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New Thermoelectric Materials with Ultra-low Thermal Conductivity

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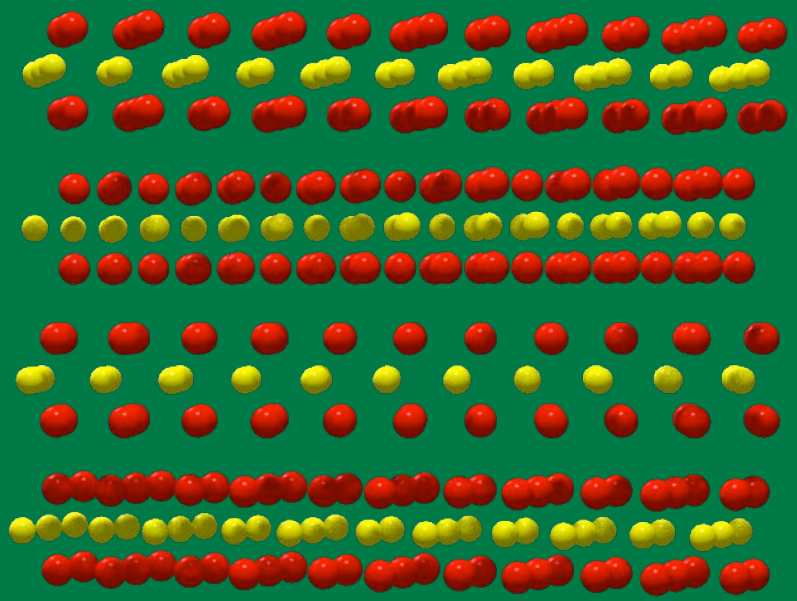
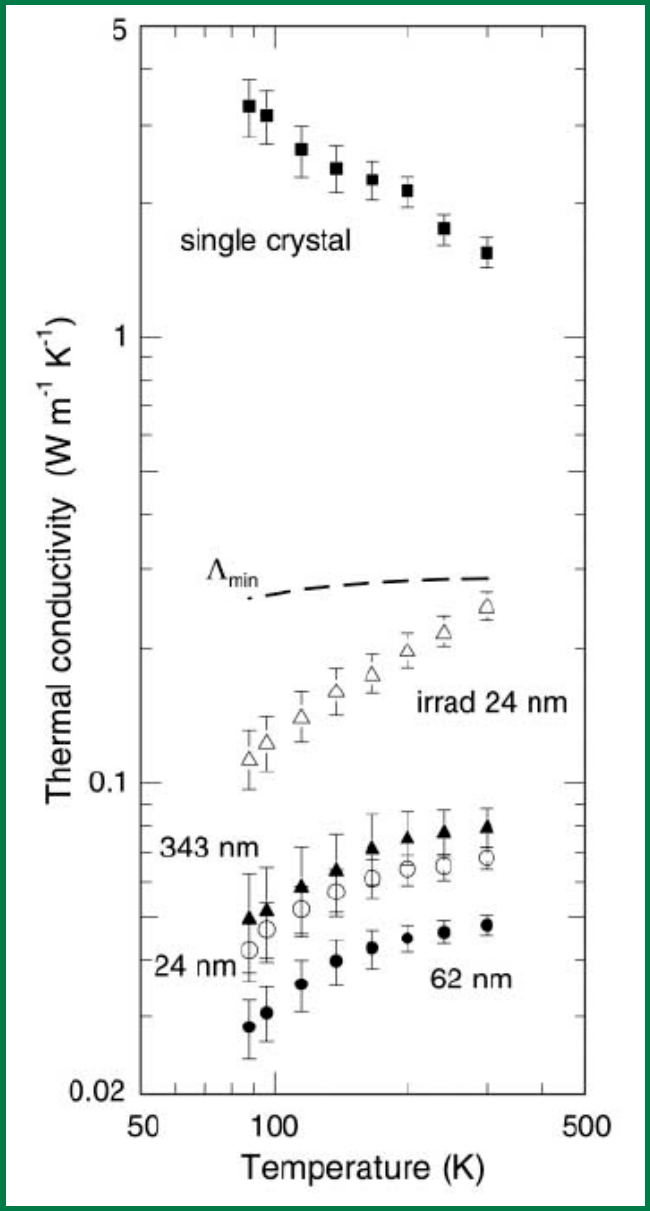
Ultralow Thermal Conductivity in WSe_2

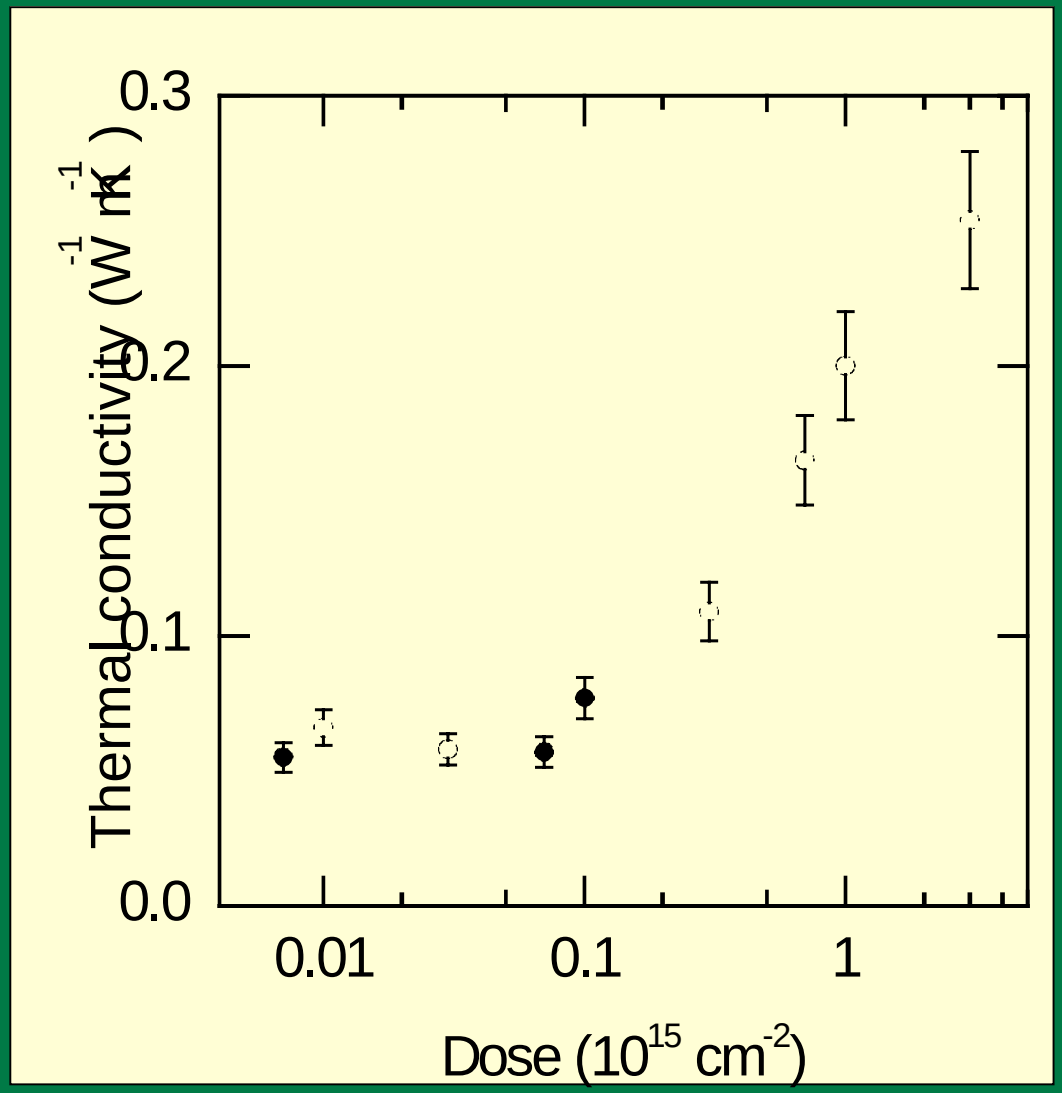
- Crystalline within sheets
- Disordered between sheets





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

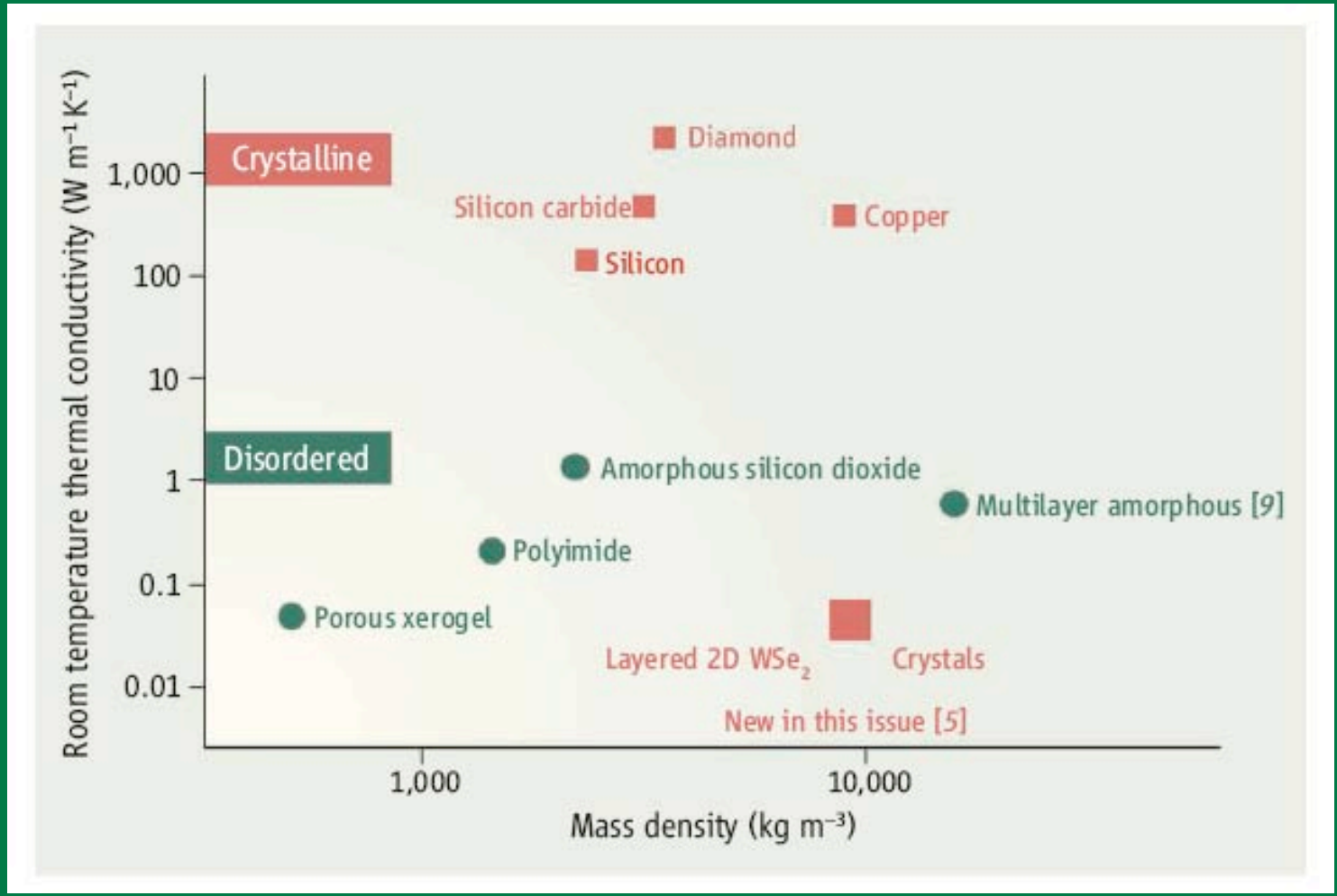
Balance of Order and Disorder Important



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

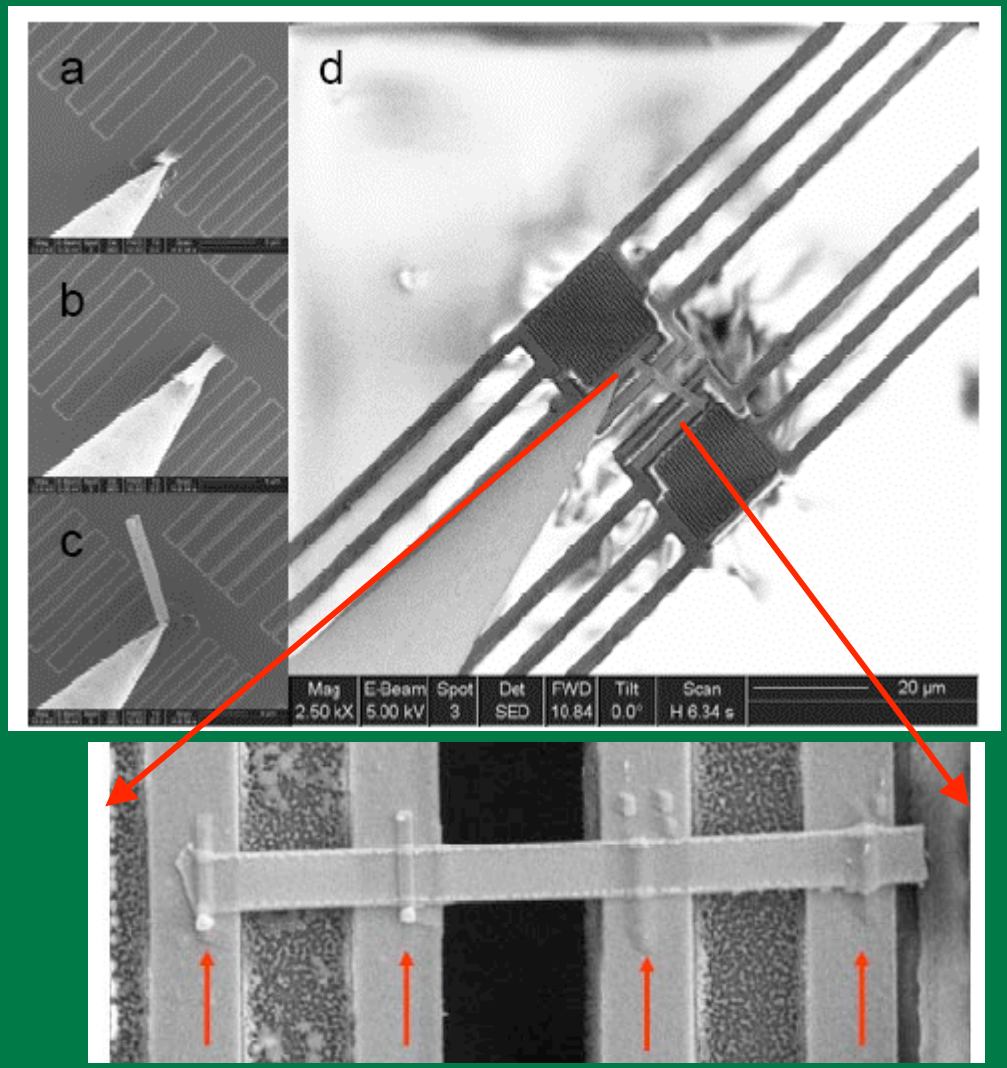
Ion damage increases the thermal conductivity!

Thermal Conductivity of Solids



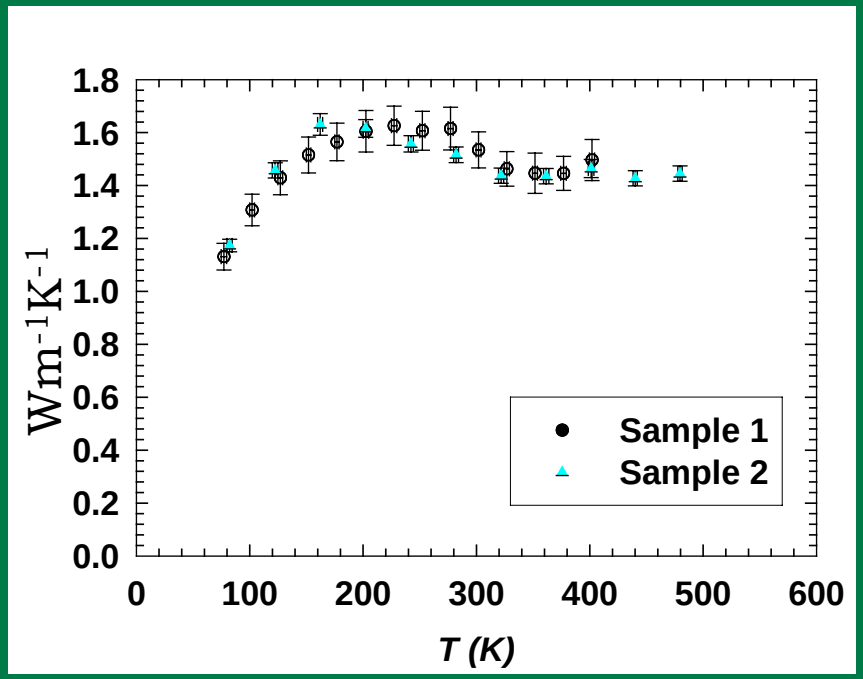
K. E. Goodson, *Science* **2007**, 315, 342.

Device Assembly for In-plane Thermal Transport

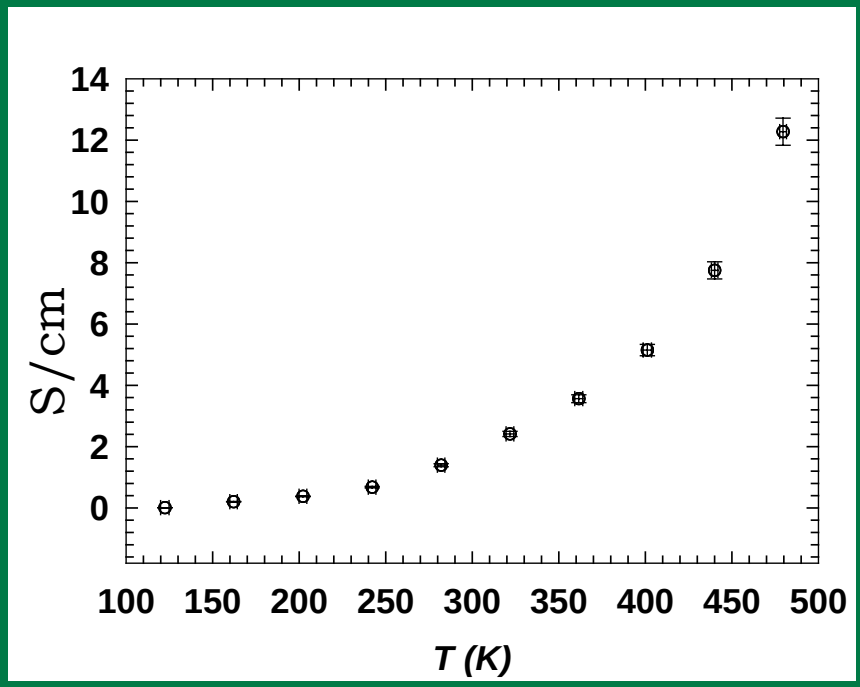


Courtesy of Dr. Li Shi, UT at Austin

WSe_2 In-plane Properties



Thermal conductivity



Electrical conductivity

Need a way to tune electricql properties

Misfit Layered Compounds

- Interleaved layers of transition metal dichalcogenides and rock salt structures
- 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
- Compounds can be metallic, semiconducting or insulating (magnetic, superconducting, etc.)
- ~10 different dichalcogenides and ~30 different rock salt constituents - lots of potential flexibility

Prior Results

- **$(YbS)_{1.24}NbS_2$** **S = 60μV/K**
  б = $1.4x10^{-5}\Omega\cdot m$
  K = $0.8Wm^{-1}K^{-1}$
  ZT = 0.1

- **$(LnS)_m(NbS_2)_n$ and $(SnS)_m(TiS_2)_n$ n,m = 1,2**
  power factor, $6\sim12x10^{-4}$ $W/m\cdot K^{-2}$ at 300K
  If the K value is ~1 $Wm^{-1}K^{-1}$,
  ZT ~ .1-.3

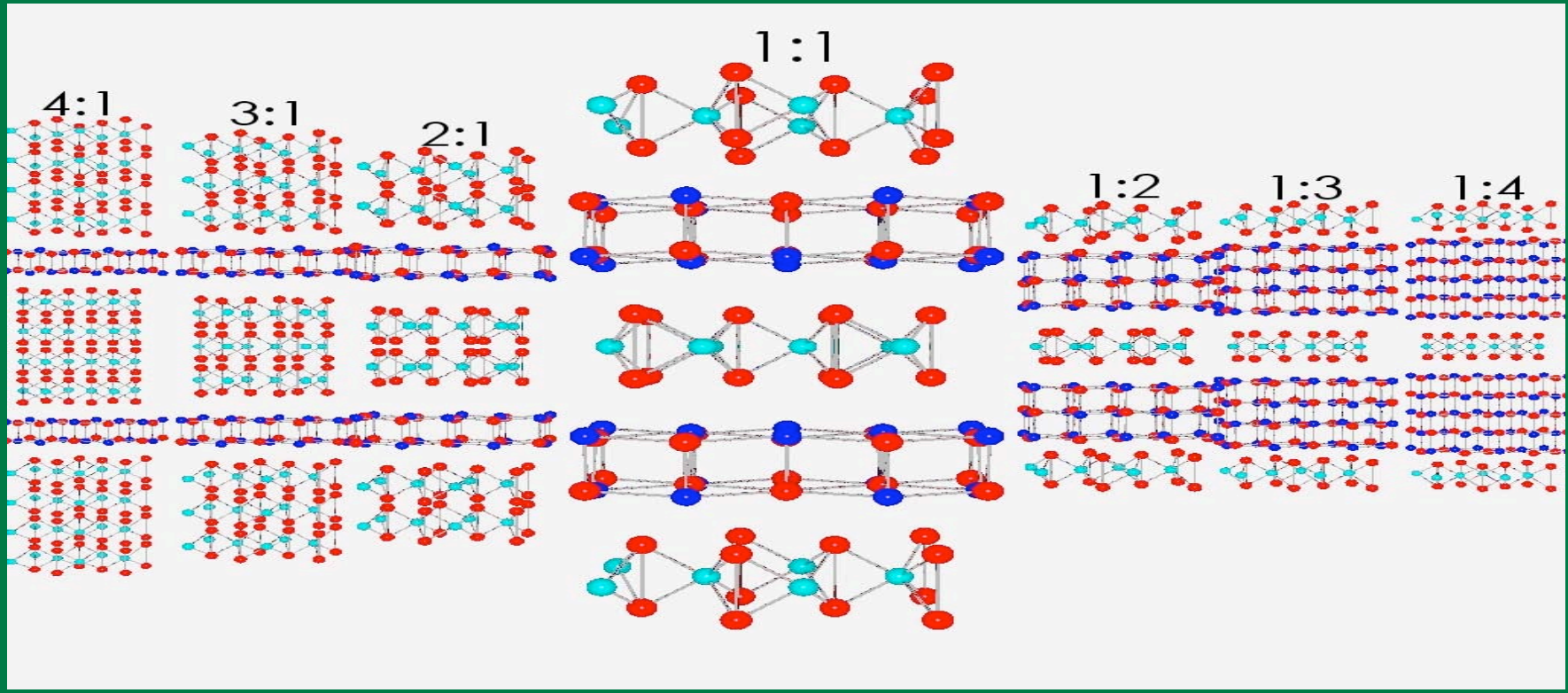
Miyazaki, Ogawa, Kajitani, Jap. J. Appl. Physics, 43 (2004) L1202

- **$(SnS)_1(TiS_2)_2$** **$K_{latttice}$ ~ 0.8 $Wm^{-1}K^{-1}$,**
  ZT ~ .4 at 400°C

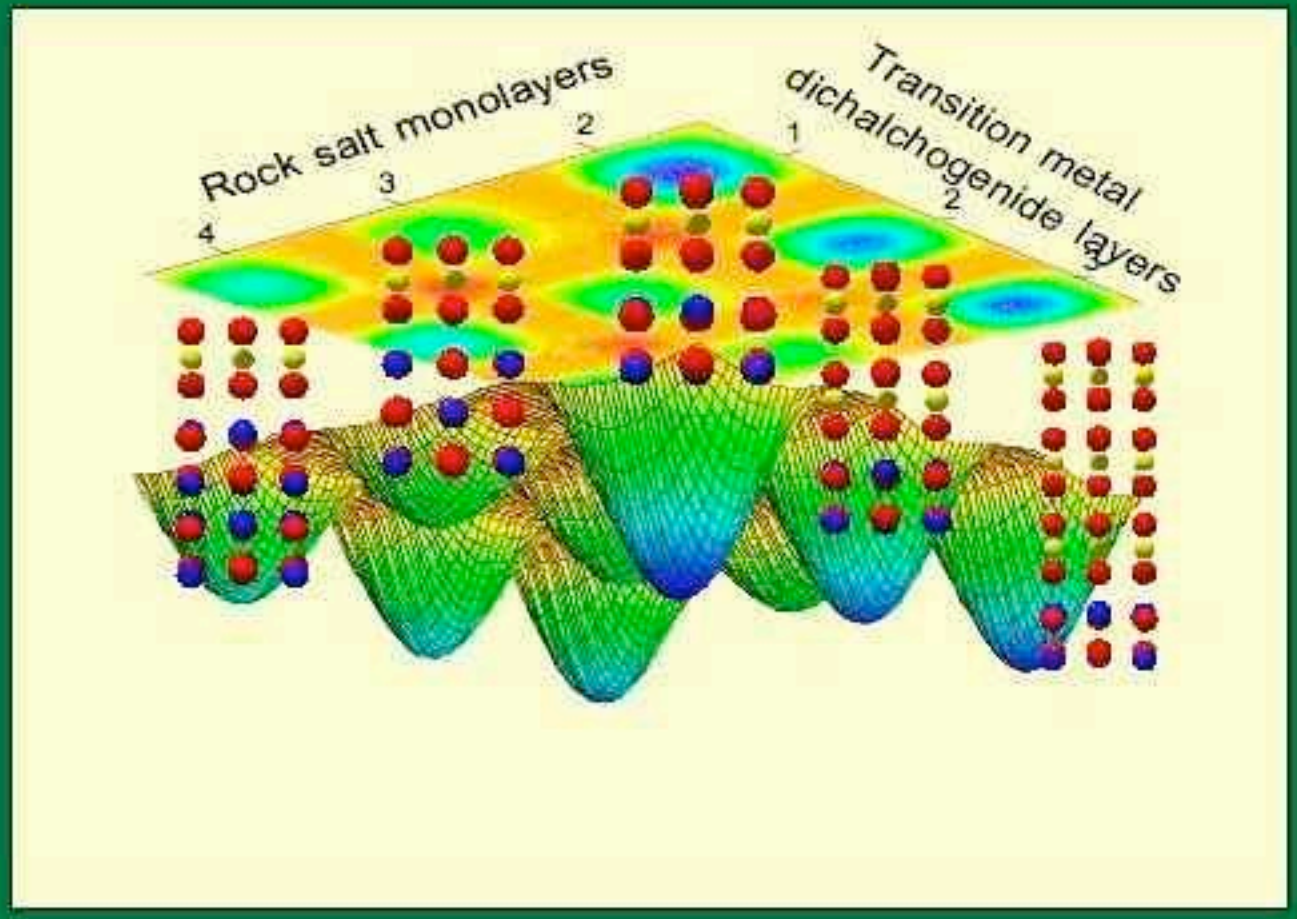
C. Wan, Y. Wang, N. Wang and K. Koumoto - ICT 2009 Freiburg

No report of controlled doping
Only one or two compounds in each family made

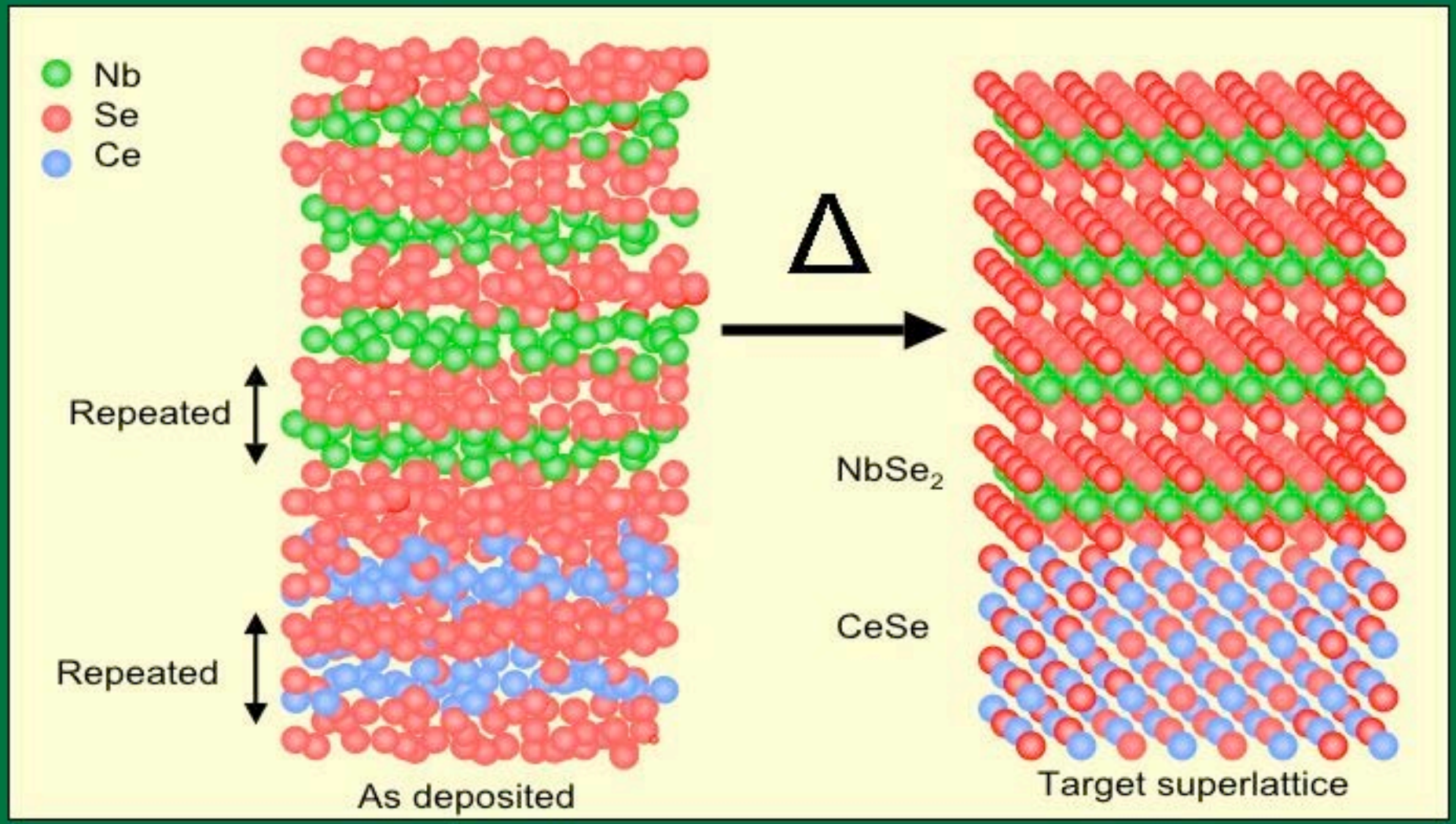
Controlled Nanostructure



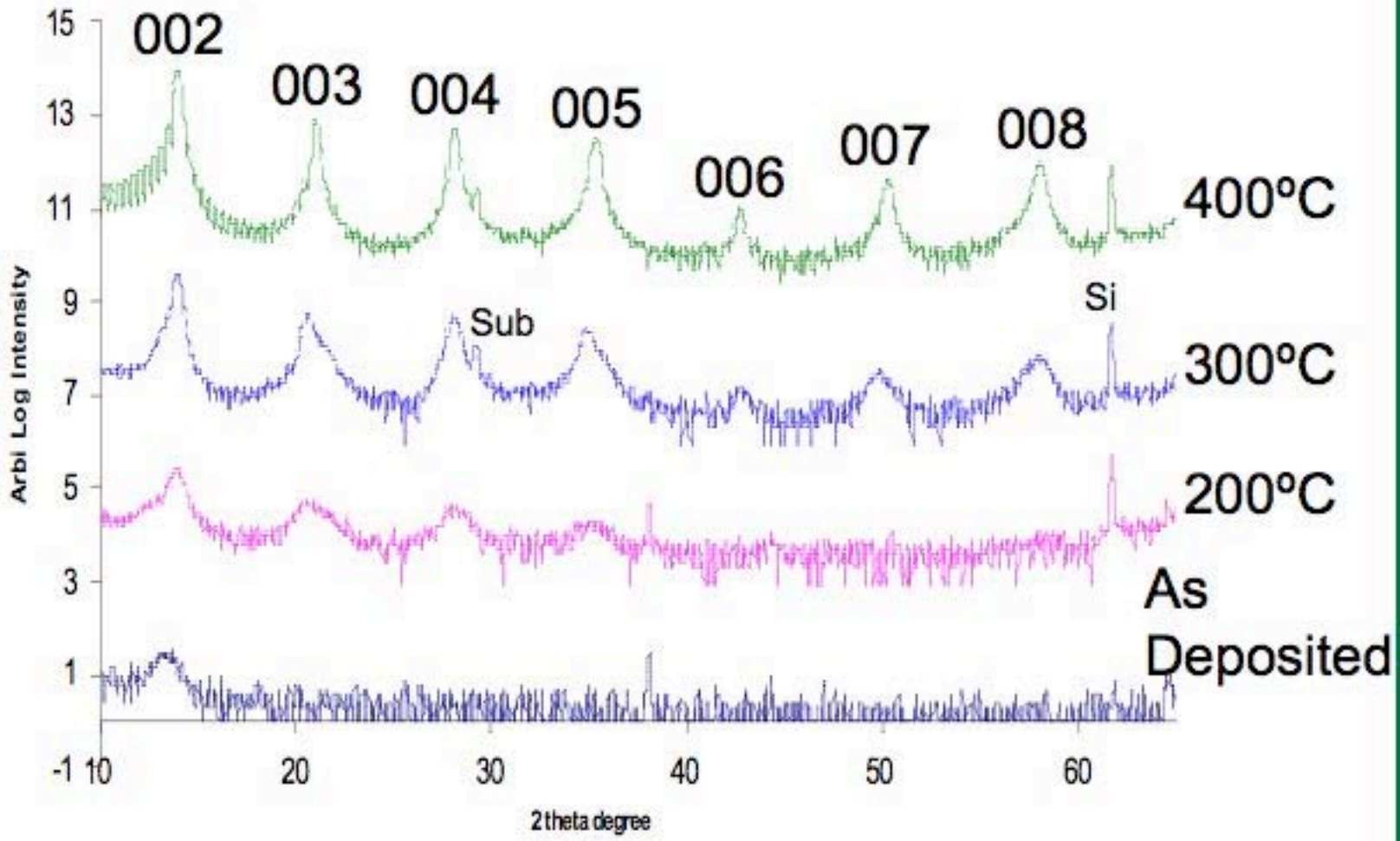
Assume local free energy minima at each value of n and m



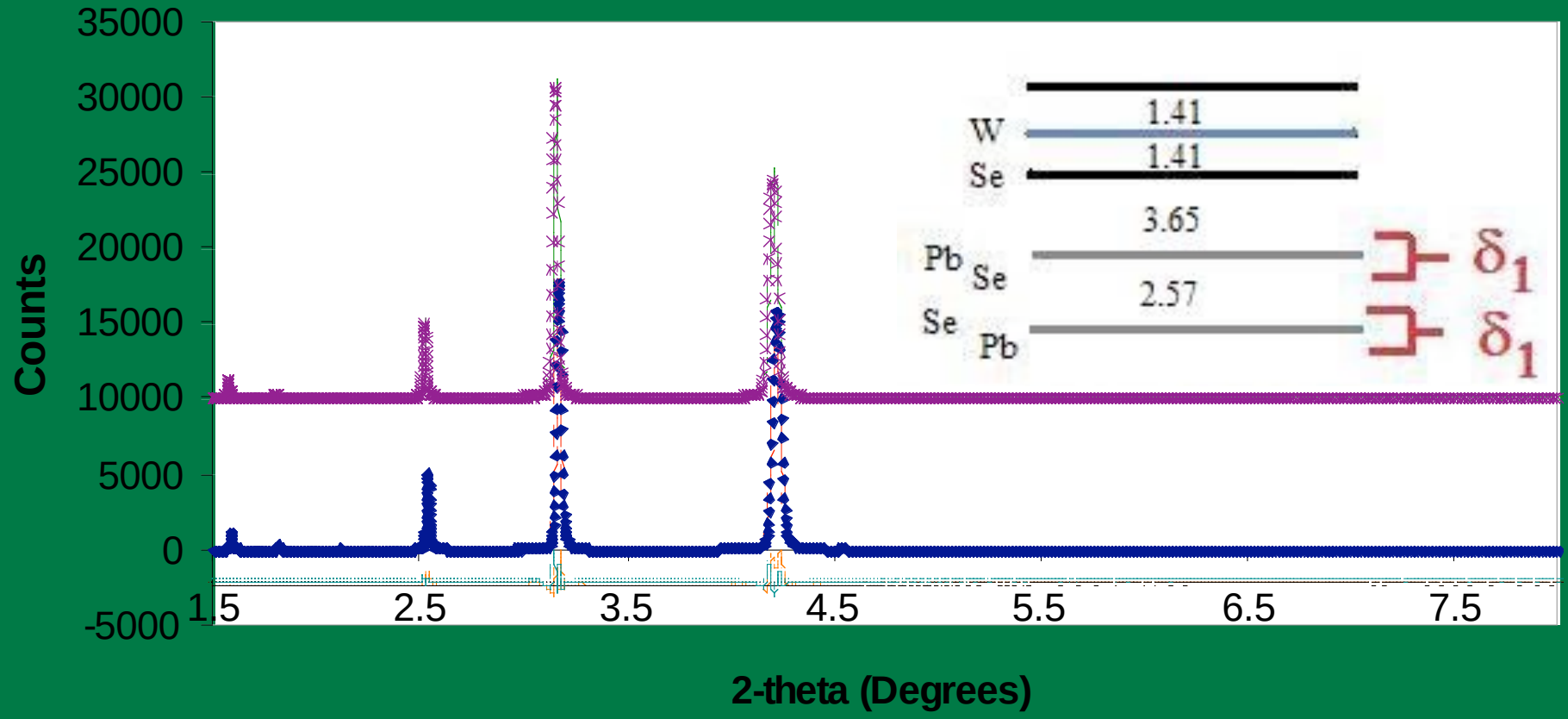
Two diffusion lengths trap nanostructure



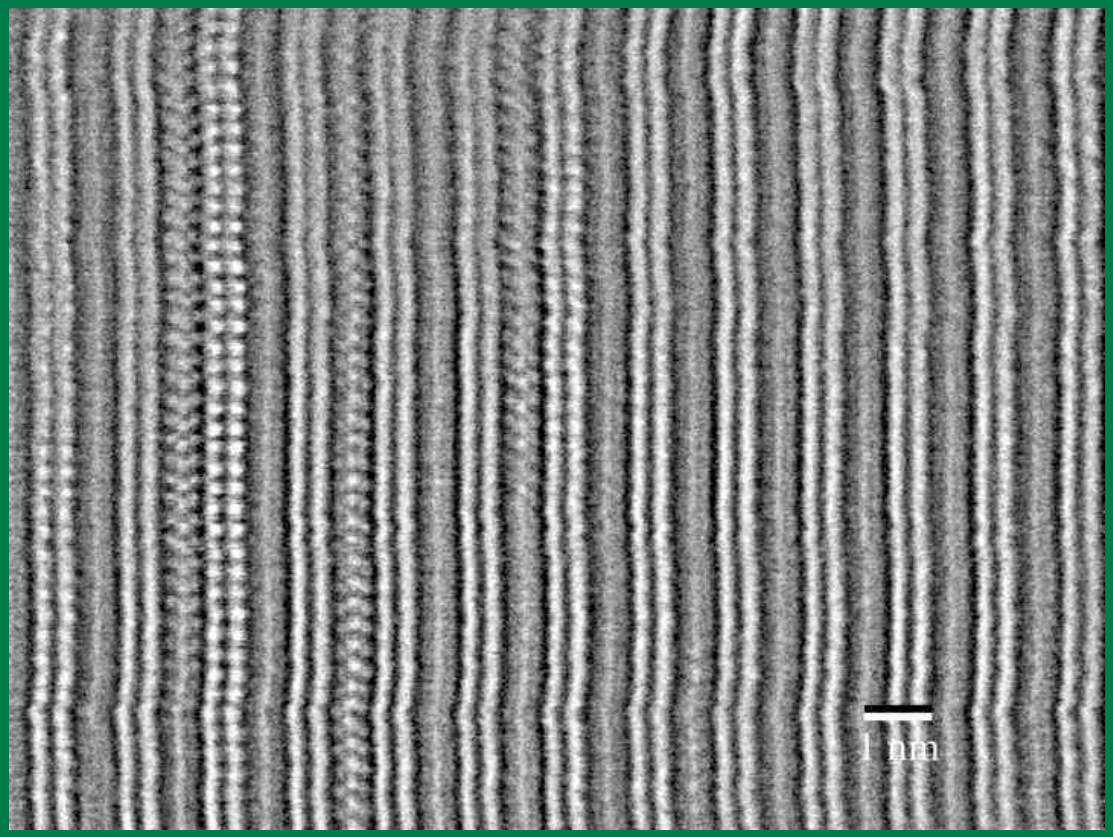
$[(PbSe)_{0.99}]_1[WSe_2]_1$ Superlattice forms with annealing



$(PbSe)_1(WSe_2)_1$ Refinement

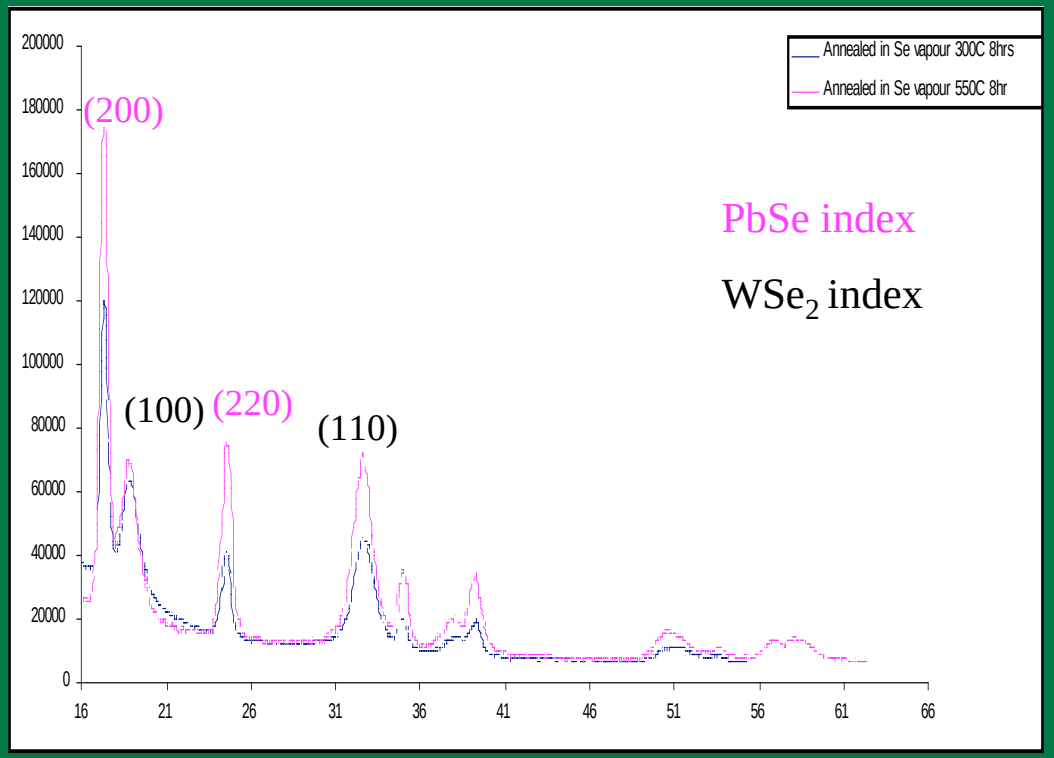


Distortion from 001 rock salt plane



$(CeS)_{1.15}TaS_2$	0.3623
$(LaS)_{1.13}TaS_2$	0.3469
$(BiS)_{1.07}TaS_2$	0.4164
$(PbS)_{1.18}TiS_2$	0.4407
$(SnS)_{1.20}TiS_2$	0.5540
$(PbS)_{1.14}NbS_2$	0.5212
$(LaS)_{1.14}NbS_2$	0.6058
$(PbS)_{1.13}TaS_2$	0.4
$(SnSe)_{1.16}NbSe_2$	0.2456
$(PbS)_{1.14}(NbS_2)_2$	0.2068
$(PbSe)_{0.99}WSe_2$	**0.228**
$(PbSe)_{0.99}MoSe_2$	**0.228**
$(SnSe)_{0.99}MoSe_2$	**0.364**

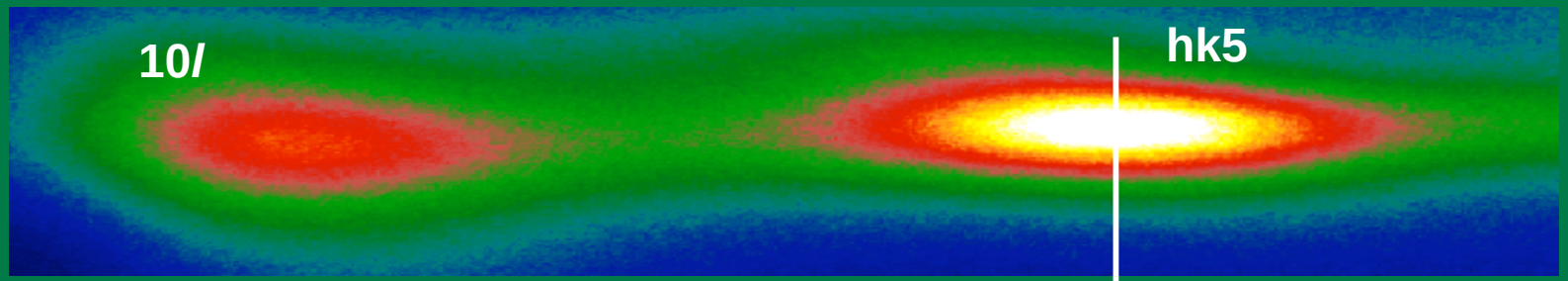
In-plane Structure $(PbSe)_1(WSe_2)_1$



Long range order within a-b planes

Grain sizes larger in PbSe than WSe_2

Short range order between a-b planes



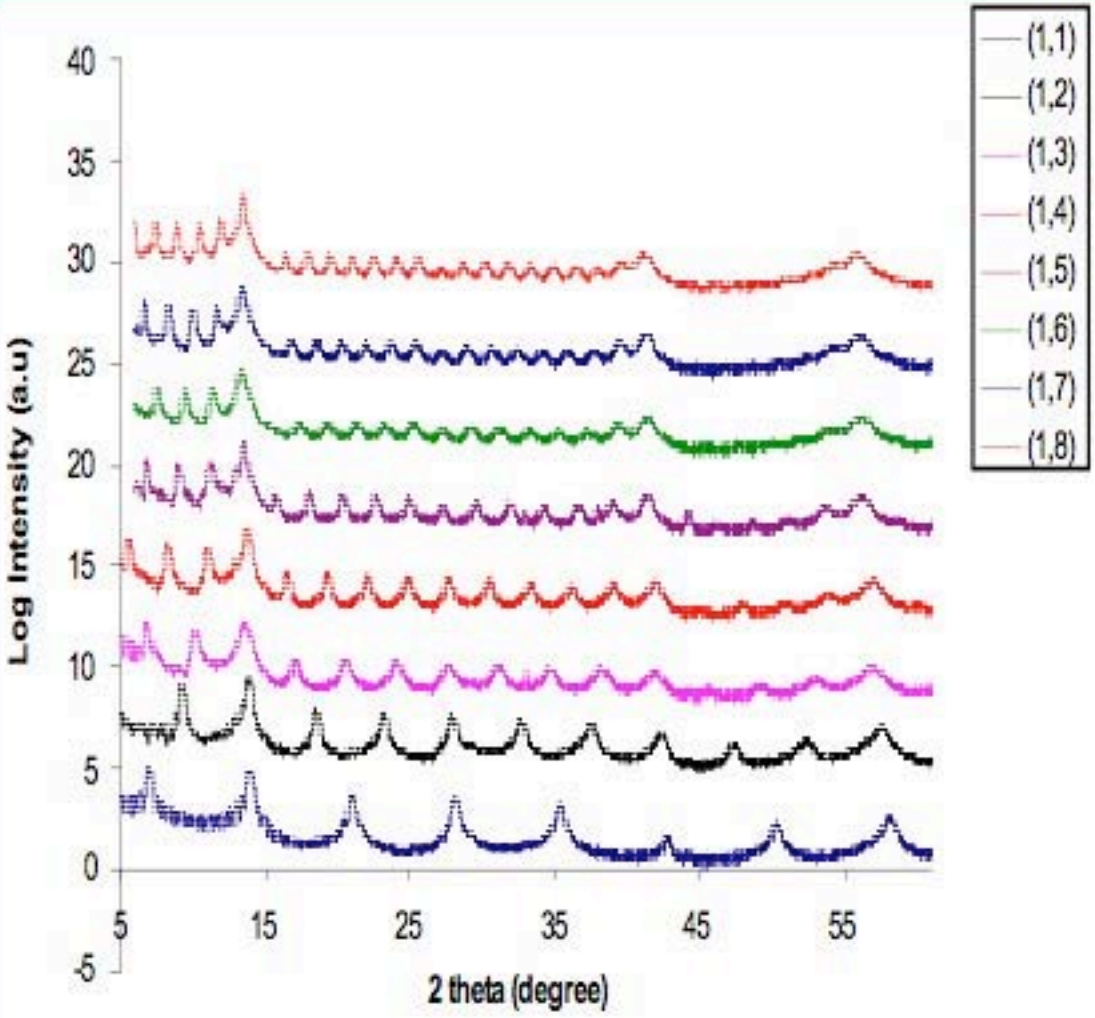
Unique Structure of Misfit compounds

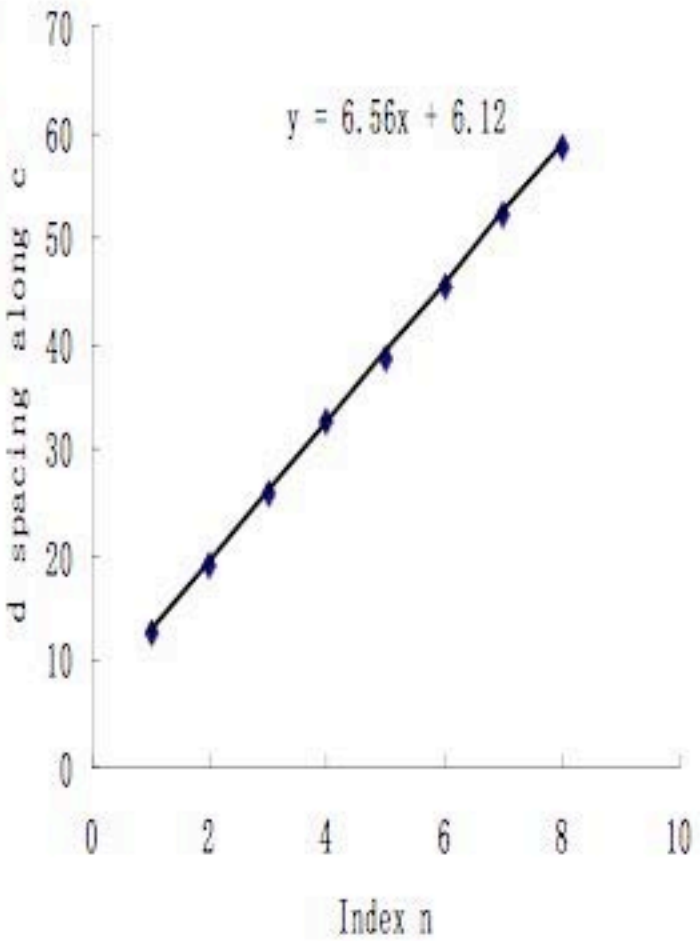
- Thermal expansion of components differ
  Planes slide over one another
  Robust to thermal cycling

- Abrupt interfaces between components with
  minimal interdiffusion
  Thermodynamically stable metal - mifit junctions
  low contact resistances possible because of
  zero or minimal interfacial phase growth.

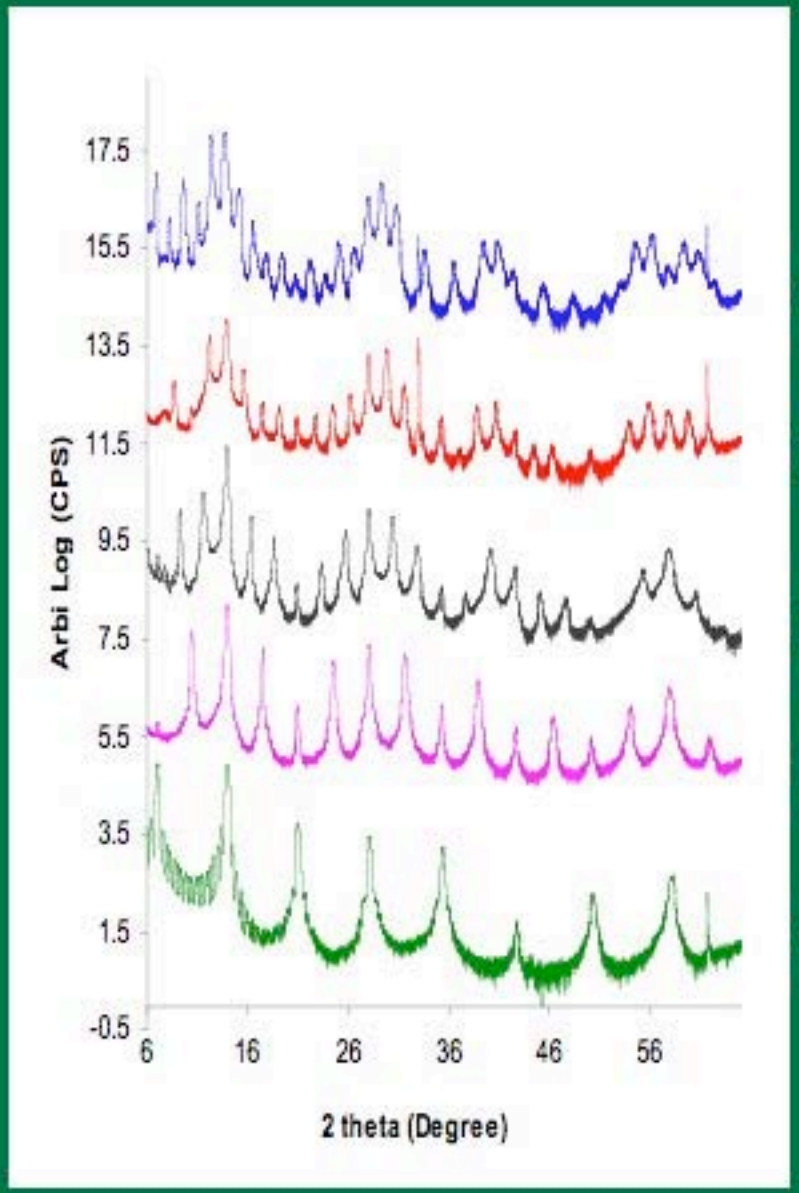
- Electron transfer between components a
  method to tune through resonance states

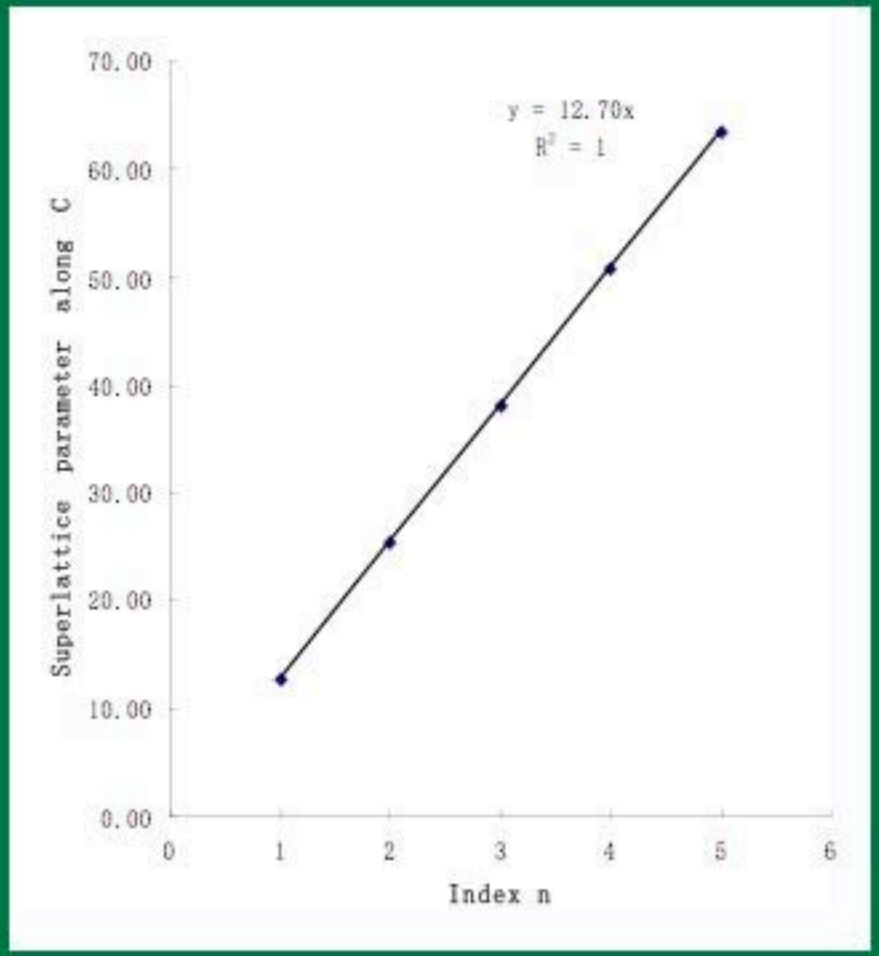
$[(PbSe)_{0.99}]_1(WSe_2)_n$



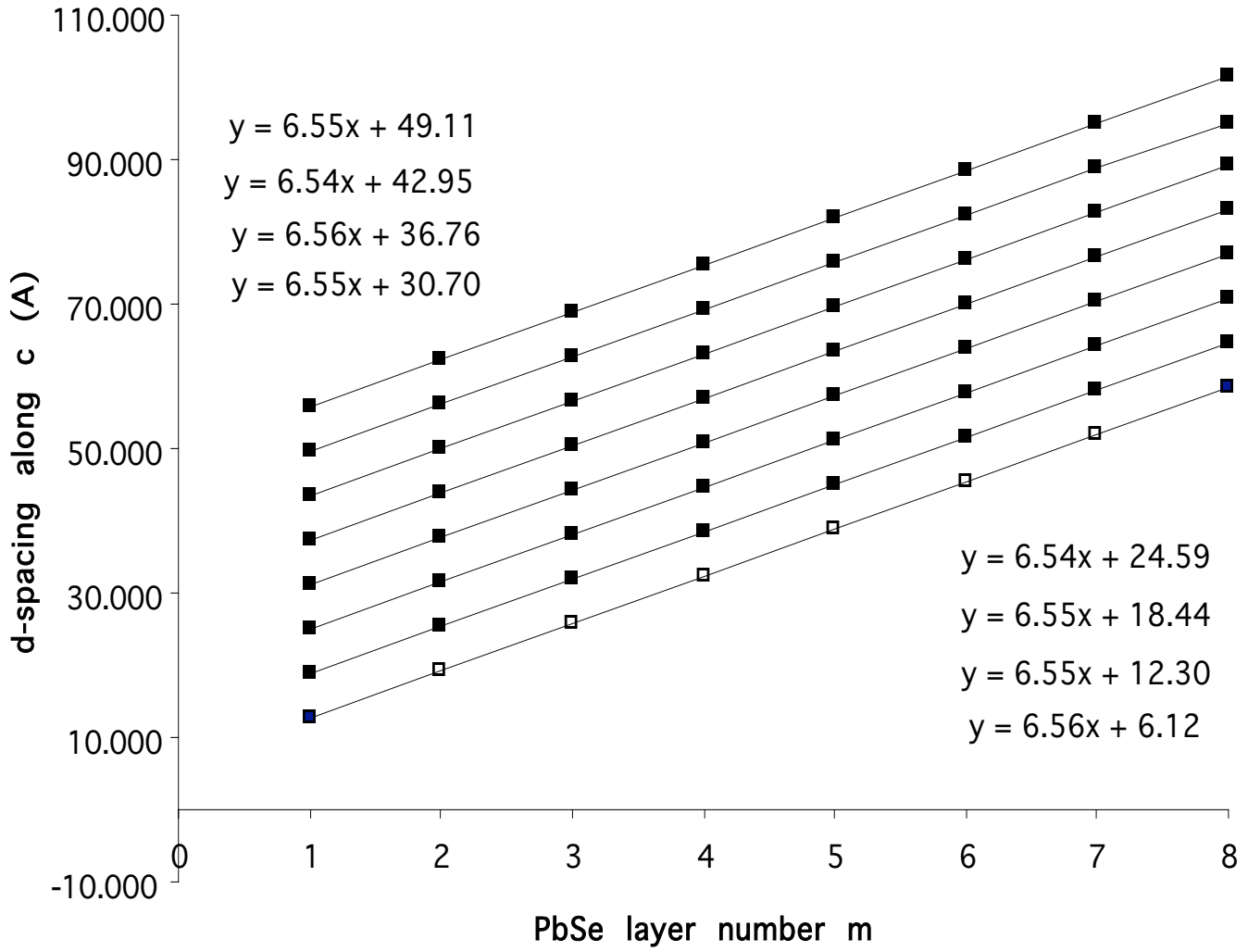


$[(PbSe)_{0.99}]_n(WSe_2)_n$ Superlattices

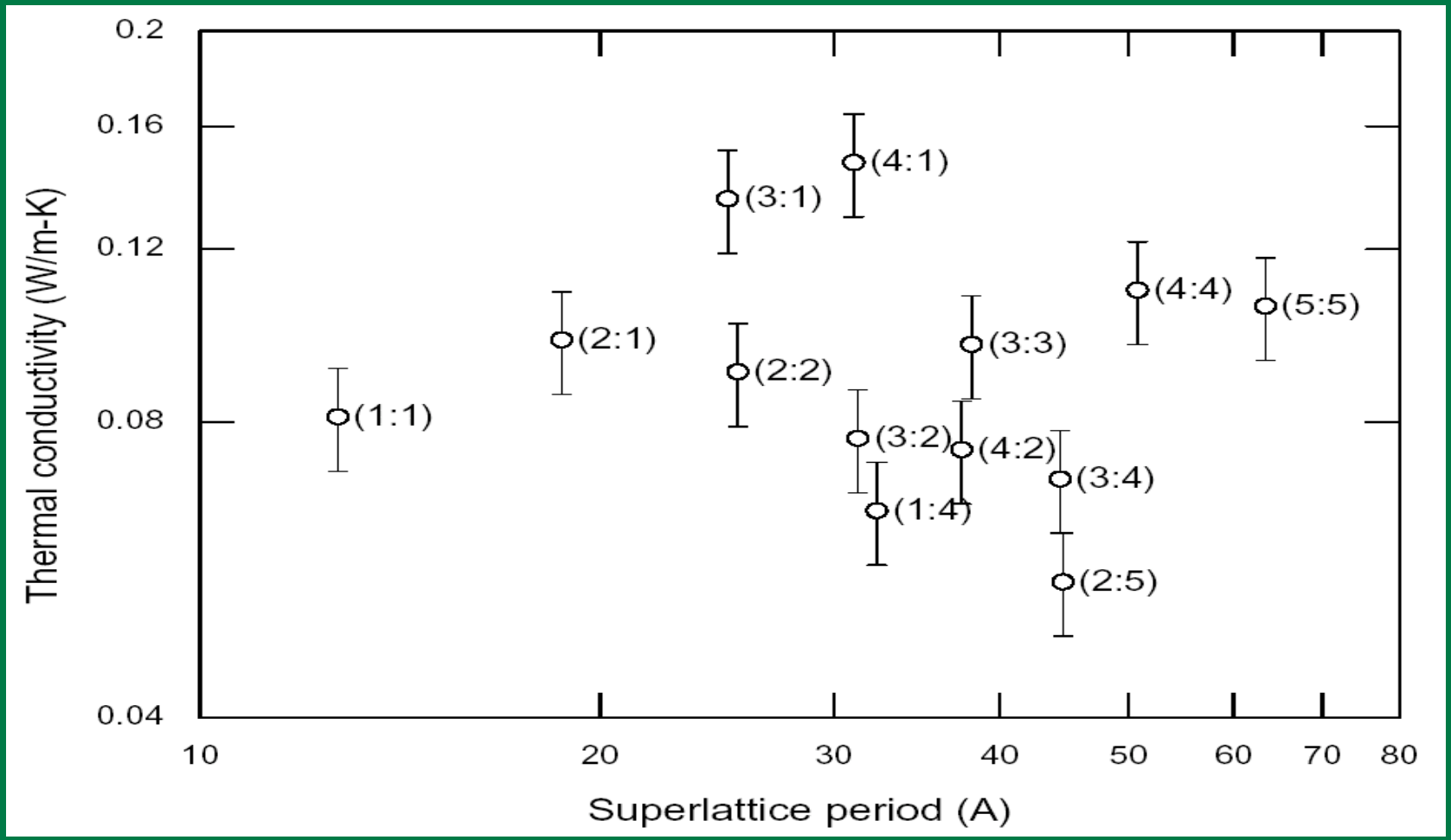




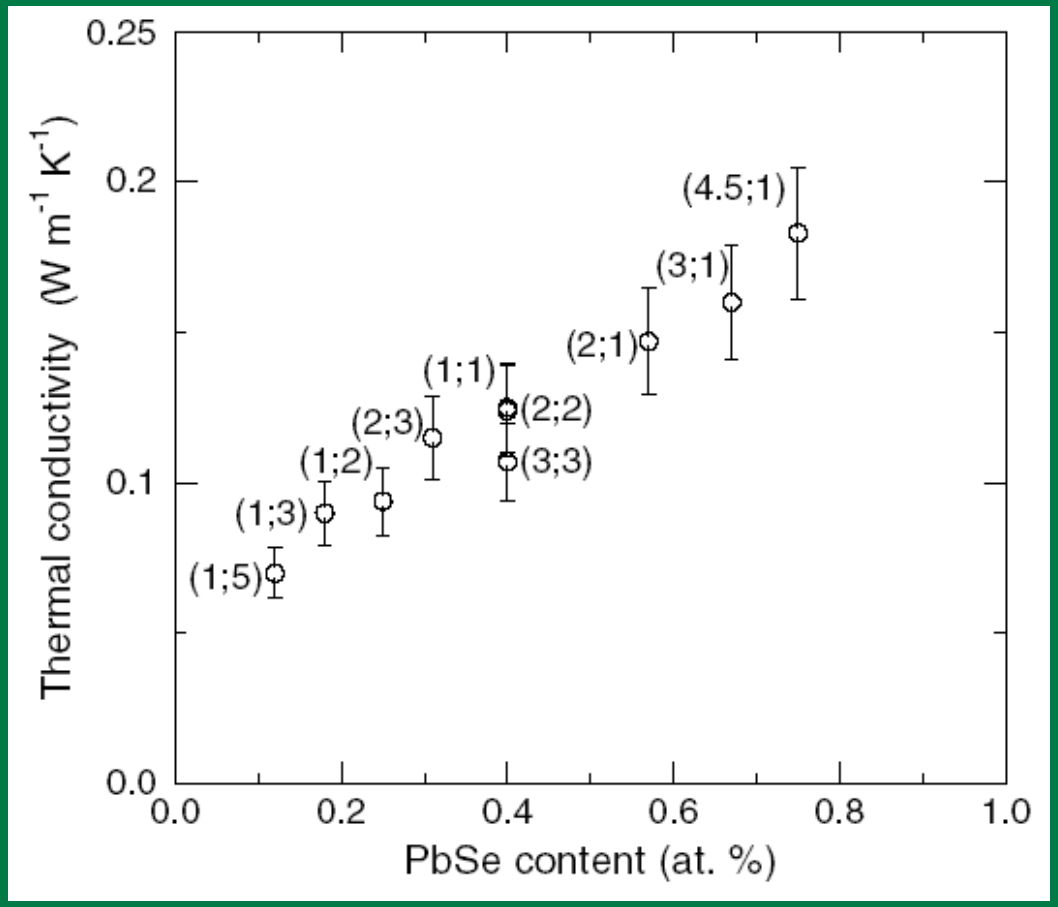
d-space of first 64 $[(PbSe)_{0.99}]_m(WSe_2)_n$

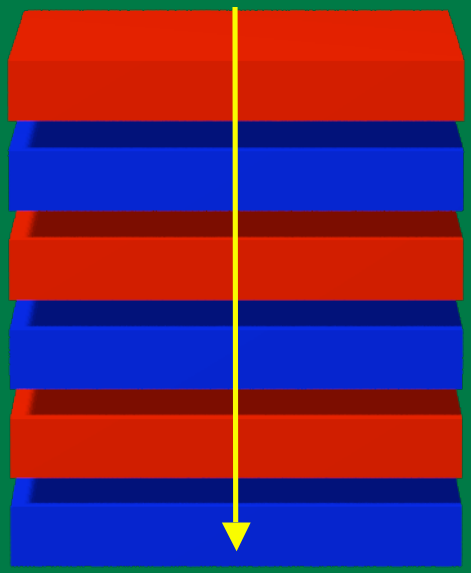


Thermal Conductivity $[(PbSe)_{0.99}]_n(WSe_2)_m$

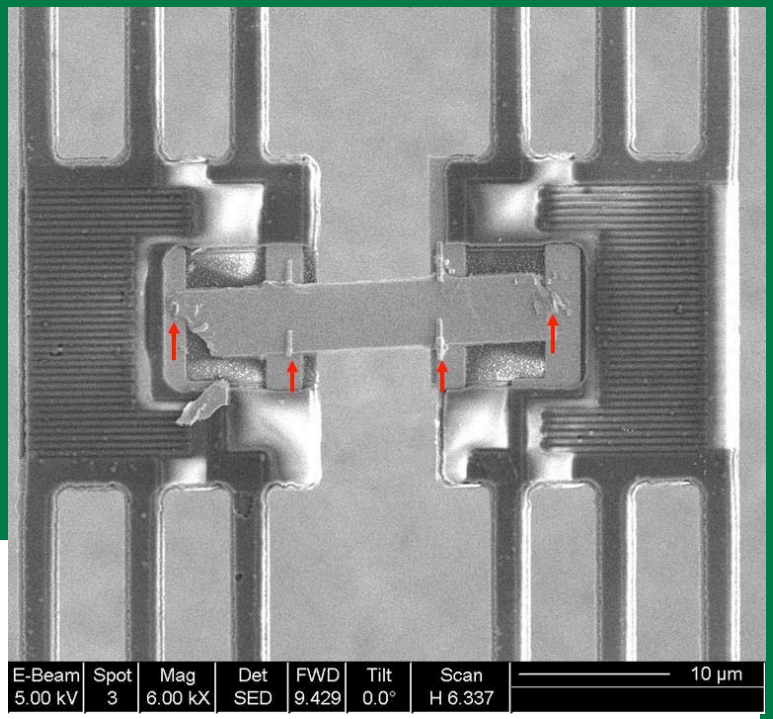


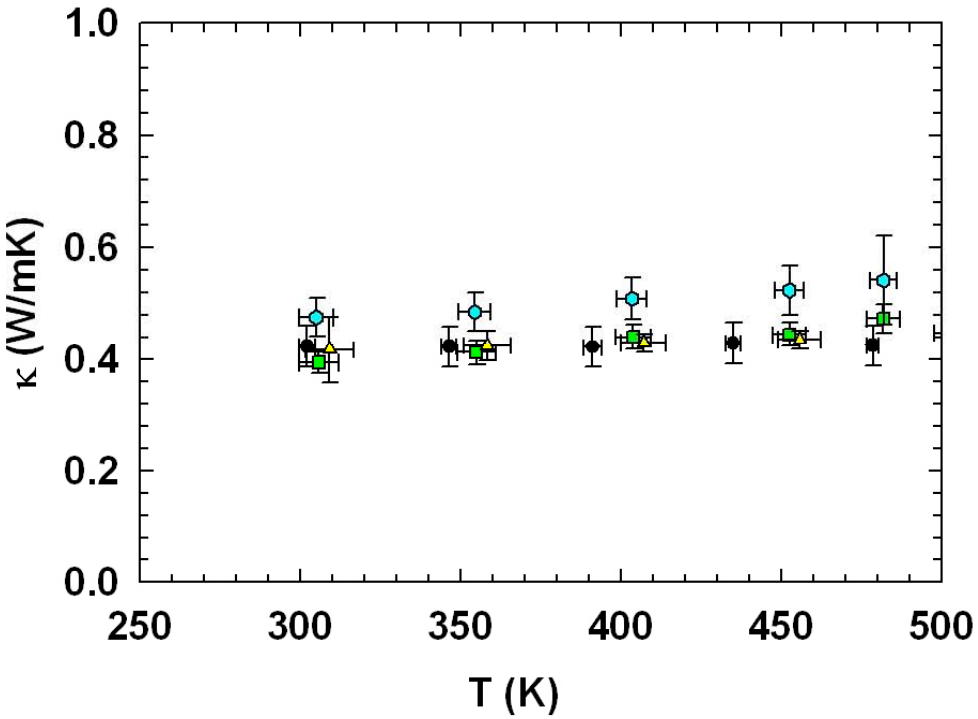
Cross Plane Thermal Conductivity $(PbSe)_n(MoSe_2)_m$





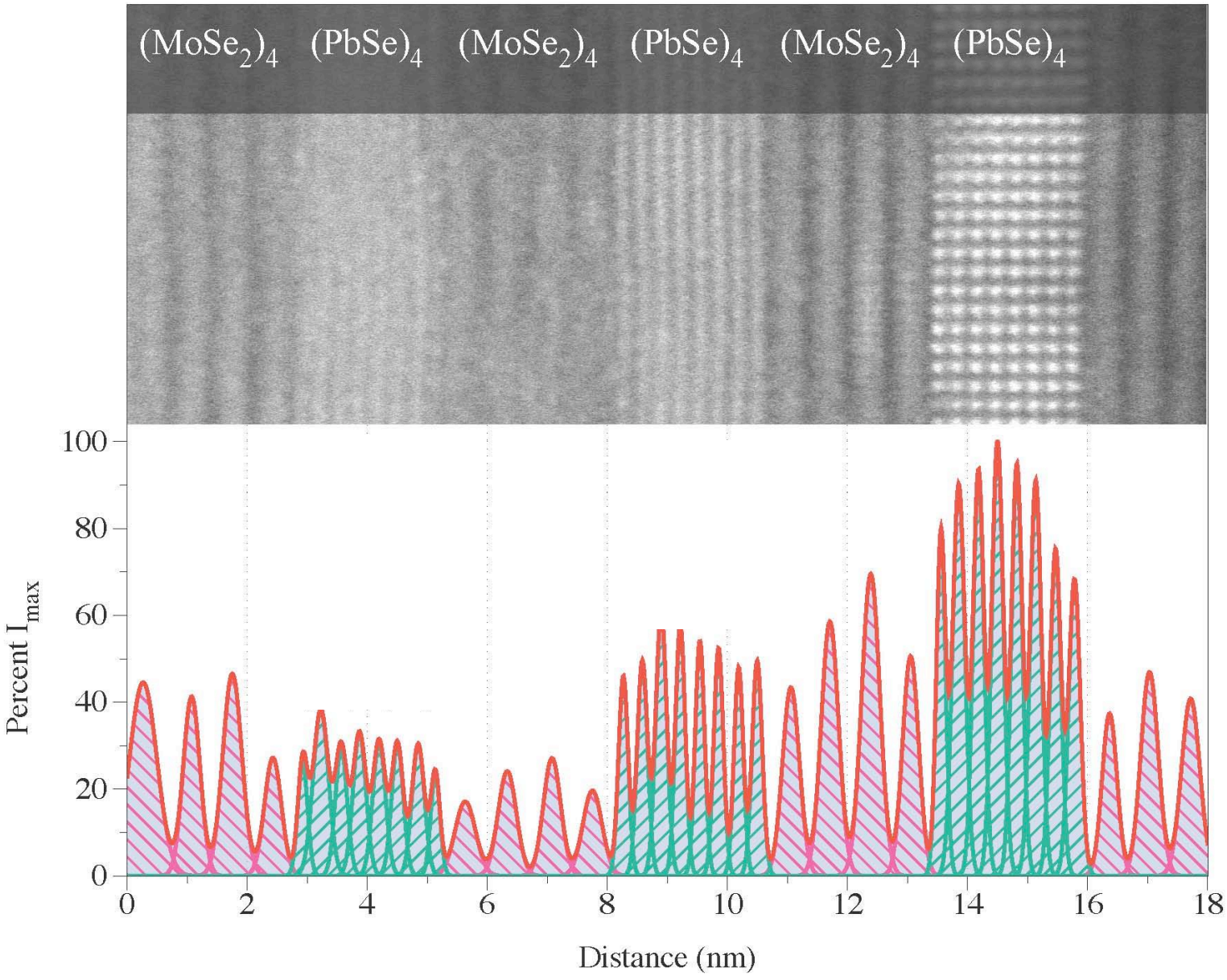
In-plane Thermal Conductivity





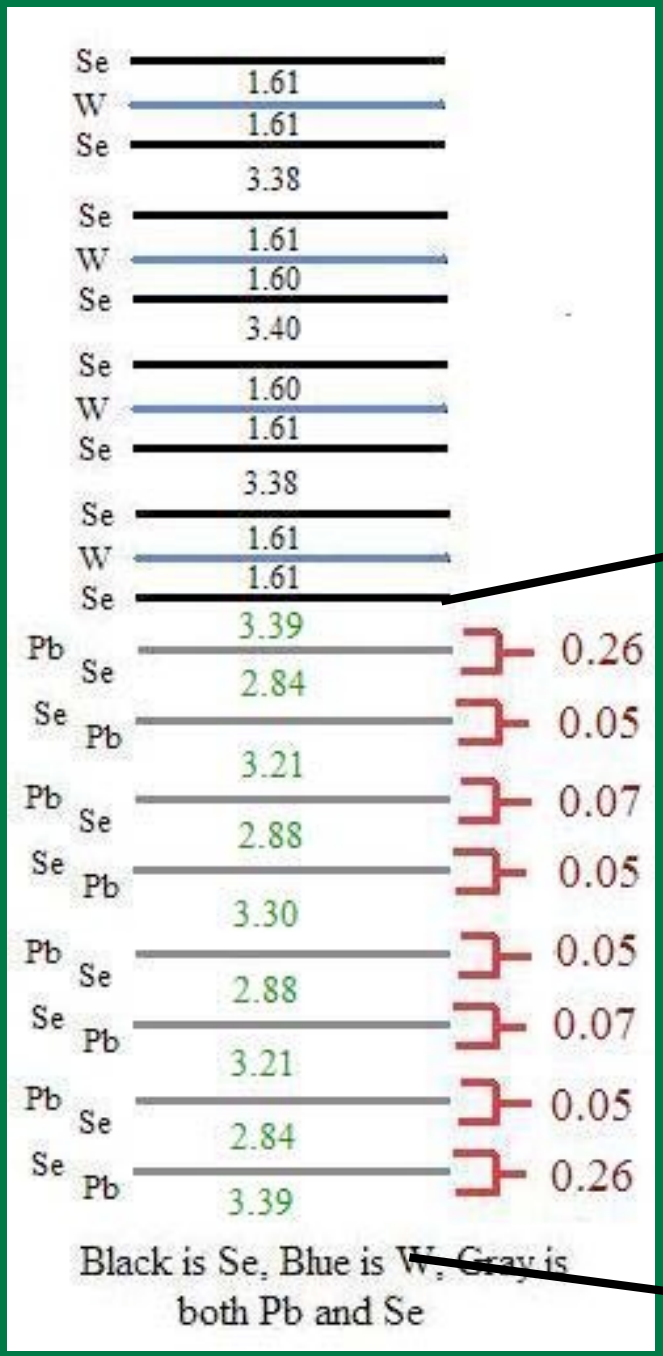
- $(PbSe)_2(WSe_2)_2$ before annealing
- $(PbSe)_3(WSe_2)_3$ after annealing
- $(PbSe)_4(WSe_2)_4$ after annealing
- $(PbSe)_2(WSe_2)_2$ after annealing

Z-contrast image of $(PbSe)_4(MoSe_2)_4$



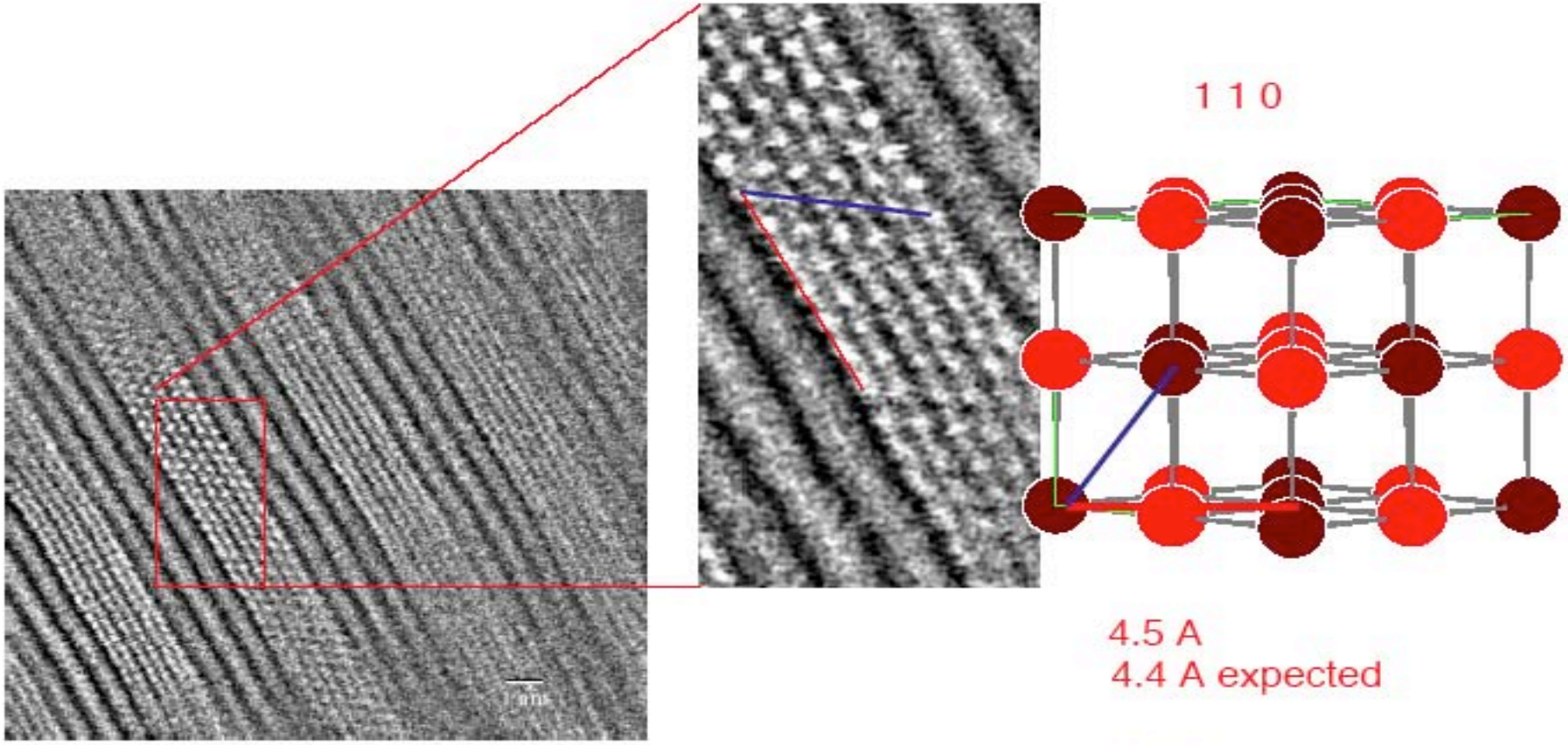
$(PbSe)_4(WSe_2)_4$

distortion in PbSe layers changes with position

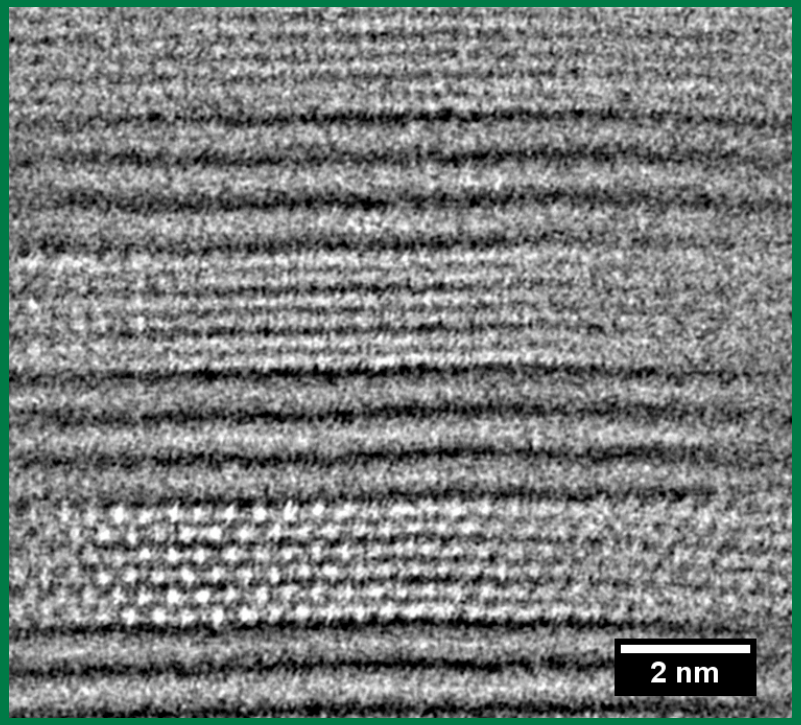


Structure of Misfit Layered Compounds

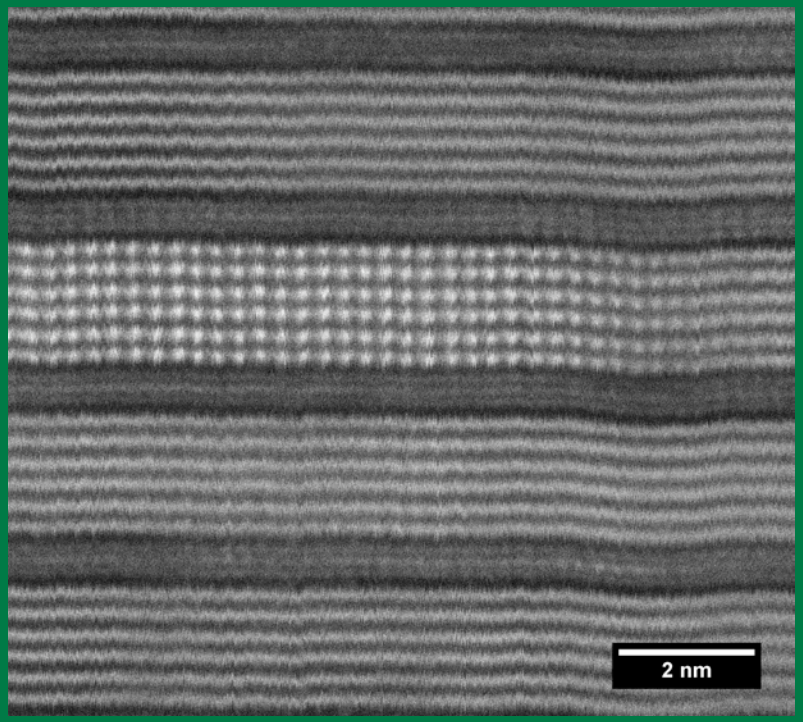
$[(PbSe)_{0.99}]_3(MoSe_2)_3$



Distortion Change with m/n ratio in $(PbSe)_n(MoSe_2)_m$ compounds



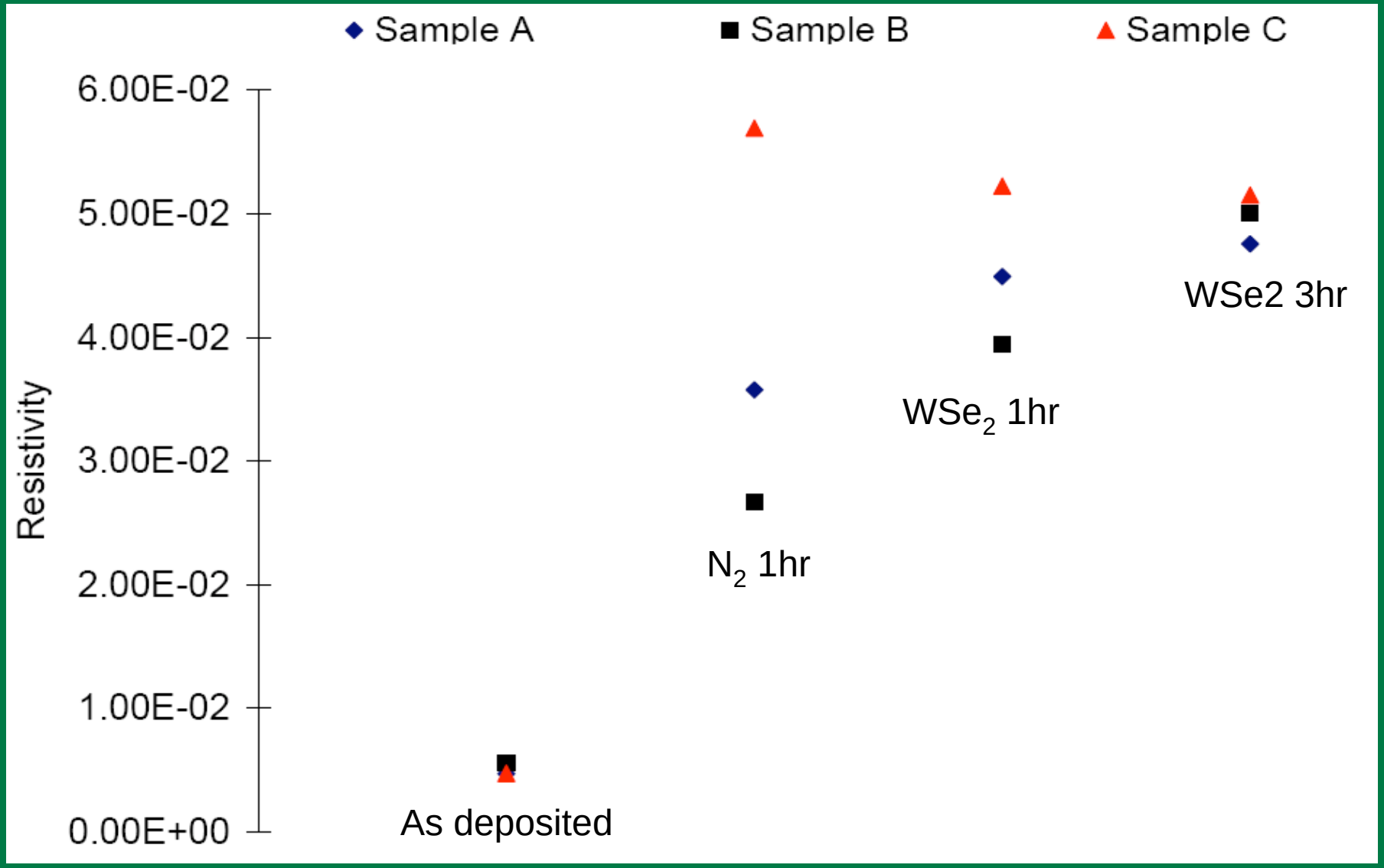
PbSe planes alternate between 0.28 and 0.35 nm separation in 3:3



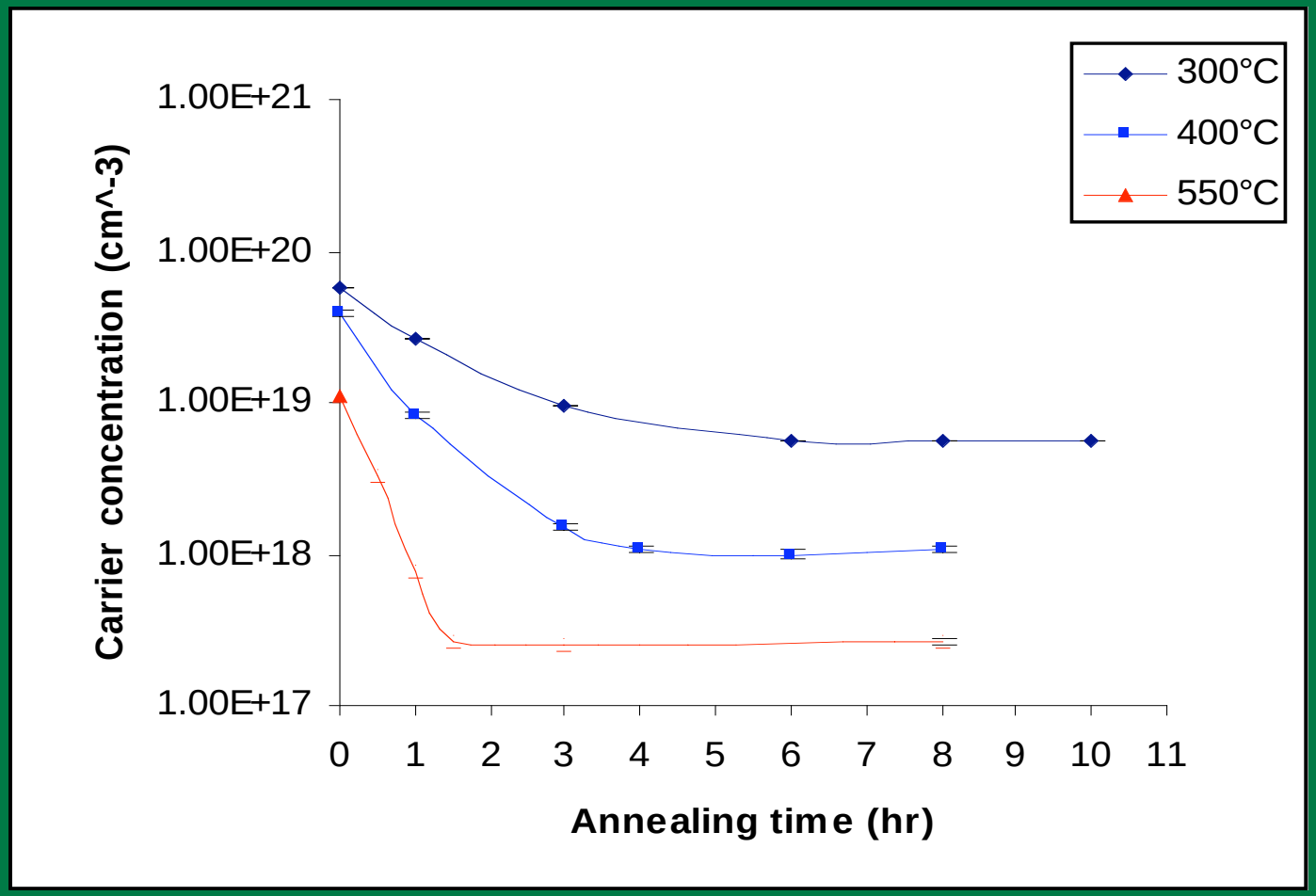
PbSe planes have a 3.1 nm separation in 3:1 compound

Annealing study [$(PbSe)_{0.99}]_1$ $(WSe_2)_1$

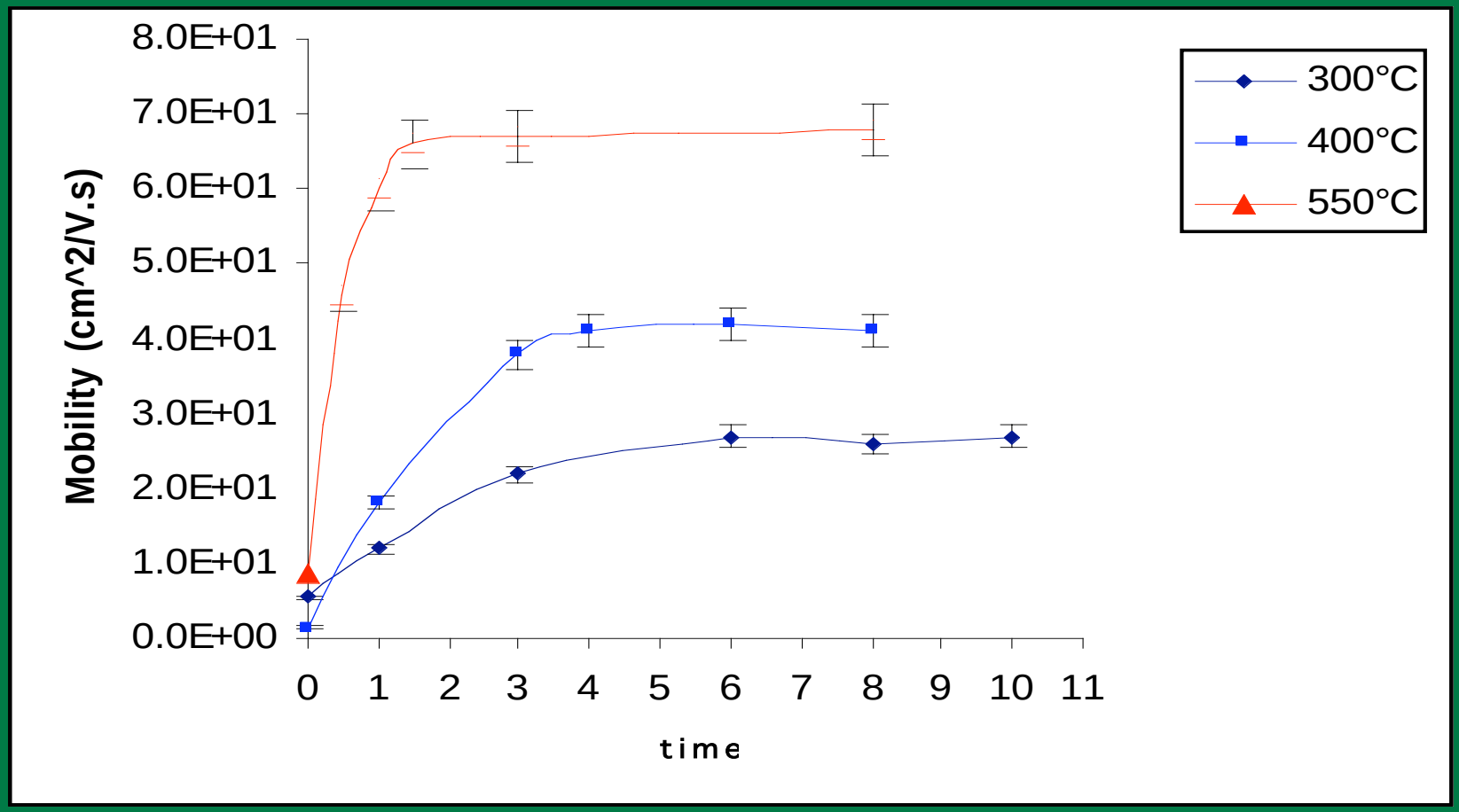
WSe_2 source of Se vapor pressure



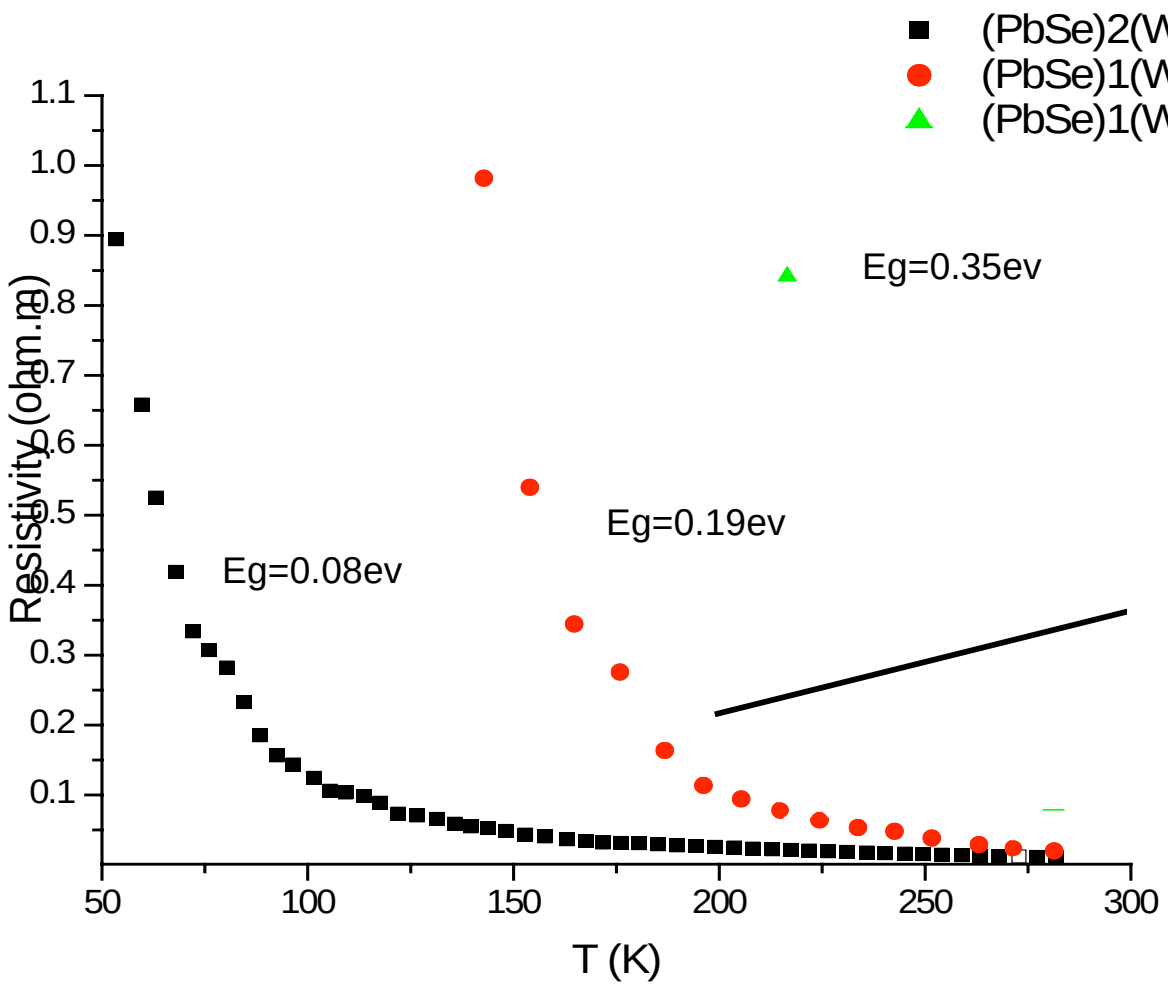
Effect of Annealing Temperature $[(PbSe)_{0.99}]_1(WSe_2)_1$

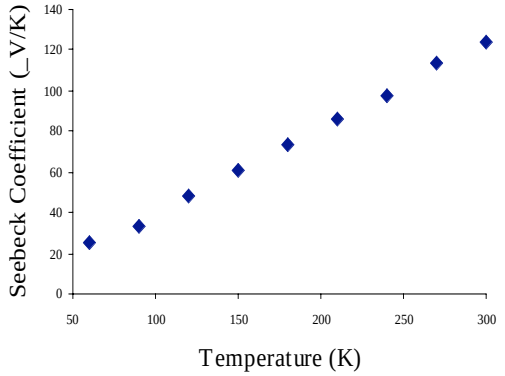


Annealing Eliminates Defects $[(PbSe)_{0.99}]_1(WSe_2)_1$



Activation Energy for Conduction varies with n/m ratio

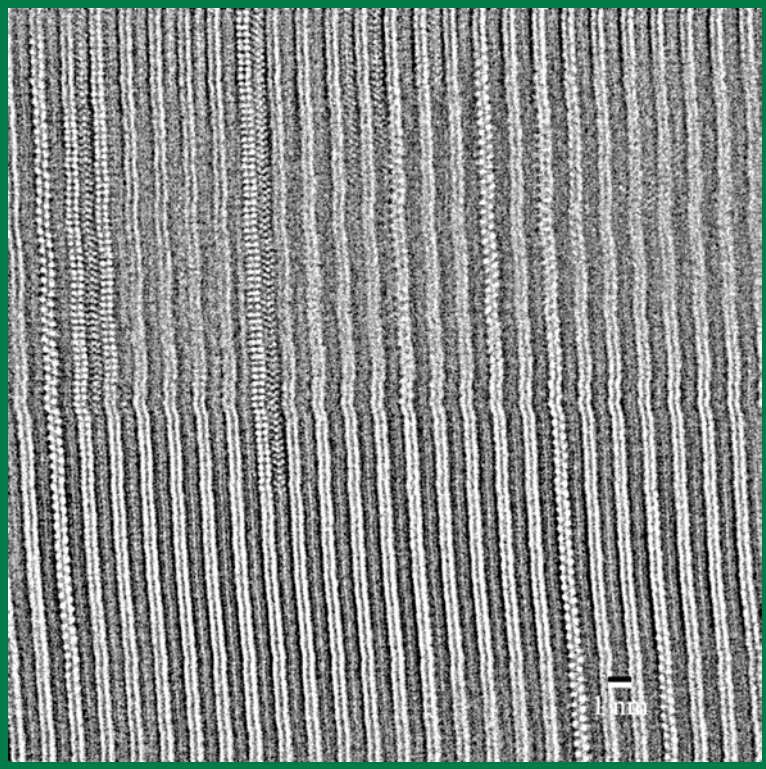


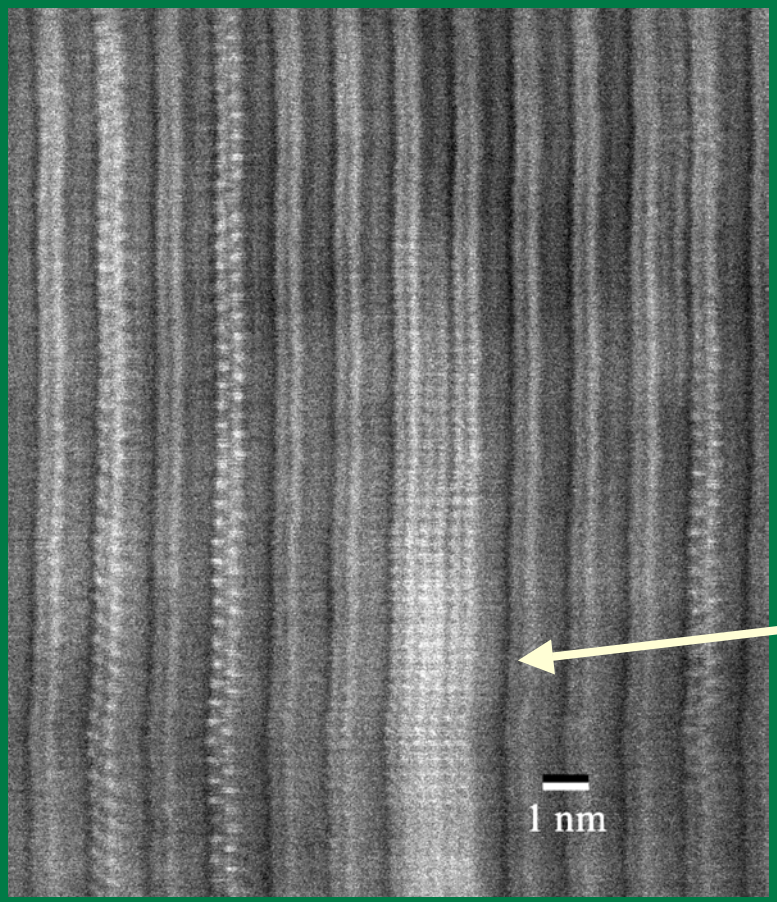


Temperature dependence of Seebeck: heavy doped semiconductors.

Intergrowth Defects in $(PbSe)_1(MoSe_2)_1$

Most of samples have regular misfit structure

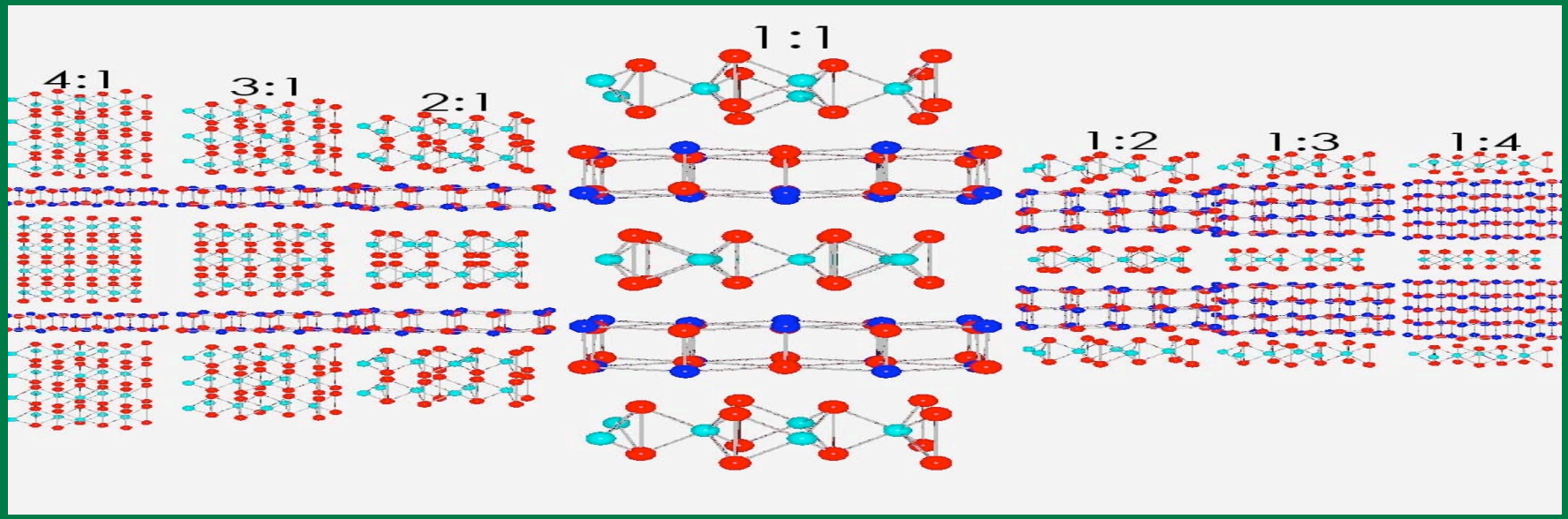




Intergrowth defects ($PbSe$-->$MoSe_2$) can be controlled by initial modulated reactant structure

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.



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