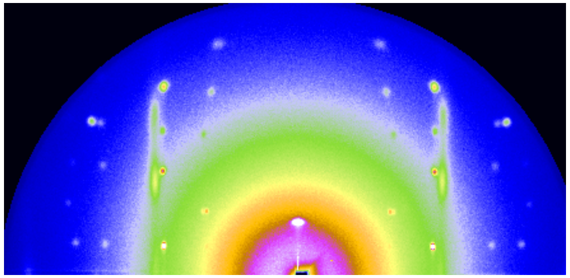

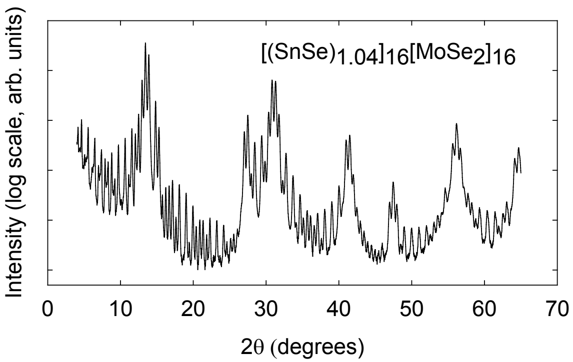

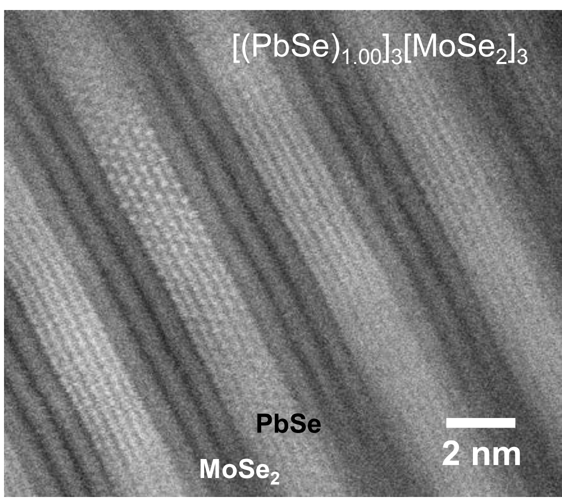

Trends in Thermoelectric Properties with Nanostructure:

Ferecrystals with Designed Nanoarchitecture

David C. Johnson

Matt Beekman,[1] Ryan Atkins,[1] Daniel B. Moore,[1] Michael D. Anderson,[1,2] Corinna Grosse,[1] Mary Smeller,[1] Colby Heideman,[1] Qiyin Lin,[1] Ngoc Nguyen,[1] Brian Lessig,[1] Ian M. Anderson,[2] Wolfgang Neumann,[3] Paul Zschack,[4]

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[2]Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD

[3]Department of Physics, Humboldt University, Berlin

[4]Advanced Photon Source, Argonne National Laboratory, Argonne, IL

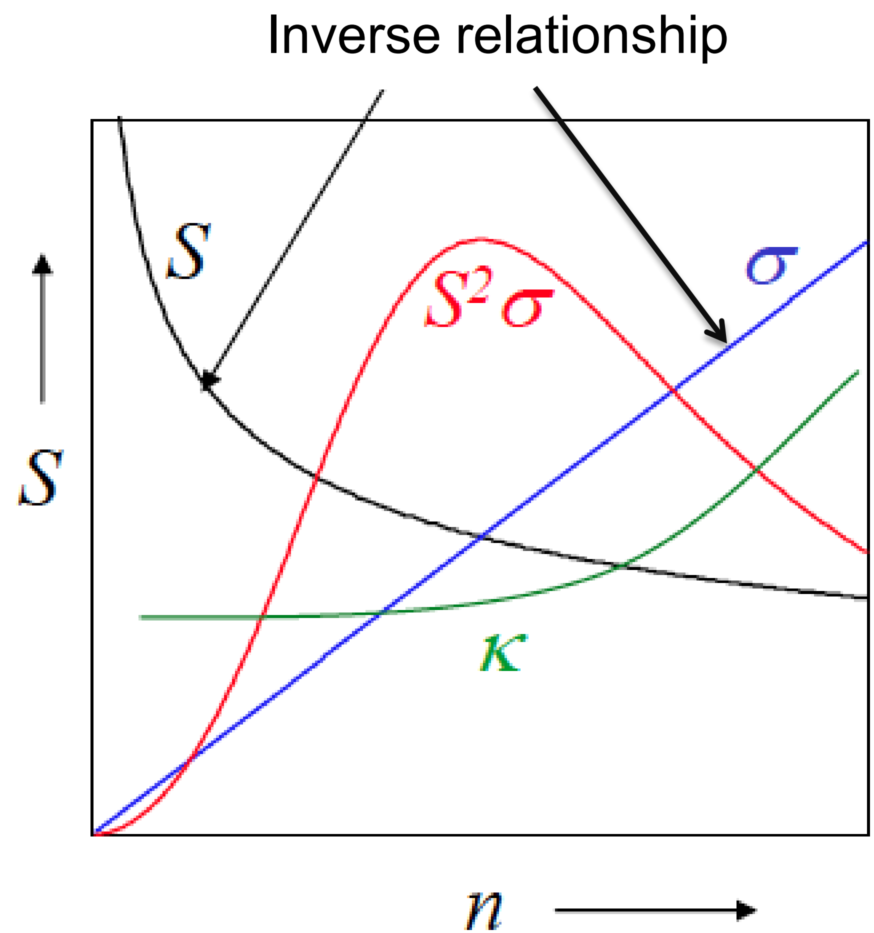
Interrelationships Limit ZT

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

$S = S(n)$

$\sigma = ne\mu$

$\kappa = \kappa_{lattice} + \kappa_{electronic}$

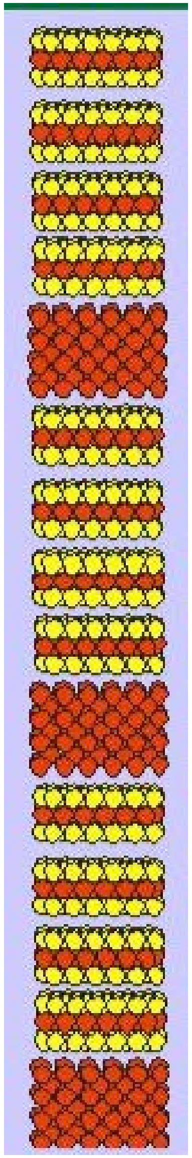


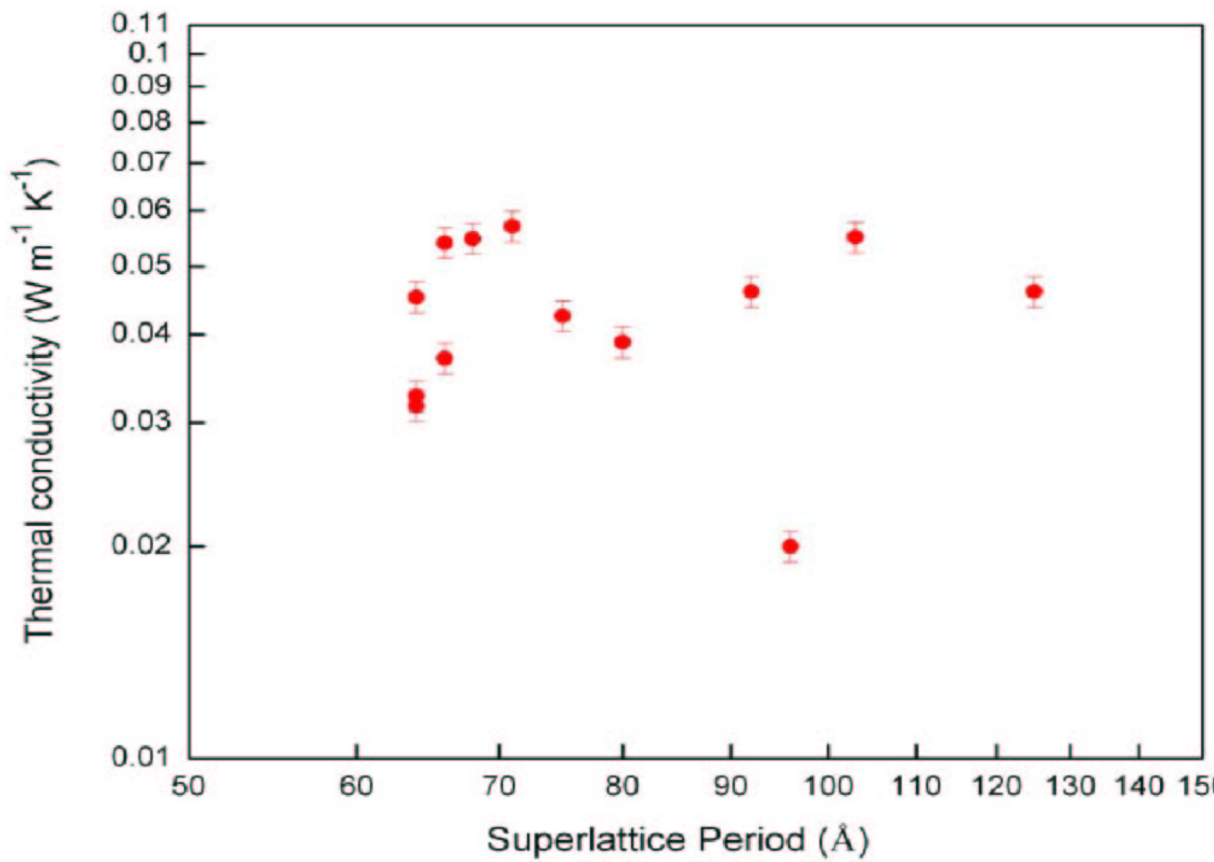
How do we design material with low $\kappa_{lattice}$?

Thermal Conductivity of $(W)_x(WSe_2)_y$

soft

hard





Lowest thermal conductivity ever measured for a fully dense solid

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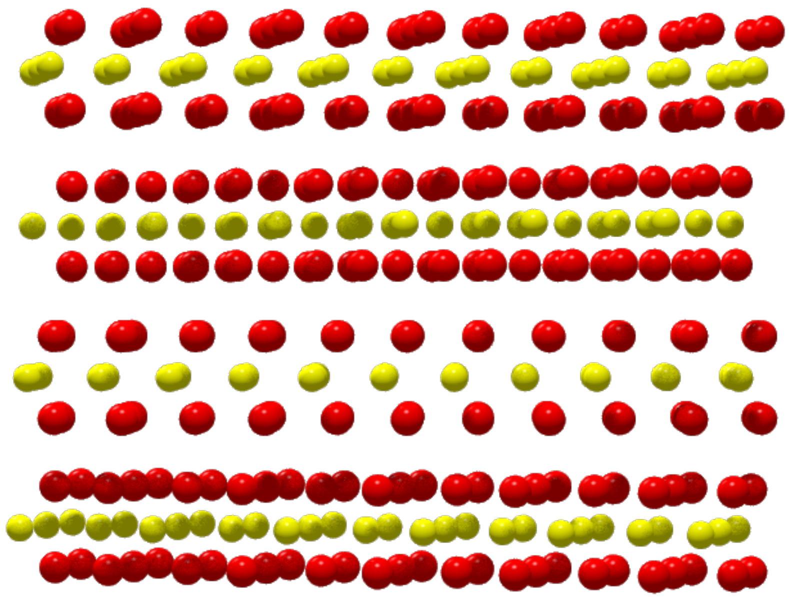
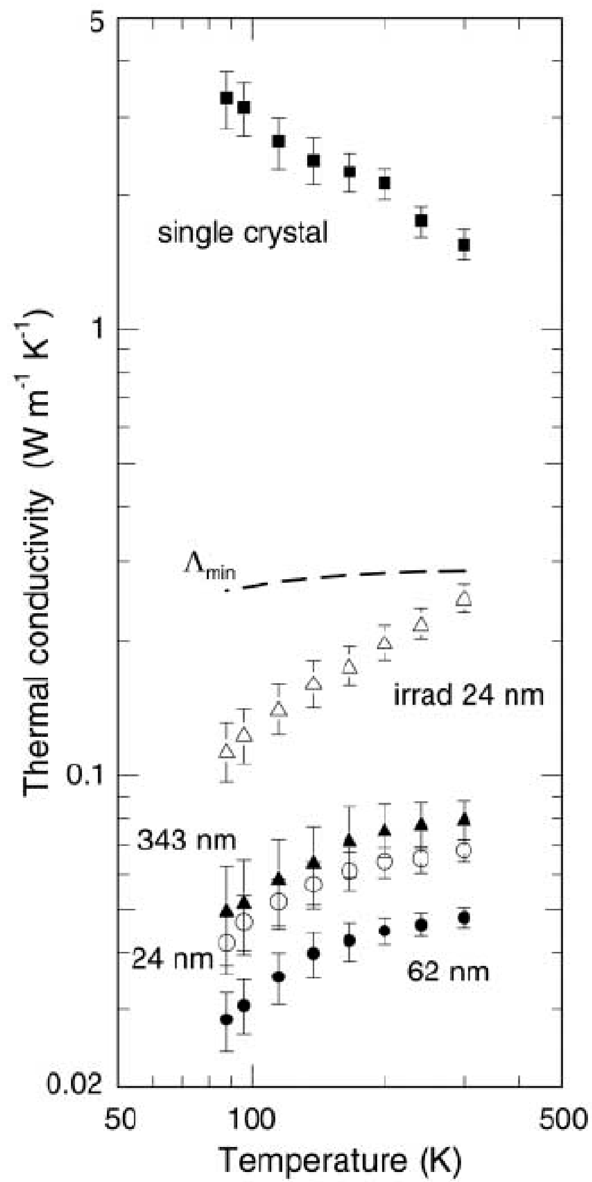
Ultralow Thermal Conductivity in WSe_2

- Crystalline within sheets
- Disordered between sheets





C. Chiritescu, D. G. Cahill, N. Nguyen, D. C. Johnson, A. Bodapati, P. Keblinski, P. Zschack, *Science* **2007**, *315*, 351.

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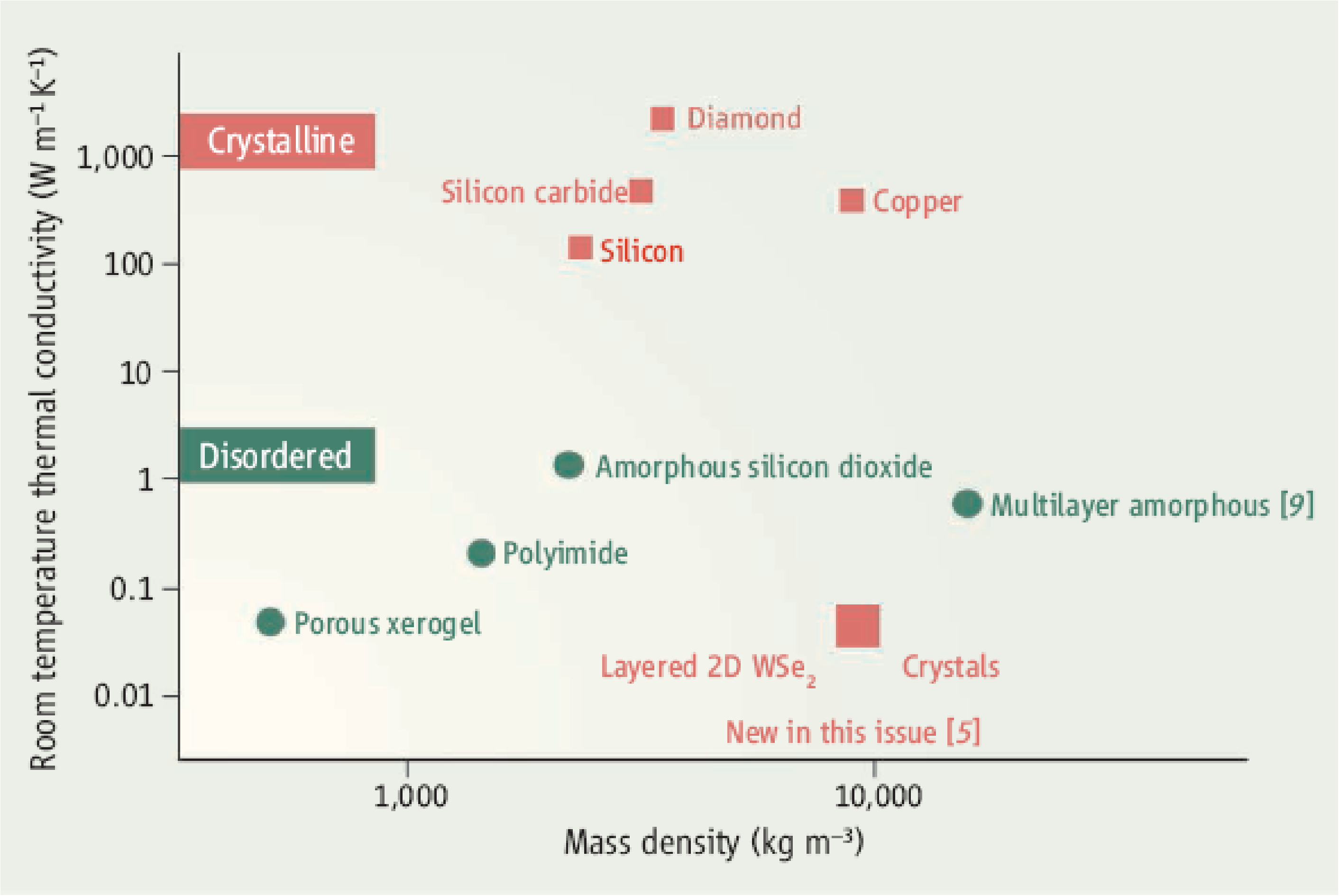
New Lower Limit



K. E. Goodson, *Science* **2007**, 315, 342.

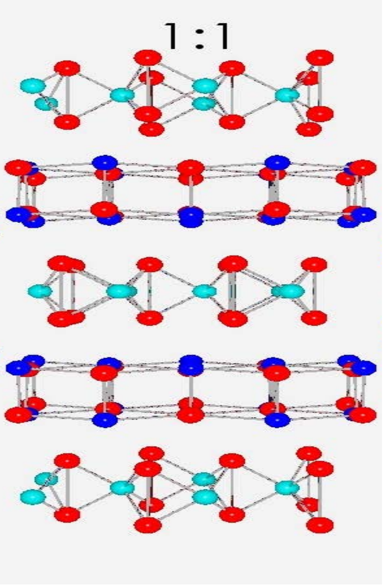
Where else might this be possible?

- Lattice mismatch in the a-b plane $[(AX)_{1+y}]_n(MX_2)_m$
- n,m = 1 forms by direct reaction of the elements at ~1000°C for ~30 compounds – mostly sulfides
- Compounds can be metallic, semiconducting or insulating (magnetic, superconducting, etc.)
- $(YbS)_{1.24}NbS_2$ S = 60μV/K $\rho = 1.4 \times 10^{-5} \Omega \cdot m$
  $K = 0.8 Wm^{-1}K^{-1}$ ZT = 0.1

  $(LnS)_m(NbS_2)_n$ and $(SnS)_m(TiS_2)_n$ n = 1, 2 m = 1
  power factor, $6{\sim}12 \times 10^{-4}\ W/m \cdot K^{-2}$ at 300K
  ZT ~ .1-.3 if the K value is ~1 $Wm^{-1}K^{-1}$,

  Miyazaki, Ogawa, Kajitani, Jap. J. Appl. Physics, 43 (2004) L1202
- $(SnS)_1(TiS_2)_2$ $K_{lattice} \sim 0.8\ Wm^{-1}K^{-1}$,
  ZT ~ .4 at 400° C

  C. Wan, Y. Wang, N. Wang and K. Koumoto - ICT 2009 Freiburg



Chalcogenide intergrowth compounds

Transition metal dichalcogenide

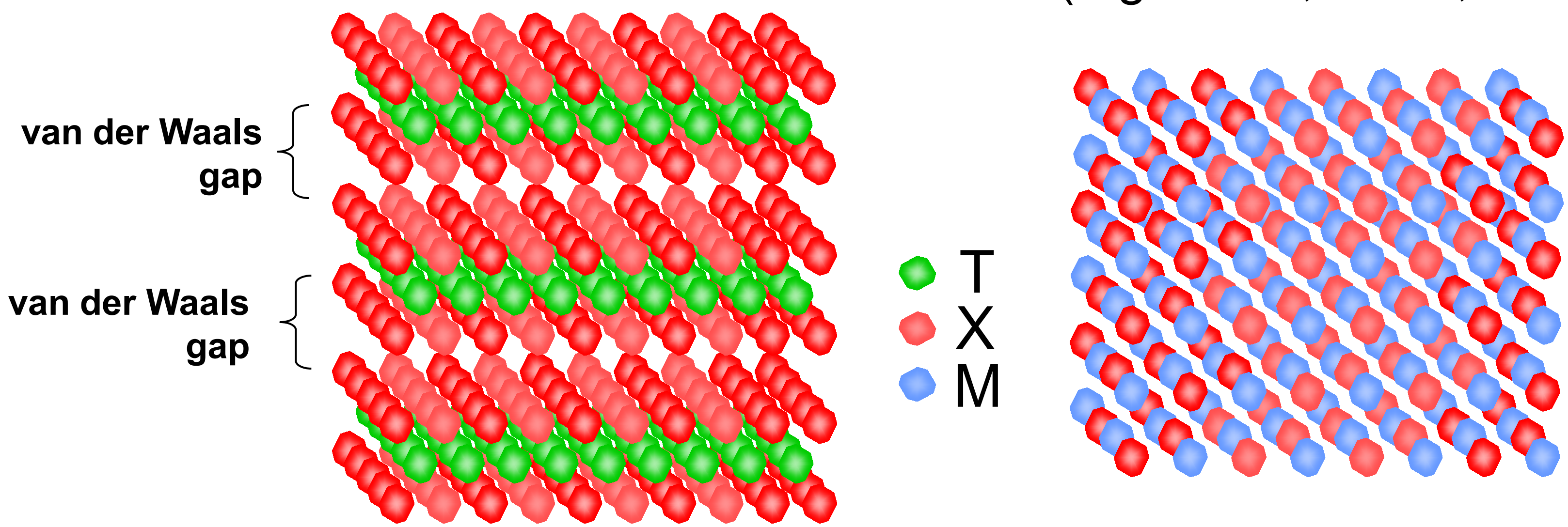
TX_2

(e.g. $TiSe_2$, $NbSe_2$, etc.)

NaCl-like monochalcogenide

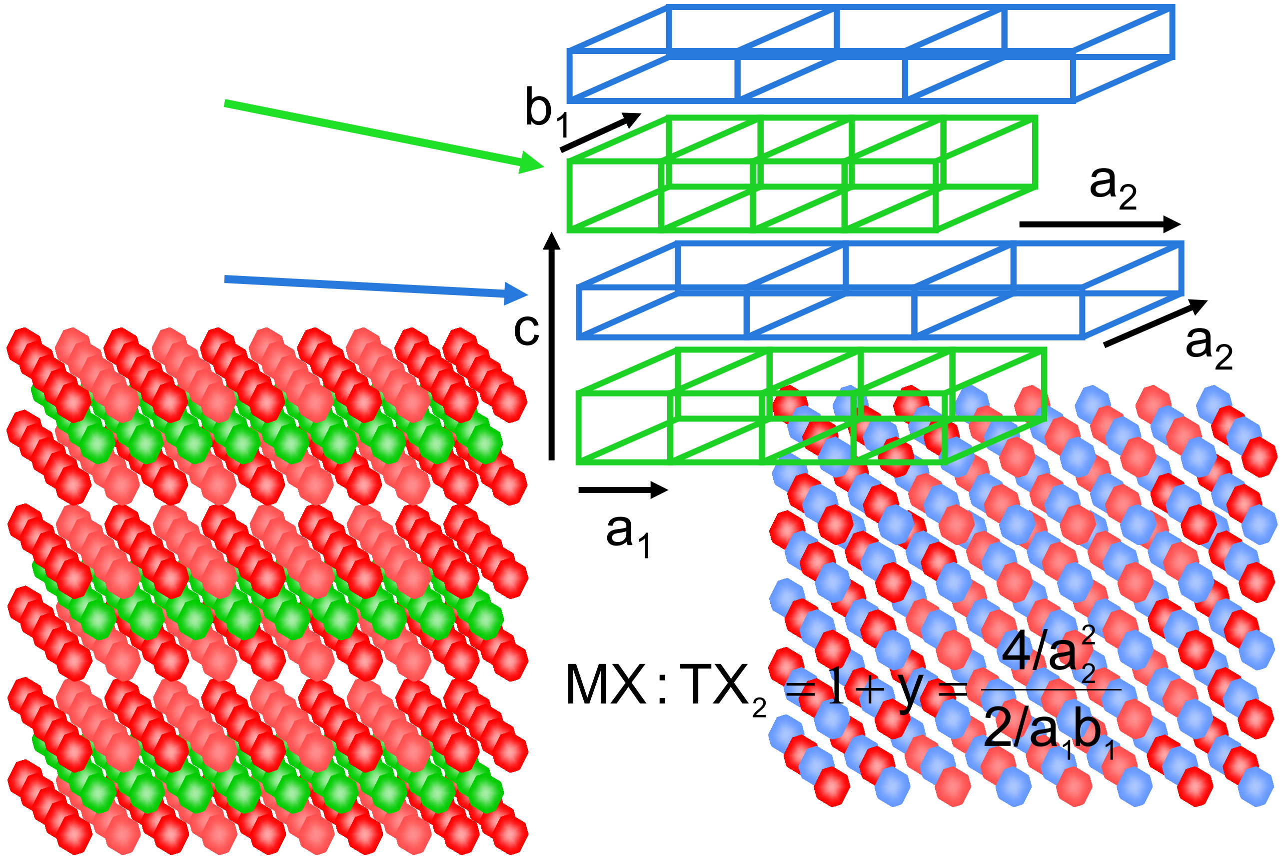
MX

(e.g. PbSe, EuSe, etc.)



Chalcogenide intergrowth compounds

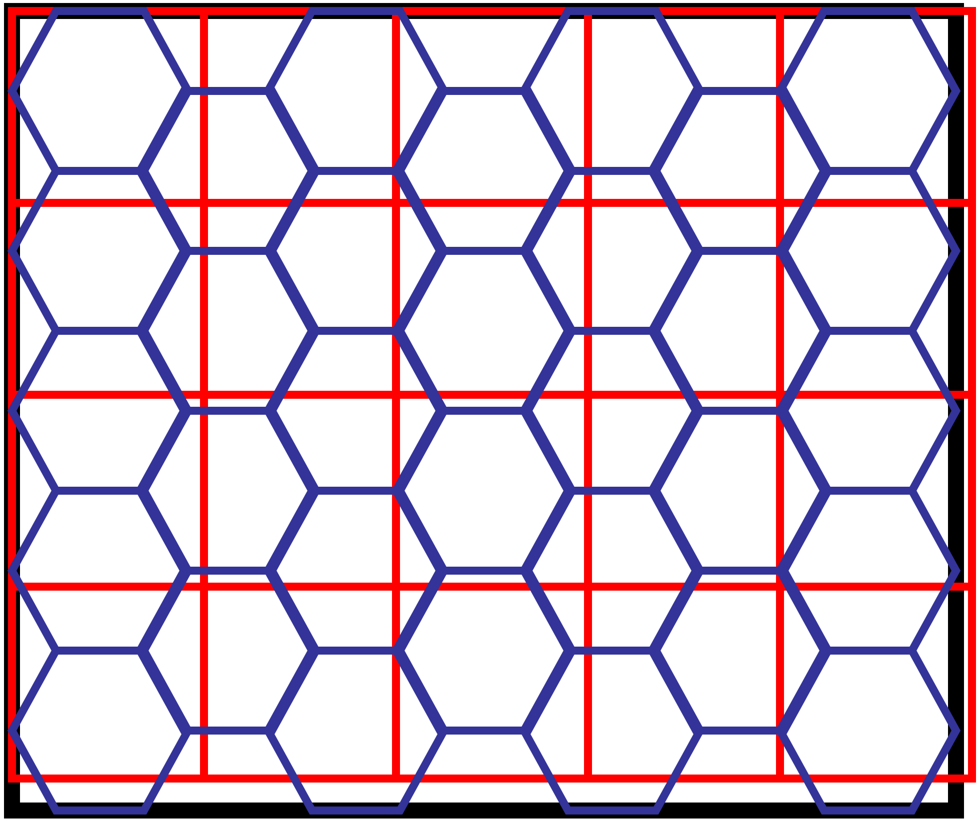
$[(MX)_{1+y}]_m[TX_2]_n$ (m, n = 1 or 2)



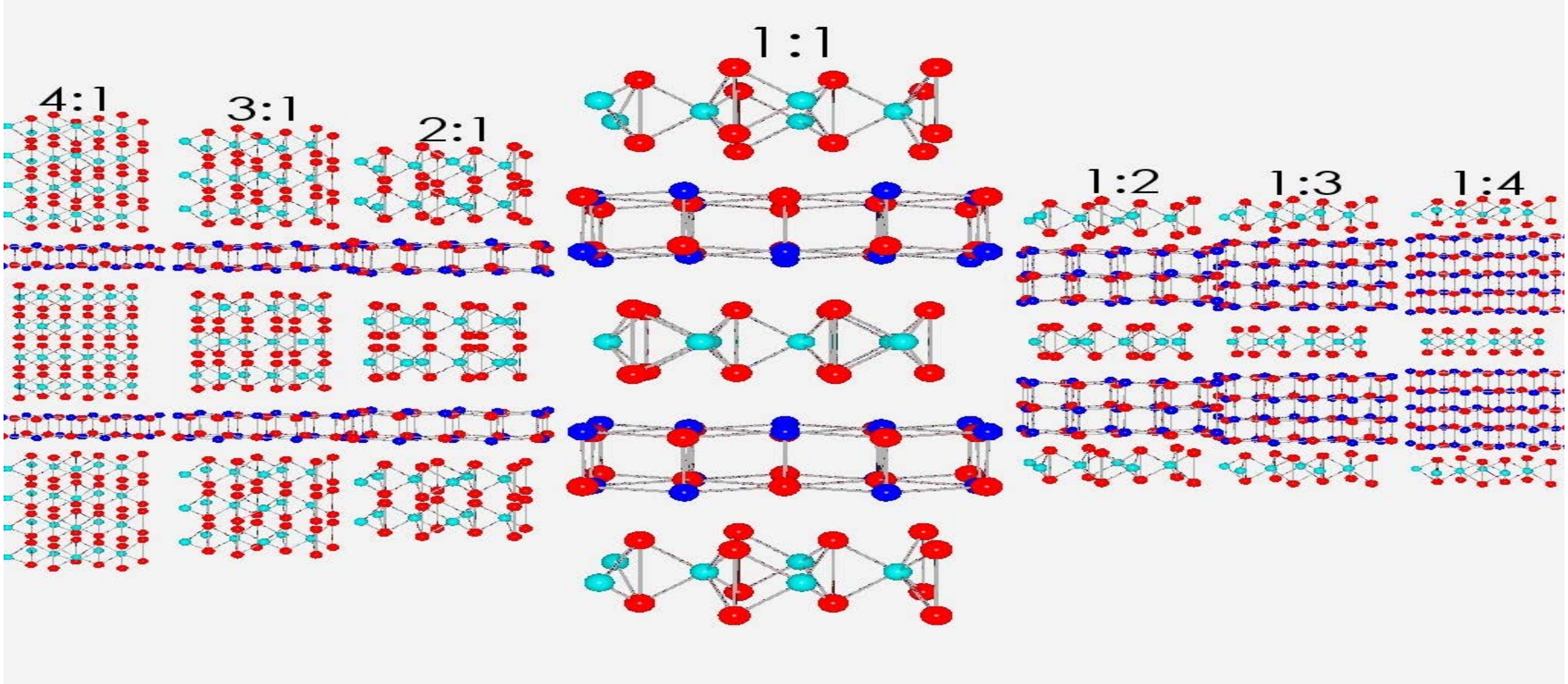
$$MX : TX_2 = 1 + y = \frac{4/a_2^2}{2/a_1 b_1}$$

Review articles:
G.A. Wiegers, Prog. Solid State Chem. **24**, 1 (1996).
A. Meerchaut, Curr. Opin. Sol. State Mater. Sci. **1**, 25 (1996).

Different atom densities in x-y plane – no epitaxy



Controlled Nanostructure



If the 1:1 structure is stable, all local bonding is satisfied in any compound, m:n. Reasonable to assume that all m:n compounds should be at least metastable.

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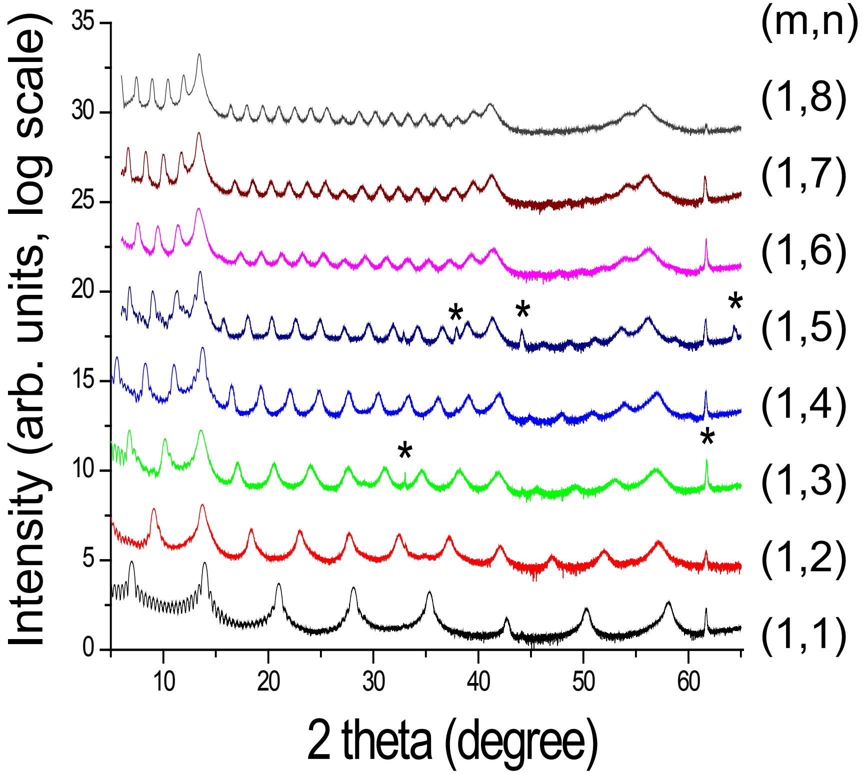
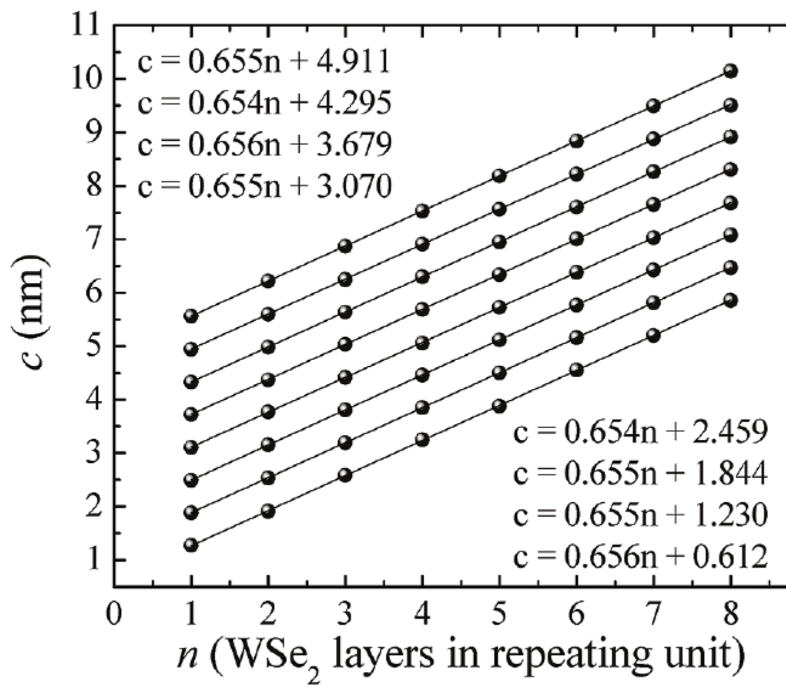
Entire families of compounds can be prepared

Only (00*l*) reflections are observed
(* indicates sample holder or substrate)



c-axis repeat thickness



First 64 members of $[(PbSe)_{0.99}]_m[WSe_2]_n$ prepared

Q. Lin et al., Chem. Mater. **22**, 1002 (2010).

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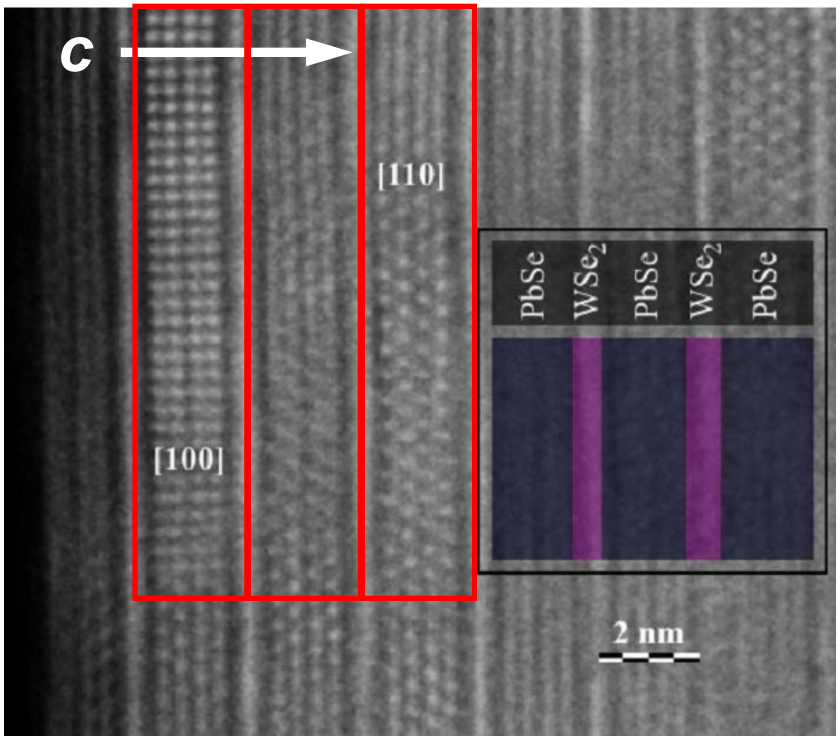
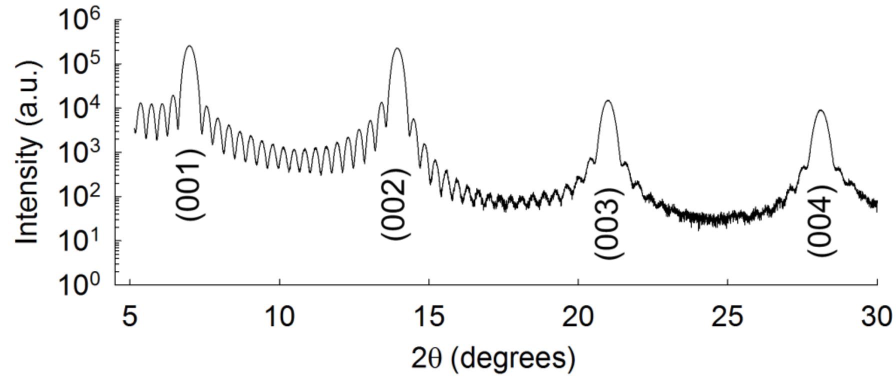
Precisely intergrown layers lacking interlayer registry

STEM image from $[(PbSe)_{0.99}]_2[WSe_2]_1$



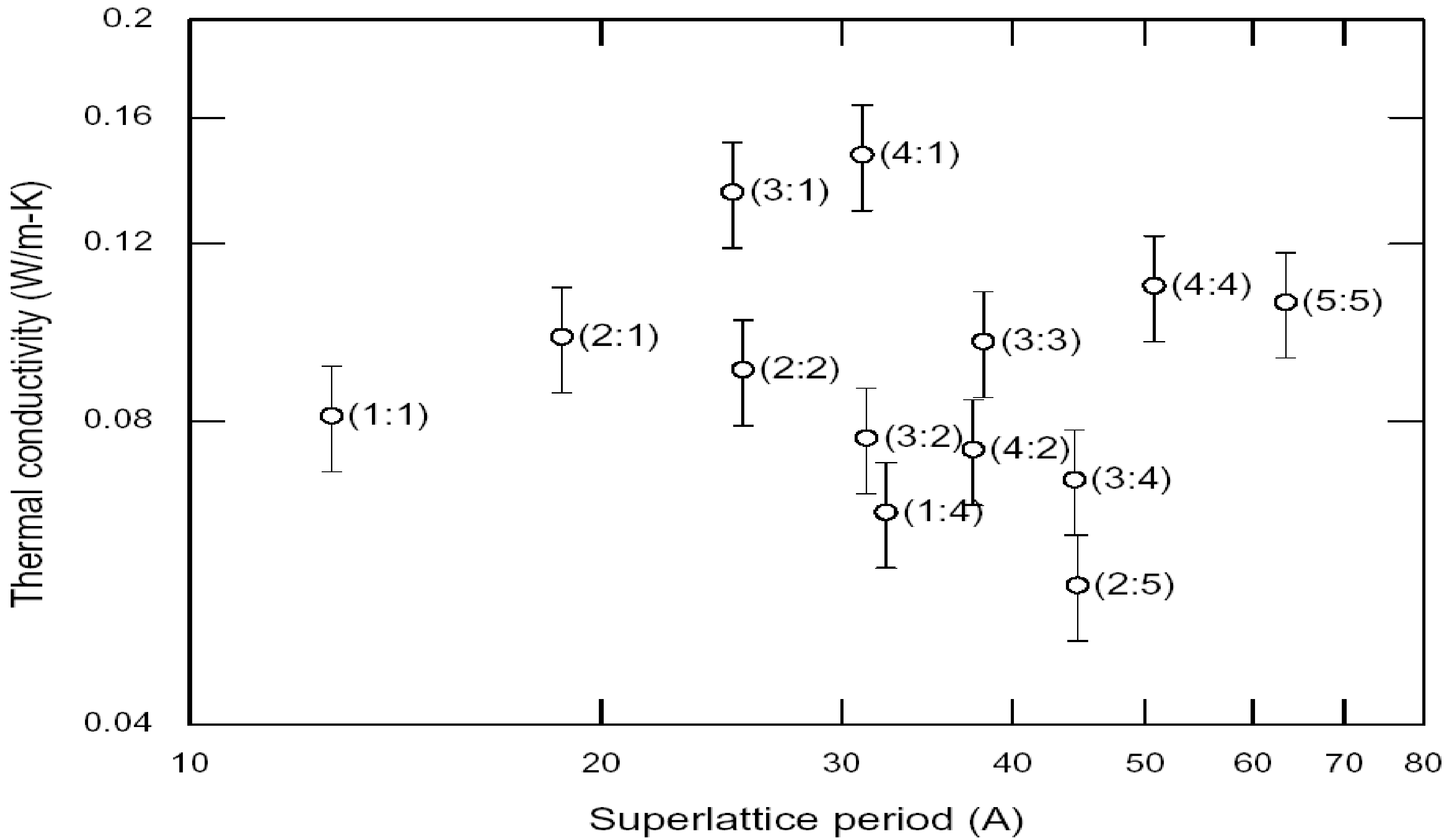
XRR from $[(PbSe)_{0.99}]_1[WSe_2]_1$



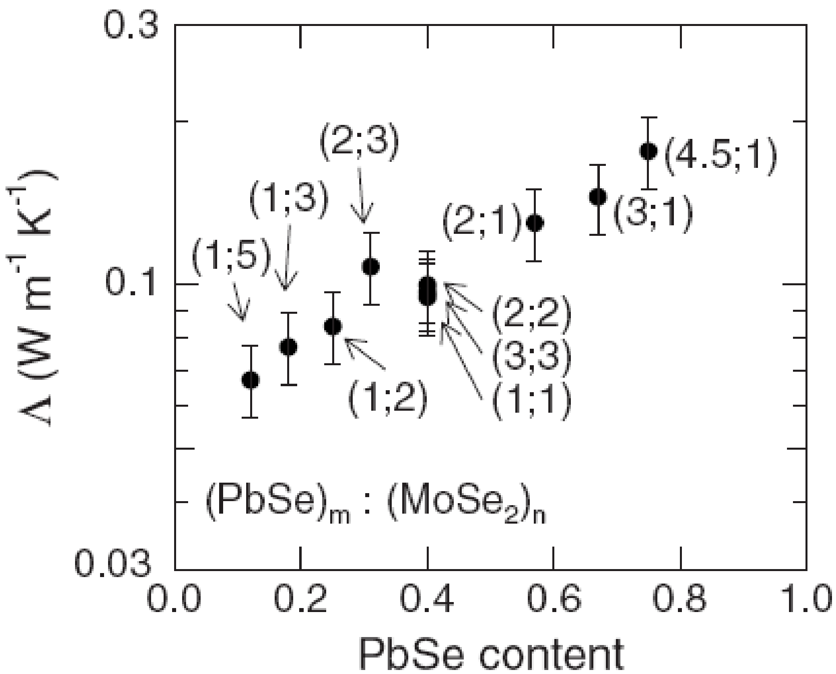
- In-plane crystallinity; crystallographically alligned components
- Atomically abrupt interfaces
- Precisely layered constituents
- Layer-to-layer mis-registration: similar to turbostratic disorder

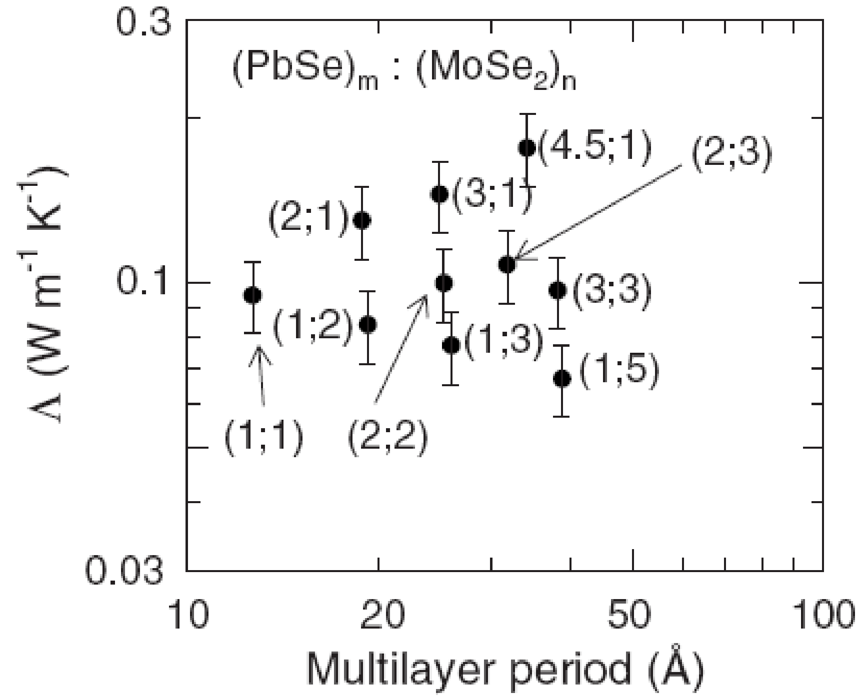
Ferecrystals – from Latin - almost

Thermal Conductivity $[(PbSe)_{0.99}]_n(WSe_2)_m$



Ultra-low cross-plane thermal conductivity





Thermoreflectance measurements:
C. Chiritescu and Prof. D.G. Cahill, University of Illinois at Urbana-Champaign

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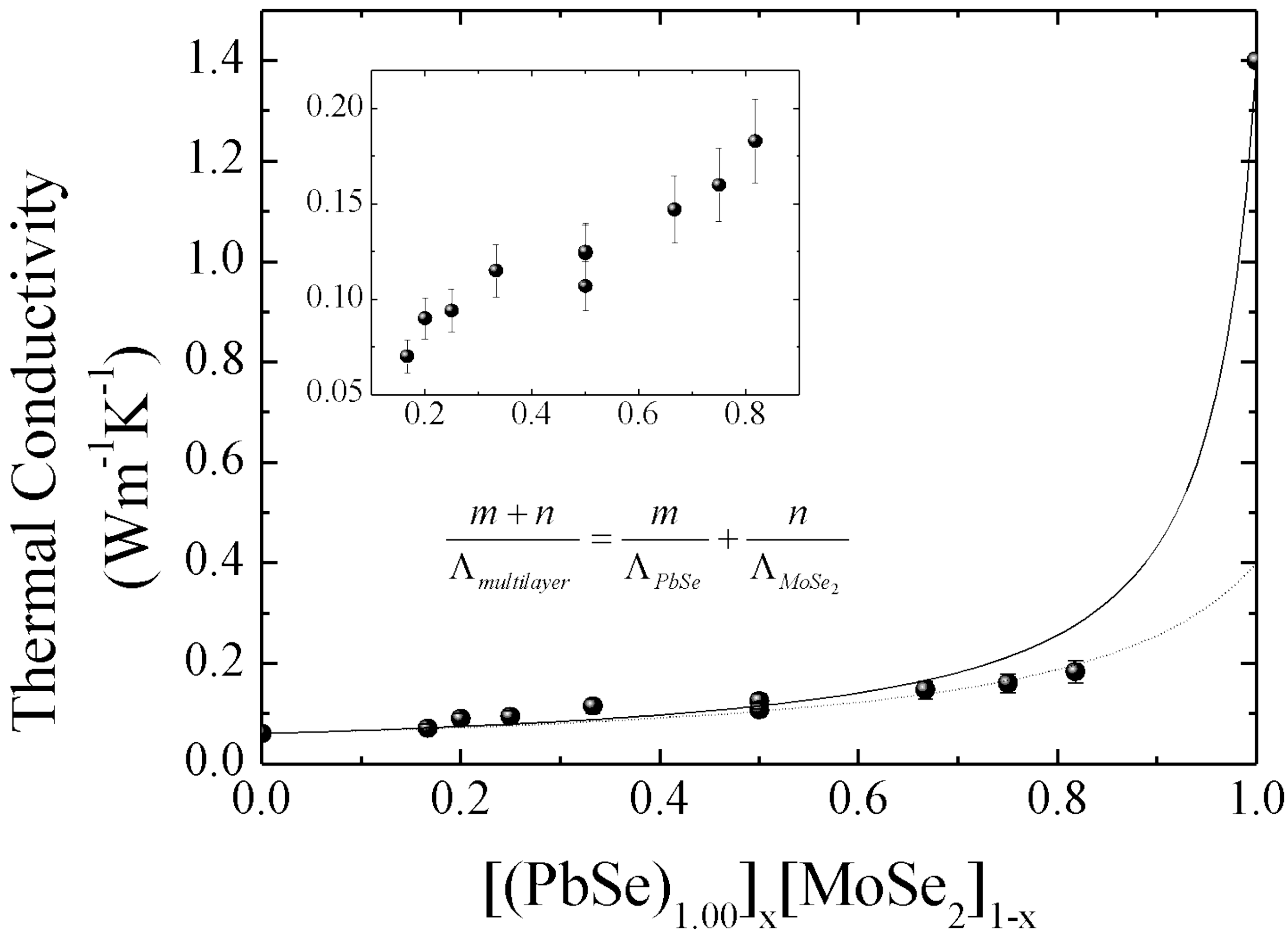
Cross Plane Thermal Conductivity – Sum of Constituents



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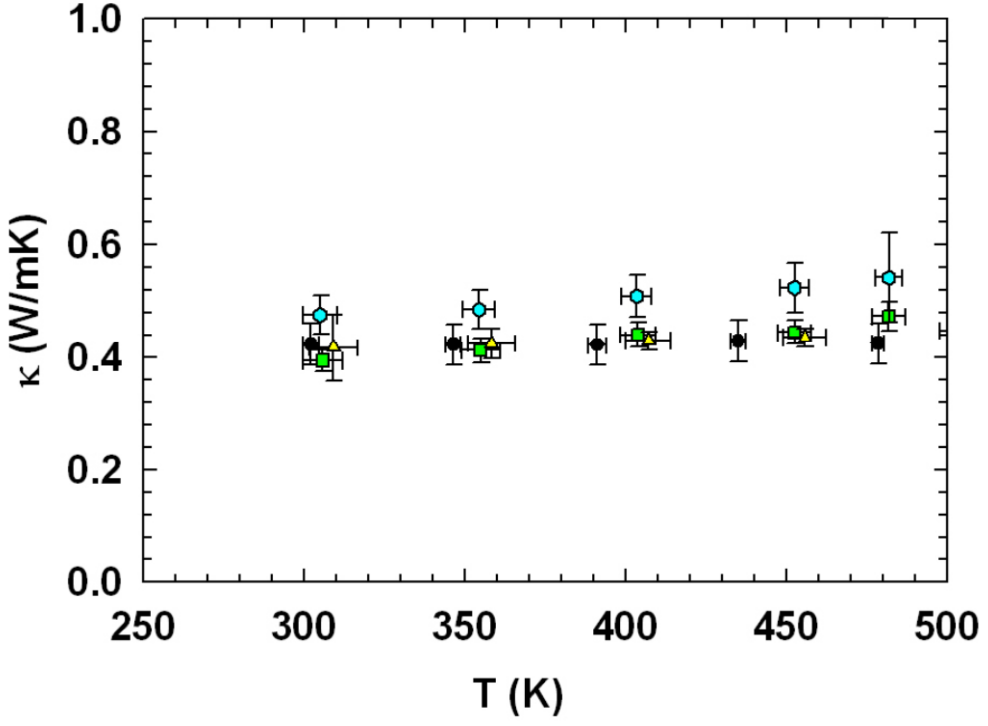
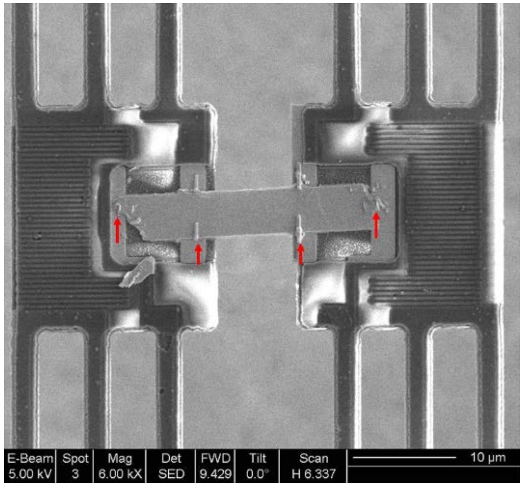
In plane Thermal Conductivity

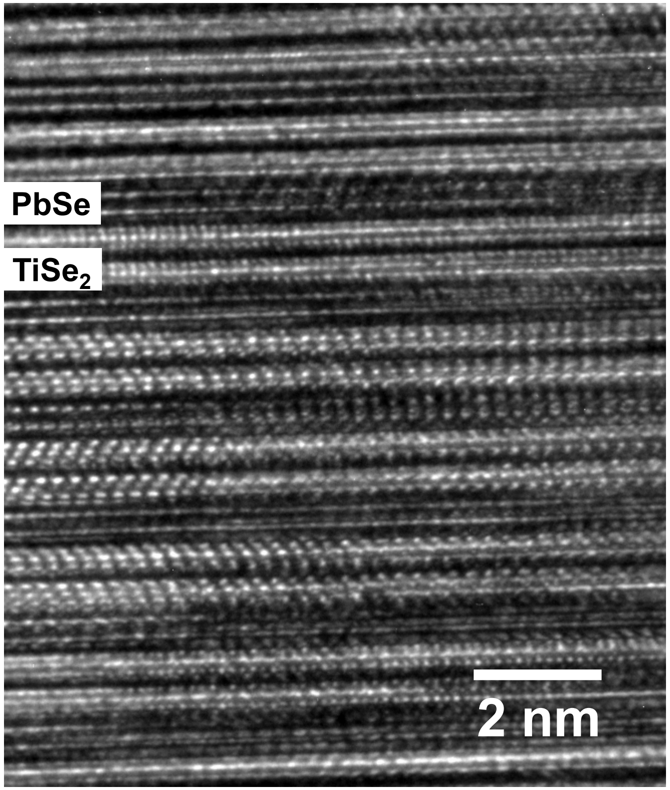
In plane thermal conductivity measurements:
A. Mavrokefalos and Professor Li Shi
University of Texas at Austin



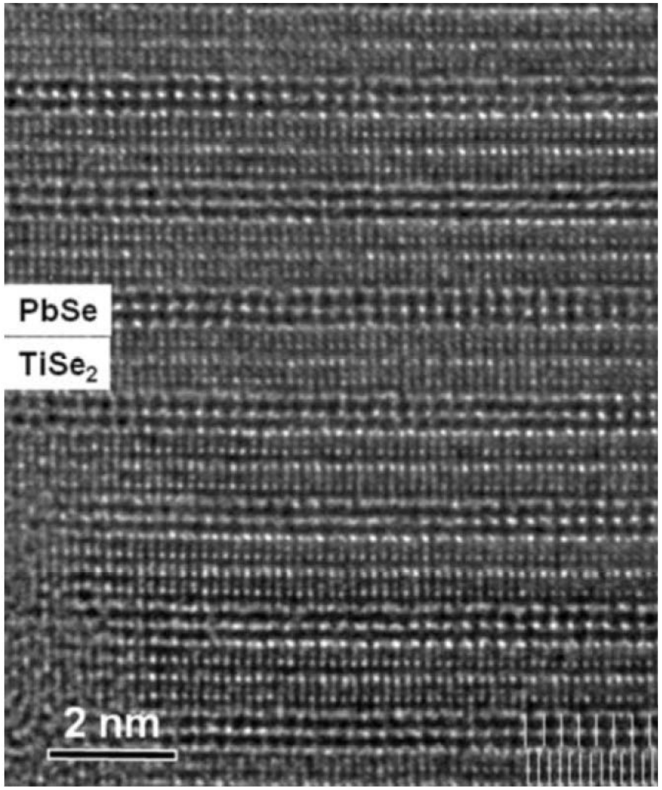


Precisely intergrown layers lacking interlayer registry

HRTEM image of $[(PbSe)_{1.16}]_1[TiSe_2]_2$:



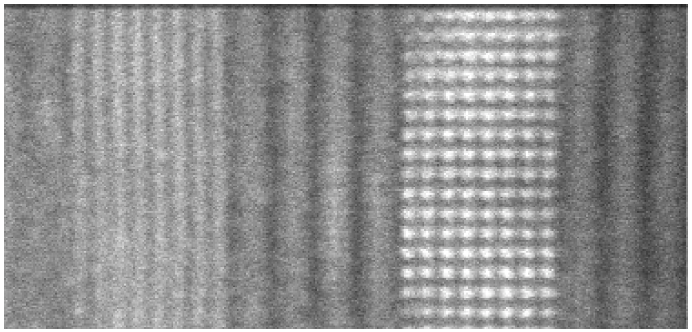
$[(PbSe)_{1.16}]_1[TiSe_2]_2$ Synthesized by direct reaction of the elements:[1]



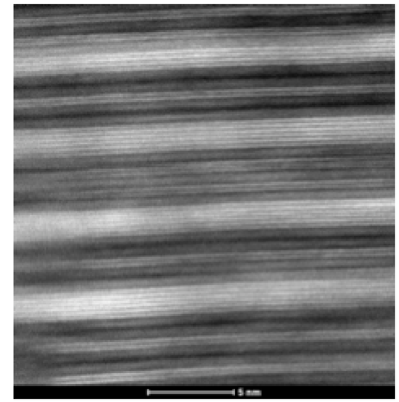
[1]N. Giang et al., *Phys. Rev. B* **82**, 7 (2010),

Isomers with controlled nanostructure

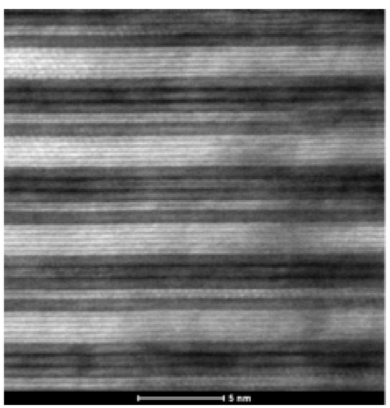
Four $(PbSe)_4(NbSe_2)_4$ Isomers



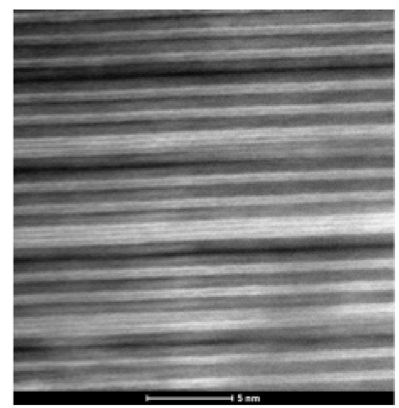
4,4,0,0,0,0



2,3,2,1,0,0

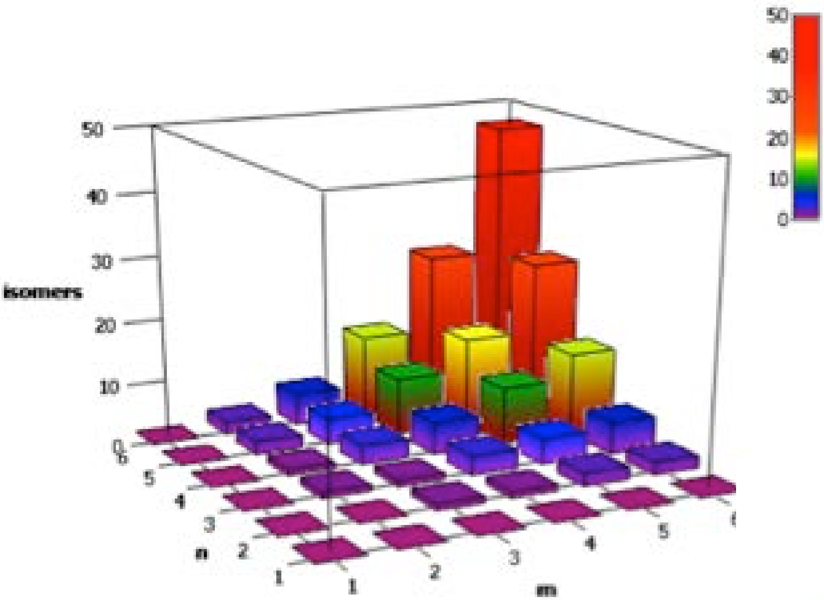


3,3,1,1,0,0

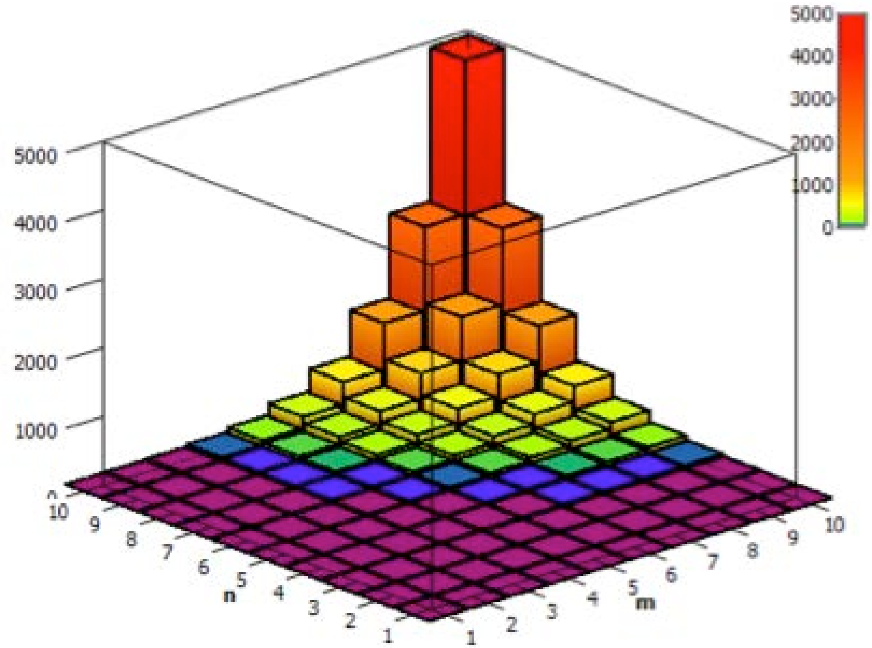


2,2,1,1,1,1

Many possible isomers …

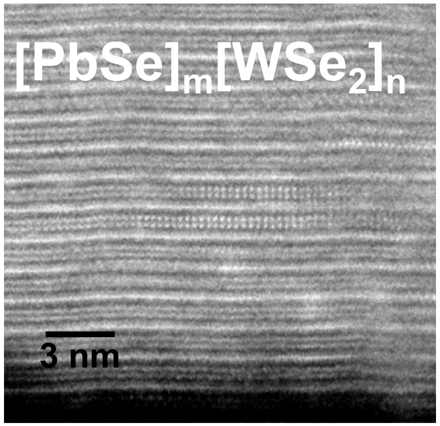


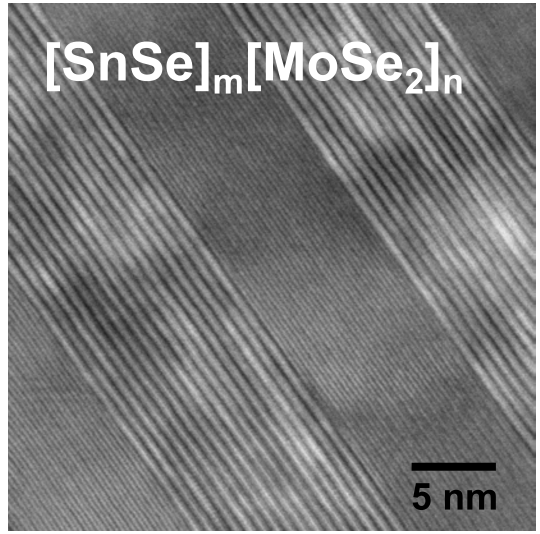
Over 200 isomers for n and m 6 or less

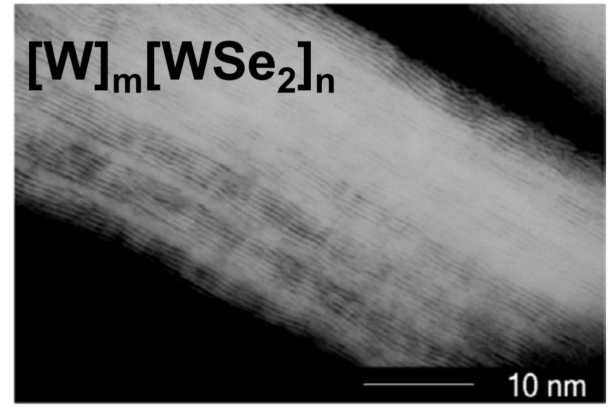


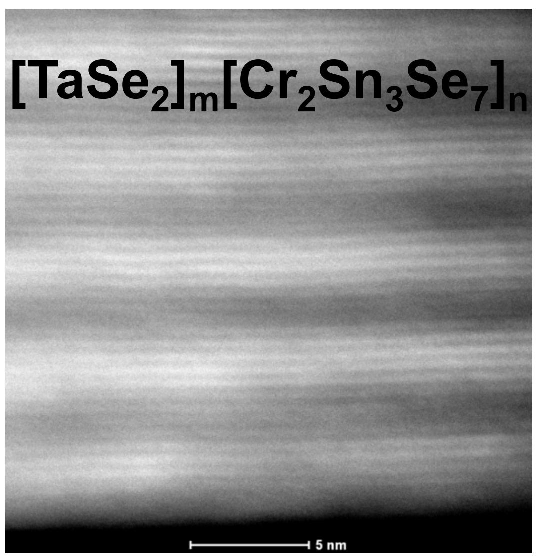
Over 20,000 isomers for n and m 10 or less

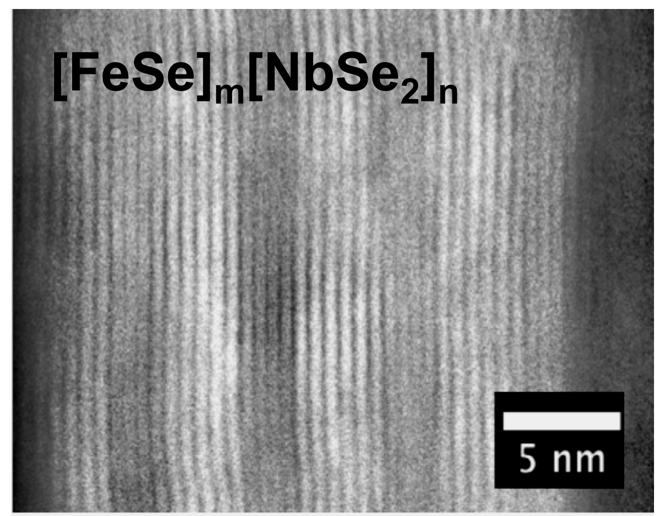
A general design principle – materials by design!



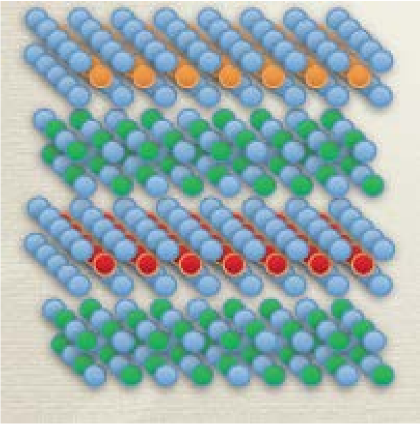


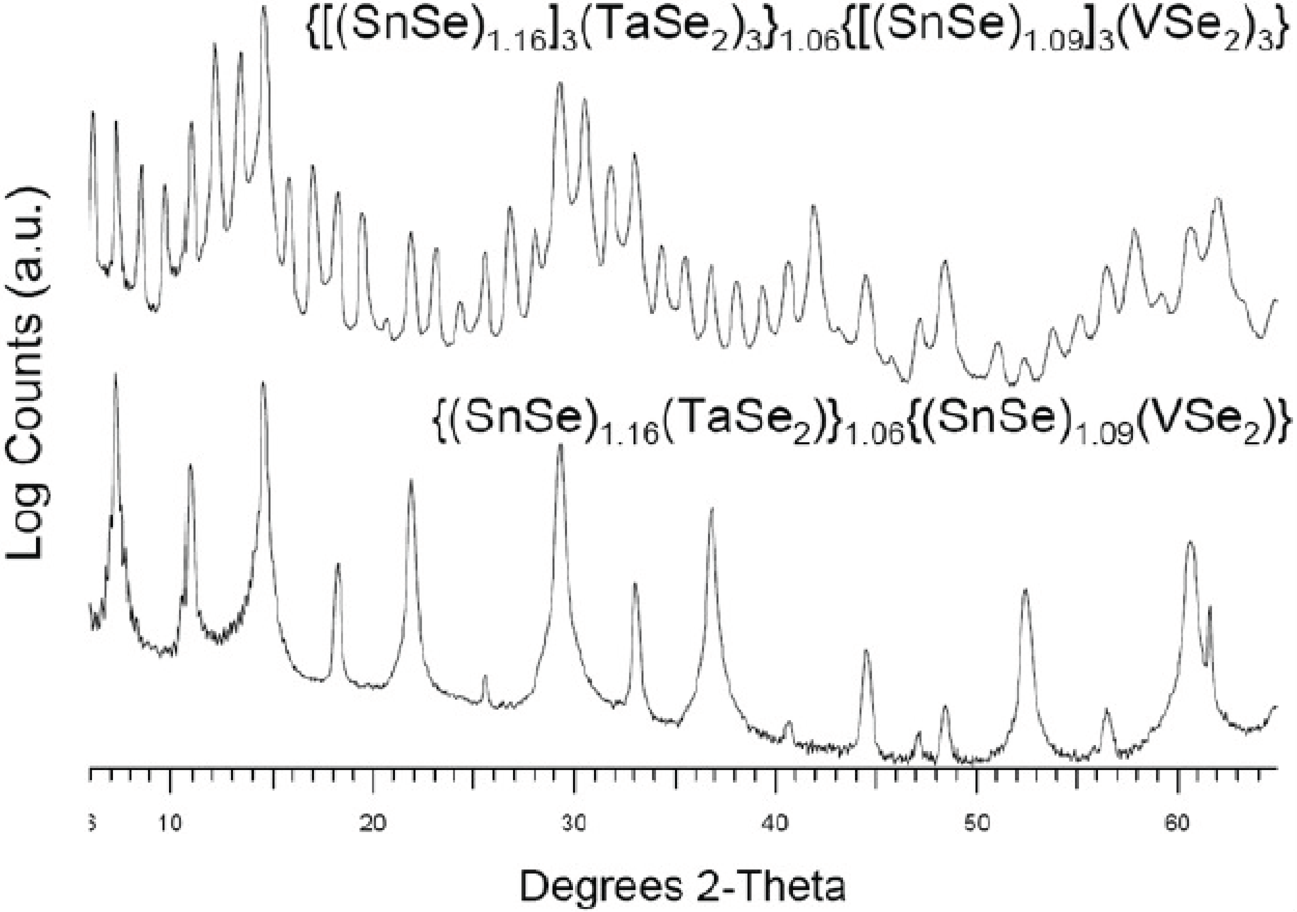






Three component ferecrystals – precisely controlled modulation doping

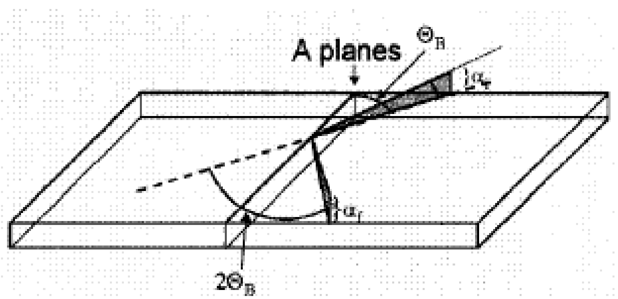




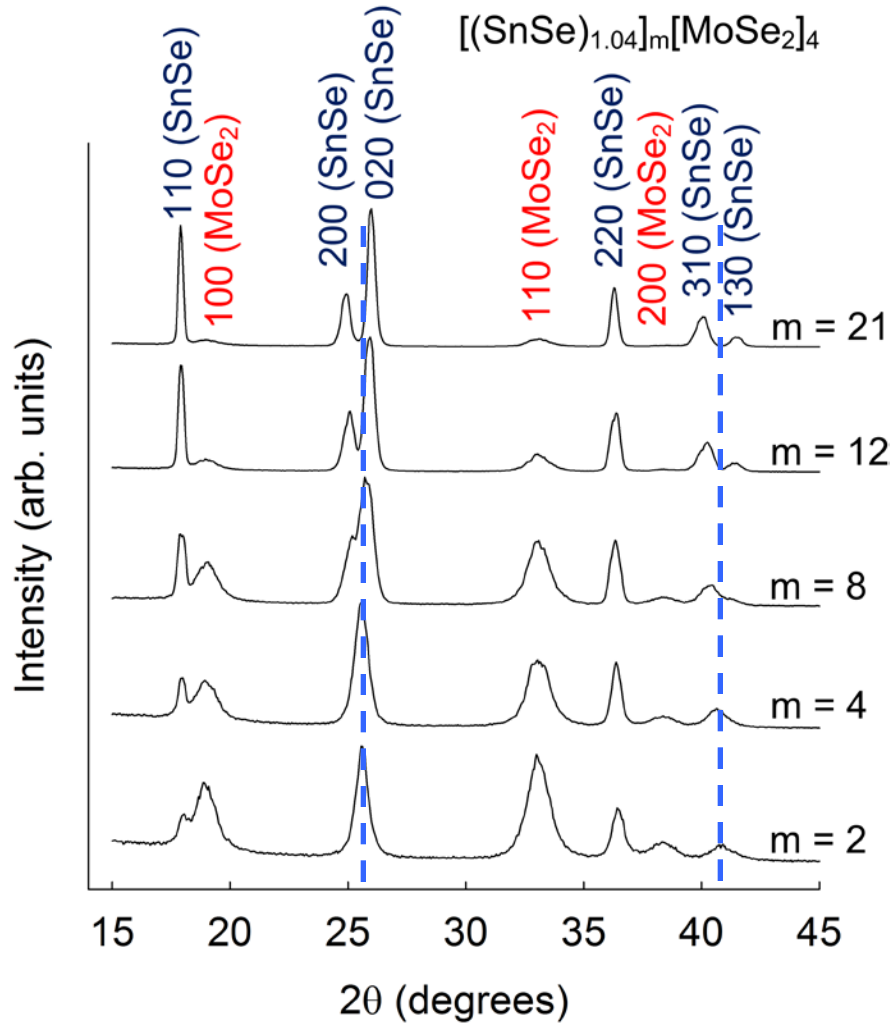
Size-induced structural transformations

In-plane Synchrotron X-ray Diffraction

($hk0$) reflections from individual components



Beam line 33-BM-C, APS
Dr. Paul Zschack



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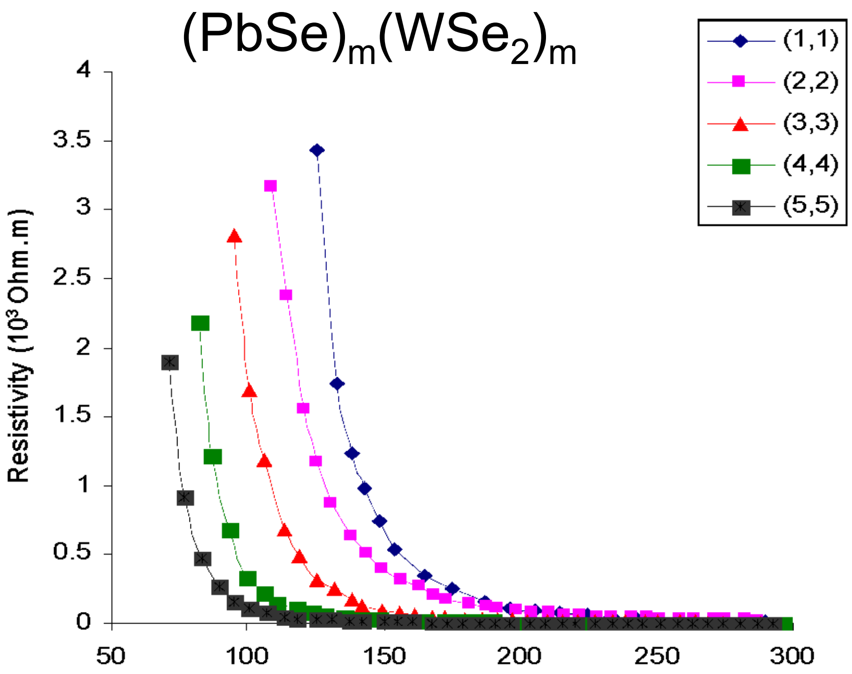
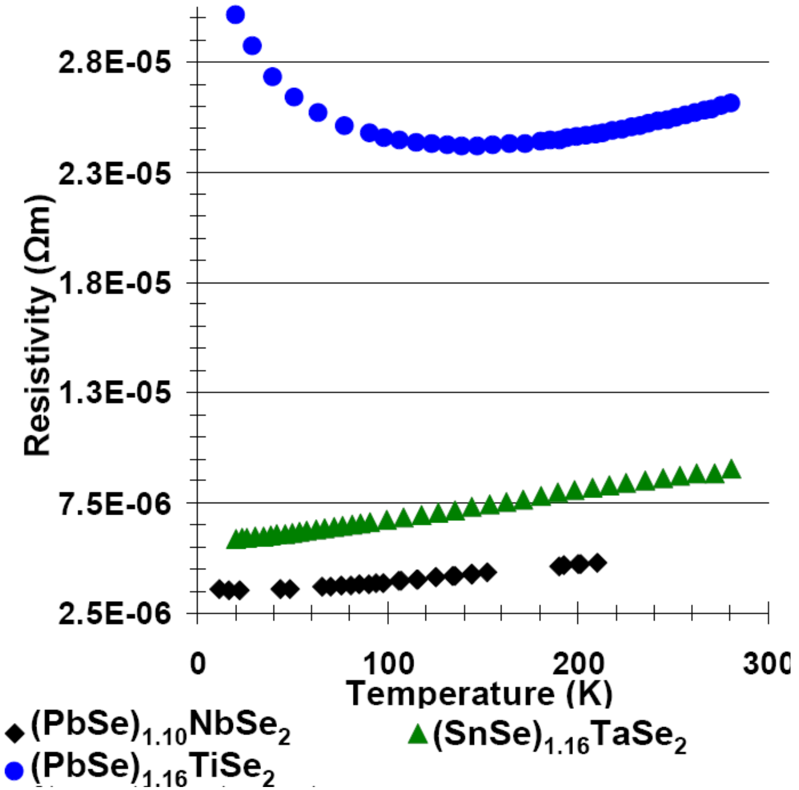
Tunable electrical properties





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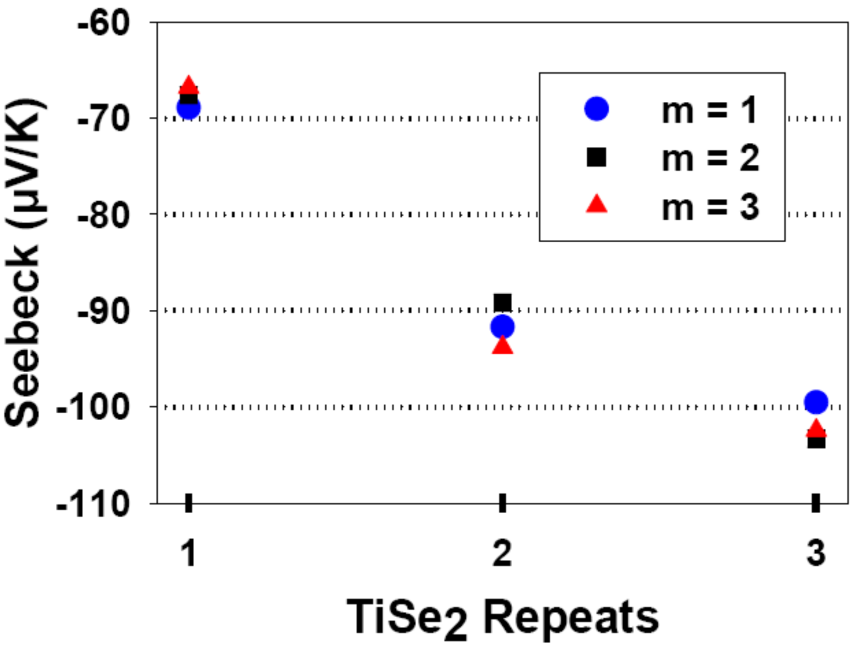
Seebeck systematically varies with number of $TiSe_2$ layers



	Seebeck	Resistivity
Misfit $(PbSe)_{1.16}(TiSe_2)_2$ (N. Giang et al.)	-50μV/K	2×10^{-4} Ωm
$(PbSe)_{1.16}(TiSe_2)_2$ ferecrystal	-92μV/K	3.7×10^{-5} Ωm

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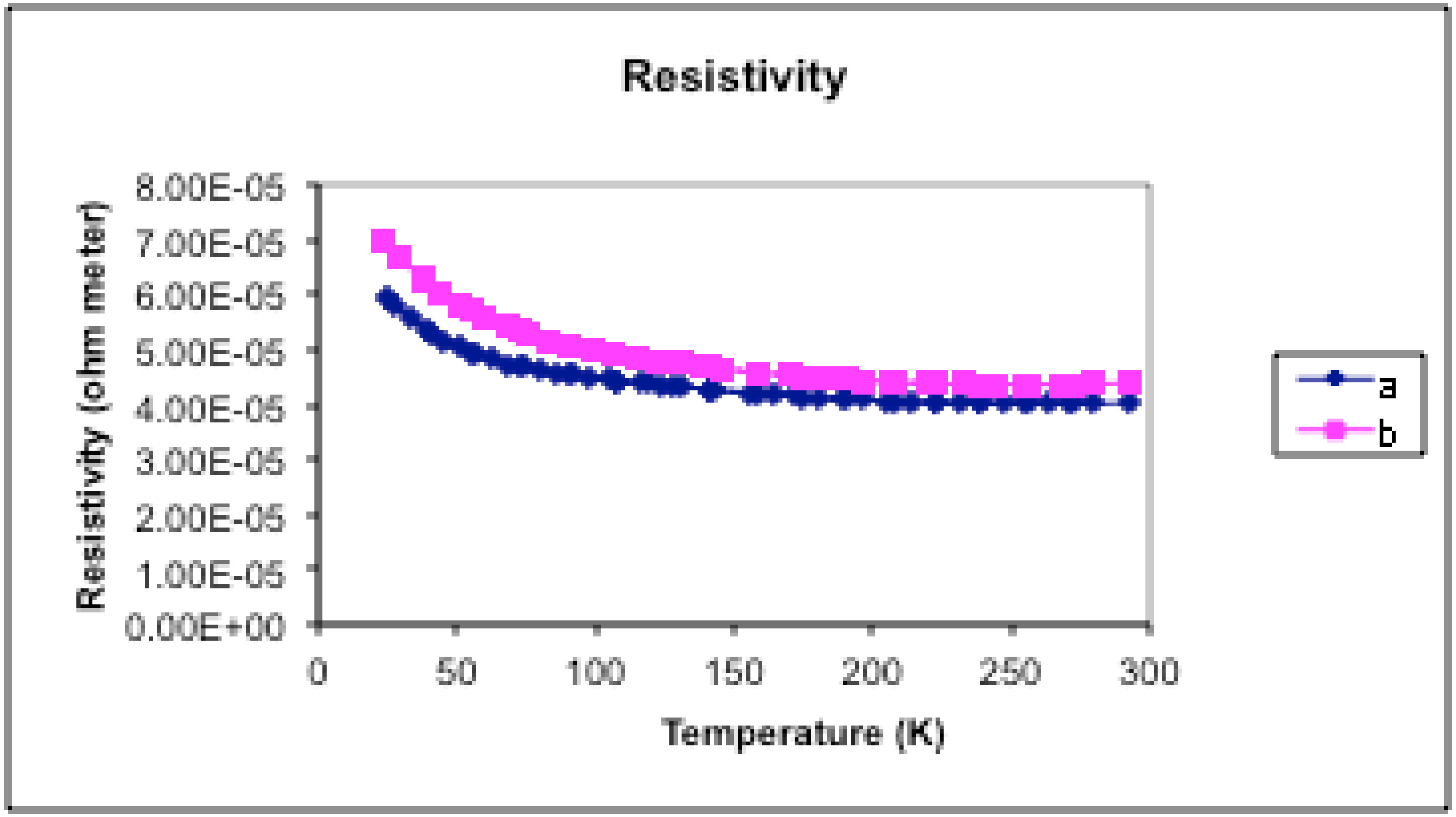
Turbostratic $TiSe_2$



Seebeck coefficients – a = -170 μV/K

b = -180 μV/K

Unusual temperature dependence!

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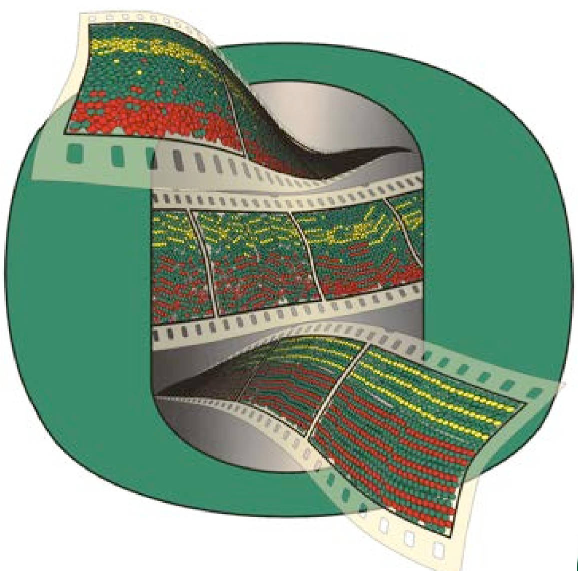
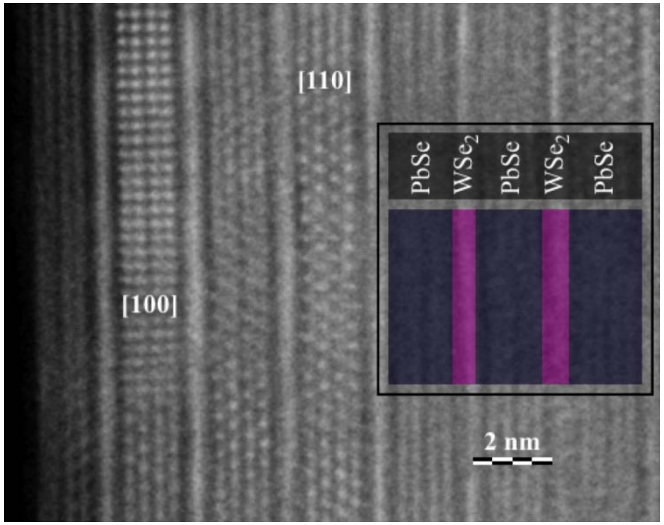
Summary

- Many new nanostructured ferecrystals can be synthesized.
- Structure of the constituent layers depends on layer thickness.
- Turbostratic disorder observed for all compounds investigated results in ultra-low thermal conductivity.
- Electrical properties depend on composition and nanostructure
- Power factor can be increased using nanostructure
    - Need to measure carrier concentrations



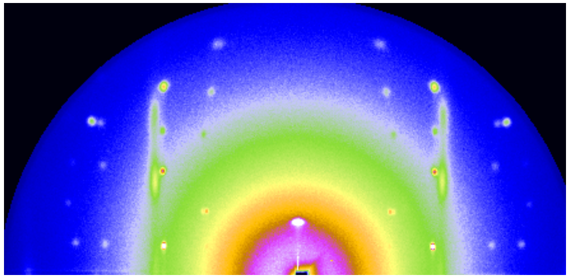


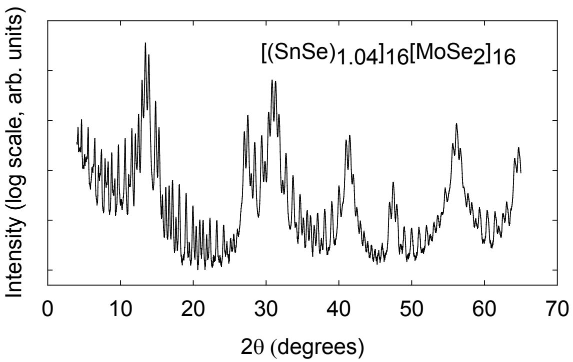
Given a family of compounds $(A)_m(B)_n(C)_p$,

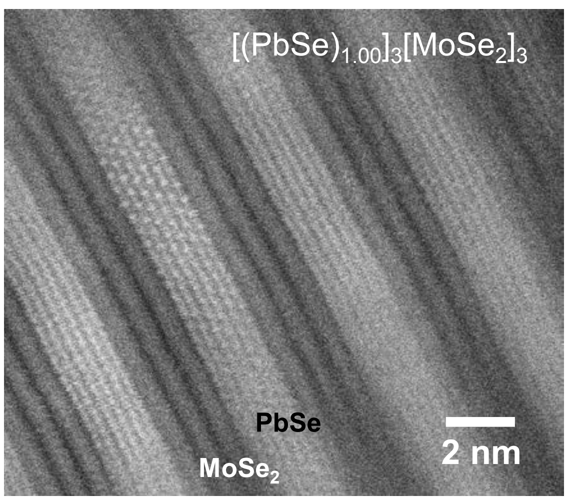
Can one calculate thermal, electrical, and/or magnetic properties?

Can one calculate the trends in properties as a function of m, n, and p?

Can one suggest which structures A, B or C should be interleaved to achieve a particular property?







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- Michael D. Anderson
- Corinna Gross
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- Colby Heideman
- Qiyin Lin

Collaborators:

- Ian M. Anderson
- Wolfgang Neumann
- Paul Zschack

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