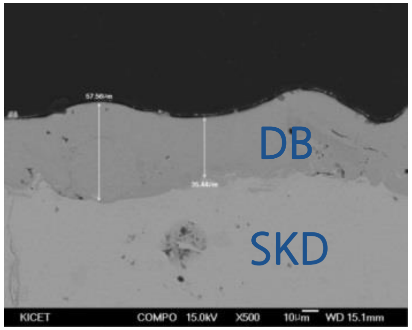
DB by TS

DB layer

DB by SS







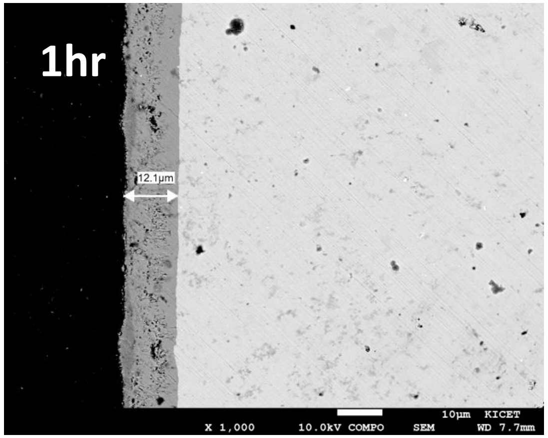
DB roughness: <~50 um

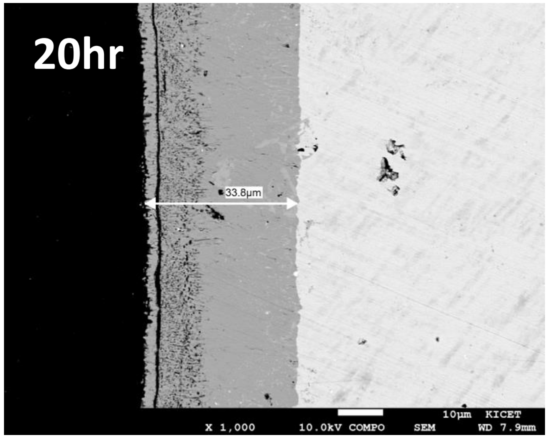
86~111 kgf/cm^2

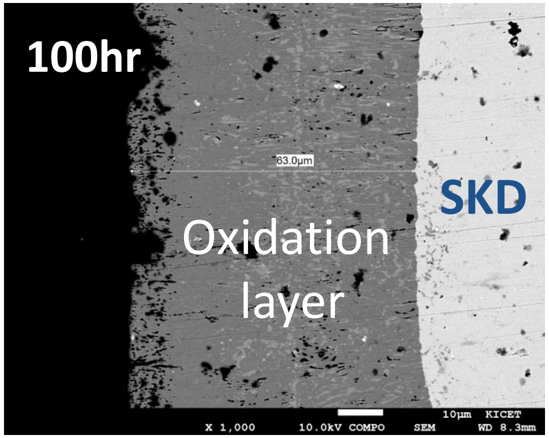
Development of Thermoelectric Modules

High Temperature Stability

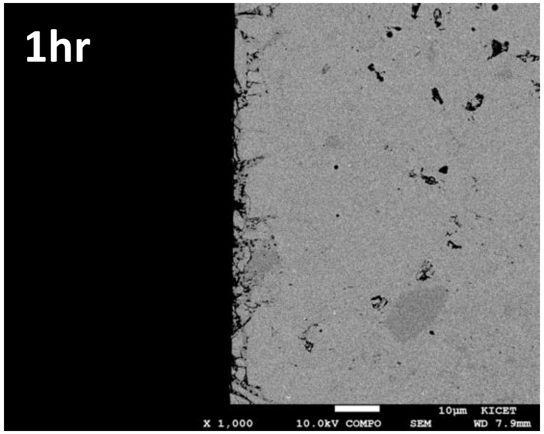
- Enhancing Technology of high temperature stability (Oxidation, Evaporation)
- Module Packaging Technology

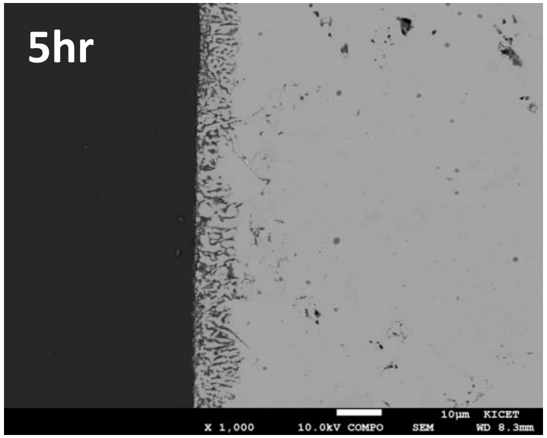


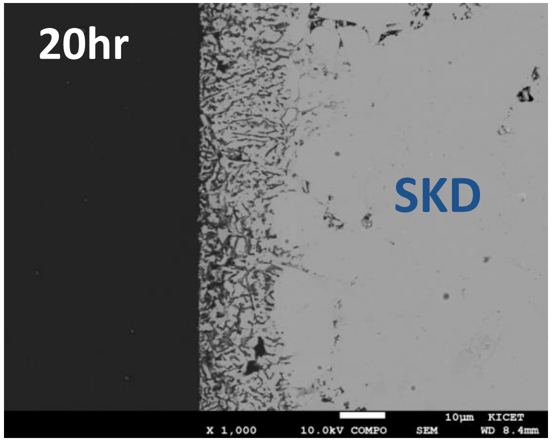




SKD @600°C in air

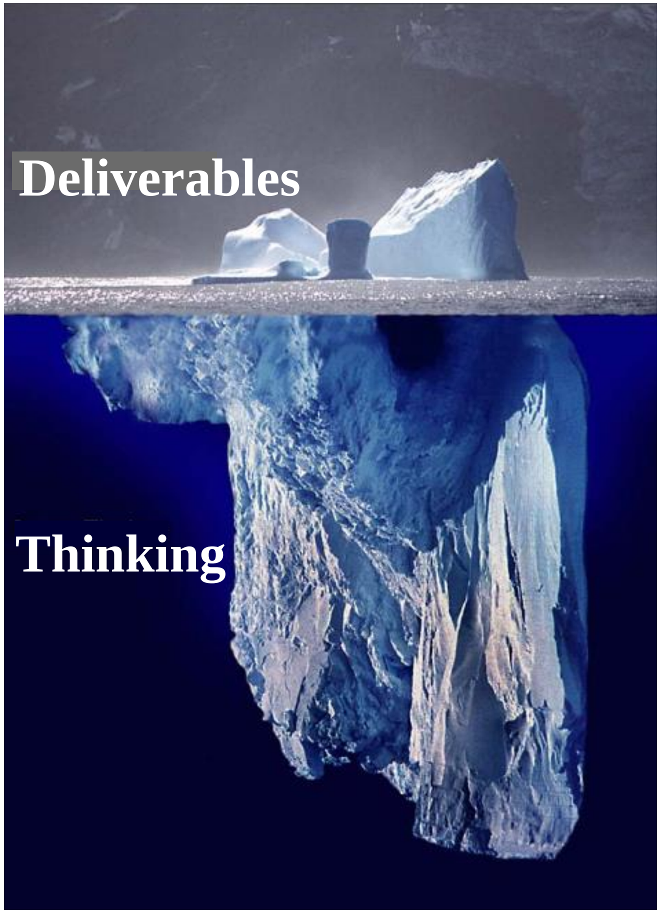


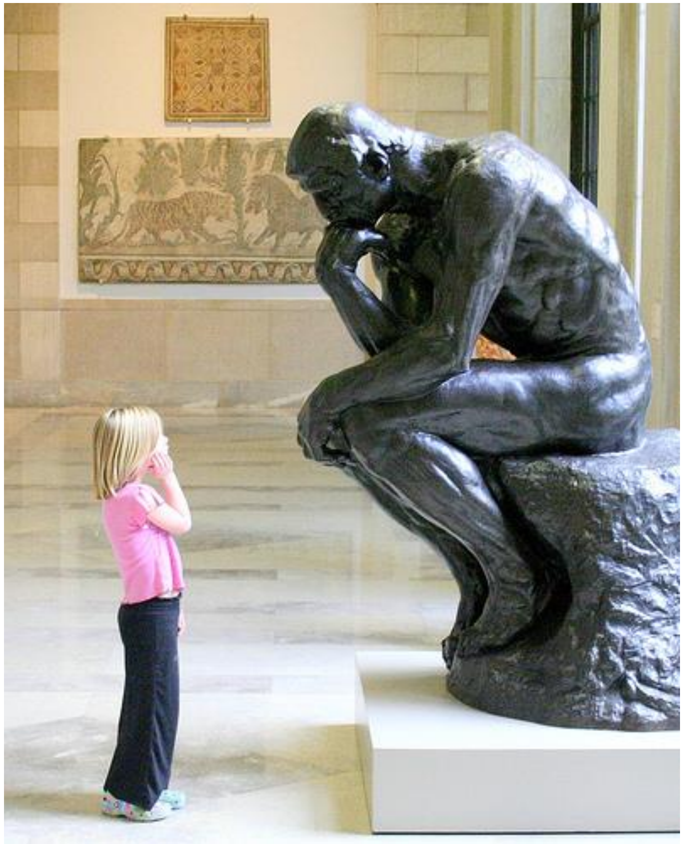




@600°C vacuum

Conclusion





Thank you for your attention!