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

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ONR

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 it 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, Cd$_{1-x}$Hg$_x$Te, Al$_{1-x}$Ga$_x$As. Very successful
  - Achieving isomorphous substitutions (making analogs)
    - K$_2$SO$_4$ $\rightarrow$ Ba$_2$SnTe$_4$
    - K$_2$MnSnS$_4$ $\rightarrow$ K$_2$ZnSnS$_4$ $\rightarrow$ K$_2$CdSnS$_4$ $\rightarrow$ K$_2$HgSnS$_4$ $\rightarrow$
    - ZrSiS $\rightarrow$ NbSiAs

Zr$^{4+}$ Si$^{2-}$ S$^{2-}$ Nb$^{5+}$ Si$^{2-}$ As$^{3-}$  Irrational synthesis…
A solid state chemist’s view of organic chemistry

At 800 °C

- CO₂
- CO
- H₂O₂
- H₂O
- H₂CO
- HCOOH
- CH₄
- C₂H₂
- C
- H
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 ($250 \, ^\circ\text{C} < T < 750 \, ^\circ\text{C}$)
- 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: $A/M/Bi/Q$

Reactivity of molten $K_2S_x$

- When $T>600$ °C: CuS, Cu$_2$S, KCuS
- In $K_2S_5$ and 350$<T<$600 °C: KCu$_4$S$_3$, KCu$_7$S$_4$
- In $K_2S_5$ and 180$<T<$350 °C: $\alpha$-KCuS$_4$, $\beta$-KCuS$_4$, KCuS$_6$, KCu$_4$S$_4$, KCu$_8$S$_6$
Investigating the A/Bi/Q system

\[ \text{A}_2\text{Q} + \text{PbQ} + \text{M}_2\text{Q}_3 \rightarrow (\text{A}_2\text{Q})_n(\text{PbQ})_m(\text{M}_2\text{Q}_3)_p \]

Map generates target compounds

Cubic materials

\[ \text{A}_m\text{B}_n\text{M}_m\text{Q}_{2m+n} \]

Phases shown are promising new TE materials

A=Ag, K, Rb, Cs
M=Sb, Bi
Q=Se, Te
Compounds discovered

- $\text{K}_2\text{Bi}_8\text{Se}_{13}$, $\text{KPbBi}_9\text{Se}_{13}$, $\text{KPb}_4\text{Sb}_7\text{Se}_{15}$
- $\text{Cs}_{1-x}\text{Pb}_{5-x}\text{Bi}_{10+x}\text{Se}_{21}$
- $\text{CsPbBi}_3\text{Te}_6$, $\text{CsPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPbBi}_3\text{Te}_6$, $\text{RbPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPb}_3\text{Bi}_3\text{Te}_8$
- $\text{KPbBiSe}_3$, $\text{K}_2\text{PbBi}_2\text{Se}_5$
- $\text{K}_2\text{Pb}_3\text{Bi}_2\text{Te}_7$, $\text{KPb}_4\text{SbTe}_6$
$CsPb_7Bi_9Se_{21}$

Sample undoped. Anticipated high ZT by doping.

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

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

DY Chung MG Kanatzidis
$KM_4Bi_7Se_{15}$ ($M = Pb, Sn$)

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

<table>
<thead>
<tr>
<th>$n$</th>
<th>1, $M_{2+n}Se_{5+n}$</th>
<th>2, $M_{4+n}Se_{8+n}$</th>
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<tr>
<td>1</td>
<td>$M_2Se_5$</td>
<td>$M_4Se_8$</td>
</tr>
<tr>
<td>2</td>
<td>$M_3Se_6$</td>
<td>$M_5Se_9$</td>
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<tr>
<td>3</td>
<td>$M_4Se_7$</td>
<td>$M_6Se_{10}$</td>
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<td>4</td>
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<td>$M_7Se_{10}$</td>
<td>$M_9Se_{13}$</td>
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<tr>
<td></td>
<td>$M_8Se_{11}$</td>
<td>$M_{10}Se_{14}$</td>
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<tr>
<td></td>
<td>$M_{11}Se_{14}$</td>
<td>$M_{14}Se_{18}$</td>
</tr>
<tr>
<td></td>
<td>(n=9)</td>
<td>(n=10)</td>
</tr>
</tbody>
</table>

1, $[M_2Se_3]_{2m}$  
2, $[M_3Se_4]_{2m}$
Design of Structure using phase homologies

\[ A_m \left[ M_{1+l}Se_{2+l} \right]_{2m} \left[ M_{2l+n}Se_{2+3l+n} \right] \]

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$_4$Te$_6$

At 225 K:
\[ \sigma \, 1733 \, \text{S/cm}, \]
\[ S \, 177 \, \mu\text{V/K}, \]
\[ \kappa \, 1.48 \, \text{W/m}\cdot\text{K} \]

AgPb$_m$SbTe$_{2+m}$(LAST-$m$)
NaPb$_m$SbTe$_{2+m}$(SALT-$m$)

Vegard's law

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

![Graph showing conductivity and lattice thermal conductivity as functions of temperature.]

- $\sigma$ (S/cm) vs. Temperature, K
- Lattice Thermal Conductivity (W/mK) vs. Temperature (K)

- $\sigma$ decreases as temperature increases.
- Lattice thermal conductivity decreases as temperature increases.

- Details on specific values and trends can be extracted from the graph.

Additional information:
- 0.35 W/mK (Harman PbTe/PbSe superlattice)
Ag$_{1-x}$Pb$_{18}$SbTe$_{20}$

Coherently embedded nanocrystals

Polychroniadis, Frangis, 2004

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

$\text{PbTe} \quad \kappa_{\text{lat}}=2.2 \ \text{W/m-K at 300 K}$
Driving force for segregation
Ag⁺/Sb³⁺ pair: stable

Dissociated state..unstable

Associated state..stable
NaPb$_{20}$SbTe$_{22}$ (SALT-20)
Best ZT Materials

![Graph showing ZT vs Temperature for various materials such as CsBi$_4$Te$_6$, β-KBiSe$_2$, TlBiTe$_6$, Na$_{0.95}$Pb$_{20}$SbTe$_{22}$, LAST, LASTT, TAGS, PbTe, Ce$_{0.9}$Fe$_3$CoSb$_{12}$, and SiGe. The graph plots ZT values against temperature in Kelvin (K), with a marked increase in ZT for certain materials at higher temperatures.]
Open framework materials from flux chemistry

Zn + Sn + xs K$_2$S$_6$ $\xrightarrow{400 \, ^{\circ} C}$ K$_6$Zn$_4$Sn$_5$S$_{17}$ + K$_2$S$_x$
K$_5$Sn[Sn$_4$Zn$_4$S$_{17}$] from molten K$_2$S$_6$

K ions loose and exchangeable

3 different type of cages
Ion-exchange experiments of $K_6Sn[Zn_4Sn_4S_{17}]$ with $Hg^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Ag^+$

$K_6Sn[Zn_4Sn_4S_{17}] + M(NO_3)_2$ (1:1, 1:2, 1:2.5, 2:1, 4.5:1)

30-40 mg
(M = Hg, Pb, Cd)

30 min stirring, RT

H$_2$O, 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
**Mercury removal: $K_6Sn[Zn_4Sn_4S_{17}]$ vs. functionalized mesoporous silicates**

<table>
<thead>
<tr>
<th>Initial concentration (ppm) of Hg</th>
<th>Material</th>
<th>Final concentration (ppm) of Hg</th>
<th>$K_d$ (ml/g)</th>
</tr>
</thead>
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<td>6.2</td>
<td>FMMS</td>
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<td>340141</td>
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<tr>
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<td>S12</td>
<td>0.23</td>
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<tr>
<td>10</td>
<td>FMMS</td>
<td>0.001</td>
<td>$10^8$</td>
</tr>
<tr>
<td>542.31</td>
<td>$K_6Zn_4Sn_5S_{17}$</td>
<td>0.001</td>
<td>$2.8 \times 10^8$</td>
</tr>
</tbody>
</table>

FMMS: functionalized monolayers on mesoporous silica

**Higher affinity of $K_6Sn[Zn_4Sn_4S_{17}]$ for Hg than functionalized silicates**
Sorting cations:
CsK(NH$_4$)$_{2.71}$Rb$_{1.29}$Sn[Zn$_4$Sn$_4$S$_{17}$]

Pore selectivity:

- **Largest cavity (K3):** Cs 100%
- **Small cavity (K1):** K 100%
- **Second large cavity (K2):** NH$_4$
  67.75%, Rb 32.25%

Manos, Kanatzidis
$K_{2x}[Sn_{3-x}Mn_xS_6]$ (KMS-1)
Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal

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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 of 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,$^8$ obtained from hexagonal-shaped crystals (Fig. L4) synthesized hydrothermally, revealed a layered structure of $K_{1.0}Mn_{0.95}Sn_{2.05}S_6$ (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

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

-- John Corbett

Some important intermetallics

Mg-Si-Al
Nb<sub>3</sub>Sn
MgB<sub>2</sub>
ZrNiSn
YbAl<sub>3</sub>
YbCu<sub>2</sub>Si<sub>2</sub>

"There is chemistry in intermetallics"

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

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Synthesis in liquid Al

Up 30% Si at 900 °C.

Al-Si phase diagram

A + B → C

Al
Quaternary intermetallics grown in liquid metals

\[ \text{Al} \]

\[ \text{RE} + \text{M} + \text{Si} \rightarrow \text{RE}_x\text{M}_y\text{Si}_z \]

Sm\(_2\)NiAl\(_4\)Si\(_7\), RE\(_4\)Fe\(_2\)Al\(_7\)Si\(_8\), RE\(_8\)Ru\(_{12}\)Al\(_{49}\)Si\(_{21}\)

The Homologous RE[AuAl\textsubscript{2}]\textsubscript{n}Al\textsubscript{2}(Au\textsubscript{x}Si\textsubscript{1-x})\textsubscript{2} series

Possible next homologue:
REAu\textsubscript{5}Al\textsubscript{10}Si: RE[AuAl\textsubscript{2}]\textsubscript{4}Al\textsubscript{2}(Au\textsubscript{x}Si\textsubscript{1-x})\textsubscript{2}
I\textsubbox{4/mmm}  4 x 34 Å
$M_3Au_7Al_{26}T$

Serendipitous discovery: TiO$_2$ cement in crucible reacted with Yb/Au/Al reaction mixture (YbAu$_3$Al$_7$)

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

$BaHg_{11}$

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

$Yb_3Au_7Al_{26}Ti$

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

$M = \text{Yb, Eu, Ca, Sr}$

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

$I \bar{4} \text{mmm}$  
Salvador, Kanatzidis

$P \ 2_1/c$
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

M. Chondroudi, U. Welp, M. Balasubramanian
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...
  - \( \text{LaO(FeAs)} \ (\text{LaO}_{1-x}\text{F}_x)(\text{FeAs}) \) superconductor up to 50 K!
- Some apparently useless materials in the 60s and 70s:
  - E.g. \( \text{LnFe}_4\text{Sb}_{12} \) (skutterudites), \( \text{ZnNiSn} \) (Heussler alloys), \( \text{CeCu}_2\text{Si}_2, \text{MgB}_2 \)
  - \( \text{La}_{2-x}\text{Ba}_x\text{CuO}_4, (\text{NH}_4)_2\text{MoS}_4 \).
- 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