Northwestern University

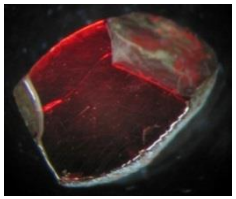
Argonne NATIONAL LABORATORY

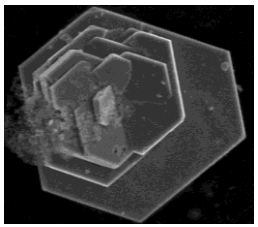
251st ACS National Meeting ,
San Diego, California, March 13-17, 2016.

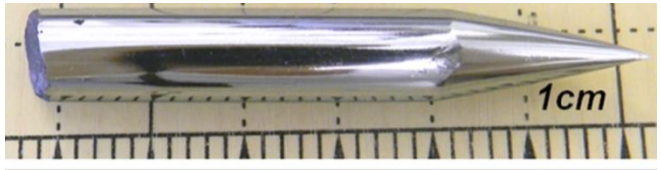
ACS Award in Inorganic Chemistry

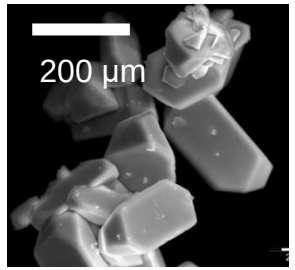
NEW INORGANIC SOLIDS FROM MOLTEN *CHALCOGENIDE* SALTS

Mercouri Kanatzidis





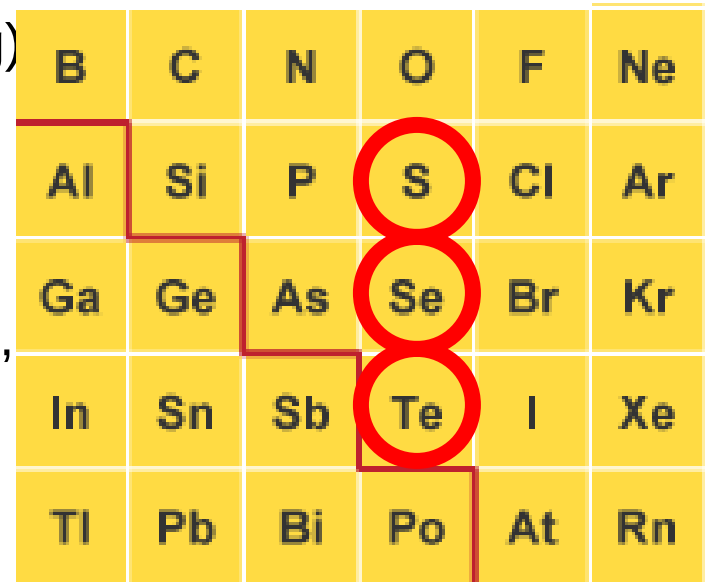




What in the world is a chalcogenide…

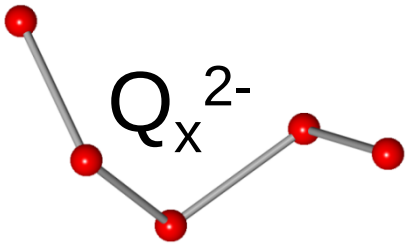
- MoS_2 (2D-physics, HDS-catalysis, H_2 catalysis
- $Ge_2Sb_2Te_5$ (non-volatile memory, computing)
- CdTe, $CuInSe_2$ (solar energy PV)
- CdZnTe, CdHgTe (hard and soft radiation detection)
- Bi_2Se_3, Bi_2Te_3, PbTe, PbSe (thermoelectrics, energy conversion, topological materials)
- CdS, CdSe (quantum dots, nanoscience…)
- $AgGaQ_2$ (Q=S, Se) (mid-IR NLO material, mid-IR laser sources, telecommunications, chemical sensing, medical applications)
- $K_xFe_{2-y}Se_2$ (unconventional superconductors)

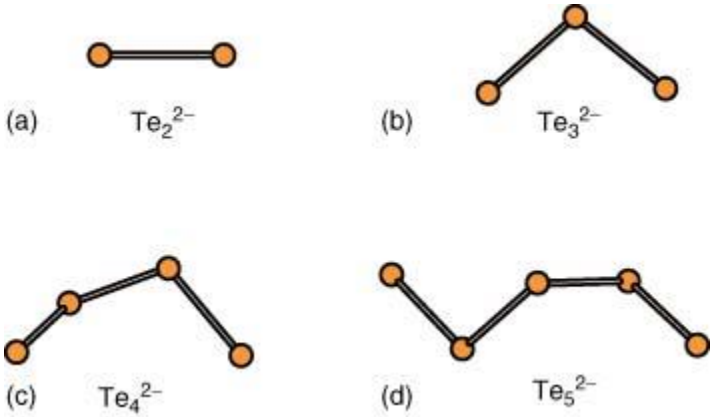
Q= S, Se, Te

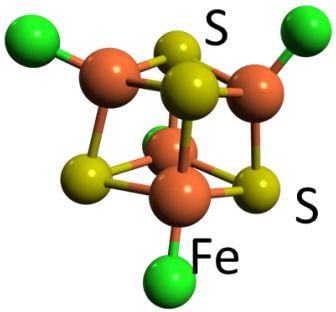


Why Chalcogenides?

- huge structural diversity
  - Formation of P-P and Q-Q (Q=S, Se) bonds
  - Redox chemistry
  - Conformational agility gives complex and interesting anions

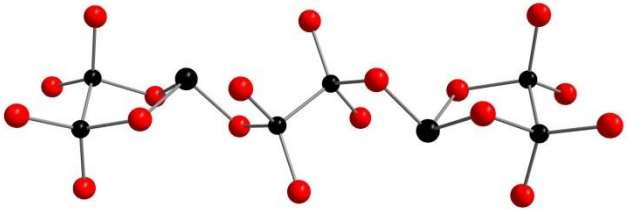




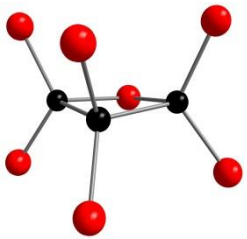


$[Fe_4S_4]$

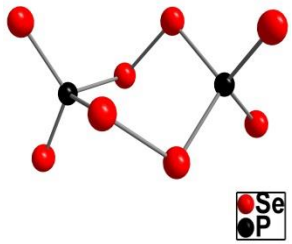
$[P_2Se_8]^{2-}$



$[P_8Se_{18}]^{6-}$



$[P_3Se_7]^{3-}$



Chung, I.; Holmes, D.; Weliky, D. P.; Kanatzidis, M. G. *Inorg.Chem.* ***2010,*** *49,* 3092.
K. Chondroudis and M.G. Kanatzidis *J. Amer. Chem. Soc*. **1997,** *119*, 2574-1575

Extended structures with Chalcogenides

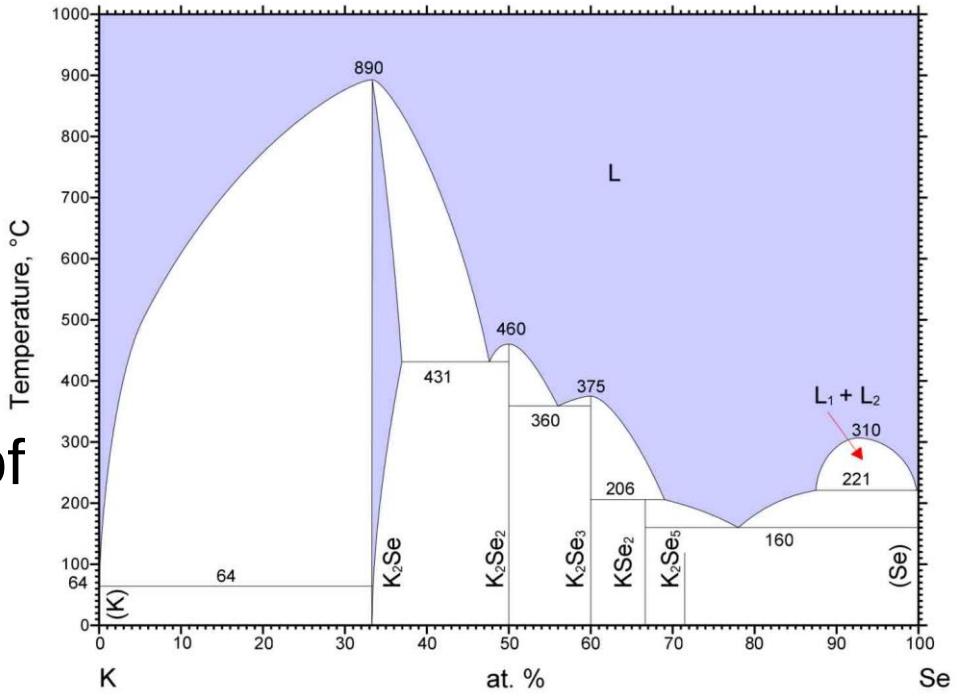
- Common chalcogenide building blocks can be further linked by addition of another metal
- Challenge: how do you prepare crystalline solid state compounds with high enough built-in structural complexity to obtain new or enhanced collective properties
- No good method existed on how combine such building blocks together to create extended solids….

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

- Lower temperatures stabilize greater numbers of compounds
- Use solvents: The molten salts (fluxes) parallel solution based synthesis
- Different fluxes can be devised for different materials. These fluxes can be reactive or non reactive.

Molten salts as solvents… Reactive polychalcogenide flux

- Flux formed from $A_2Q + [Q_x]^{2-} \rightarrow A_2Q_{x+1}$
- (Q=S, Se, Te)
- Low (200°-600°C) reaction temperatures allow access of kinetically stable phases
- Increased diffusion created by formation of a ‘solvent’
- Unreacted flux washed away



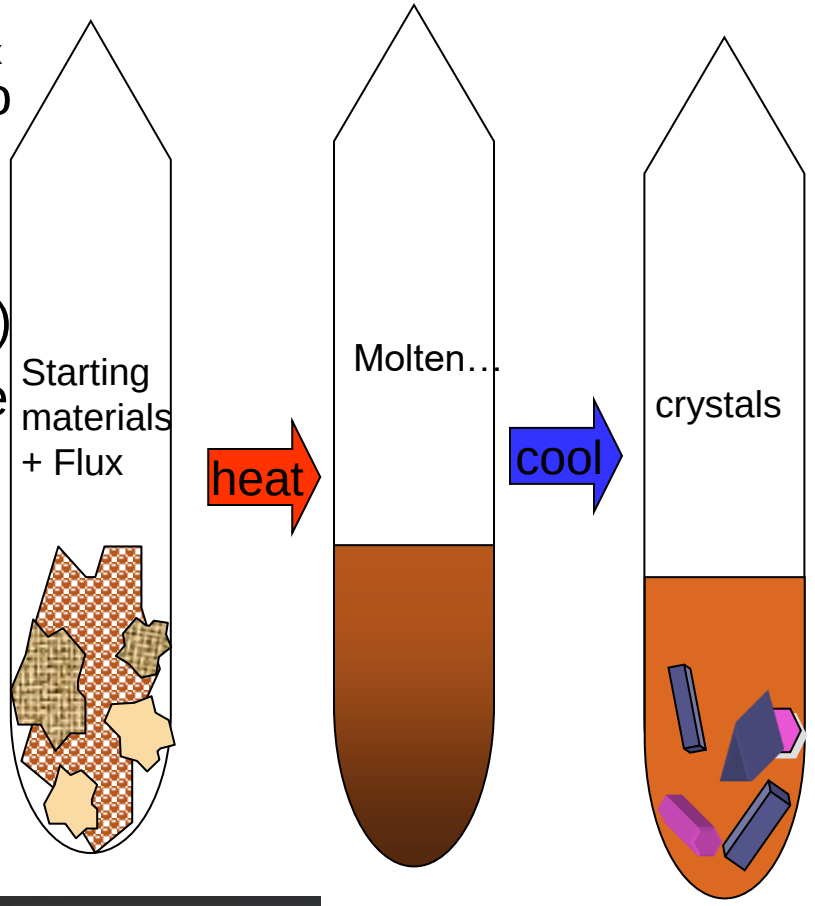
Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202.
Kanatzidis, M. G. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 139.
Sangster, J. and Pelton, A.D. *J. Phase Equilib.* **1997**, *18*, 177.

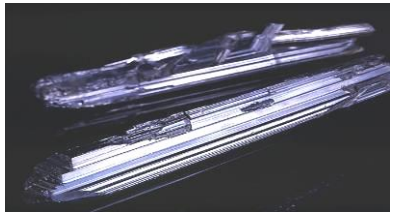
Molten salts (fluxes) as solvents

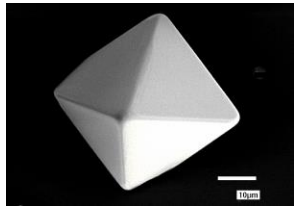
- Molten chalcogenide salts ($Na_2Se + Se_x \rightarrow Na_2Se_x$) as Reagents and Solvents to synthesize new compounds

ADVANTAGES

- Low temperatures (250 $^oC < T < 550\ ^oC$)
- 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: e.g. A/Bi/Se or quaternary: A/M/Bi/Se)

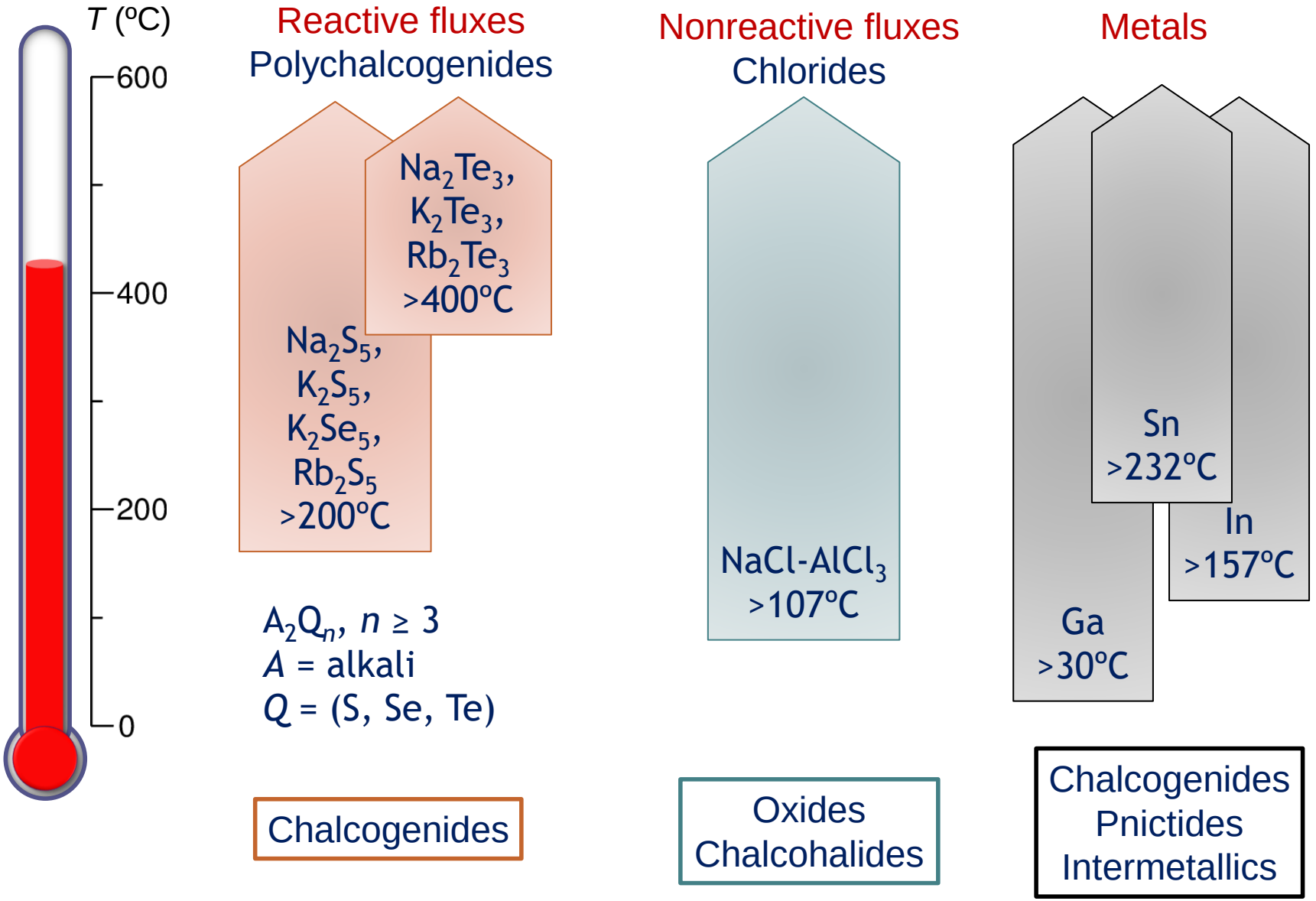






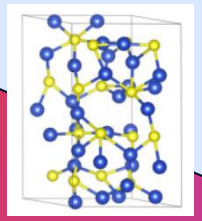
T.K. Bera, J.I. Jang, J.H. Song, C.D. Malliakas, A.J. Freeman, J.B. Ketterson and M.G. Kanatzidis *J. Am. Chem. Soc.* **2010,** *132*, 3484-3495

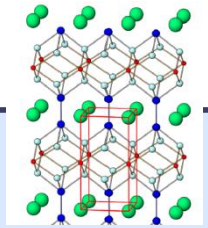
A wealth of solvents for low T reactions



Example: Reactivity of liquid K_2S_x

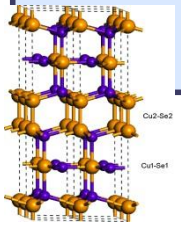
- CuS, Cu_2S, $KCuS$



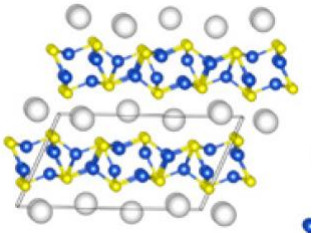


- KCu_4S_3, KCu_7S_4

800-900 °C



- KCu_8S_6

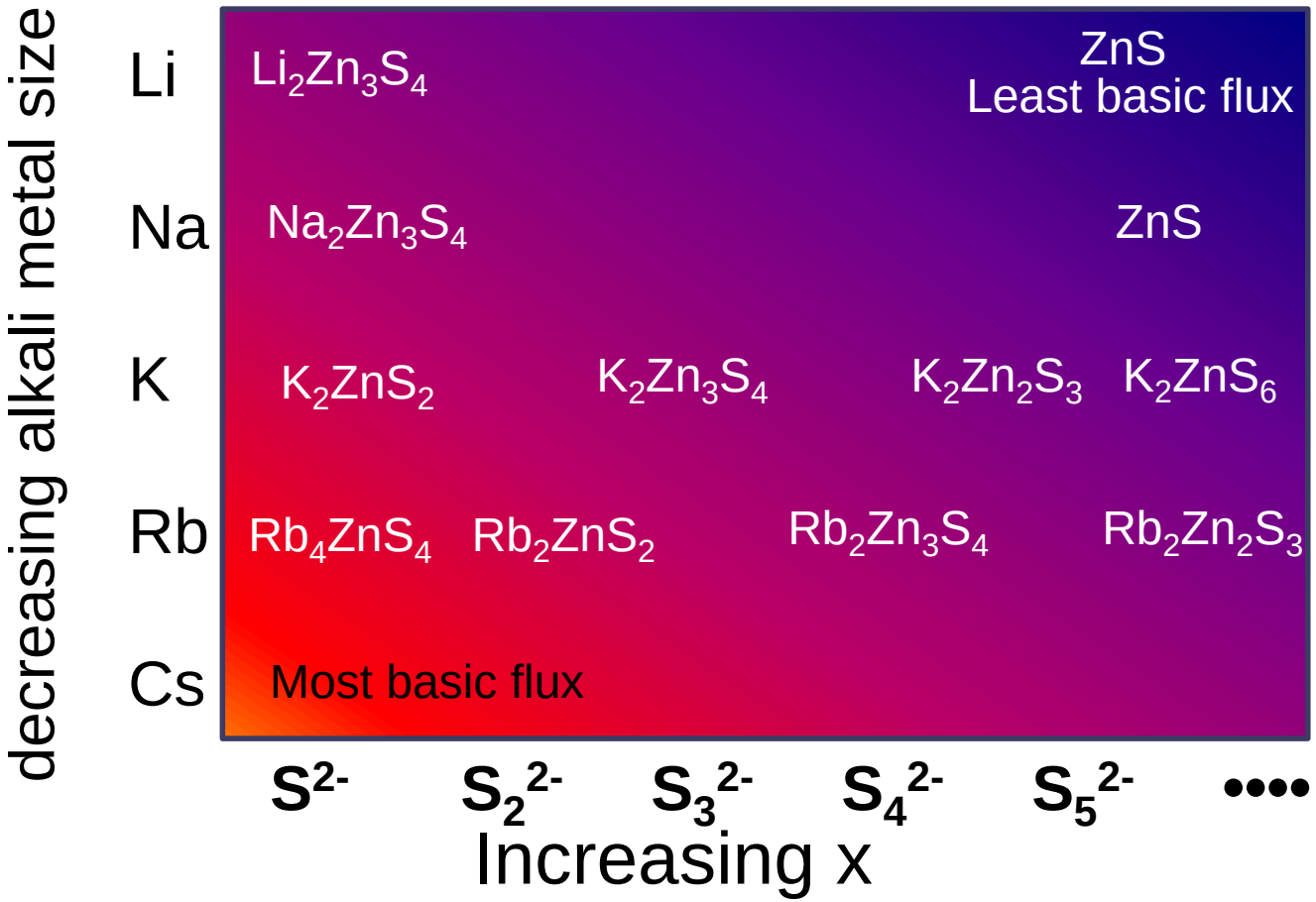


180-400 °C

- α-$KCuS_4$, β-$KCuS_4$,
- $KCuS_6$, KCu_4S_4

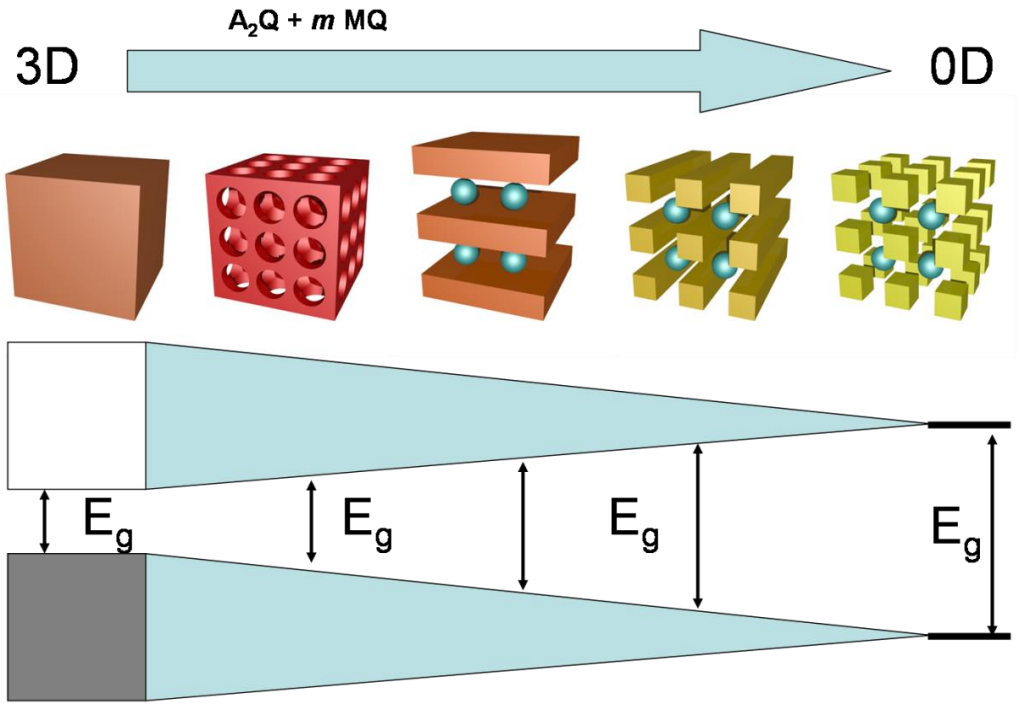
Tuning *basicity* in A_2Q_x controls reaction outcomes..

$$MQ + xs\ A_2Q_x \rightarrow A_zM_nQ_m + A_2Q_y$$



Bandgap increase through dimensional reduction of a covalent framework

- **by introducing A_2Q into MQ: $(A_2Q)_n(MQ)_m$**

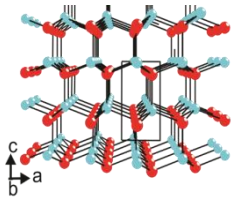


- From CdTe (1.4 eV) to $Cs_2Cd_3Te_4$ (E_g~2.3 eV) Z =(55, 48, 52)
- From HgTe (0 eV) to $Cs_2Hg_3Te_4$ (E_g~2.0 eV) Z =(55, 80, 52)

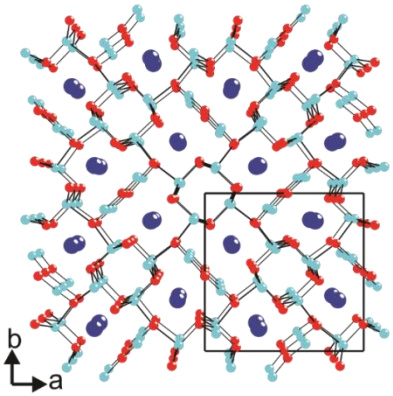
K. Biswas, Q. Zhang, I. Chung, J.H. Song, J. Androulakis, A.J. Freeman and M.G. Kanatzidis *J. Am. Chem. Soc.* **2010,** *132*, 14760.
J. Androulakis, J.; S.C. Peter, H. Li, C.D. Malliakas, J.A. Peters, Z. Liu, B.W. Wessels, J.H. Song, H. Jin, A.J. Freeman and M.G. Kanatzidis *Adv. Mater.* **2011**, *23*, 4163

A specific example…

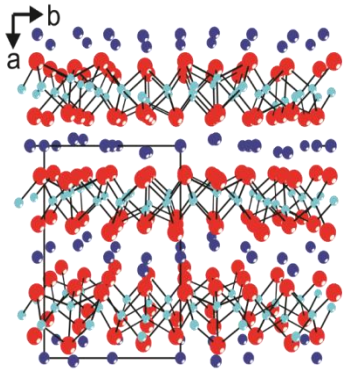
CdS :: 3D



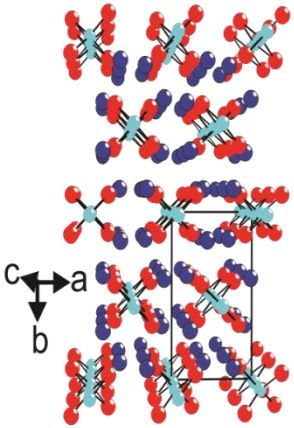
$K_2M_6S_7$ :: 3D



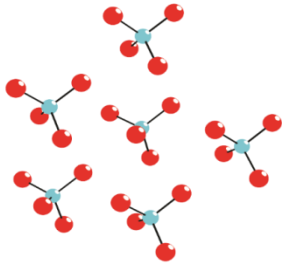
$K_2Cd_3S_4$ :: 2D



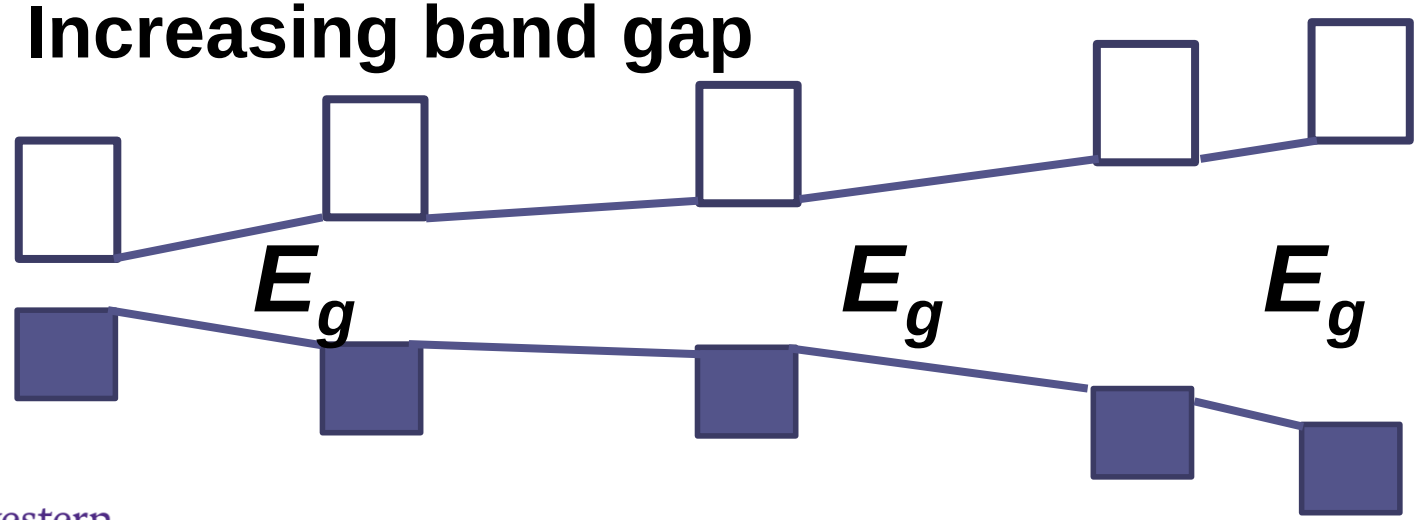
Na_2CdS_2:: 1D



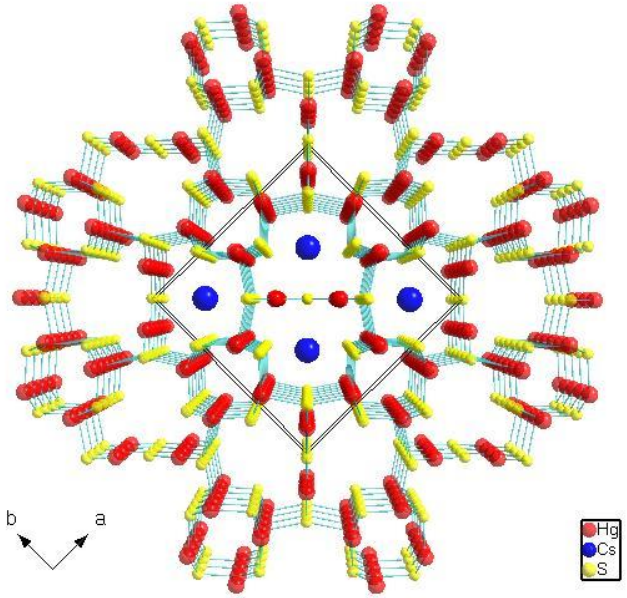
Na_6CdS_4:: 0D

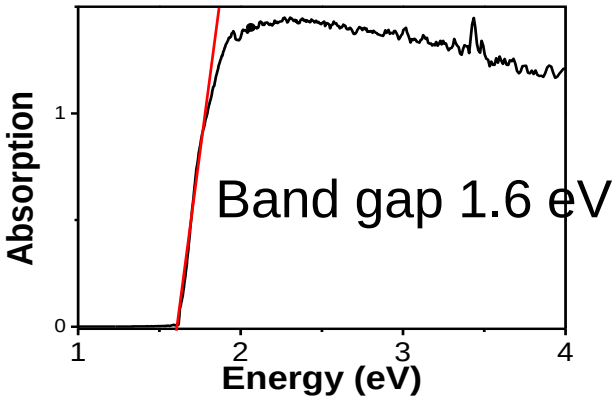


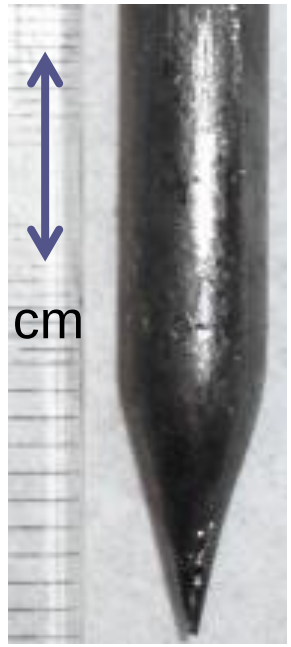
Increasing band gap



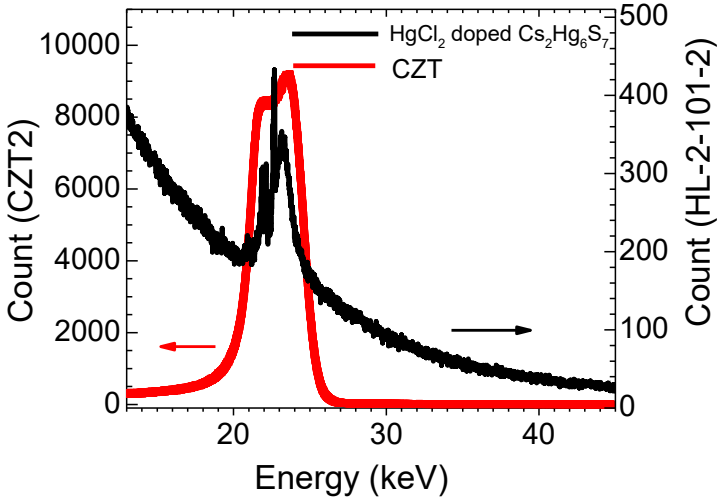
$Cs_2Hg_6S_7$: A new X-ray and γ-ray detector from dimensional reduction

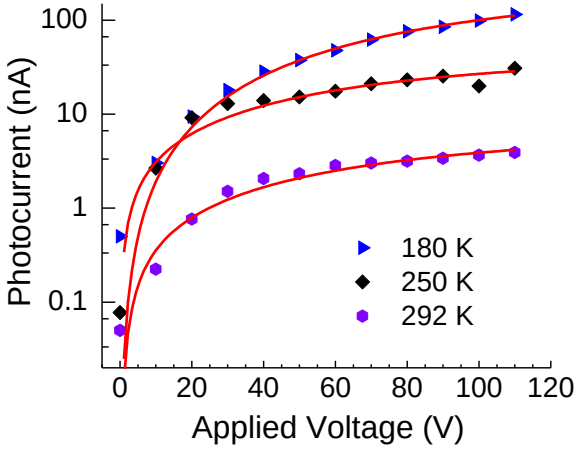






Ag X-ray response

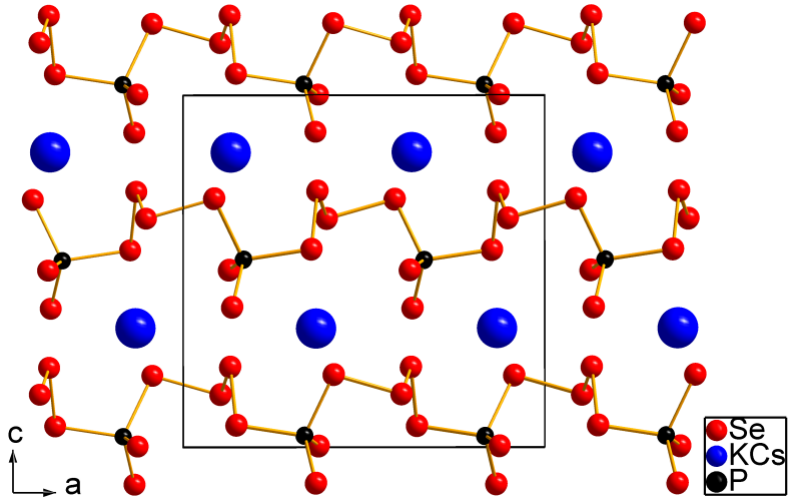


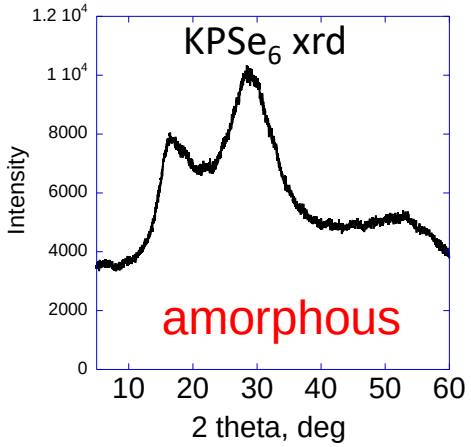


With Bruce Wessels

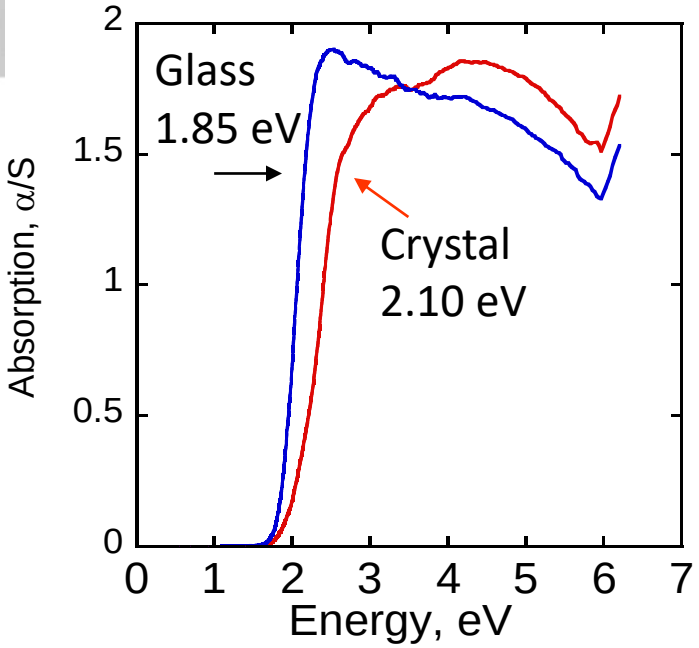
J.A. Peters, N.K. Cho, Z.F. Liu, B.W. Wessels, H. Li, J. Androulakis and M.G. Kanatzidis *J. Appl. Phys.* **2012,** *112,* 063702

$KPSe_6$ crystal and glass





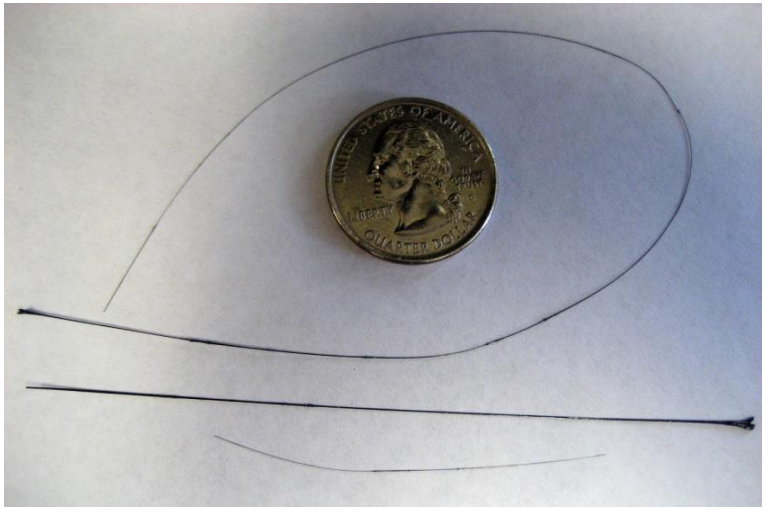
- $APSe_6$ (A = K, Rb)
  - Polar structure $Pca2_1$
  - $KPSe_6$ $\chi^{(2)}$ = 151.3 pm V^{-1}
  - $RbPSe_6$ $\chi^{(2)}$ = 149.4 pm V^{-1}
  - Phase-matchable

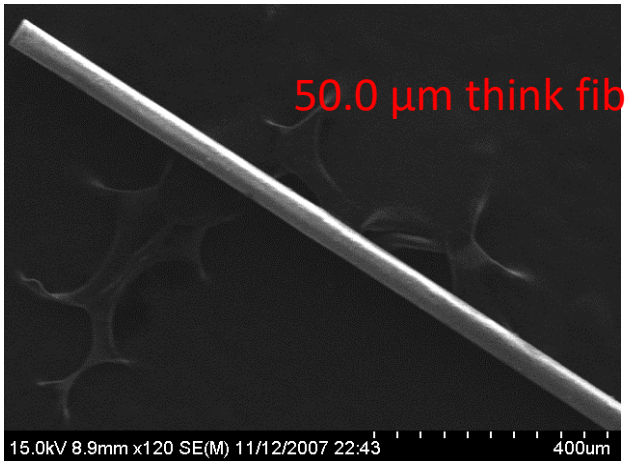


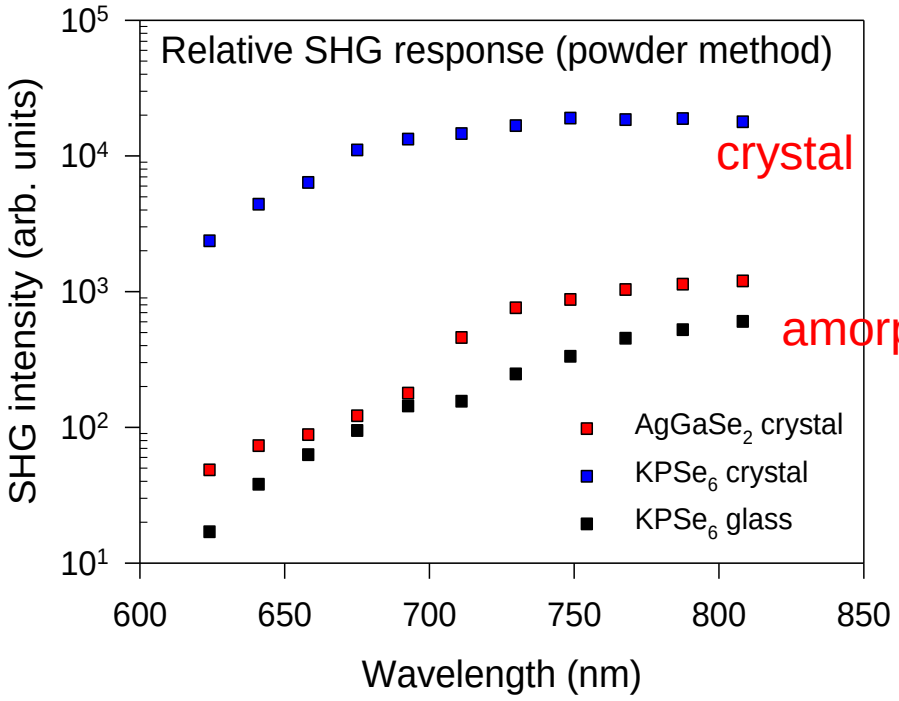
Haynes, A. S.; Saouma, F. O.; Otieno, C. O.; Clark, D. J.; Shoemaker, D. P.; Jang, J. I.; Kanatzidis, M. G., *Chem Mater*, **2015,** *27*, 1837,
I. Chung, M.G. Kim, J.I. Jang, J. He, J.B. Ketterson and M.G. Kanatzidis *Angew. Chem. Int. Ed.* **2011,** *50*, 10867

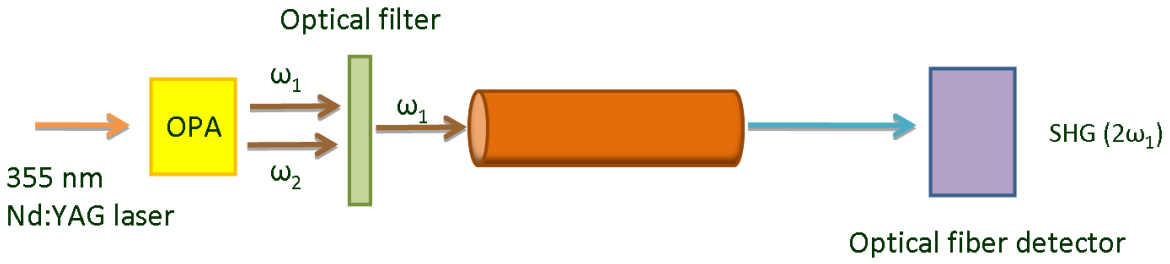
$KPSe_6$ amorphous fiber

Nonlinear optic second harmonic generation









I. Chung, J.I. Jang, C.D. Malliakas, J.B. Ketterson and M.G. Kanatzidis *J. Am. Chem. Soc.* **2010,** *132*, 384-389

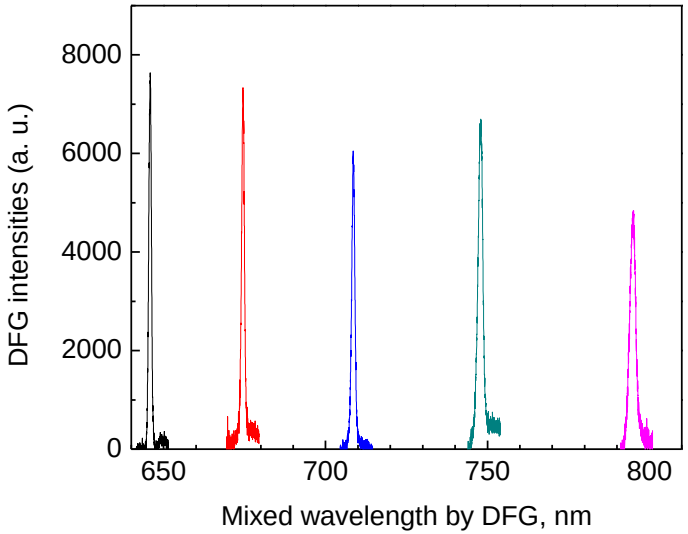
With Professor John Ketterson, NU

Waveguide mode and Difference frequency generation (DFG) from amorphous $KPSe_6$ fiber

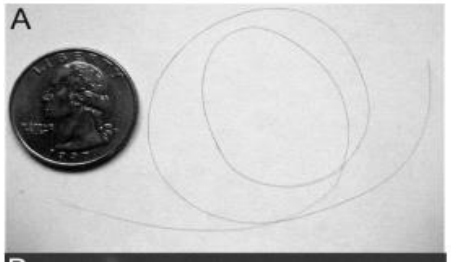
$\omega 1 + \omega 2 = \omega 3$

$\omega 1 - \omega 2 = \omega 4$

Largest permanent NLO response from any glass!



Used incident beams		Calculated mixed light
λ_1 (nm)	λ_2 (nm)	λ_{DFG} (nm)
1575.0	458.3	646.4
1477.4	467.3	683.4
1420.5	473.3	709.8
1350.1	481.6	748.8
1282.1	490.9	795.6



I. Chung, J.I. Jang, C.D. Malliakas, J.B. Ketterson and M.G. Kanatzidis *J. Am. Chem. Soc.* **2010,** *132*, 384-389

$KPSe_6$ crystal: ~160 pm /V

$KPSe_6$ glass : ~9-14 pm/ V

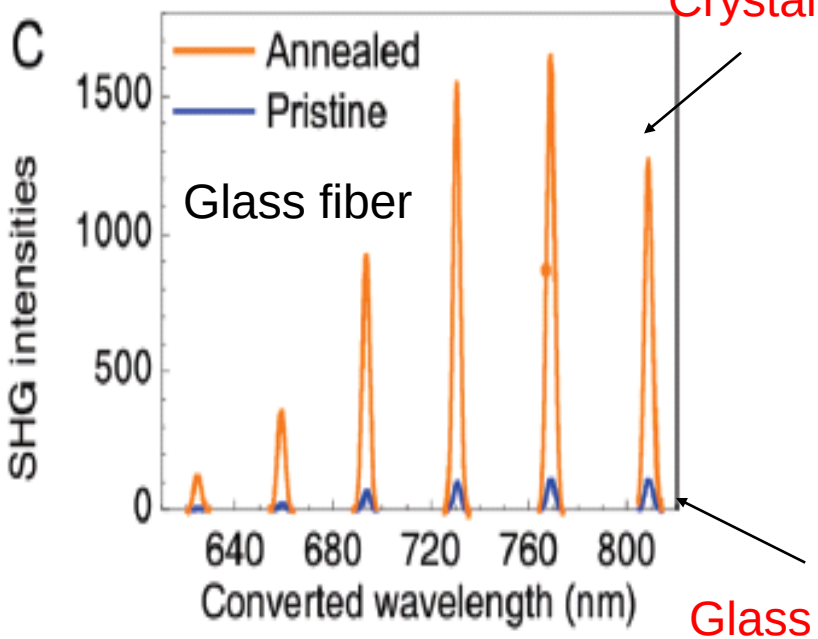
Benchmarks: $ZnGeP_2$: ~75 pm/ V

$AgGaSe_2$: ~40 pm/ V

$KTiPO_4$: ~16.6 pm /V

$KNbO_3$: ~10.8 – 27 pm /V

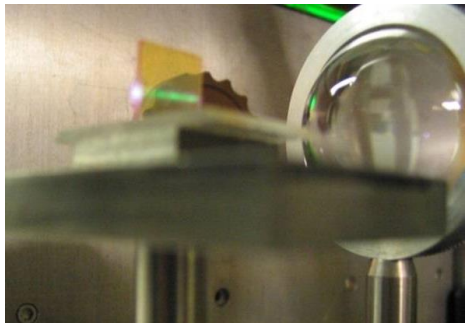
$KPSe_6$: Major SHG enhancement with fiber annealing



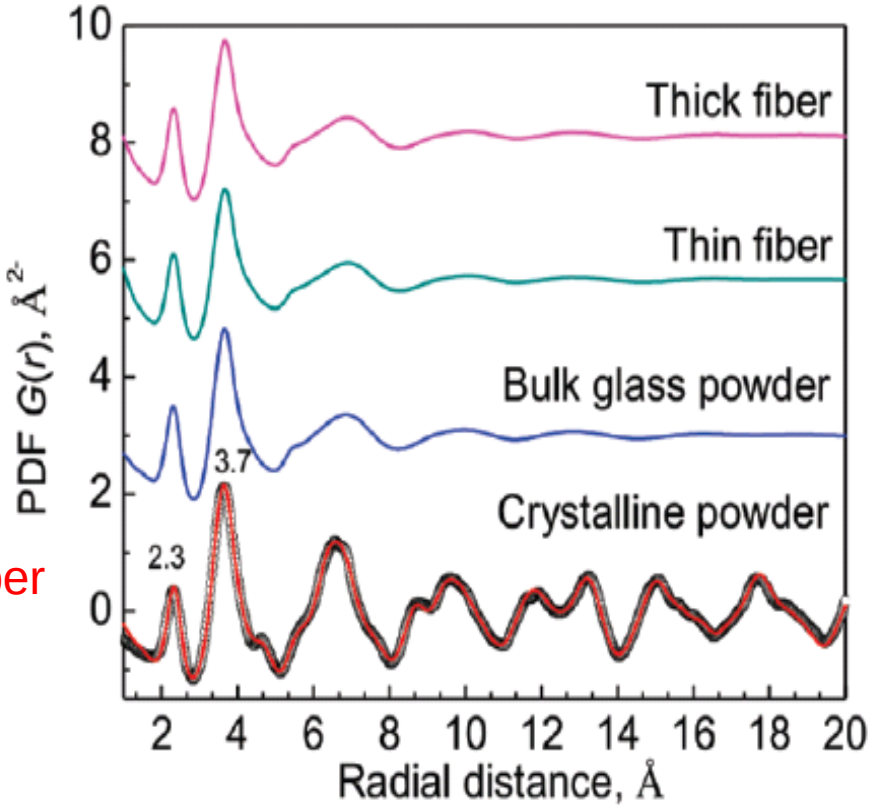
Crystal fiber

Glass fiber

Propagating SHG signal



Pair distribution functions



The local structure of the amorphous form is the same as the crystal

Investigating the A/Bi/Q system

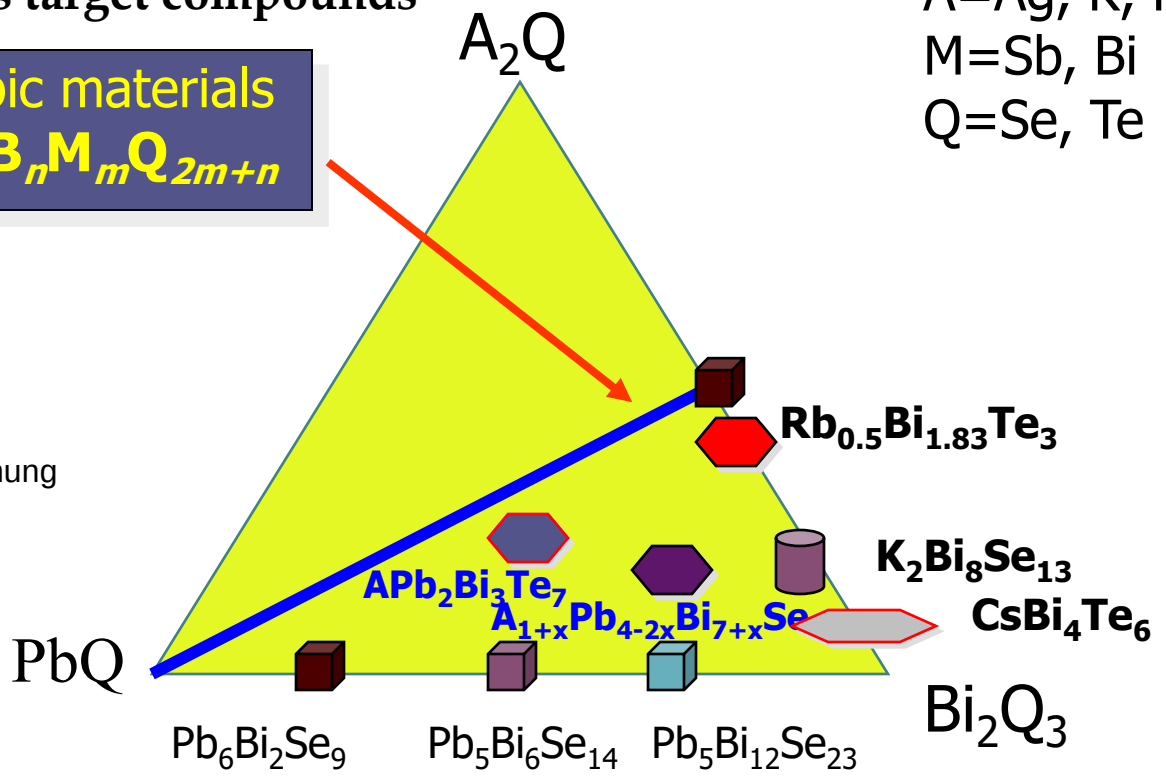
$$A_2Q + PbQ + M_2Q_3 \longrightarrow (A_2Q)_n(PbQ)_m(M_2Q_3)_p$$

Map generates target compounds

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

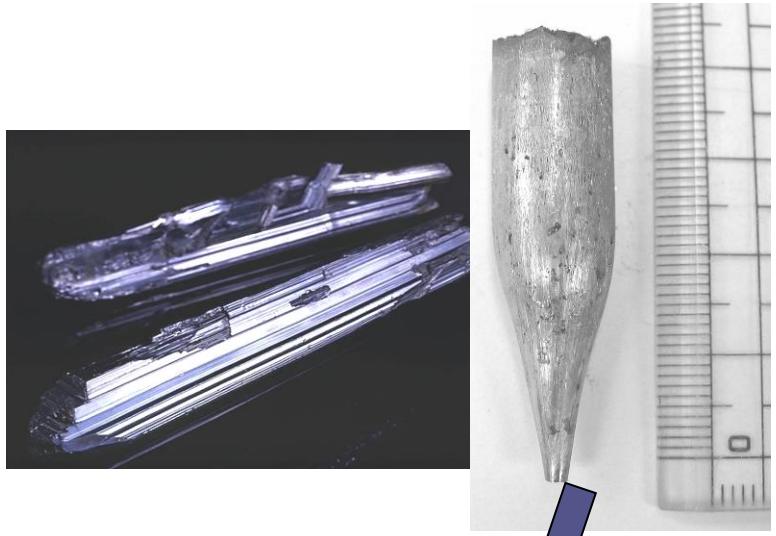
Cubic materials
$A_mB_nM_mQ_{2m+n}$

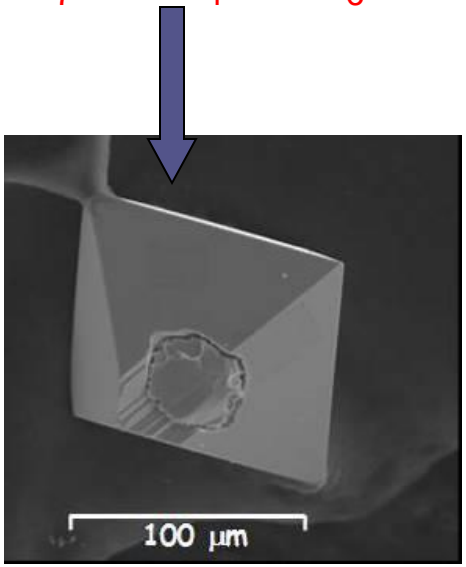
Duck Young Chung

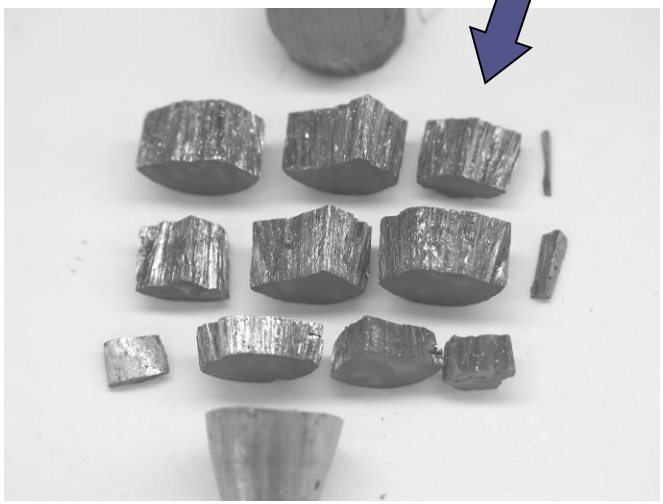


A wealth of compounds

- $K_2Bi_8Se_{13}$, $KPb_7Bi_9Se_{21}$, $KPb_4Sb_7Se_{15}$
- $CsPb_5Bi_{10}Se_{21}$
- $CsPbBi_3Te_6$, $CsPb_2Bi_3Te_7$, $RbPbBi_3Te_6$, $RbPb_2Bi_3Te_7$, $RbPb_3Bi_3Te_8$,
- $KPbBiSe_3$, $K_2PbBi_2Se_5$
- $K_2Pb_3Bi_2Te_7$, KPb_4SbTe_6

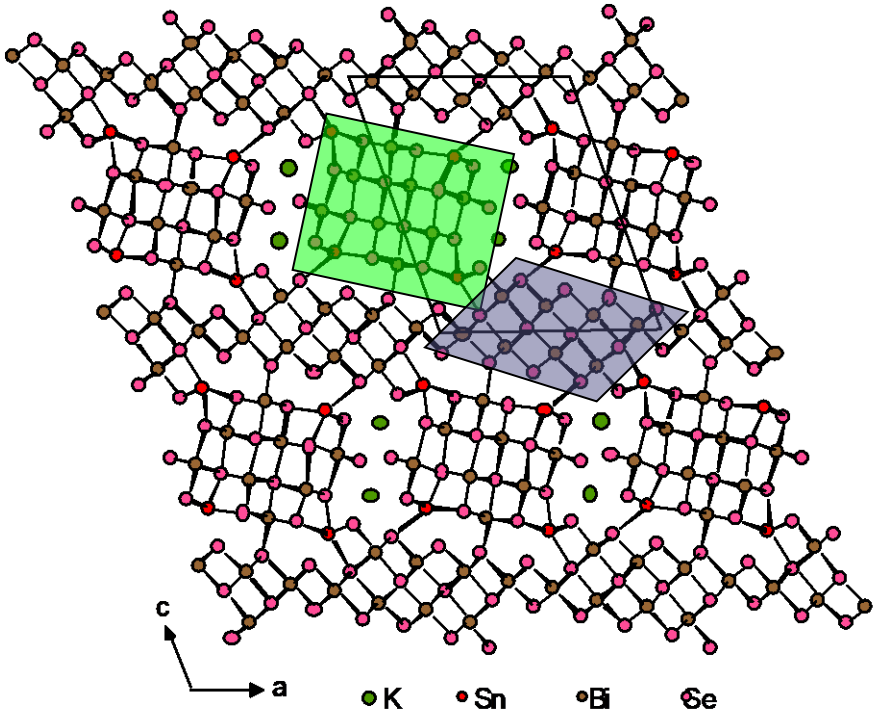




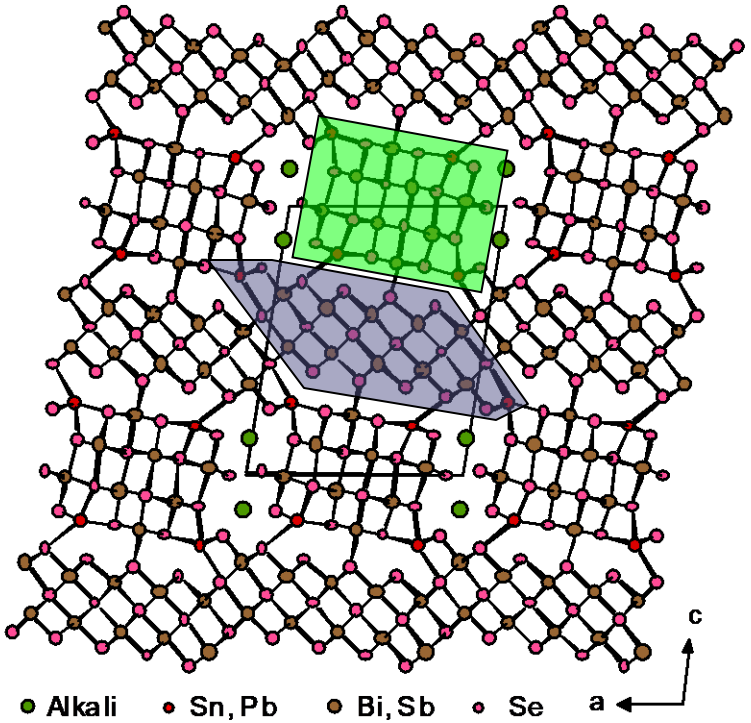


$KM_3Bi_7Se_{14}$ vs. $KM_4Bi_7Se_{15}$

(M= Sn, Pb)



$K_{2.5}Bi_{8.5}Se_{14}$, $K_{1.45}Sn_{2.10}Bi_{7.45}Se_{14}$

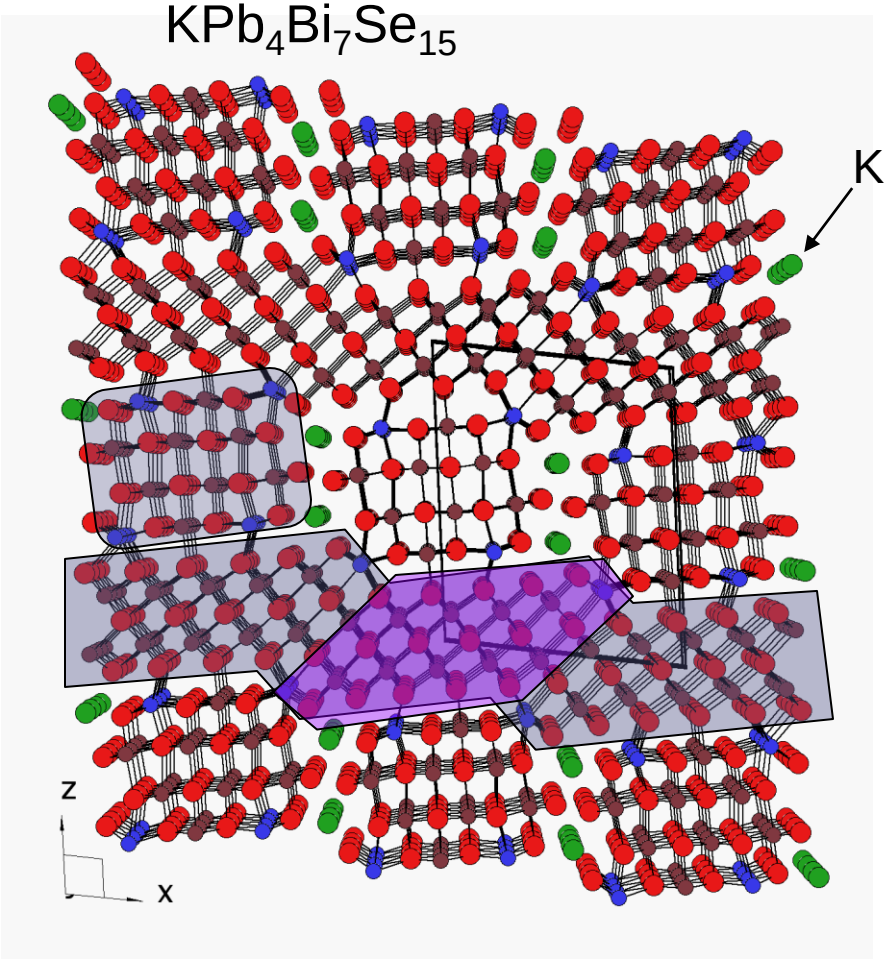


$KSn_4Bi_7Se_{15}$, $KPb_4Bi_7Se_{15}$, $KPb_4Sb_7Se_{15}$, $RbPb_4Sb_7Se_{15}$

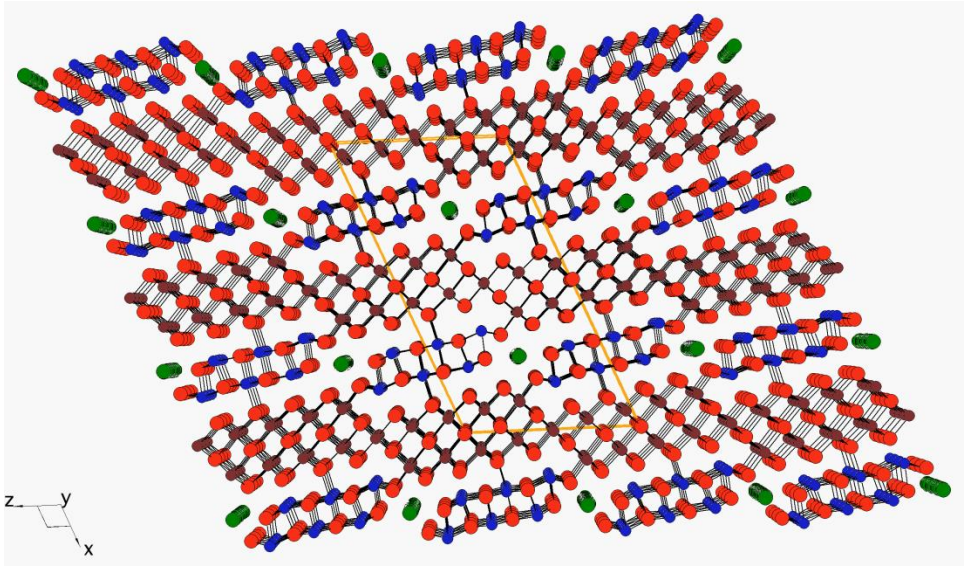
Northwestern University

M.G. Kanatzidis, *Acc. Chem. Res.* **2005**, *38*, 111. 359

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

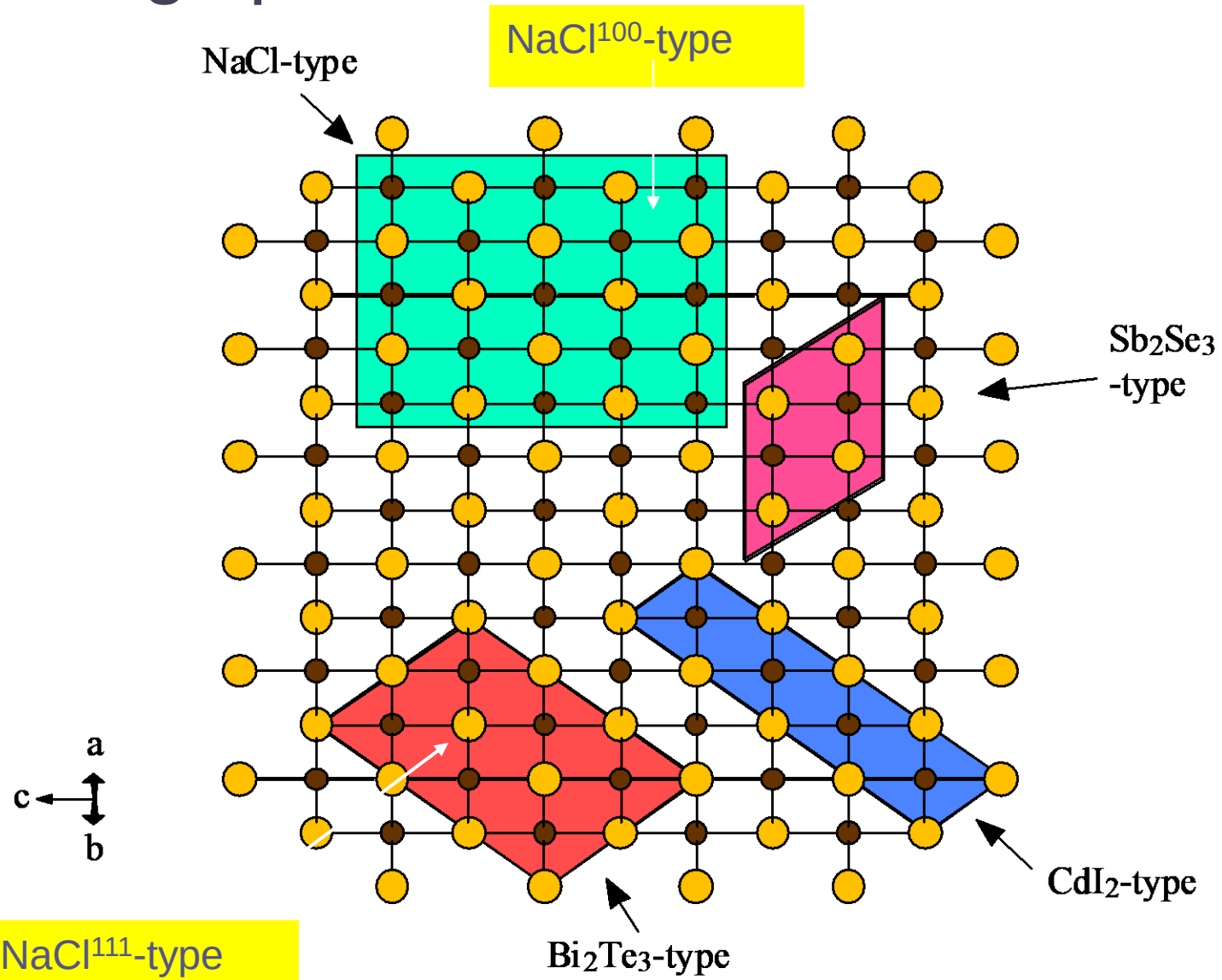


$CsPb_7Bi_9Se_{21}$



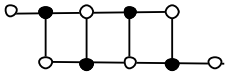
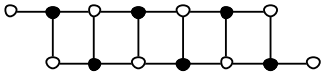
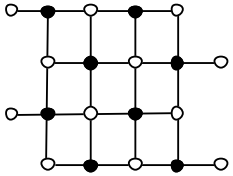
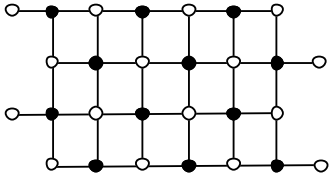
Narrow gap semiconductors

Carving up the NaCl lattice

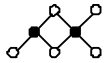
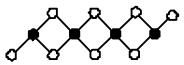
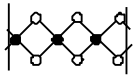
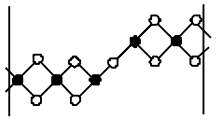
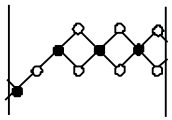
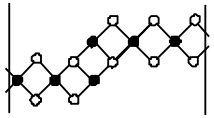
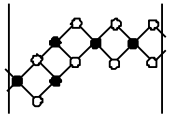
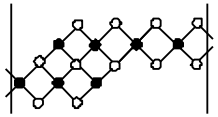
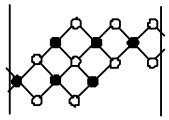
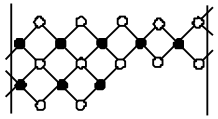
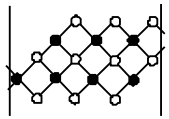
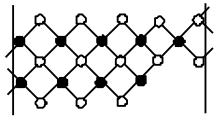
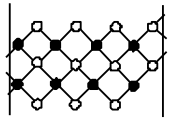
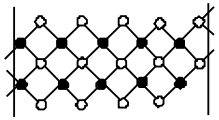
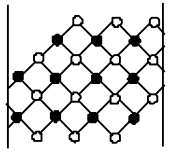
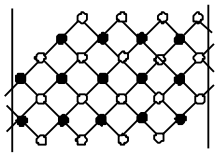


Modular Chemistry : $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$

A series is born…

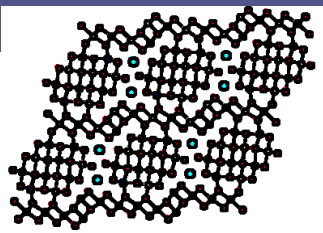
m \ l	1, $[M_2Se_3]_{2m}$	2, $[M_3Se_4]_{2m}$
1	 M_4Se_6	 M_6Se_8
2	 M_8Se_{12}	 $M_{12}Se_{16}$

Adjustable modules

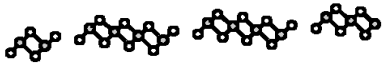
n \ l	1, $M_{2+n}Se_{5+n}$	2, $M_{4+n}Se_{8+n}$
0	 M_2Se_5	 M_4Se_8
1	 M_3Se_6	 M_5Se_9
2	 M_4Se_7	 M_6Se_{10}
3	 M_5Se_8	 M_7Se_{11}
4	 M_6Se_9	 M_8Se_{12}
5	 M_7Se_{10}	 M_9Se_{13}
6	 M_8Se_{11}	 $M_{10}Se_{14}$
	 $M_{11}Se_{14}$ (n=9)	 $M_{14}Se_{18}$ (n=10)

M.G. Kanatzidis, *Acc. Chem. Res.* **2005**, *38*, 111. 359

Member generating scheme

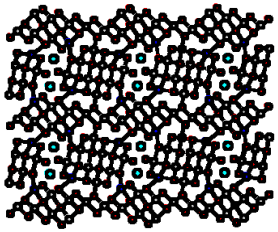


$Rb_{1+x}Sn_{1-2x}Bi_{7+x}Se_{12}$

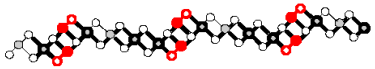


M_4Se_8-layer (n = 0)

+ 2 MSe



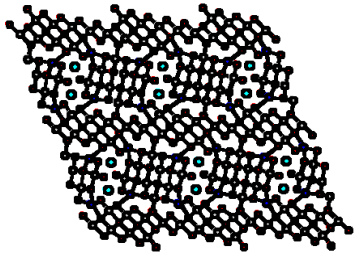
β-$K_2Bi_8Se_{13}$, $K_{1+x}M'_{2-2x}Bi_{7+x}Se_{13}$, $Sr_4Bi_6Se_{13}$-type (~ 20 compounds)



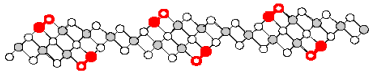
M_6Se_{10}-layer (n = 2)

?
(e.g. $KSnBi_{11}Se_{18}$)

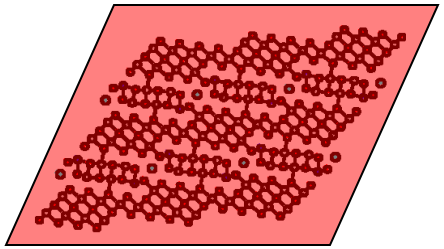
+ 2 MSe



$K_{2.5}Bi_{8.5}Se_{13}$, $A_{1+x}M'_{3-2x}Bi_{7+x}Se_{14}$



M_8Se_{12}-layer (n = 4)

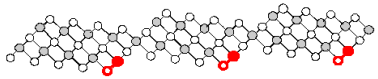


$A_{1-x}M'_{3-x}Bi_{11+x}Se_{20}$

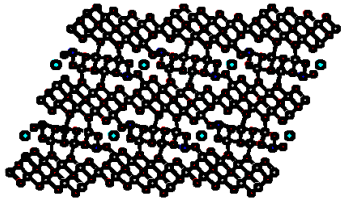
Predicted

+ 1 MSe

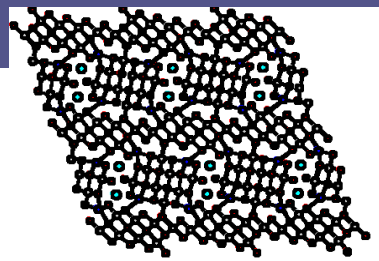
?
(e.g. $K_2Sn_7Bi_{14}Se_{29}$)



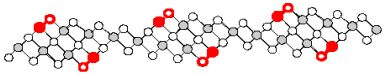
M_9Se_{13}-layer (n = 5)



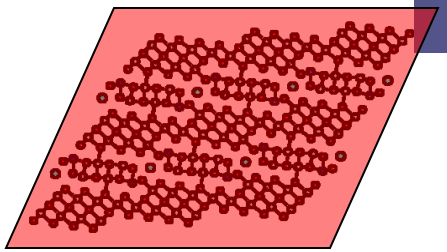
$A_{1-x}M'_{4-x}Bi_{11+x}Se_{21}$



$K_{2.5}Bi_{8.5}Se_{13}$, $A_{1+x}M'_{3-2x}Bi_{7+x}Se_{14}$



M_8Se_{12}-layer (n = 4)



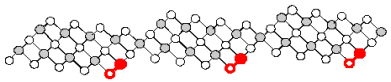
$A_{1-x}M'_{3-x}Bi_{11+x}Se_{20}$

Predicted

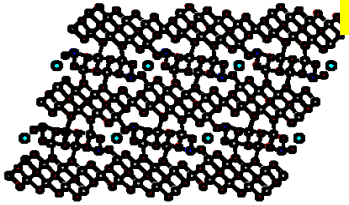
Member generating scheme

+ 1 MSe

?
(e.g. $K_2Sn_7Bi_{14}Se_{29}$)

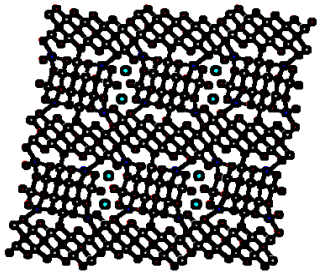


M_9Se_{13}-layer (n = 5)

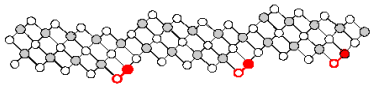


$A_{1-x}M'_{4-x}Bi_{11+x}Se_{21}$

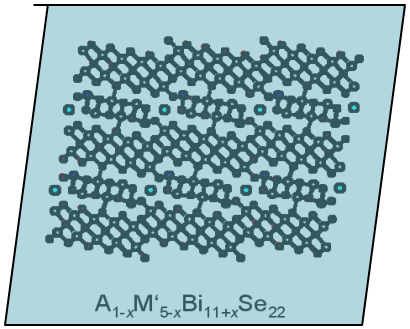
+ 1 MSe



$A_{1+x}M'_{4-2x}M''_{7+x}Se_{15}$



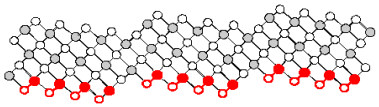
$M_{10}Se_{14}$-layer (n = 6)



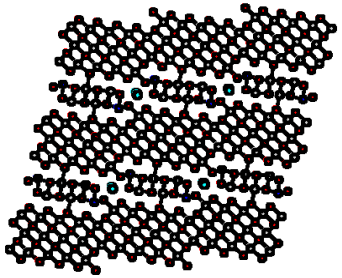
$A_{1-x}M'_{5-x}Bi_{11+x}Se_{22}$

+ 4 MSe

?
(e.g. $K_2Sn_{14}Bi_{14}Se_{34}$)



$M_{14}Se_{18}$-layer (n = 10)

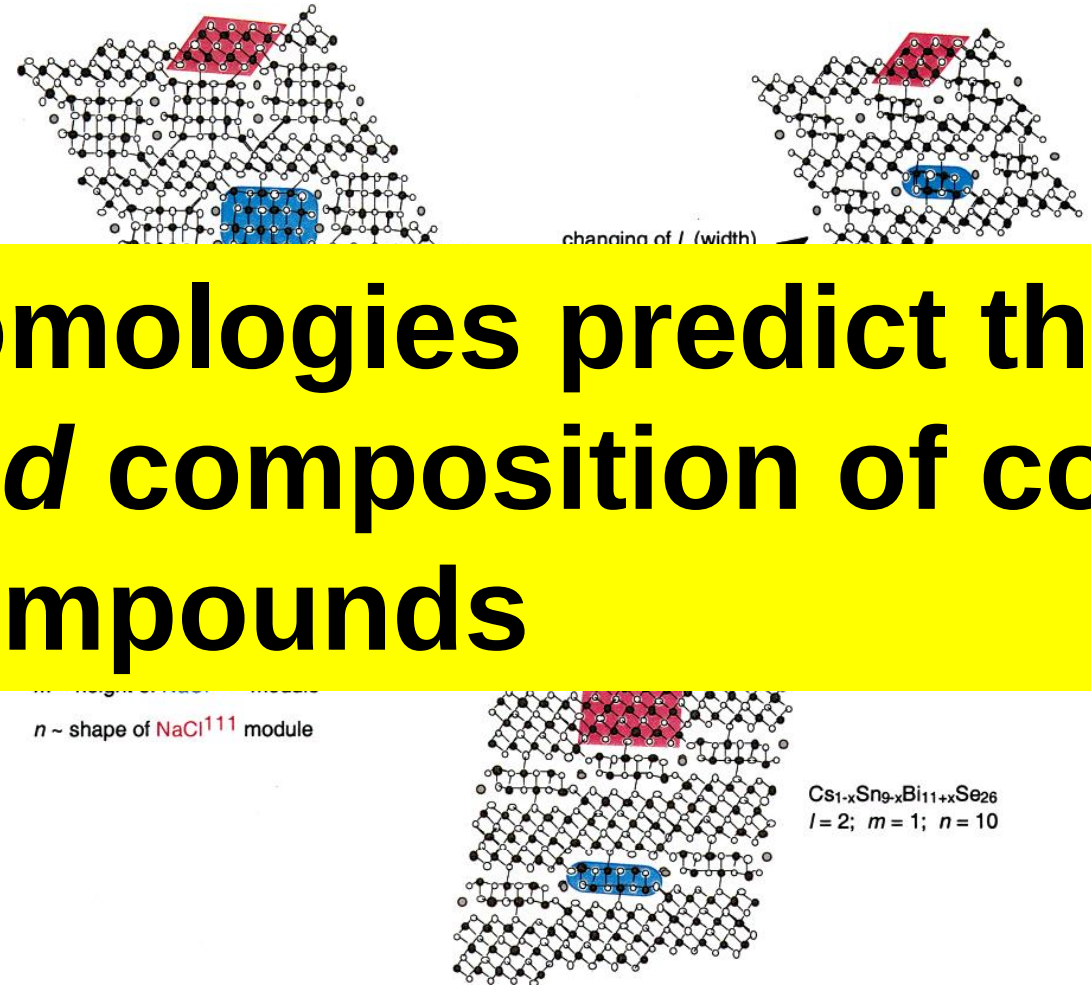


A = K, Rb, Cs, Sr, Ba

Mrotzek and Kanatzidis
Accounts of Chemical Research,
2003

Prediction of Structure using phase homologies

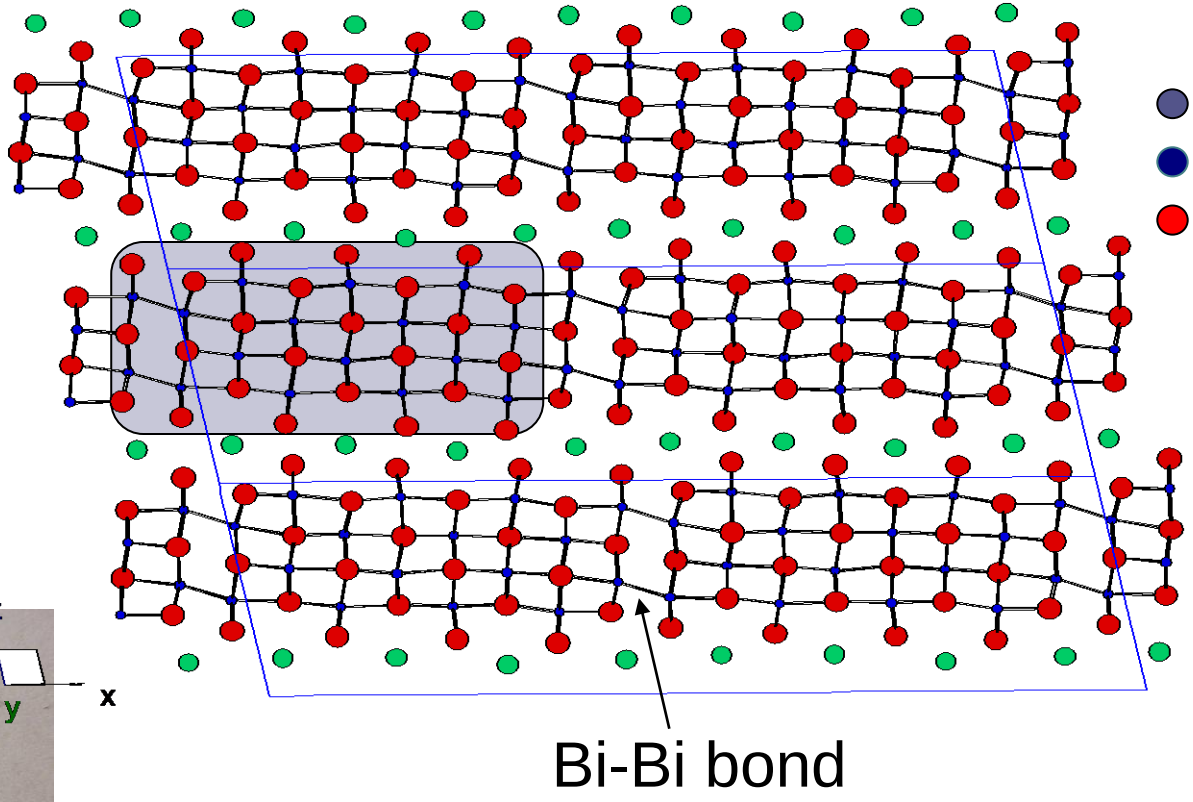
$A_m [M_{1+l} Se_{2+l}]_{2m} [M_{2l+n} Se_{2+3l+n}]$



homologies predict the structure *and* composition of countless compounds

M.G. Kanatzidis, *Acc. Chem. Res.* **2005**, *38*, 111. 359

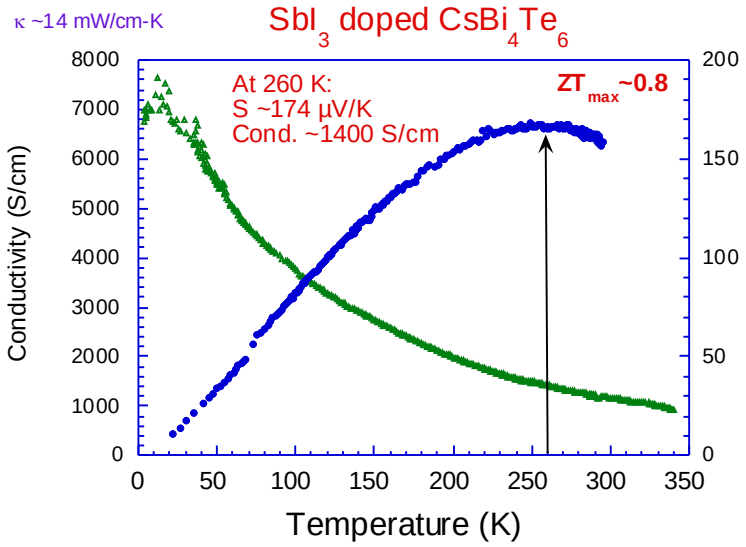
$CsBi_4Te_6$

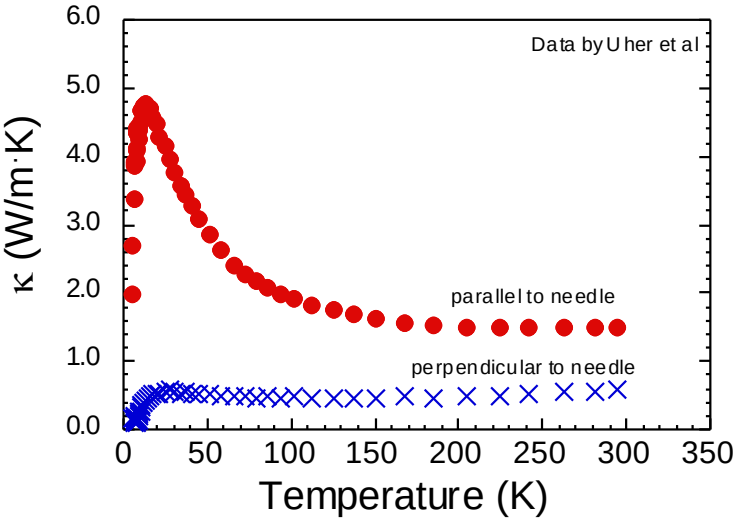


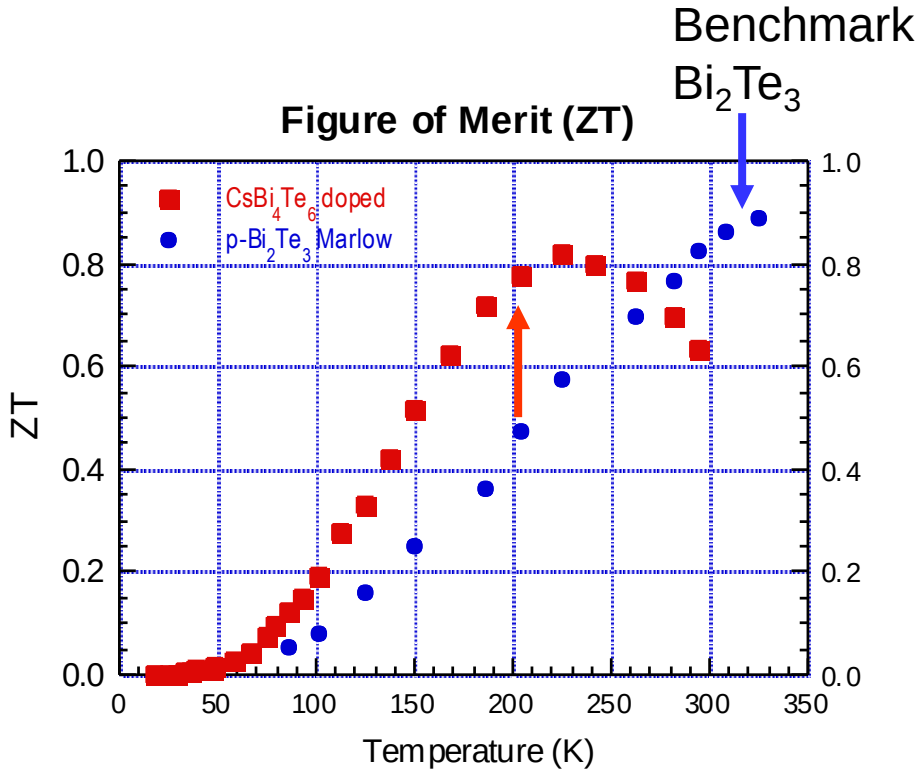
C.D. Malliakas, D.Y. Chung, H. Claus and M.G. Kanatzidis *J. Am. Chem. Soc.,* 2013, *135,* 14540-14543.

High performance thermoelectric material $CsBi_4Te_6$

At 225 K :
σ 1733 S/cm,
S 177 μV/K,
κ 1.48 W/m·K







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

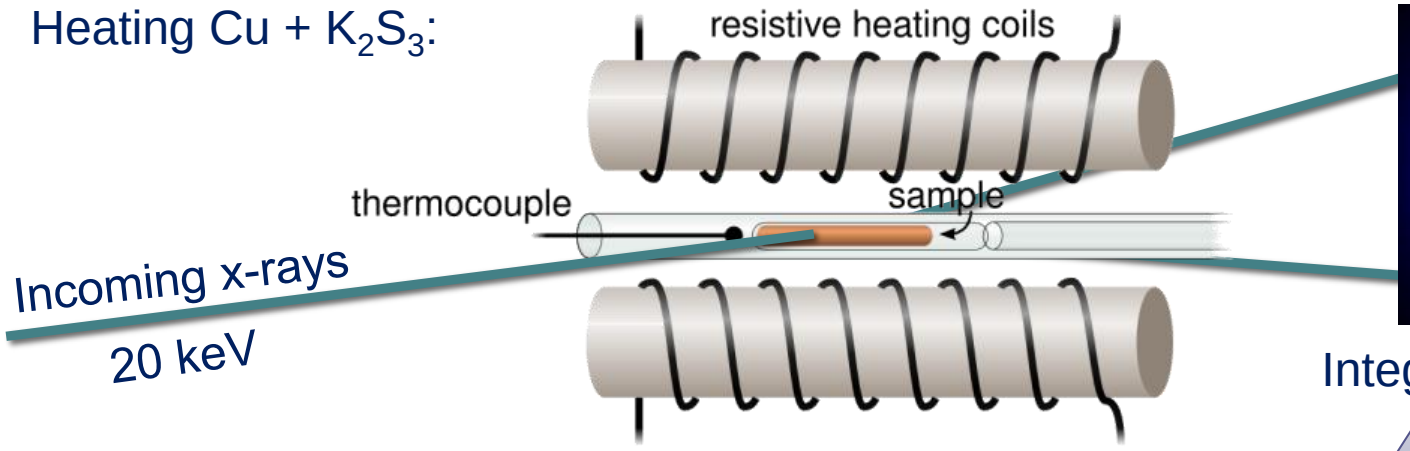
What if we could be aware of all phases present in a given reaction system?

These reactions give many new compounds, but mechanisms are poorly understood:
Do crystals form on cooling? Or at high temperature? Or on heating?
Is the system in equilibrium? *In situ* synthesis can shed light to these questions…

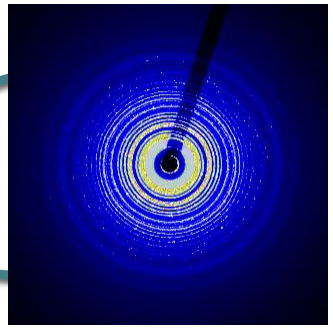
P. J. Chupas *et al, J. Appl. Cryst*. **41** 822 (2008)

Anatomy of *in situ* synthesis

Heating Cu + K_2S_3:



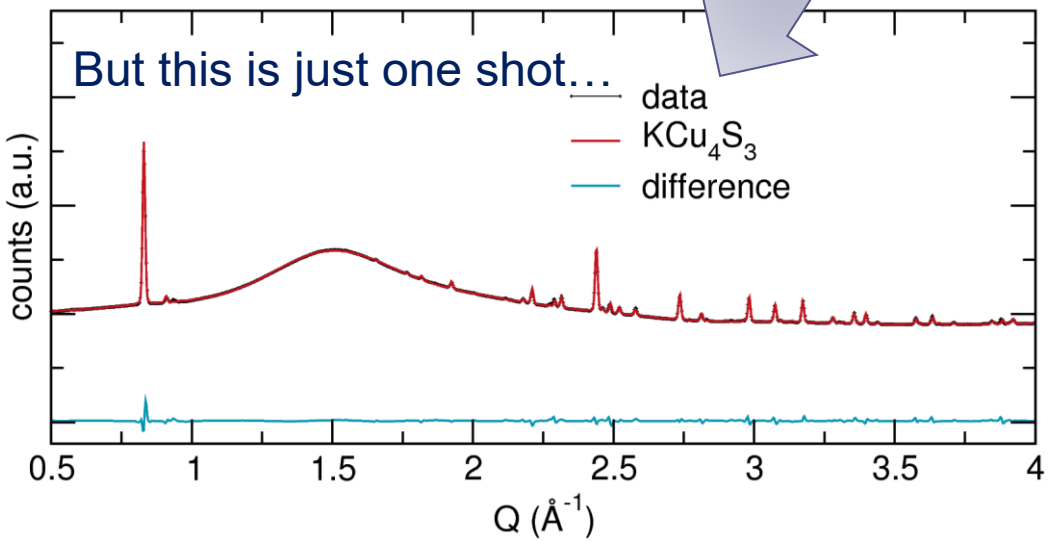
2D detector



Integrate for 1D pattern

Data:

Rietveld refinement identifies phases



Shoemaker, D. P.; Hu, Y. J.; Chung, D. Y.; Halder, G. J.; Chupas, P. J.; Soderholm, L.; Mitchell, J. F.; Kanatzidis, M. G., *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10922

Anatomy of *in situ* synthesis

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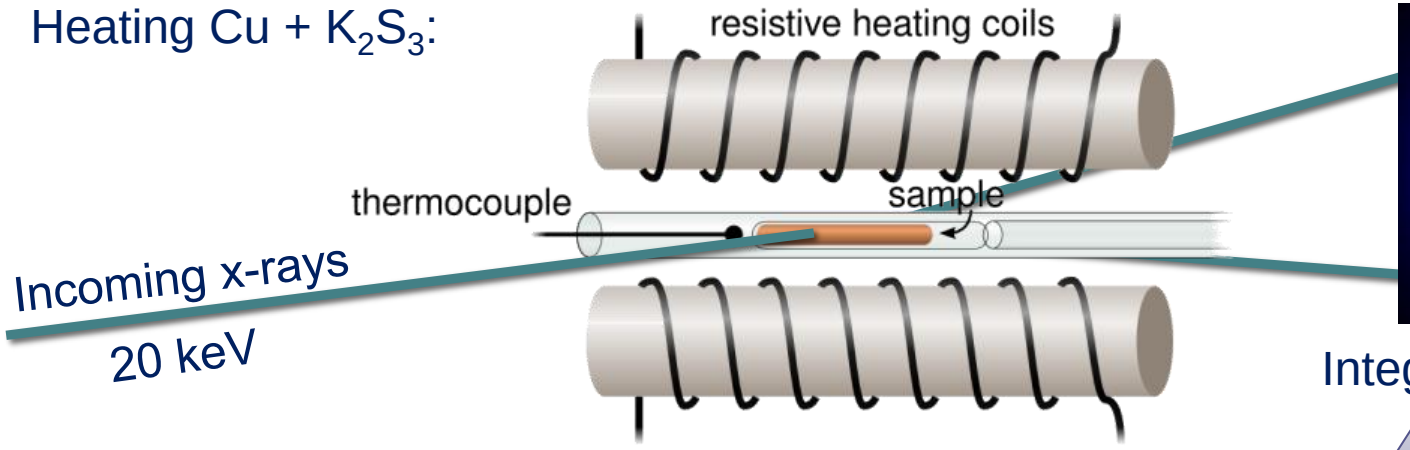
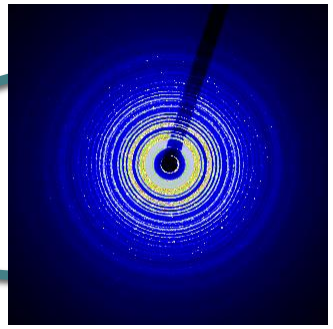
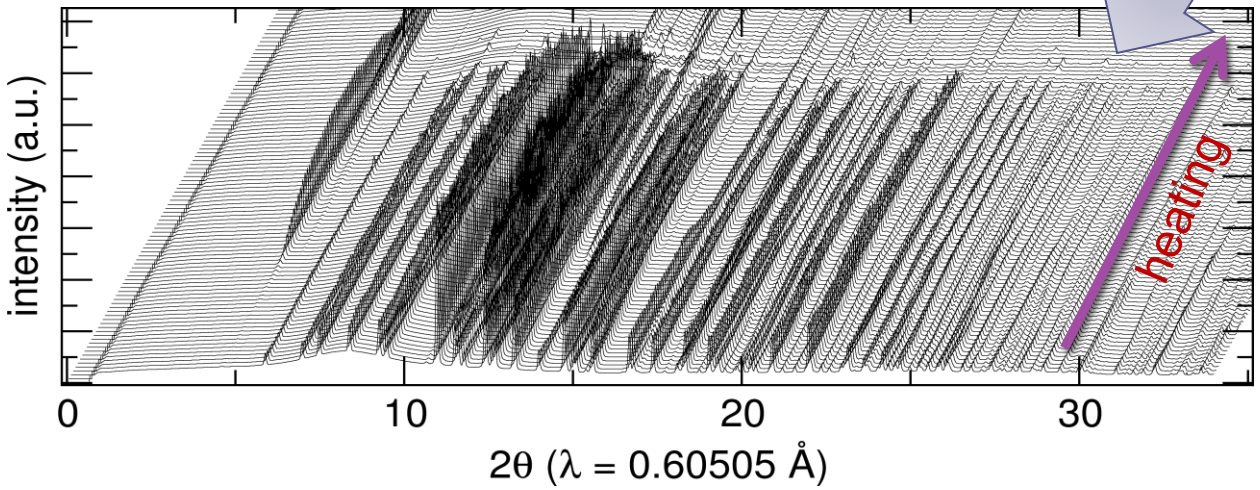


2D detector



Integrate for 1D pattern

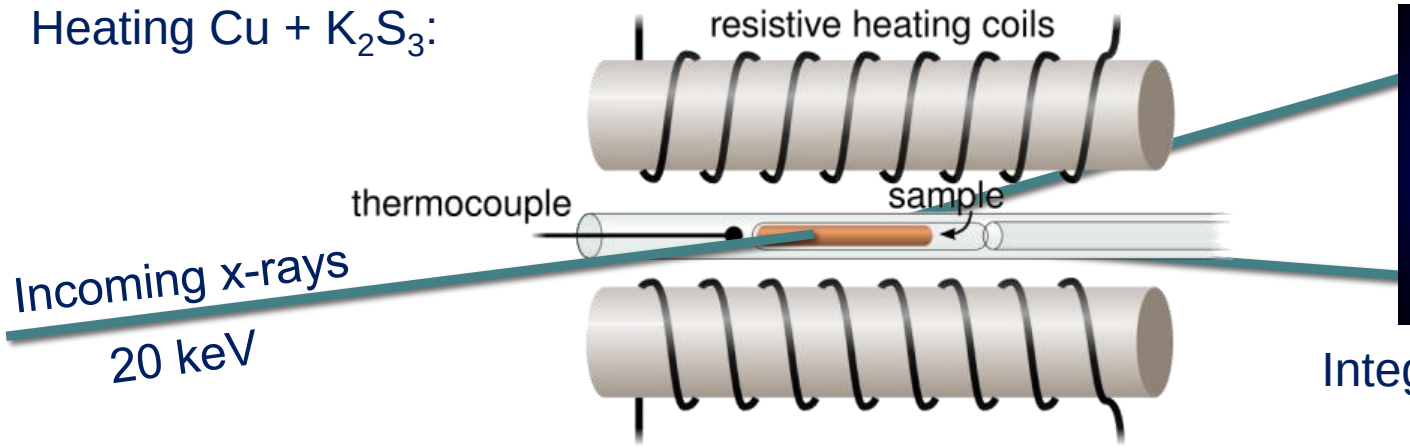
Data:



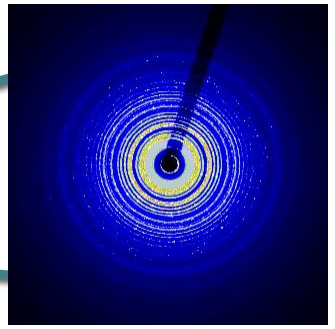
Shoemaker, D. P.; Hu, Y. J.; Chung, D. Y.; Halder, G. J.; Chupas, P. J.; Soderholm, L.; Mitchell, J. F.; Kanatzidis, M. G., *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10922

Anatomy of *in situ* synthesis

Heating Cu + K_2S_3:

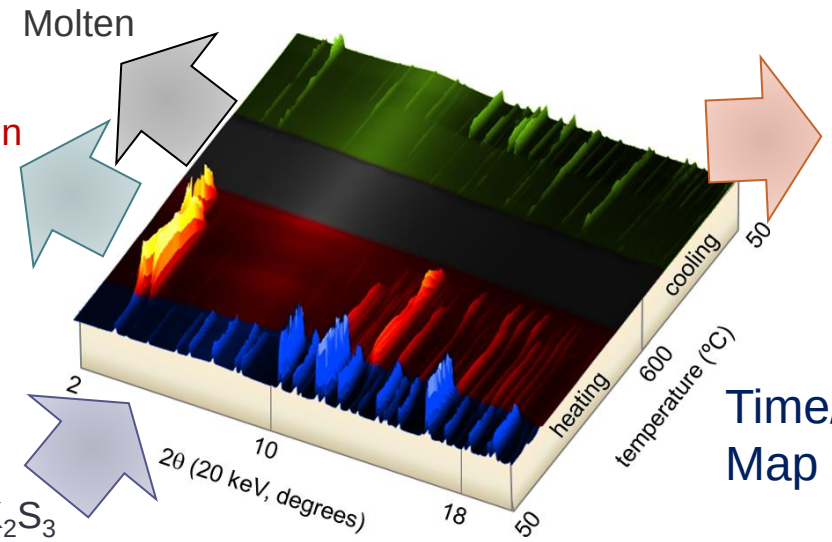


2D detector



Integrate for 1D pattern

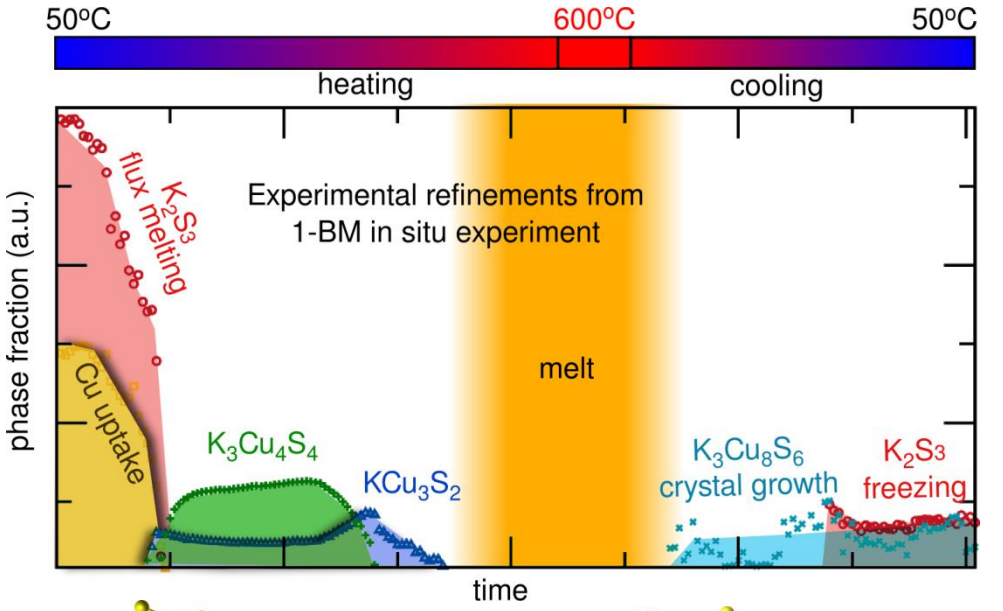
Data:

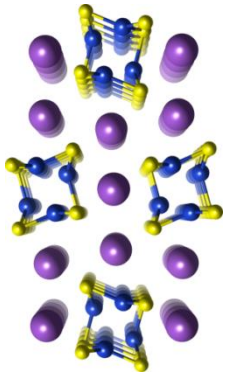


Time/Temperature dependence
Map molten and crystalline regions

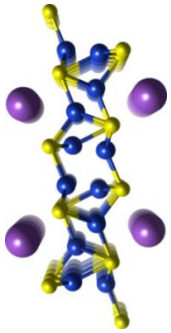
Shoemaker, D. P.; Hu, Y. J.; Chung, D. Y.; Halder, G. J.; Chupas, P. J.; Soderholm, L.; Mitchell, J. F.; Kanatzidis, M. G., *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10922

In situ (panoramic) synthesis map of Cu + K_2S_3

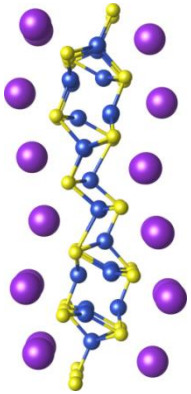




New phase
$K_3Cu_4S_4$



KCu_3S_2



$K_3Cu_8S_6$

New phases form on heating, different phase upon cooling

Similarities between phases imply the ability to tailor linkages and topology

Materials discovery: New $K_3Cu_4S_4$ phase

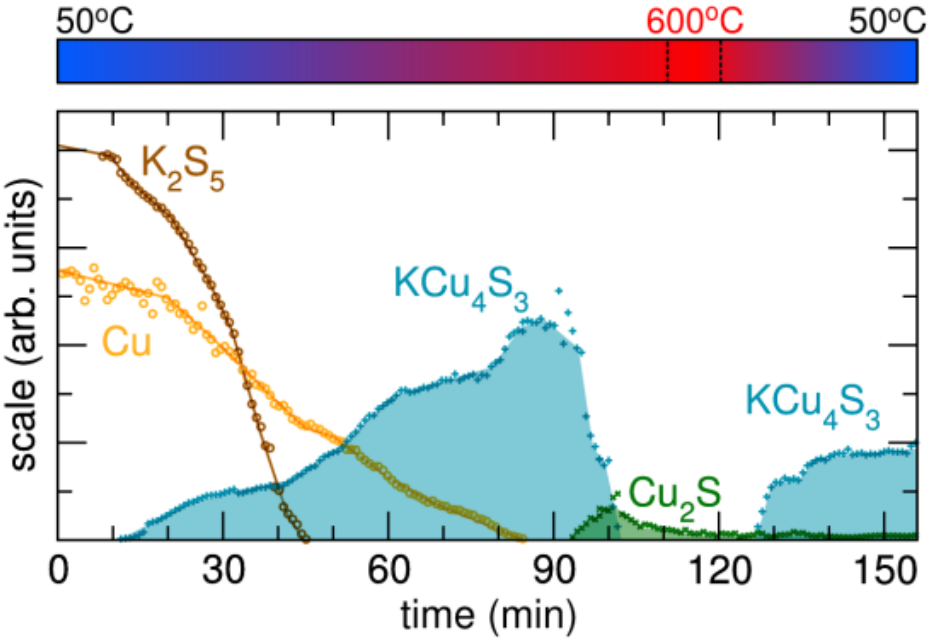
Crystal growth: Conditions found for $K_3Cu_8S_6$

Synthesis tuning: What happens when we change the reaction, for example the sulfur content?

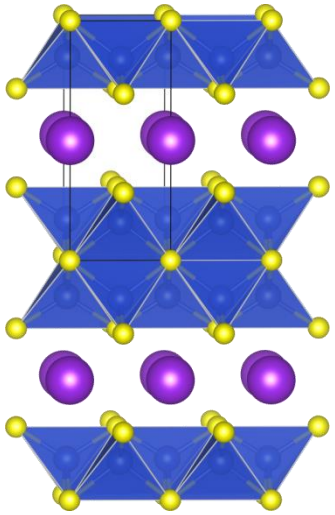
Shoemaker, D. P.; Hu, Y. J.; Chung, D. Y.; Halder, G. J.; Chupas, P. J.; Soderholm, L.; Mitchell, J. F.; Kanatzidis, M. G., *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 10922

Changing flux sulfur content, Cu + K_2S_5

Panoramic synthesis

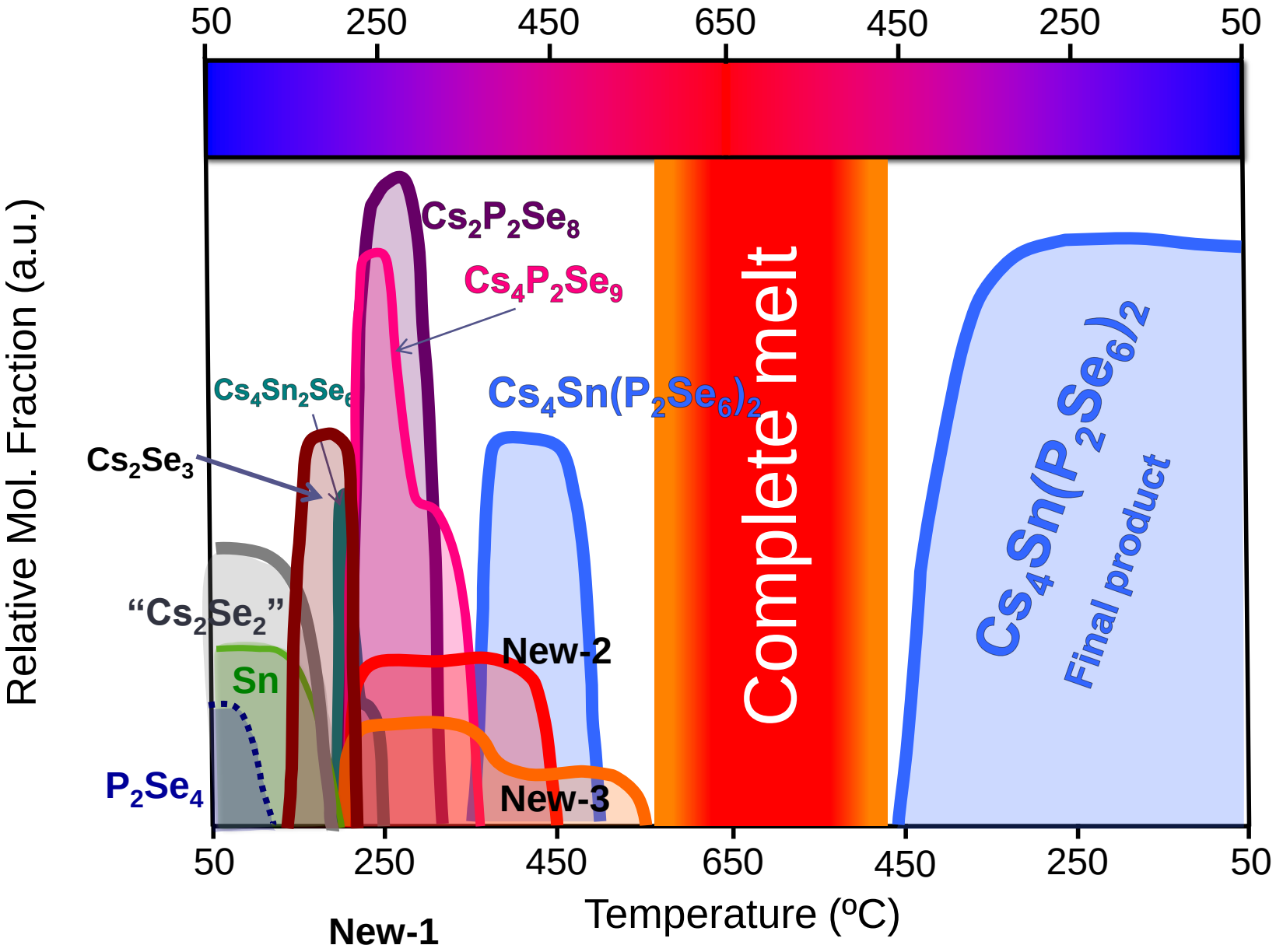


One phase, one single motif:
CuS_4 tetrahedra in KCu_4S_3



Increased S—S bond character in melt and product
Powder on heating, crystals on cooling
When is the crossover from 1-D Cu-S chains?

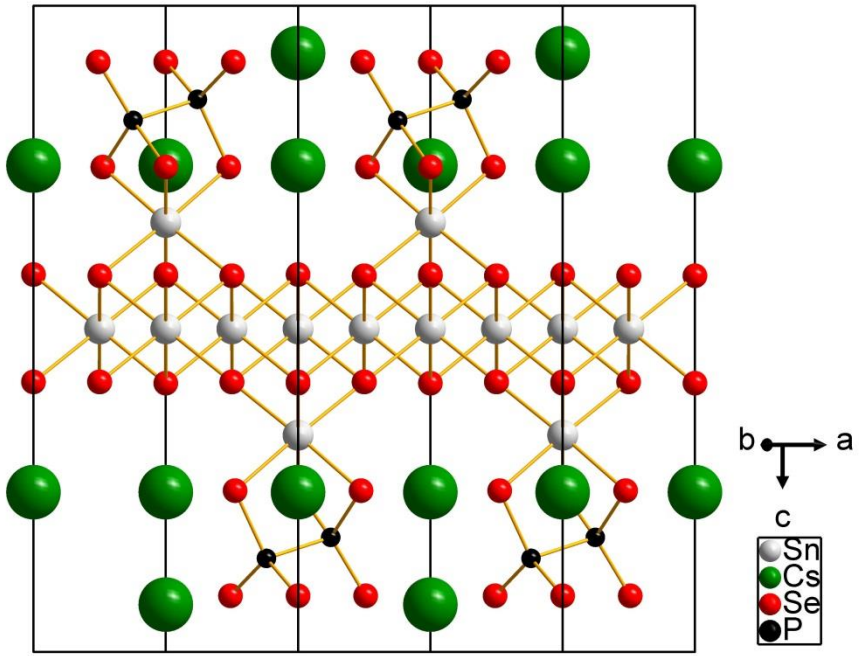
From Cu + K_2S_x reactions we find new phases and conditions for crystal growth
Can we use these tools to find new phases efficiently?



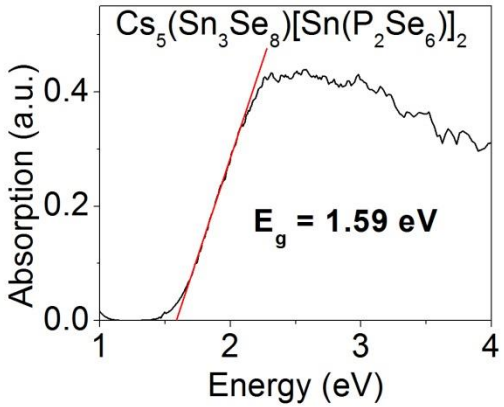
New-3 = $Cs_4Sn_5P_4Se_{20}$

Northwestern University

$Cs_4Sn_5P_4Se_{20}$

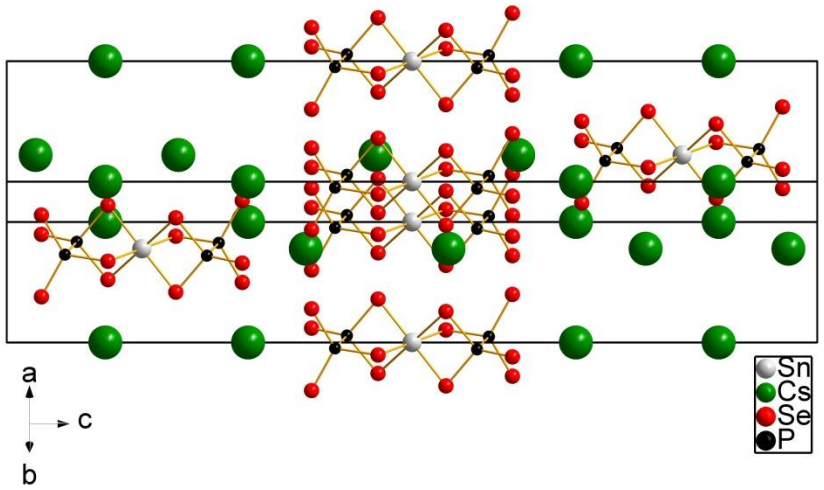


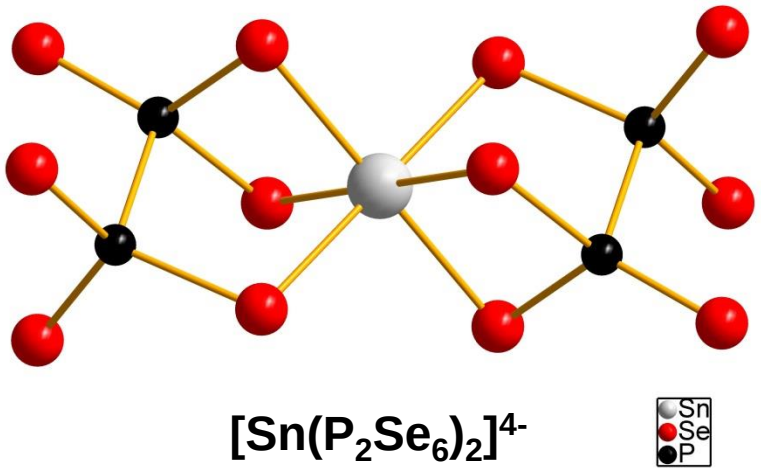
Trigonal *P*-3*m*
a = 7.695(1)
c = 18.797(4)
V = 964.03(3)
Z = 1



A new 2D semiconductor!

$Cs_4Sn(P_2Se_6)_2$





$[Sn(P_2Se_6)_2]^{4-}$

A new coordination complex

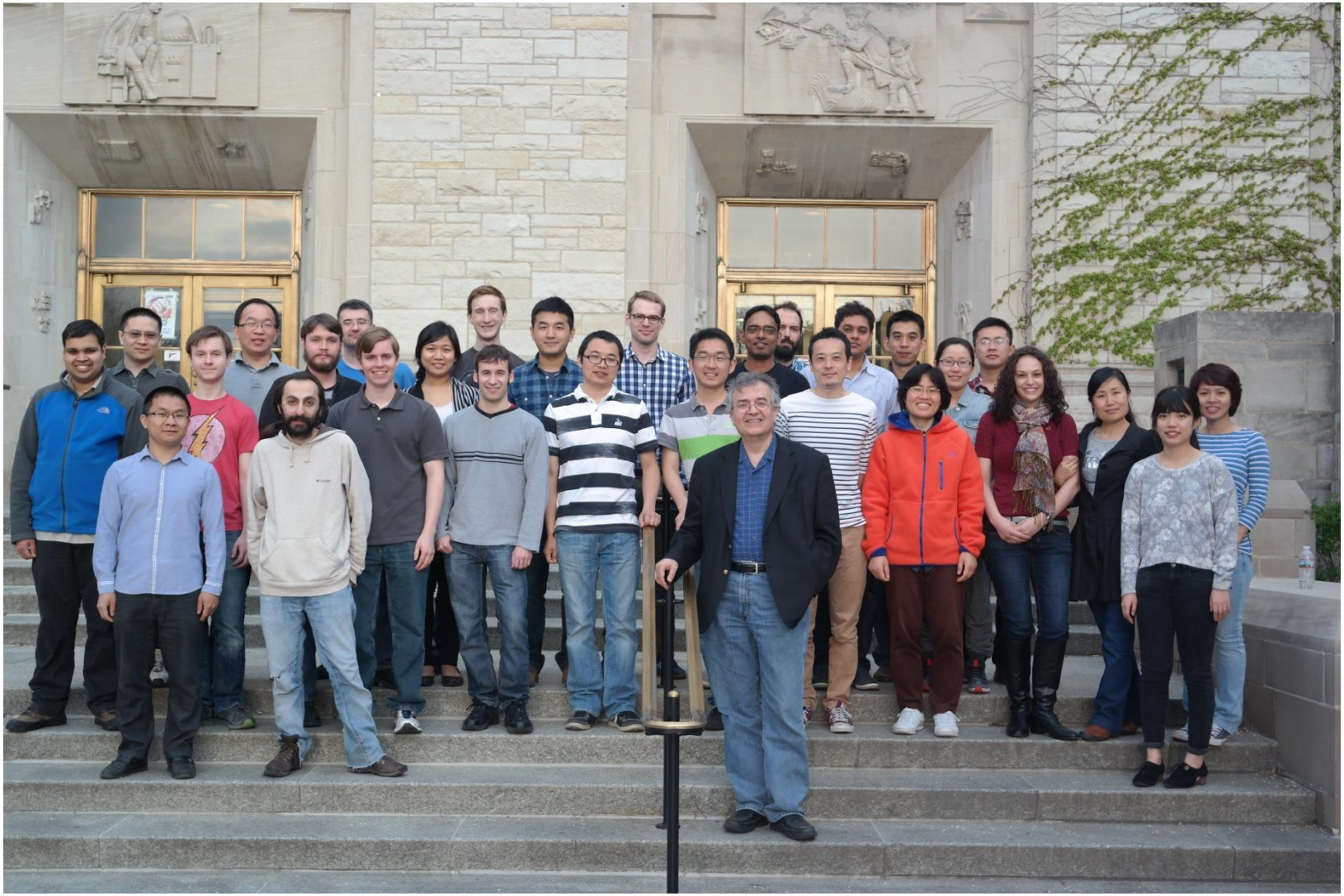
Northwestern University

2005

2009

2007

2012



2015

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National Science Foundation
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Relevant Research and Results . . .Yesterday, Today, and Tomorrow

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DARPA

NNSA
National Nuclear Security Administration

DTRA
Defense Threat Reduction Agency

DOW CORNING

NASA

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