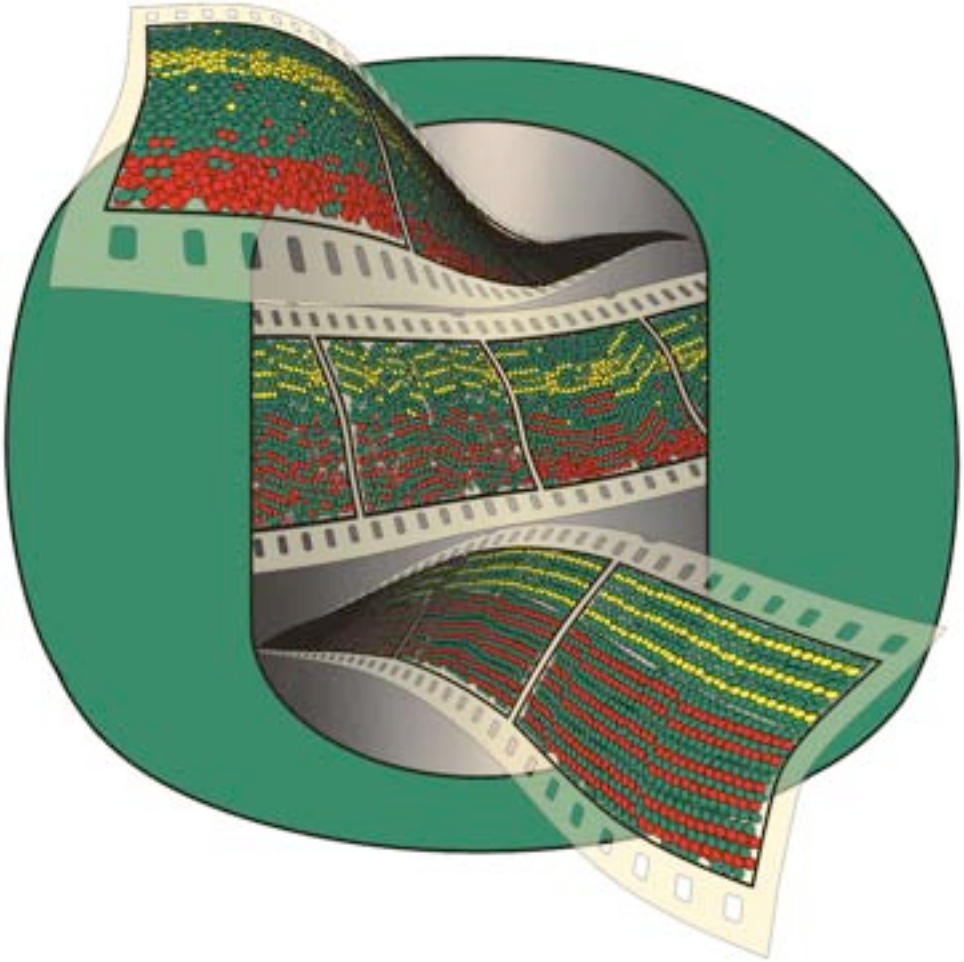
Ferecrystals: Thermoelectric Materials Poised Between the Crystalline and Amorphous States



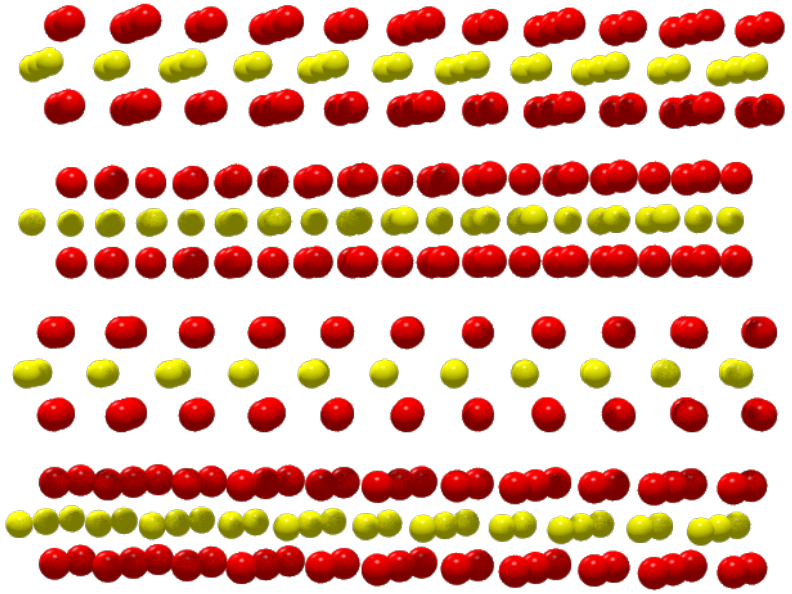
David C. Johnson

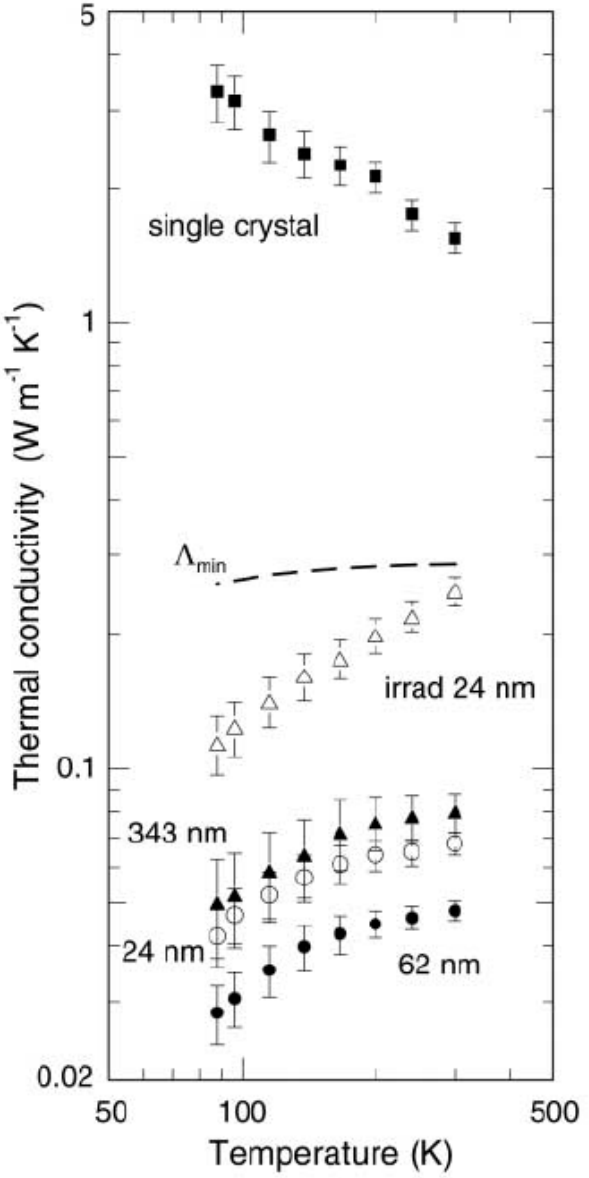
Department of Chemistry
and
Materials Science Institute

University of Oregon

Ultralow Thermal Conductivity in WSe_2

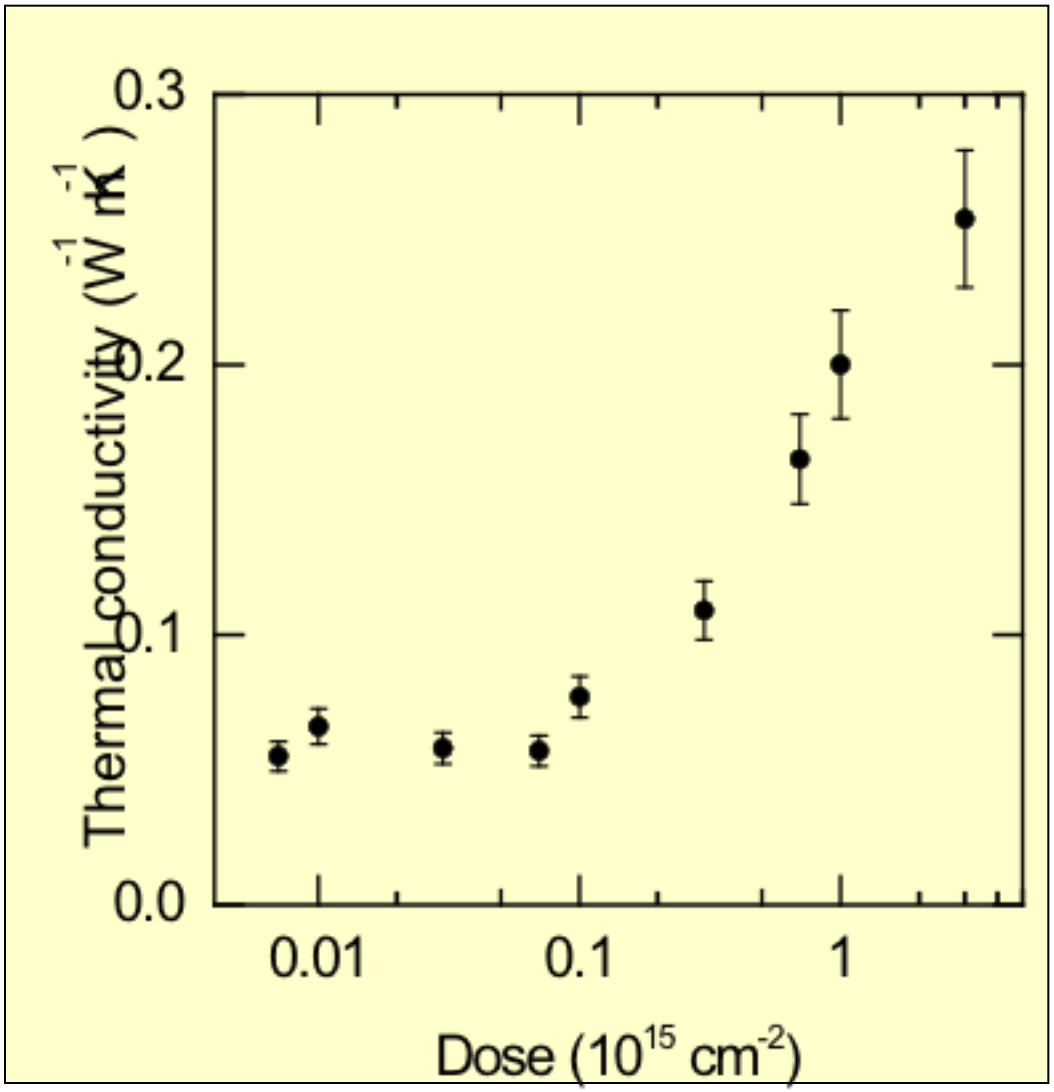
- Crystalline within sheets
- Disordered between sheets





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

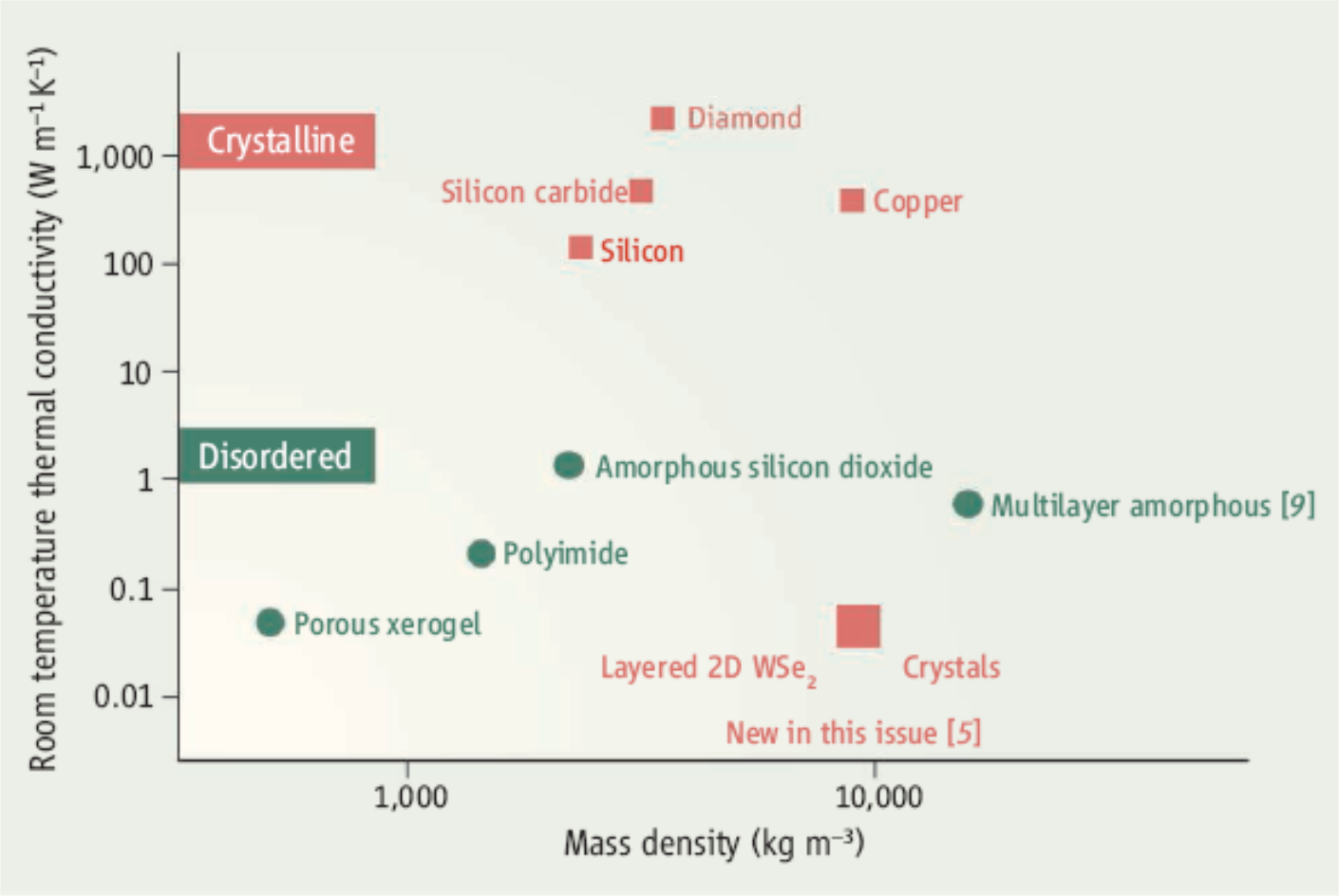
Balance of Order and Disorder Important



Ion damage destroys order in a-b plane and along c.

Ion damage increases the thermal conductivity!

Thermal Conductivity of Solids



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

Proposed New Paradigm

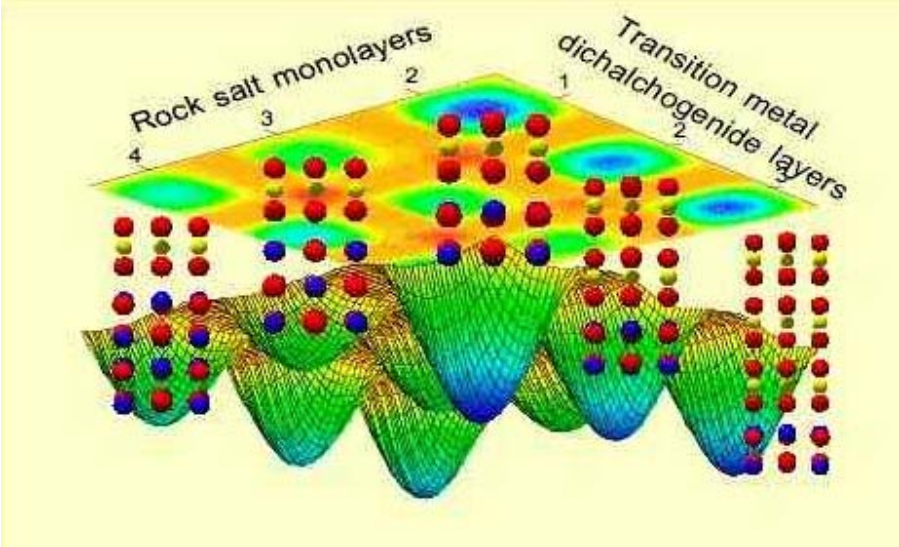
Molecular chemistry – based on combining standard bonding geometries to make new molecules

Assumption: satisfying local coordination results in a kinetically stable molecule

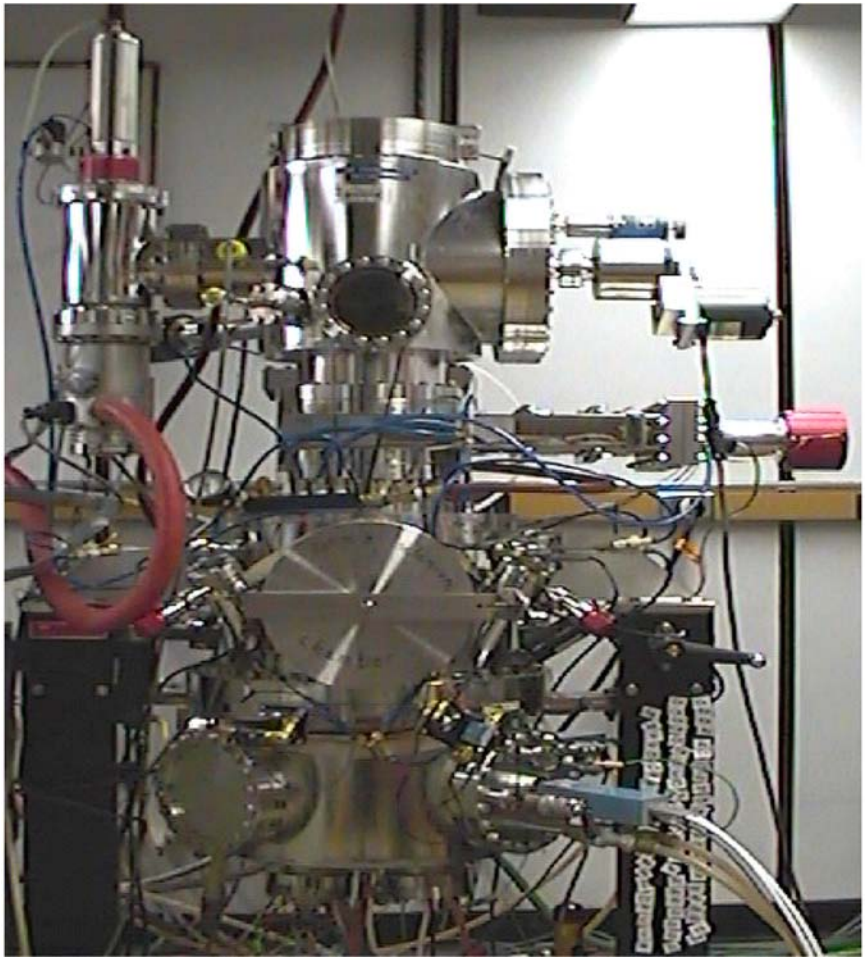
Can we apply the same rules to extended inorganic solids?

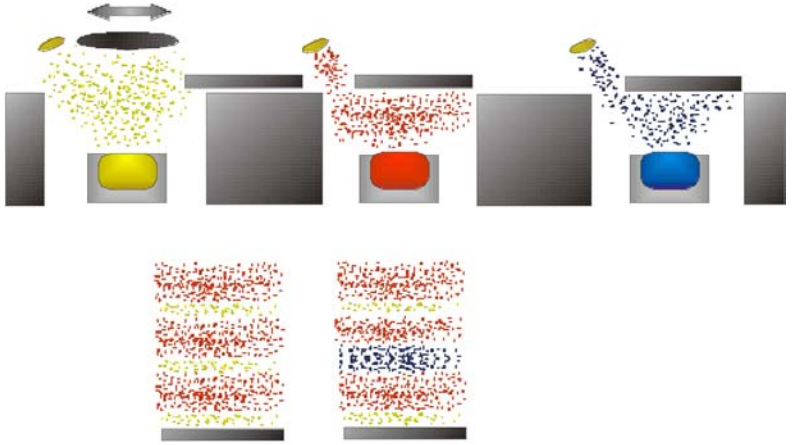
Assumption: satisfying local coordination results in a kinetically stable extended solid

Does this let us prepare families of new structurally related materials?



Key to Synthesis
Control of Diffusion Lengths and Deposition Sequence

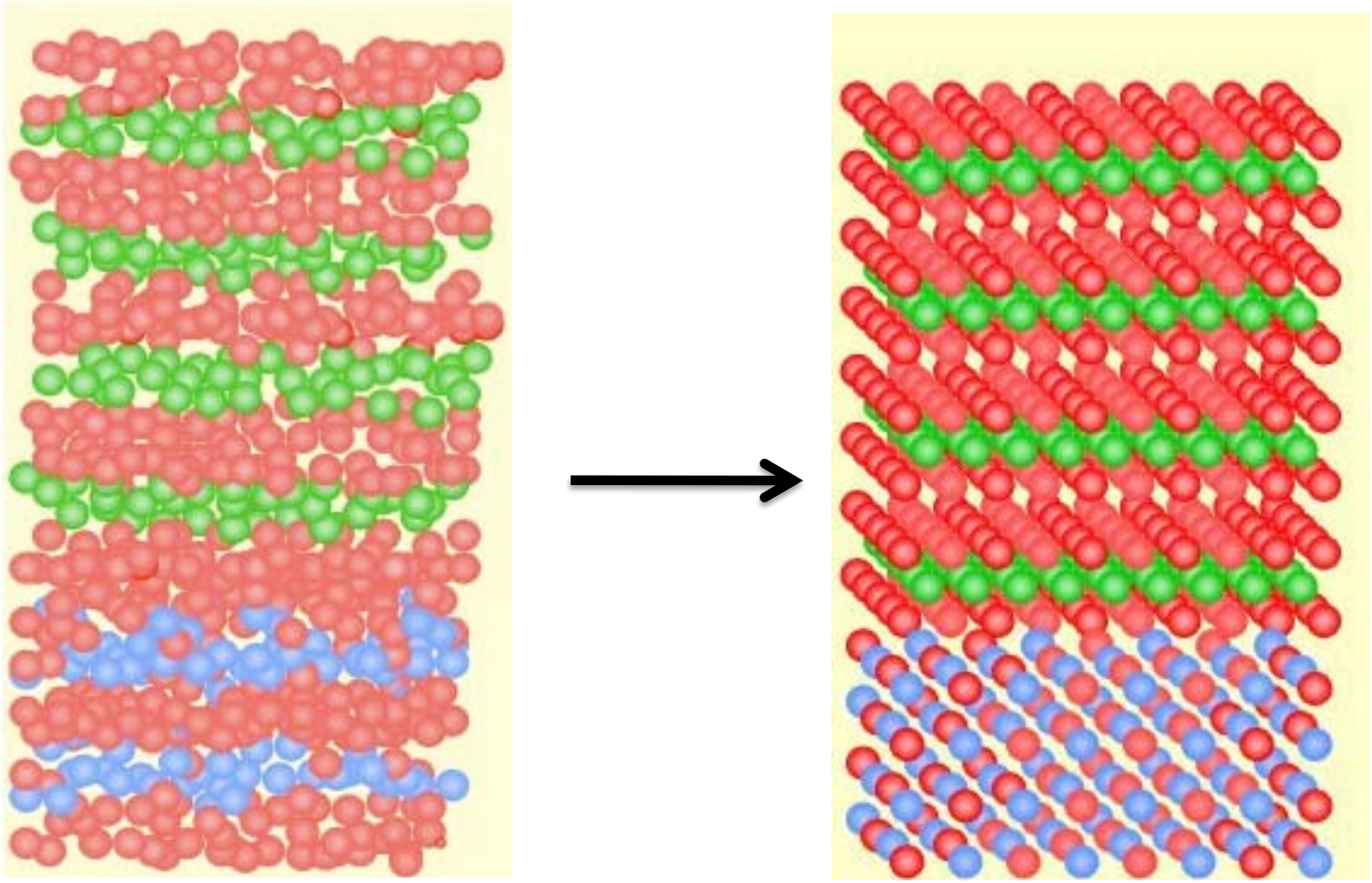




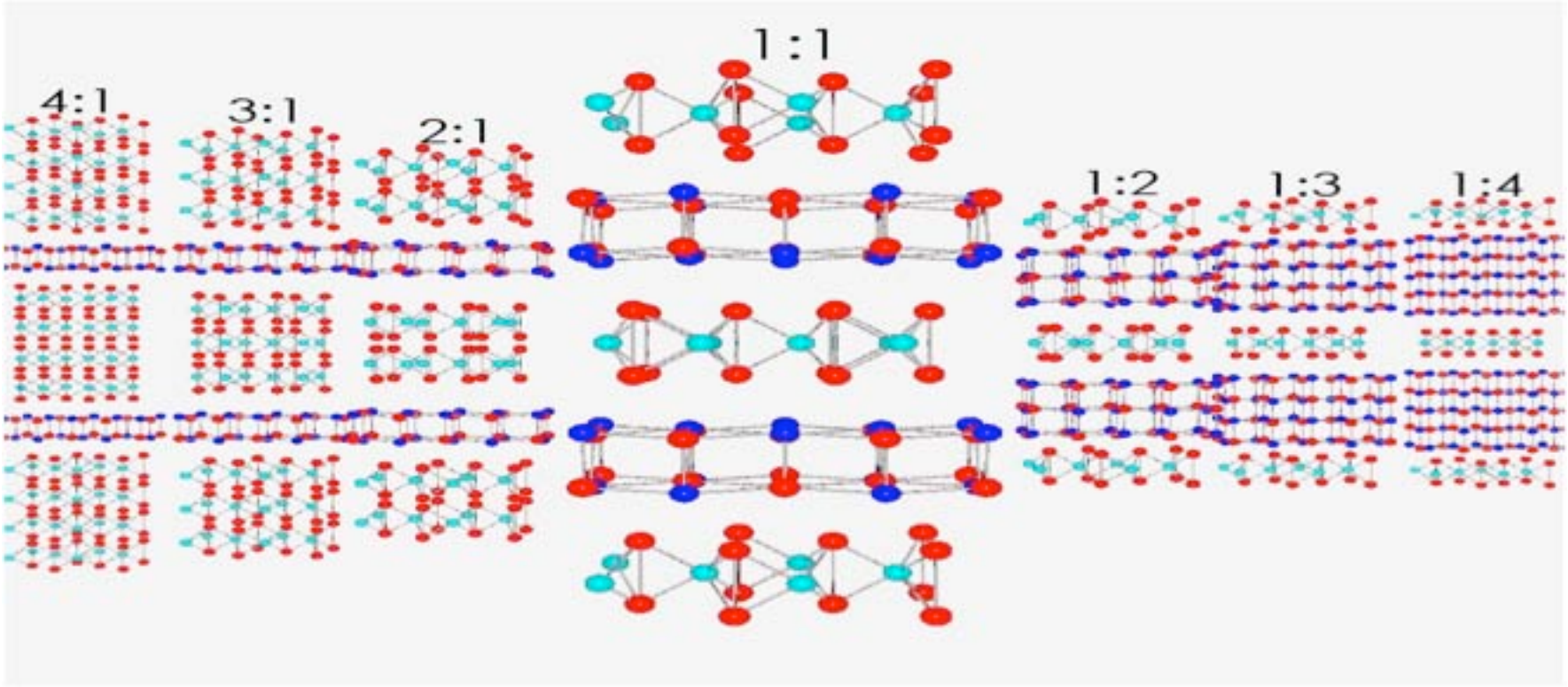
Can create simple or complex layer sequences.

Sub-Angstrom control of thickness

Composition profile of reactant controls reaction kinetics

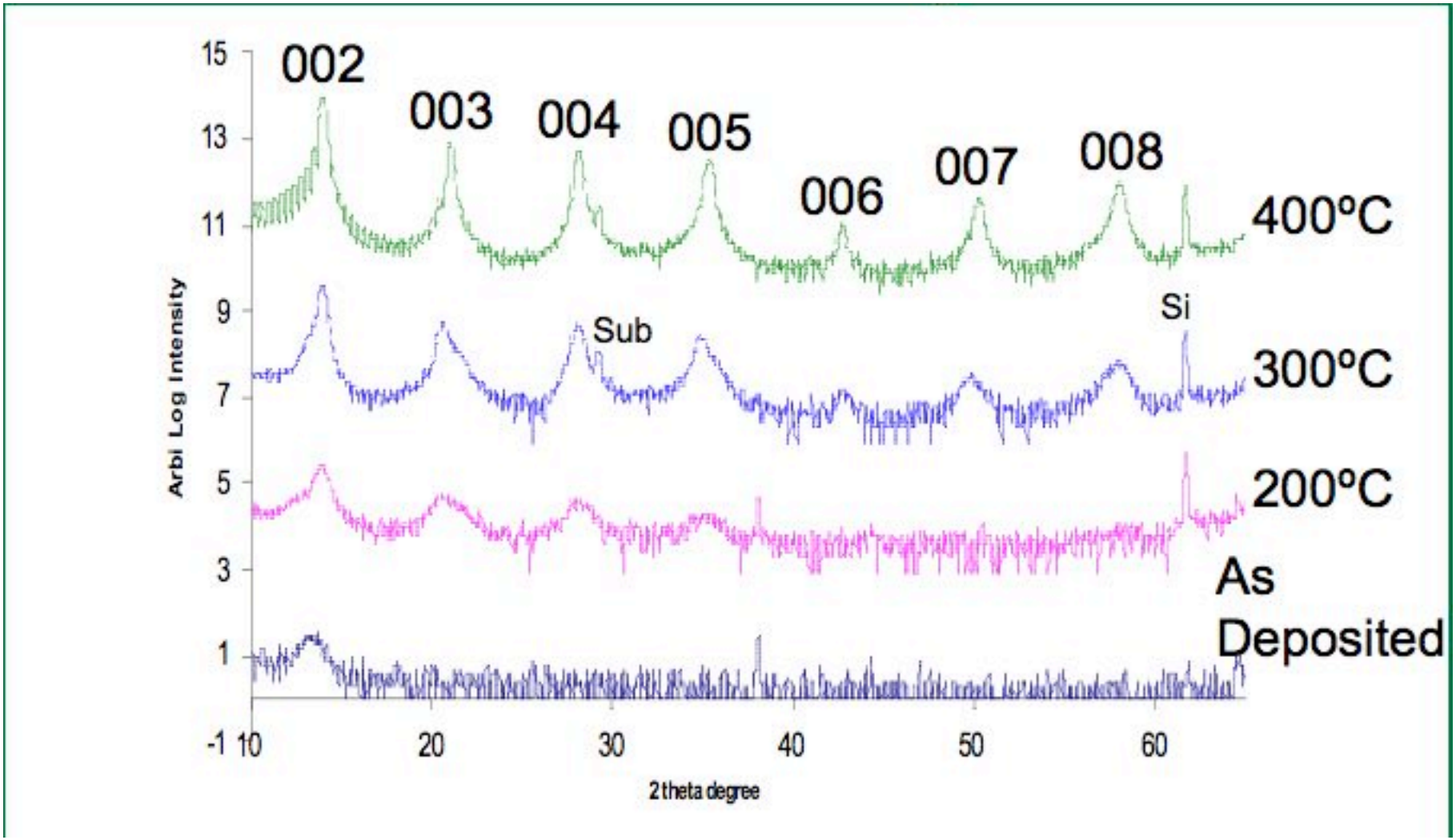


Designed Nanostructure

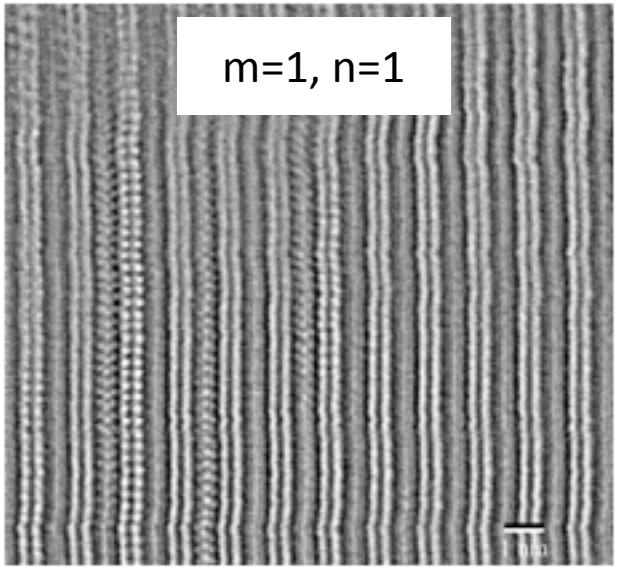


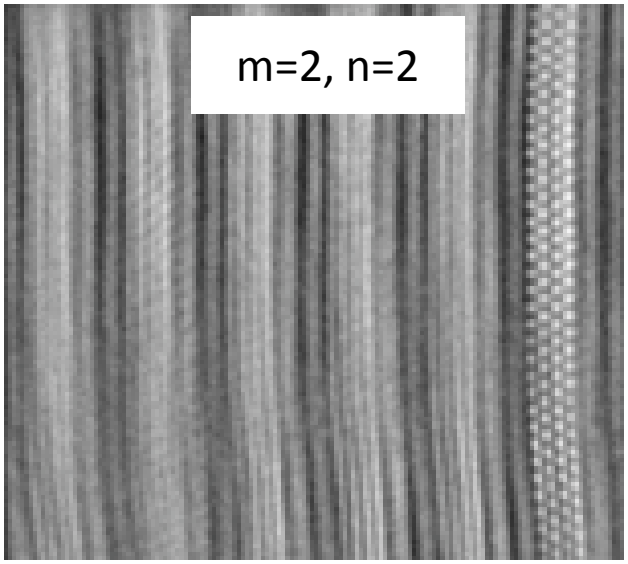
If the 1:1 structure is stable, all local bonding is satisfied in any compound m:n. m:n compounds should be at least metastable, just like all hydrocarbons that satisfy local bonding rules are at least metastable…

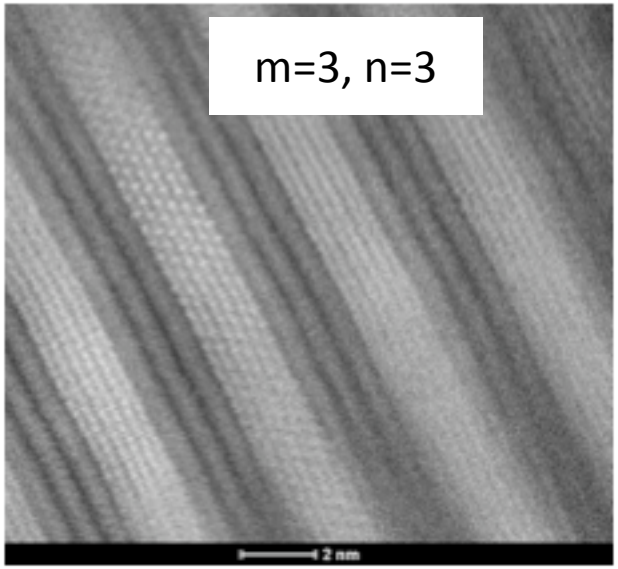
$[(PbSe)_{0.99}]_1[WSe_2]_1$ forms on annealing

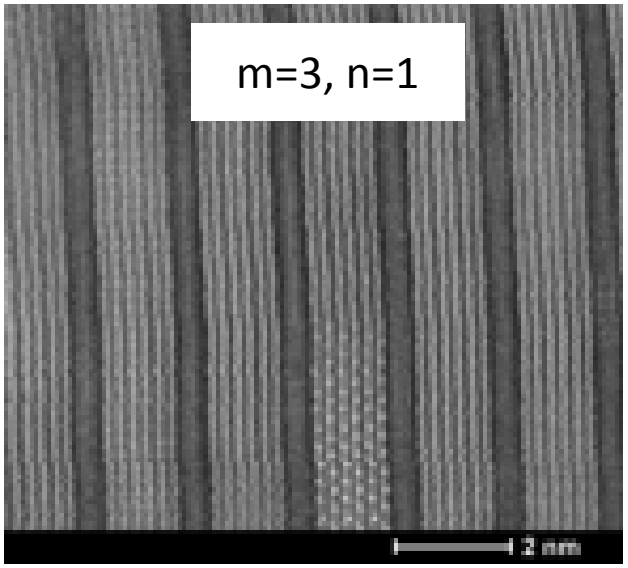


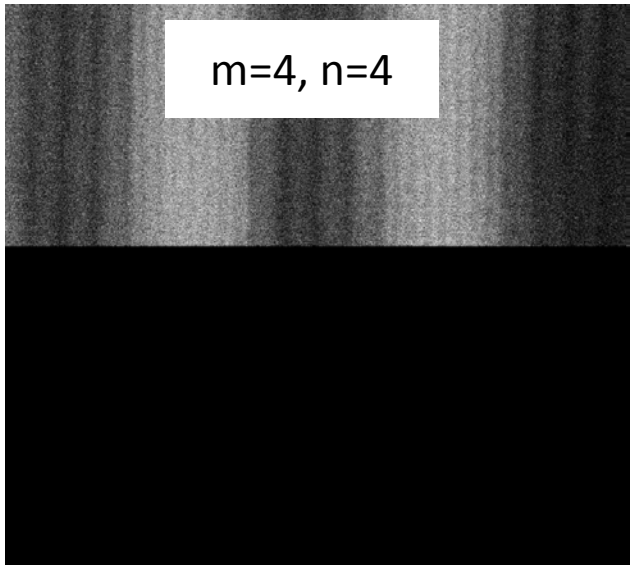
$[(PbSe)_{1.00}]_m(MoSe_2)_n$

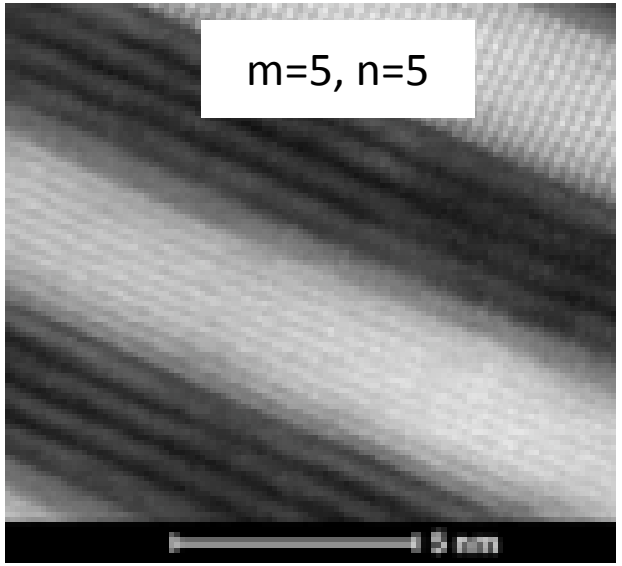




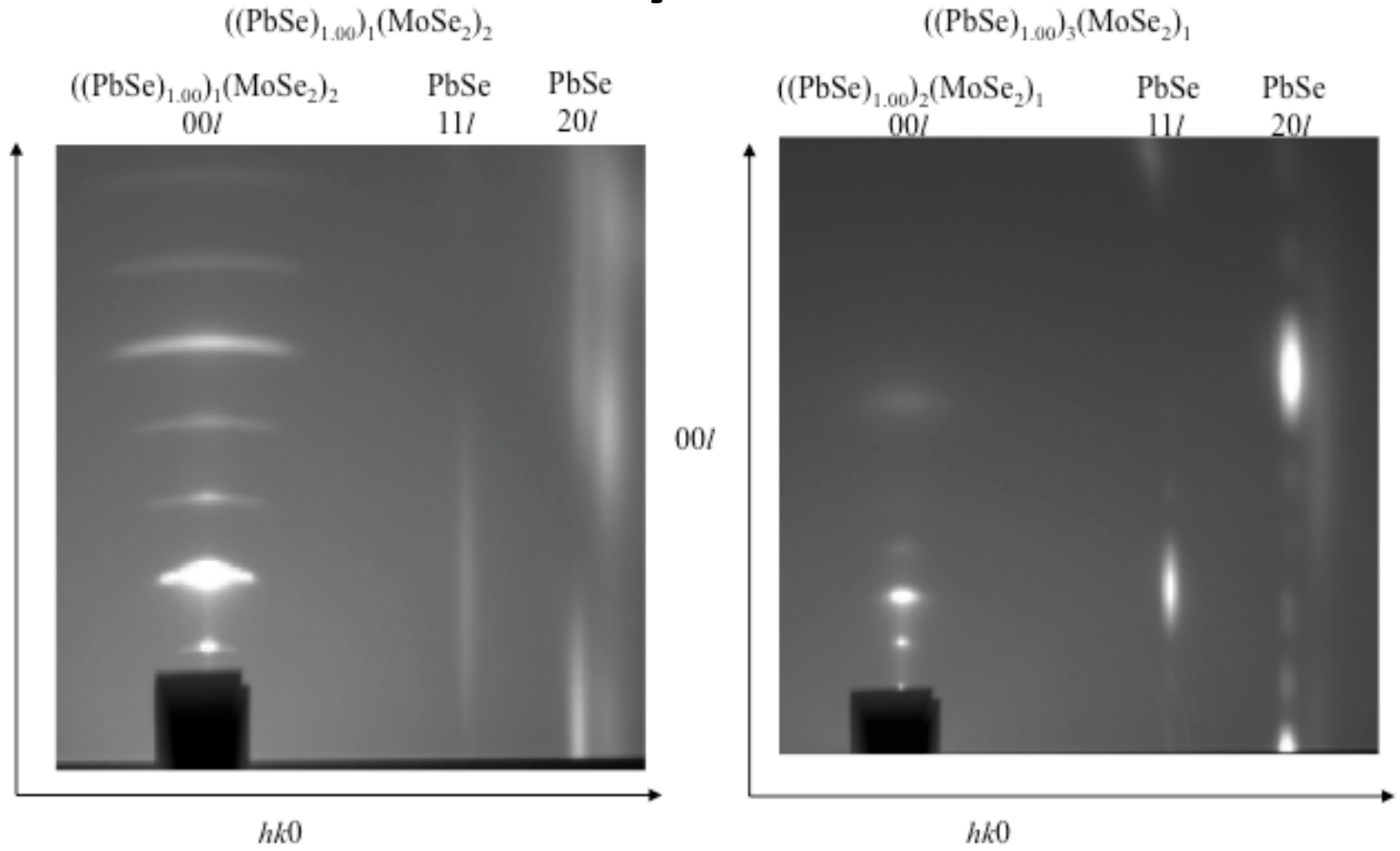




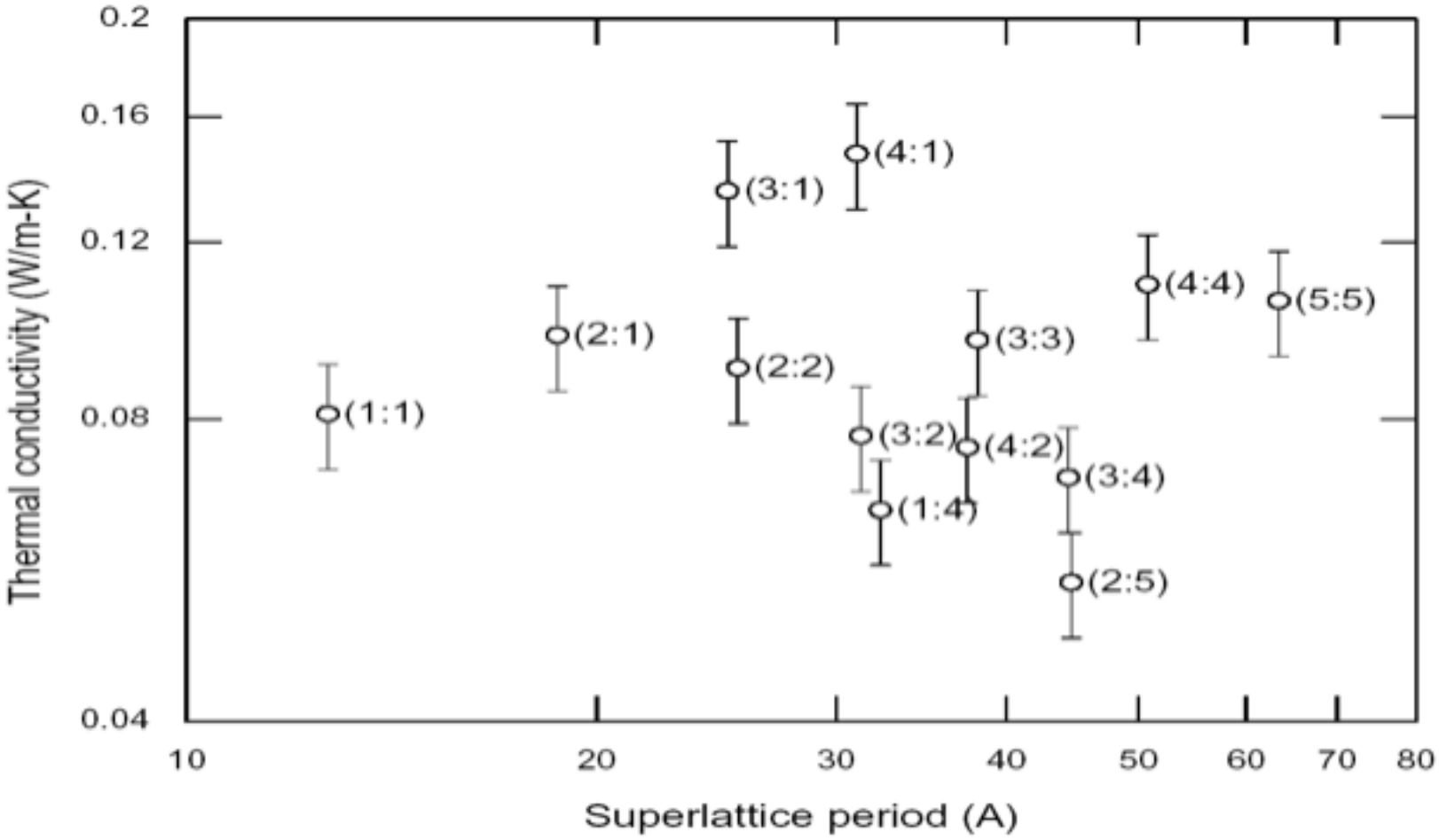




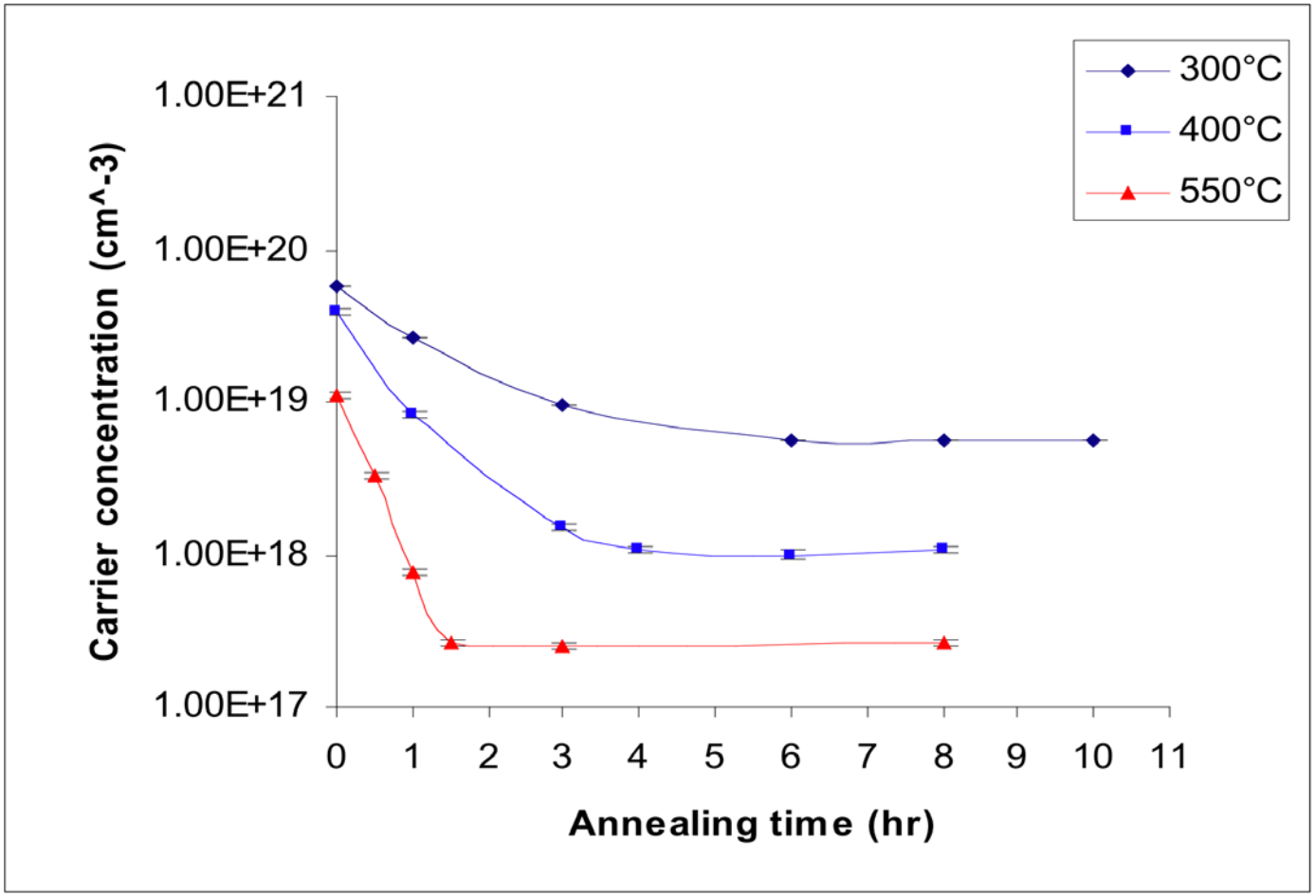
Aligned relationship between the PbSe and $MoSe_2$ layers, but where is the superlattice crystal?



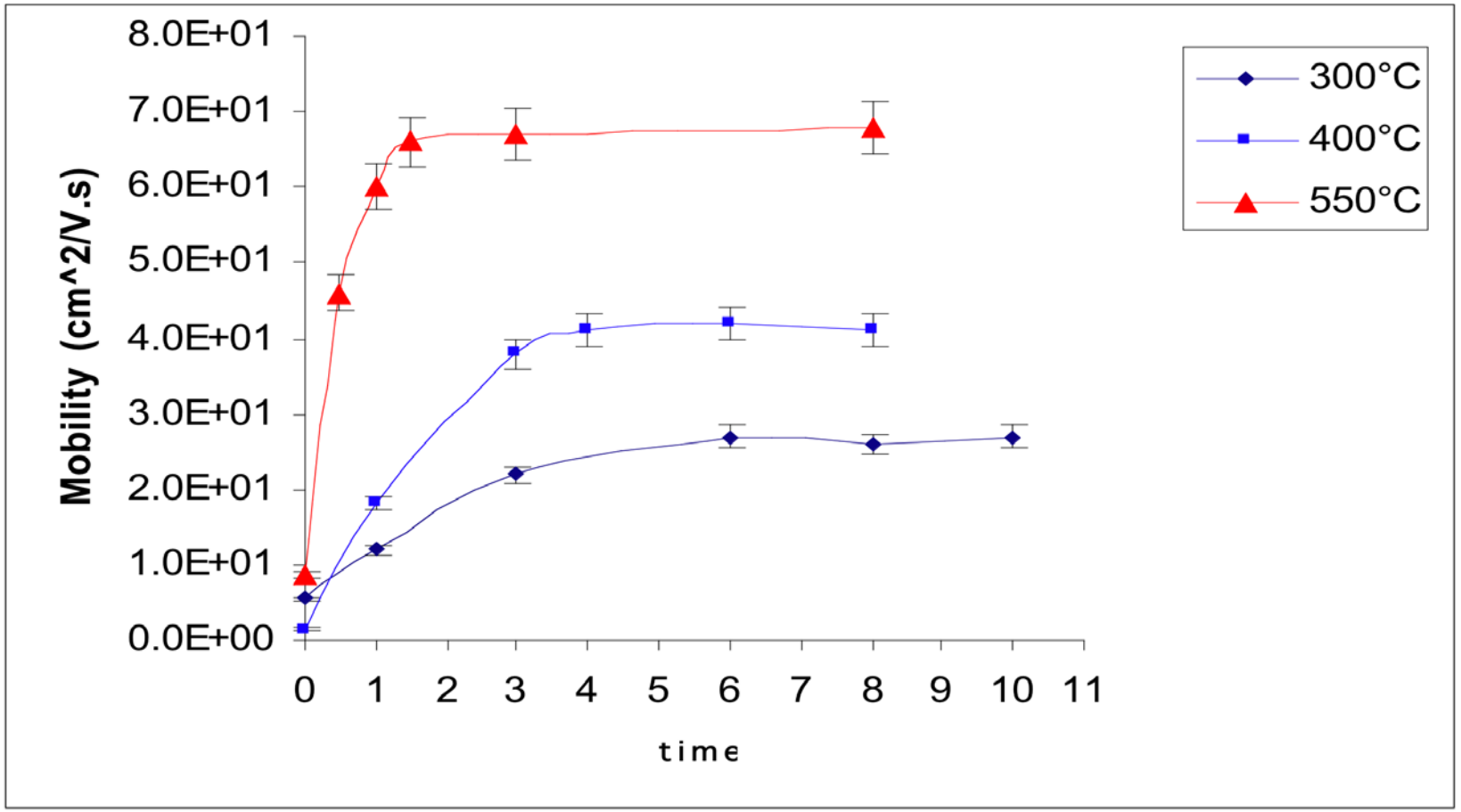
Ferecrystals – from the Latin fere – meaning “almost”
have ultra low thermal conductivities



Synthesis traps defects - annealing in chalcogen vapor reduces defect levels

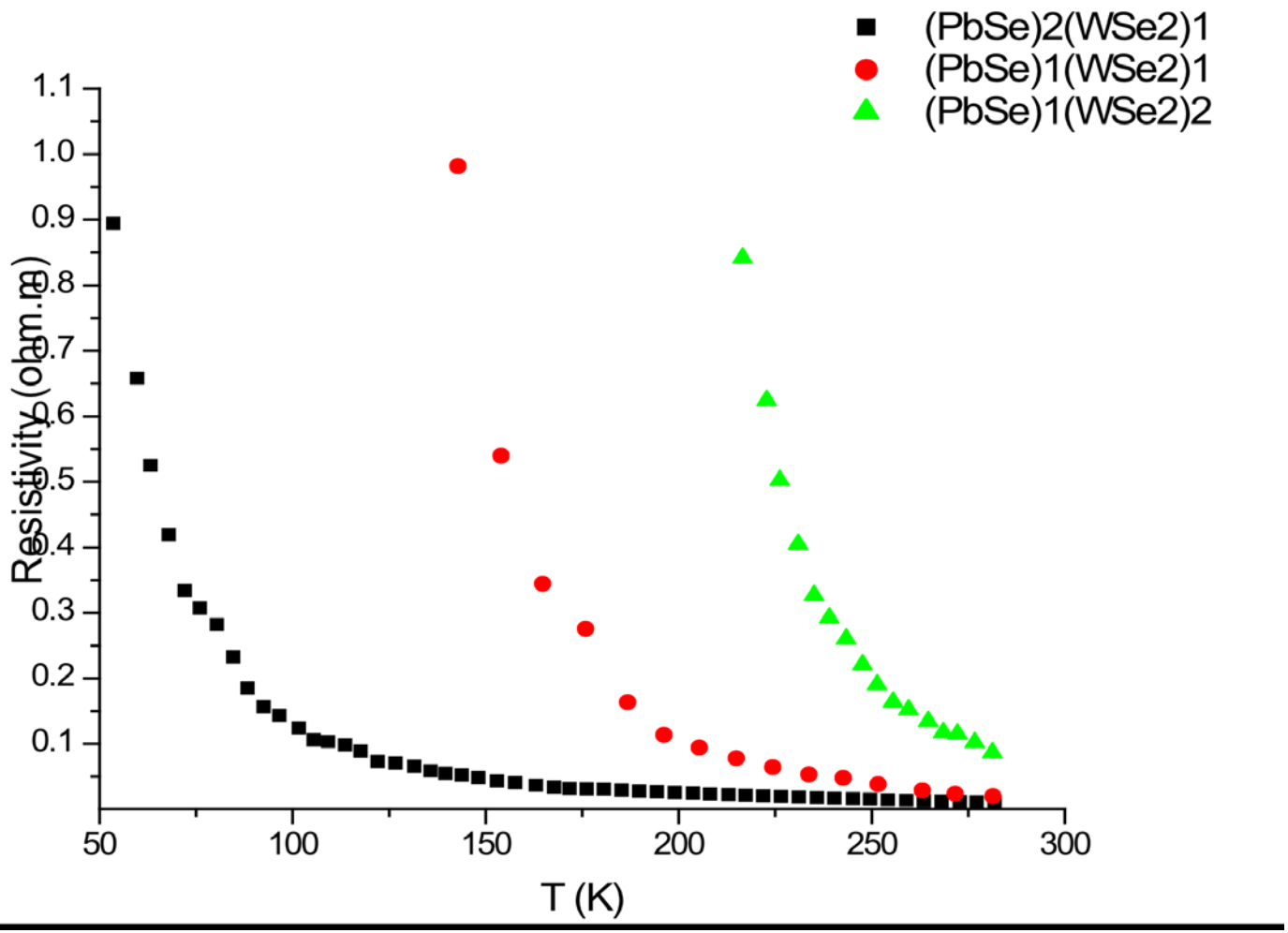


Annealing increases mobility - $[(PbSe)_{0.99}]_1(WSe_2)_1$



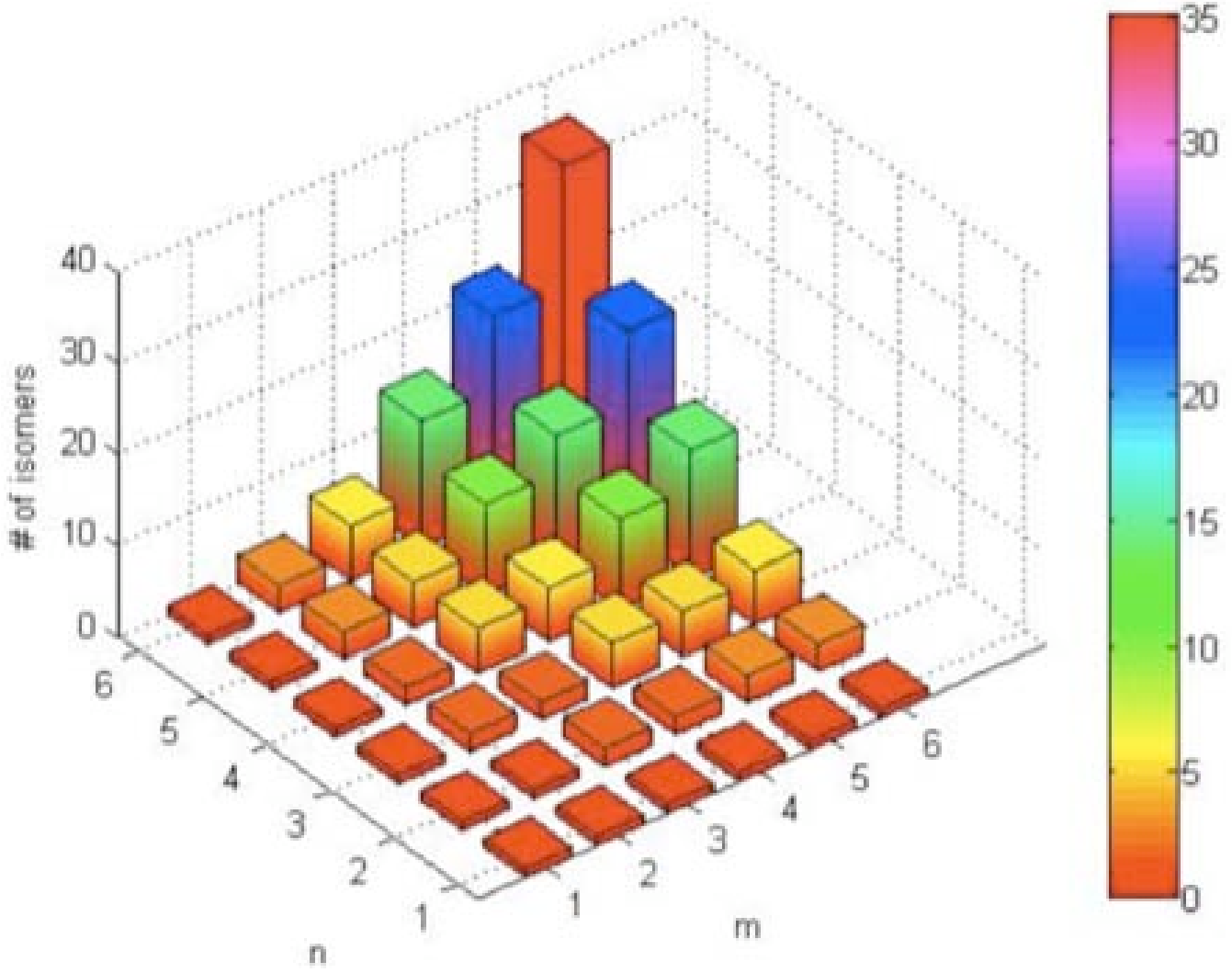
High mobility may result from aligned nature of PbSe and WSe_2nanograins

Activation energy for electrical conduction changes with nanostructure



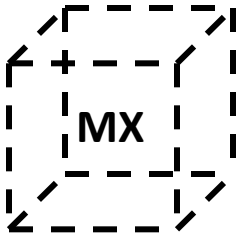
Many Possible Nanostructured Isomers!

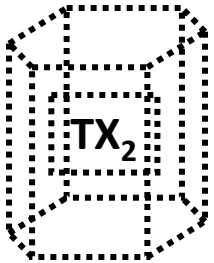
many more in ternary systems

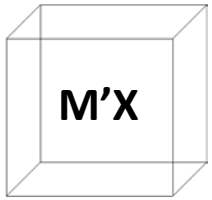


New Ferecrystal intergrowths

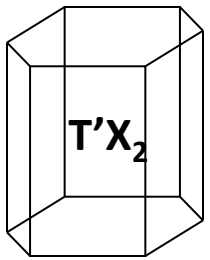
ABAC:
$(TX_2)_m$
$(MX)_n$
$(TX_2)_p$
$(M'X)_q$

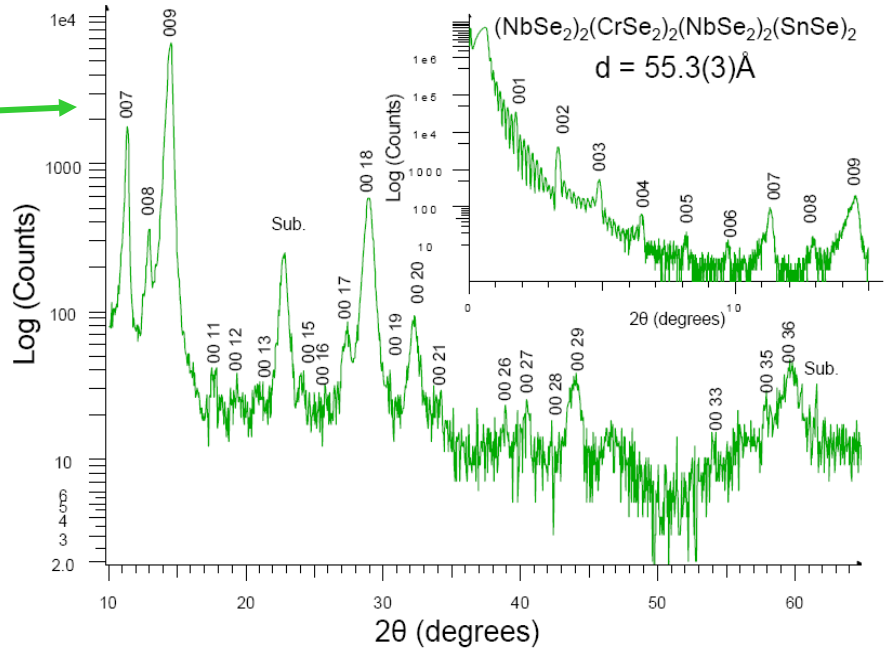


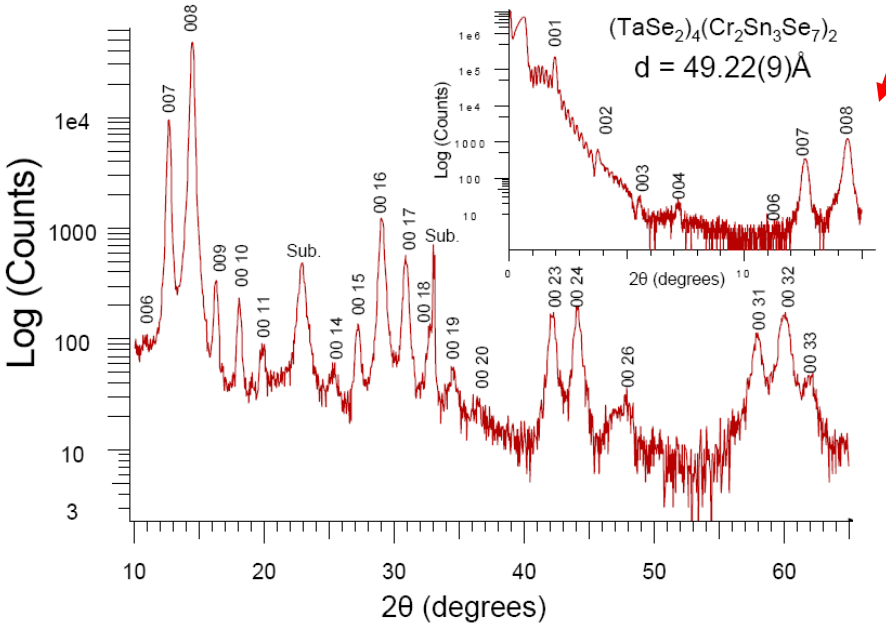




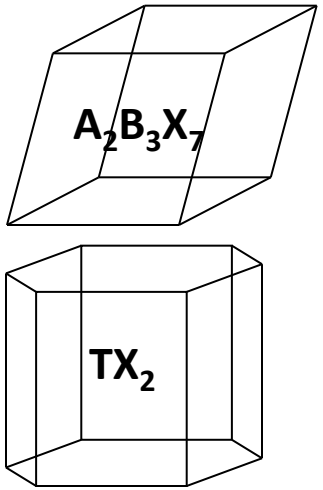
ABCD:
$(TX_2)_m$
$(MX)_n$
$(T'X_2)_p$
$(M'X)_q$



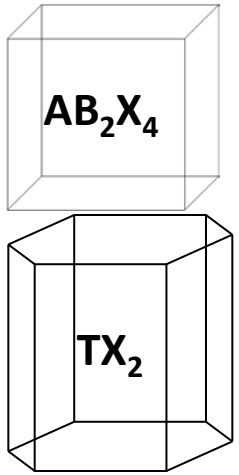




$(TX_2)_m(A_2B_3X_7)_n$
hexagonal-monoclinic

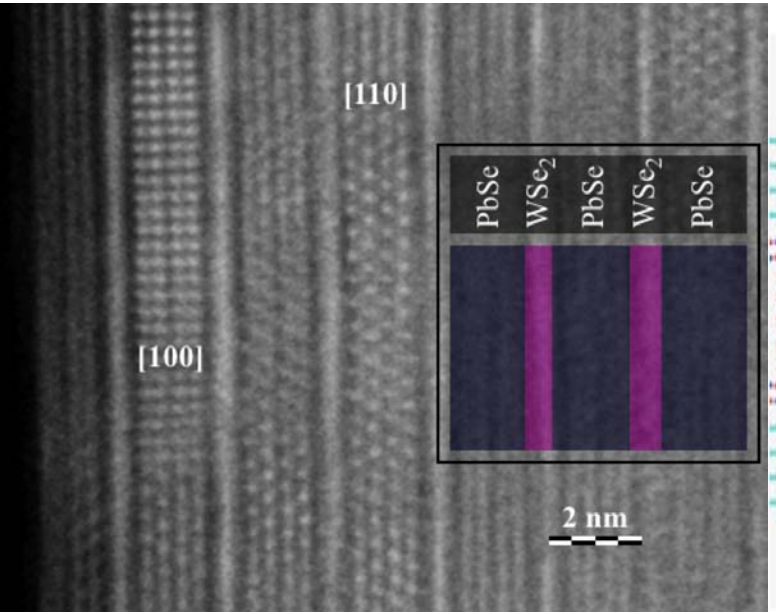


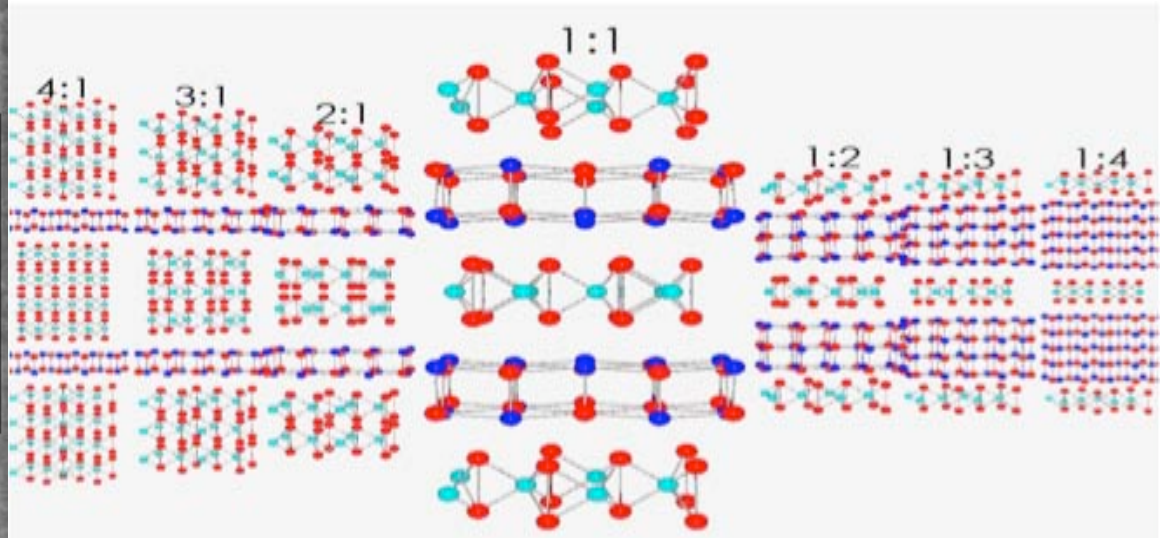
$(TX_2)_m(AB_2X_4)_n$
hexagonal-spinel



Summary

- Nanostructure effects structure of the constituent layers.
- Structure effects properties
- A turbostratic disorder observed for all compounds investigated leading to a reduced thermal conductivity.
- Carrier concentration controlled by annealing in Se vapor
- New “nano chemistry” using multi component ABC and ABAC nanostructure and local chemical bonding criteria is upon us.
- Much to understand about charge transfer between layers, controlled doping and interplay between nanostructure and properties





Acknowledgements

Graduate Students

Myungkeun Noh
Fred Harris
Mary Smeller
Clay Mortensen
Ngoc Nguyen
Colby Heideman
Qiyin Lin

Collaborators

Paul Zschack - APS
David Cahill
Catalin Chirtescu
Li Shi
Anastassios Mavrokefalos
Harold Bottner
Raimar Rostek
Ian Anderson
Mike Anderson

Funding

ONR Murdock Foundation
Asahi KaseiARL Air Force NSF
Department of Education NIST
State of Oregon - ETIC and ONAMI