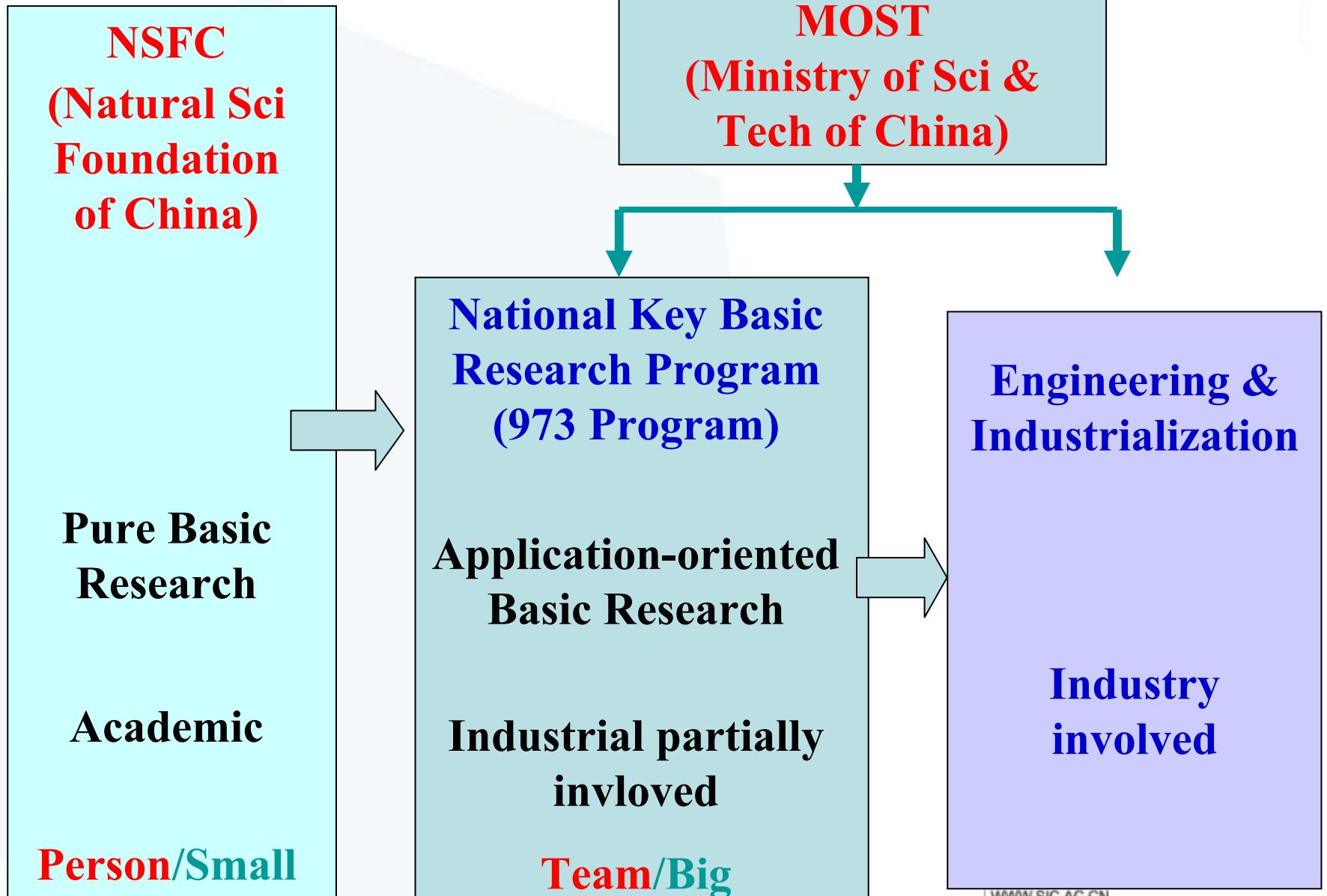


Overview of Research on Thermoelectric Materials and Devices in China

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Shanghai Institute of Ceramics
Chinese Academy of Sciences
Shanghai, China

Sept 30, 2009



Institutions:

1. Shanghai Institute of Ceramics, CAS (Shanghai)
2. Wuhan University of Technology (Wuhan)
3. Zhejiang University (Hangzhou)
4. Tsinghua University (Beijing)
5. Tianjin University (Tianjin)
6. Shandong University (Jinan)
7. Beijing University of Sci. and Tech. (Beijing)
8. Tianjin Power Source Institute (Tianjin)
9.

Scientists:

Chen Lidong, Zhang Wening, ... (Shanghai)
Zhang Qingjie, Tang Xinfeng, ... (Wuhan)
Zhao Xinbin, ... (Zhejiang)

1. New thermoelectric compounds: *special* structures

- ◆ 3-dimentional caged compounds
- ◆ 2-dimentional layered compounds
- ◆ New concept TE materials

Tuning the electron correlation; Other compounds;

2. Nano and bulk nanocomposite materials

Goal: $ZT \sim 2.0$

3. Devices and module fabrication

Goal: Efficiency $\sim 20\%$

4. Industrial applicartions

Phase 1: Hybrid PV+TE power generation;

Automobile waste heat recovery;

Special power generation

--- Mainly supported by China government (973)

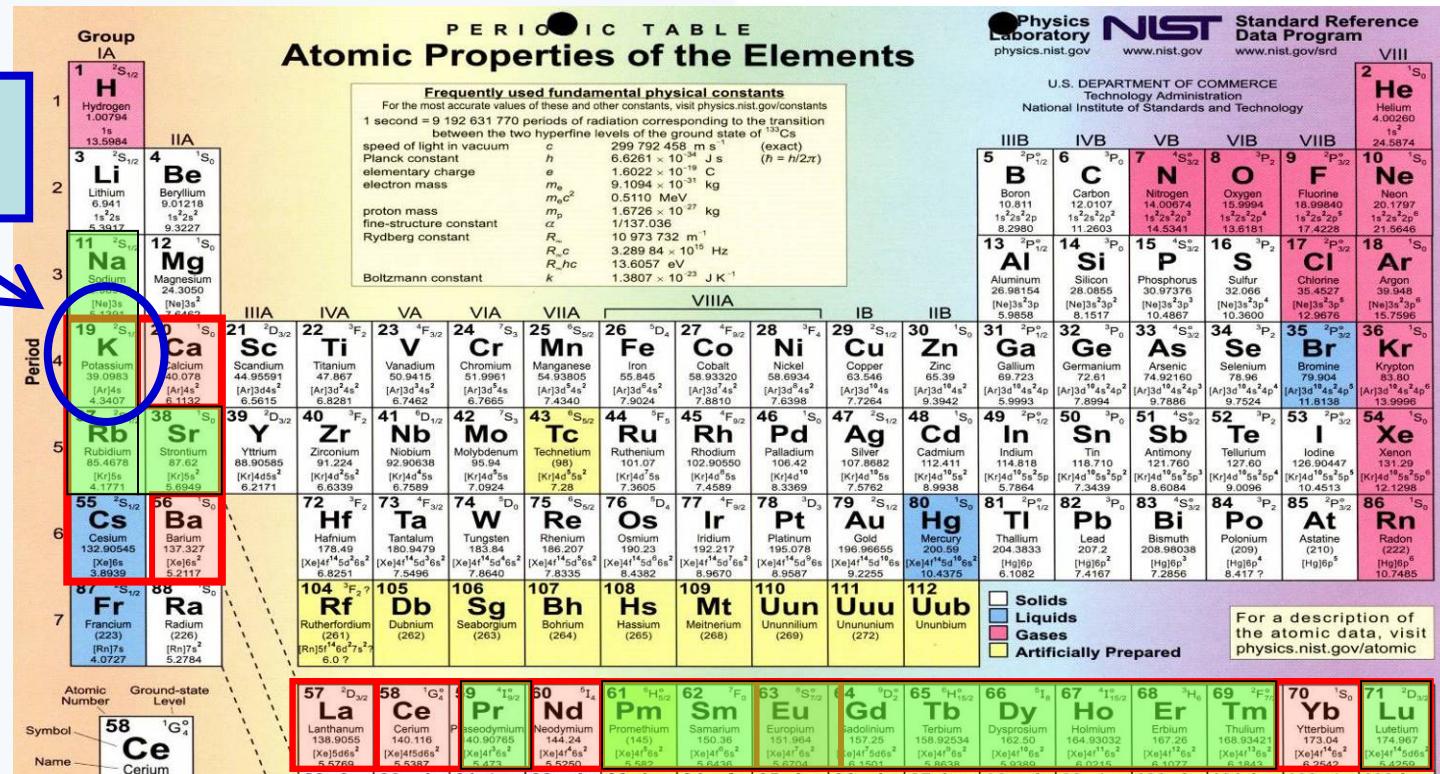
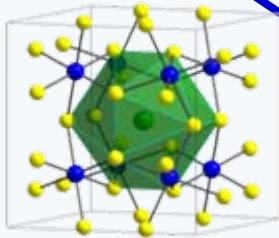


The Electronegativity-based Selection Rule

The Δx -based selection rule ($\Delta x = x_{Sb} - x_I > 0.80$):

- Most of atoms form no stable filled phase ;
- RE and AE atoms do form stable filled phases;
- AM-filled CoSb_3 — novel filled phases ?

Novel filled
 CoSb_3 ?

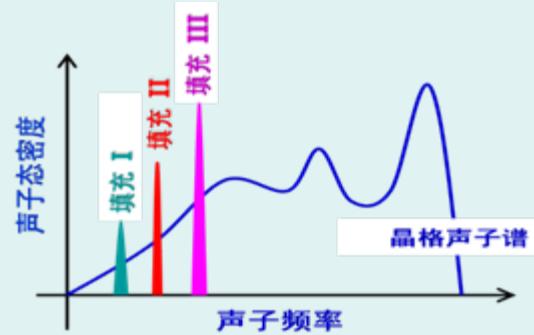


AM-filled CoSb_3 : 2007 Goldsmid Award (Dr. Pei YZ);
Pei, Chen, Zhang, APL (2009,2007); Mei, Zhang, Chen, PRB (2007).

Optimal Combinations of multiple fillers

Optimal Combinations of multiple fillers :

“Using fillers with largely different rattling frequencies to realize wide-spectrum phonon scattering, especially for the low-frequency phonons ”



	Filler atom	Rattling ω_0 (cm^{-1})
稀土 (RE)	La	68
	Ce	55
	Eu	59
	Yb	43
碱土 (RE)	Ba	94
	Sr	91
碱金属 (AM)	Na	113
	K	142

□ Bad combinations :

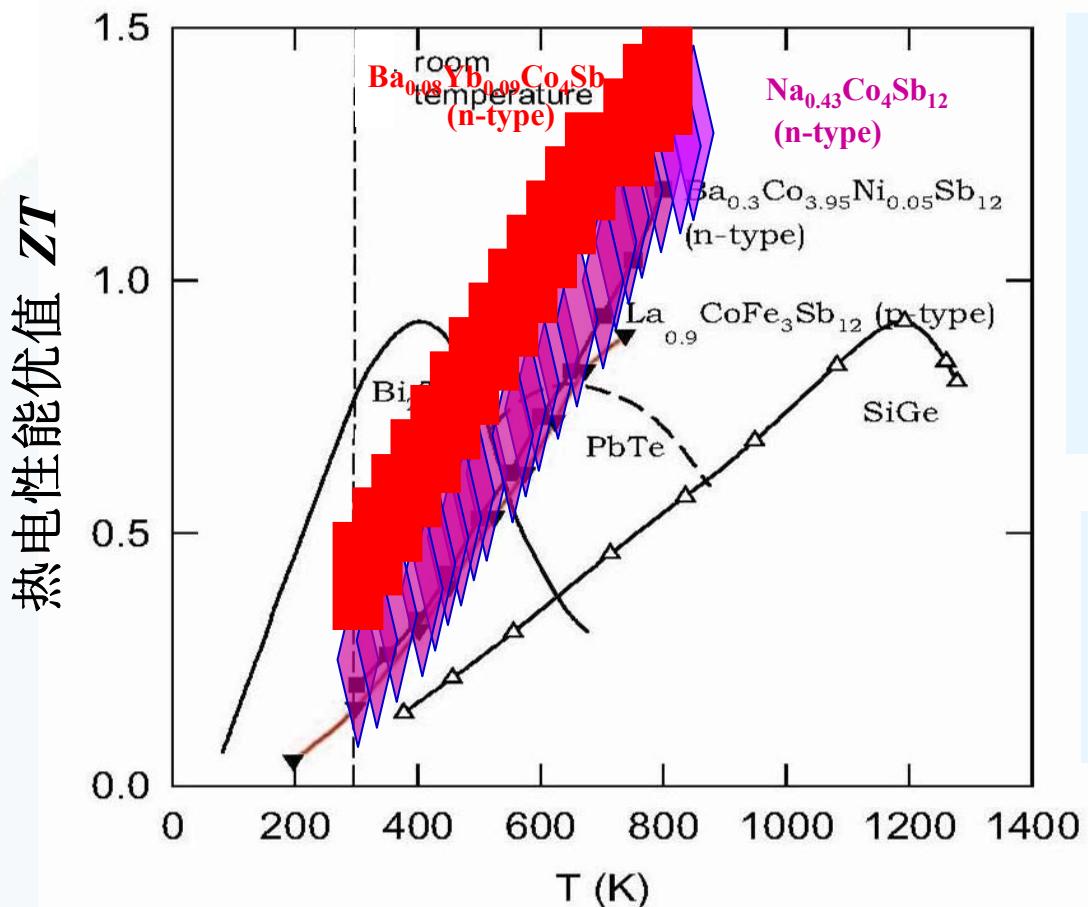
REs (Mischmetal)
AEs (Ba + Sr)

□ Good combinations :

Dual : Ba + Yb , Ba + Ce ,
Yb + Na , ...

Triple : Yb + Ba + Na , ...

ZTs of the Ba-Yb dual-filling CoSb₃



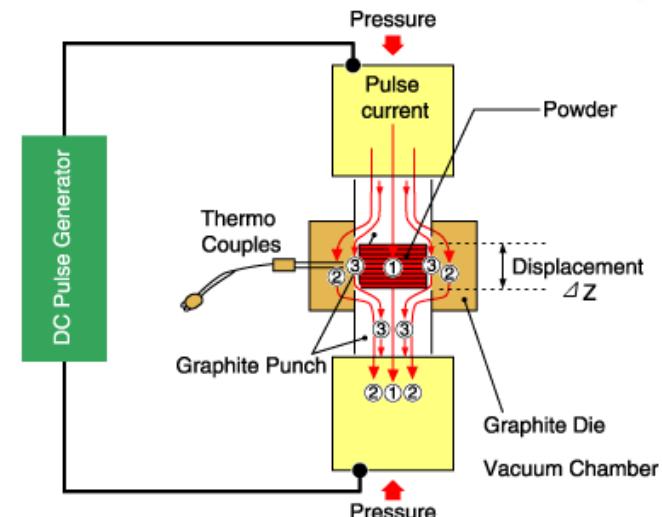
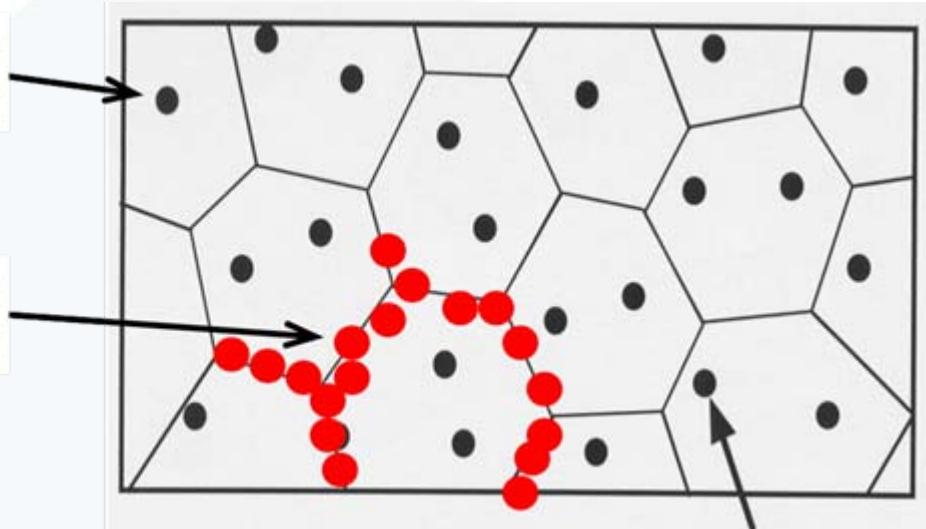
Ba-Yb dual-filled CoSb₃ reaches $ZT \sim 1.36 @ 850K$, Best among the CoSb₃-based bulk materials ! (2008)

A series of dual-filled CoSb₃ ($\sim 1.4 @ 850K$) could be obtained easily.

Yang, Zhang, Chen et al, Appl. Phys. Lett. 91, (2007)
Shi, Yang, Chen, Zhang, et al, Appl. Phys. Lett. 92, (2008)
US patent - with GM, 2008, #61036715

晶粒内的
纳米颗粒

界面上的
纳米颗粒

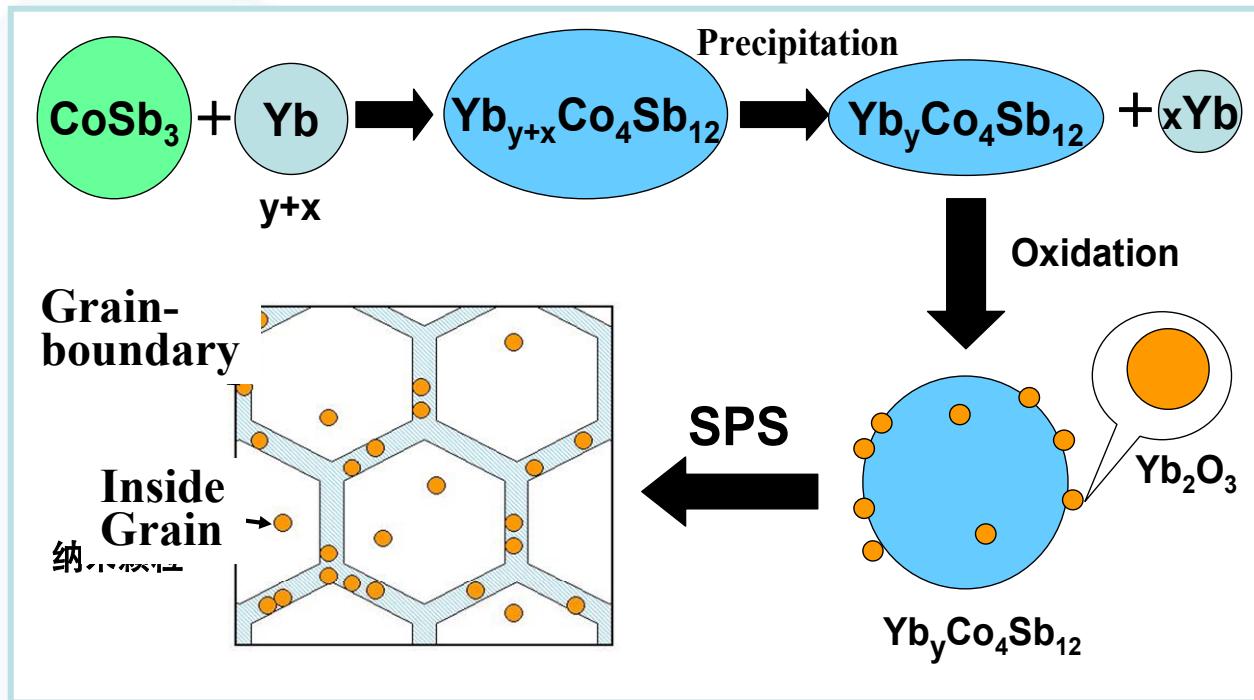


SPS : Non-equilibrium

Bulk nanocomposite :

- In situ nanoparticle formation plus SPS
- melt-spinning(MS) plus SPS
- Chemical synthesis plus SPS
- Mechanical alloy(MA) plus SPS

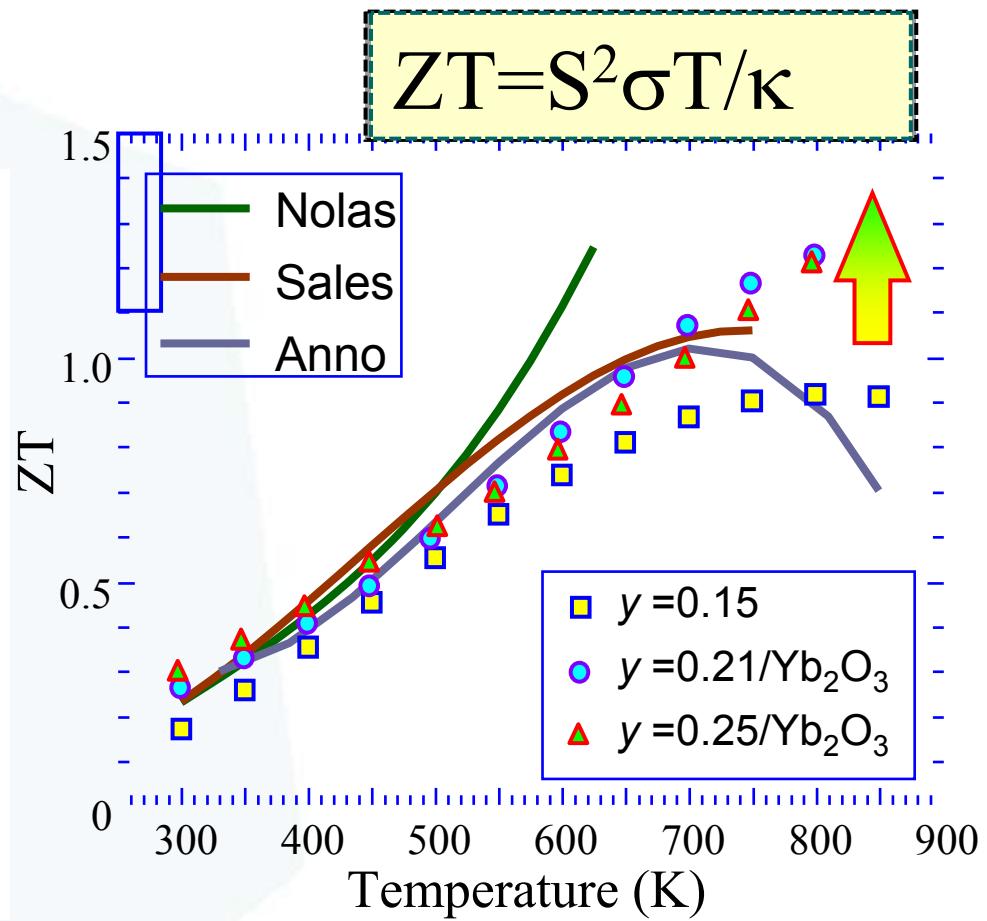
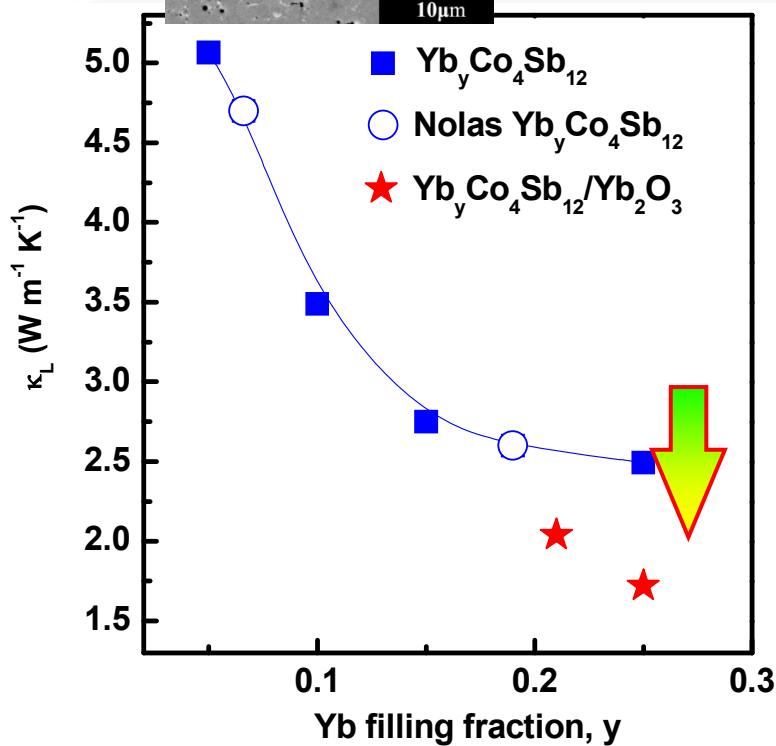
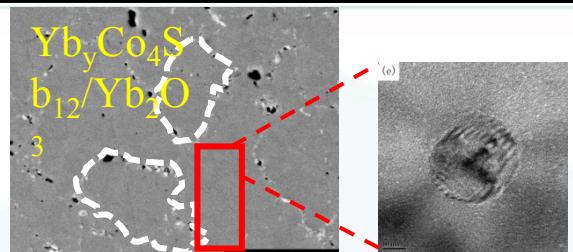
In-situ preparation of $\text{Yb}_y\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3$ nano-composites



Selective oxidation of Yb leads to the formation of homogeneously dispersed nano-size oxide particles.
→ served as effective phonon scattering centers.

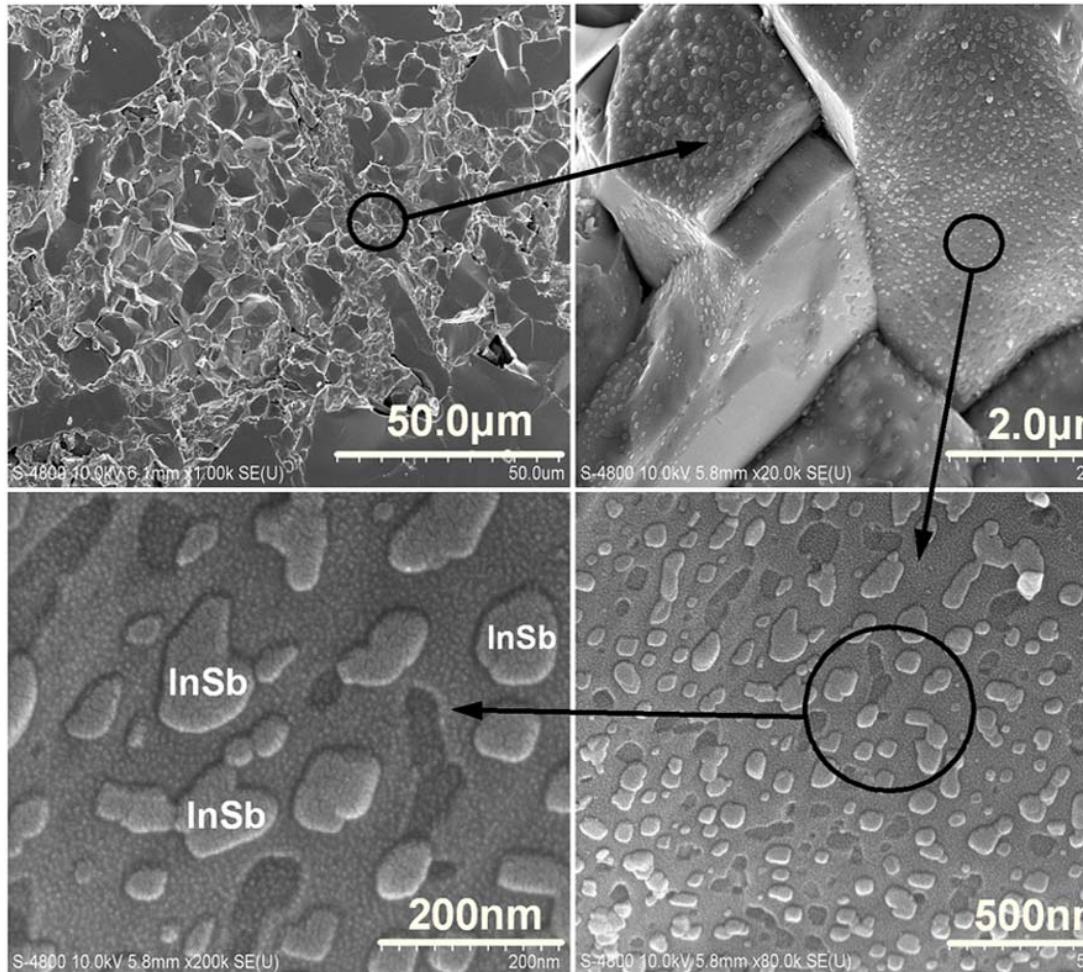
Chen, Zhang, Appl. Phys. Lett. (2006); J. Appl. Phys. (2005, 2007); China patent

TE performance of $\text{Yb}_y\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3$



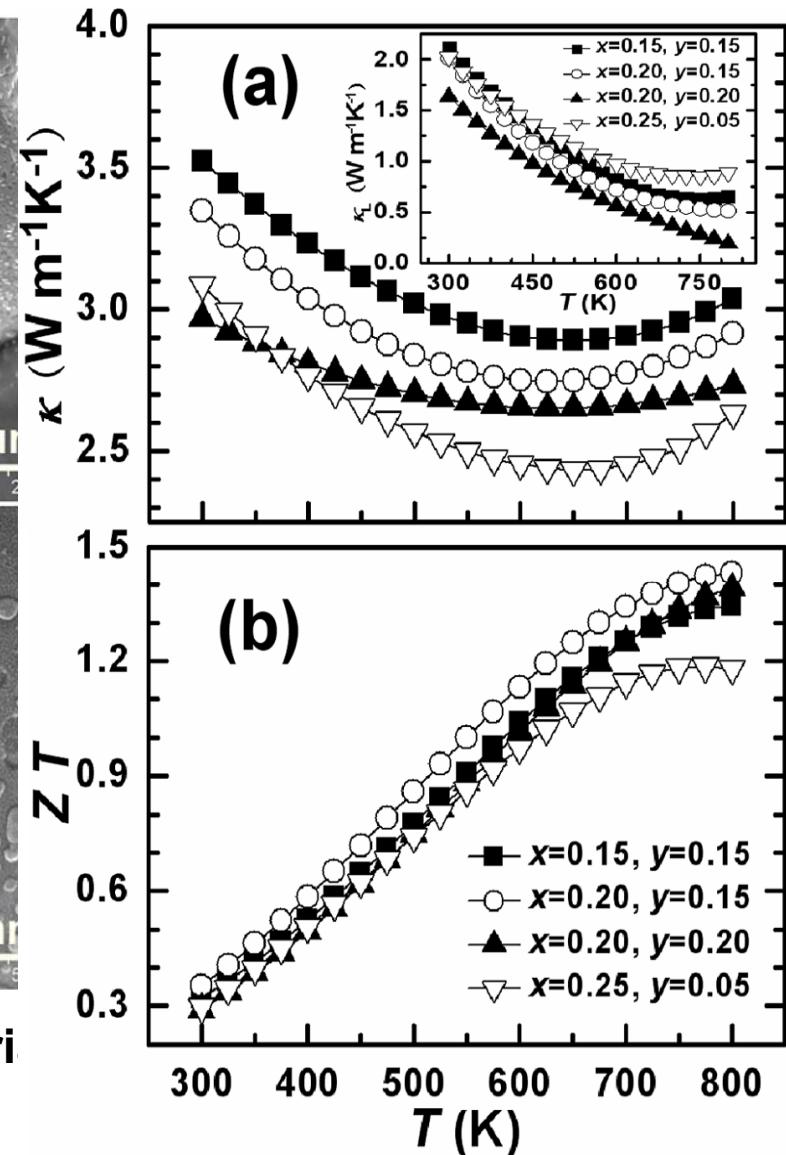
κ_L was greatly depressed by the Yb_2O_3 nano particles dispersed inside grain and on the grain-boundary. $ZT \sim 1.3$

$\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12}/\text{InSb}$ composites

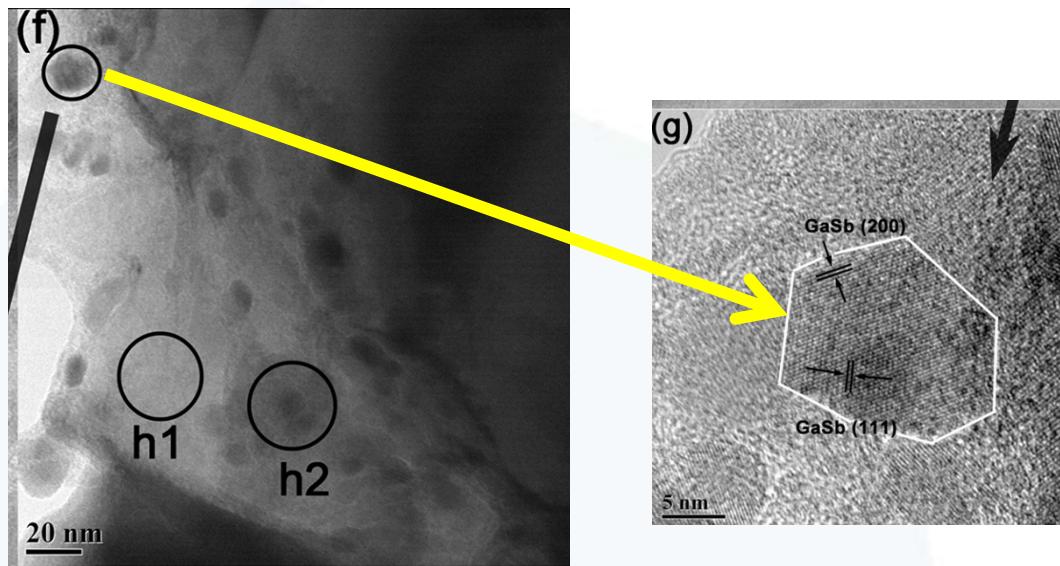


FESEM photos of $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ bulk materi

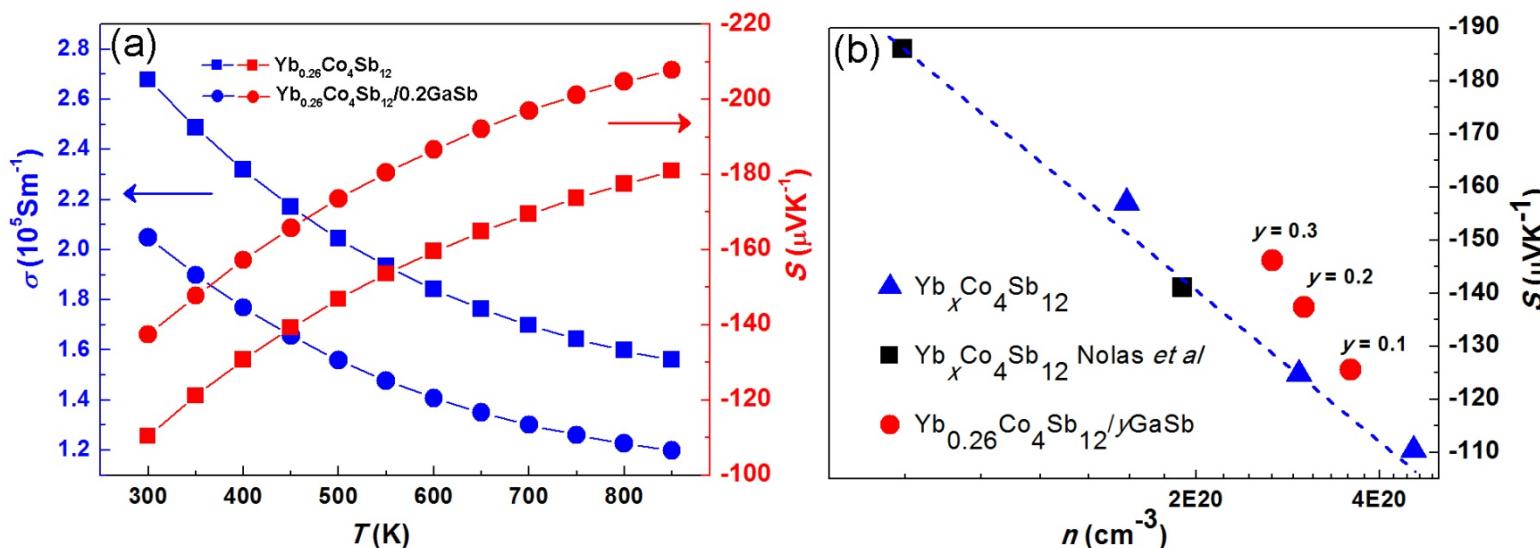
Li, Tang et al., APL(2008)- Wuhan.



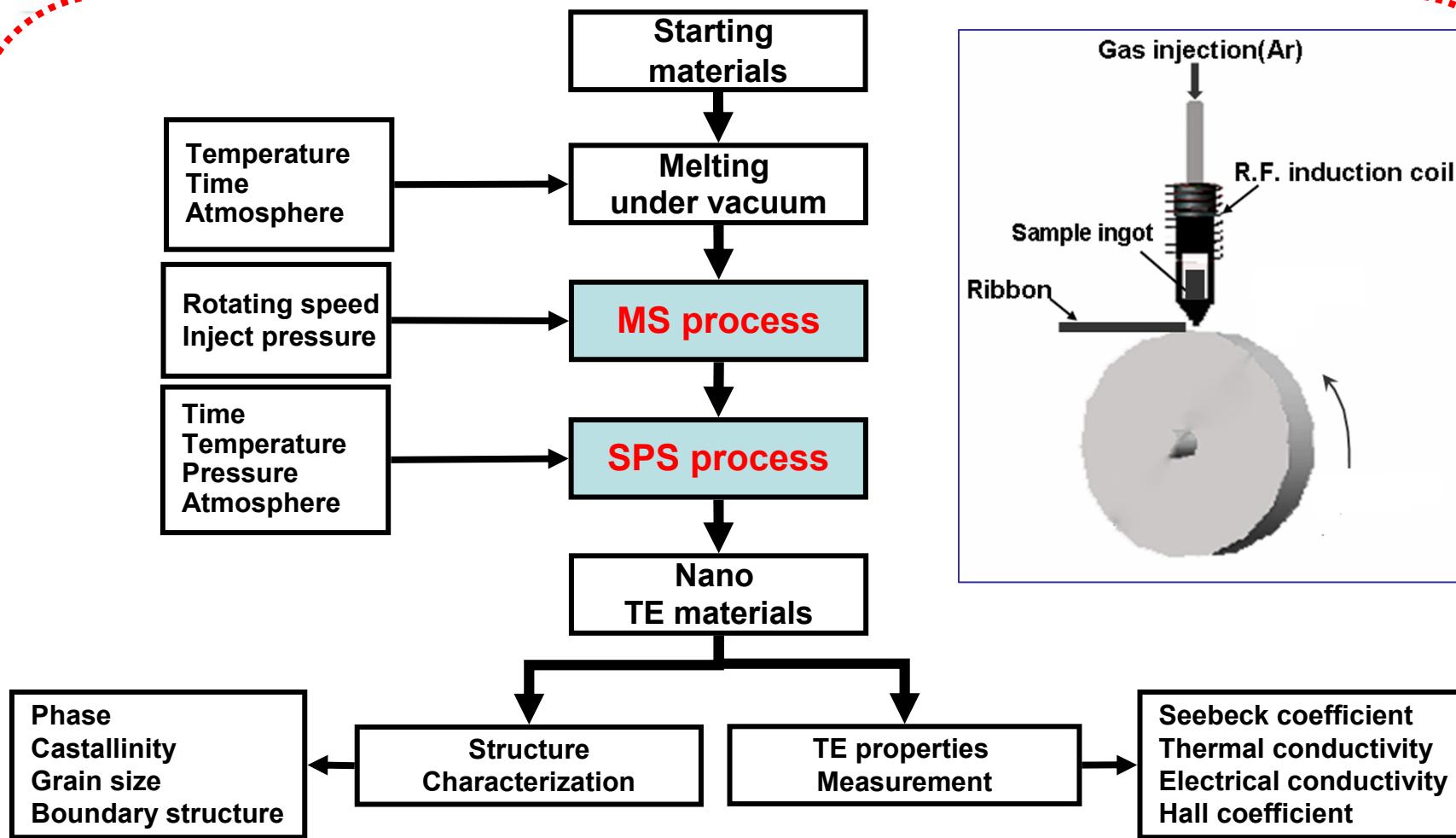
In-situ formed $\text{Yb}_y\text{Co}_4\text{Sb}_{12}/\text{GaSb}$ nano-composites



- ◆ GaSb: 5-10 nm
- ◆ Grain boundary & inside grain
- ◆ S also improved
- ◆ ZT > 1.4



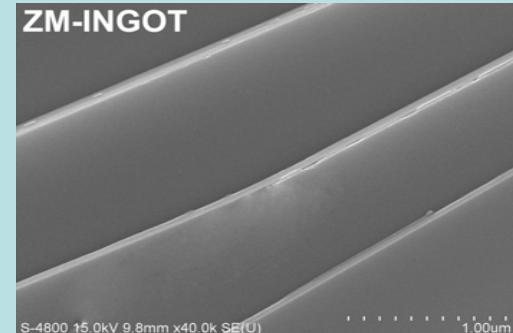
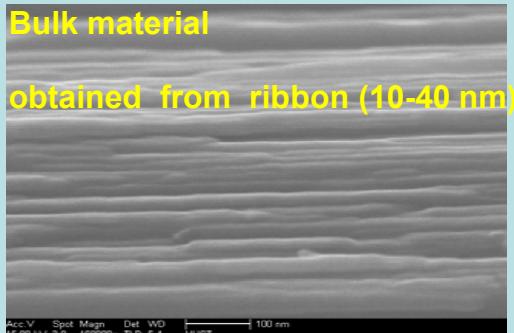
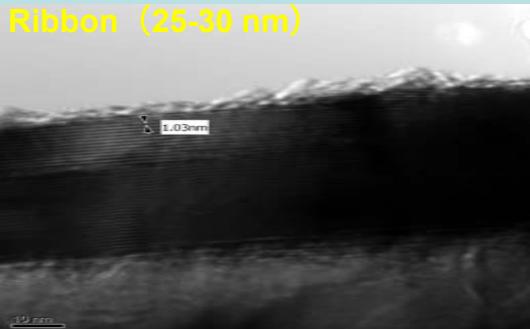
MS-SPS Technology



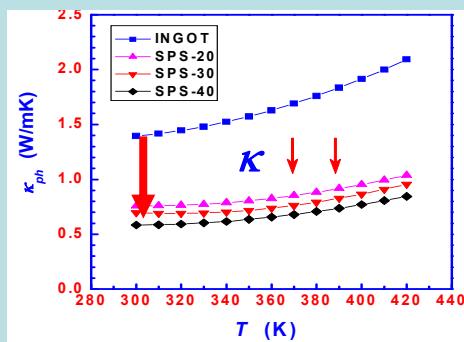
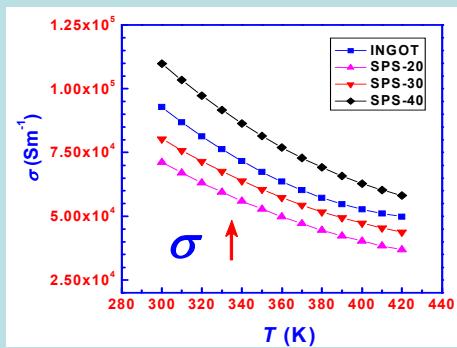
The MS technique has been widely used to prepare amorphous alloys, but it has not been reported to apply for preparing TE materials with fine nanostructure before our work. By our work, we have found that the MS technique can give us considerable control over the resulting nanostructures in TE materials.

Nanostructure by MS-SPS

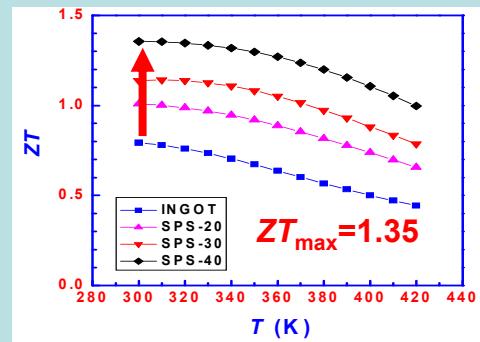
A p-type Bi_2Te_3 material with layered nanostructure was obtained by MS+SPS technology, the TE properties were greatly enhanced with the nanostructure and the highest ZT values reaches **1.35** at 300 K.



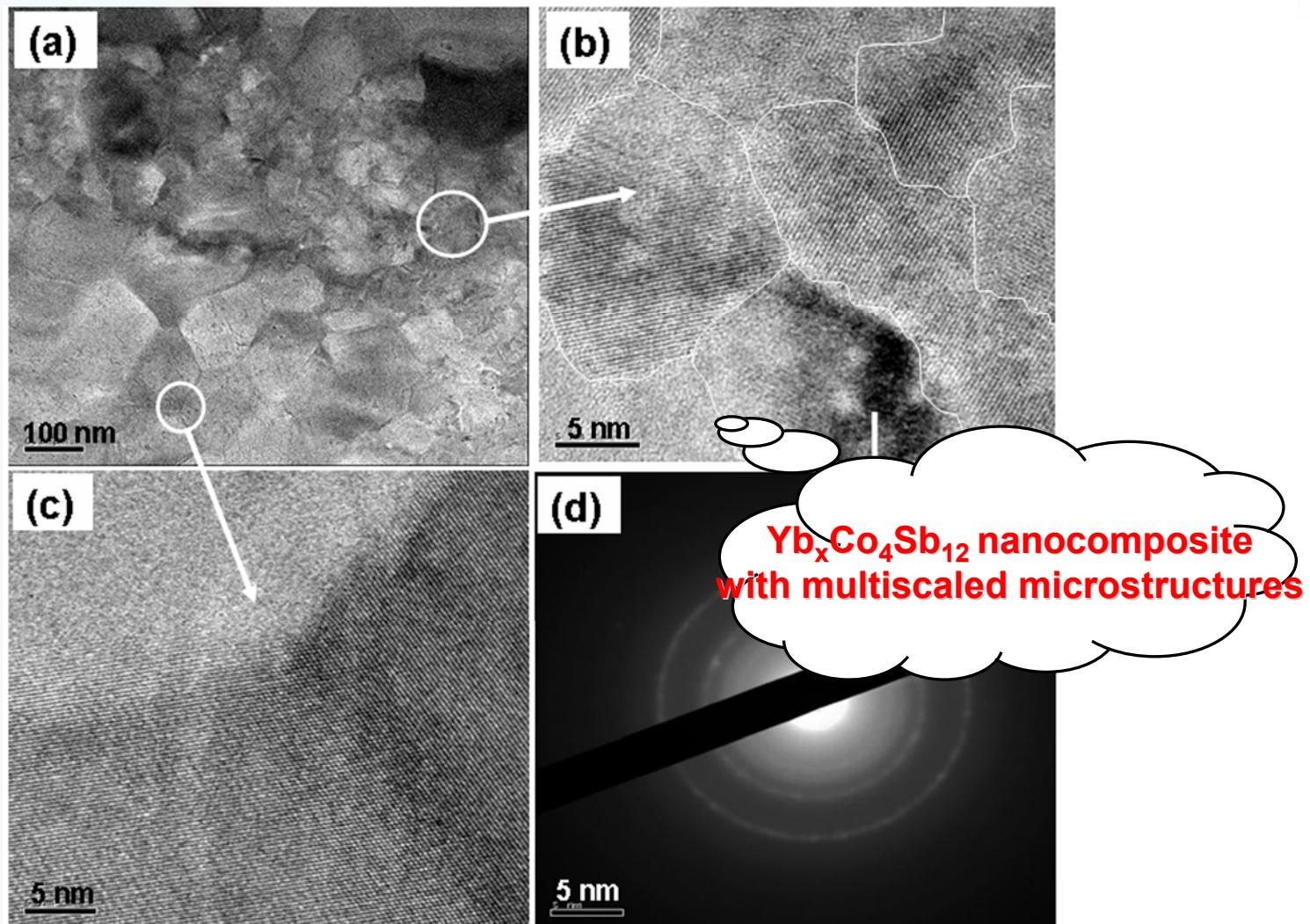
P-type Bi_2Te_3 with layer nanostructure



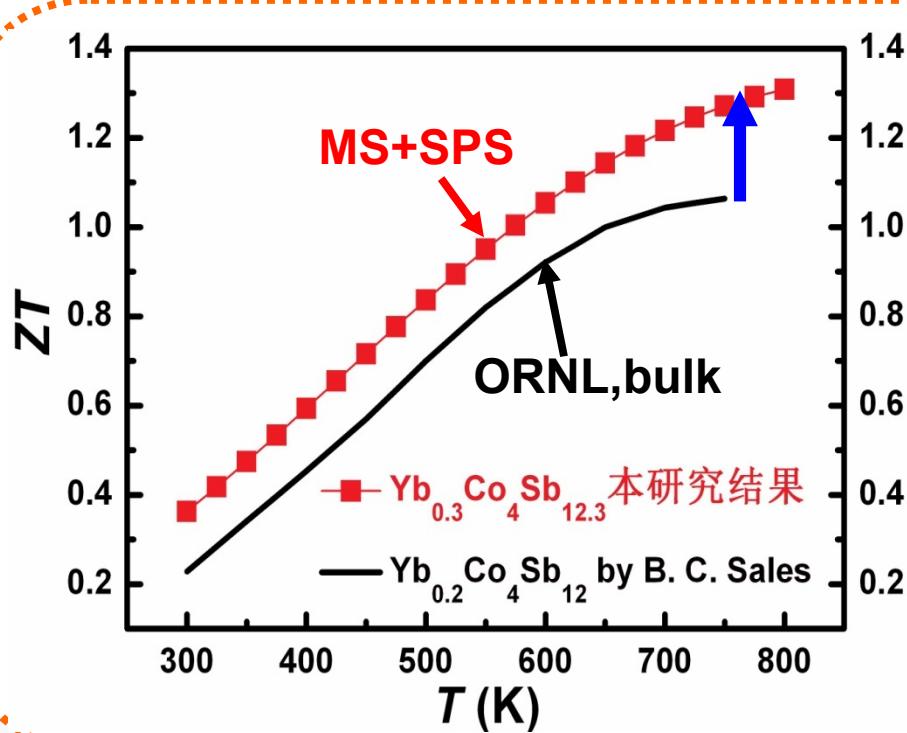
Zone melting sample(0.2-2 μm)



MS/SPS Results for $\text{Yb}_x\text{Co}_4\text{Sb}_{12}$



MS/SPS Results for $\text{Yb}_y\text{Co}_4\text{Sb}_{12}$



Tranditional (B. Sales, ORNL)

$$ZT_{\max} = 1.05 \text{ (750K)}$$

MS+SPS

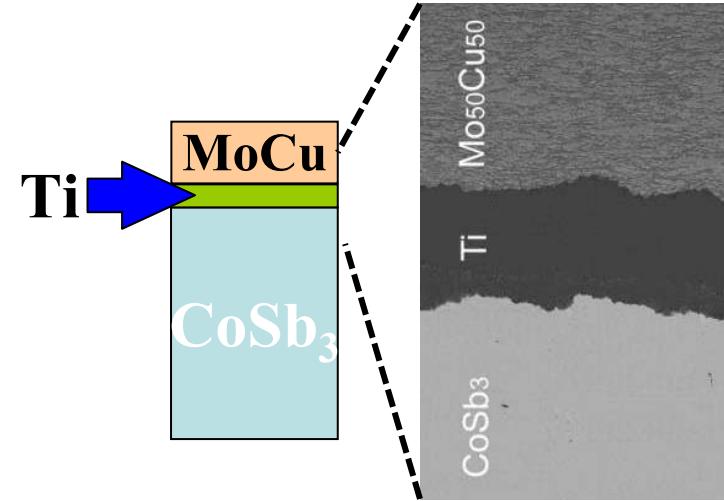
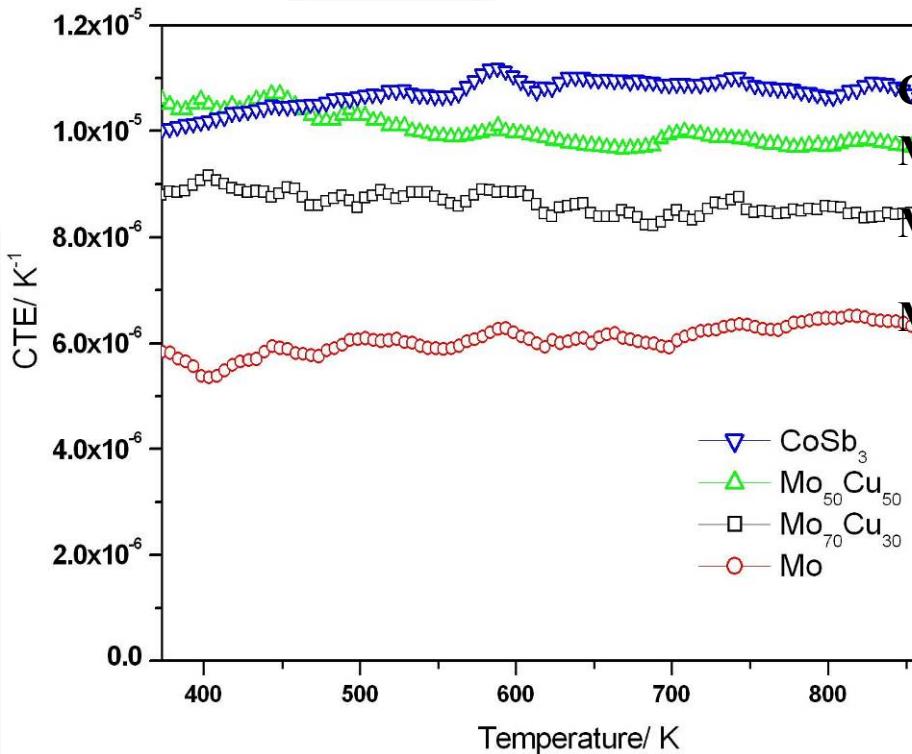
$$ZT_{\max} = 1.30 \text{ (800K)}$$

$$ZT \geq 1.0 \quad (T \geq 570K)$$

Induction Melting + MS + SPS

- 制备时间从传统方法的 9-10天 缩短至40小时以内
- Yb填充CoSb₃基ZT值由1.05提高到1.30, 提高了25%

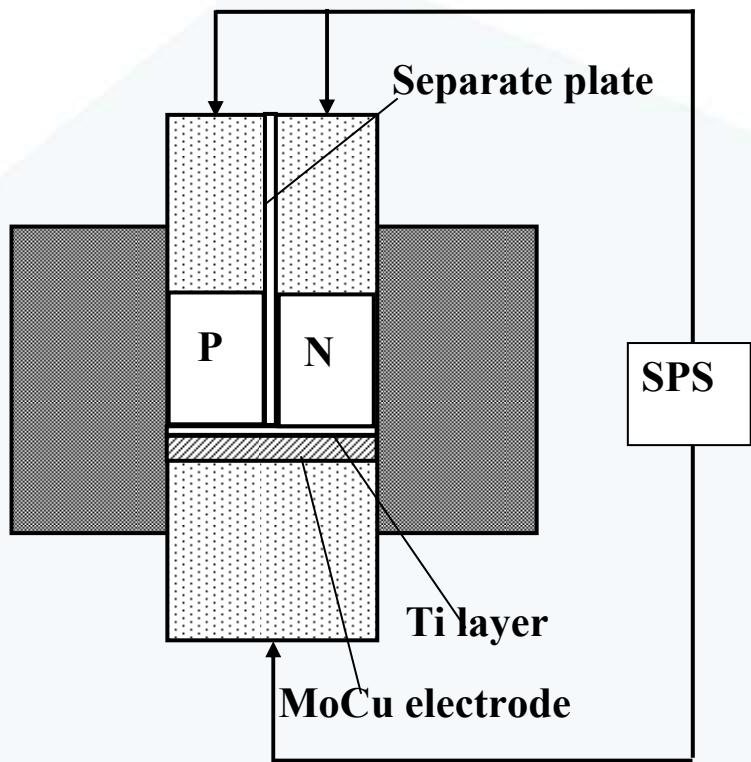
CTE comparison between CoSb_3 and Mo-Cu alloys



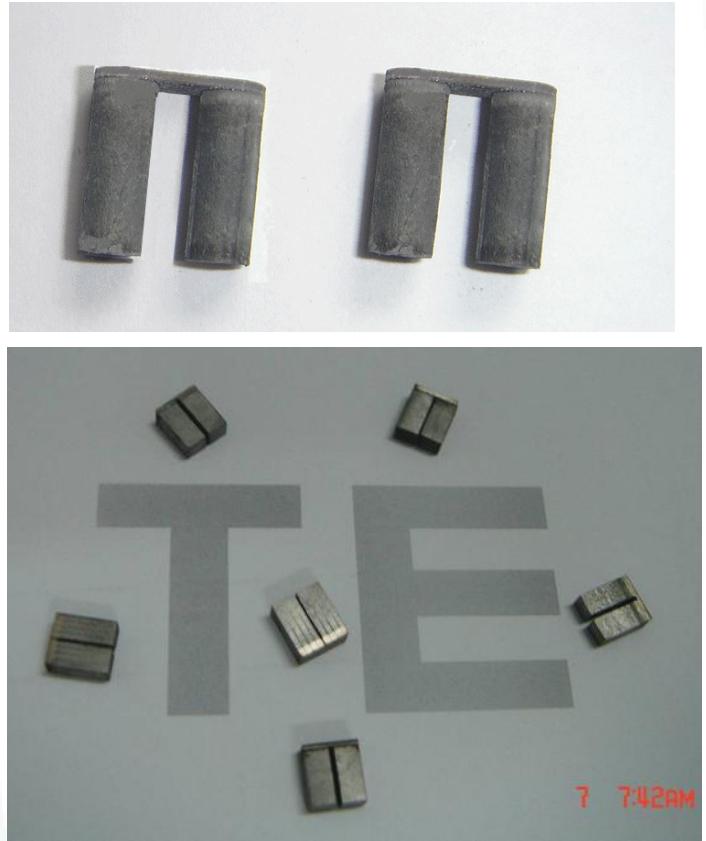
Co Sb_3 is joined with MoCu alloys with inserting Ti-interlayer.

CTE can be tuned by changing the Mo-Cu alloy composition. $\text{Mo}_{50}\text{Cu}_{50}$ shows close CTE values with skutterudite in the whole temperature range.

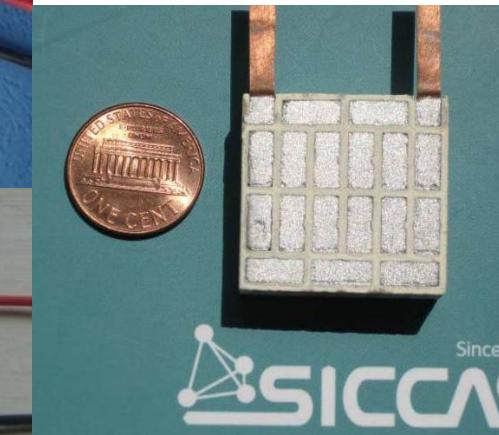
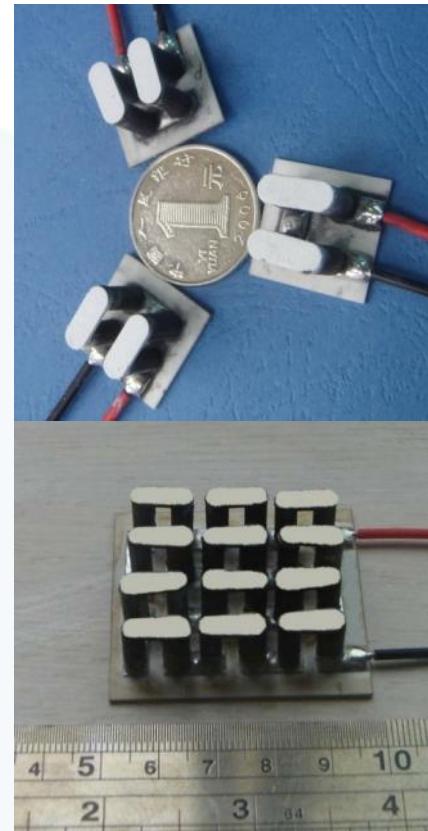
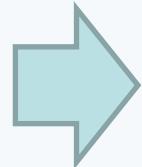
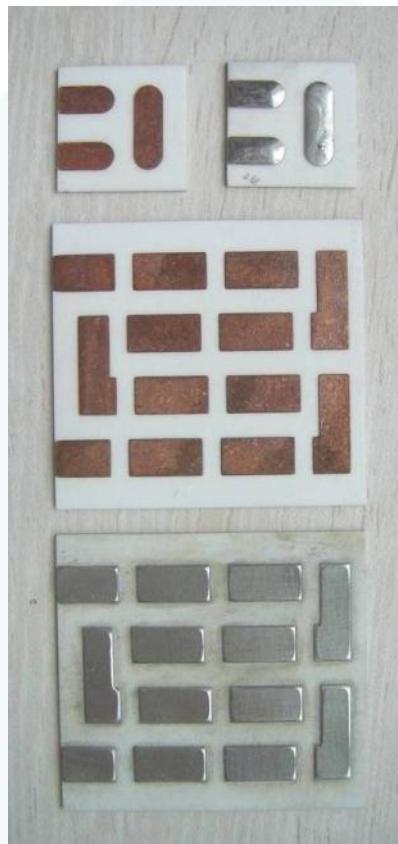
Fabrication of π -shaped CoSb₃ element : *SPS one step sintering*



Schematic of π -shaped element
fabrication by SPS one step sintering



Design and Fabrication of Filled CoSb₃ TE module

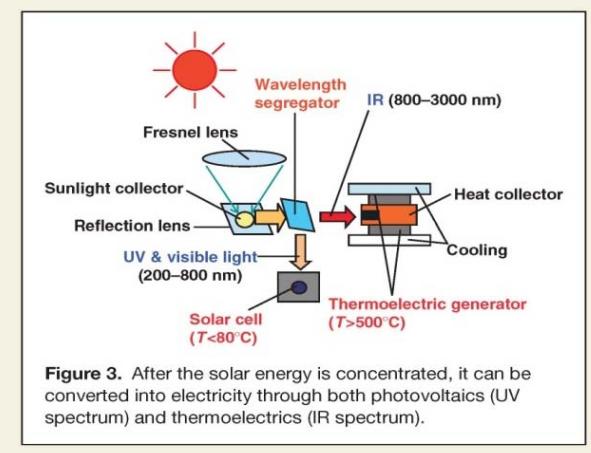
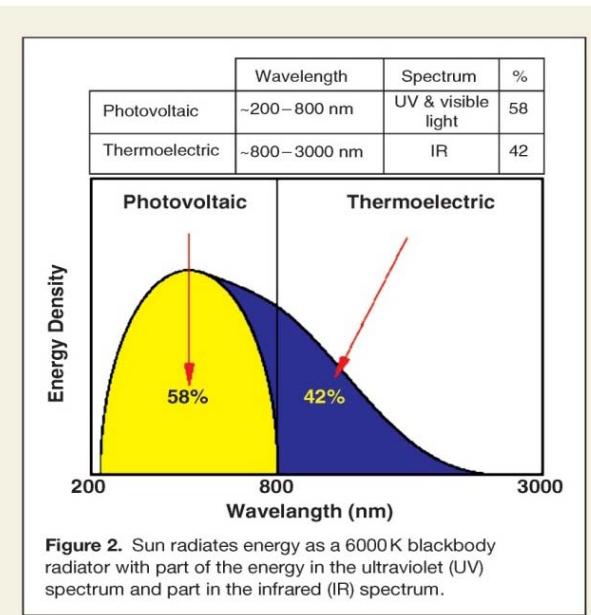


Metalized AlN substrate

Demonstrated module

SICCAS, cooperate with Corning

Hybrid PV-TE Power Generation System

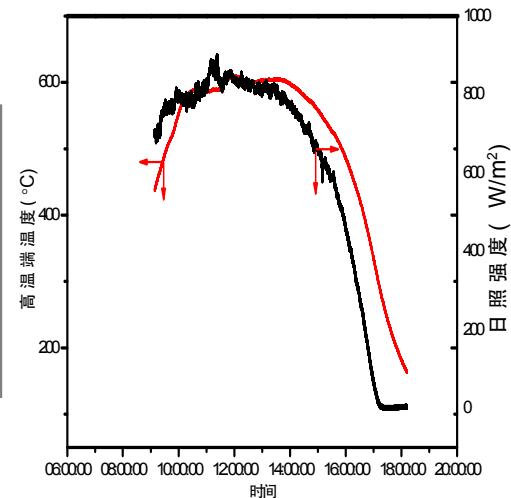


Prototype
(Running at Wuhai, Neimeng)



Bi₂Te₃-based TE Module

- T_high : 270°C
- 装备地点 : 乌海市
- Service : >1 year



SIC-SAIC TE power generation program

*Partially Funded by Shanghai Automotive Industry Science
and Technology Development Foundation*

- ◆ **Main team members:**

Shanghai Institute of Ceramics

SAIC Motor Technical Center

- ◆ **Period:**

Phase I: From 2009 to 2012

Phase II:

- ◆ **Project goal:**

*Demonstrate 500W generator installed into a 2.5L car with a
fuel economy improvement of 8-10%*

Summary

Research on thermoelectrics has been improved very much, and we Chinese scientists have caught up with world level quickly in recent years.

We are close to the end of the phase-I 973 program (national key basic research program).

Thank you for your attention!

Look forward to seeing you on
ICT2010, Shanghai, China





Shanghai Inst of Ceramics,
Chinese Academy of Sciences
Shanghai 200050

Basic Research on Inorganic Materials

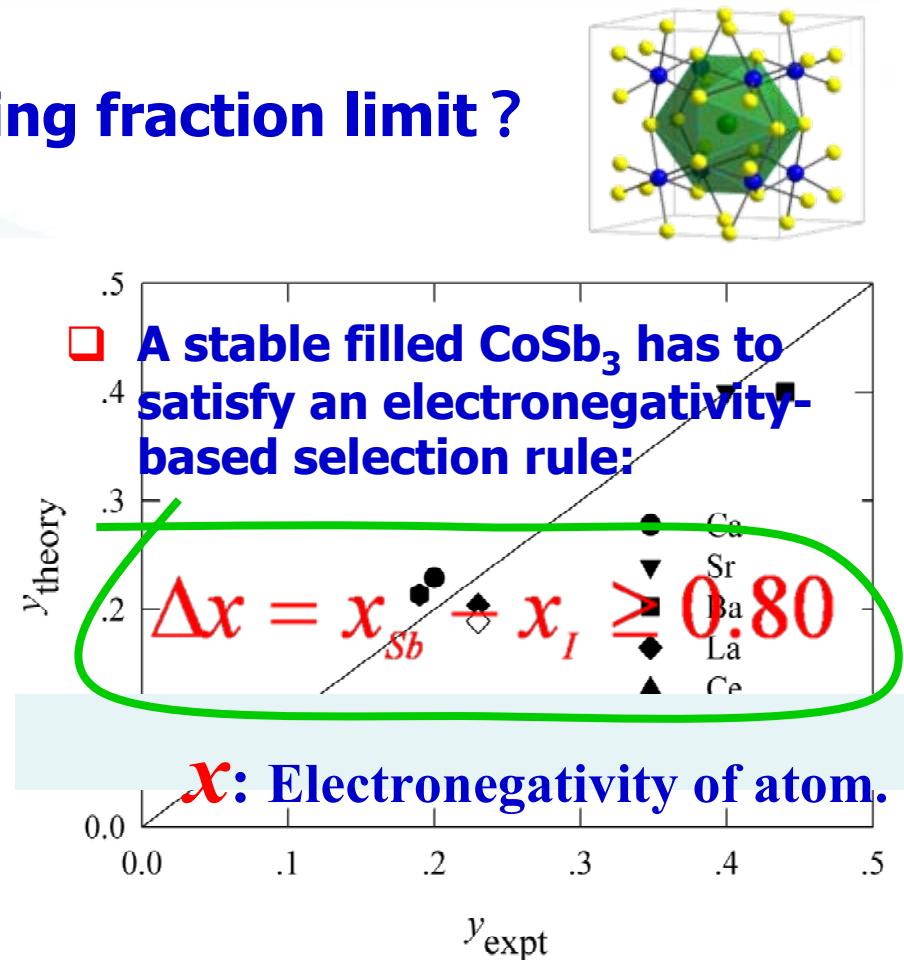
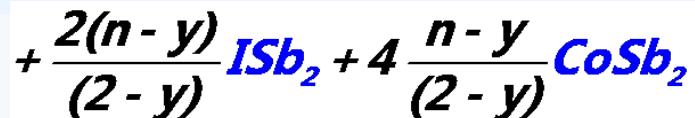
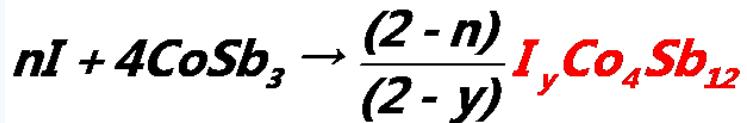
- Rank as one of the best research institutes in China;
 - Focus on non-metallic inorganic materials;
 - Expand much research areas in recent years.
-
- ① Advanced Structural Ceram.
 - ② Functional Ceramics and its Applications in IT
 - ③ Bio-Materials
 - ④ New Energy Materials
 - ⑤ Eco-materials
 - ⑥ Synthetic Crystals
 - ⑦ Industrial Ceramics improved by high tech & Ancient Ceramics
 - ⑧ Space Materials Science
- 
 - Ceramics
 - Glass
 - Crystals
 - Inorganic coatings
 - Composites

FFL and Electronegativity-based Selection Rule

Point : What controls the filling fraction limit ?

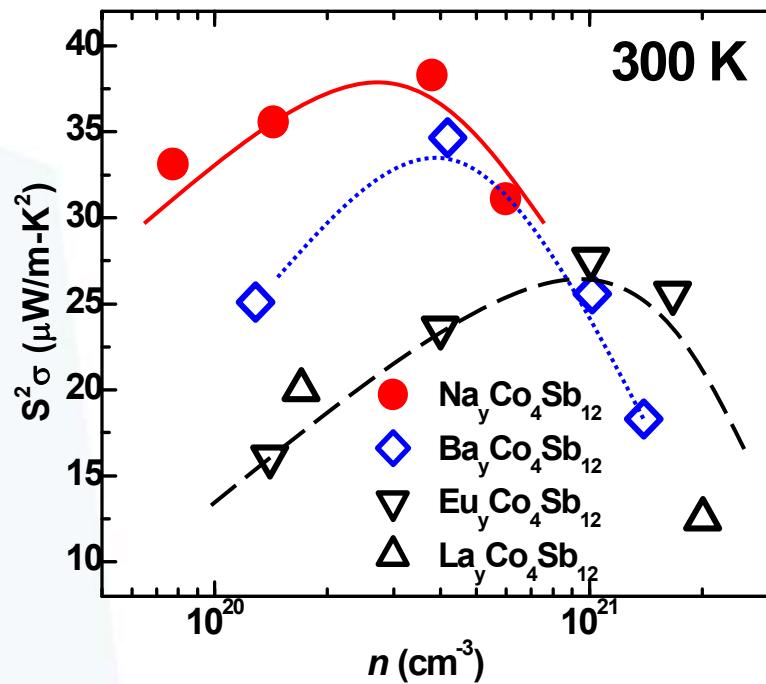
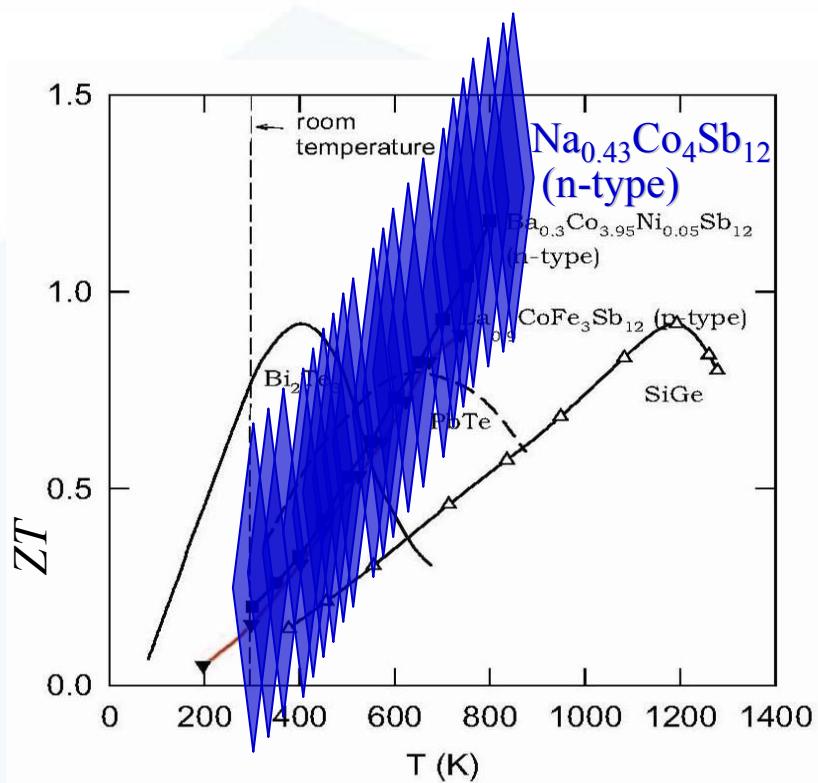
	Ca	Ba	La	Ce	Yb
Exptl FFL	0.20	0.44	0.23	0.10	0.19

- Competition between the filled phase and possible secondary phases determines the FFL.



Shi, Zhang*et.al, Phys. Rev. Lett. (2005).
FFL: Theoretical predictions
Shi, Zhang*et.al, Phys. Rev. B. (2007).
agree well with experimental data.
Shi, Zhang*et al, Acta Mater. (2008).

Alkali-metal-filled skutterudites: $\text{Na}_y\text{Co}_4\text{Sb}_{12}$ and $\text{K}_y\text{Co}_4\text{Sb}_{12}$

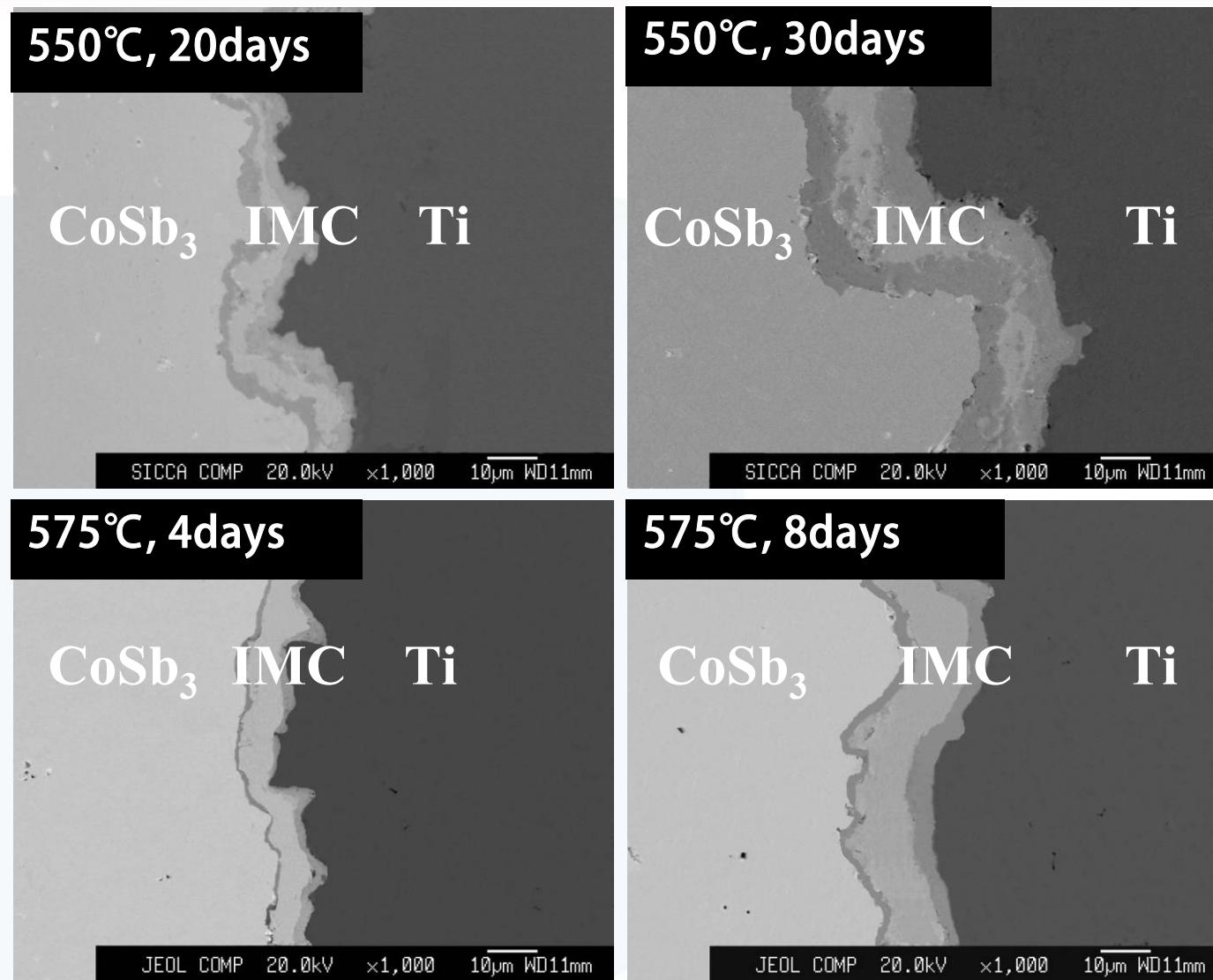


- ◆ Na and K has a maximum filling fraction (up to 65%) reported.
- ◆ $\text{Na}_y\text{Co}_4\text{Sb}_{12}$ shows the highest power factor and ZTs among all single filled SKTs.

AM-filled CoSb_3 : 2007 Goldsmid Award (Dr. Pei YZ);

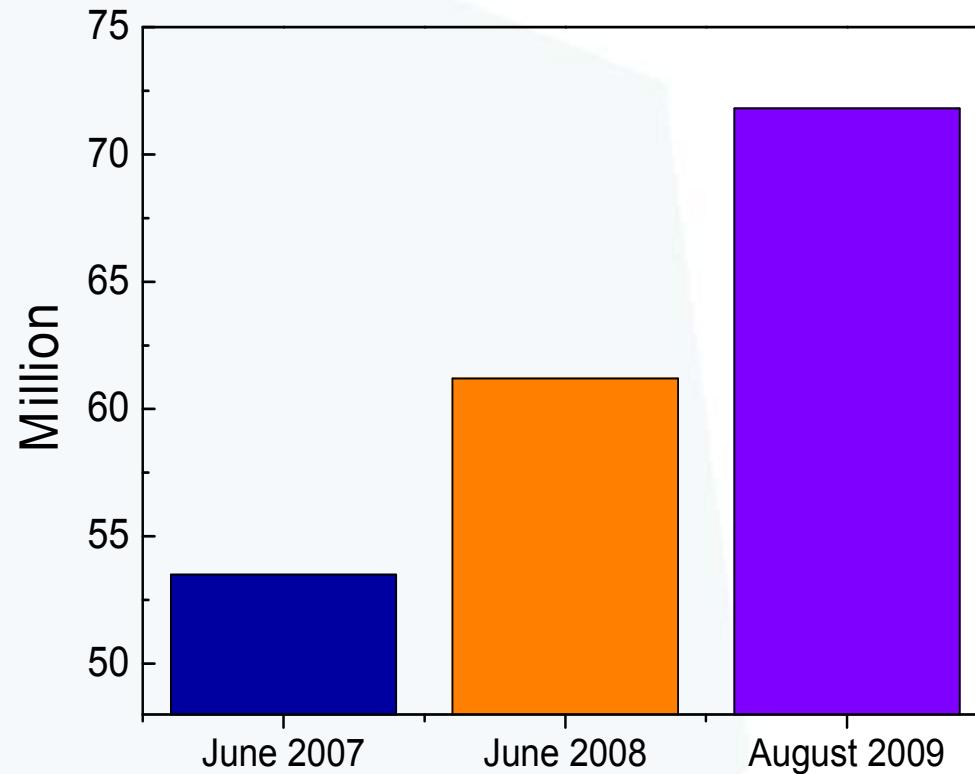
Pei, Chen, Zhang, APL (2009,2007); Mei, Zhang, Chen, PRB (2007).

Thermal durability: interfacial change after thermal aging



TEM of CoSb₃/Ti/Mo-Cu joint after thermal aging at different conditions

Vehicle in China



主要技术经济指标

建成5~10kW热电—光电复合发电分布式电站示范系统

- 复合发电系统的发电效率： $\geq 20\%$
- 温差发电（热电发电）的发电贡献率： $\geq 5\%$
- 复合发电系统建造成本：
 $< 4500 \text{ \$/kW}$ (100倍聚光比)
 $< 3300 \text{ \$/kW}$ (400倍聚光比)