



What to expect from exploratory synthesis: intermetallics, chalcogenides and thermoelectrics

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Mercouri G. Kanatzidis
Department of Chemistry, Northwestern University
and Argonne National Laboratory

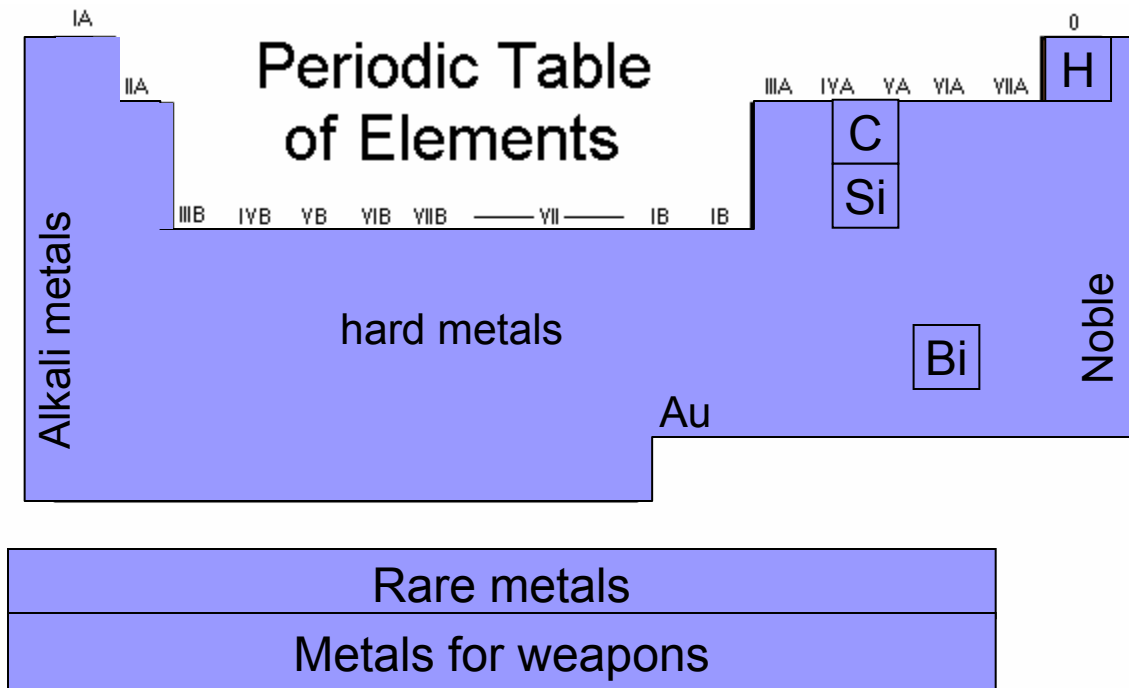




Outline

- Why exploratory synthesis
- Chalcogenides
 - Thermoelectrics
 - Unusual structures and homologies
 - Ion exchangers
- Intermetallics
- Conclusions

The periodic table according to some...





Why Do Exploratory Synthesis?

- **New Materials**

- Advance the cutting edge of what is possible
- New compositions, new structures
- Unusual properties
- New synthesis methods (synthetic toolbox...)
- Learn more about structure/property relationships
- Discover the unpredictable

- The elucidation of a structure can help us think logically as to what experimentation can be done with it.

- Predicting the outcome of a solid state reaction is difficult, if not impossible, which makes exploratory synthesis an invaluable tool.

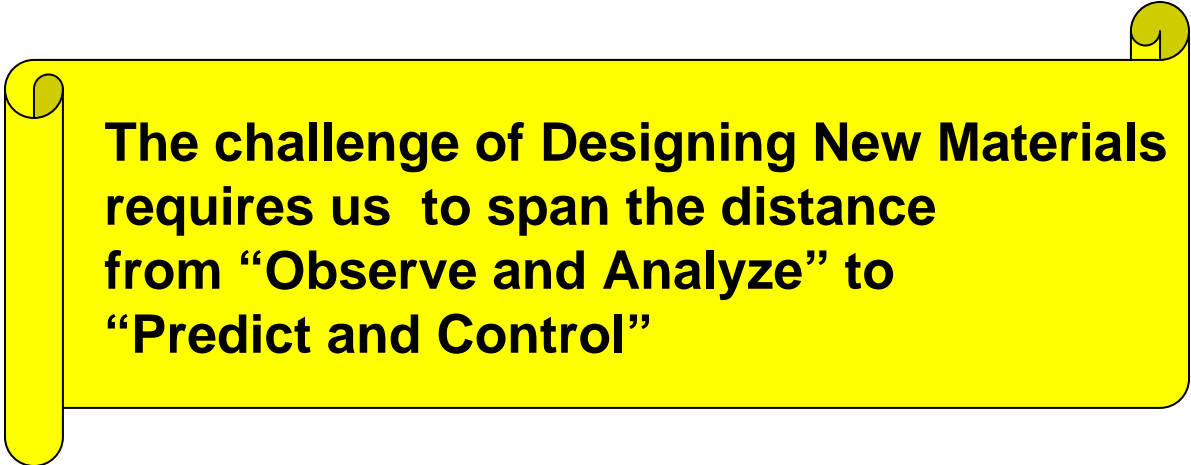
- **Expand the shelf...**

- **Ultimate goal: design of materials**



First: define “Design”

- Design Structure/composition
 - Design Function
 - Design Synthesis
- “Design” is a word rich with ambiguity and highly dependent on context



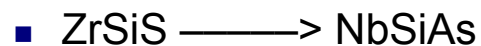
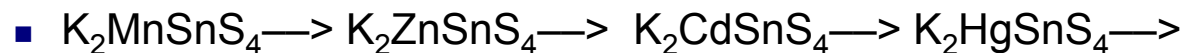
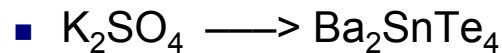
The challenge of Designing New Materials requires us to span the distance from “Observe and Analyze” to “Predict and Control”

Many Levels of Design

- Highest Level: Target a property you want, then synthesize a material which has the property
- High Level: Envision a structure, then synthesize it
- Moderate: Adjust (or optimize) a property systematically by making small changes in a known material

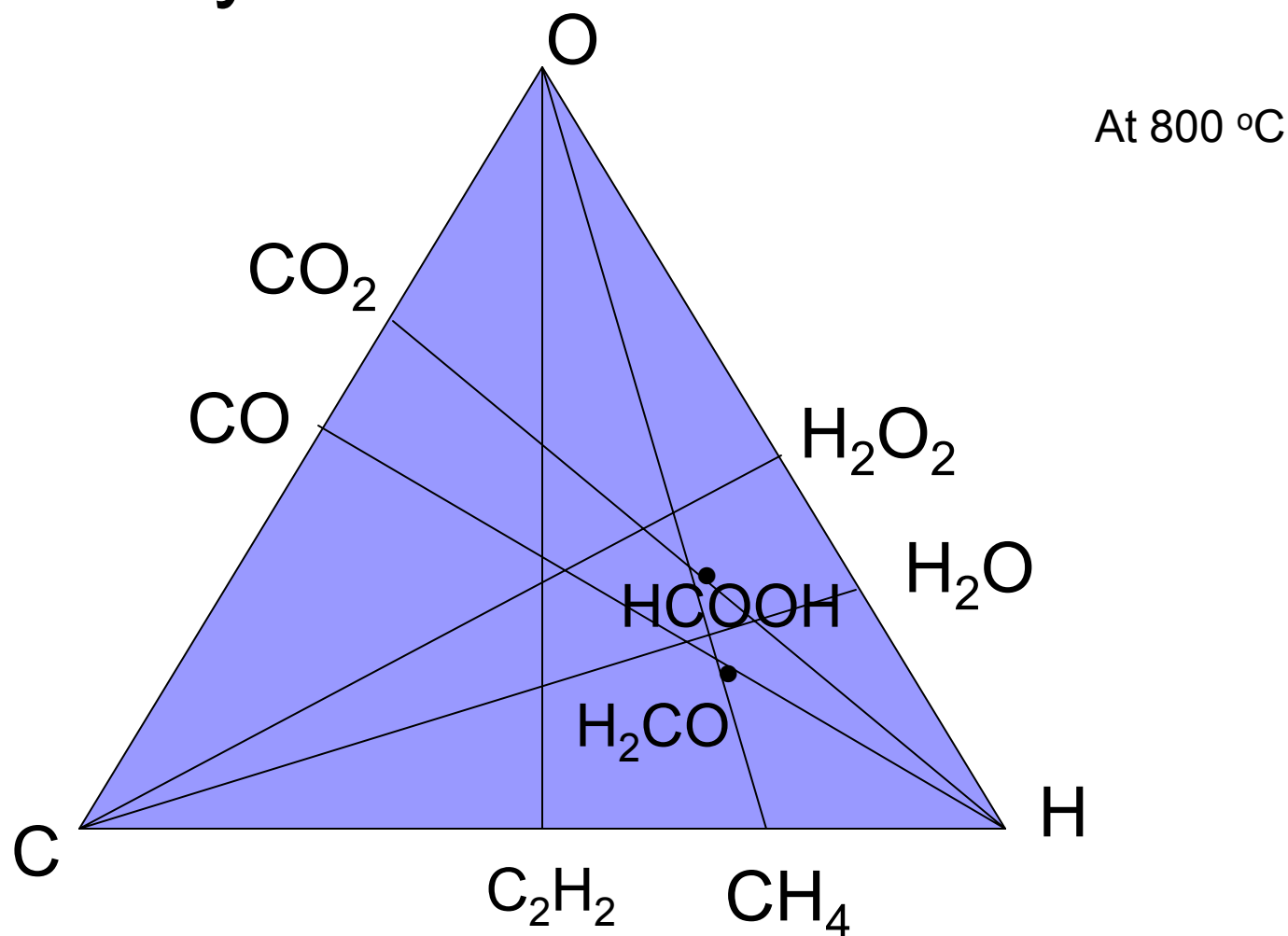
→ Band gap engineering is an example, $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$, $\text{Al}_{1-x}\text{Ga}_x\text{As}$. Very successful

→ Achieving isomorphous substitutions (making analogs)



Irrational synthesis...

A solid state chemist's view of organic chemistry





An organic chemist's view of solid state chemistry: **Turn down the heat...use solvents**

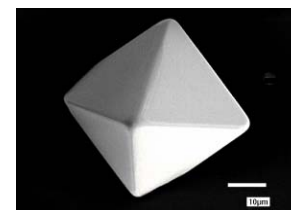
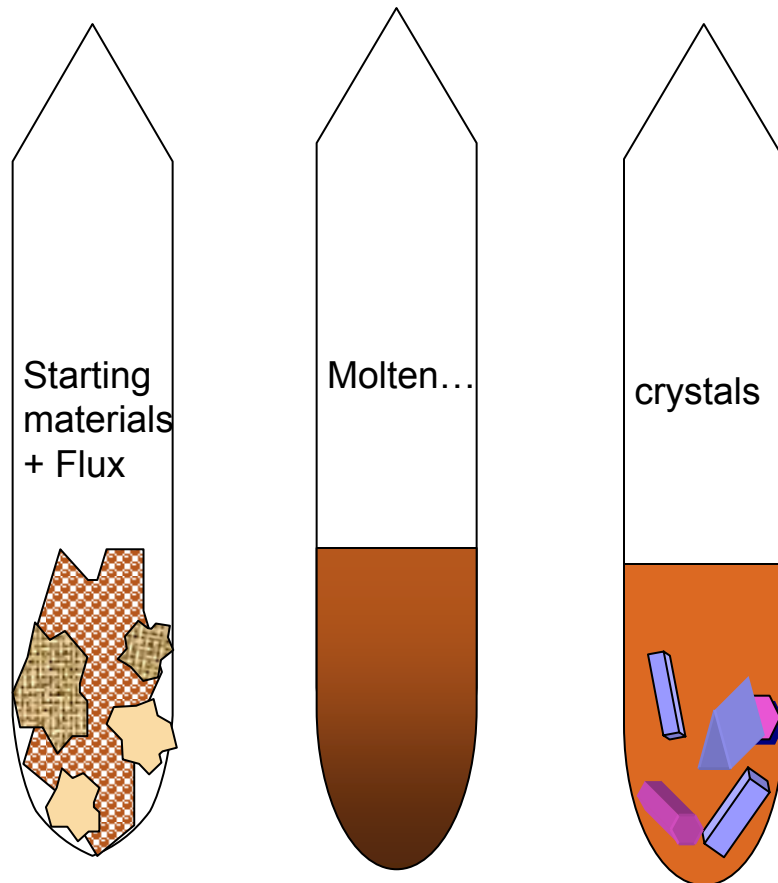
- Lower temperatures stabilize greater numbers of compounds
- Need solvents: The molten salt method parallels solution based synthesis
- Different fluxes can be devised for different materials. These fluxes can be reactive or non reactive.

Polychalcogenide Flux

- Molten chalcogenide salts ($A_2Q + Q_x \rightarrow A_2Q_x$) as **Reagents and Solvents** to synthesize new compounds

ADVANTAGES

- Low temperatures ($250\text{ }^\circ\text{C} < T < 750\text{ }^\circ\text{C}$)
- Can produce compounds not accessible by other methods
 - Kinetic products / Thermodynamic products
- Conducive to large crystal growth
- Ability to produce in pure form more complicated compounds such as ternary: A/Bi/Q or quaternary: A/M/Bi/Q)

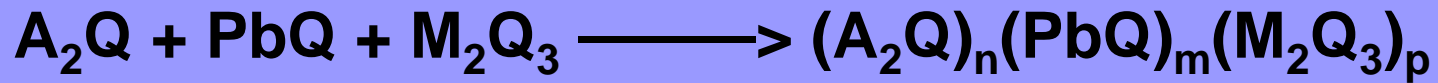


M. G. Kanatzidis and A. Sutorik *Progress in Inorganic Chemistry* 1995, 43, 151-265.

Reactivity of molten K_2S_x

- When $T > 600$ °C: CuS , Cu_2S , $KCuS$
- In K_2S_5 and $350 < T < 600$ °C : KCu_4S_3 , KCu_7S_4
- In K_2S_5 and $180 < T < 350$ °C : α - $KCuS_4$, β - $KCuS_4$, $KCuS_6$, KCu_4S_4 , KCu_8S_6

Investigating the A/Bi/Q system



Map generates target compounds

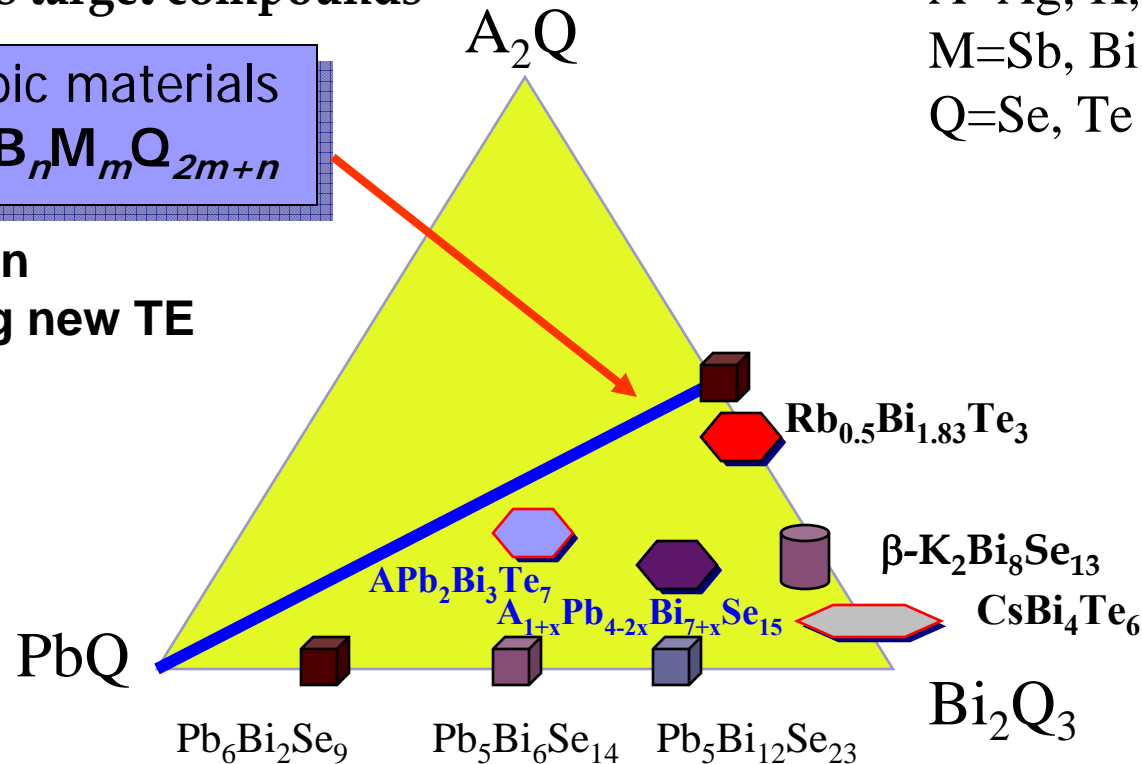
Cubic materials
 $A_m B_n M_m Q_{2m+n}$

A=Ag, K, Rb, Cs

M=Sb, Bi

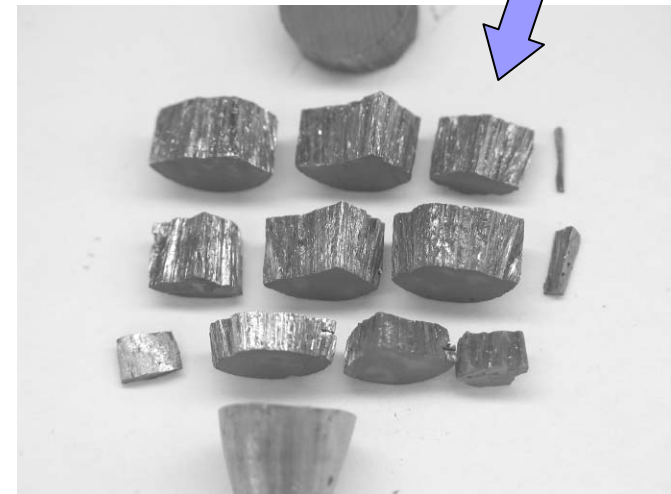
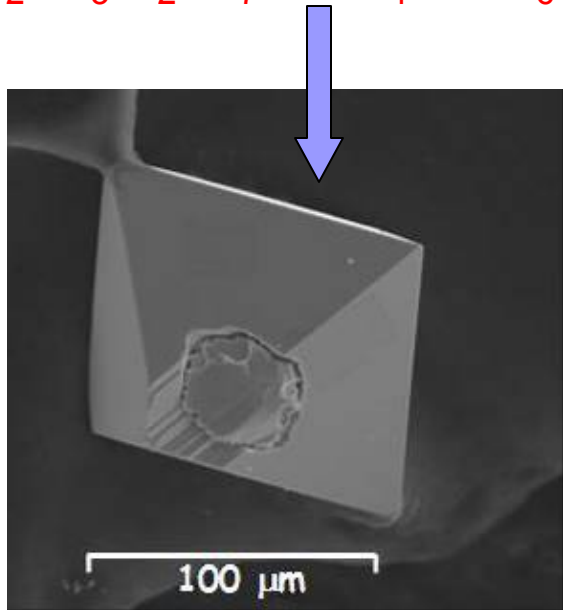
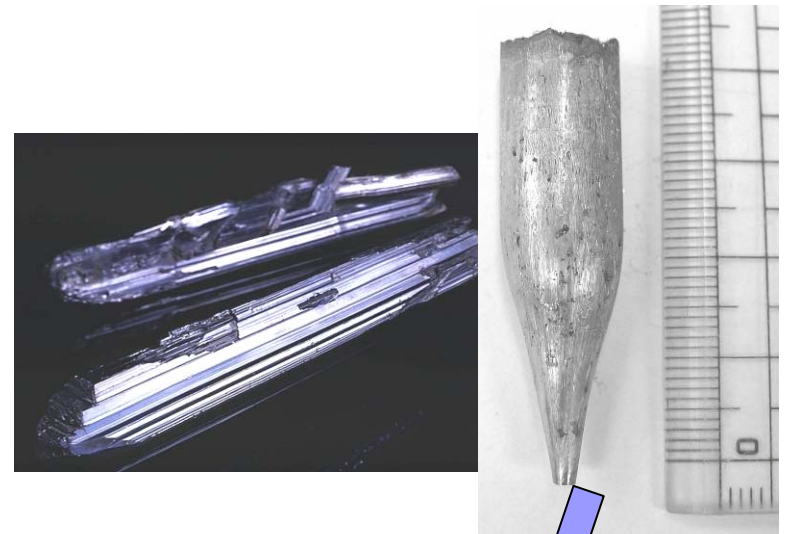
Q=Se, Te

Phases shown
 are promising new TE
 materials

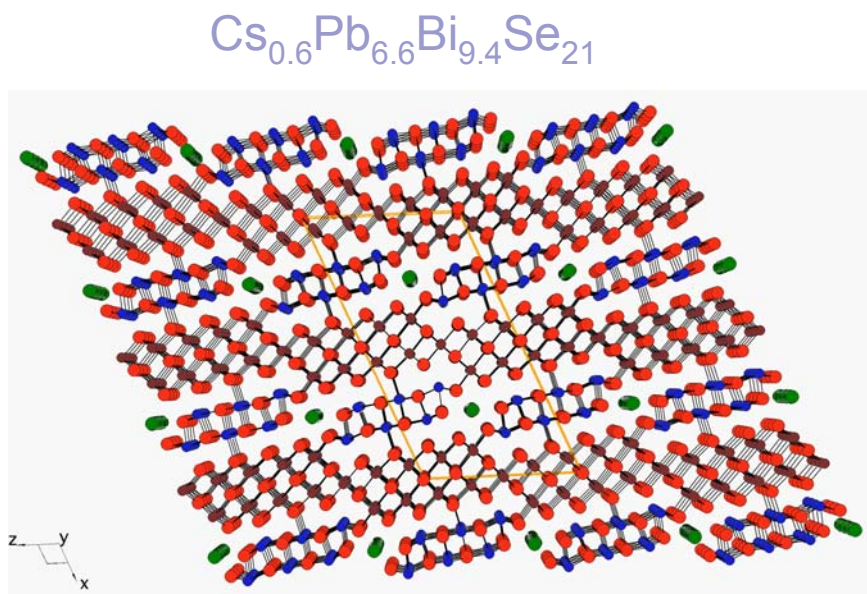
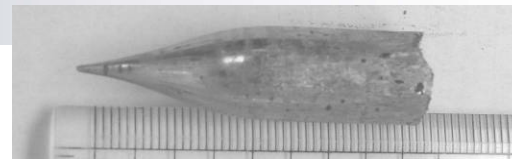


Compounds discovered

- $\text{K}_2\text{Bi}_8\text{Se}_{13}$, $\text{KPbBi}_9\text{Se}_{13}$, $\text{KPb}_4\text{Sb}_7\text{Se}_{15}$
- $\text{Cs}_{1-x}\text{Pb}_{5-x}\text{Bi}_{10+x}\text{Se}_{21}$
- $\text{CsPbBi}_3\text{Te}_6$, $\text{CsPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPbBi}_3\text{Te}_6$,
 $\text{RbPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPb}_3\text{Bi}_3\text{Te}_8$,
- KPbBiSe_3 , $\text{K}_2\text{PbBi}_2\text{Se}_5$
- $\text{K}_2\text{Pb}_3\text{Bi}_2\text{Te}_7$, $\text{KPb}_4\text{SbTe}_6$



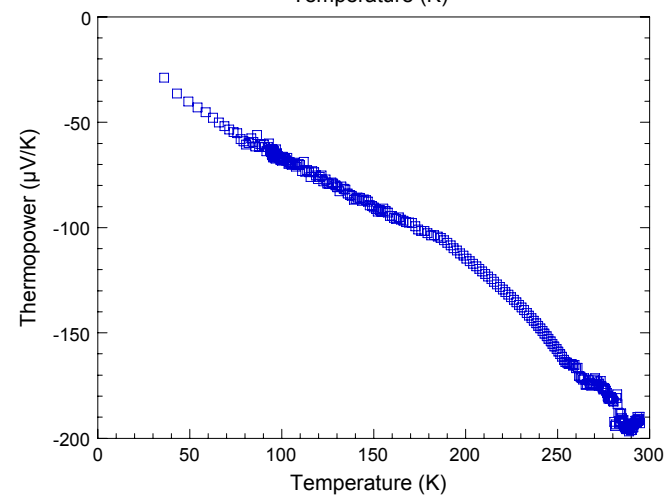
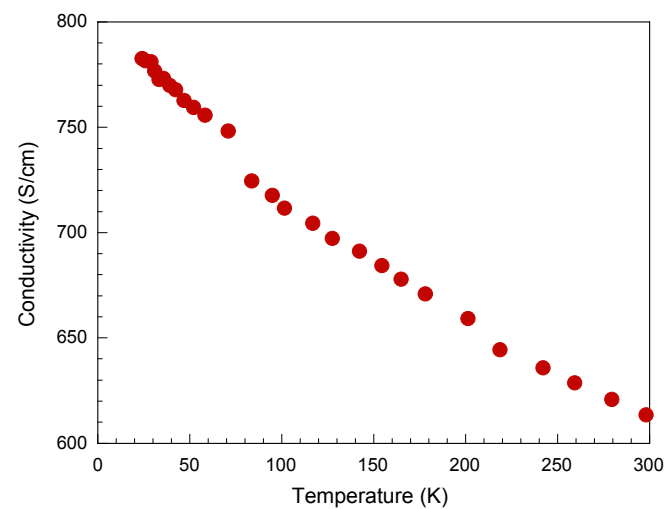
$CsPb_7Bi_9Se_{21}$



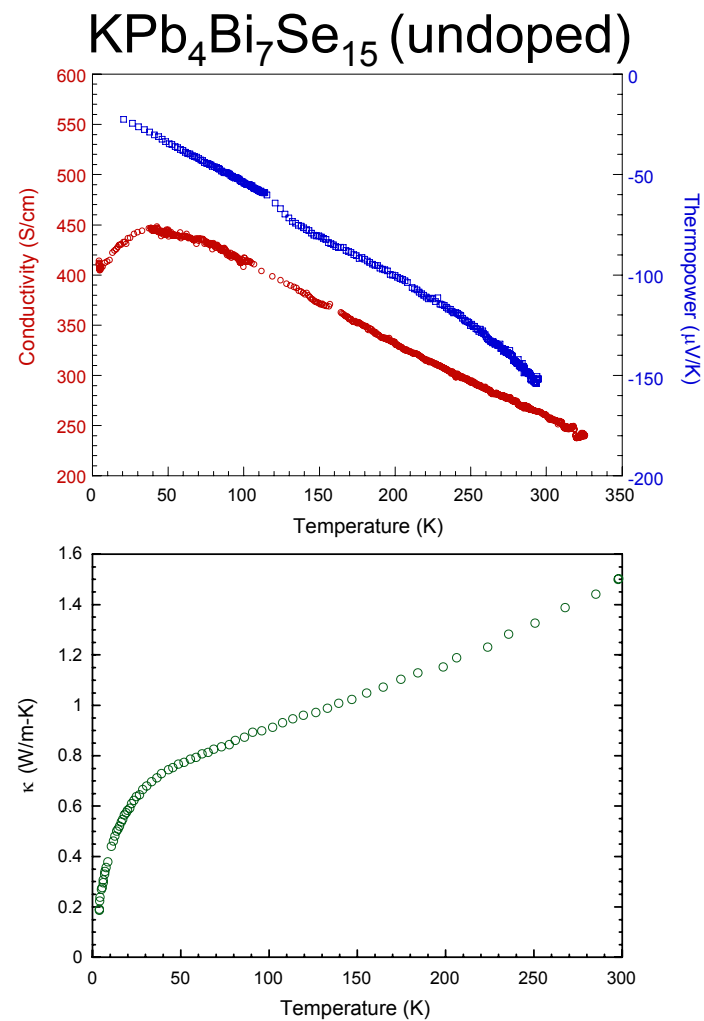
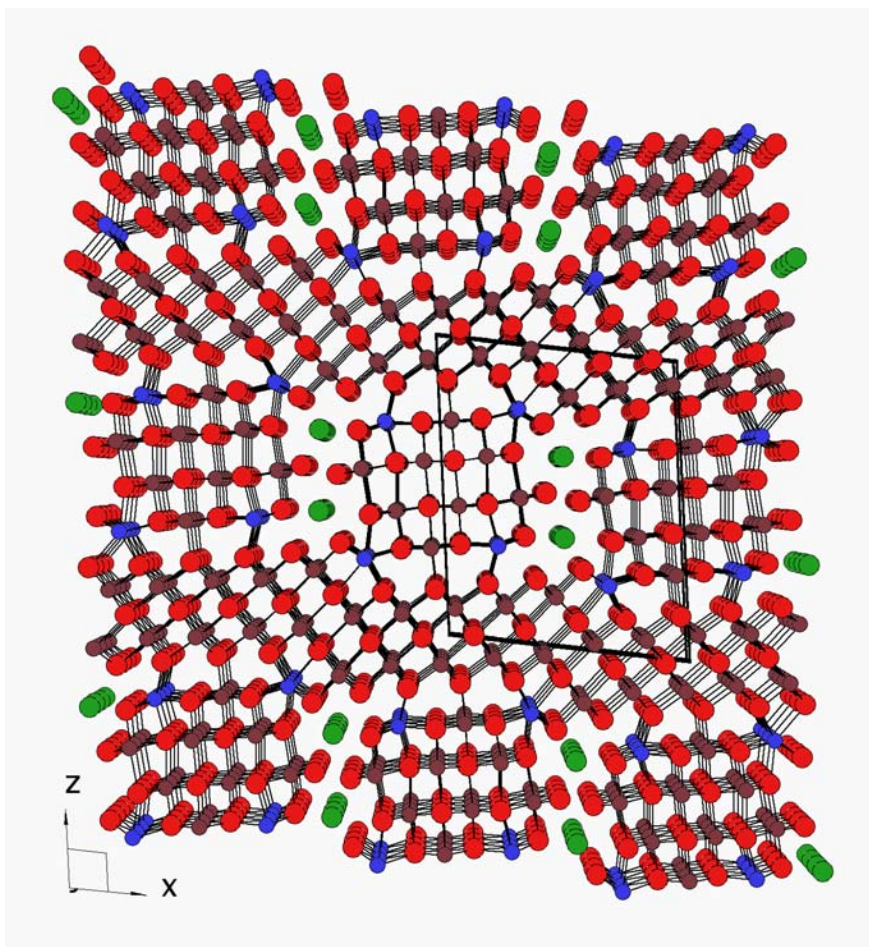
$$ZT_{300\text{K}} = 0.6$$

Sample undoped.
Anticipated high ZT by doping.

$$ZT = (\sigma S^2 / \kappa) T$$



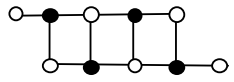
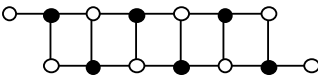
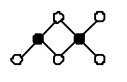
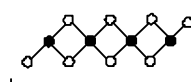
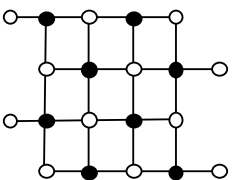
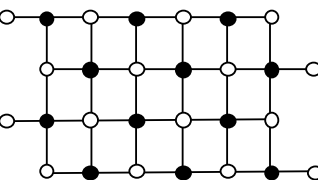
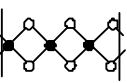

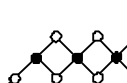
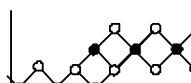
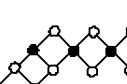
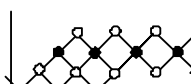
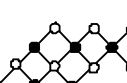
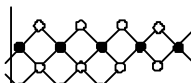
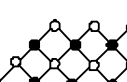


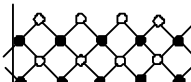

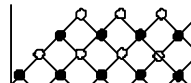
$KM_4Bi_7Se_{15}$ ($M = Pb, Sn$)



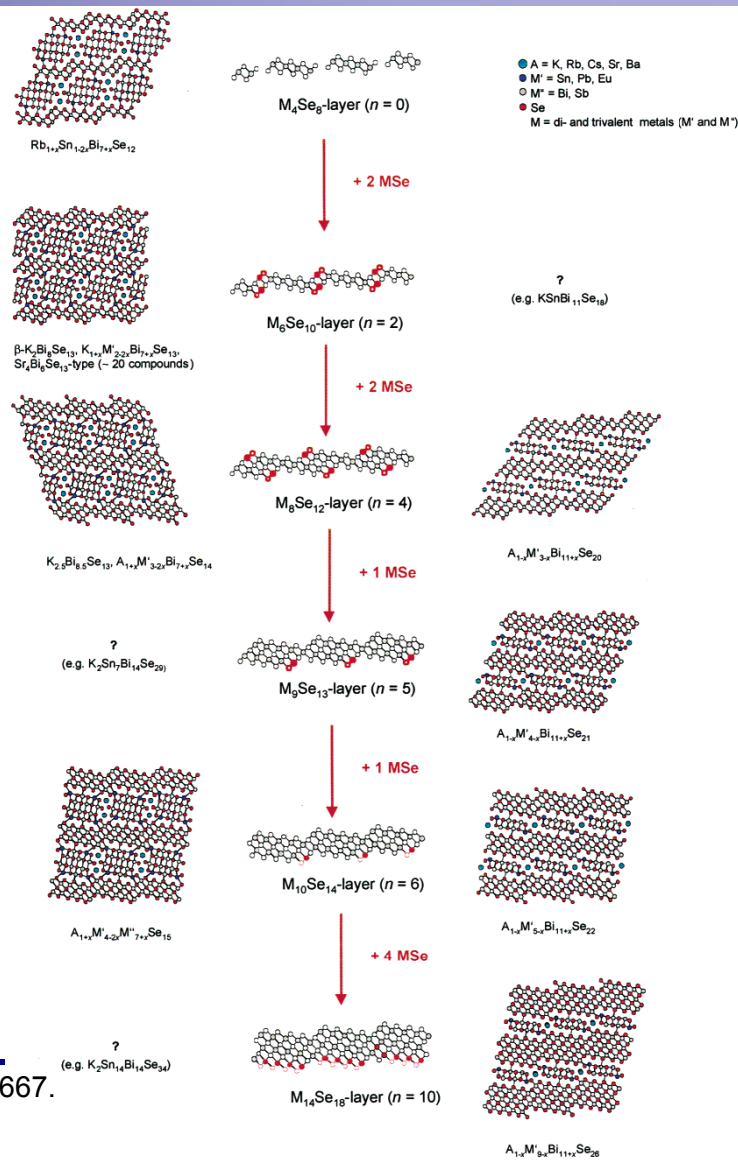
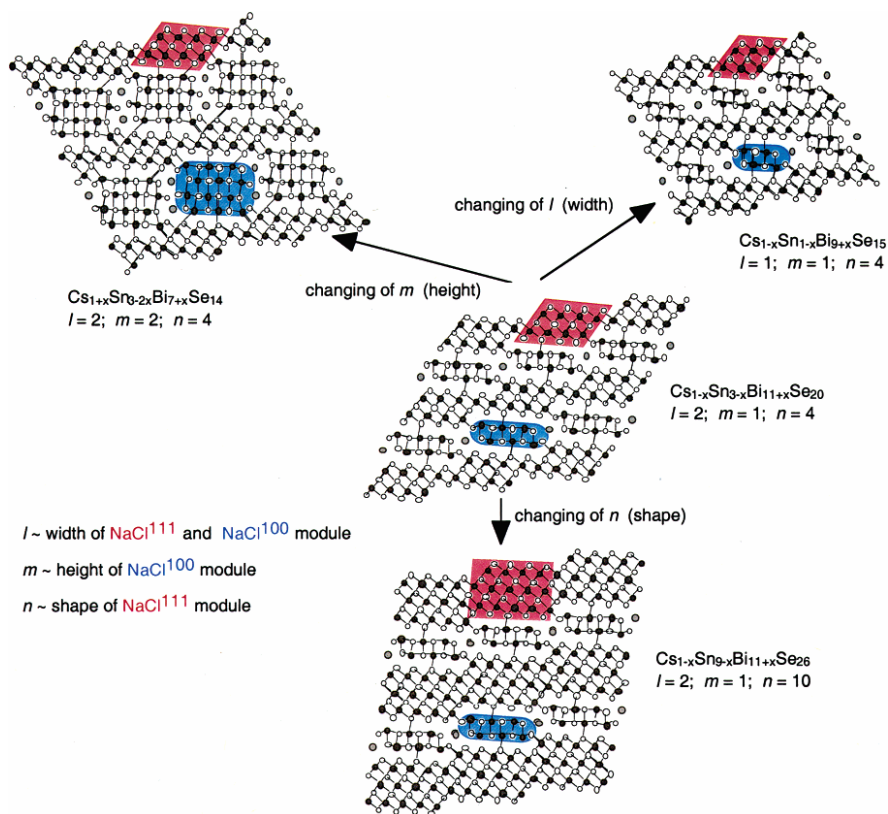
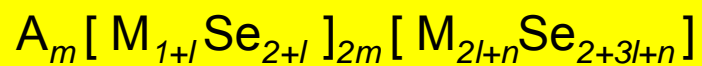
K.-S. Choi, D.-Y. Chung, A. Mrotzek, P. Brazis,
C. R. Kannewurf, C. Uher, W. Chen, T. Hogan, M.G. Kanatzidis *Chem. Mater.* **2001**, *13*, 756.



Chemistry : $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$

$m \setminus$	1, $[M_2Se_3]_{2m}$	2, $[M_3Se_4]_{2m}$	$n \setminus$	1, $M_{2+n}Se_{5+n}$	2, $M_{4+n}Se_{8+n}$
1	 M_4Se_6	 M_6Se_8	0	 M_2Se_5	 M_4Se_8
2	 M_8Se_{12}	 $M_{12}Se_{16}$	1	 M_3Se_6	 M_5Se_9
			2	 M_4Se_7	 M_6Se_{10}
			3	 M_5Se_8	 M_7Se_{11}
			4	 M_6Se_9	 M_8Se_{12}
			5	 M_7Se_{10}	 M_9Se_{13}
			6	 M_8Se_{11}	 $M_{10}Se_{14}$
				 $M_{11}Se_{14}$ (n=9)	 $M_{14}Se_{18}$ (n=10)

Design of Structure using phase homologies



A. Mrotzek, D.-Y. Chung, T. Hogan, M.G. Kanatzidis *J. Mater. Chem.* **2000**, 10, 1667.

A. Mrotzek, M.G. Kanatzidis, *J. Solid State Chem.* **2002**, 167, 299.

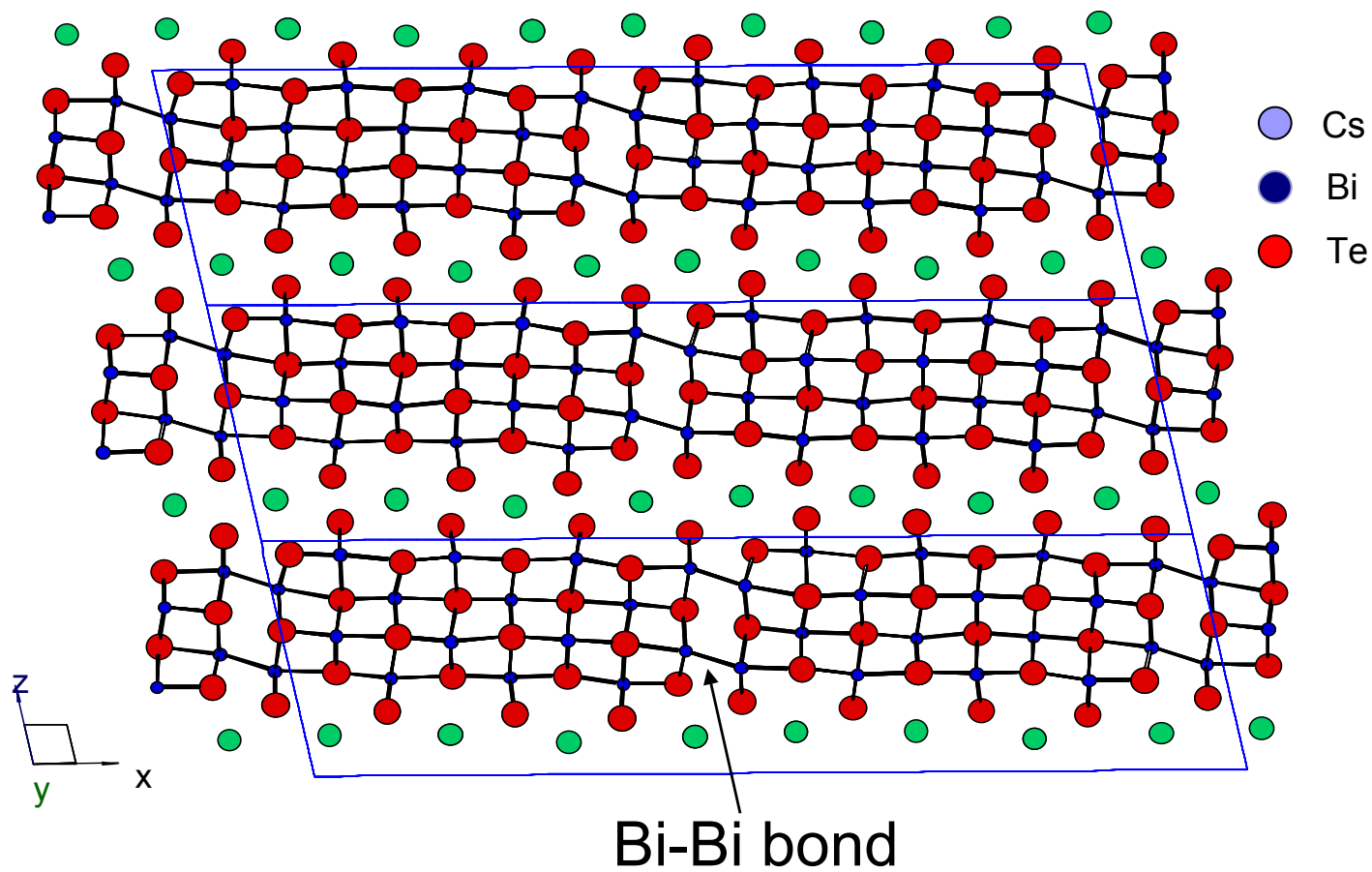
A. Mrotzek, M.G. Kanatzidis, *Acc. Chem. Res.* **2003**, 36, 111.



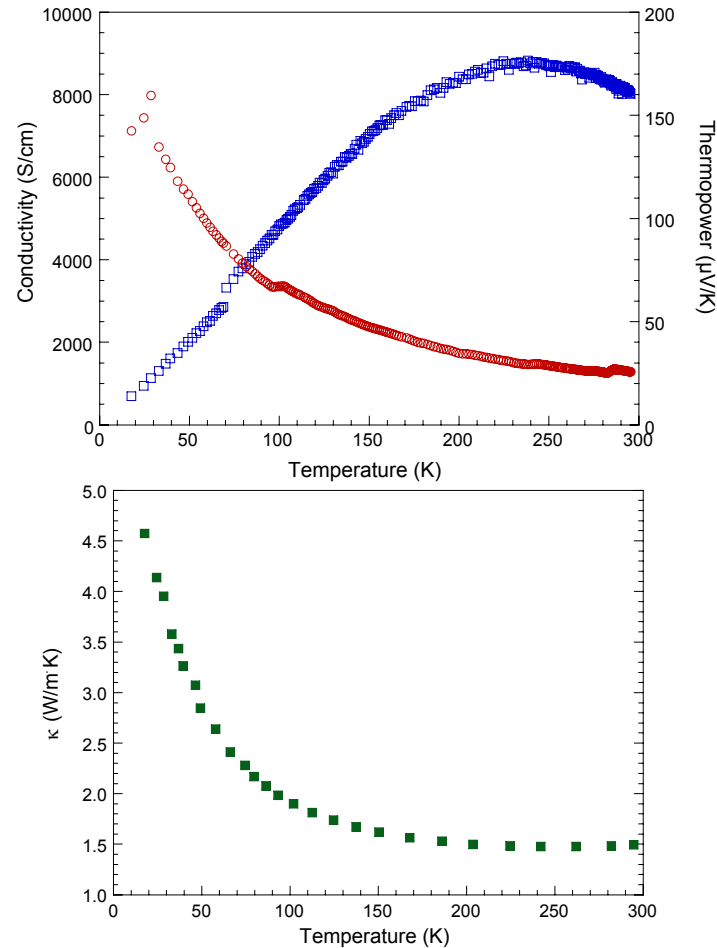
Selection criteria for TE candidate materials

- Narrow band-gap semiconductors
- Heavy elements
 - High mobility, low thermal conductivity
- Large unit cell, complex structure
 - low thermal conductivity
- Highly anisotropic or highly symmetric...
- Complex compositions
 - low thermal conductivity, electronic structure

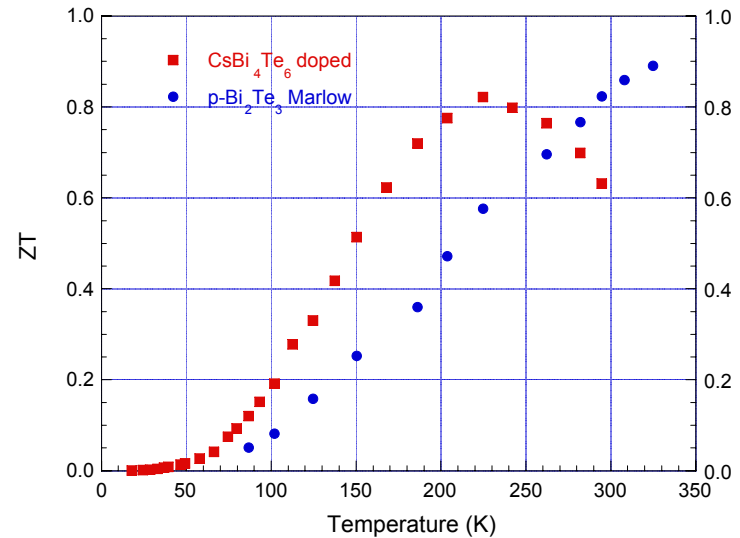
$CsBi_4Te_6$



0.05 % SbI_3 -doped $CsBi_4Te_6$

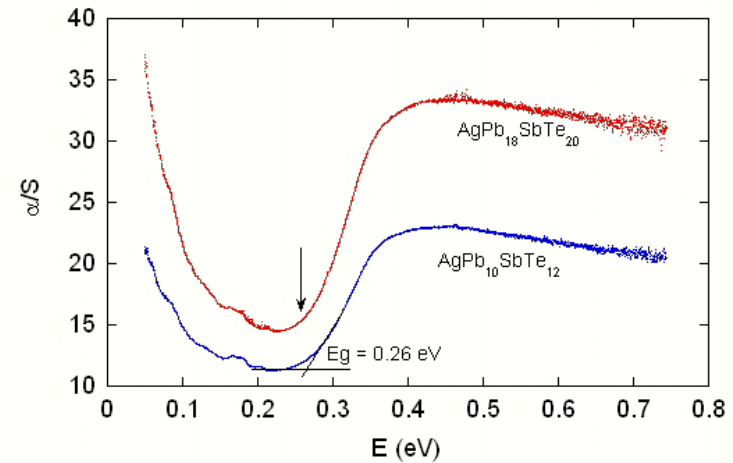
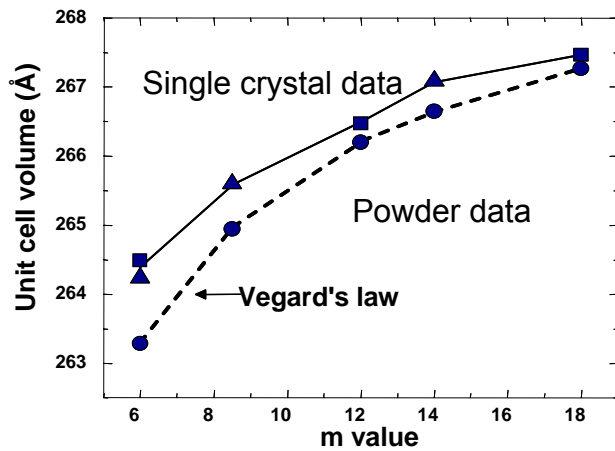
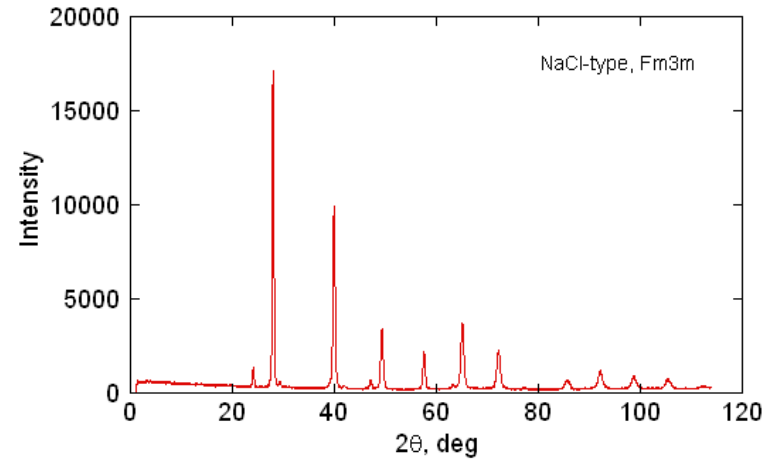
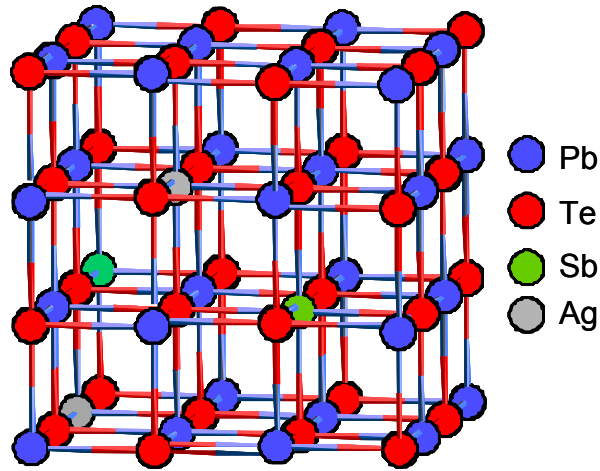


At 225 K :
 σ 1733 S/cm,
 S 177 $\mu V/K$,
 κ 1.48 W/m·K



D.-Y. Chung, T. Hogan, M. Rocci-Lane, P. Brazis, J. Ireland, C. Kannewurf, M. Bastea, C. Uher, and M. Kanatzidis, *Science*, **2000**, 287, 1024

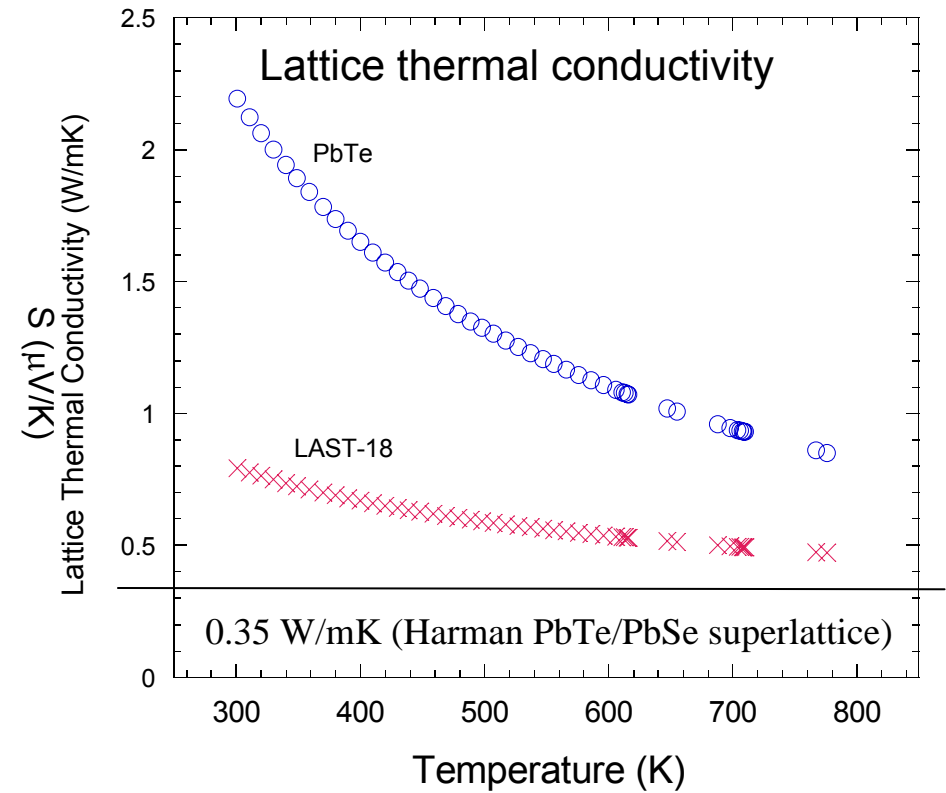
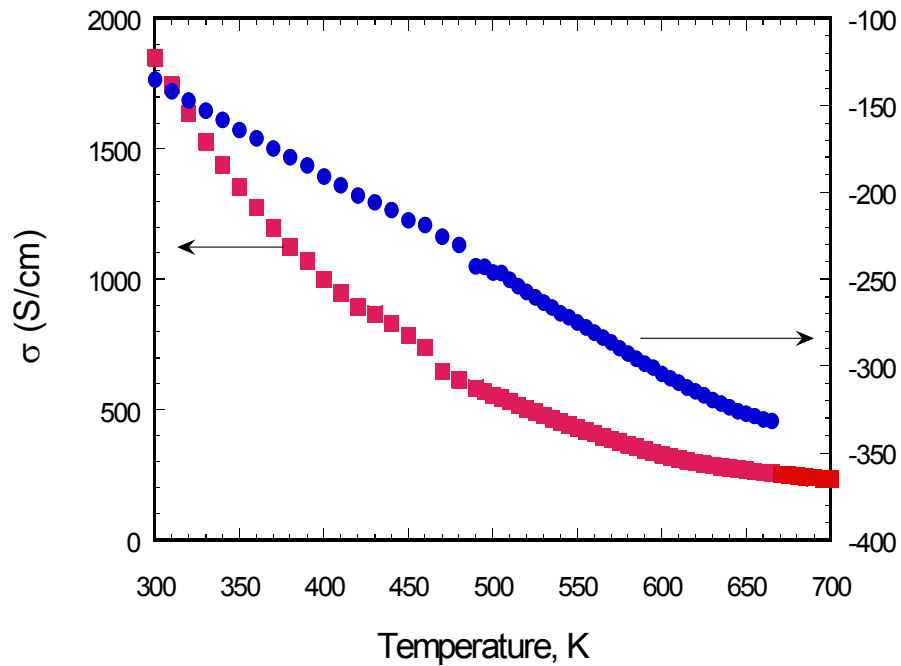
AgPb_mSbTe_{2+m} (LAST-m) NaPb_mSbTe_{2+m} (SALT-m)

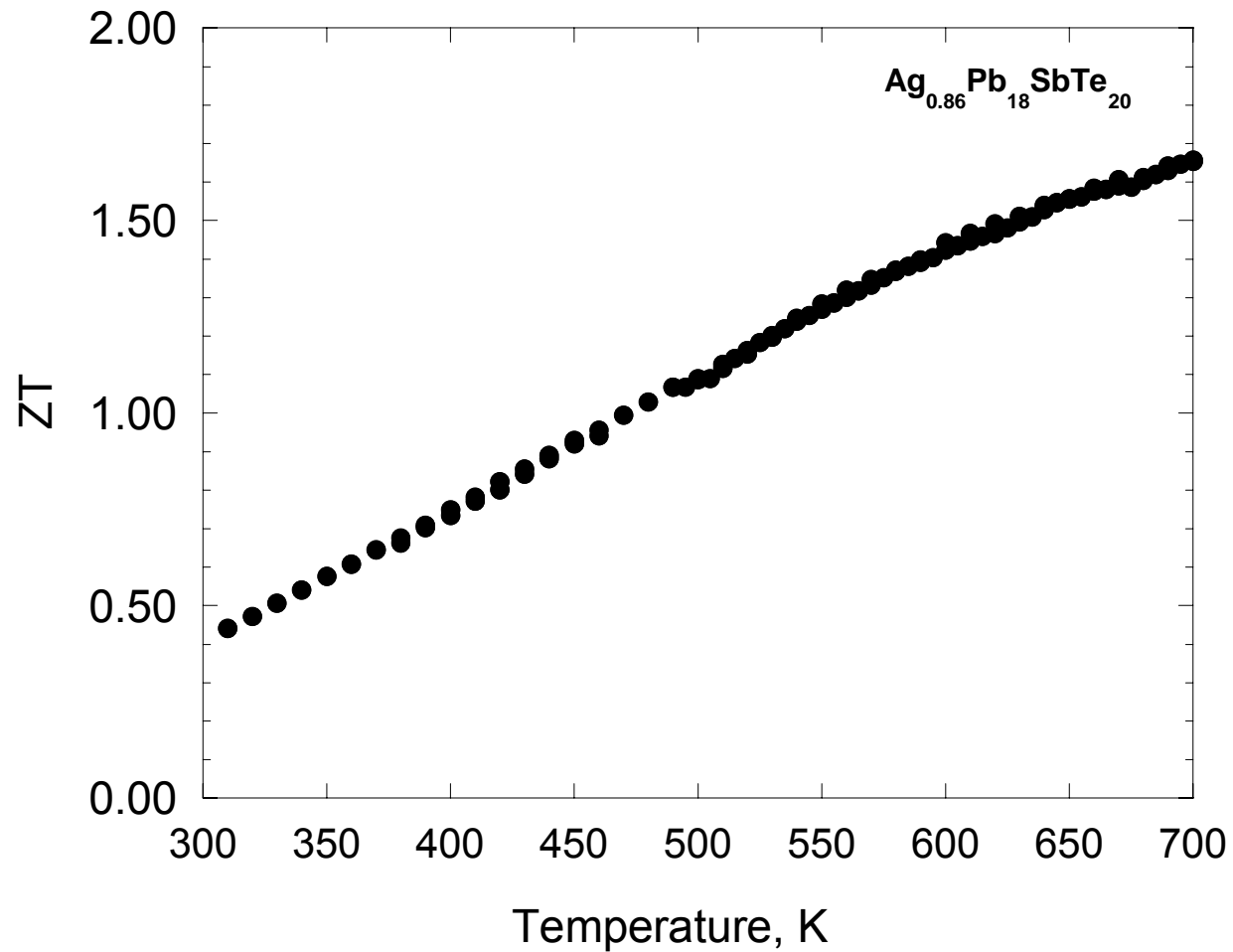


(1) (a) Rodot, H. *Compt. Rend.* **1959**, 249, 1872-4.

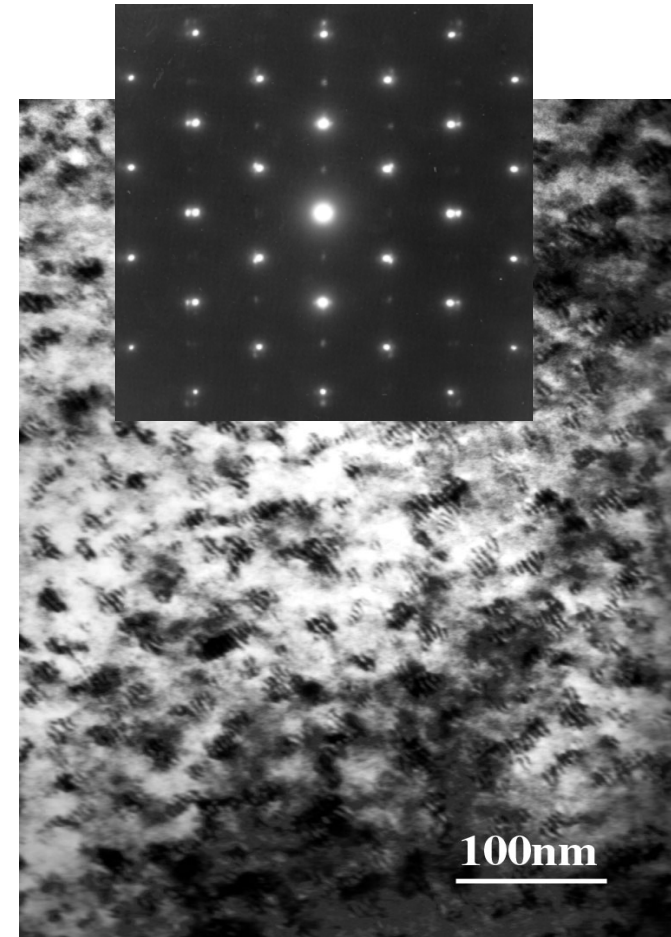
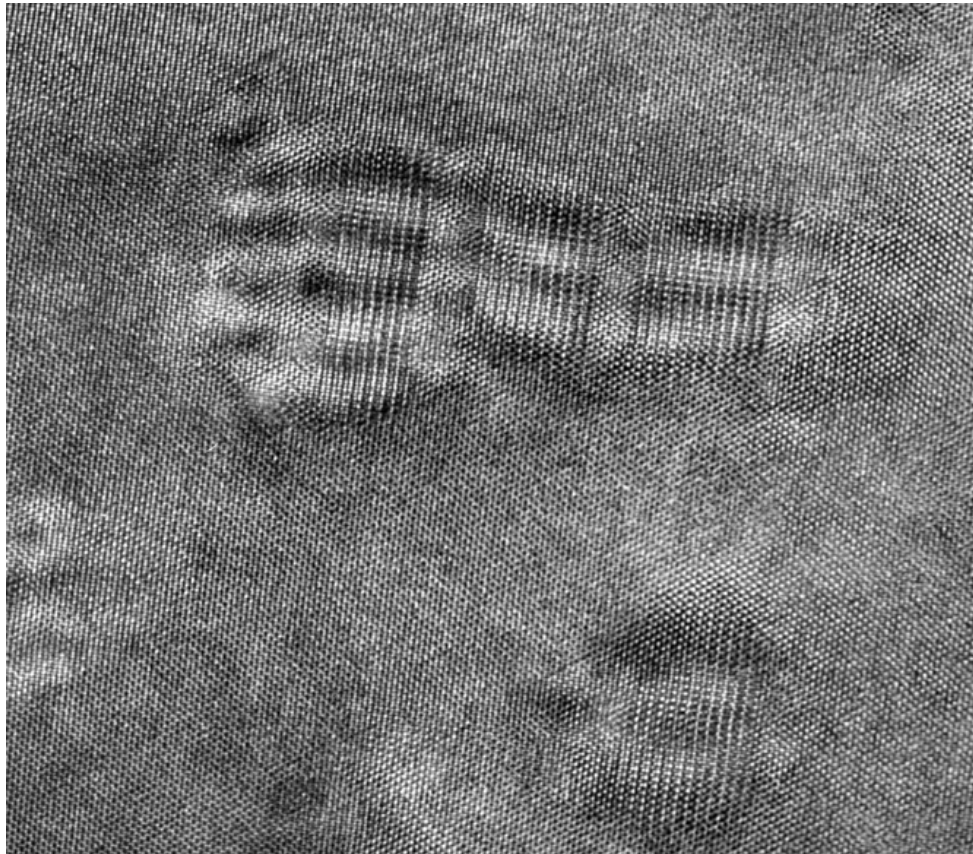
(2) (a) Rosi, F. D.; Hockings, E. S.; Lindenblad, N. E. *Adv. Energy Convers.* **1961**, 1, 151.

Properties of $\text{Ag}_{1-x}\text{Pb}_{18}\text{SbTe}_{20}$





Coherently embedded nanocrystals

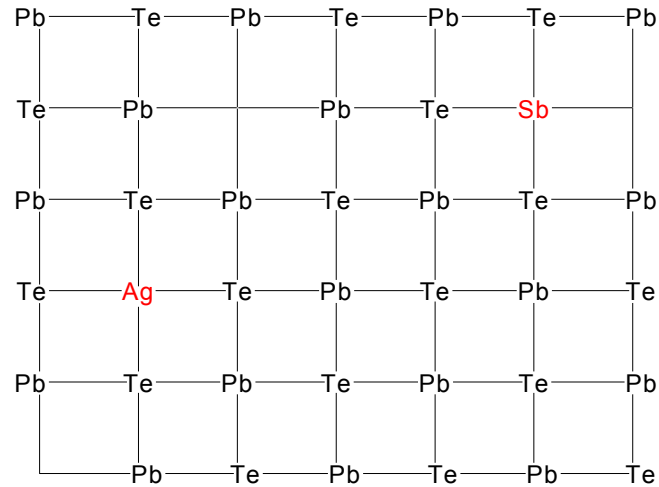


Polychroniadis, Frangis, 2004

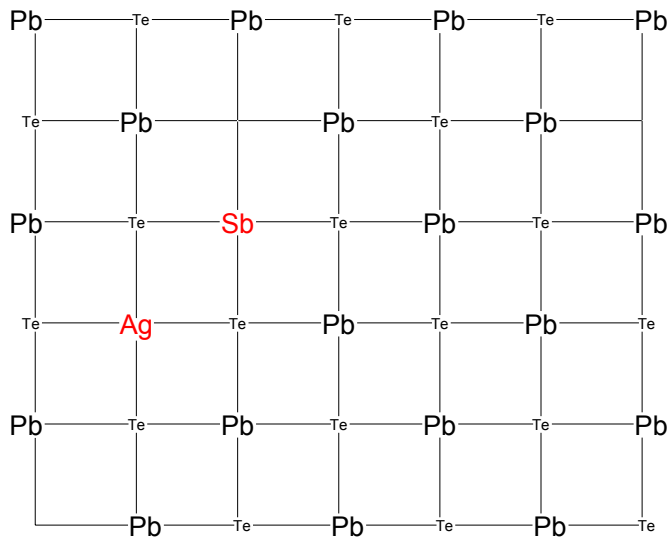
LAST-18 $\kappa_{\text{latt}}=1.2$ W/m-K at 300 K
PbTe $\kappa_{\text{latt}}=2.2$ W/m-K at 300 K

Driving force for segregation

Ag⁺/Sb³⁺ pair: stable

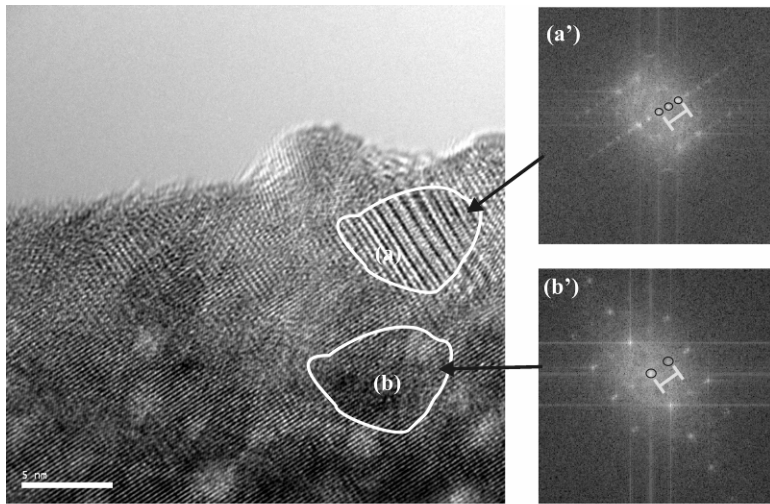


Dissociated state..unstable

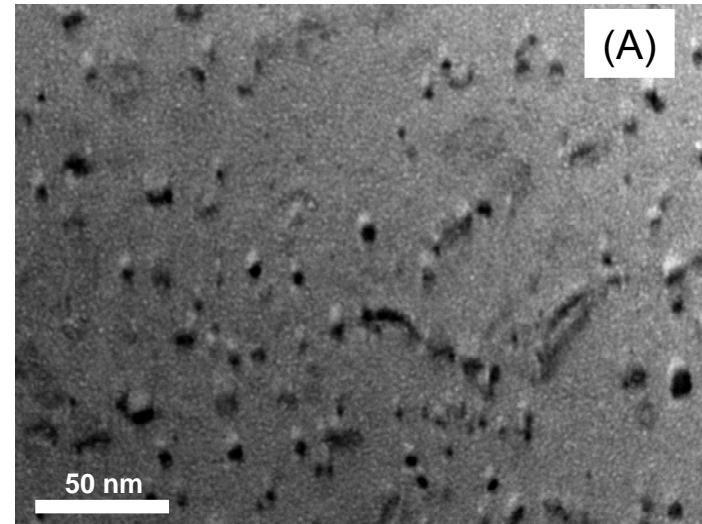


Associated state..stable

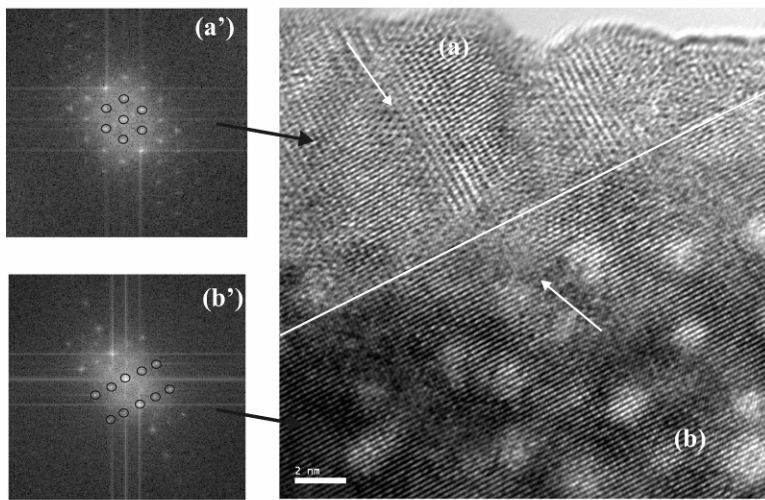
NaPb₂₀SbTe₂₂ (SALT-20)



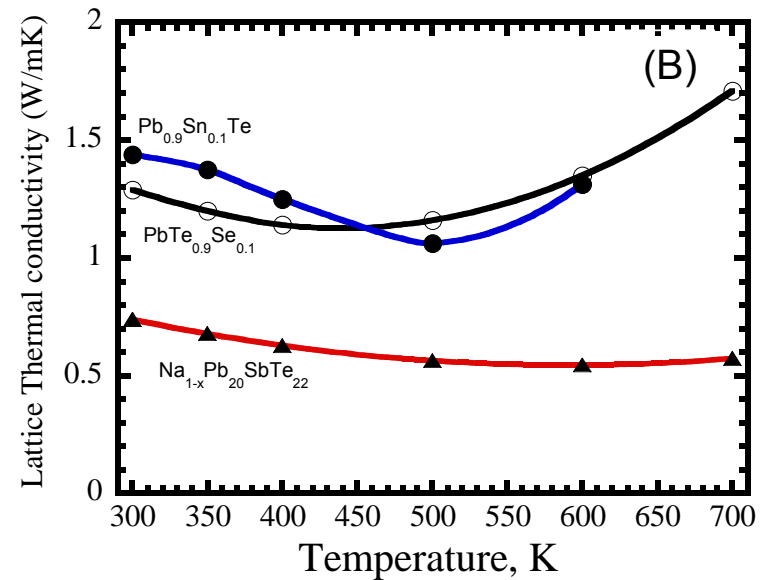
(A)



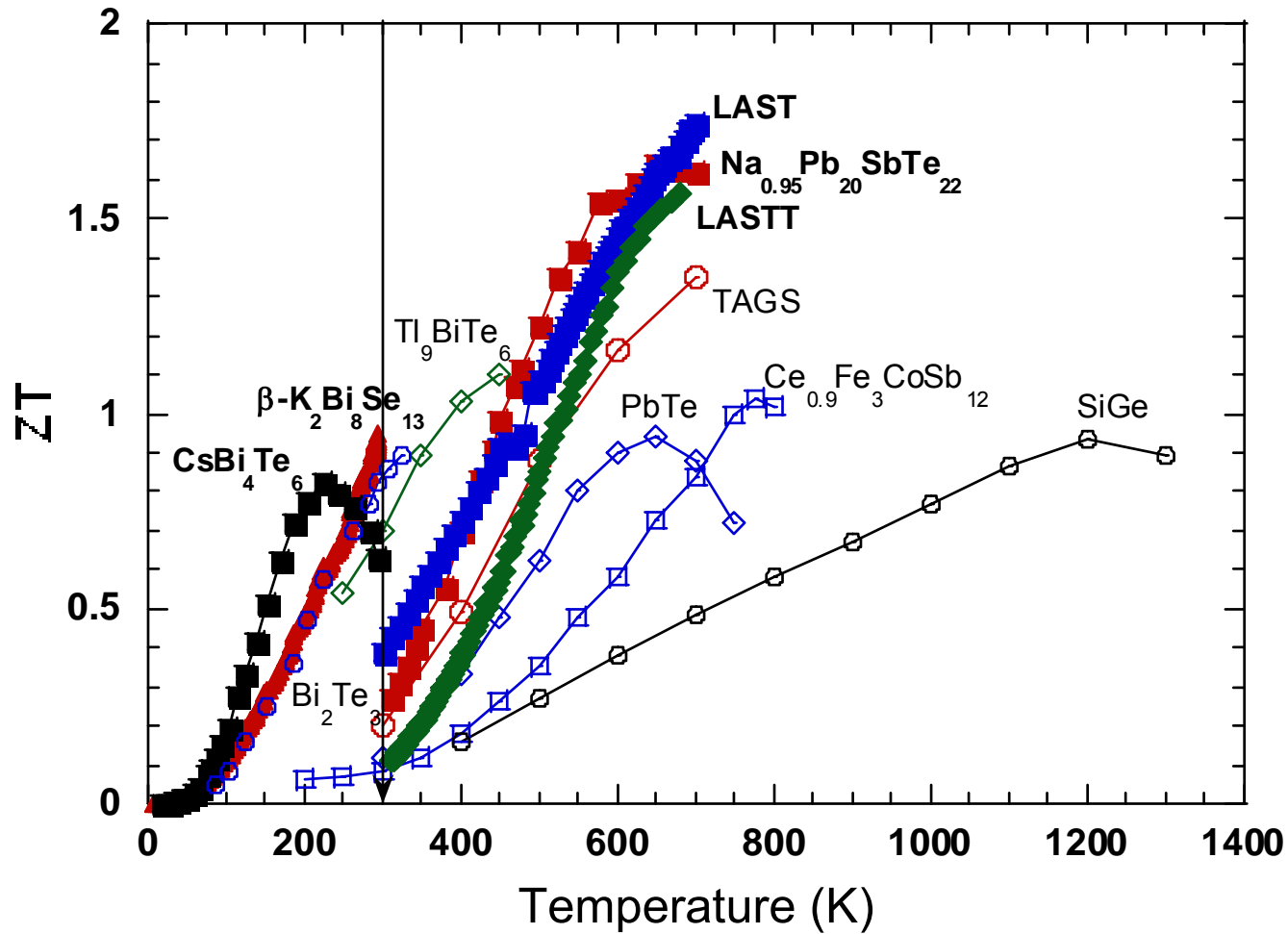
(A)



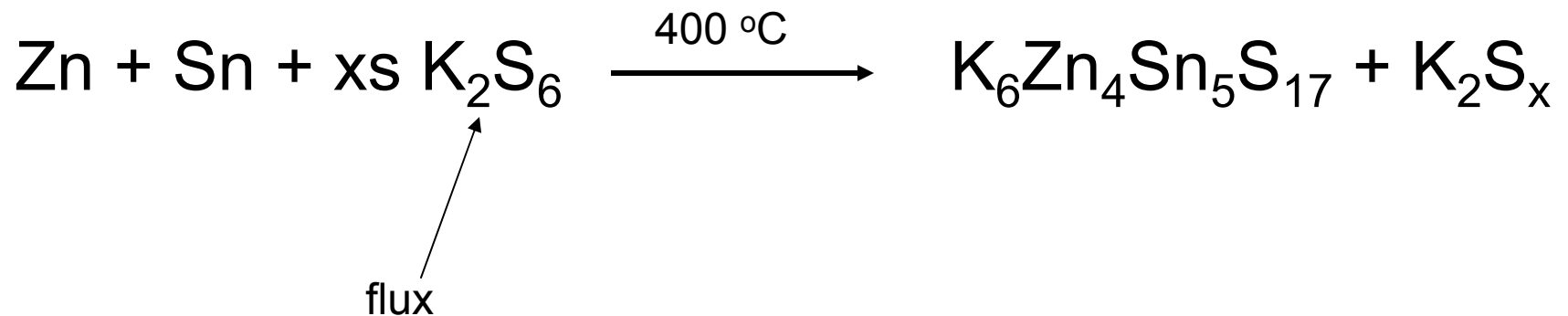
(B)



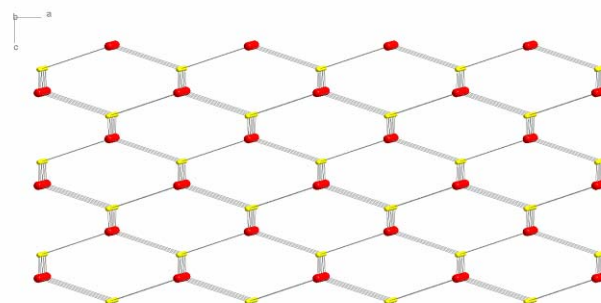
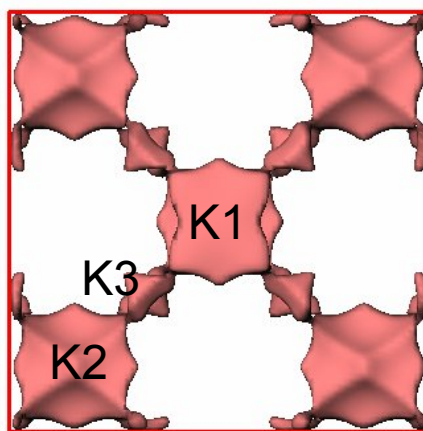
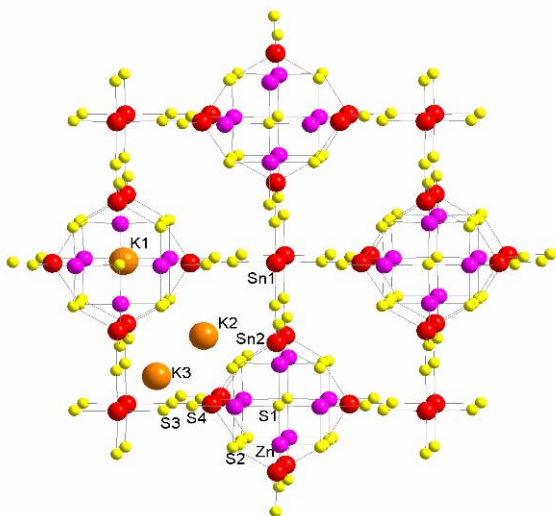
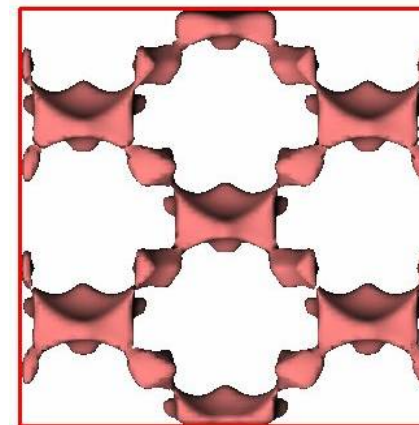
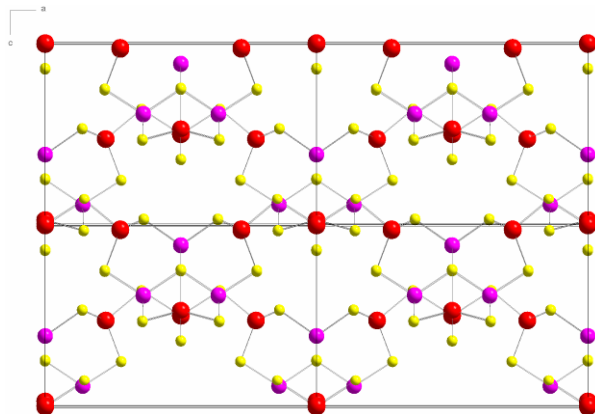
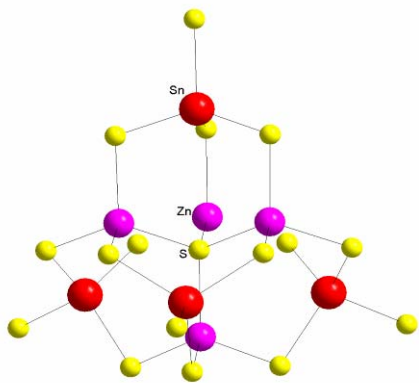
Best ZT Materials



Open framework materials from flux chemistry



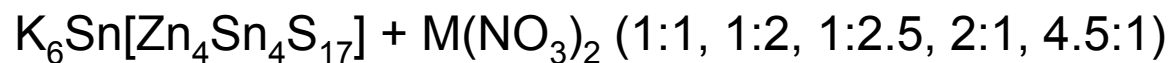
$K_5Sn[Sn_4Zn_4S_{17}]$ from molten K_2S_6



K ions loose and exchangeable

3 different type of cages

Ion-exchange experiments of $\text{K}_6\text{Sn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}]$ with Hg^{2+} , Pb^{2+} , Cd^{2+} , Ag^+



30-40 mg

(M= Hg, Pb, Cd)

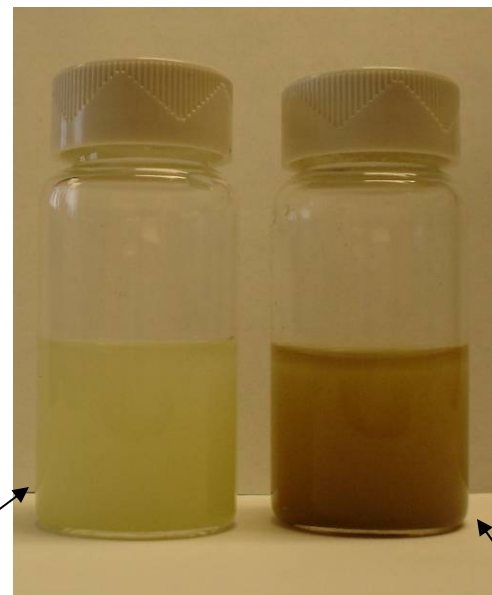
30 min
stirring, RT
→
 H_2O , 16 ml

Reduces:

Hg^{2+} conc. from 400 ppm to <3 ppb

Pb^{2+} conc. from 400 ppm to <50 ppb

Cd^{2+} conc. from 400 ppm to <0.5 ppm



$\text{K}_6\text{Sn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}] (\text{H}_2\text{O})$

$\text{K}_6\text{Sn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}]$
+ 2.5 $\text{Hg}(\text{NO}_3)_2 (\text{H}_2\text{O})$

Mercury removal: $K_6Sn[Zn_4Sn_4S_{17}]$ vs. functionalized mesoporous silicates

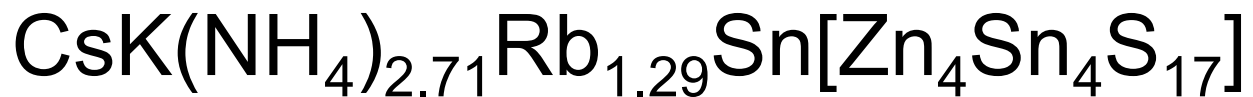
Initial concentration (ppm) of Hg	Material	Final concentration (ppm) of Hg	K_d (ml/g)
6.2	FMMS	0.0007	340141
3	PMPS	0.00016	3812400
10.76	S12	0.23	4248
10	FMMS	0.001	10^8
542.31	$K_6Zn_4Sn_5S_{17}$	0.001	2.8×10^8



FMMS: functionalized monolayers on mesoporous silica

Higher affinity of $K_6Sn[Zn_4Sn_4S_{17}]$ for Hg than functionalized silicates

Sorting cations:

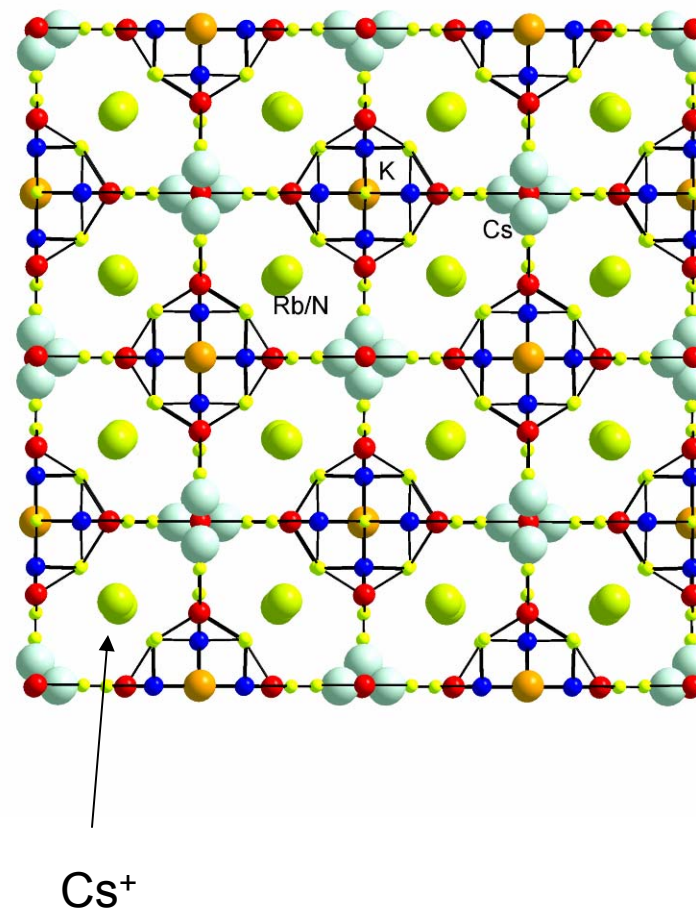


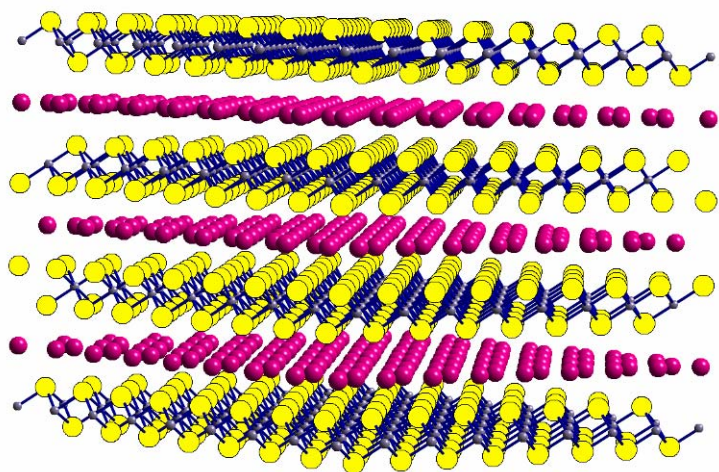
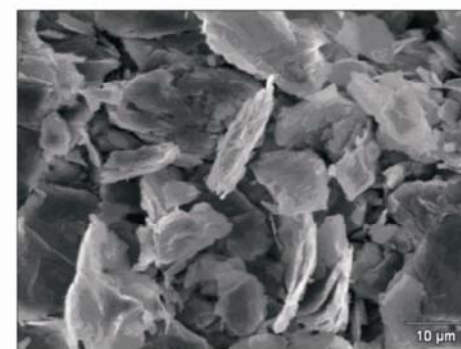
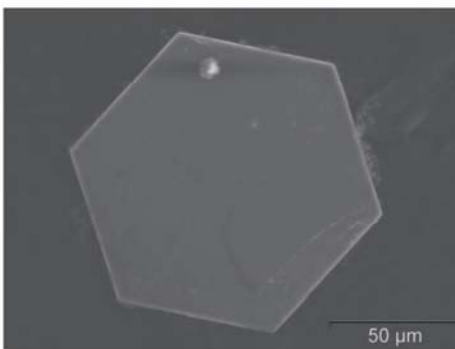
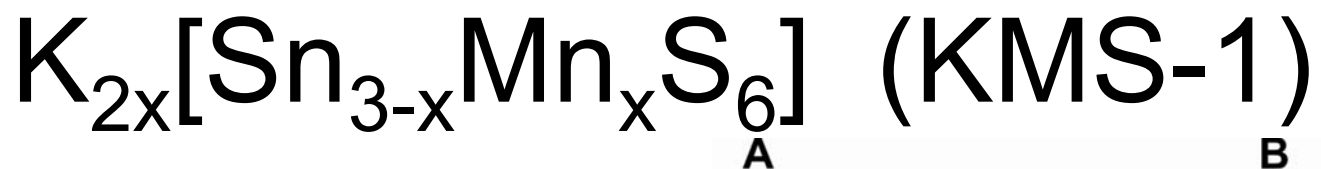
Pore selectivity:

Largest cavity (K3): Cs 100%

Small cavity (K1): K 100%

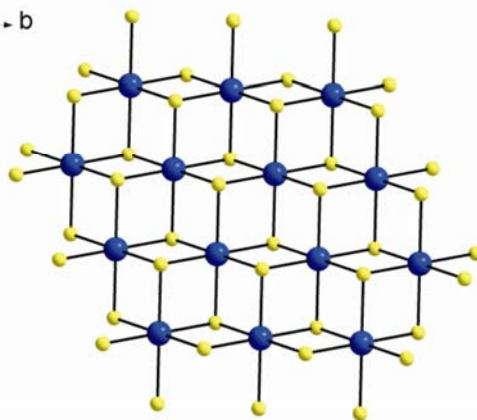
**Second large cavity (K2): NH₄
67.75%, Rb 32.25%**





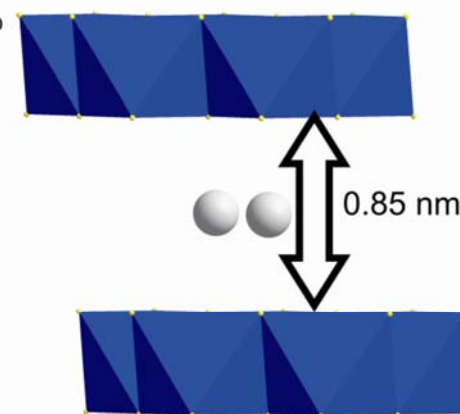
C

a
b
c



D

a
b
c



Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal

Manolis J. Manos*, Nan Ding*, and Mercouri G. Kanatzidis*^{†‡}

*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208; and [†]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Edited by James L. Dye, Michigan State University, East Lansing, MI, and approved January 4, 2008 (received for review December 6, 2007)

In this article, we report the family of robust layered sulfides $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5-0.95$) (KMS-1). These materials feature hexagonal $[Mn_xSn_{3-x}S_6]^{2x-}$ slabs of the CdI_2 type and contain highly mobile K^+ ions in their interlayer space that are easily exchangeable with other cations and particularly strontium. KMS-1 display outstanding preference for strontium ions in highly alkaline solutions containing extremely large excess of sodium cations as well as in acidic environment where most alternative adsorbents with oxygen ligands are nearly inactive. The implication of these results is that simple layered sulfides should be considered for the efficient remediation of certain nuclear wastes.

chalcogenide | environmental remediation | ion exchange | layered materials | nuclear waste

Current growing interest in nuclear power as a potential solution for global energy may also raise serious environmental and health concerns due to highly radioactive nuclear waste. ^{90}Sr is one of the major heat producers and biohazards in nuclear wastes. The removal of radioactive strontium is essential to reducing the risk of human exposure to radiation and for the considerable cost savings due to minimization of the storage

Na^+ ions. This property is highly relevant to the problem of nuclear waste remediation and points to the class of metal sulfide compounds as a highly promising source of materials for helping to solve it.

Results and Discussion

The KMS-1 materials can be easily prepared on a multigram scale and high purity with solid-state or hydrothermal synthesis techniques. They are extremely stable in atmosphere and water, while they display high thermal stability [see supporting information (SI) Figs. 5–7 (complete materials, instrumentation, and methods are provided in *SI Materials and Methods*, SI Figs. 5–12, and SI Table 2)]. Single-crystal data,[§] obtained from hexagonal-shaped crystals (Fig. 1A) synthesized hydrothermally, revealed a layered structure of $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$ (CdI_2 structure type). The layer is built up by edge-sharing “Mn/Sn” S_6 octahedra with Mn and Sn atoms occupying the same crystallographic position and all sulfur ligands being three-coordinated (Fig. 1C). K^+ ions are found between the layers and are positionally disordered, a feature that gives them high mobility and the ability to exchange with other ions particularly with strontium (Fig. 1D).

Indeed, polycrystalline samples (Fig. 1B) of KMS-1 can com-

Exploration of Intermetallics Using Liquid Al and Ga



Linus Pauling

"The great field of chemistry comprising the compounds of metals with one another have been largely neglected by chemists in the past ... "



"There is chemistry
in intermetallics"
-- John
Corbett

Some important intermetallics

Mg-Si-Al
Nb₃Sn
MgB₂
ZrNiSn
YbAl₃
YbCu₂Si₂

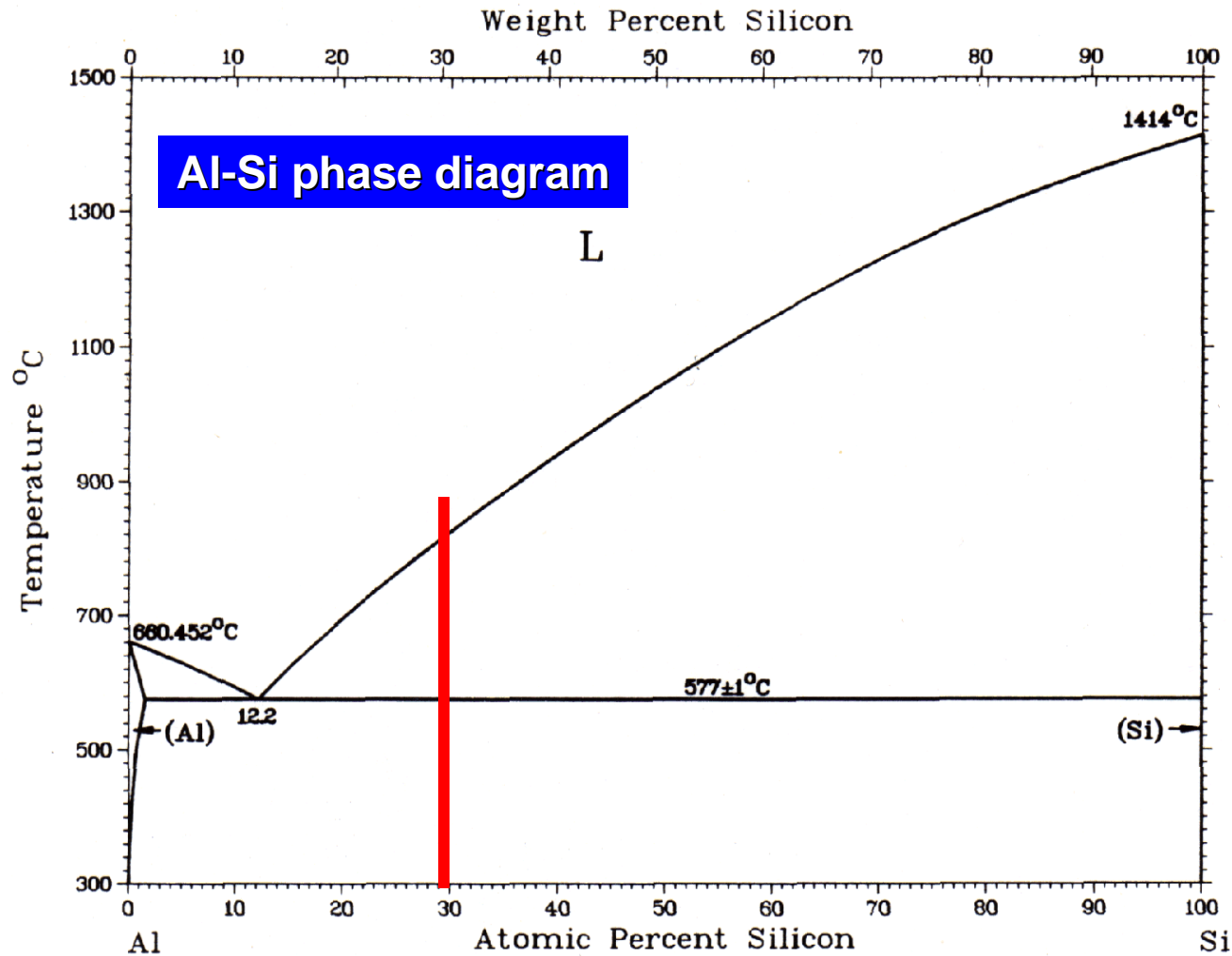
Traditional solid state synthesis--combine stoichiometric ratios and heat to high temperature



Some Statistics ...

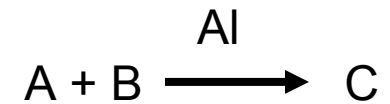
- **Binary Systems:** A_xB_y
~ 20,000 compounds known; about 80% of all possible combinations
- **Ternary Systems:** $A_xB_yC_z$
Only ~ 5% of 100,000 possible combinations have been discovered
- **Quaternary Systems:** $A_xB_yC_zQ_m$
Only few representatives are known

Synthesis in liquid Al

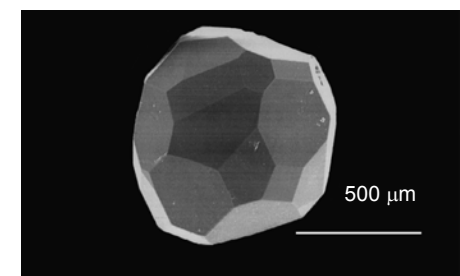
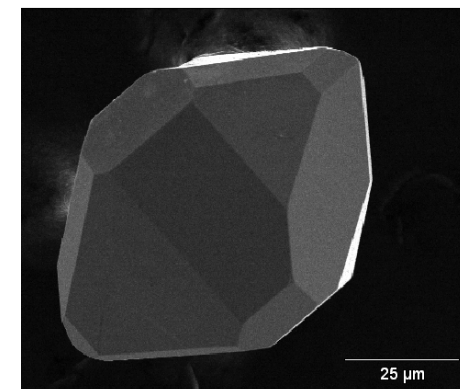
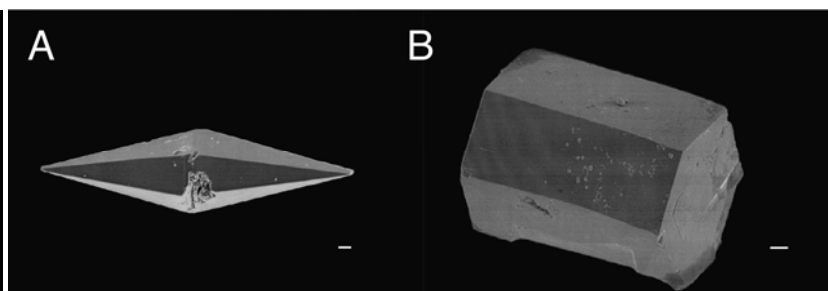
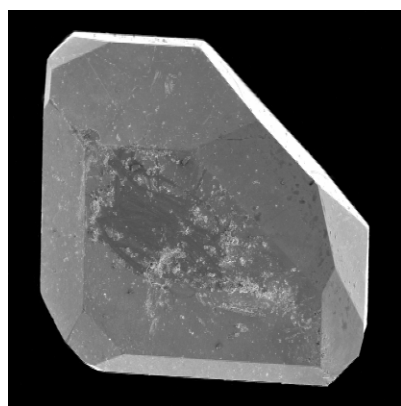
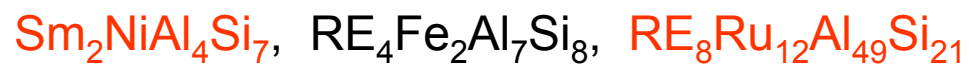


Al-Si phase diagram

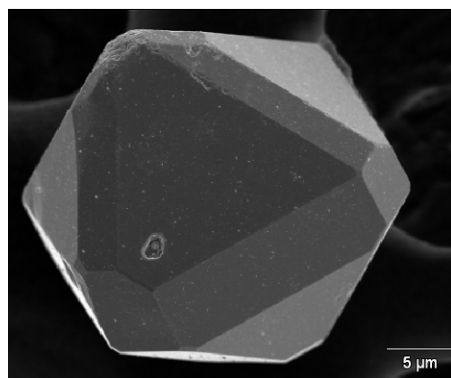
Up 30%
Si at 900 °C.



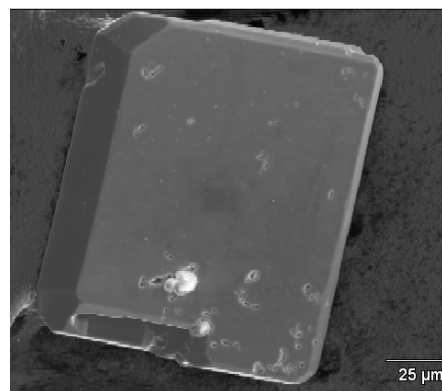
Quaternary intermetallics grown in liquid metals



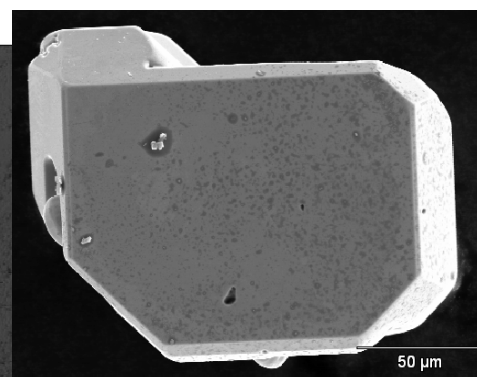
MnSi_2



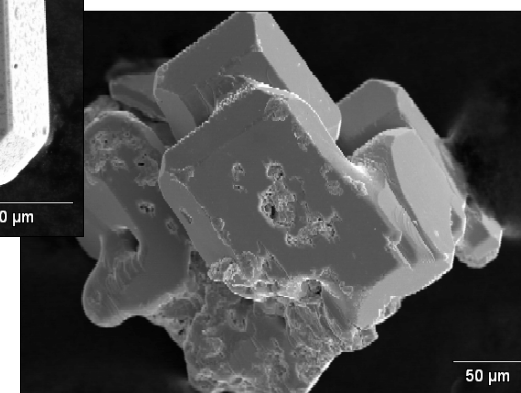
RuIn_3



Yb_2NiSi



YbNiSi



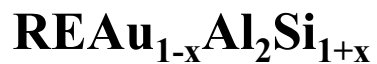
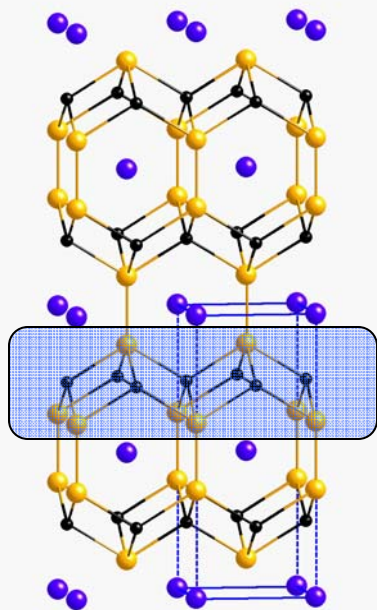
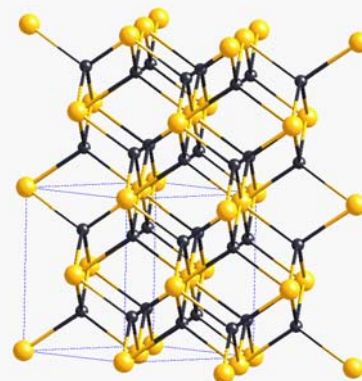
YbCoGe_2

The Homologous RE[AuAl₂]_nAl₂(Au_xSi_{1-x})₂ series

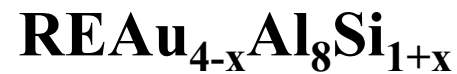
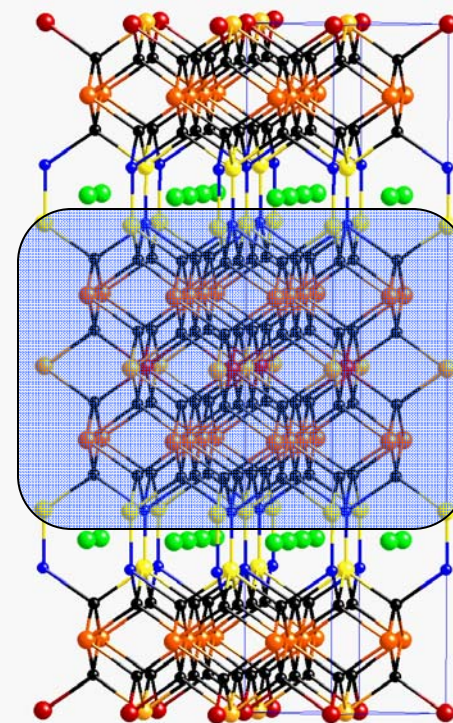
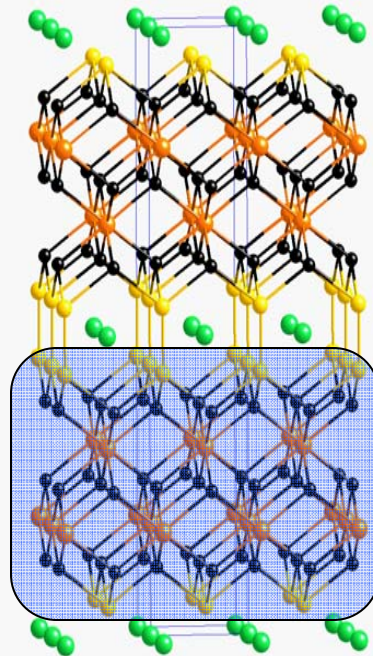
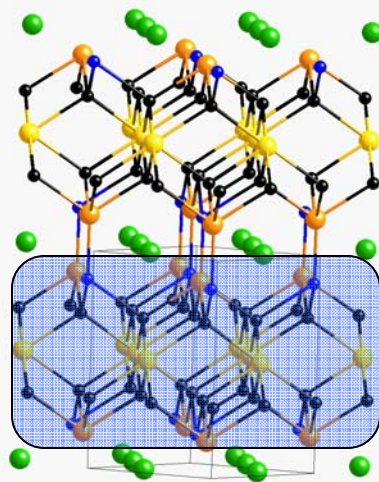
Possible next homologue:



I4/mmm 4 x 34 Å



BaAl₄ type

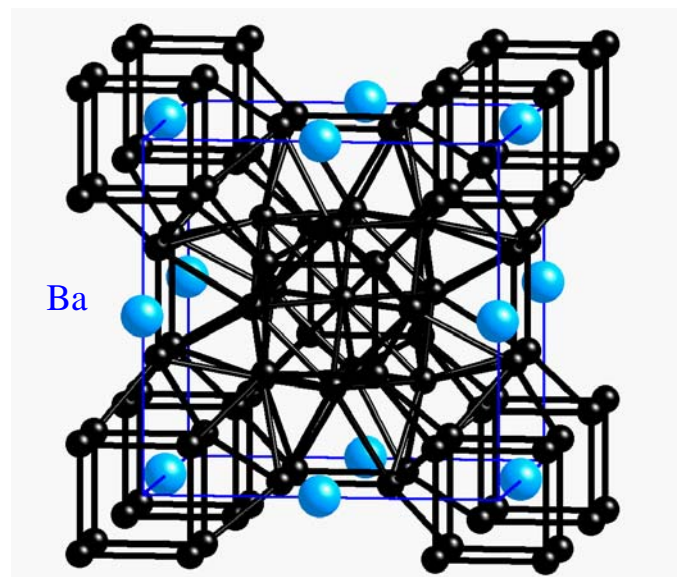


$M_3Au_7Al_{26}T$

Serendipitous discovery: TiO_2 cement in crucible reacted with Yb/Au/Al reaction mixture ($YbAu_3Al_7$)

Gold analogs form only with divalent or mixed-valent M ions: Ca, Sr, Eu, Yb.

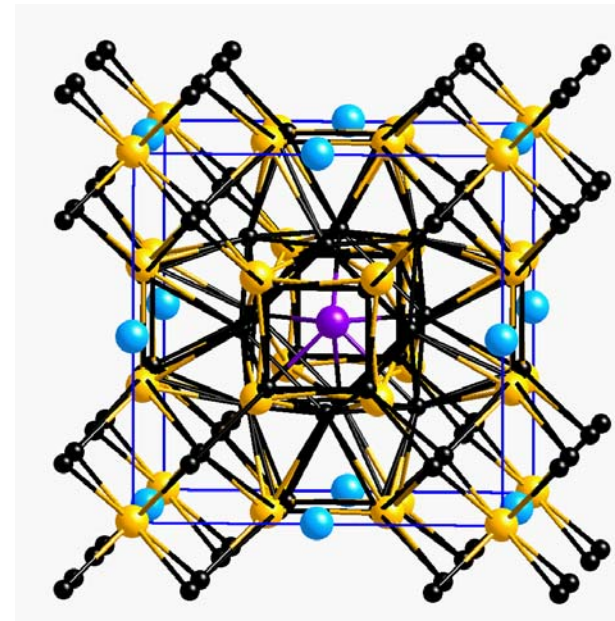
M = Yb, Eu, Ca, Sr



$BaHg_{11}$

$Pm-3m$, $a = 9.60^1$

Empty
 Hg_8 cube



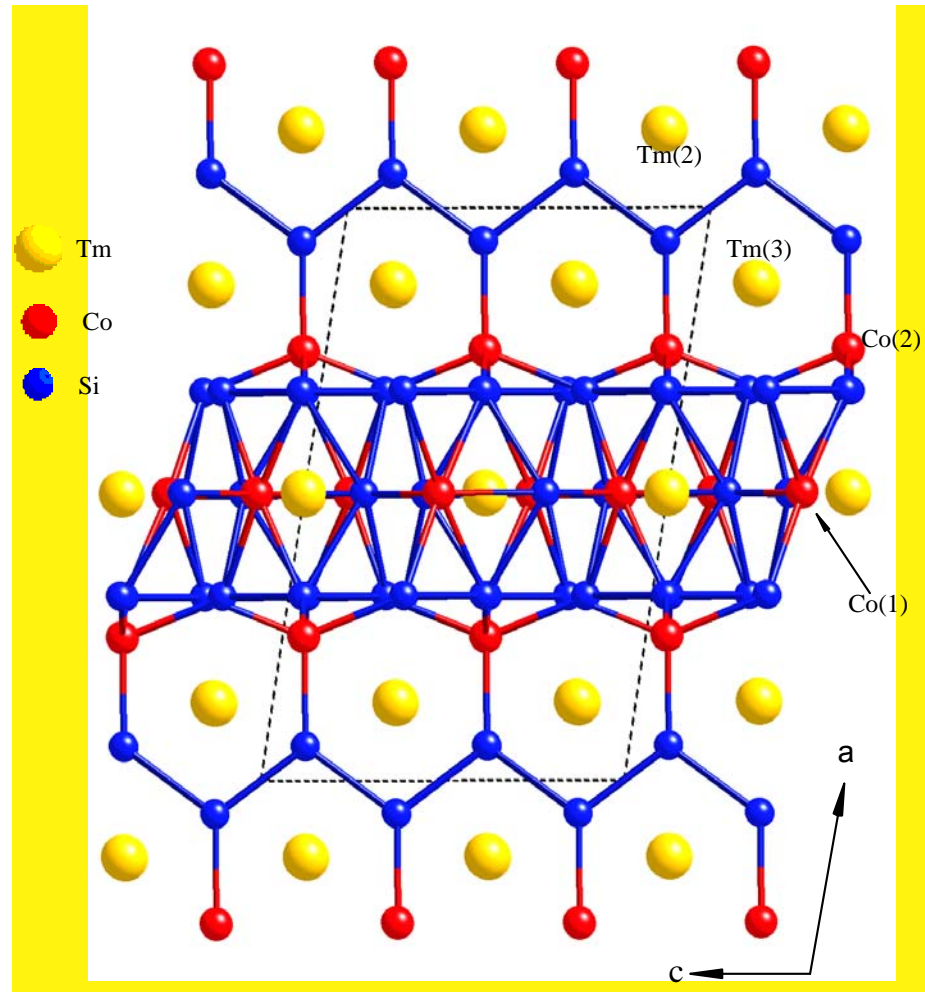
$Yb_3Au_7Al_{26}Ti$

$Pm-3m$, $a = 8.6509(6)^1$

Au - Stuffed
 Al_8 cube

¹Zarechnyuk, et al. *Inorg. Mater.* **1967**, 3, 153

Chemistry in liquid Ga: $\text{RE}_5\text{Co}_4\text{Si}_{14}$



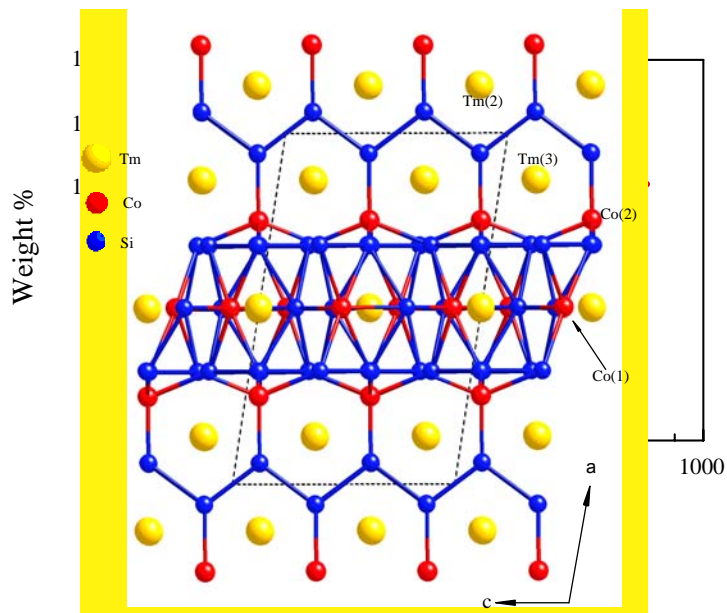
$I4/mmm$

Salvador, Kanatzidis

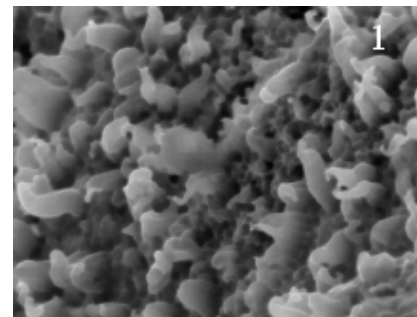
$P2_1/c$

Resistance to Oxidation

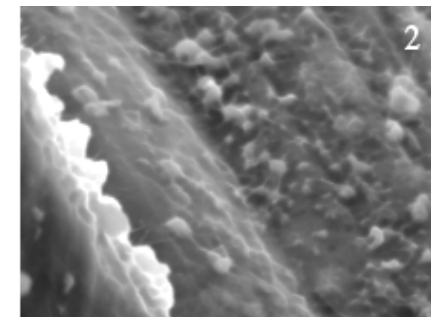
Melting point > 1200 °C



After 900 °C for 12h



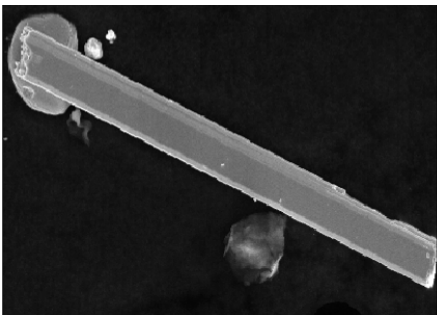
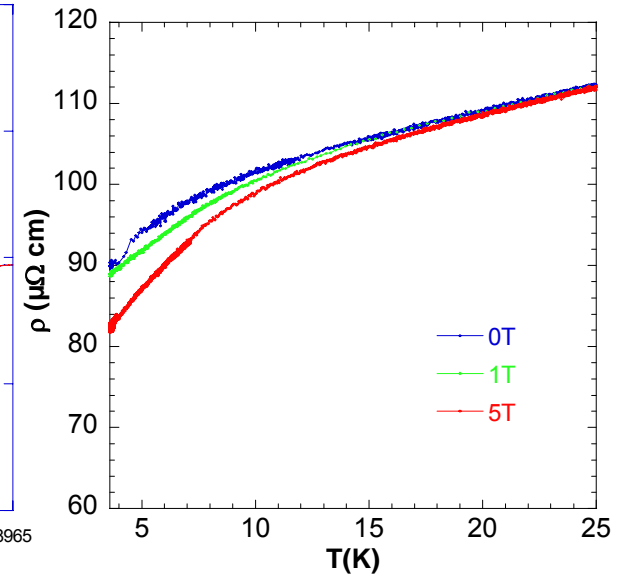
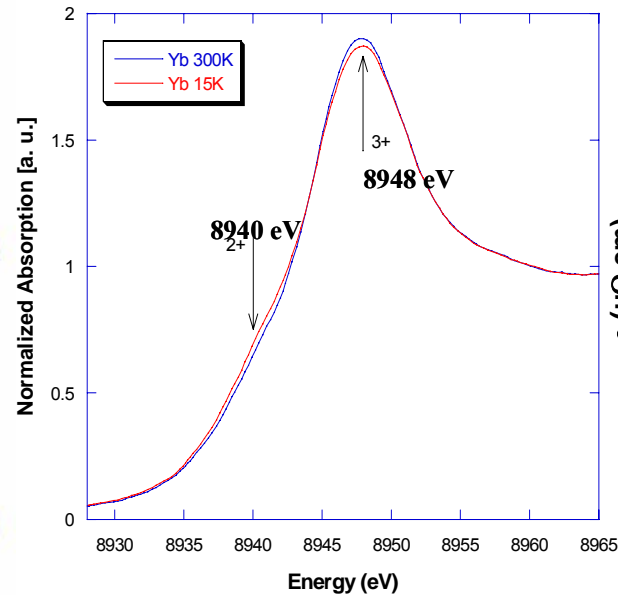
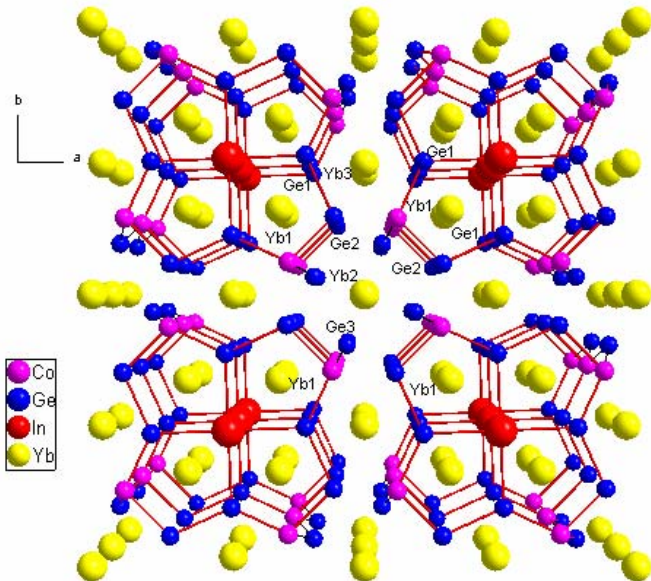
(100)



(101)

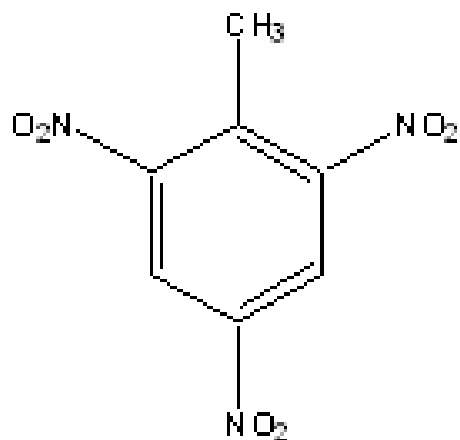
Yb₇Co₄InGe₁₂ - crystal structure

X-Ray Absorption Near Edge Spectroscopy (XANES)

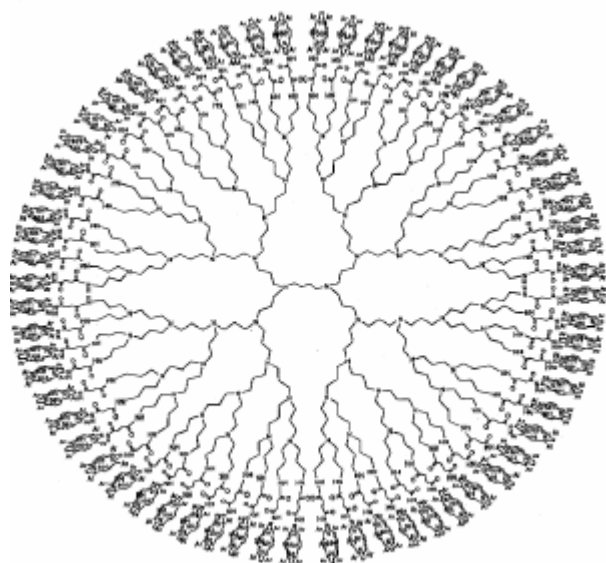


- 👉 Poor metallic behavior
- 👉 Negative magneto-resistance: suppression of spin-scattering of conduction & f-electrons in a high field
- 👉 frequently seen in Kondo systems, heavy fermion systems

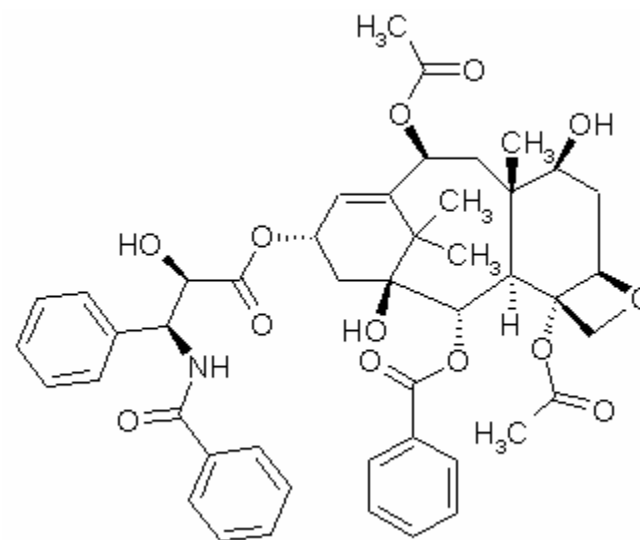
exploratory synthesis leads to “synthesis by design”



TNT

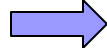


5th generation dendrimer



Taxol

Exploratory synthesis



Reactivity principles
And patterns



Design

Conclusions

- Exploratory synthesis is the foundation of synthetic chemistry
- Synthesis methodologies are critical to materials discovery
- Apparently “useless” materials today may be the hot materials of tomorrow..
 - $\text{LaO}(\text{FeAs})$ ($\text{LaO}_{1-x}\text{F}_x$)(FeAs) superconductor up to 50 K!
- Some apparently useless materials in the 60s and 70s:
 - E.g. $\text{LnFe}_4\text{Sb}_{12}$ (skutterudites), ZnNiSn (Heussler alloys), CeCu_2Si_2 , MgB_2
 - $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{NH}_4)_2\text{MoS}_4$.
- If it doesn't exist, you can't measure it.
- Grand challenge: design of specific compounds to obtain specific properties: e.g. superconductors, thermoelectrics, photovoltaics, magnets, ferroelectrics, etc.

“Expect the unexpected or you may not find it...” Heraclitus, 500 BC

Collaborators

- Tim Hogan, MSU
- S. D. (Bhanu) Mahanti, Dept. of Physics, MSU
- Ctirad Uher, U of Michigan
- Simon Billinge, Physics, MSU
- Eldon Case, MSU
- Harold Schock, MSU
- Bruce Cook, Iowa State
- Ulrich Welp, Argonne NL
- Art Freeman, Northwestern
- David Seidman, Northwestern

