Selection Criteria for Candidate Materials

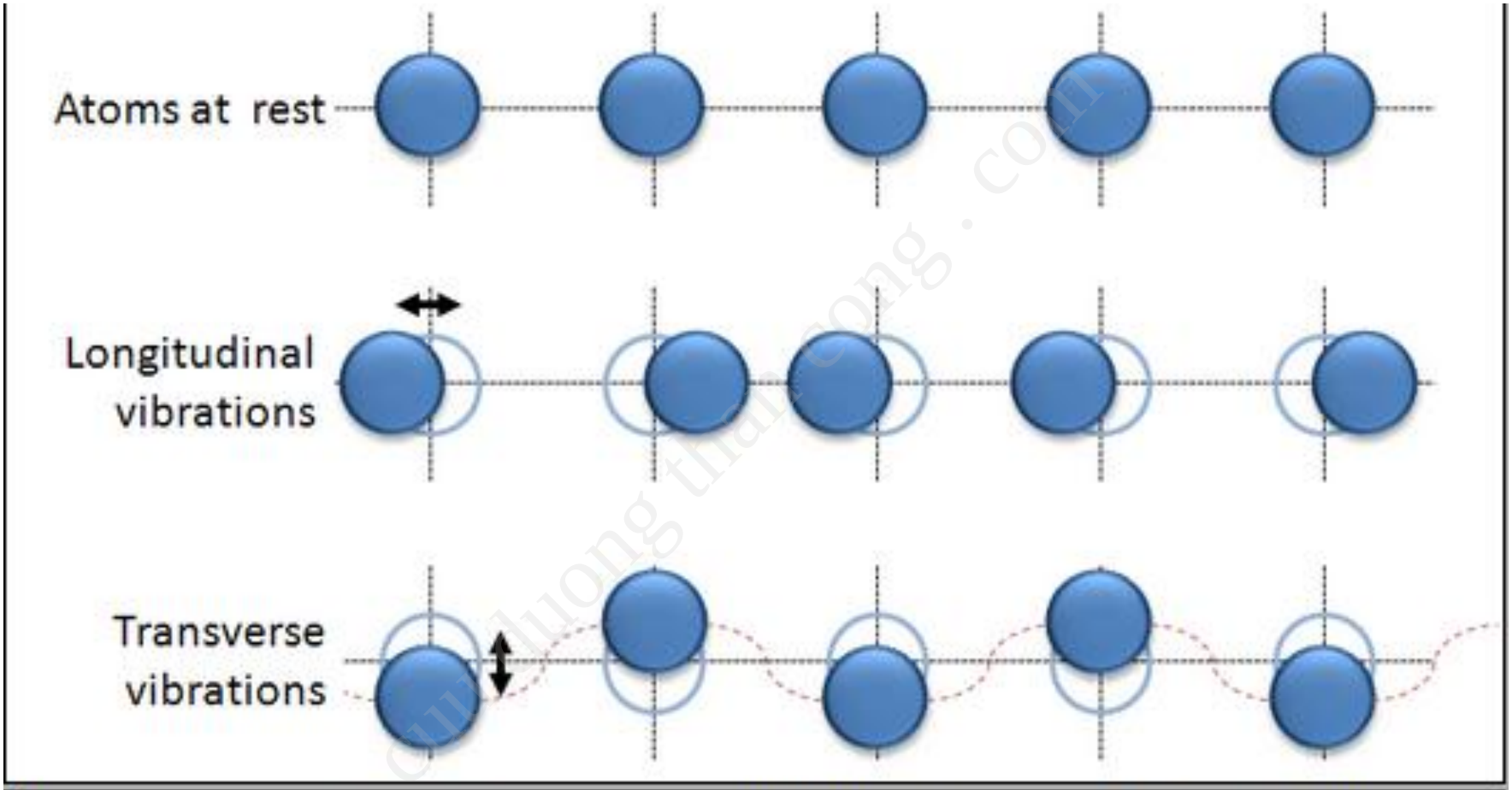
$$zT = \frac{S^2 \sigma}{\kappa_l + \kappa_e}$$

Increasing zT

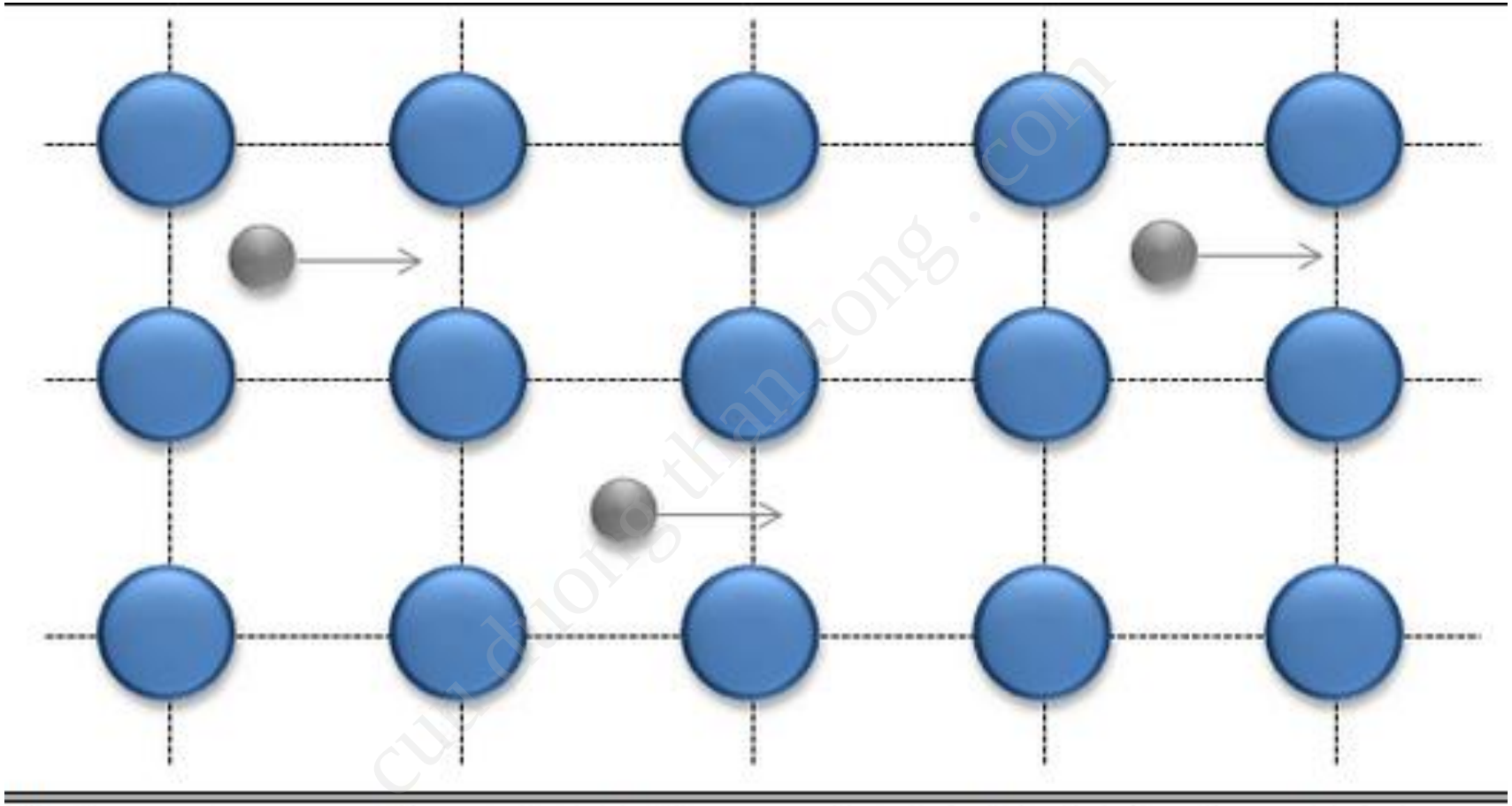
Reducing Thermal Conductivity

One of the primary methods for increasing the **zT** is to reduce the thermal conductivity.

- ✓ The thermal conductivity of a material is made up of two components, the lattice component and the electronic component.
  - ❖ The electronic component of the thermal conductivity comes from the heat that is transfered through the material via the charge carriers and is directly related to the electrical conductivity (**σ** in the numerator). Therfore, reducing κ_e is not beneficial to the **zT**.
  - ❖ The lattice component of the thermal conductivity is a result of heat transfer via lattice vibrations, also known as phonons. κ_l is independent of the numerator and thus reducing this value can contribute to an increase in the final **zT** value.



Phonons are vibrations that move through the lattice carrying heat (κ_l). These vibrations happen in the longitudinal and transverse directions.



Electrons also move through the lattice carrying heat. Scattering these electrons can reduce the κ_e; however scattering electrons reduces electrical conductivity and is detrimental to the **zT** value.

There are several methods for reducing the lattice thermal conductivity of a material. Each of these methods involves scattering the phonons as they move through the lattice at different length scales.

The three methods discussed below scatter phonons in three different scales: angstroms, nanometers, and microns.

1. Angstroms:

Substitution and doping methods involve replacing a fraction of one of the original elements in the host material with an isoelectronic atom (substitution) or an atom with ±1 electron (n or p-type doping).

This "impurity" atom is randomly dispersed throughout the unit cells of the material and has a different size and mass than the atoms in the host matrix. Therefore, the phonons traveling through the lattice experience a defect and are scattered on the atomic or angstrom length scale.

2. Nanometers:

Phonons are scattered on the nanometer length scale by using nanoinclusions. These inclusions are nano-scale particles incorporated into the material during synthesis or sintering which may be made of the same compound or a unique material.

The nano-inclusions cause the phonons traveling through the material at the nanometer scale to experience a defect and scatter, reducing the thermal conductivity.

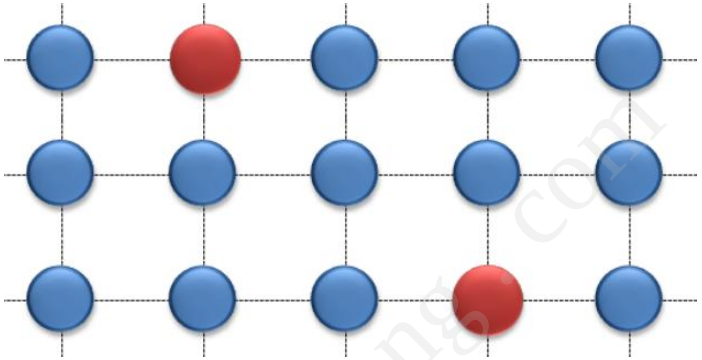
3. Microns:

Grain boundary engineering is used to scatter the long wavelength phonons in the range of several microns. This is done by powder processing and adjusting the sintering parameters in order to reduce the final grain size of the material.

As phonons encounter a grain boundary they are scattered, thus increasing the number of grains can reduce the lattice thermal conductivity on the micron length scale.

Each of these methods may be incorporated into a material individually or in combination. Depending on the intrinsic thermal conductivity of the material, the different methods may have different effectiveness in enhancing the overall zT value.

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



Host atoms (blue) throughout the unit cell are replaced by atoms with one more or one less electron (red), changing the carrier concentration of the material

Increasing Power Factor

The numerator of the above **zT** equation is often referred to as the power factor. By increasing this value the **zT** of a material can be enhanced. The primary method for increasing the power factor is doping.

Doping is done by replacing one of the host atoms with an element with ± one electron (compared to the host element). In doing this, the carrier concentration of the compound can be tailored to the optimal level. Doping concentrations are usually rather low (<15%) and often reach a solubility limit where the compound cannot be formed homogeneously with large concentrations of the dopant atom.

The Seebeck coefficient and electrical conductivity are both dependant on the carrier concentration and carrier mobility. Thus the ability to tailor the carrier concentration via atomic doping is critical to optimizing the power factor.

Selection Criteria for Candidate Materials

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

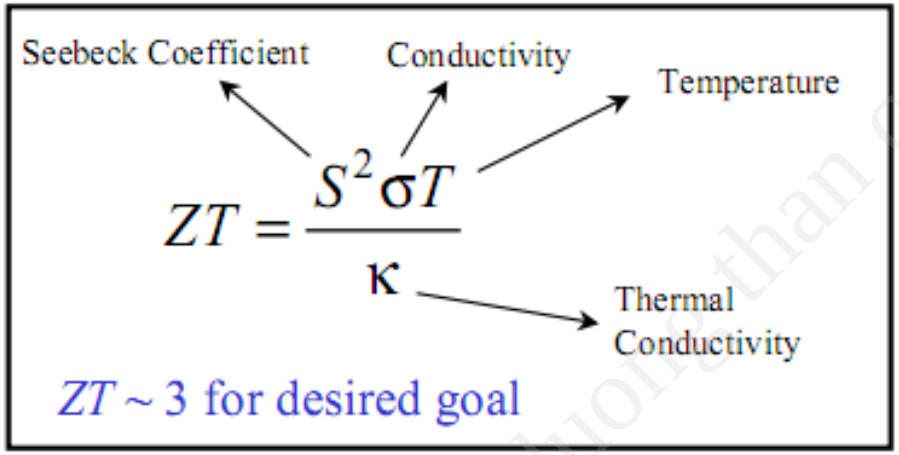
m = effective mass
τ = scattering time
r = scattering parameter
k_{latt} = lattice thermal conductivity
T = temperature
γ = band degeneracy

Guiding Principles:

- ✓ ‰Narrow band-gap semiconductors : For operation at room temperature
- ✓ ‰Heavy elements : High μ, low κ
- ✓ ‰Large unit cell, complex structure : low κ
- ✓ ‰Highly anisotropic or highly symmetric
- ✓ ‰Complex compositions : low κ, complex electronic structure
- ✓ ‰Mass Fluctuation : low κ
- ✓ ‰High density of states near the Fermi level : high Seebeck coefficient

Motivation for Nanotechnology in Thermoelectricity

(2D quantum wells, 1D nanowires, 0D quantum dots)



Difficulties in increasing ZT in bulk materials:

$S \uparrow \Longleftrightarrow \sigma \downarrow$

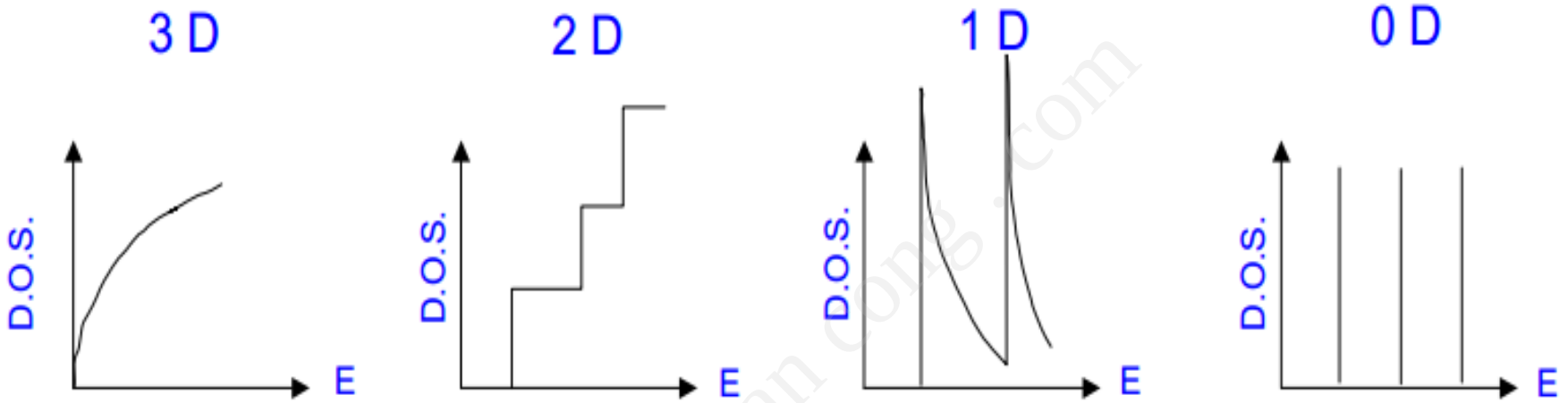
$\sigma \uparrow \Longleftrightarrow S \downarrow$ and $\kappa \uparrow$

$\Rightarrow$ A limit to Z is rapidly obtained in conventional materials

$\Rightarrow$ So far, best bulk material ($Bi_{0.5}Sb_{1.5}Te_3$) has $ZT \sim 1$ at 300 K

Low dimensional physics gives additional control:

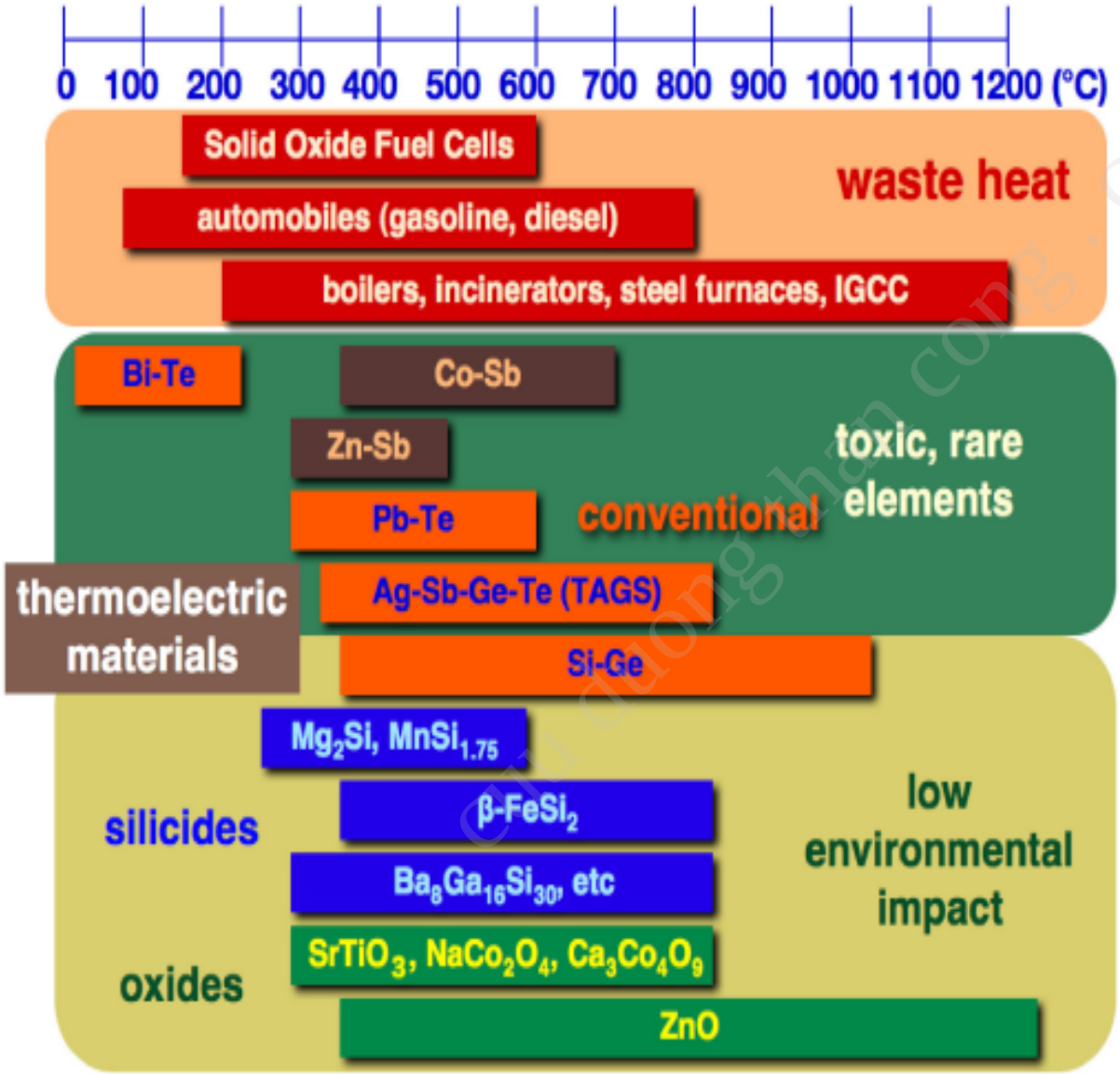
- Enhanced density of states due to quantum confinement effects
  $\Rightarrow$ Increase S without reducing σ
- Boundary scattering at interfaces can reduce κ more than σ
- Possibility of materials engineering to further improve ZT

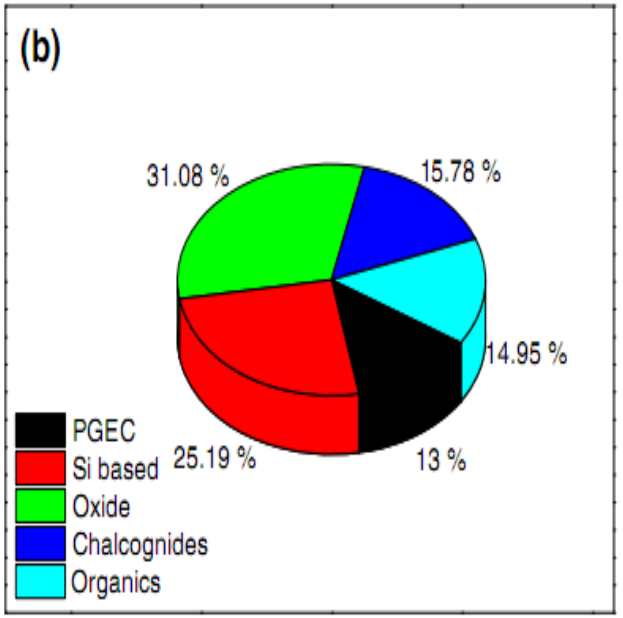


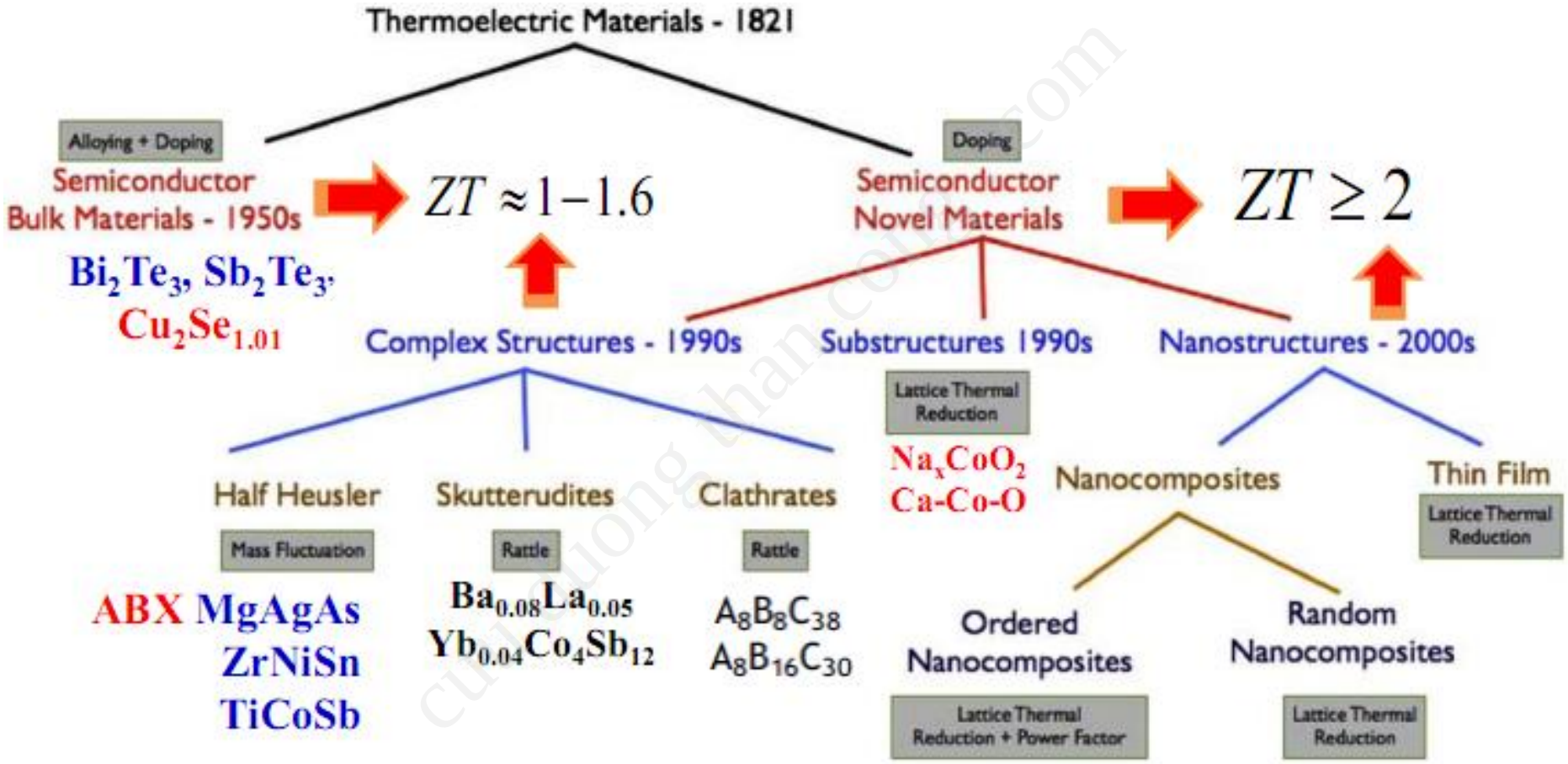
- (D.O.S.) more favourable (stronger dependence of DOS on E)

➔ increase of α without increasing ρ

- additional degree of freedom (size) for tailoring of the transport
- possibility to explore the anisotropy of transport properties
- chance to decrese $\lambda_{lattice}$ due to phonon scattering on interfaces
- $ZT_{0D} > ZT_{1D} > ZT_{2D} > ZT_{3D}$







Bulk & Film--->Nano Materials

Bismuth telluride (Bi_2Te_3) and its alloys are good thermoelectric materials below room temperature.

Above room temperature the relatively narrow band gap causes mixed conduction due to both electrons and holes. This leads to reduced Seebeck coefficient.

Bismuth telluride can be alloyed with Sb_2Te_3 or Bi_2Se_3, which reduces thermal conductivity considerably. Pseudo-ternary system of Bi_2Te_3-Sb_2Te_3-Sb_2Se_3 has also been formed .

Problems with tellurium arise, since it is scarce, toxic and volatile at high temperatures. Therefore the use of tellurium is limited.

Lead telluride (PbTe) was found to have good thermoelectric properties at temperatures in the range of 300–700 K.

Similar materials are such as PbS and PbSe, which belong to chalcogenides system.

Chalcogenide is chemical compound including at least one chalcogen ("ore former") ion (usually S, Se or Te) and electropositive element.

Lead chalcogenides have a FCC structure and are polar semiconductors with a mixed ionic-covalent bond with the electrons travelling mainly in the cation (Pb) sublattice and the holes in the anion chalcogenide sublattice.

PbTe has high mean atomic weight and a multi-valley band structure. The band gap at 300 K is 0.32 eV, which produces higher Seebeck effect than that of bismuth telluride.

Also its thermoelectric figure of merit (*ZT*) is higher when the temperature is raised although it has better lattice thermal conductivity than bismuth telluride.

PbTe- SnTe system have been studied since 1961.

Lead telluride forms isomorphous solid solutions with lead selenide and tin telluride, which leads to lower thermal conductivity and improved *ZT* values.

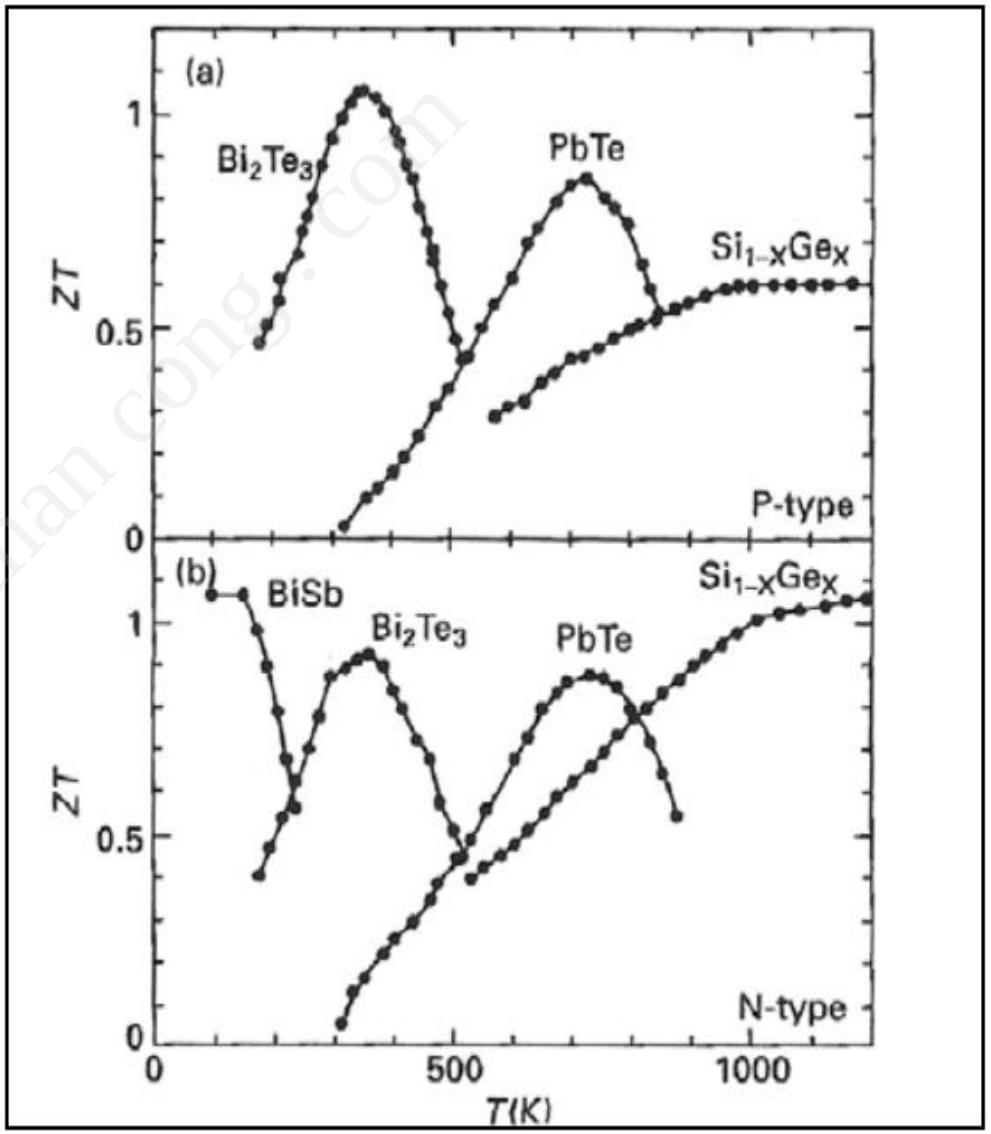
Band gap goes to zero at Pb0.4Sn0.6Te and therefore lower compositions of tin telluride are required to ensure adequate band gap leading to *ZT* values near 1 for n-type PbTe-SnTe alloys at 700 K.

Another system that gives similar properties are AgSbTe2 and GeTe.

SiGe alloys are superior materials for thermoelectric generation.

Silicon has a large band gap and therefore silicon rich alloys, such as Si0.7Ge0.3, are suitable for high temperature applications because problems with minority carrier dominance do not arise.

The large phonon scattering ensures low thermal conductivity without affecting the electron mobility.



Skutterudites (ReTm4M12) are complex materials containing rare earth elements (Re), transition metals (Tm) and metalloids (M).

Binary skutterudites have chemical formula of ReTm4M12, where Re is rare earth element, Tm is transition metal and M is metalloid.

Binary skutterudites have the chemical formula of TmM3 and relatively high thermal conductivity, but the Seebeck coefficient is also relatively large.

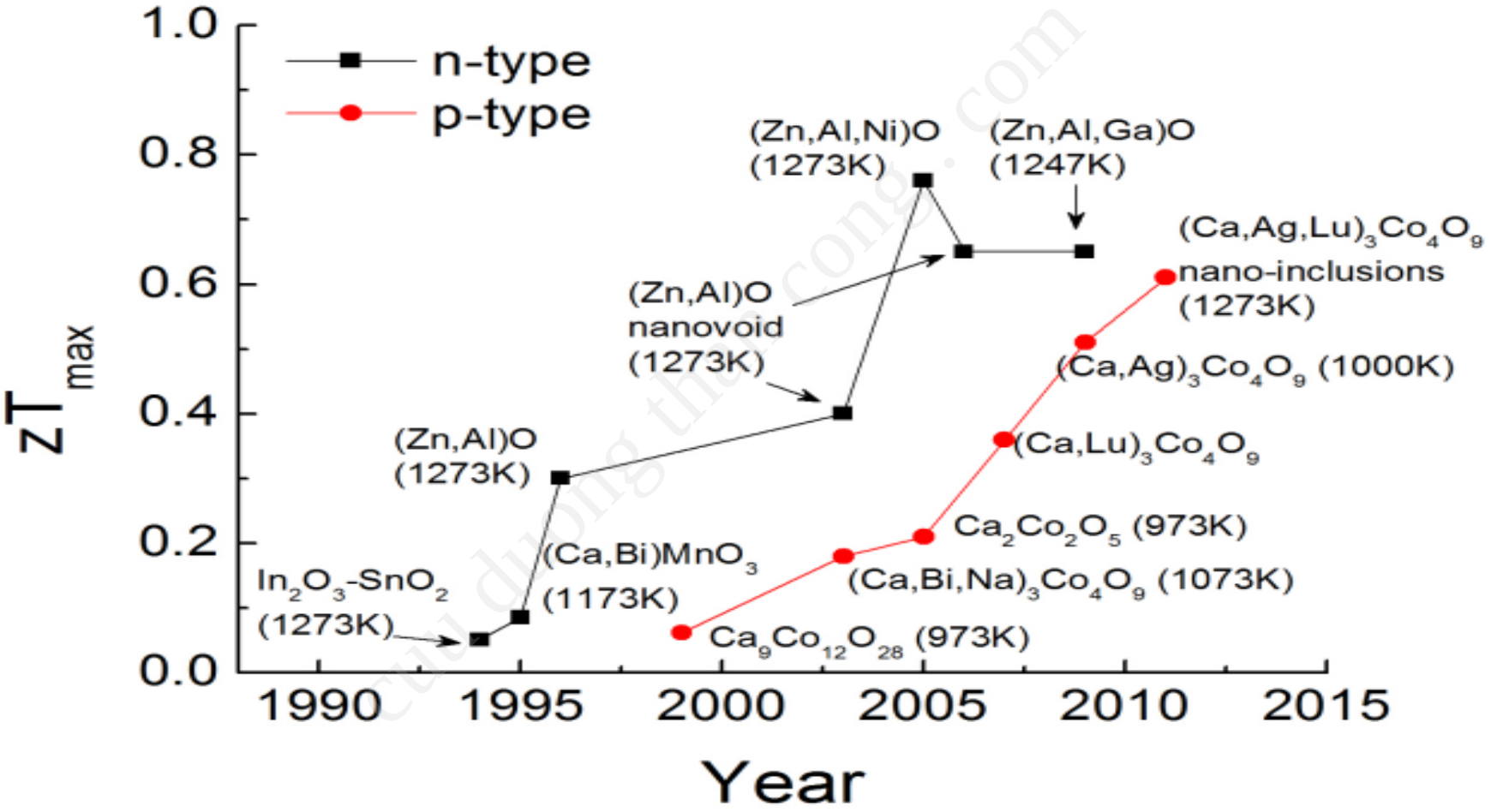
The crystal structure of binary skutterudites has two large empty spaces in each unit cell. When the empty space is occupied by relatively heavy rare earth element, the result will be reduced thermal conductivity due to rattling of the heavy element within loosely bound lattice.

The figure of merit (ZT) has been found to be higher than unity at 700 K.

Metal oxide thermoelectric materials

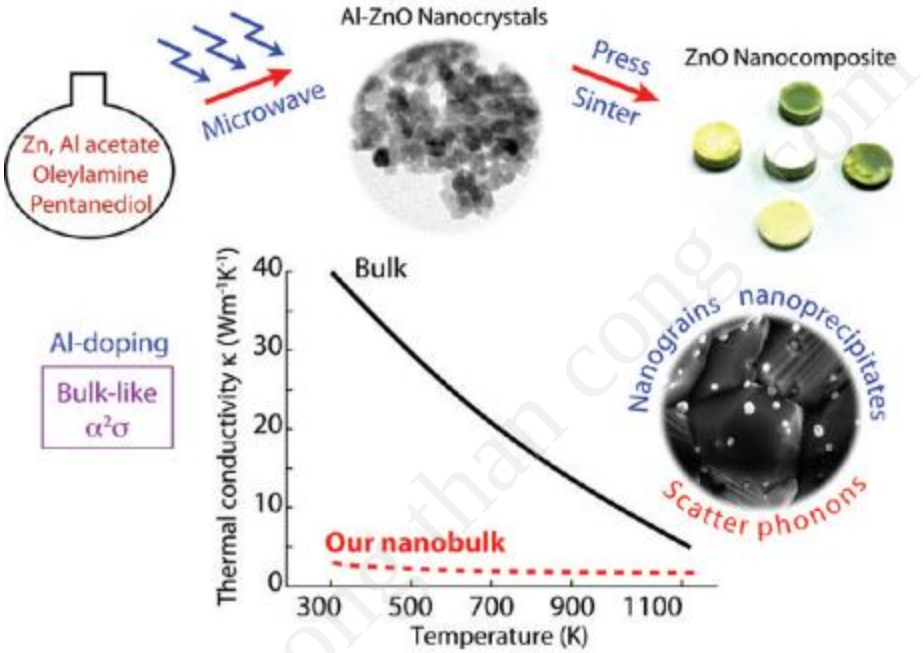
A two-dimensional electron gas (2DEG) in $SrTiO_3$. The 2DEG demonstrates a Seebeck coefficient *S* that is enhanced by a factor of ~5 compared with the bulk and an optimized *ZT* that reaches 2.4, twice that of conventional thermoelectric materials.

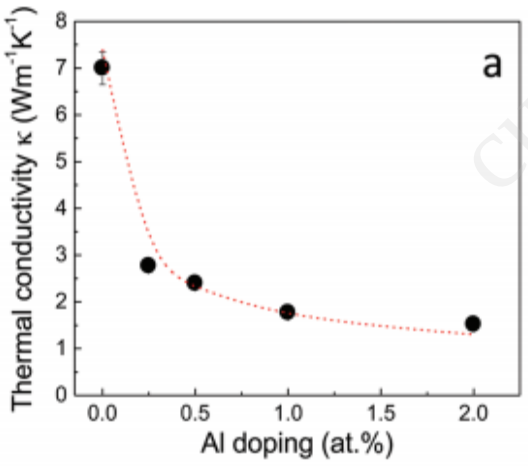
Other new oxide materials developed in Japan are such as Na_2CoO_4, $CaMnO_3$, $(ZnO)(In_2O_3)$, ZnO and $CuAlO_2$.

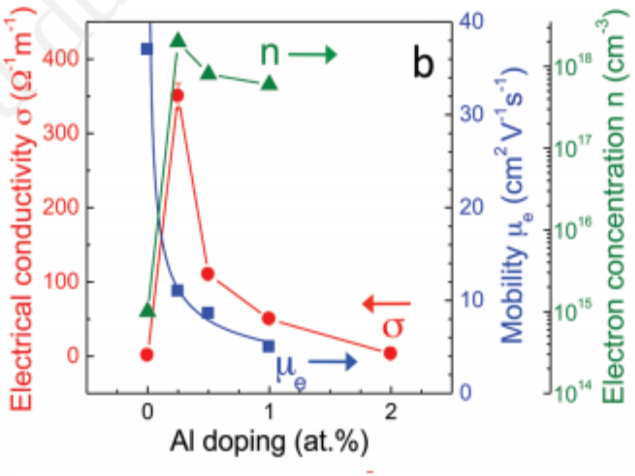


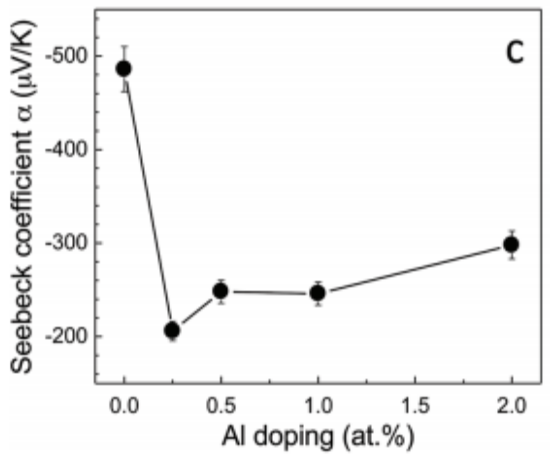
Al-Doped Zinc Oxide Nanocomposites with Enhanced Thermoelectric Properties

Nano Lett. 2011, 11, 4337–4342



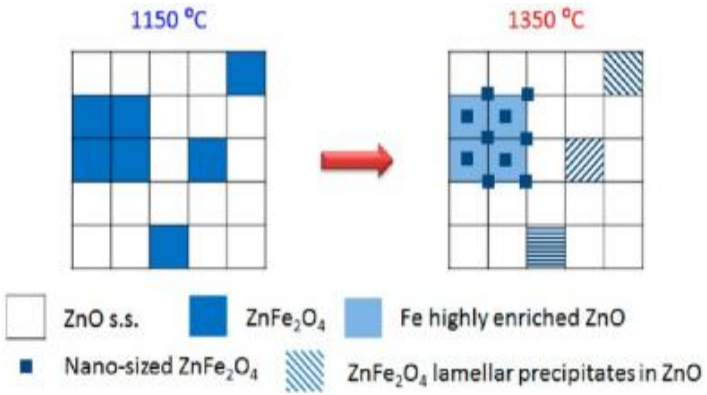


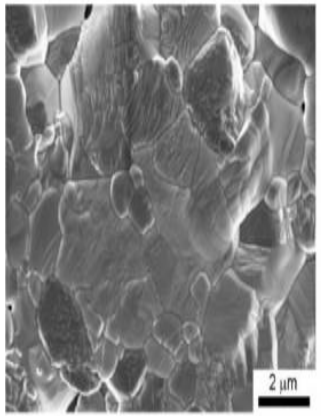




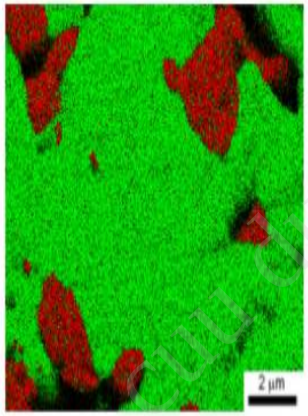
Thermoelectric Transport Properties of Fe-Enriched ZnO with High-Temperature Nanostructure Refinement

ACS Appl. Mater. Interfaces 2015, 7, 7927−7937

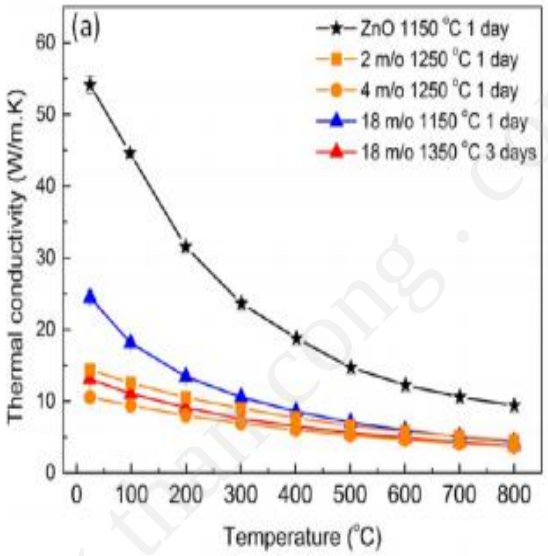


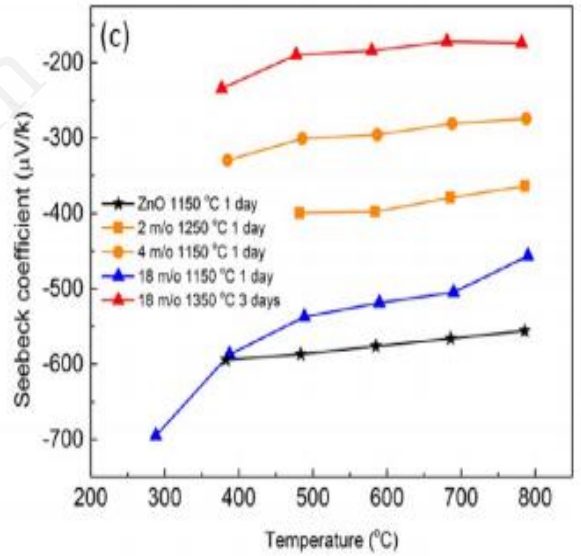


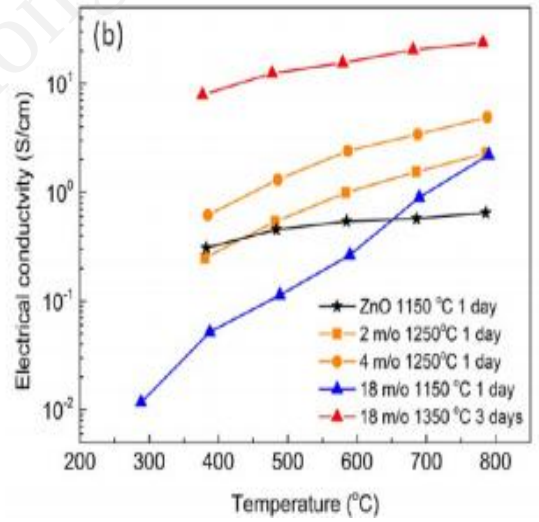
(a) SEM image

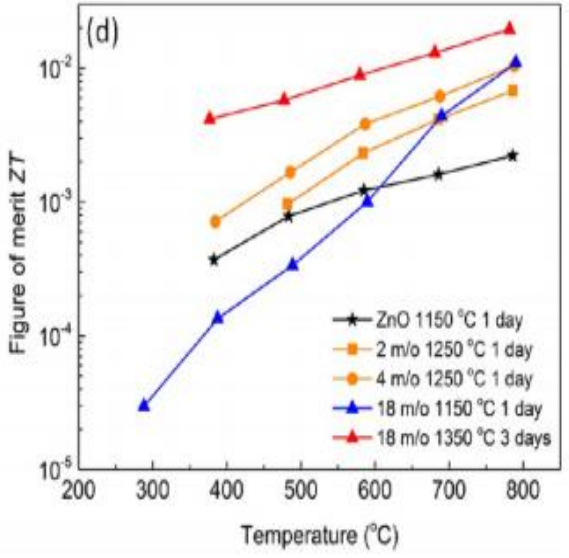


(b) EDS map: Zn L (green) and Fe L (red)

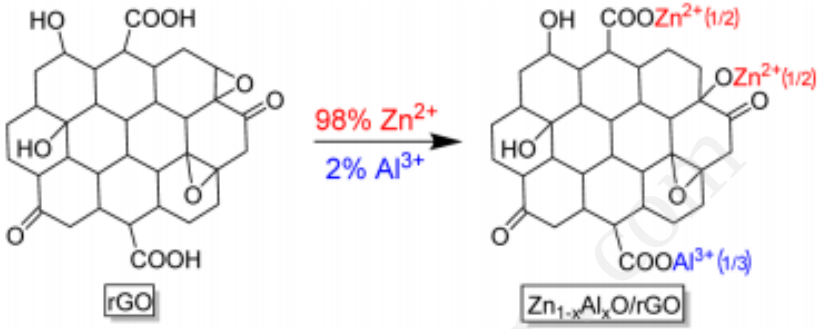


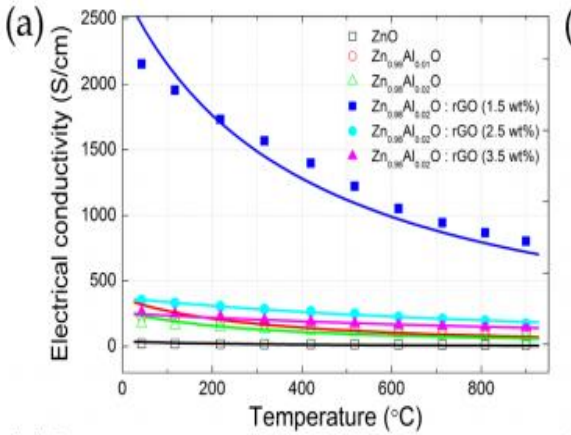


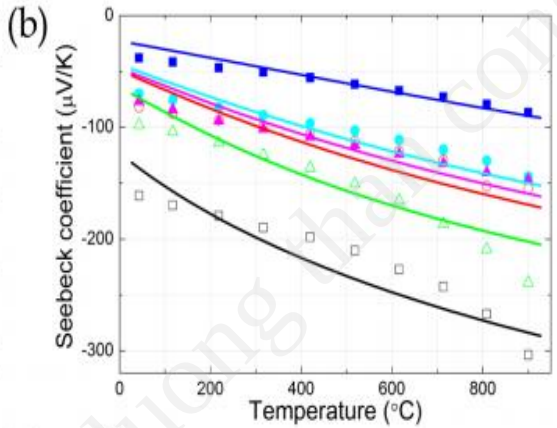


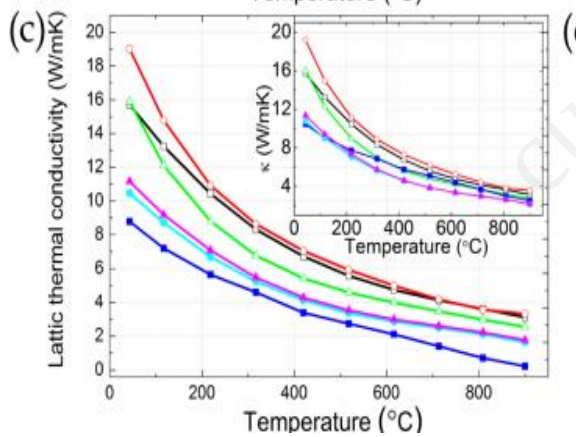


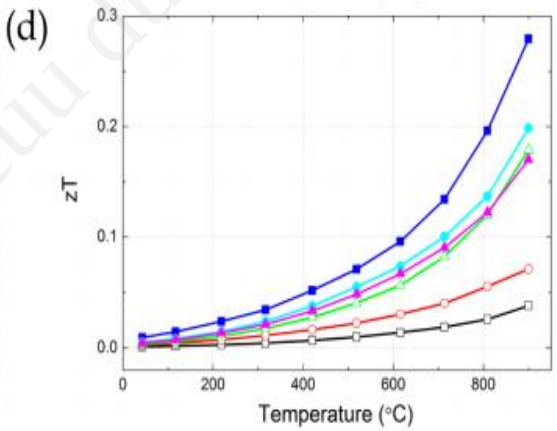
One-Step Chemical Synthesis of ZnO/Graphene Oxide Molecular Hybrids for High-Temperature Thermoelectric Applications

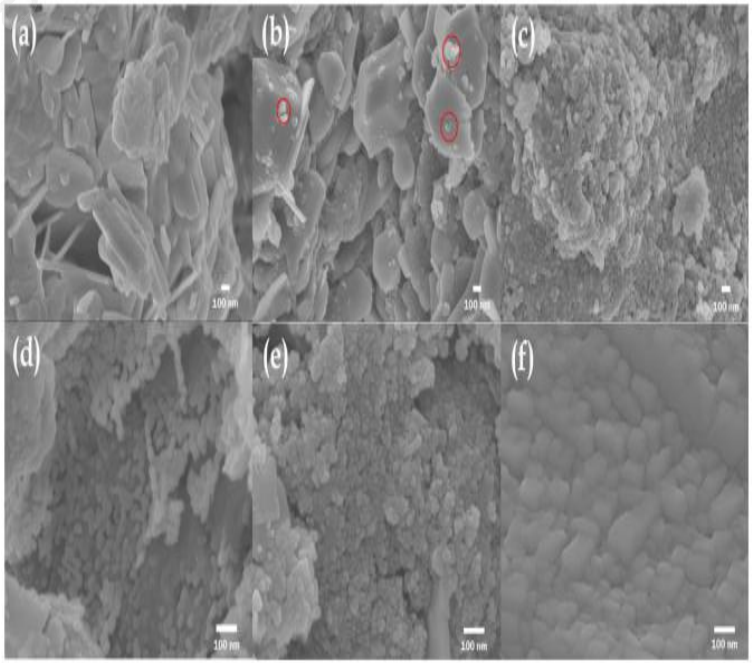












ACS Appl. Mater. Interfaces 2015, 7, 3224−3230

Enhanced thermoelectric performance of Al-doped ZnO thin films on amorphous substrate

Shrikant Saini[1†], Paolo Mele[1†], Hiroaki Honda[2], Dave J. Henry[3], Patrick E. Hopkins[3], Leopoldo Molina-Luna[4], Kaname Matsumoto[5], Koji Miyazaki[6], and Ataru Ichinose[7]

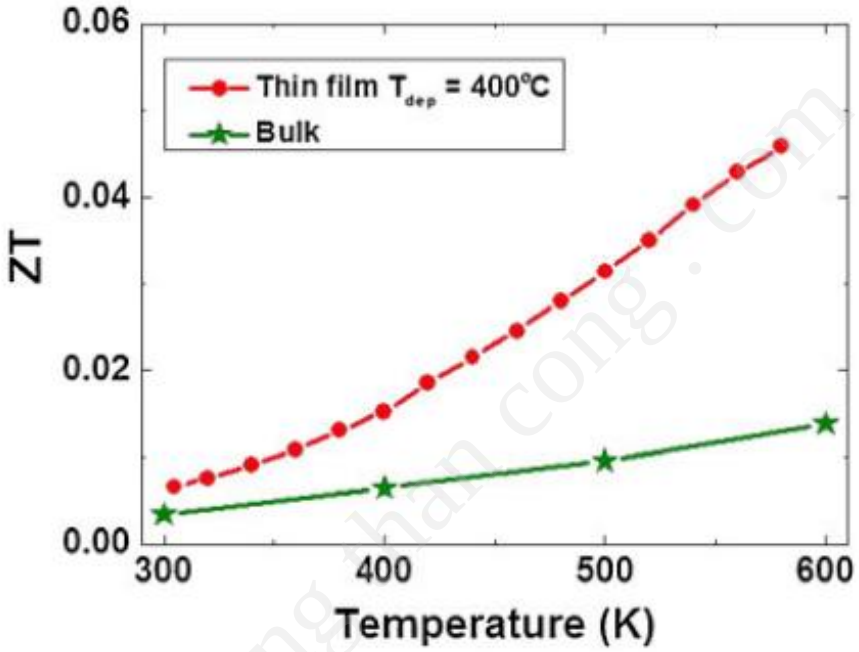


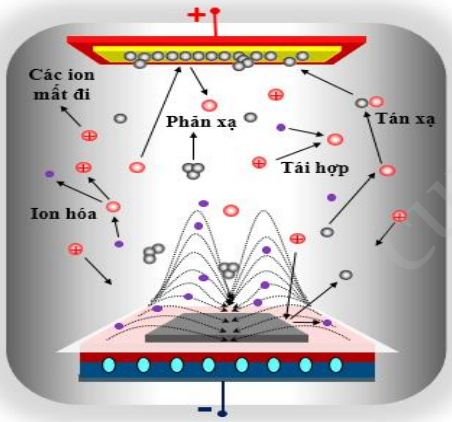
Fig. 5. (Color online) Dimensionless figure of merit at elevated temperatures using thermal conductivity at 300 K for AZO thin film deposited at 400 °C compared with our previously reported bulk material[16] of same composition.

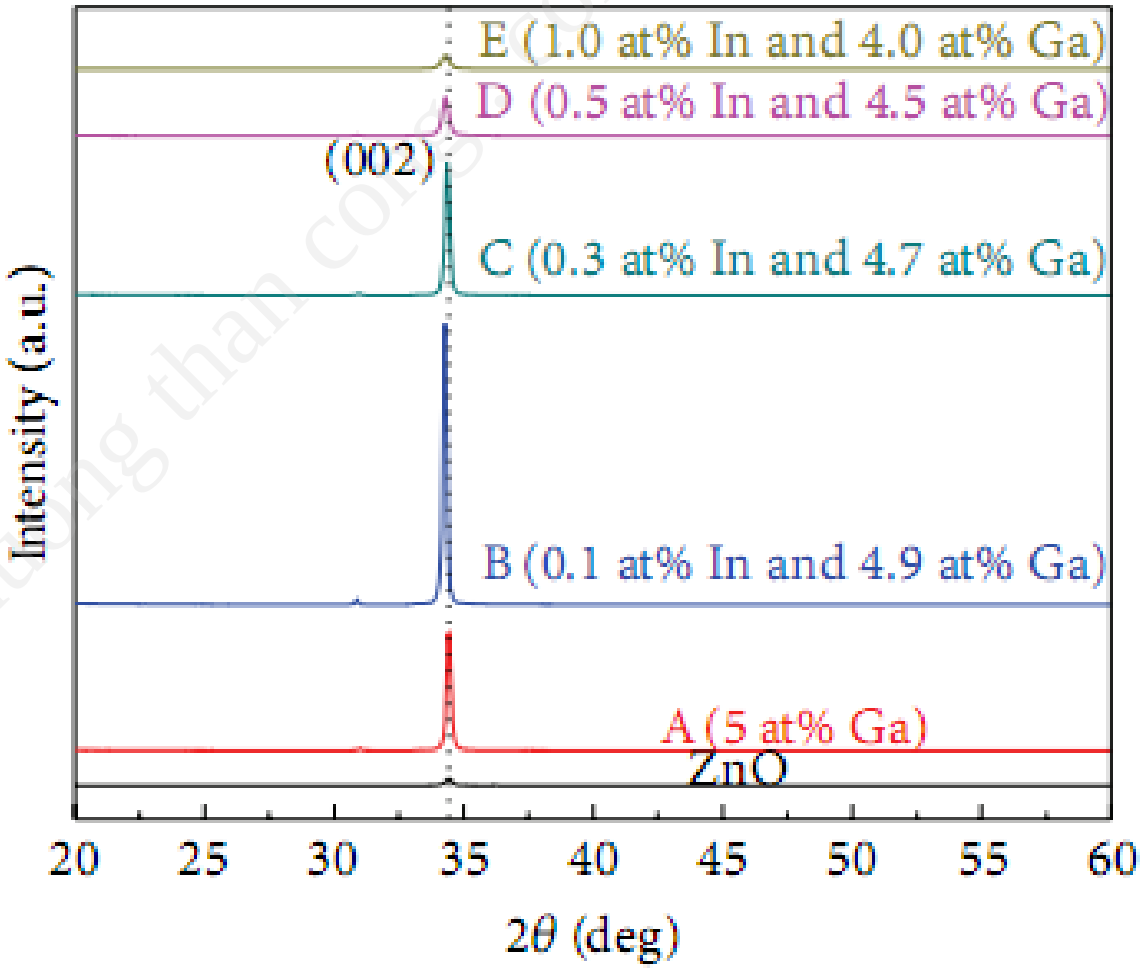
2% Al-doped ZnO (AZO) thin films fabricated at 300 °C by pulsed laser deposition (PLD) on amorphous fused silica demonstrated the high quality crystallinity and grain connection, which correlates to the high thermoelectric performance: electrical conductivity $\sigma = 923$ S/cm and Seebeck coefficient $S = -111$ μV/K at 600 K. Its power factor ($S^2 \cdot \sigma$) is 1.2×10^{-3} W m^{-1} K^{-2}, twofold better than films deposited on crystalline $SrTiO_3$ under the same experimental conditions. Using our measured thermal conductivity (κ) at 300 K (4.89 W m^{-1} K^{-1}), the figure of merit, $ZT = (S^2 \cdot \sigma \cdot T/\kappa)$, is calculated as 0.045 at 600 K, 5 times larger than ZT of our previously reported bulk ZnO.

Japanese Journal of Applied Physics **53**, 060306 (2014)

Structural properties of as-deposited IGZO thin films

Target		A	B	C	D	E
Impurity	at% In	0	0.1	0.3	0.5	1
	at% Ga	5	4.9	4.7	4.5	4.0

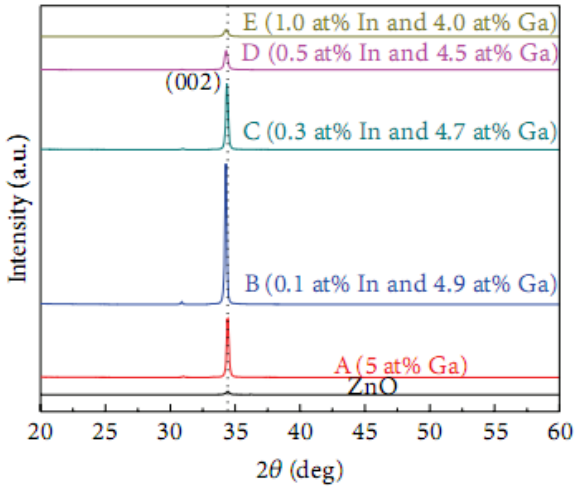




Advances in Condensed Matter Physics. 971528 (2014)

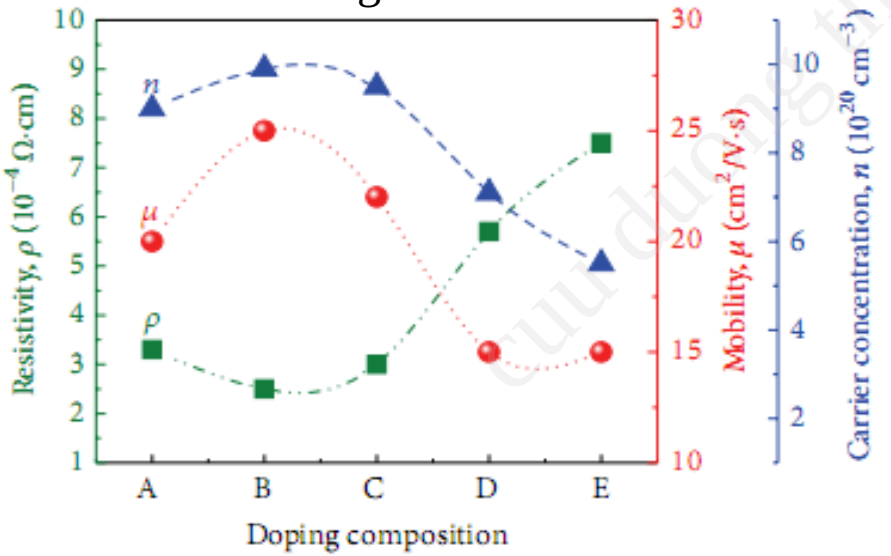
Thin Solid Films. 583, 201 (2015)

Electrical properties of as-grown and post-annelaed IGZO thin films

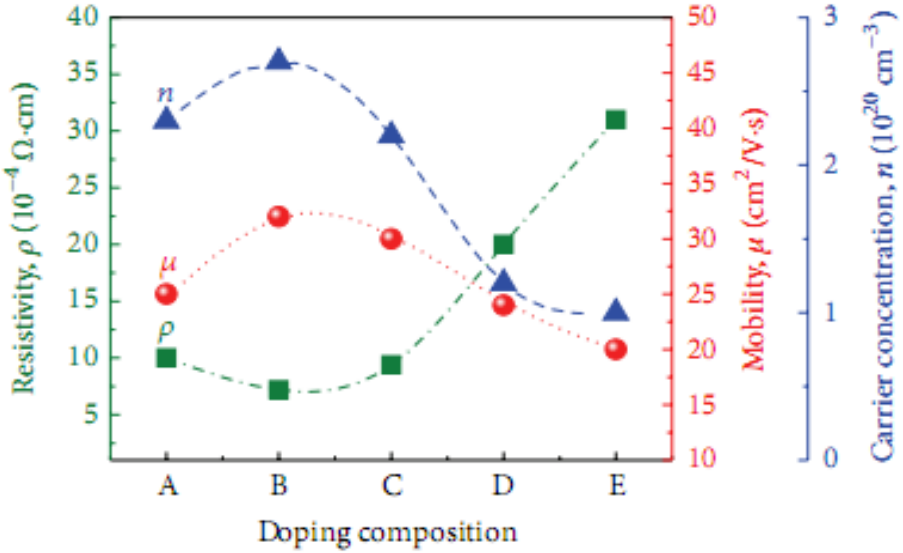


Target		A	B	C	D	E
Impurity	at% In	0	0.1	0.3	0.5	1
	at% Ga	5	4.9	4.7	4.5	4.0

As-grown



Post-annealed



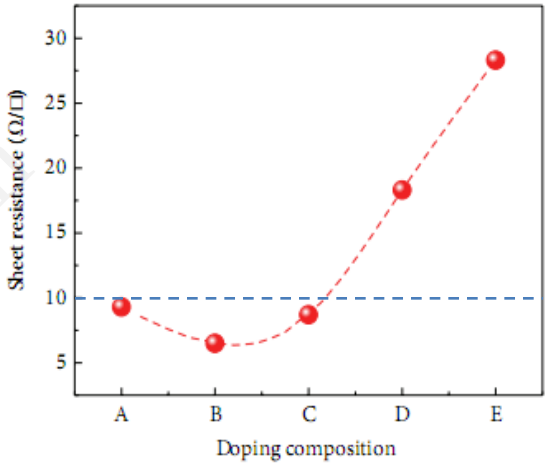
Advances in Condensed Matter Physics. 971528 (2014)

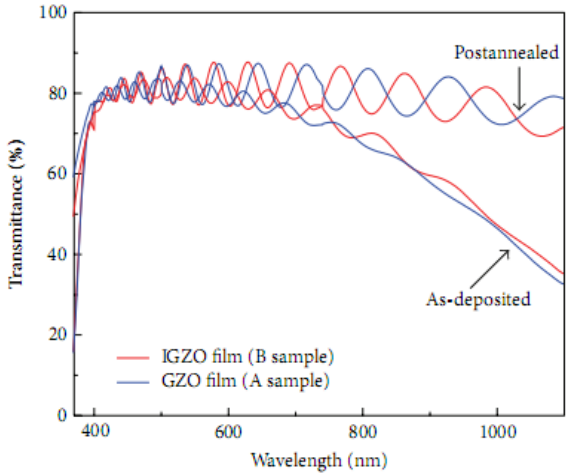
Thin Solid Films. 583, 201 (2015)

Electrical and Optical properties of post-annelaed thin films

Target		A	B	C	D	E
Impurity	at% In	0	0.1	0.3	0.5	1
	at% Ga	5	4.9	4.7	4.5	4.0

	Sample	Electron density (10^{20} cm^{-3})	Electron mobility (cm^2/V·s)	Conductivity (10^3 Ω^{-1}·cm^{-1})	Sheet resistance (Ω/□)	Transmittance (%)	
						Visible (400-750 nm)	NIR (750-1100 nm)
As-deposited	GZO	9.7	20	3.1	3.0	78.3	54.3
	IGZO	9.9	25	4.0	2.2	78.9	56.0
Post-annealed							
400 °C	GZO	6.0	22	2.1	4.2	77.8	65.5
	IGZO	8.2	30	4.0	2.2	76.7	57.9
450 °C	GZO	5.0	26	2.1	4.3	79.2	70.0
	IGZO	5.3	33	2.9	3.0	79.7	66.6
500 °C	GZO	2.3	25	1.0	9.4	81.7	78.3
	IGZO	2.7	32	1.4	6.6	83.9	79.6

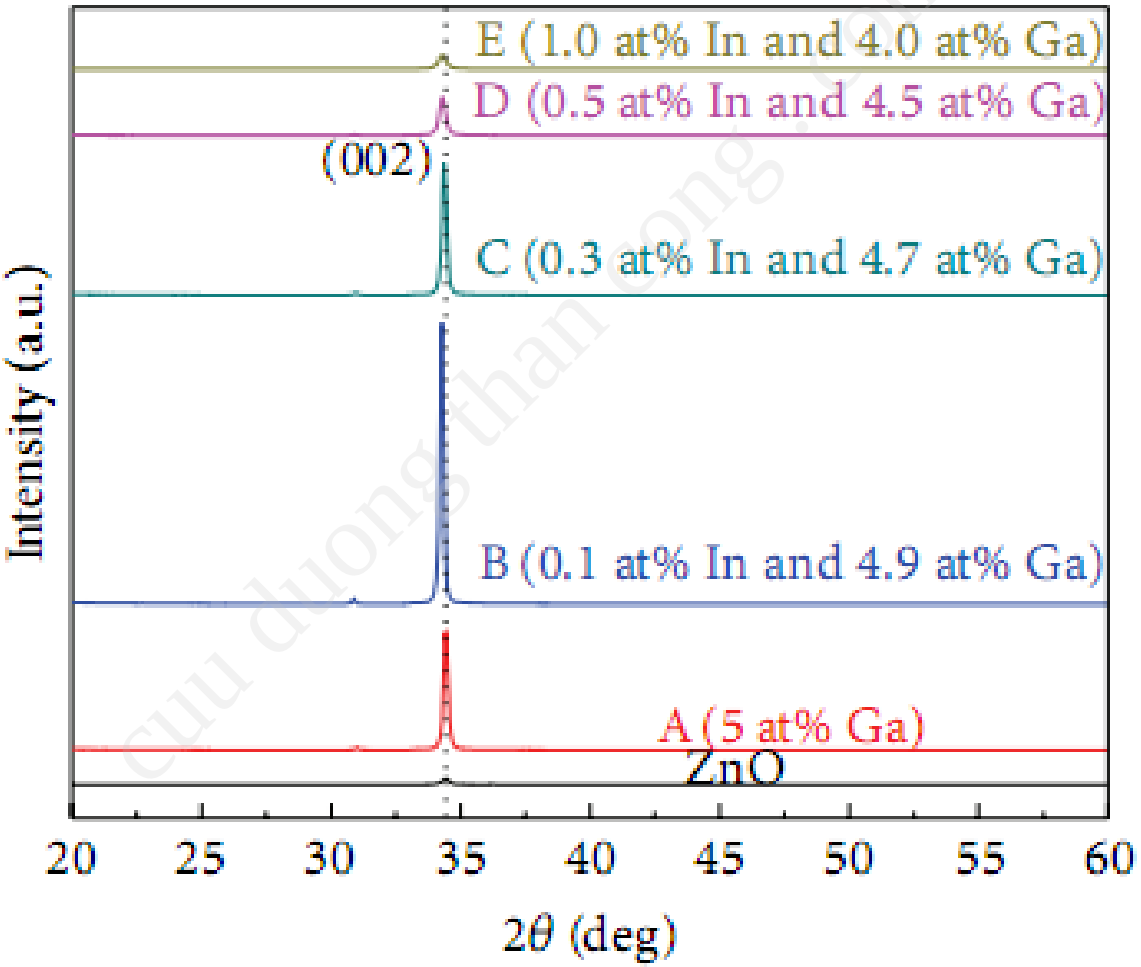




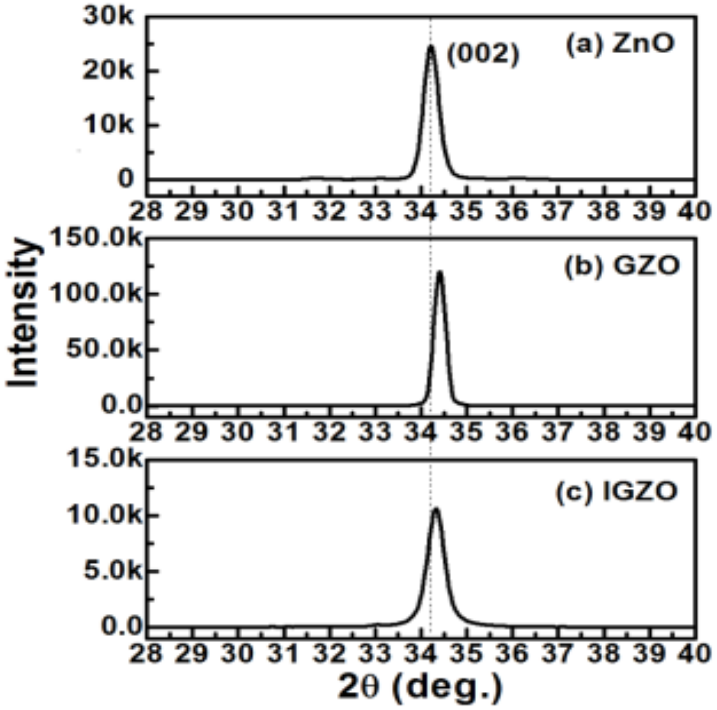
GZO and IGZO are good as Transparent conducting electrode.

Advances in Condensed Matter Physics. 971528 (2014)
Thin Solid Films. 583, 201 (2015)

Thermoelectric properties of 0.5 %at In and 4.5 %at Ga co-doped ZnO thin films



Structure properties



$$\varepsilon = [2C^2_{13} - C_{33}(C_{11} + C_{12})/2C_{13}] \; [(c_f - c_o)/c_o]$$

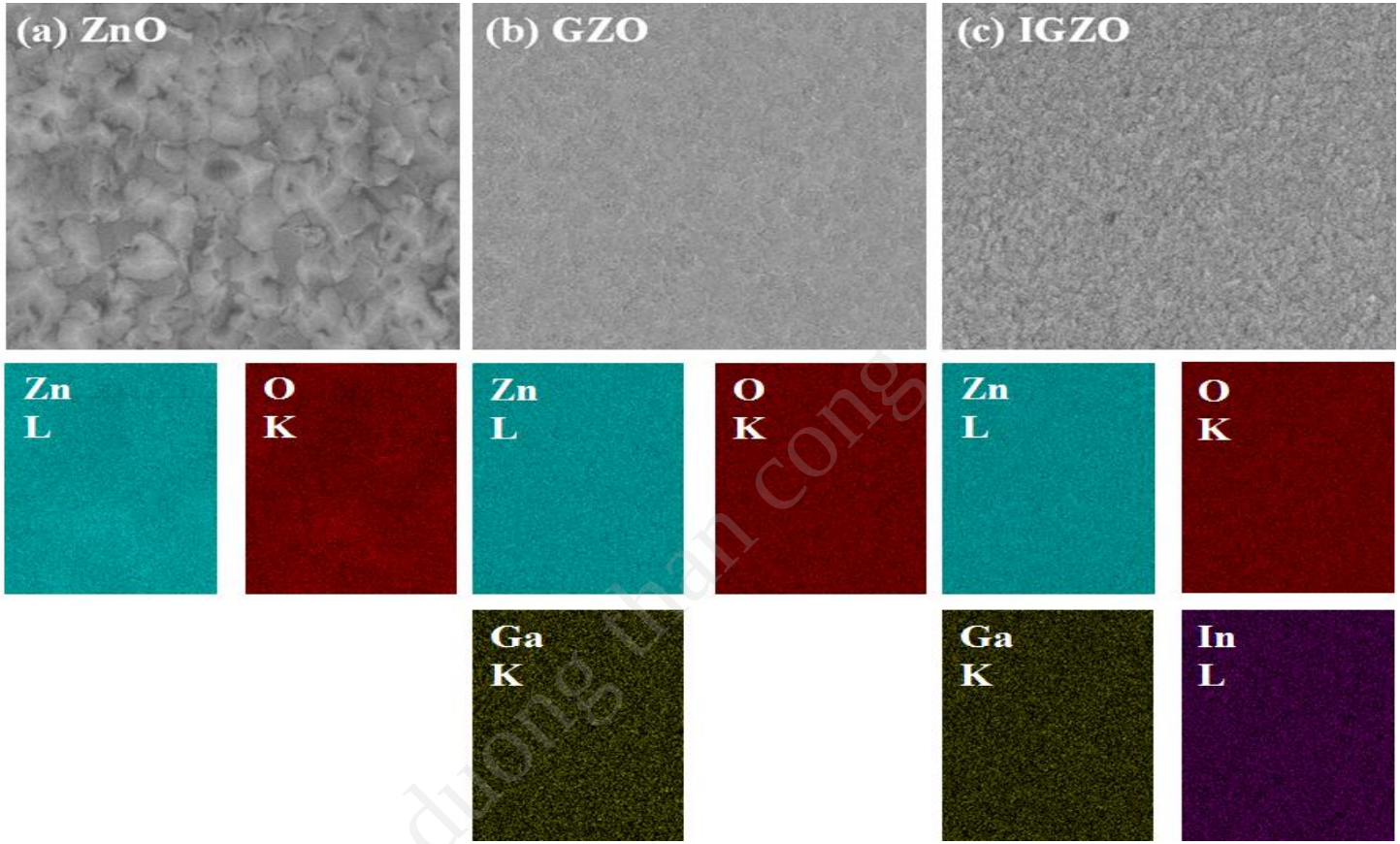
C_{ij} are the elastic stiffness constants for ZnO (C_{11} = 209.7, C_{33} = 210.9, C_{12} = 121.1, and C_{13} = 105.1 GPa), and c_f and c_o = 0.52 nm are the lattice parameters of the ZnO films and strain-free ZnO bulk.

$$c_f = 2d_{002} = \lambda/\sin\theta$$

The dislocation density was evaluated from the following relation $\delta = 1/D^2$

	2θ (002) (deg)	Grain size D (nm)	Dislocation density δ (x 10^{-3} nm)	Residual stress ε (GPa)
ZnO	34.21	21.6	2.14	– 1.5034
GZO	34.42	27.3	1.34	– 0.1522
IGZO	34.33	18.8	2.83	– 0.7292

FESEM - EDS



✓ **Ga and In dopants distribute uniformly in the host ZnO structure.**

	O K	Zn L	Ga L	In L	Si K	Total
ZnO	52.57	47.17			0.26	100
GZO	52.91	43.70	2.82		0.57	100
IGZO	53.45	43.25	2.59	0.33	0.38	100

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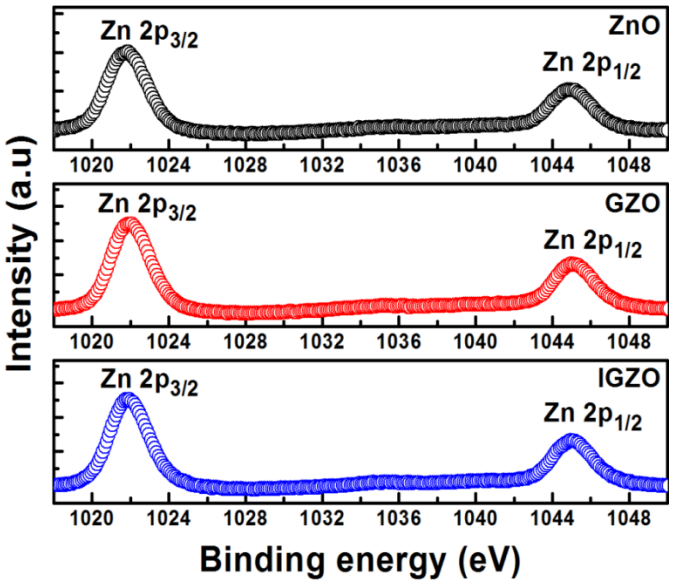
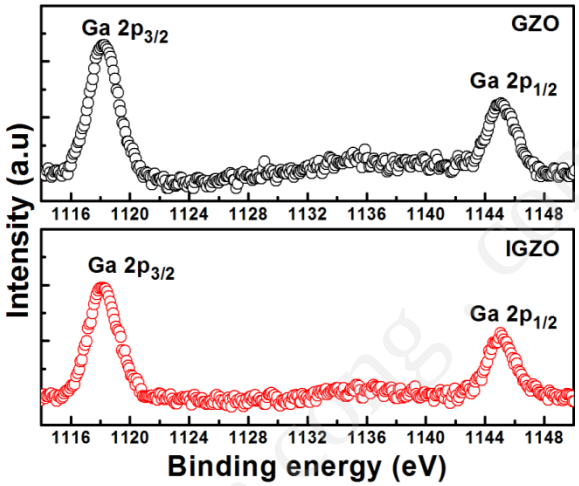
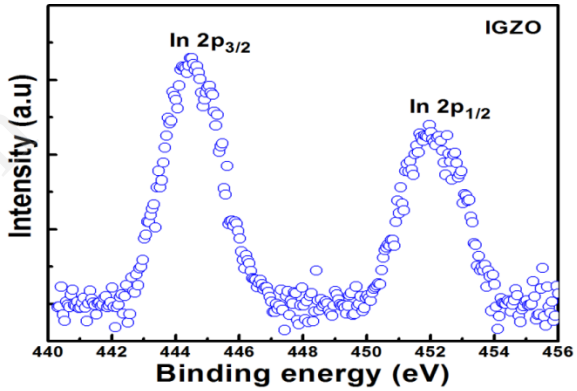
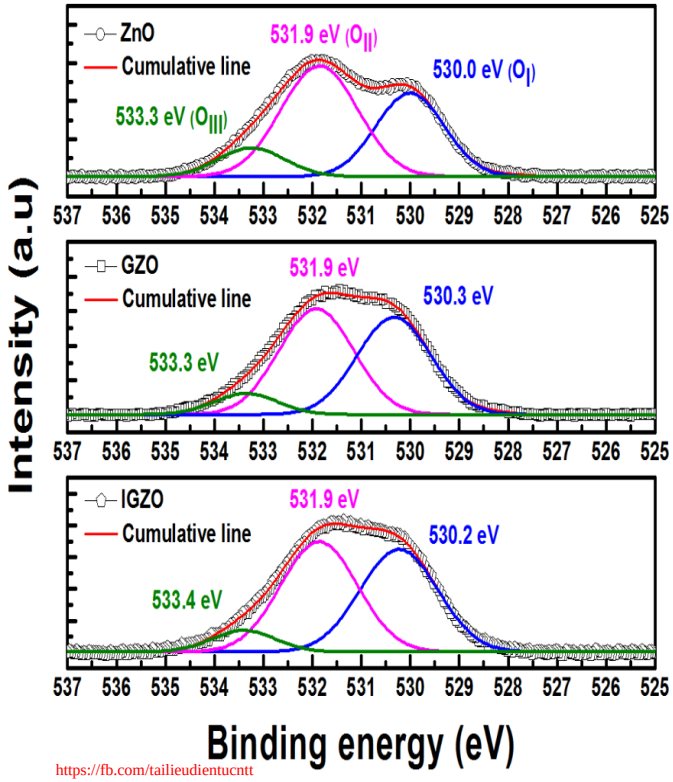
Chemical states - XPS







- ✓ **Chemical states of Zn, Ga, In: +2, +3, +3 → In^{3+} and Ga^{3+} substiute Zn^{2+} sites → donate electrons**
- ✓ **Oxygen vacancies exit → donate electrons**



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Electrical properties and Crystallinity

	2θ (002) (deg)	Grain size D (nm)	Dislocation density δ (x 10^{-3} nm)	Residual stress ε (GPa)
ZnO	34.21	21.6	2.14	– 1.5034
GZO	34.42	27.3	1.34	– 0.1522
IGZO	34.33	18.8	2.83	– 0.7292

	O K	Zn L	Ga L	In L	Si K	Total
ZnO	52.57	47.17			0.26	100
GZO	52.91	43.70	2.82		0.57	100
IGZO	53.45	43.25	2.59	0.33	0.38	100

$$\Lambda = h(3\pi^2 n)^{1/3}\mu/2\pi e$$

h is the Plank constant, n is the electron density, and μ is the electron mobility

	Electron density (10^{19} cm^{-3})	Electron mobility ($cm^2/V.s$)	Resistivity (10^{-2} Ωcm)	Sheet resistance (Ω/□)	Mean free path Λ (nm)	Grain size (nm)
ZnO	9.4	5.7	1.170	80	0.52	21.6
GZO	164.0	12.5	0.031	2.7	2.97	27.3
IGZO	97.4	8.7	0.074	6.4	1.74	18.8

Correlation between crystallinity and electrical properties

	Electron density (10^{19} cm^{-3})	Electron mobility (cm^2/V.s)	Resistivity (10^{-2} Ωcm)	Sheet resistance (Ω/□)	Mean free path Λ (nm)	Grain size (nm)
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	2θ (002) (deg)	Grain size D (nm)	Dislocation density δ (x 10^{-3} nm)	Residual stress ε (GPa)
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GZO	34.42	27.3	1.34	−0.1522
IGZO	34.33	18.8	2.83	−0.7292

$$O_O^x \rightarrow V_O^{\circ\circ} + 2e' + \frac{1}{2}O_2\,(g)$$

$$V_i^x + Zn\,(s) \rightarrow Zn_i^{\circ\circ} + 2e'$$

$$Ga_2O_3 \xrightarrow{ZnO} 2Ga_{Zn}^{\circ} + V_{Zn}'' + 3O_O^x + 3ZnO$$

$$Ga_2O_3 \xrightarrow{ZnO} 2Ga_{Zn}^{\circ} + 2e' + 2O_O^x + \frac{1}{2}O_2\,(g)$$

$$In_2O_3 \xrightarrow{ZnO} 2In_{Zn}^{\circ} + V_{Zn}'' + 3O_O^x + 3ZnO$$

$$In_2O_3 \xrightarrow{ZnO} 2In_{Zn}^{\circ} + 2e' + 2O_O^x + \frac{1}{2}O_2\,(g)$$

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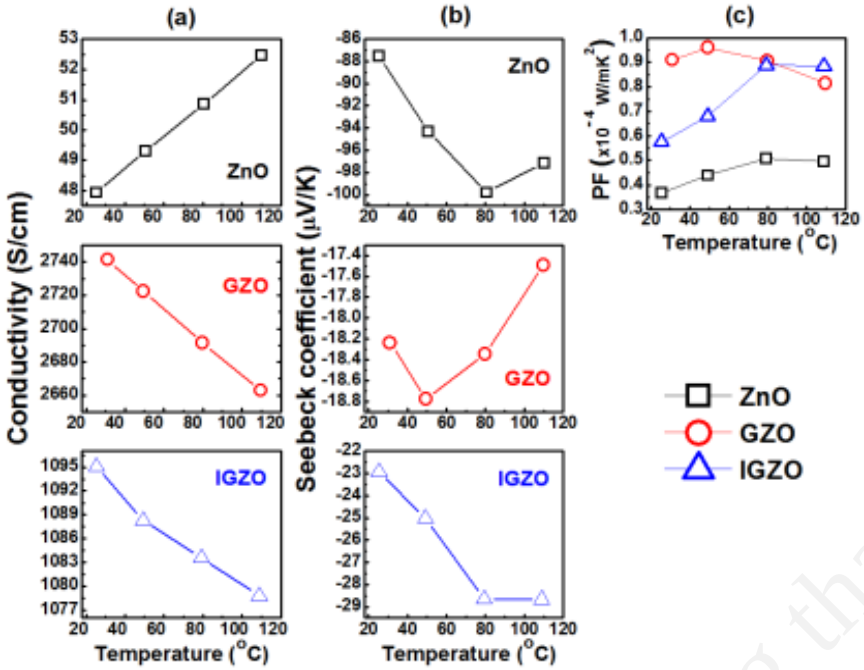
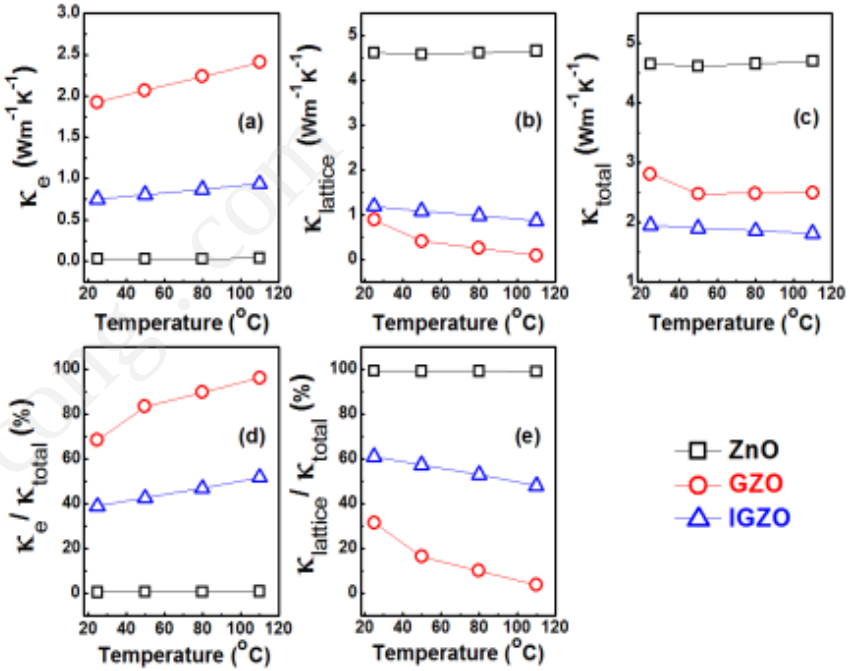
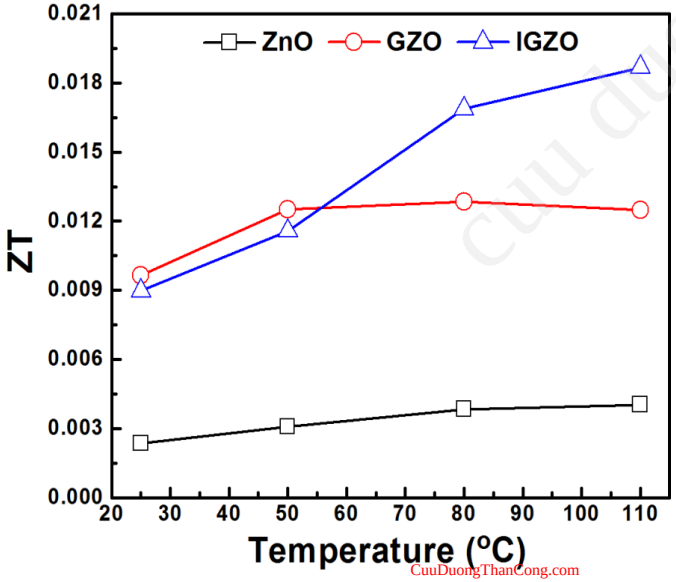
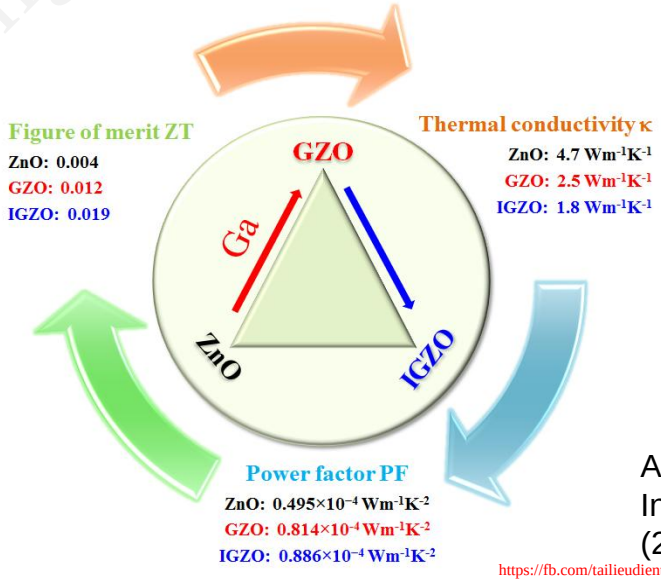
Thermoelectric properties









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