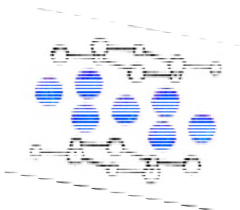
Utilizing Magnetic Semiconductors and Bottom-up Nanostructuring Methods for Enhanced Thermoelectrics

[1] National Institute for Materials Science (NIMS)
WPI MANA & NOIC
[2] Hiroshima University
[3] University of Tsukuba

Takao Mori [1-3]

2/14/2017 EPSRC Thermoelectric Network Meeting @Univ. Manchester

MANA Thermal Energy Materials Lab

熱エネルギー変換材料グループ

NIMS Permanent Senior Scientists

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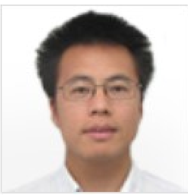

研究員
熱エネルギー変換材料グループ

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Fahim

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Postdoctoral fellows (NOIC, JSPS, CREST)

Gabin

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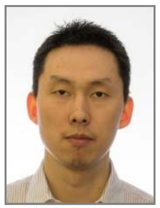


Guo

Amir

Jean-Baptiste

Anastasiia

Summary:

1. Introduction

Necessity to realize TE!

2. Ways to enhance TE

Selective scattering of phonons

Nanostructuring

Novel concepts for power factor

Nanocomposite: Hybrid effect

Magnetic semiconductor

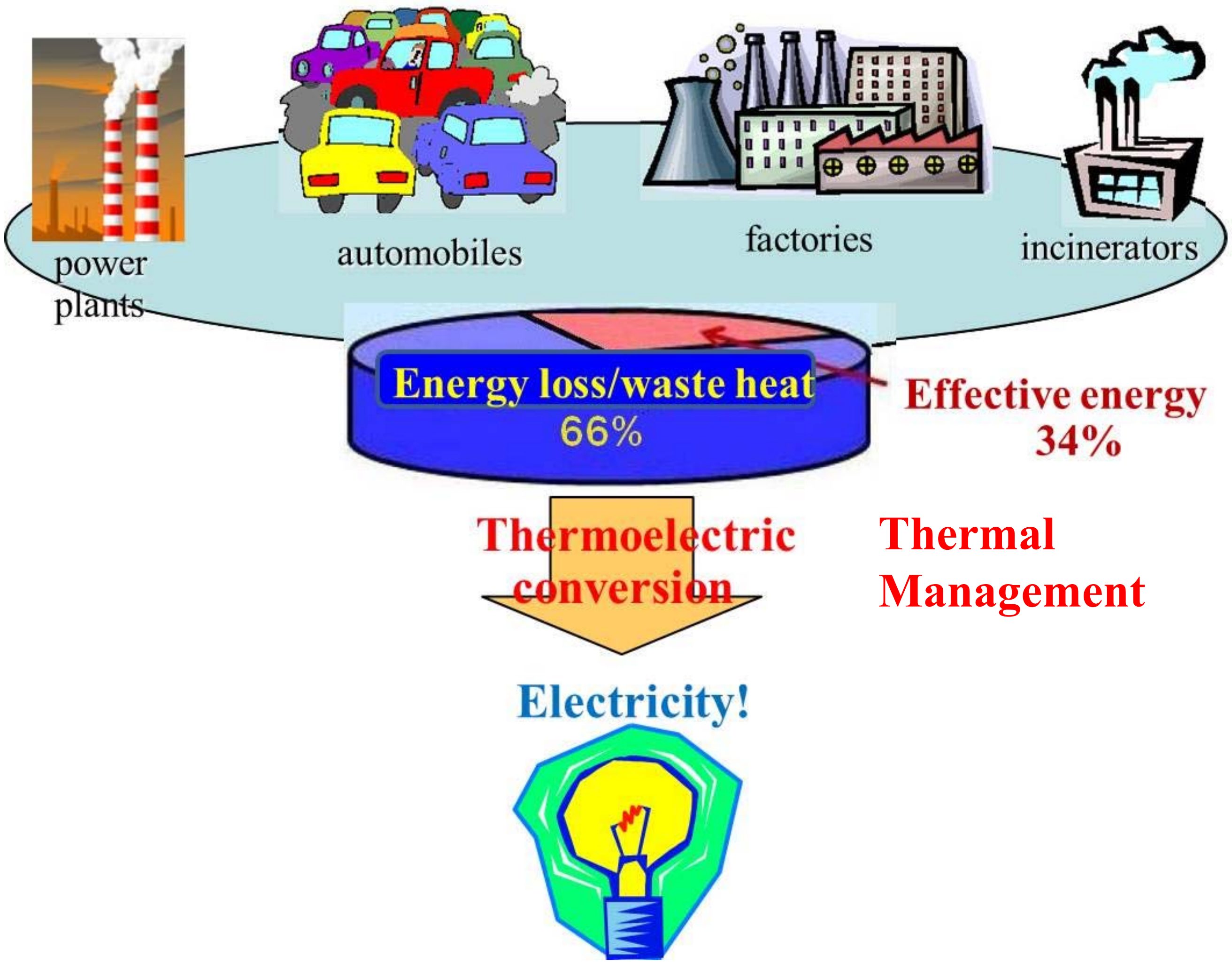
Measurements

3. Novel materials

1. Introduction

Thermoelectrics & Thermal management

Japan Primary Energy Consumption 2.4×10^{19} J (2005)



Must find ways to realise the first wide-scale application of Thermoelectrics and develop more advanced Thermal Management technology

Ubiquitous waste heat and so many possible TE application

Present Status

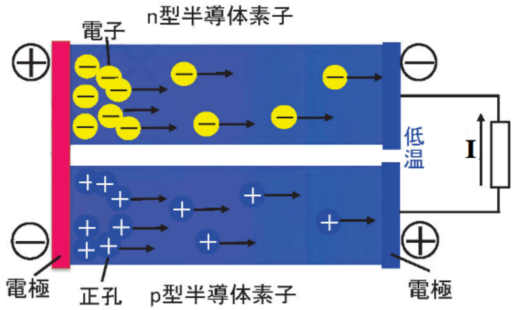
Why no wide-scale applications yet?

1. Materials performance

Figure of merit:

$$ZT = \alpha^2 \bullet \sigma / \kappa \bullet T$$

$$\Delta V = \alpha \Delta T$$



α = Seebeck coefficient (large) σ = electrical conductivity (large)

κ = thermal conductivity (small)

α x σ σ x κ

Also

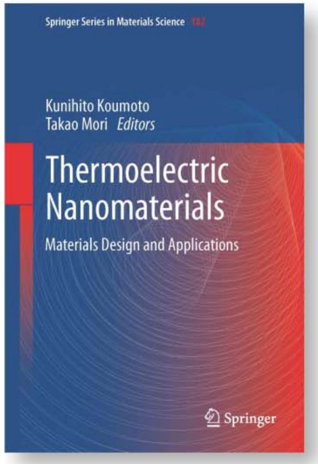
2. Projects were vertically structured 3. NP was too "early"

4. p, n

Time is ripe for a Breakthrough!

Nanotech + rapid developments in materials science

Worldwide race now ignited!



2013, XIII, 387 p. 190 illus., 72 illus. in color.

Printed book

Hardcover

- ► **129,99 € | £117.00 | $179.00**
- ► ***139,09 € (D) | 142,99 € (A) | CHF 173.50**

eBook

For individual purchases buy at a lower price on springer.com. Also available from libraries offering Springer's eBook Collection.

- ► **springer.com/ebooks**

K. Koumoto, Nagoya University, Nagoya, Japan; **T. Mori**, National Institute for Materials Science, Tsukuba, Japan (Eds.)

Thermoelectric Nanomaterials

Materials Design and Applications

Series: Springer Series in Materials Science, Vol. 182

- ► **Presents a new concept of thermoelectrics**
- ► **Presents atomic-scale and nanoscale materials design concepts for creating thermoelectric materials**
- ► **Includes a large number of recent breakthroughs which have dramatically enhanced thermoelectric performance**
- ► **Displays the application of thermoelectrics in a large emerging energy market**

Presently, there is an intense race throughout the world to develop good enough thermoelectric materials which can be used in wide scale applications. This book focuses comprehensively on very recent up-to-date breakthroughs in thermoelectrics utilizing nanomaterials and methods based in nanoscience. Importantly, it provides the readers with methodology and concepts utilizing atomic scale and nanoscale materials design (such as superlattice structuring, atomic network structuring and properties control, electron correlation design, low dimensionality, nanostructuring, etc.). Furthermore, also indicates the applications of thermoelectrics expected for the large emerging energy market. This book has a wide appeal and application value for anyone being interested in state-of-the-art thermoelectrics and/or actual viable applications in nanotechnology.

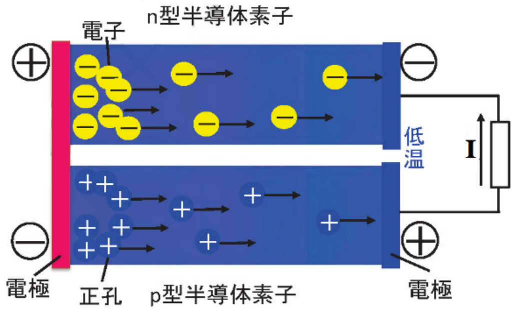
Ubiquitous waste heat and so many possible TE application

Present Status

Why no wide-scale applications yet?

1. Materials performance

$V = \alpha \Delta T$



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Time is ripe for a Breakthrough!

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2. Ways to enhance TE

2. Ways to enhance TE

σ x κ

A. Selective scattering of phonons

lower κ_L

B. Enhancement of power factor:

Nanocomposites (hybrid effect), magnetic semiconductors, etc.

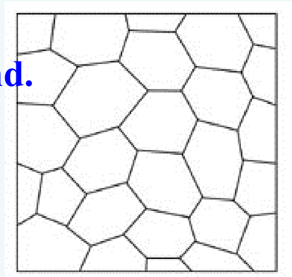
Nanostructuring

Selective scattering of phonons

Key is in developing actual processes for nanostructuring & selective scattering

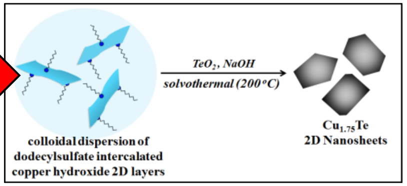
Electric. cond.

Thermal Cond



Proper scale for each material

2. Bottom-up Processes



Low TC !

Nanosheet fabrication of TE materials!

e.g. J. Mat. Chem. A (2014)

1. Mechanical methods

Spark plasma sintering (SPS)

High power (8000 A) High pressure

NIMS has long developed insights from structural materials

・NIMS Nanomeas.

(a)

Fine powder

FAST SPS HEATING

Fine nano/micro-structure obtained!

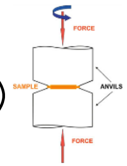
Ballmilling, MA, etc.

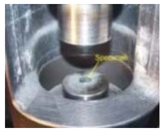
Intermetallic & ceramics
Process: κ↓ ρ↓ !
Company materials +30%ZT

J. Mat. Chem. C (2013)

(b)

HPT, SPD

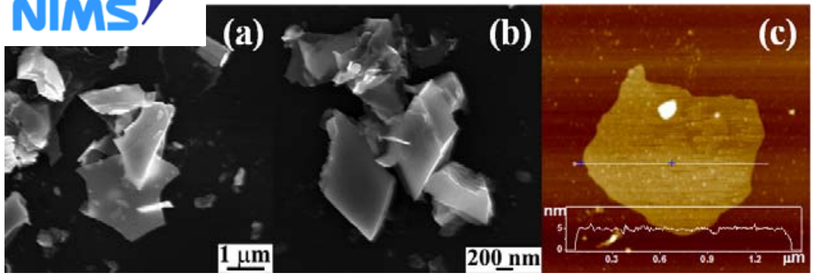




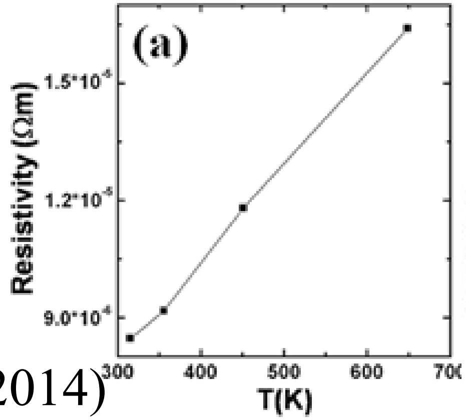
Nano-structure

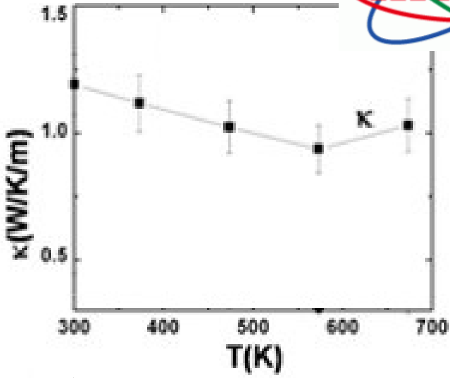
Processes for further enhancement of high performance TE materials

$CuTe_{1.75}$ Nanosheets



C. Nethravathi *et al.* J. Mat. Chem. A (2014)



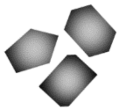


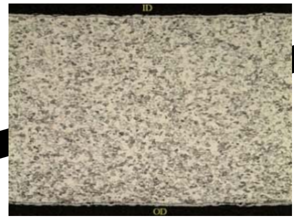
Lowering of thermal conductivity achieved without sacrificing so much electrical conductivity

Now Bi_2Te_3-type

As first attempt, nanosheets just quick compact with SPS with no optimization

FAST SPS HEATING

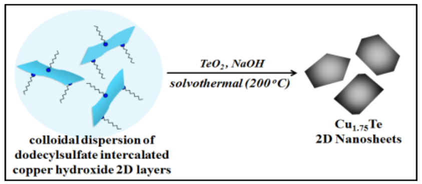




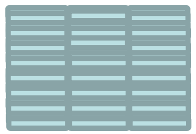
"Only" 30% ZT enhancement

Porosity NG

Next: Control of integration of NS



Chemical Hierarchical Design

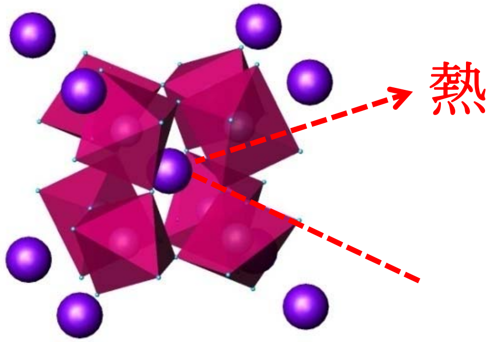


ZT ↑

Novel concepts:

New materials: Rare earth-free high performance skutterudites (CoSb$_3$-based compounds)

Considered as the champion mid- high temperature TE material.
Many companies worldwide involved



Normal enhancement of TE:
"Rattling" of RE atoms in the cage structure

RE-free!

Cage modification + Nanostructuring
Rare earth-free & Oxidation resistant high ZT skutterudites！

nano tech 2016 Grand Award!: Project Award (Green Nanotechnology)
Largest nanotechnology conf. in the world (40,000+ participants)

ZT~1.6 (1.8)

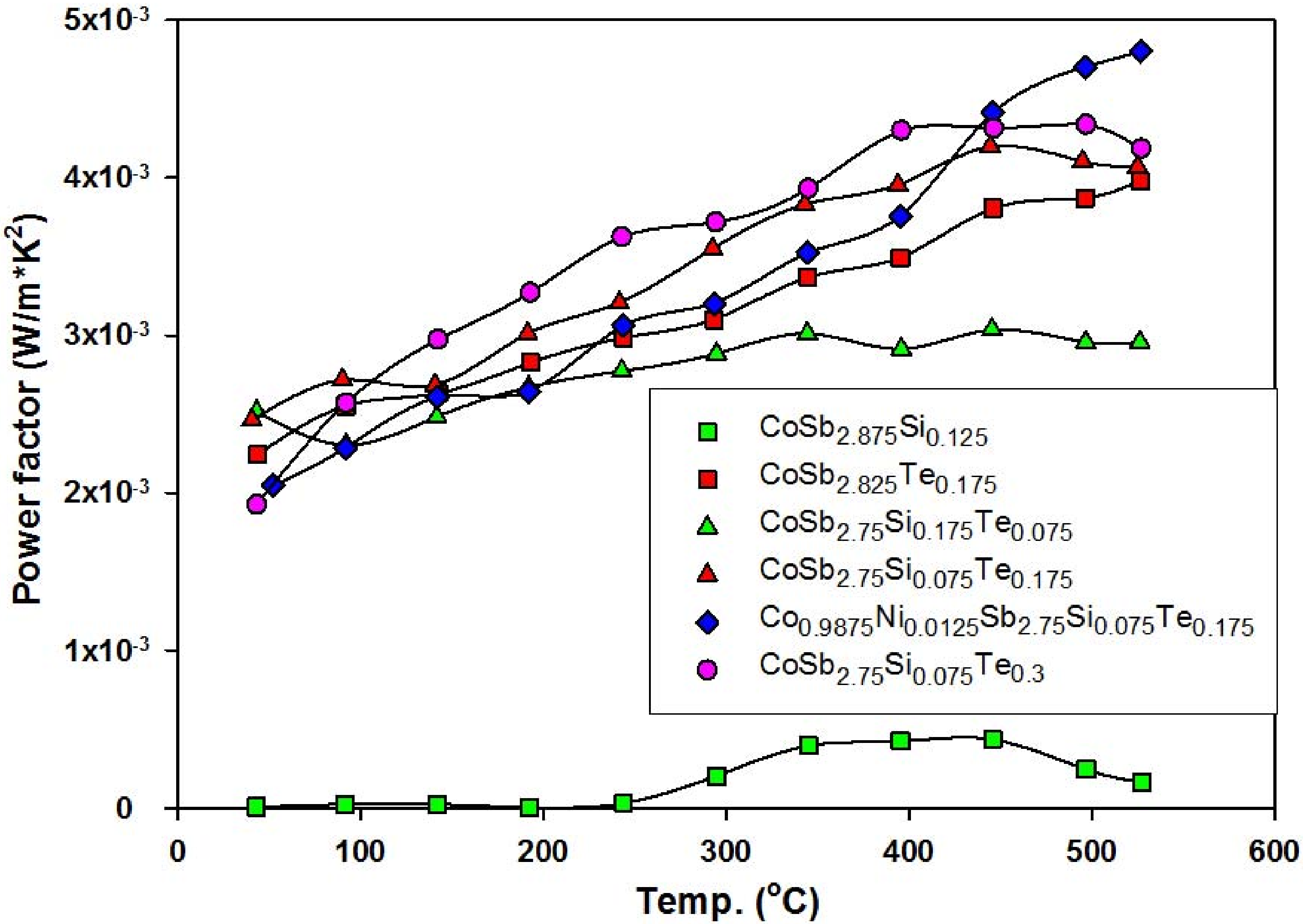
Patent submitted

Nano Energy 31, 152 (2017) doi:10.1016/j.nanoen.2016.11.016

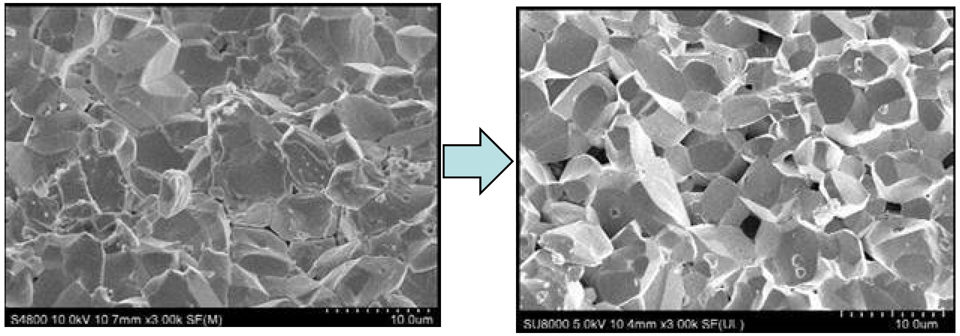
Variety of control over phonon scattering!

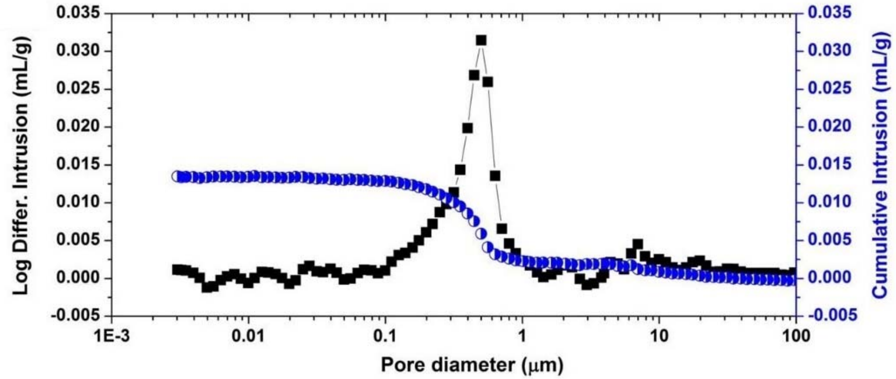
Power factor

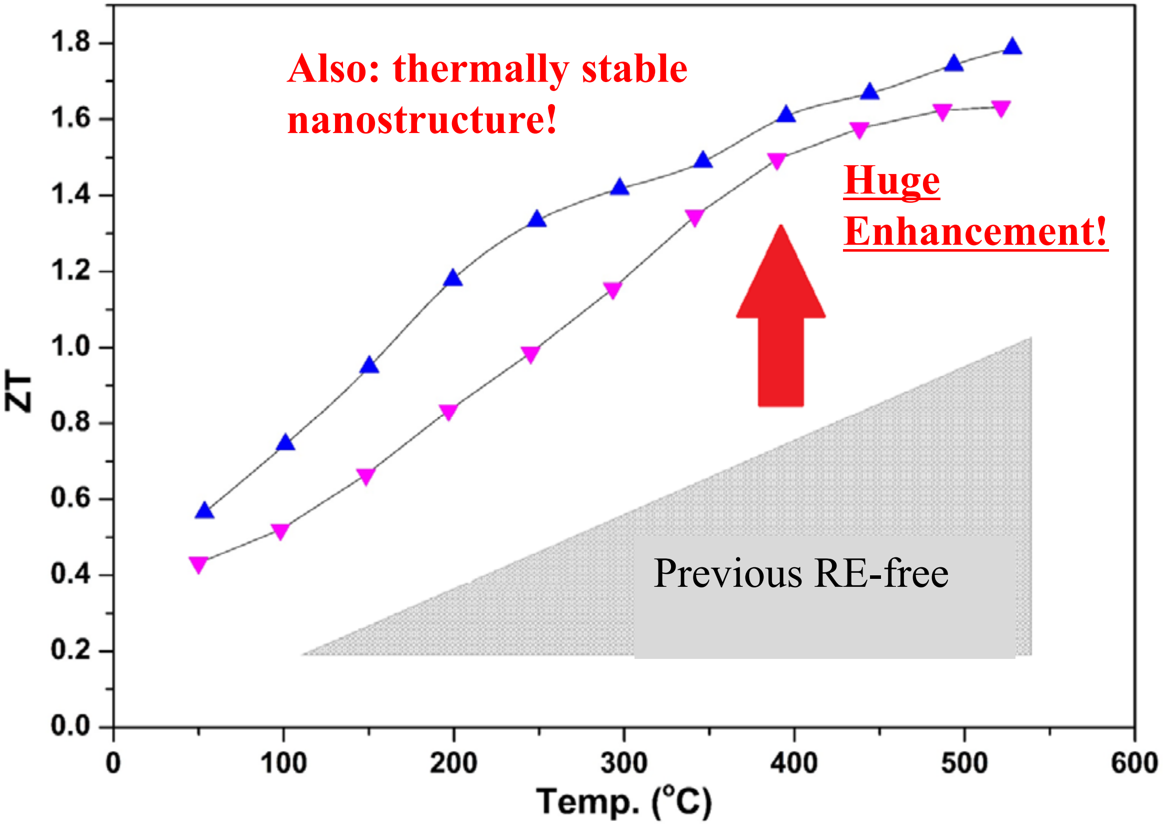
>4mW/m*K^2



Utilize phase diagrams!







Nano Energy **31, 152 (2017) doi:10.1016/j.nanoen.2016.11.016**

High power SPS
(SPS-1080)

Max. 8000 A
+800^{o}C/min.

100 mm diam.
samples OK

Ways to enhance TE

A. Selective scattering of phonons

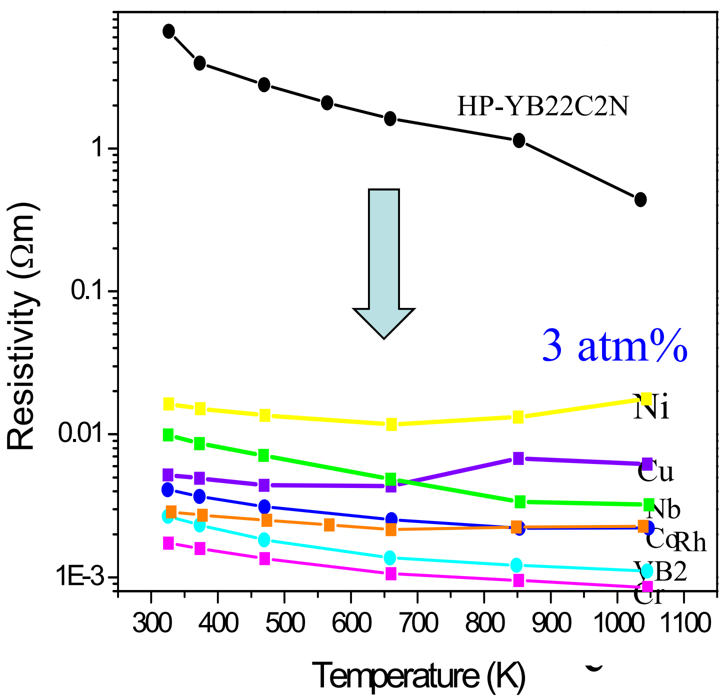
B. Enhancement of power factor: $\alpha \times \sigma$?

Nanocomposites (hybrid effect),
Magnetic semiconductors, etc.

Hybrid effect

TM dope +heat treatment → $YB_{22}C_2N$

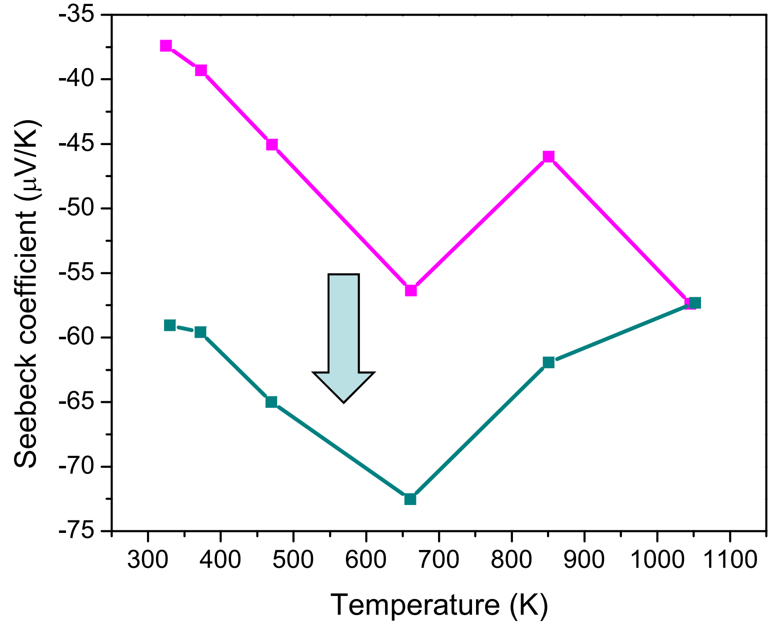
1. Huge reduction of resistivity!



2. Certain TM enhance Seebeck also!

Heat treatment effect!

Co, V

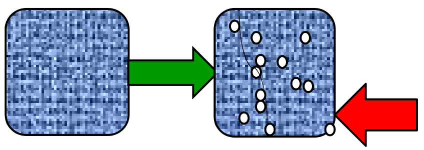


Electrical resistivity ~10,000% improved

Simult.!

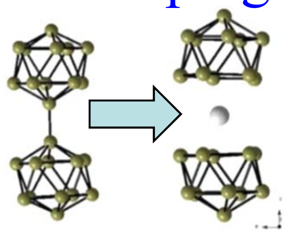
Seebeck enhancement 180%

Hybrid effect! Conductive path



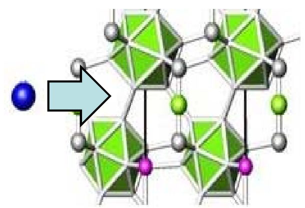
Just confirmed!

Intrinsic doping

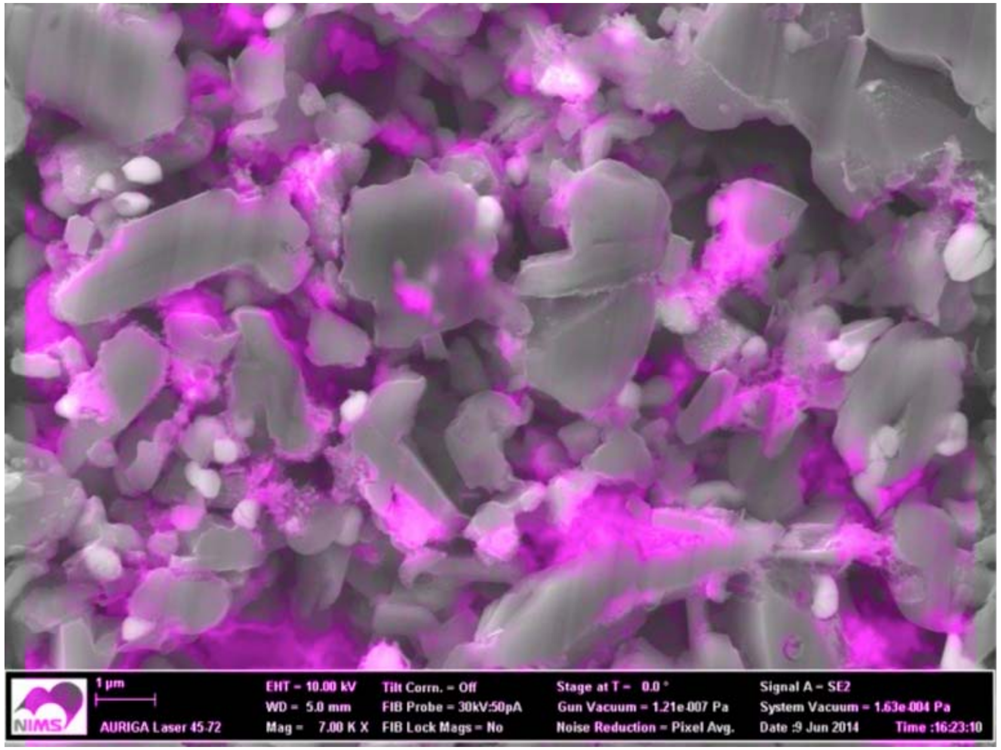


or

Electronic struct.



V distribution



Partially connected

Like a nano "spider web" partially covering the surfaces!

Scripta Materialia, 111, 44 (2016)

Hybrid effect?

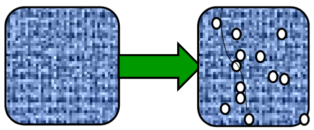
TM dope +heat treatment

Electrical conductivity ~10000% improved

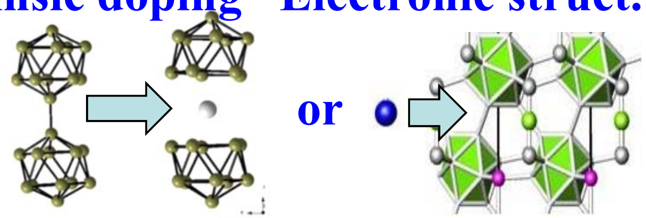
Simultaneous!

Seebeck enhancement 180%

Partial conductive path



Intrinsic doping **Electronic struct.**



Advanced thermal nanoscale measurements (and electrical)

Measurement of thin film thermal conductivity
Thermoreflectance method

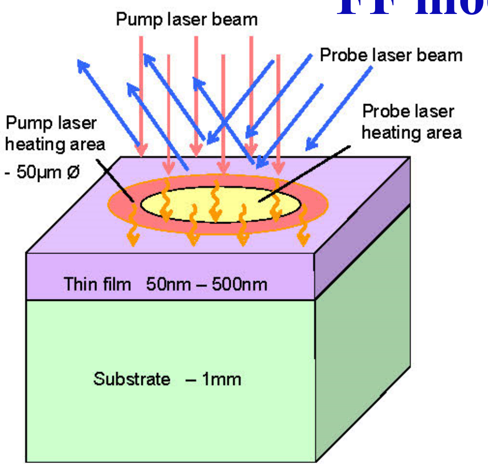
Utilizing picosecond lasers

Pump-probe

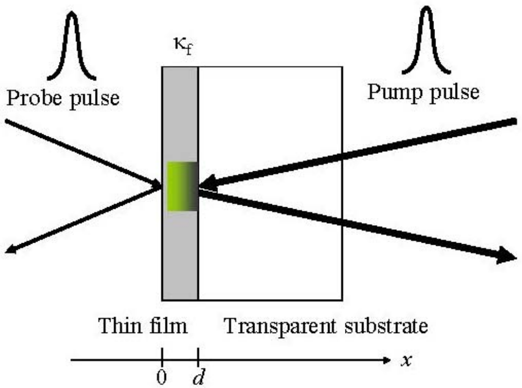
PicoTherm
Pico-TR

10 nanometer thick nanofilm (ceramics, etc. with relatively low κ) measurement possible!

FF mode



RF mode



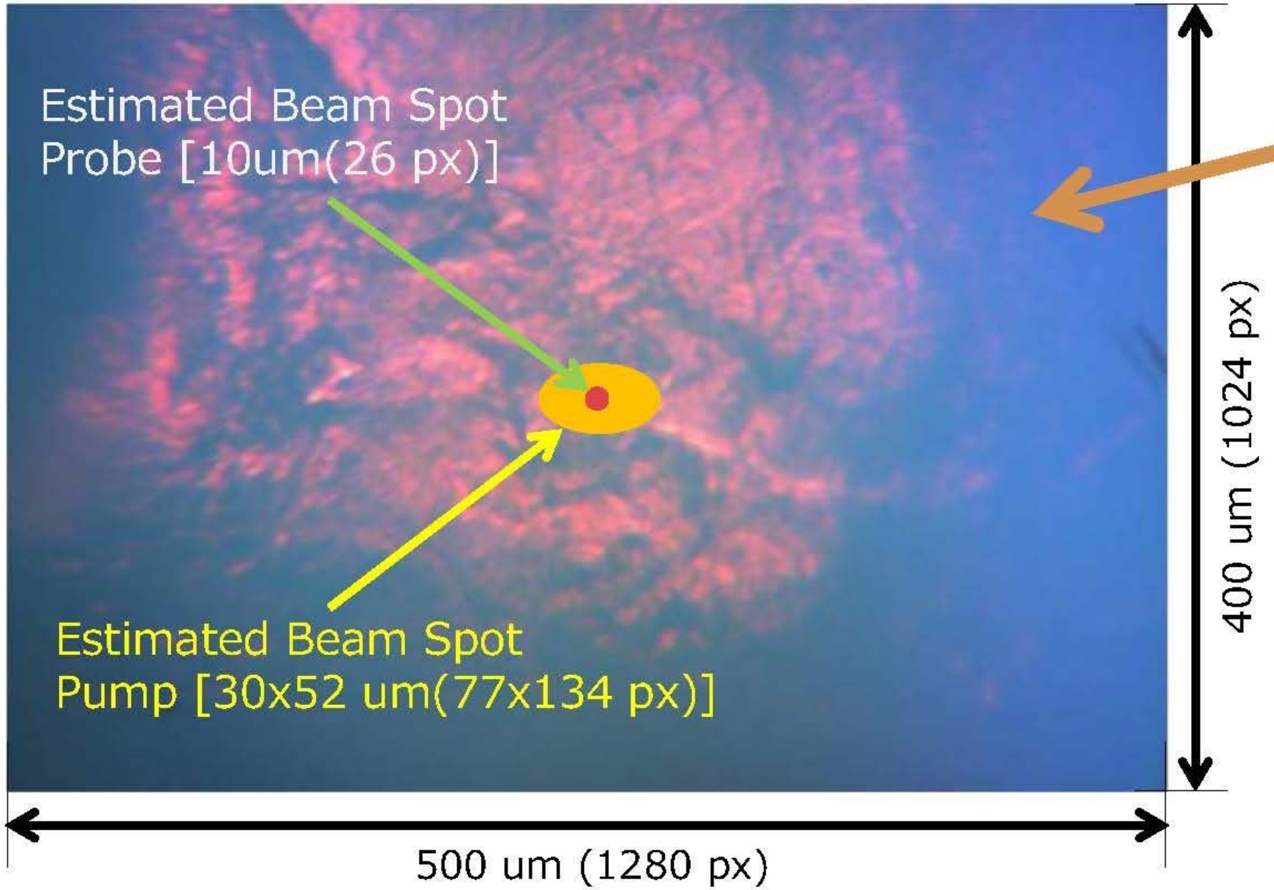
Advanced development of thermal evaluation

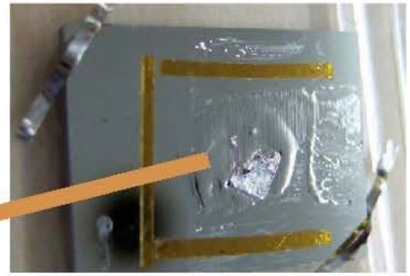
Analysis of validity and range of FF mode

Further modification to be able to measure microcrystals also

System change: Beam size successfully focused to ~3μm

PicoTR Remodeling: Sample-Surface Monitoring System

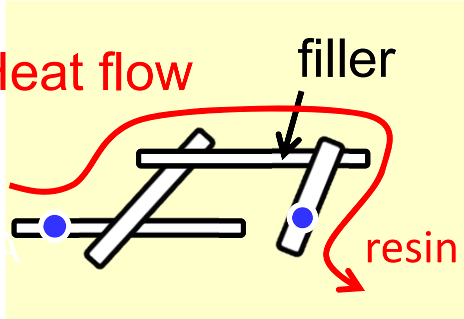




Good resolution for finding sampling point.

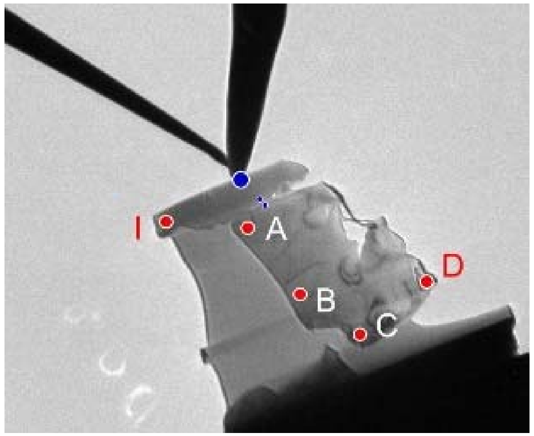
Thermal evaluation on the nanoscale

e.g.



Vital for developing thermal properties of composites

Development of a novel in-situ TEM thermal probe method!



300 kV JEM-3100FEF HRTEM

Patent filed

Nanoscale evaluation of Heat flow・Thermal resistance

Huge insight for TE nanomaterials also!

Nano-Seebeck measurements being developed also

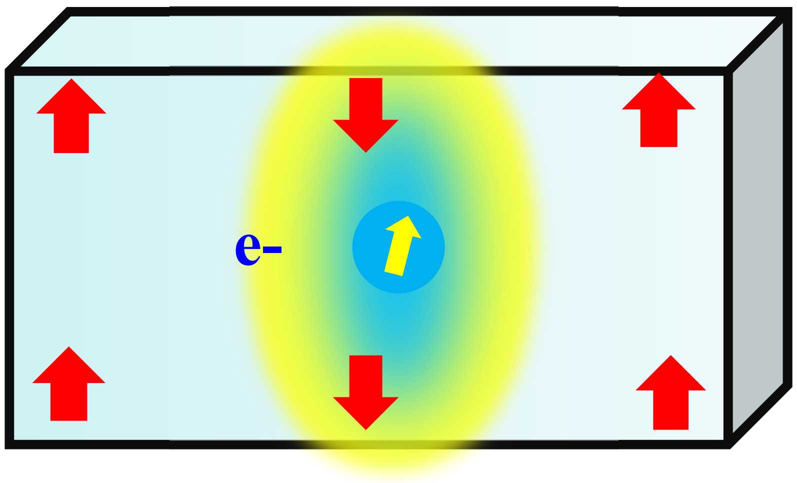
Ways to enhance TE

A. Selective scattering of phonons

B. Enhancement of power factor: $\alpha \times \sigma$?

Nanocomposites (hybrid effect),
Magnetic semiconductors, etc.

Magnetic semiconductors



- Strong interaction between carrier and magnetic moment

Enhanced effective mass ?

Large Seebeck coefficients ?
High Power Factor?

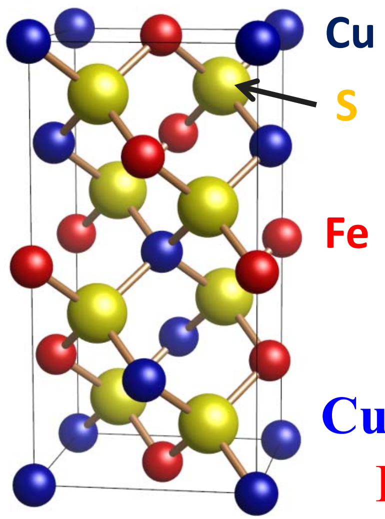
New concepts for TE functionalization

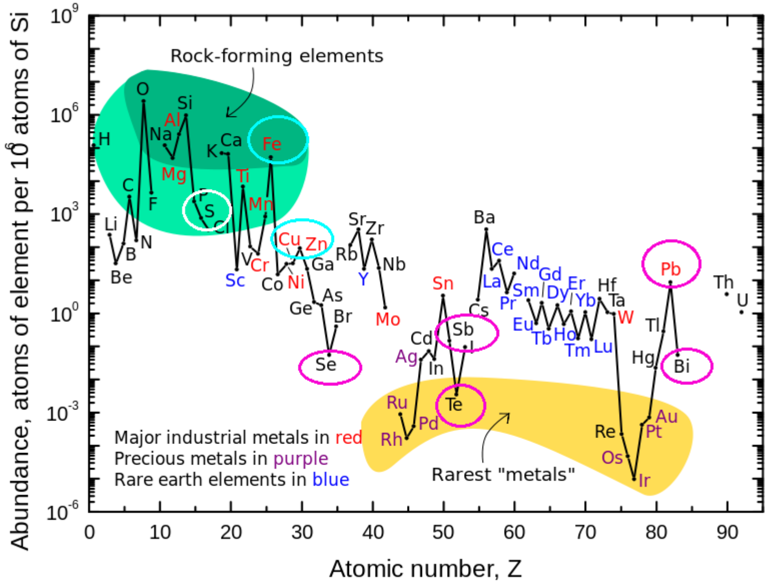
$CuFeS_2$-based magnetic semiconductors

High power factor @RT
Develop as Replacement for Bi_2Te_3!

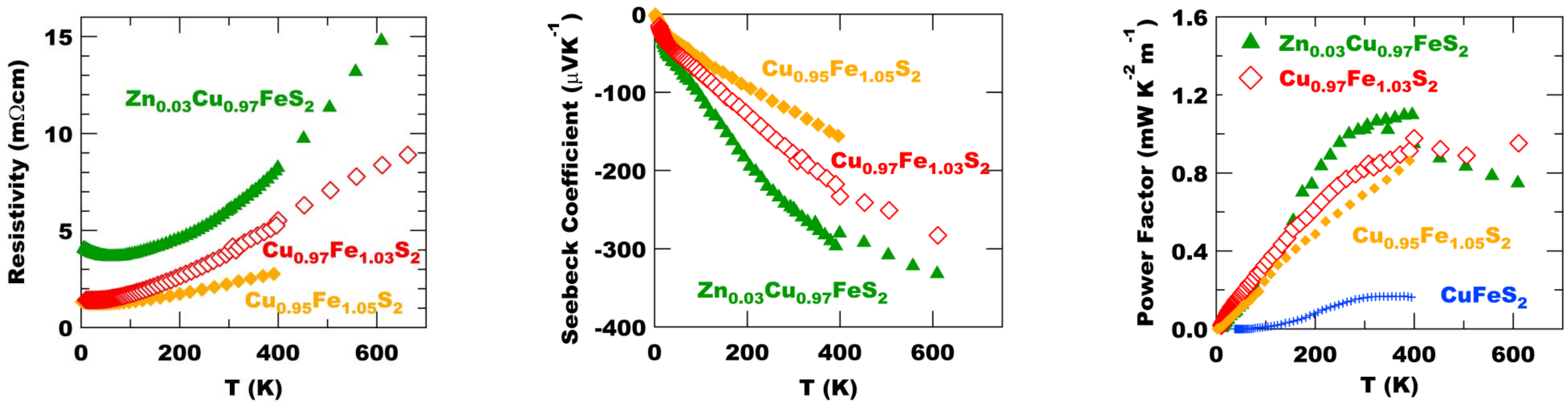
Naohito TSUJII and Takao MORI

APEX 6 (2013) 043001 *Selected SPOTLIGHT*

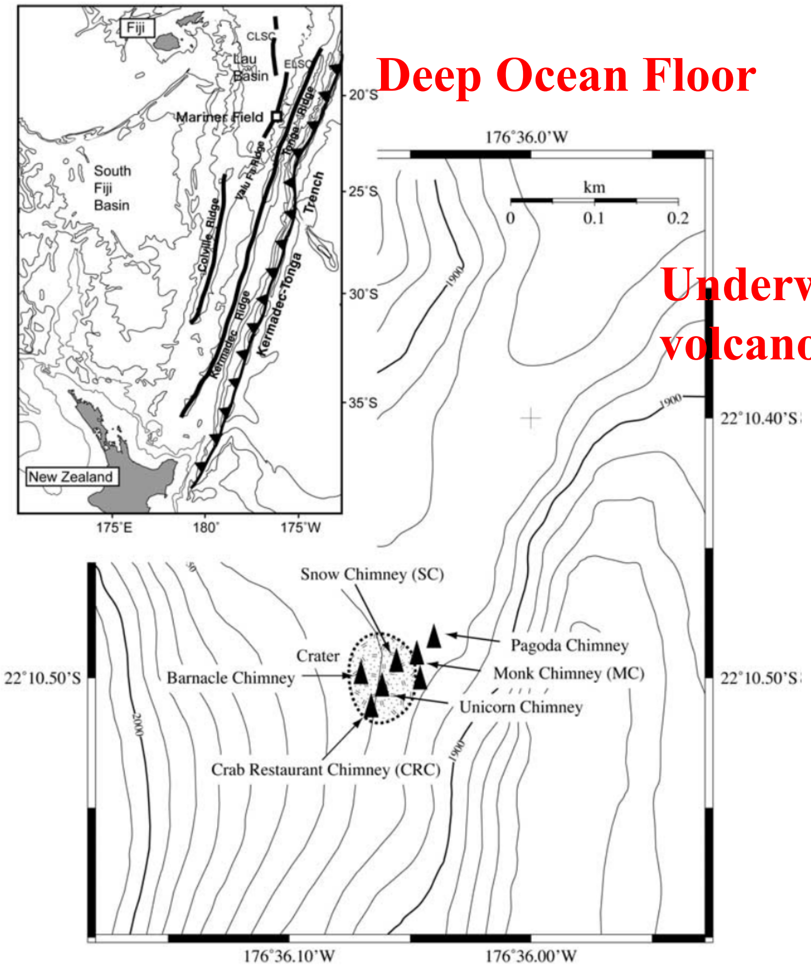




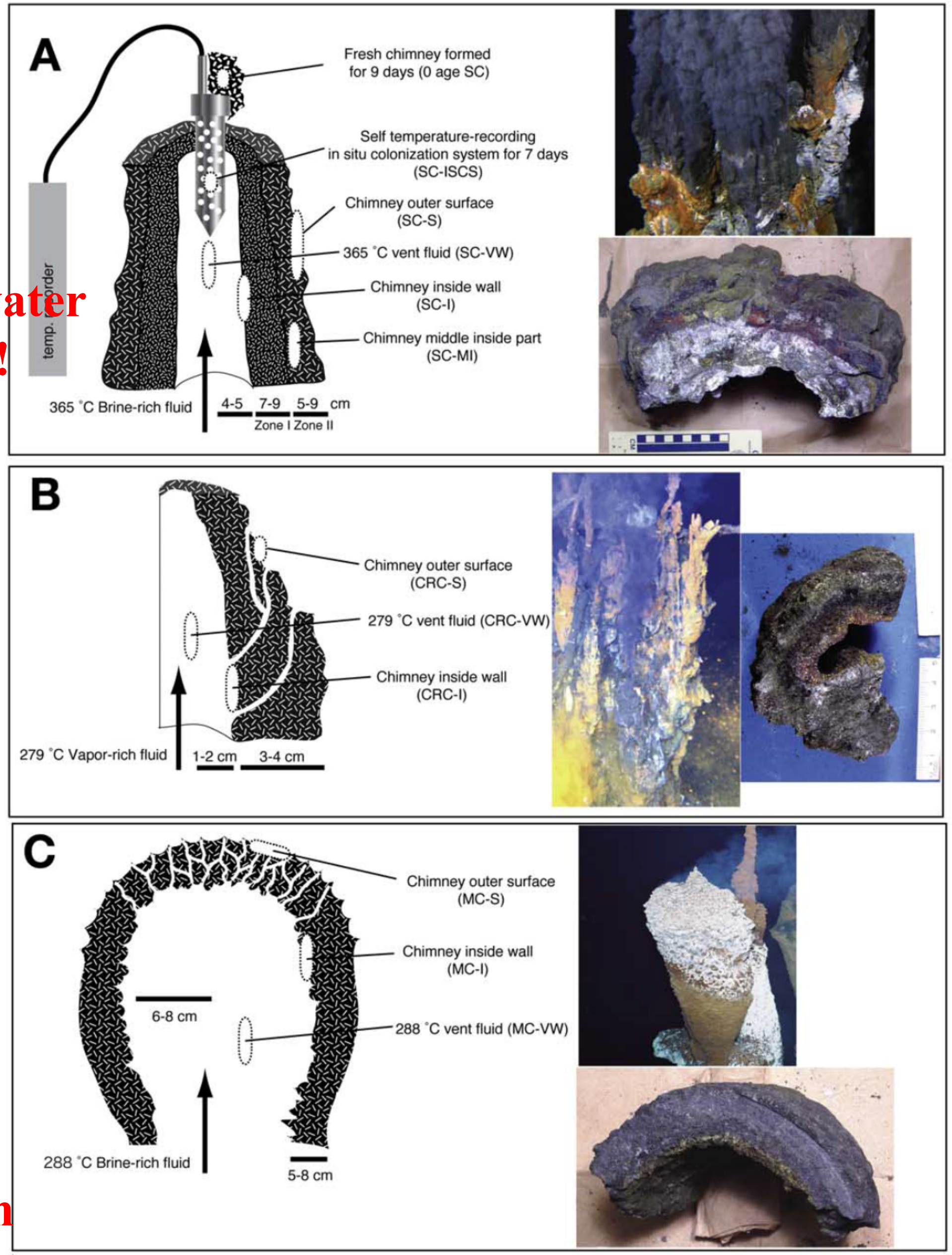
Enhanced TE indicated from magnetic interactions!

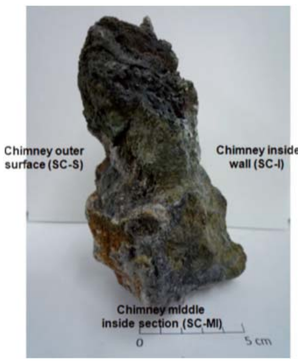


Deep Ocean Floor



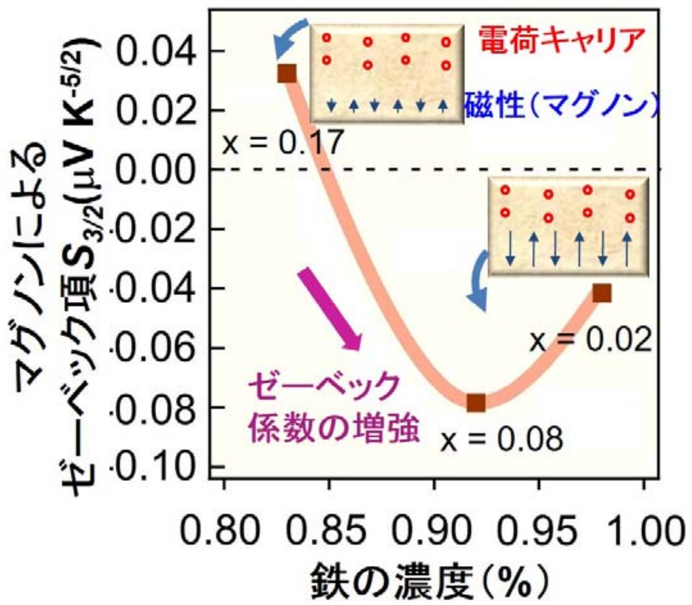
Underwater volcano!





TE electricity generated on the ocean floor!

Ang et al., Angew. Chem. Int. Ed. 54, 12909 (2015)

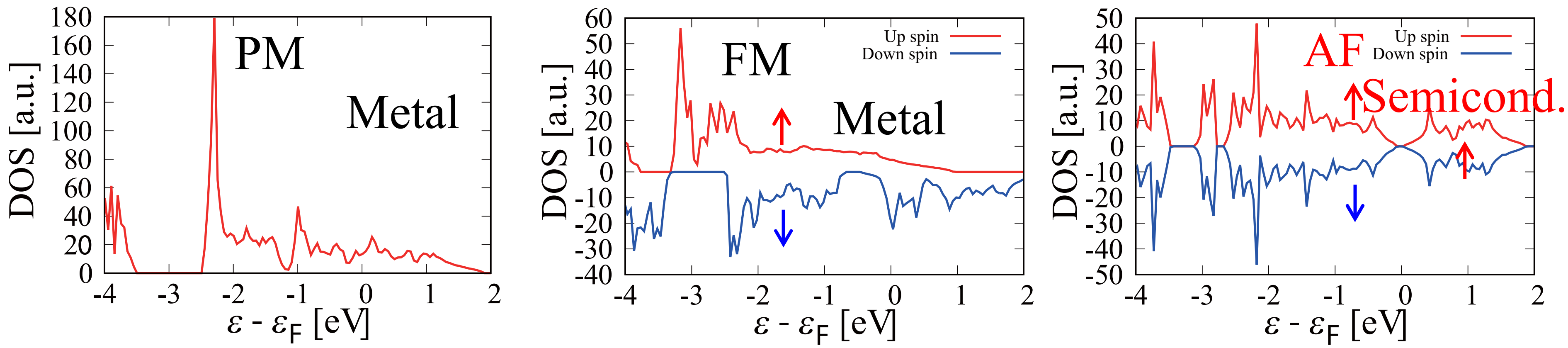


Ang et al., Angew. Chem. Int. Ed. 54, 12909 (2015)

Carrier-magnon scattering enhancement

Theory: H. Takaki, N. Kobayashi et al. (U. Tsukuba) Mori CREST team

$CuFeS_2$ First principles calc. based on DFT



Appl. Phys. Lett. in press (2017)

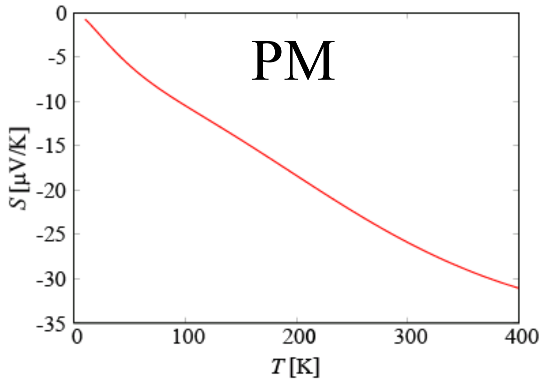
Theory: H. Takaki, N. Kobayashi et al. (U. Tsukuba) Mori CREST team

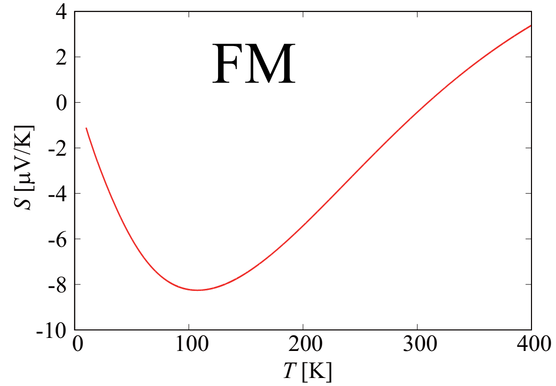
$CuFeS_2$ First principles calc. based on DFT

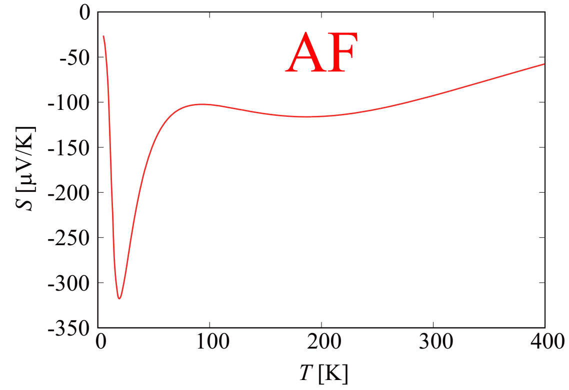
Nonequilibrium Green function formalism

$$S(\mu,T) = -\frac{1}{eT}\frac{L_1(\mu,T)}{L_0(\mu,T)} \qquad L_n(T) = \frac{2}{h}\int_{-\infty}^{\infty} d\varepsilon(\varepsilon-\mu)^n\left(-\frac{\partial f_{FD}}{\partial \varepsilon}\right)\bigg|_{\varepsilon=\mu} \mathcal{T}(\varepsilon)$$

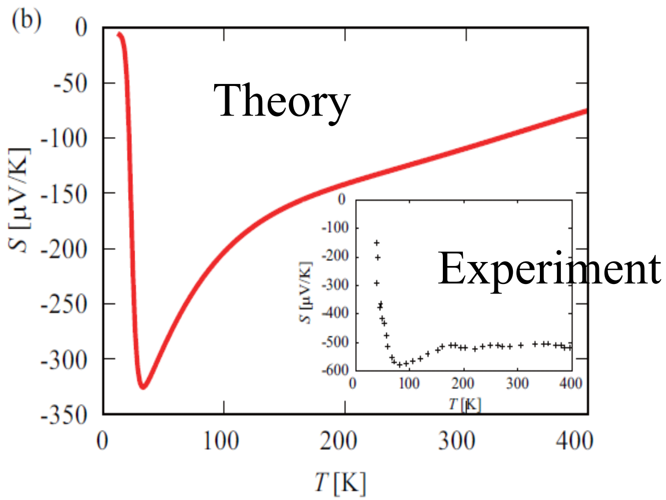
$\mathcal{T}(\varepsilon) = \mathrm{Tr}\left[G^r\Gamma_L G^a \Gamma_R\right]$

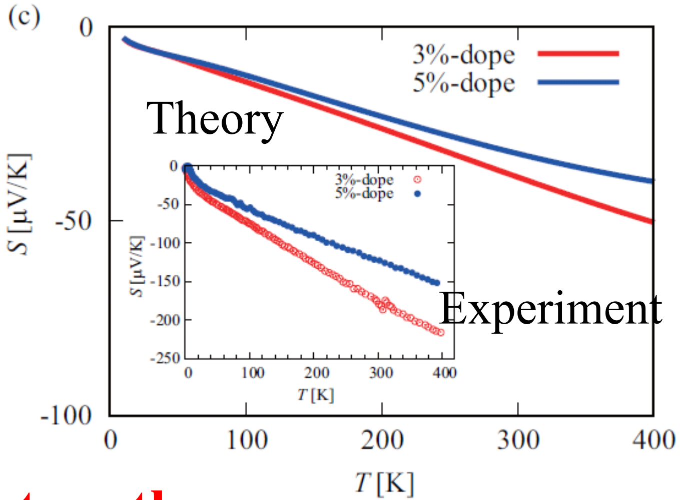






Only AF state has large Seebeck!





Temperature dependence well reproduced

Gap in magnitude indicates other effects still in play

Appl. Phys. Lett. in press (2017)

@High temperature applications

e.g. Topping cycle in power plants
(ZT~0.7 potentially increase output by 6%)

Scripta Materialia
Viewpoint Set
2016

3. Novel inorganic materials
Material Design

Novel borides, sulfides, silicides, oxides, nitrides

High temperature TE applications

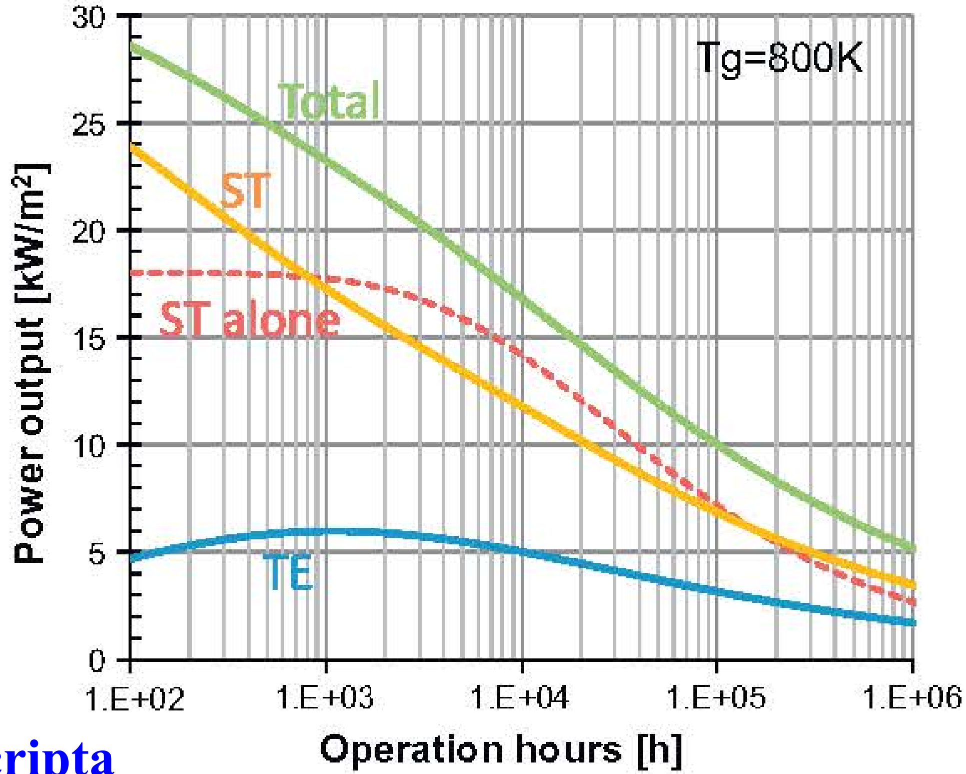
Borides

Topping cycles!

Power plants

Large gap in temperature between steam turbines and incinerating temp.

Power output enhancement from high temp. TE!



K. Yazawa and A. Shakouri, in Scripta Materialia Viewpoint Set (2016)

Review: T. Mori, "Perspectives of High-Temperature Thermoelectric Applications and p-type and n-type Aluminoborides", JOM, DOI 10.1007/s11837-016-2069-9

In Mori Lab

ZEM-5

Seebeck and electrical conductivity measurement up to 1500 K

PEM-2

Evaluation of thermal energy flow and maximum power output = TE efficiency%
Up to 1100 K

Material Design

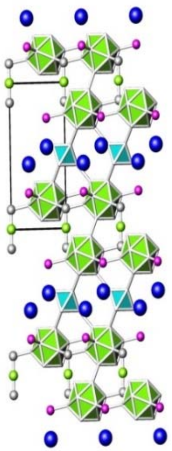
e.g. Control of atoms in voids of structures

p type boron carbide "B_4C"
Emin et al., 1984
ZT≈1.0@1000℃

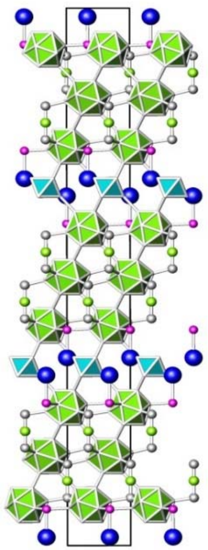
Lack of n-type counterpart

Void control Insertion of Metal ion R
Network structure

$RB_{17}CN$ n type



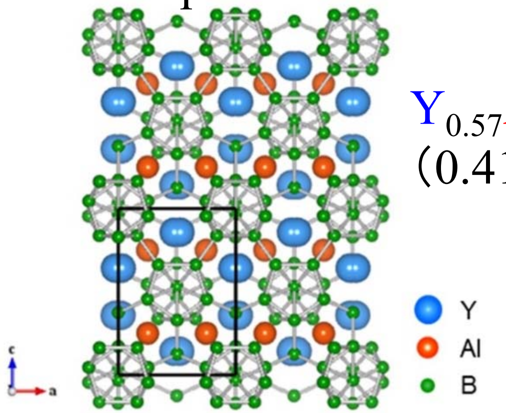
$RB_{22}C_2N$



Dalton Trans., (2014)

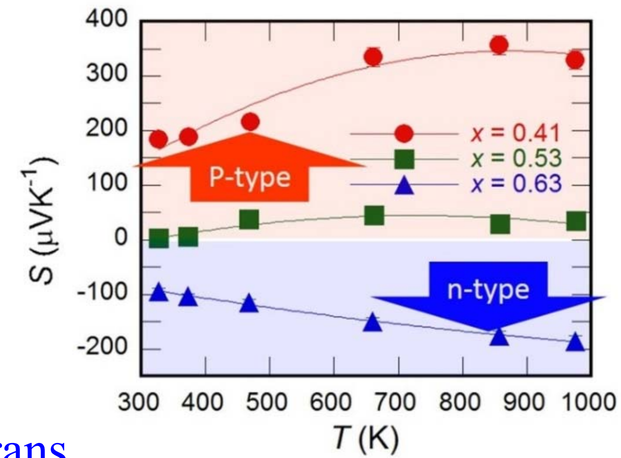
25 year old problem solved!

Void control Al atom occupancy
Excellent p- and n- control



$Y_{0.57}Al_xB_{14}$
($0.41 \le x \le 0.63$)

Large p- and n-type *S*



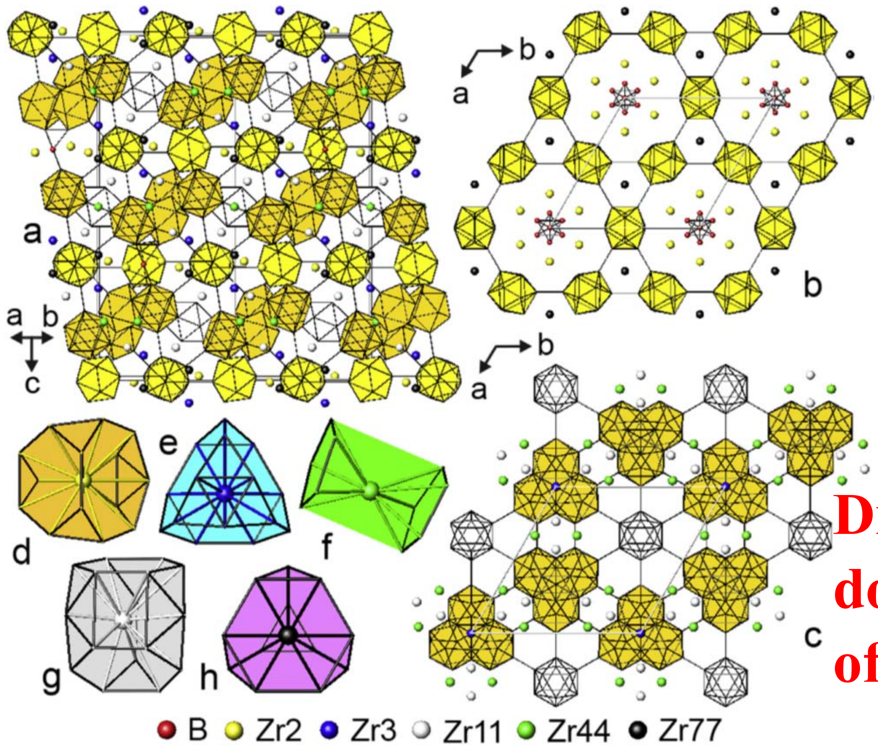
Best matching p-n!

S. Maruyama et al
Appl. Phys. Lett. (2012)
J. Appl. Phys. (2014)
STAM (2014)

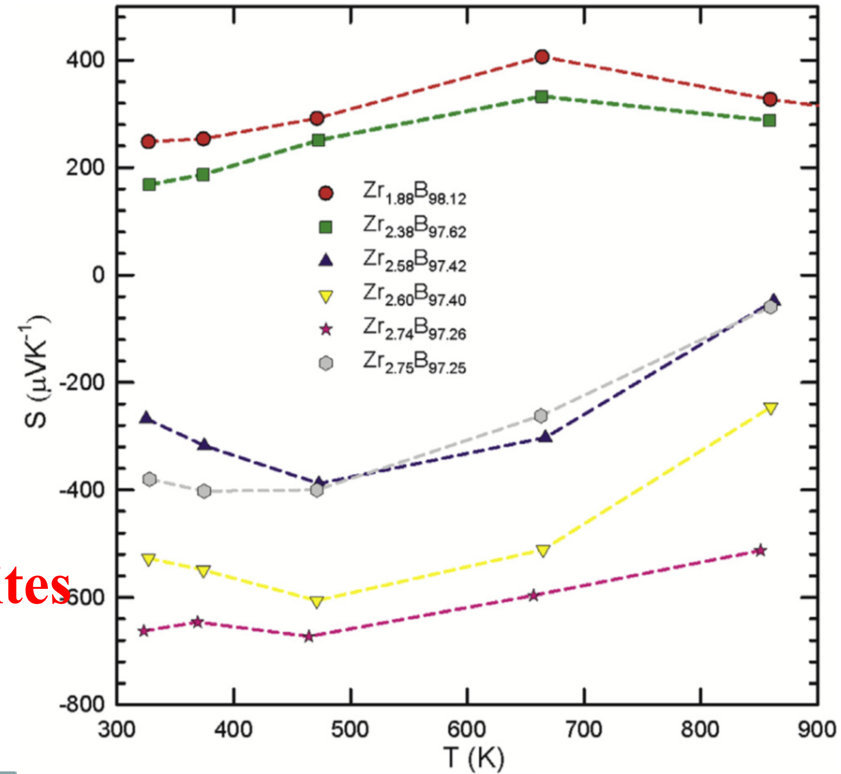
Other promising borides for p n control

➡ **Elemental boron! Strategic doping of voids!**

Sologub et al. Acta Materialia, 122, 378-385 (2017).

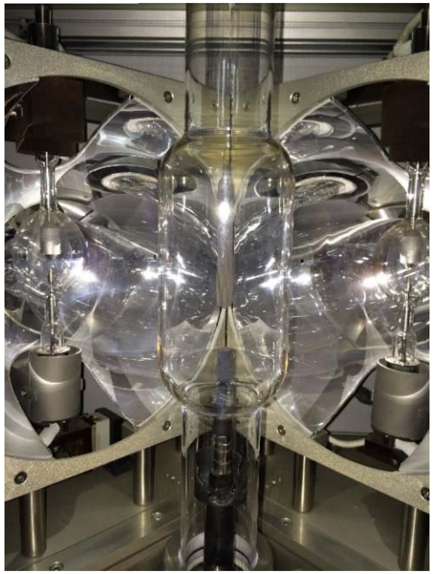


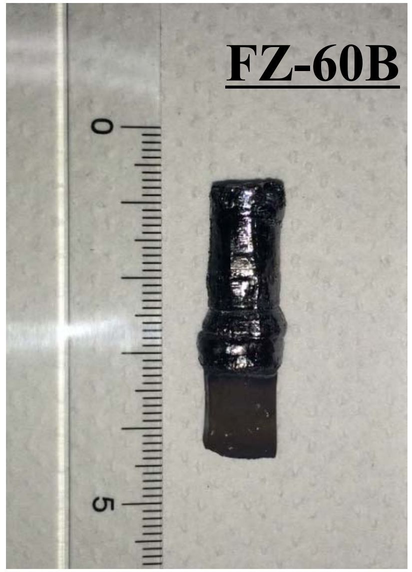
Diverse doping sites of β-B!

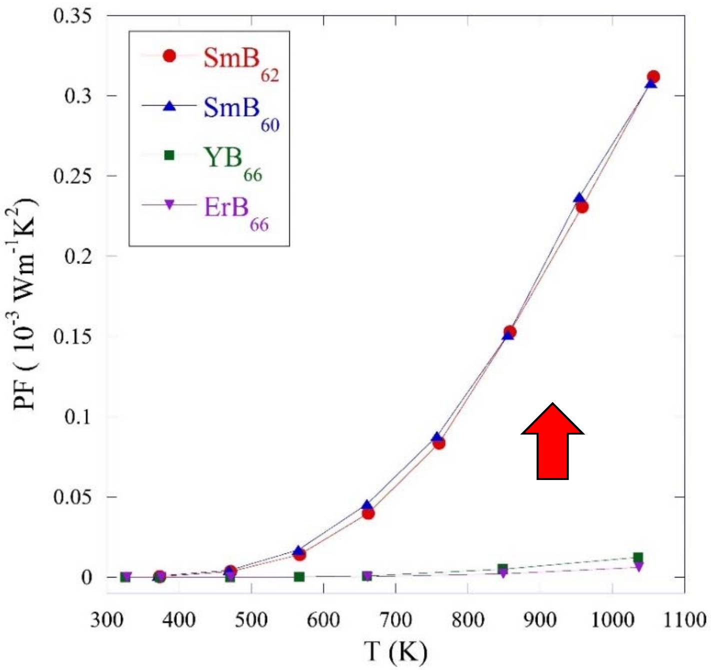


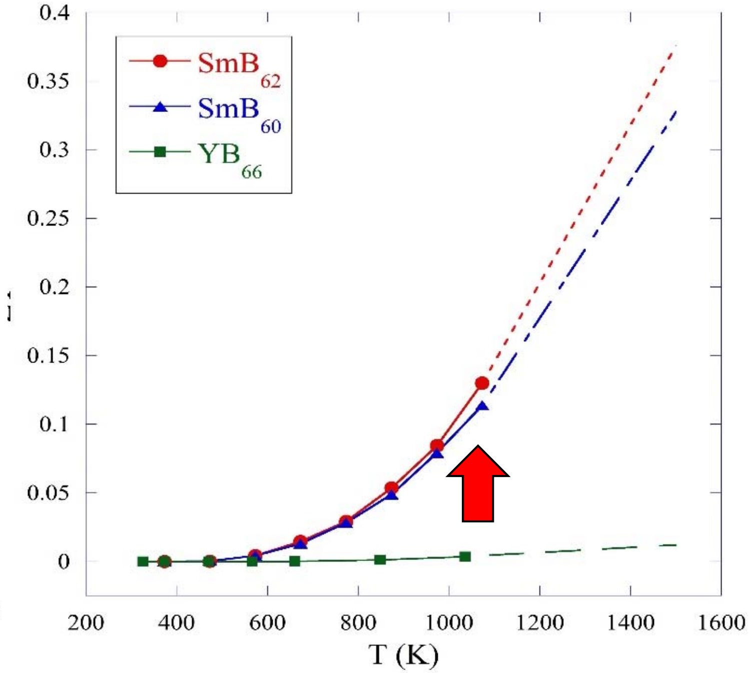
Excellent (S>200 μV/K) p-type or n-type in a material with a single crystal structure and composed of the exact same relatively abundant elements

TE enhancement discovered in SmB_{66}!







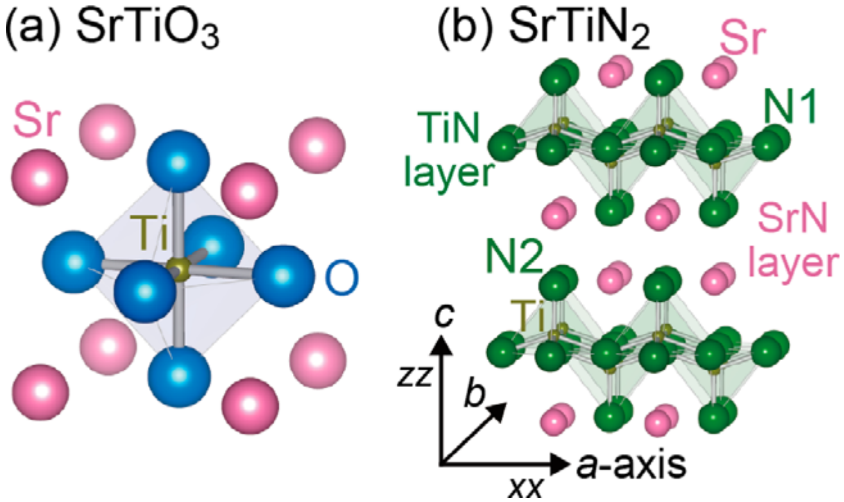


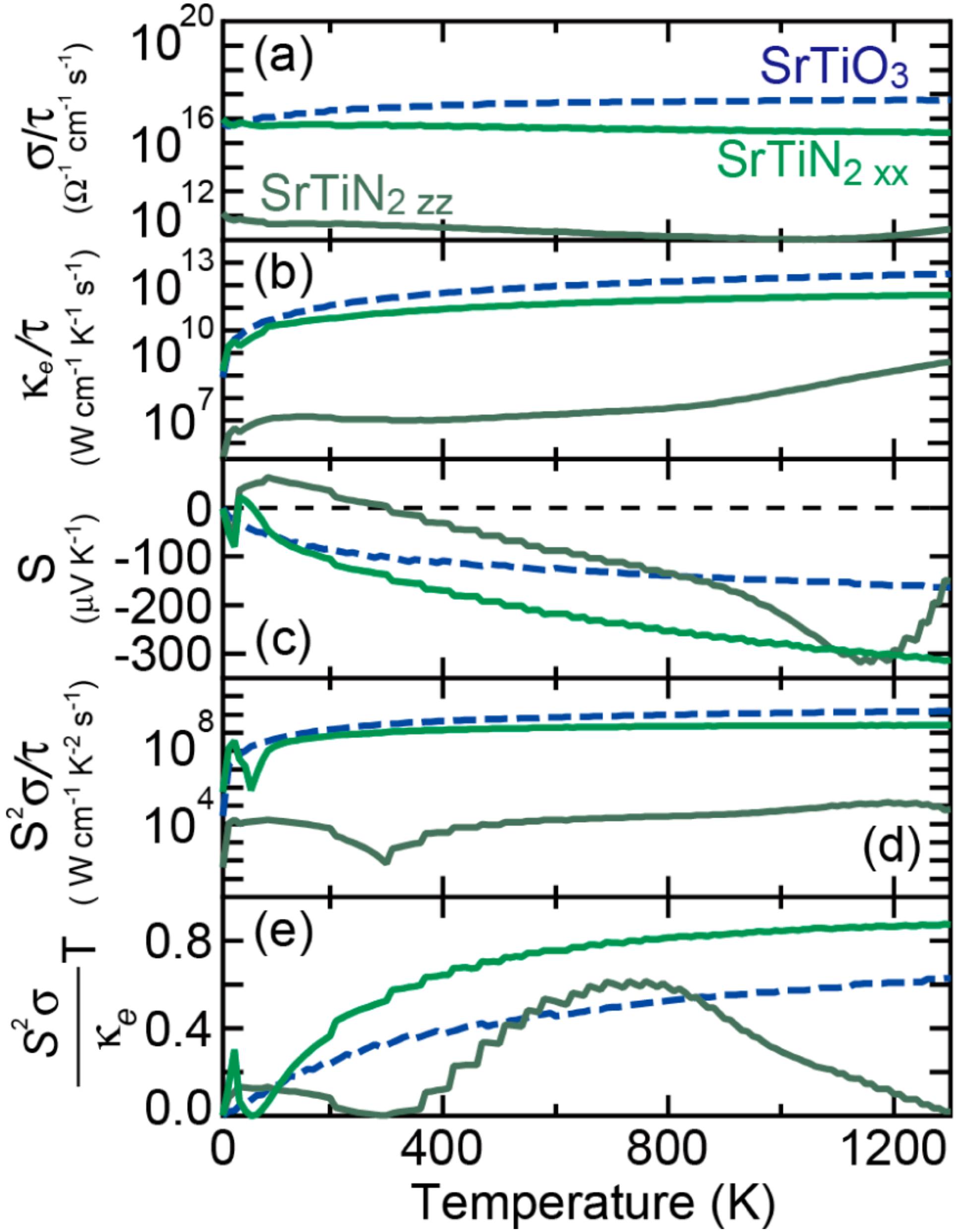
Mixed valency indicated!

ZT ~40 times enhancement due to Sm!

J. Materiomics (2015)

Layered nitrides can be quite promising for TE





I. Ohkubo and T. Mori

Chem. Mater., 26, 2532 (2014)
Chem. Mater., 27, 7265 (2015)

Inorg. Chem. 2014

Layered nitrides may be more higher performing TE systems than oxides!

Fabrication and evaluation of modules (Novel magnetic sulfides)

Summary:

1. Introduction

Necessity to realize TE!

2. Ways to enhance TE

Selective scattering of phonons

Nanostructuring

Novel concepts for power factor

Nanocomposite: Hybrid effect

Magnetic semiconductor

Measurements

3. Novel materials

Thank you!

■ NIMS, MANA Thermal Energy Materials Lab

- **Thermoelectric Materials & Thermal Management**
- **Different fields+Company researchers: Open Innovation**
- **World class, state of the art facilities →Top papers and products**

Collaboration is welcome!

In Open Innovation Lab:
Over 40 researchers from
Companies, NIMS, & Univ.

Contact:
MORI.Takao@nims.go.jp