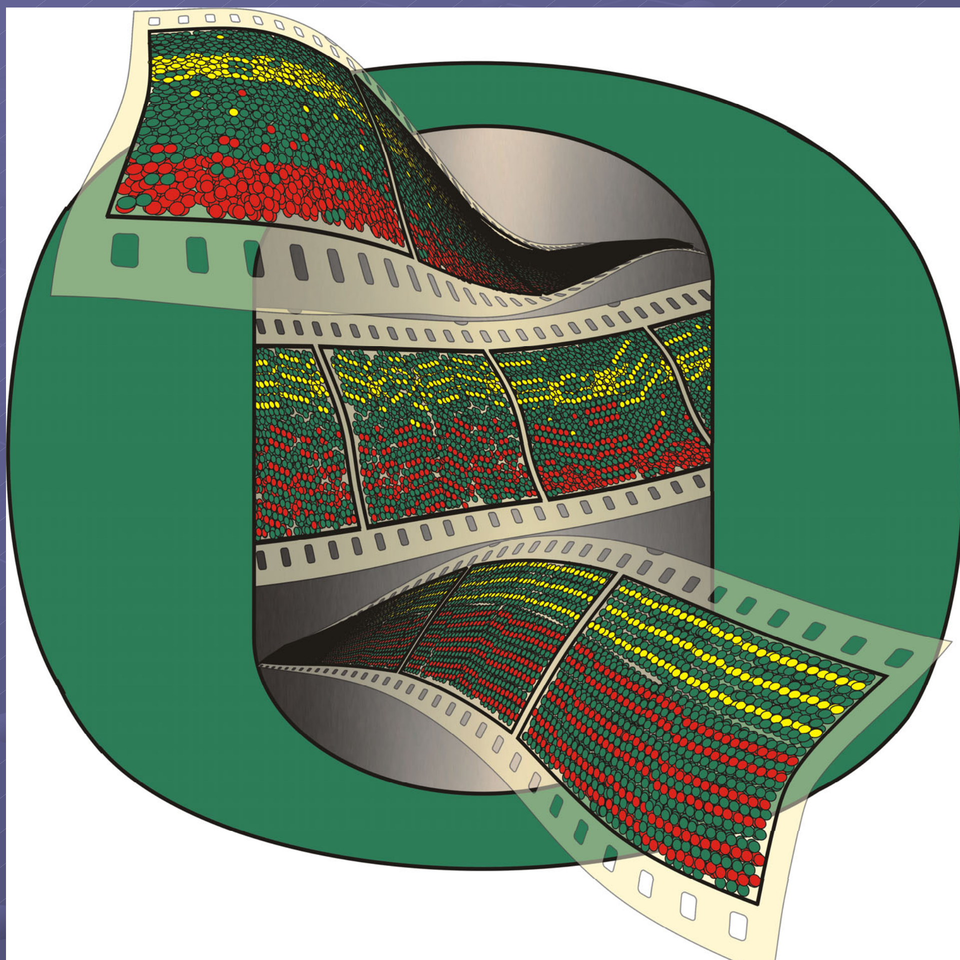
Crystal Engineering of Novel Thermoelectric Materials



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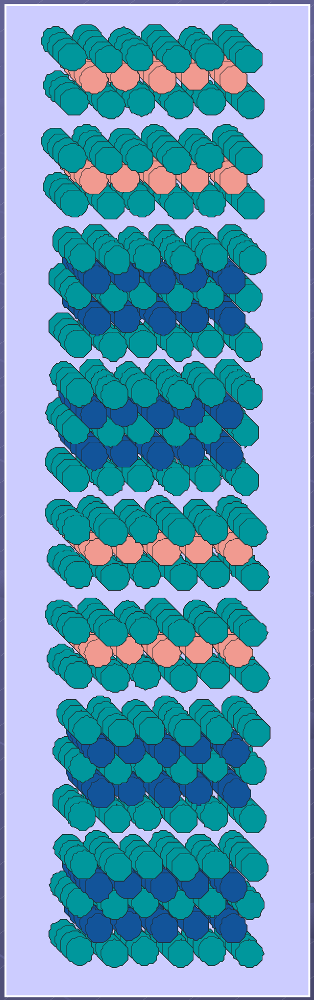
18 Feb 2004

What is a superlattice?

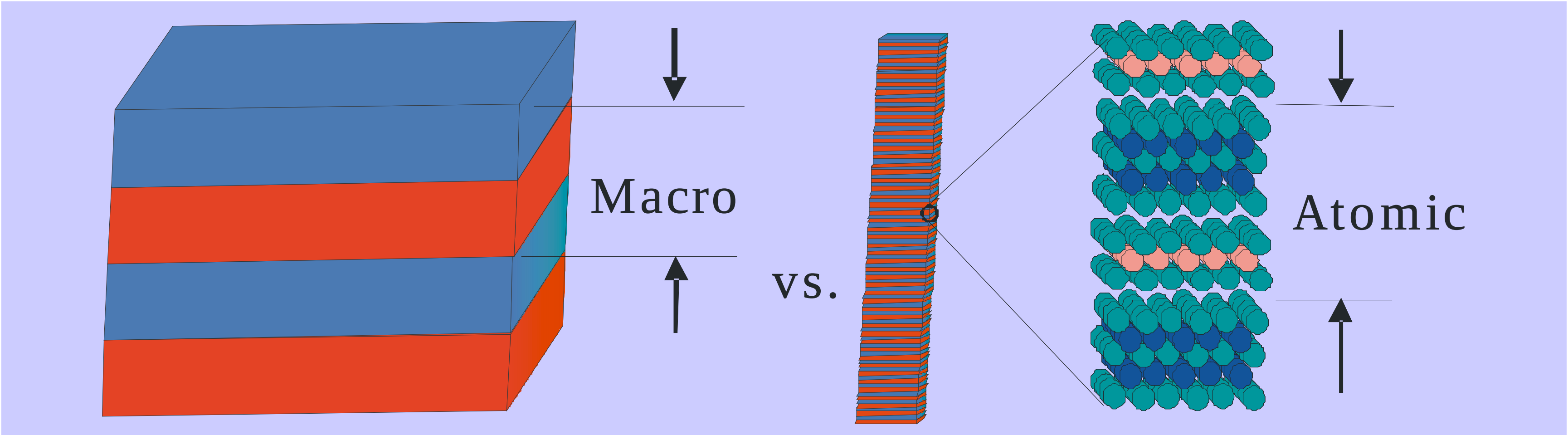


Quick Review

- Two or more materials are alternated
- The resulting structure is then repeated
- Layers within a superlattice are crystallographically aligned with one another

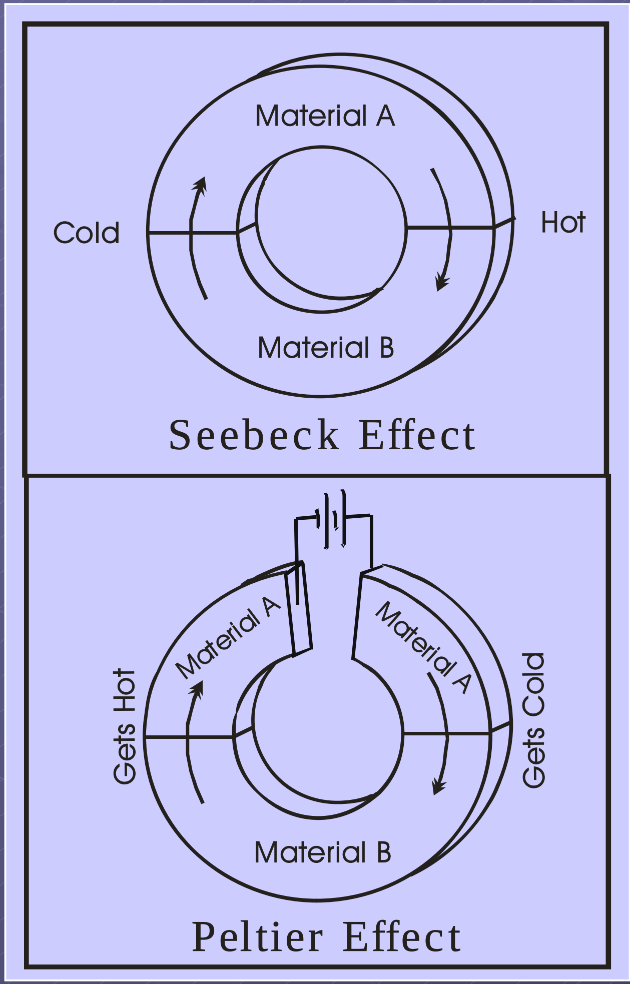
Why are Superlattices Interesting

Fundamental Understanding



- Composites are well understood on the macro scale
- What happens to the above alternating material as the layers get thinner?
- One unit cell of each material → new properties?

Thermoelectric Materials

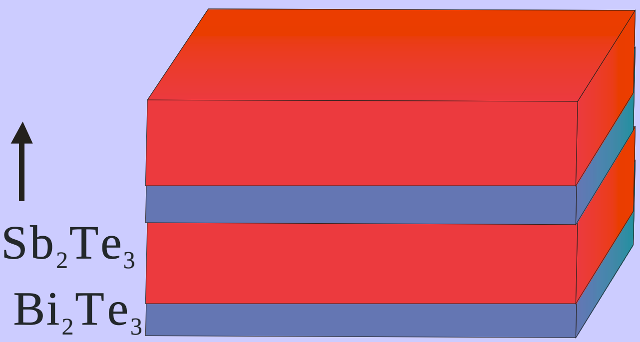


$$ZT = \left(\frac{\sigma S^2}{K_e + K_\ell} \right) T$$

- ZT = Normalized Thermoelectric Eff.
- σ = electrical Conductivity
- S = Seebeck Coefficient
- K_e = Thermal Conductivity (Electronic)
- K_l = Thermal Conductivity (Lattice)
- T = Temperature

Superlattices and Thermoelectrics

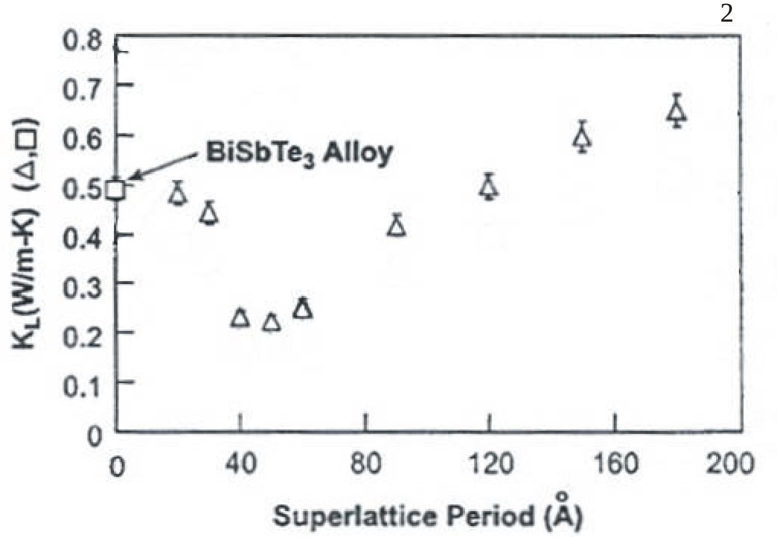
Venkatasubramanian, et al. have shown evidence that superlattice structures lower thermal conductivities from the values of bulk components



50 Å Sb_2Te_3
10 Å Bi_2Te_3

ZT~ 2.4 in p-type Bi_2Te_3 / Sb_2Te_3 [1]
ZT~ 1.4 in n-type Bi_2Te_3 / $Bi_2Te_{2.83}Se_{0.17}$

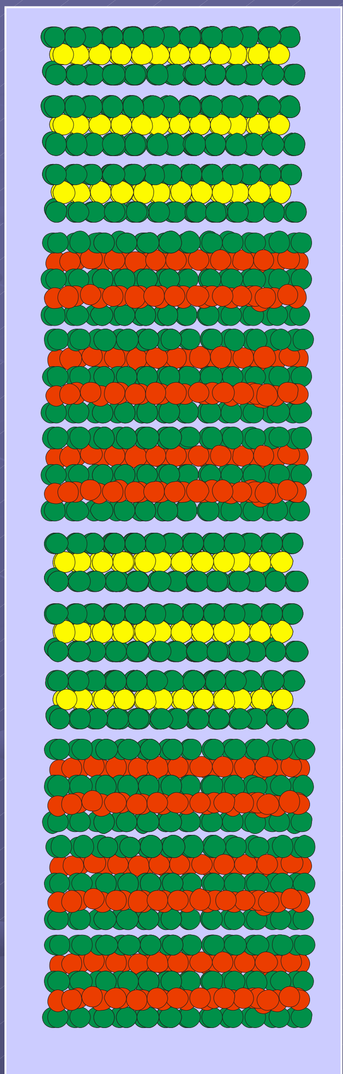
[2]



Highest ZT ever reported in a bulk alloy at 300K:
ZT ~ 1.14 - p-type $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$

(1) Venkatasubramanian, R.; Slivola, E.; Colpitts, T.; O'Quinn, B. Nature 2001, 413, 597
(2) Venkatasubramanian, R. Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 61, 3091.

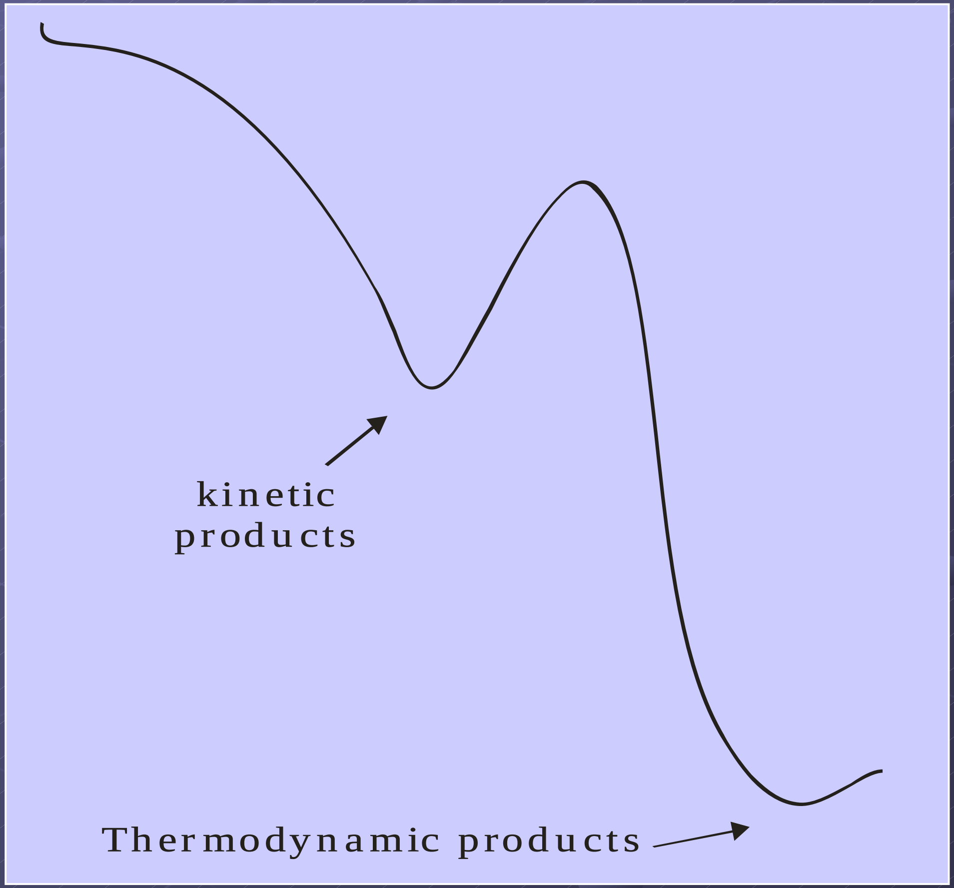
$[(Bi_2Te_3)_x(TiTe_2)_y]$ Superlattices



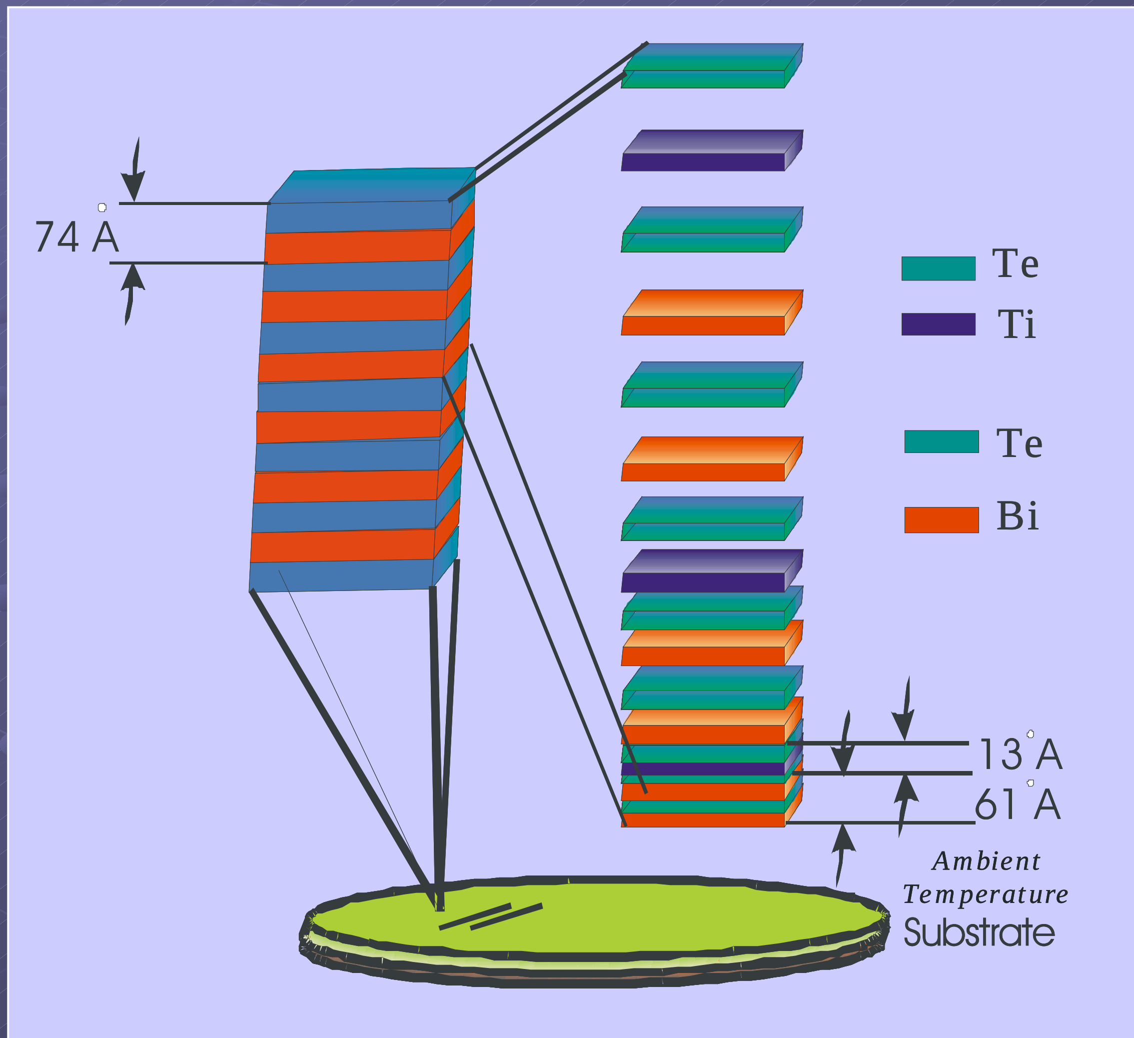
- Thermal conductivity reduction should hold true for other superlattice structures
- Van der Waals gaps should make clean interfaces between layers
- Interesting Properties?
  - Bi_2Te_3 – Semiconductor
  - $TiTe_2$ – Semi-Metal

A Low Temperature Technique is Required

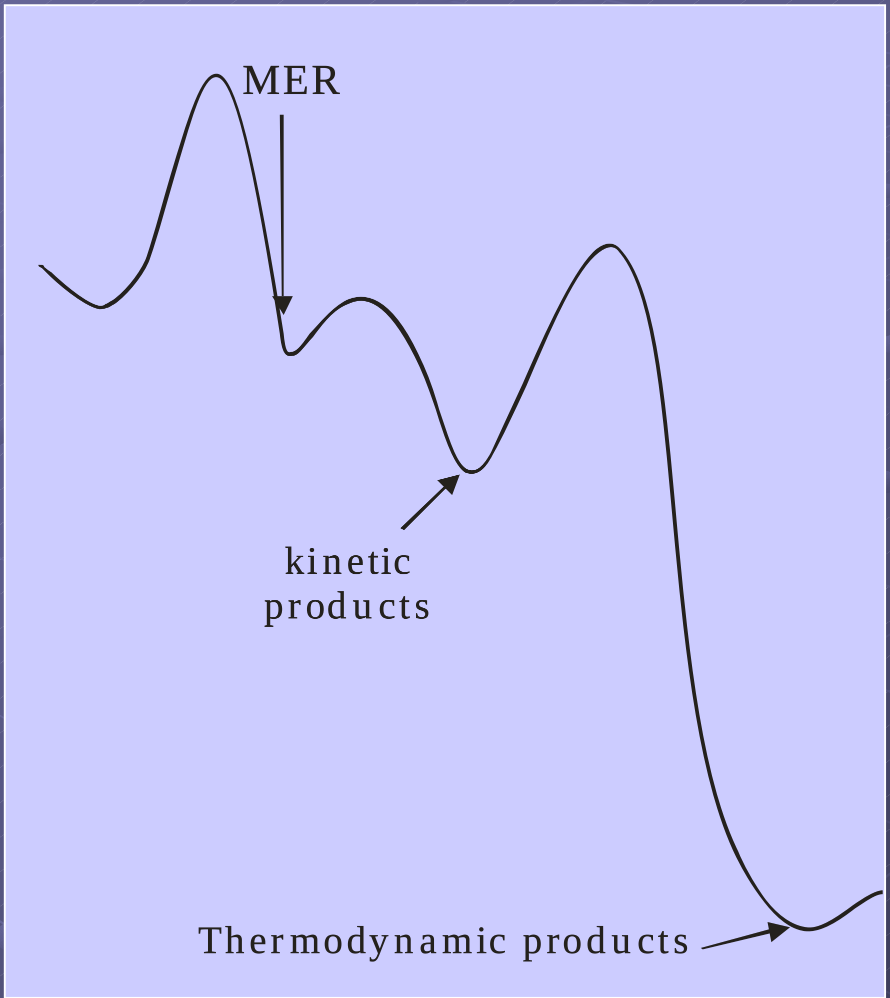
One of the main problems for trapping kinetic products in the solid state is overcoming diffusion



Modulated Elemental Reactants (MER)

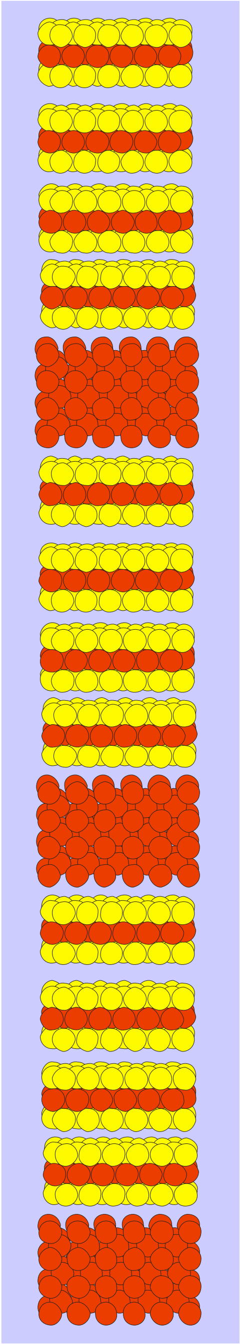


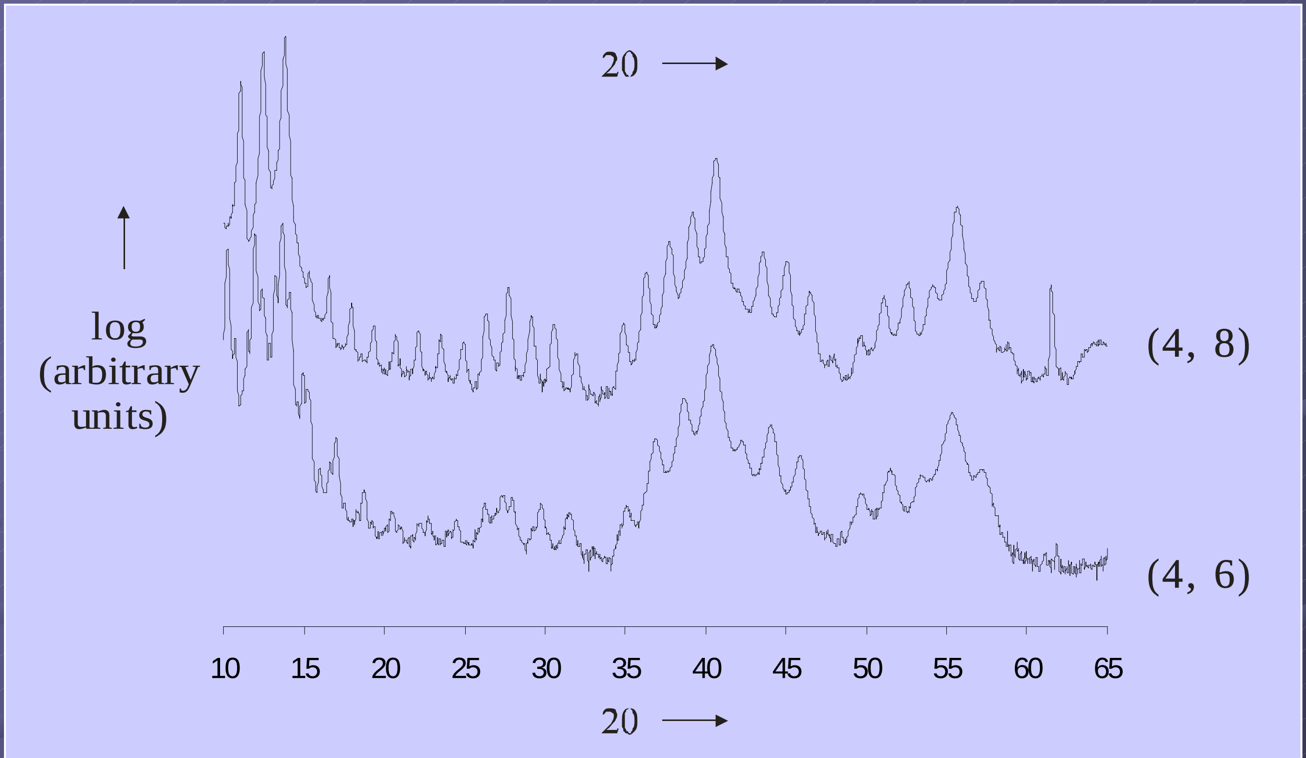
Modulated Elemental Reactants (MER)

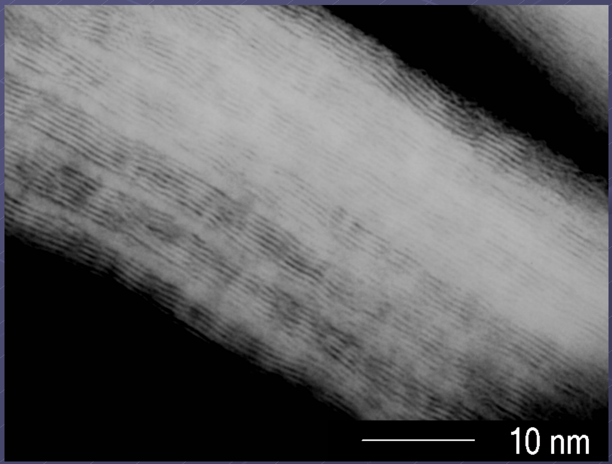


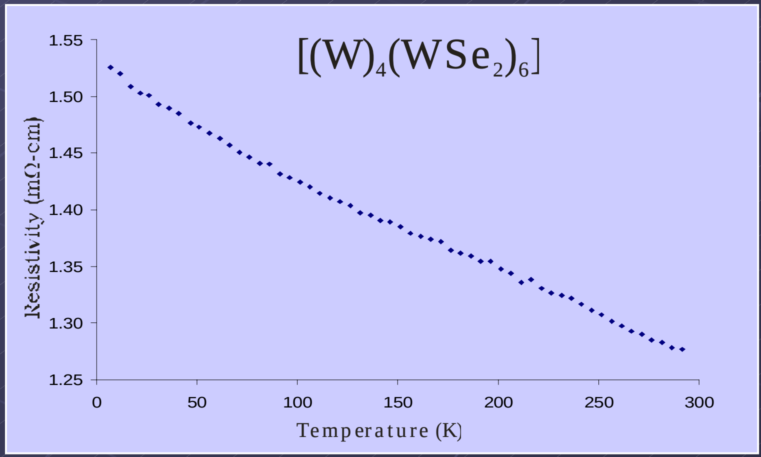
- Gentle annealing of the reactant stack (<500°C) causes the kinetic product to form

$[(W)_x(WSe_2)_y]$ Superlattices

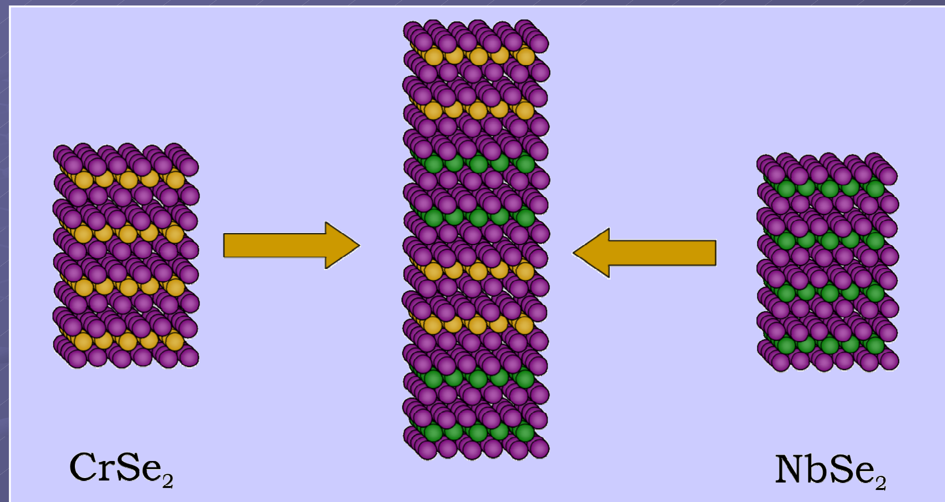


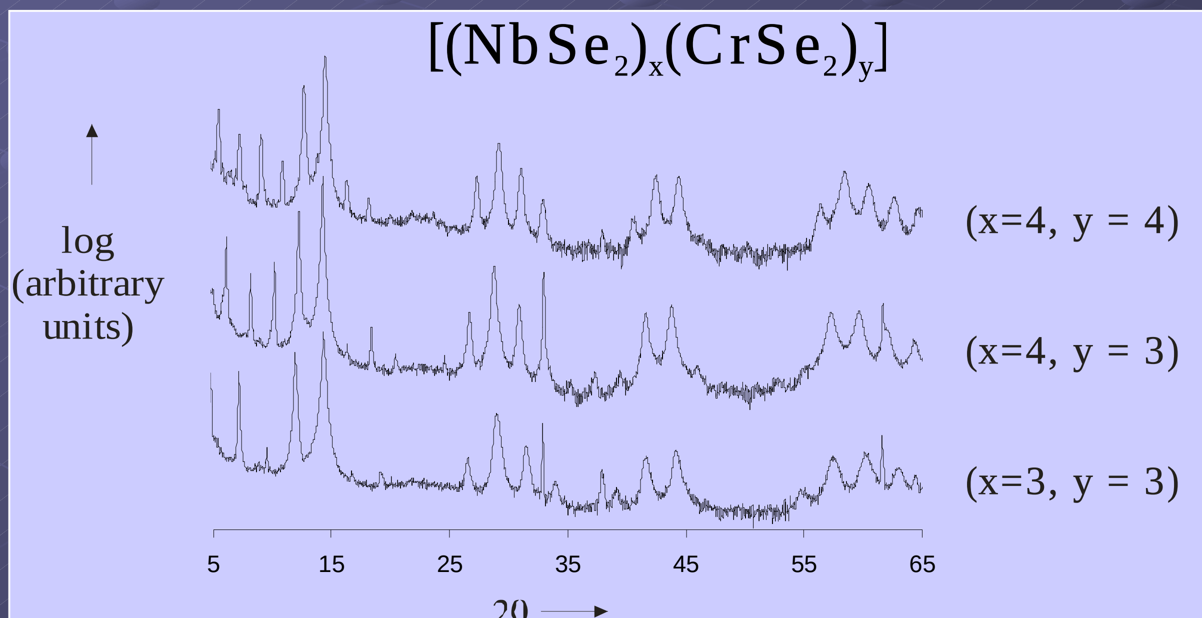




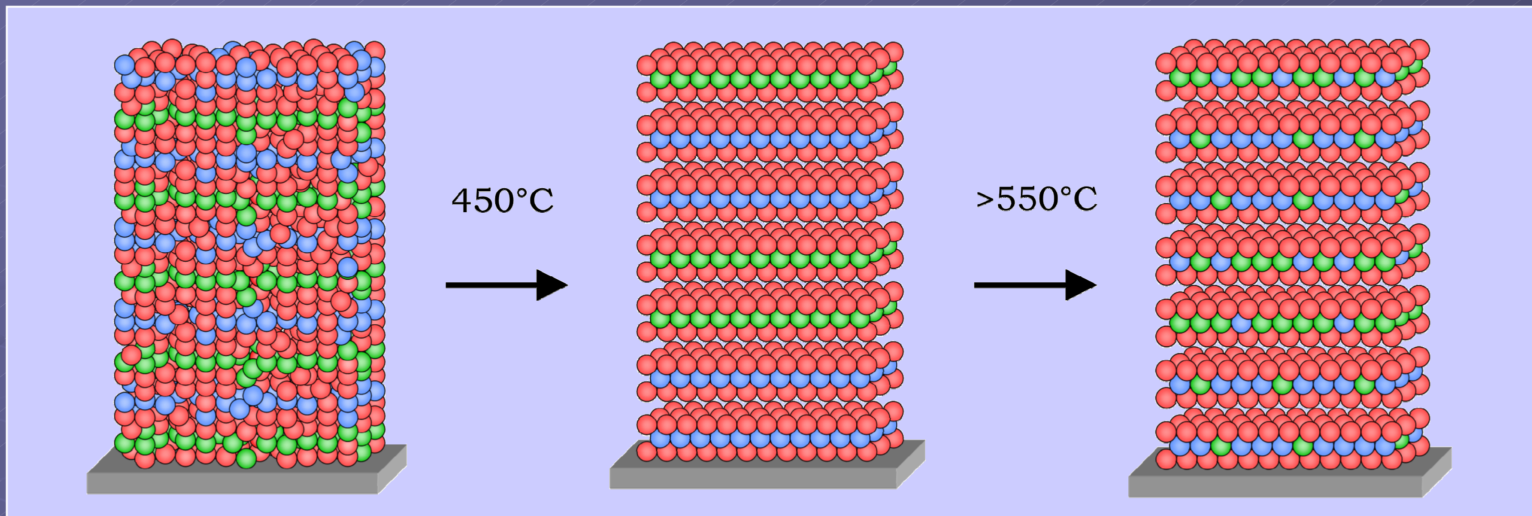


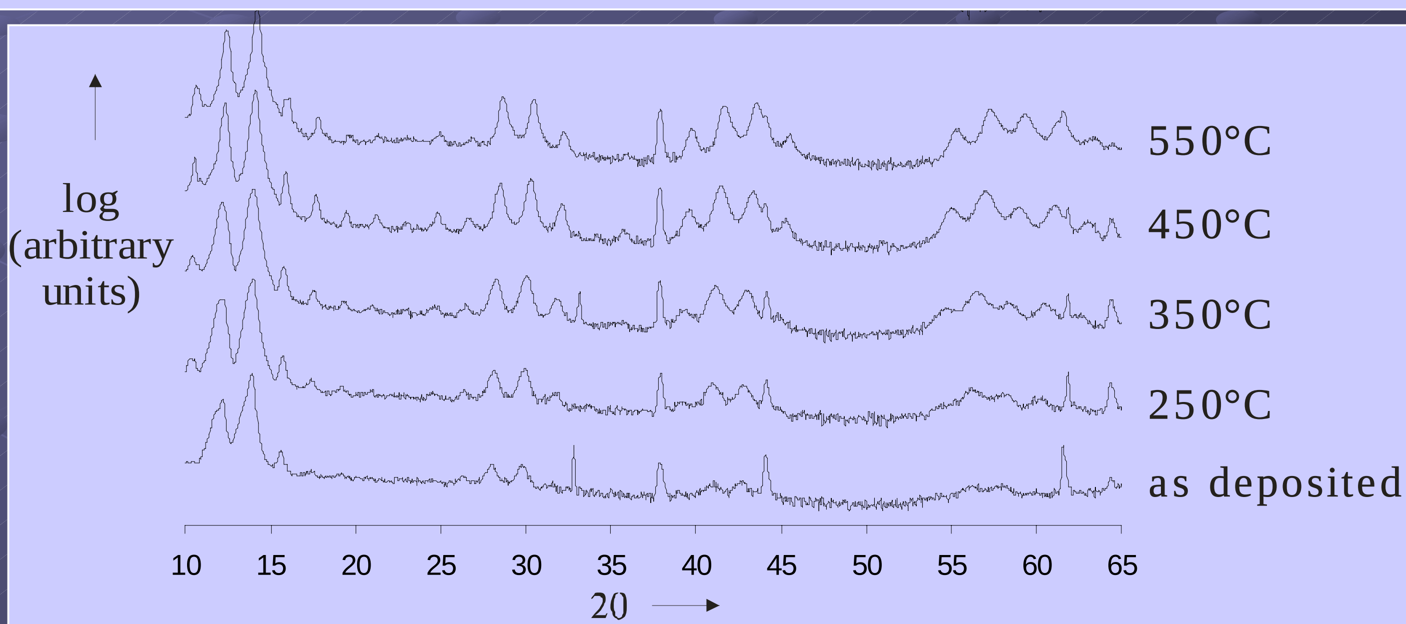
$[(NbSe_2)_x(CrSe_2)_y]$



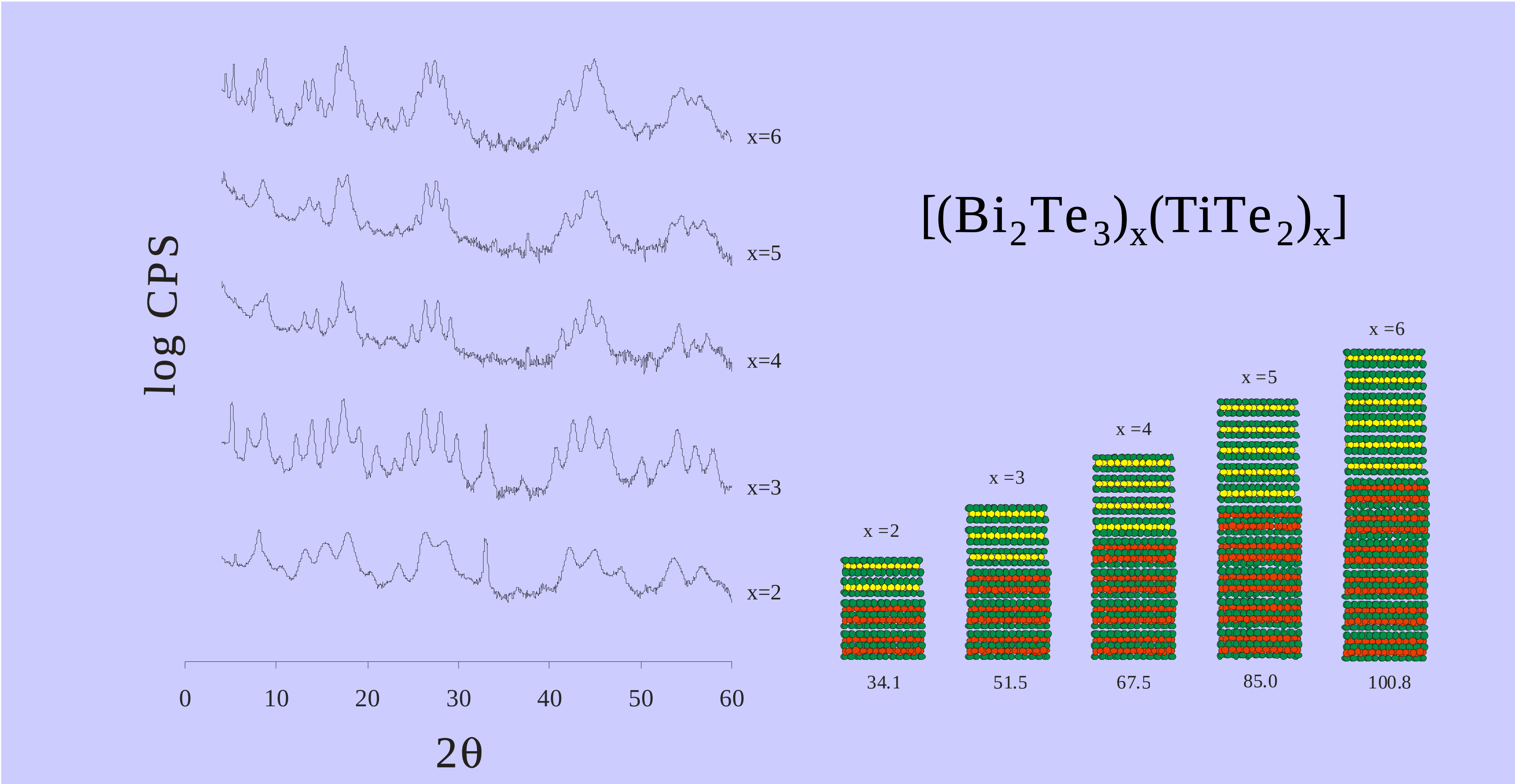


$[(TaSe_2)_x(VSe_2)_y]$





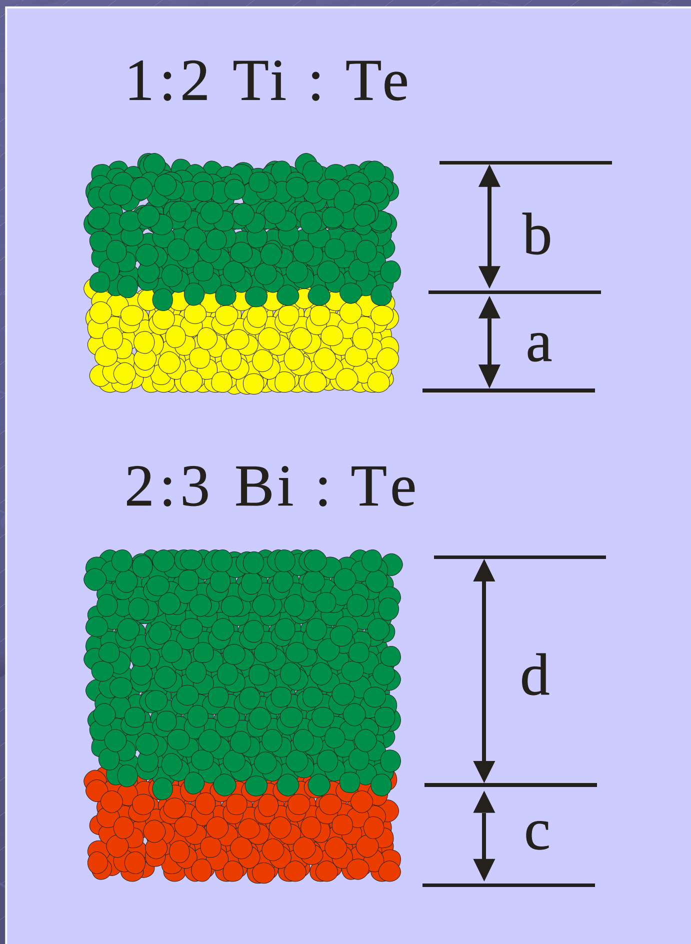
Unit Cell Control



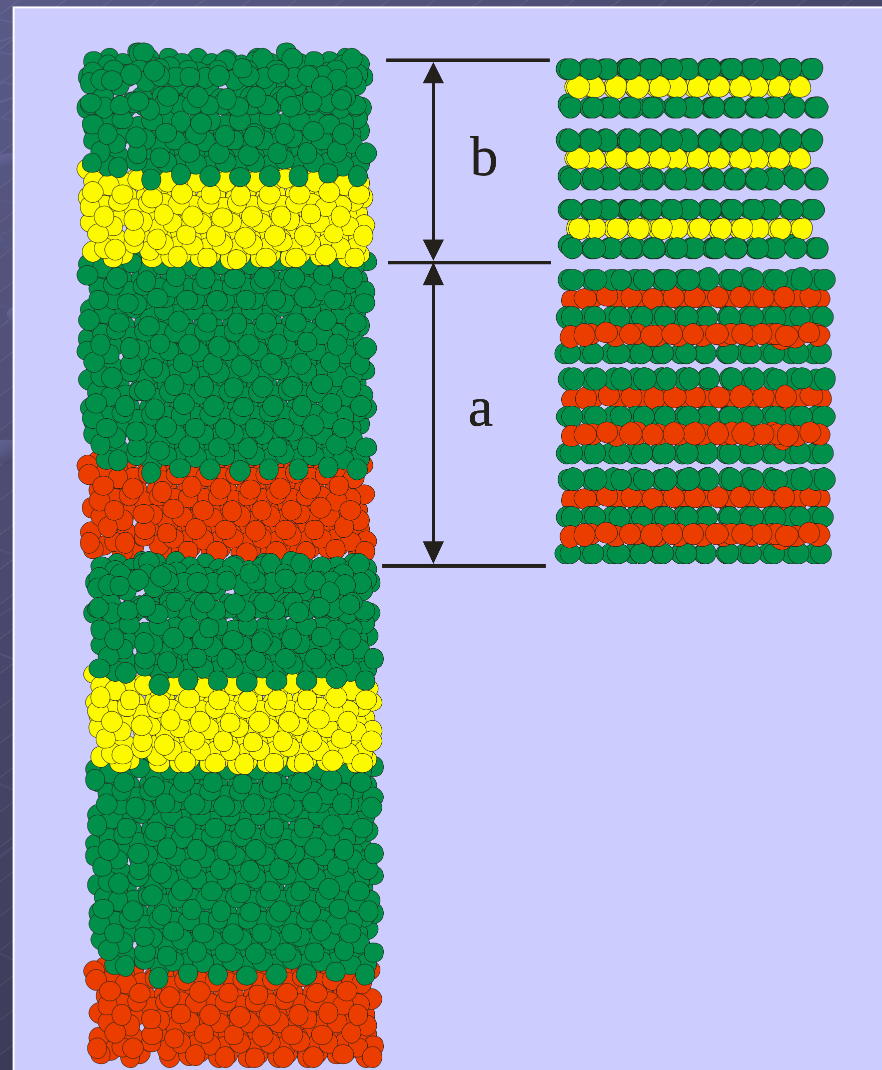
F. R. Harris, S. Standridge, C. Feik, D. C. Johnson,
Angew. Chem. Int. Engl **2003**, *42*, 5296.

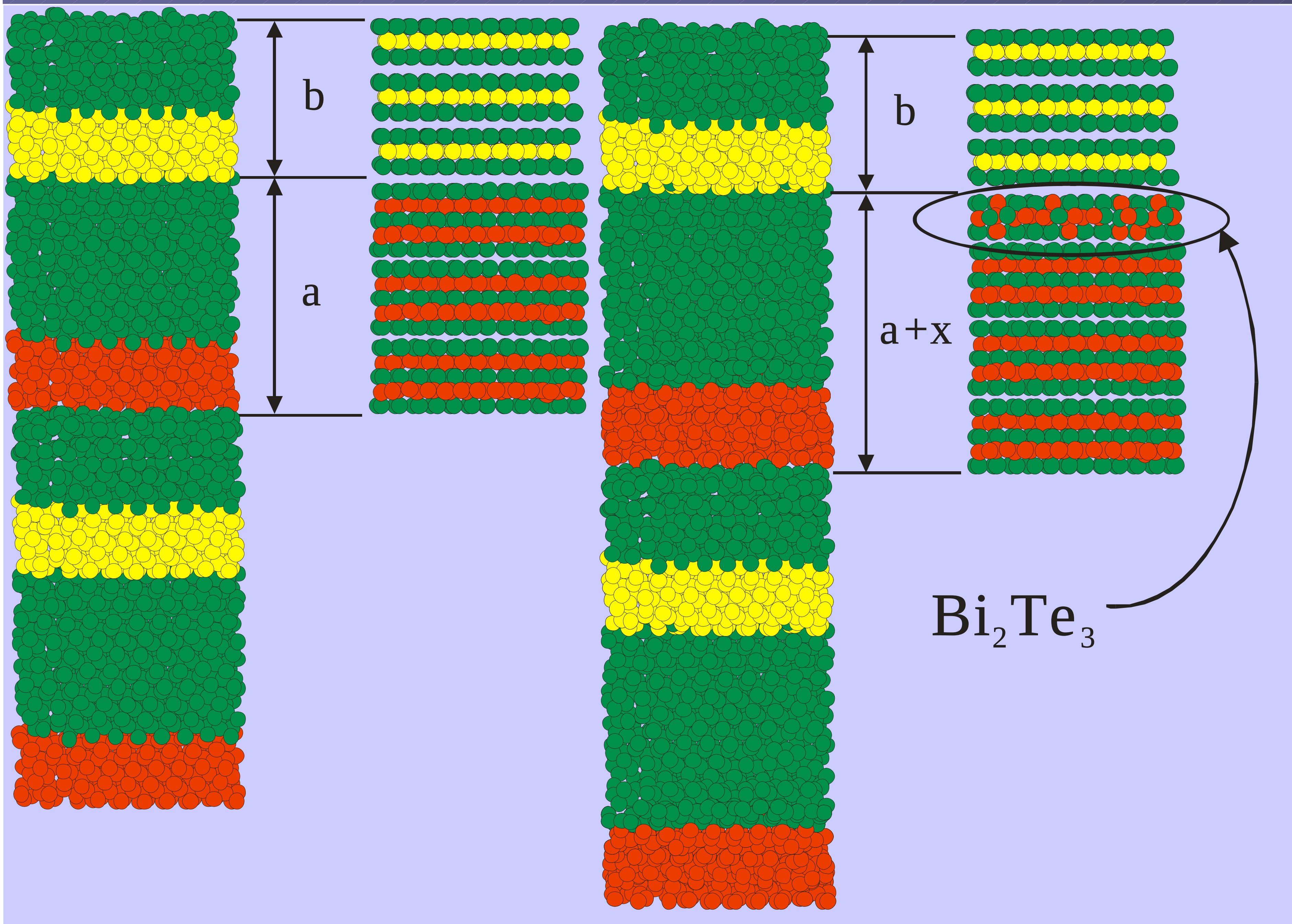
Two Main Calibrations

Stoichiometric



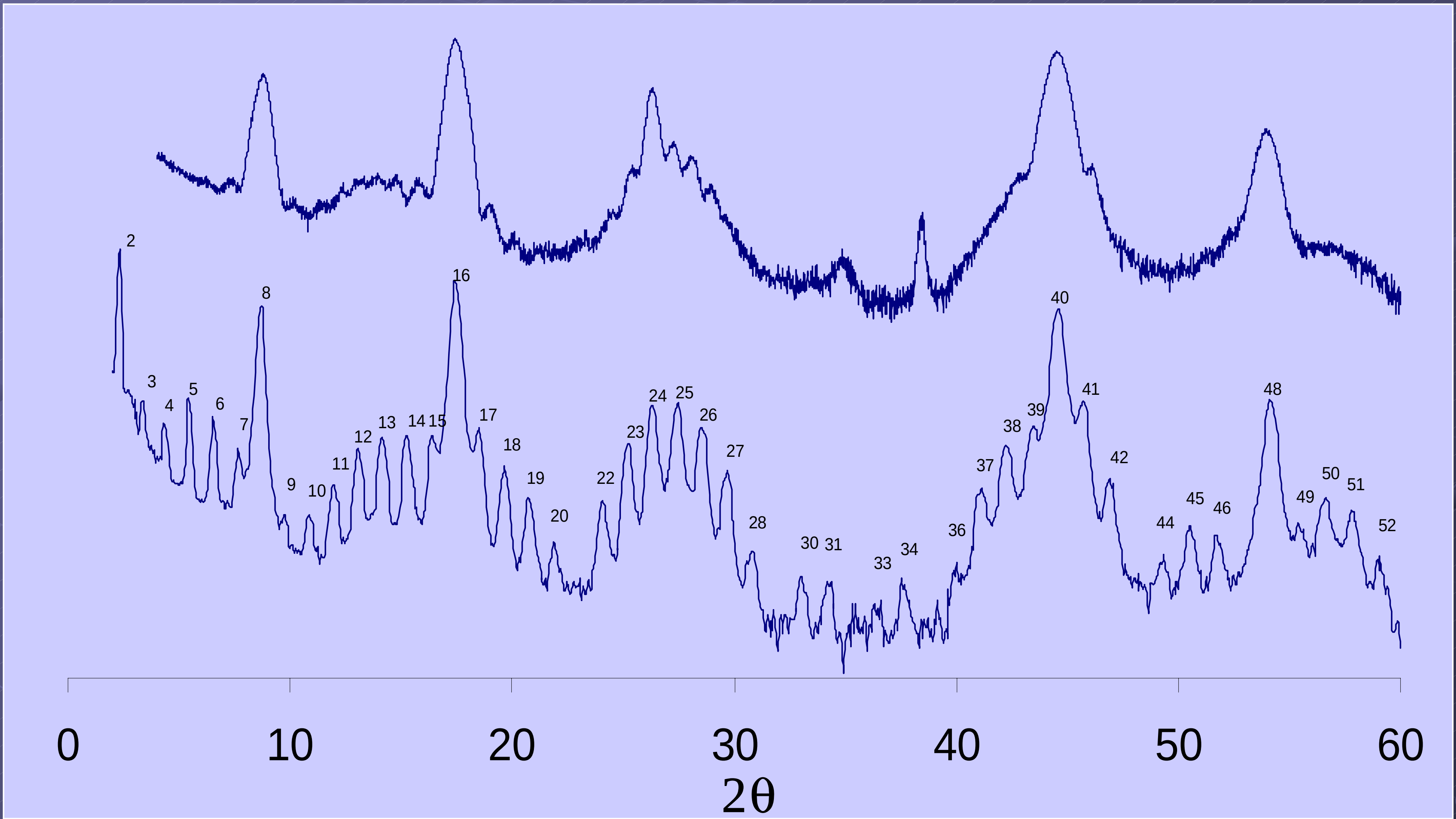
Absolute Amount



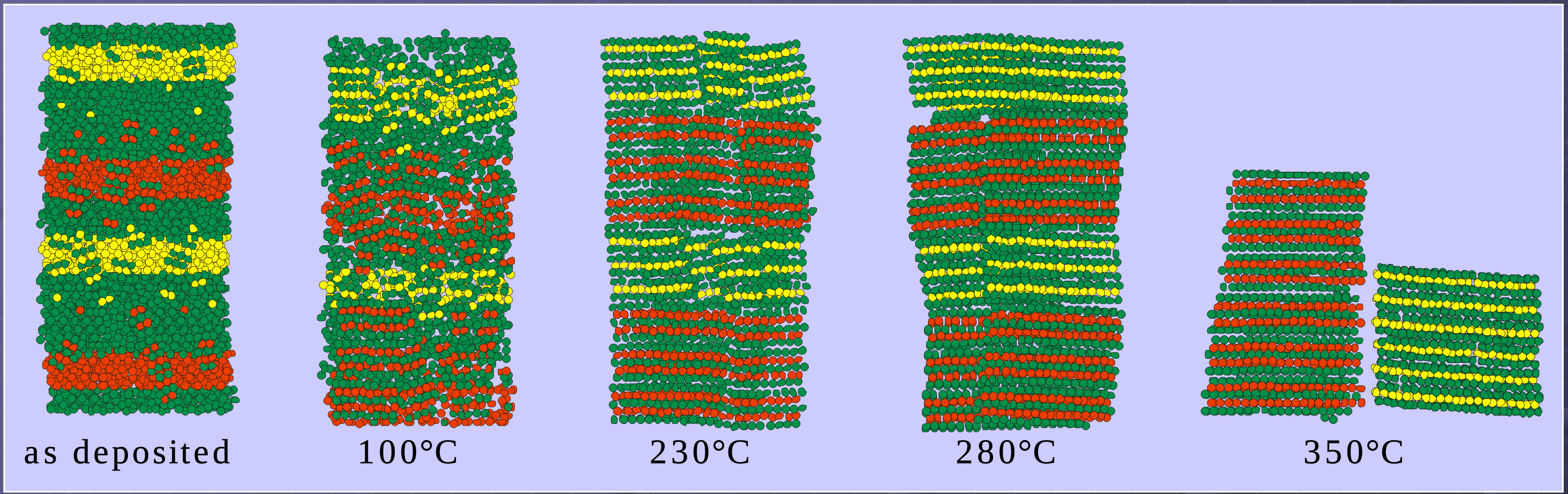

b
a
b
a+x
Bi_2Te_3

Calibration of Component Layers

Absolute Thickness is Critical



Proposed Mechanism



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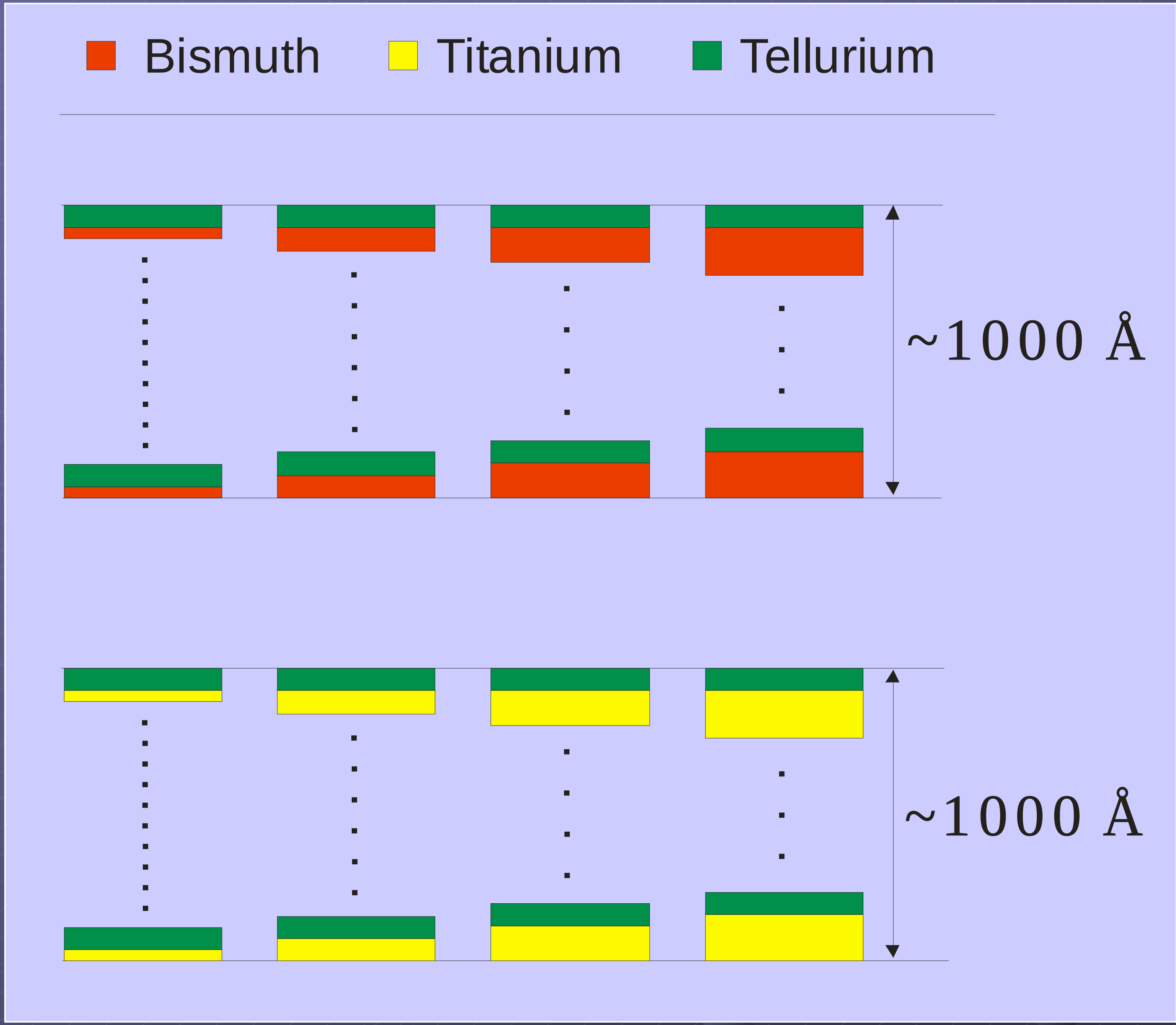
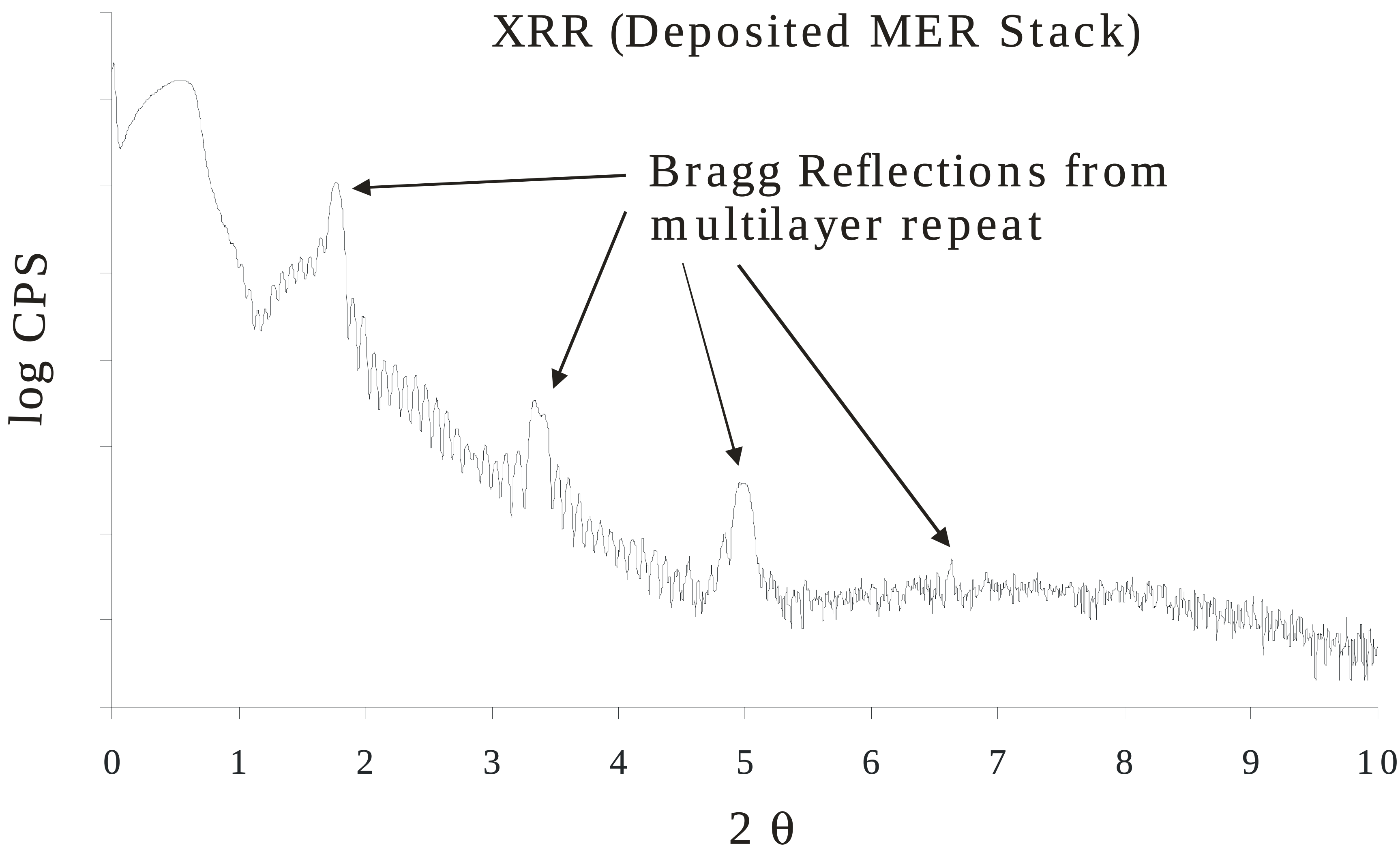
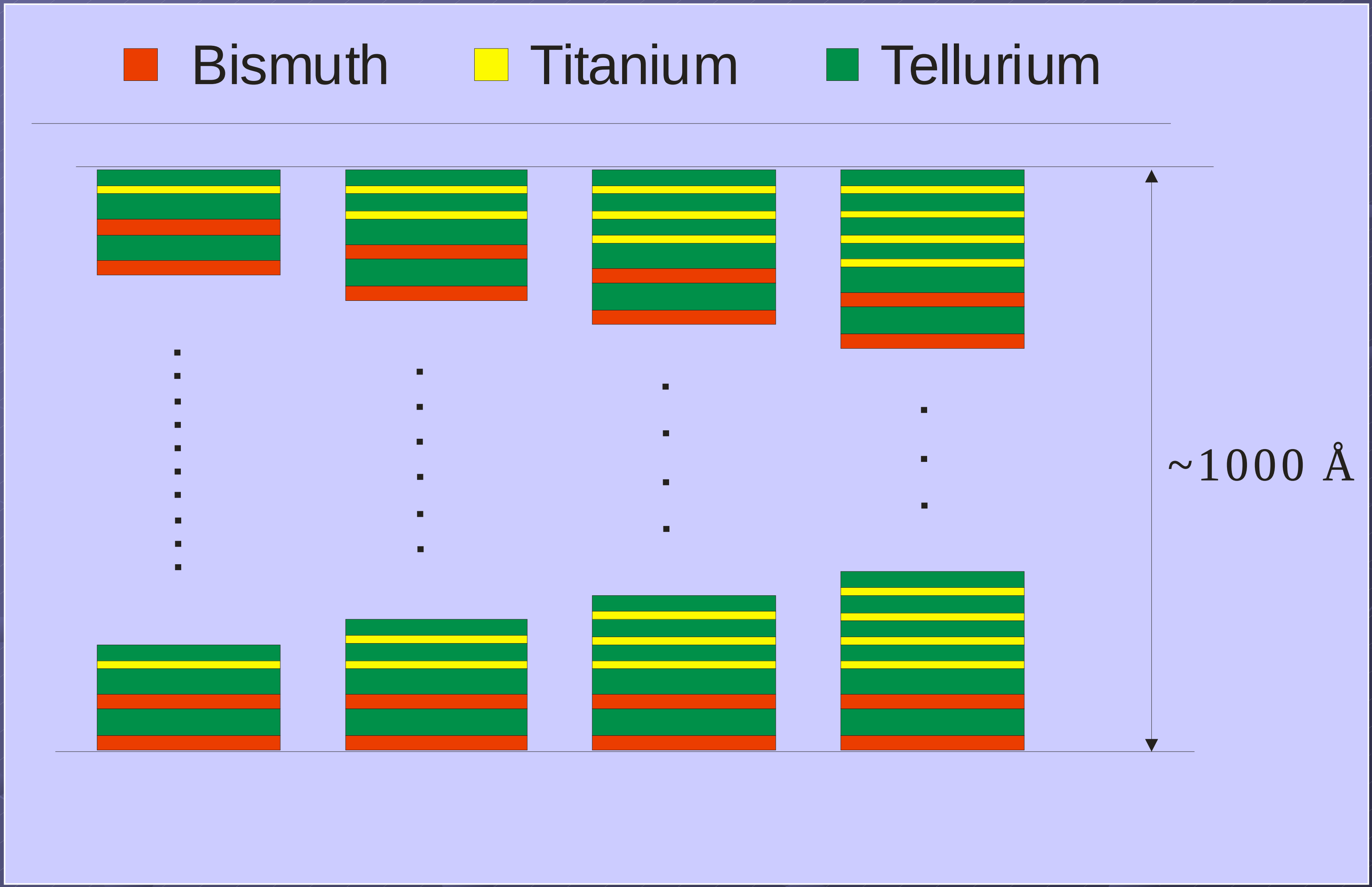

Bismuth
Titanium
Tellurium
~1000 Å
~1000 Å

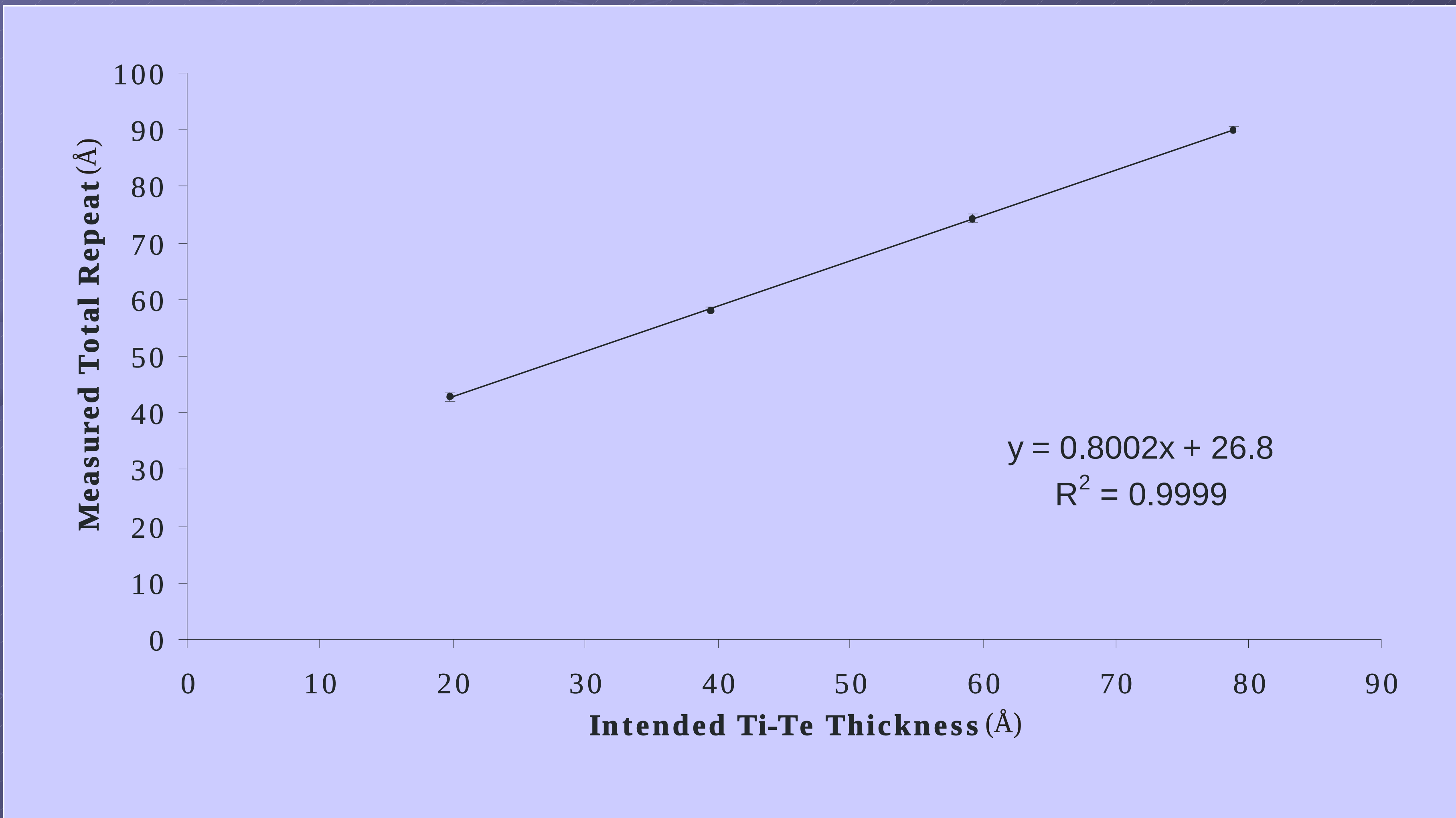
Deposited Reactant Stacks



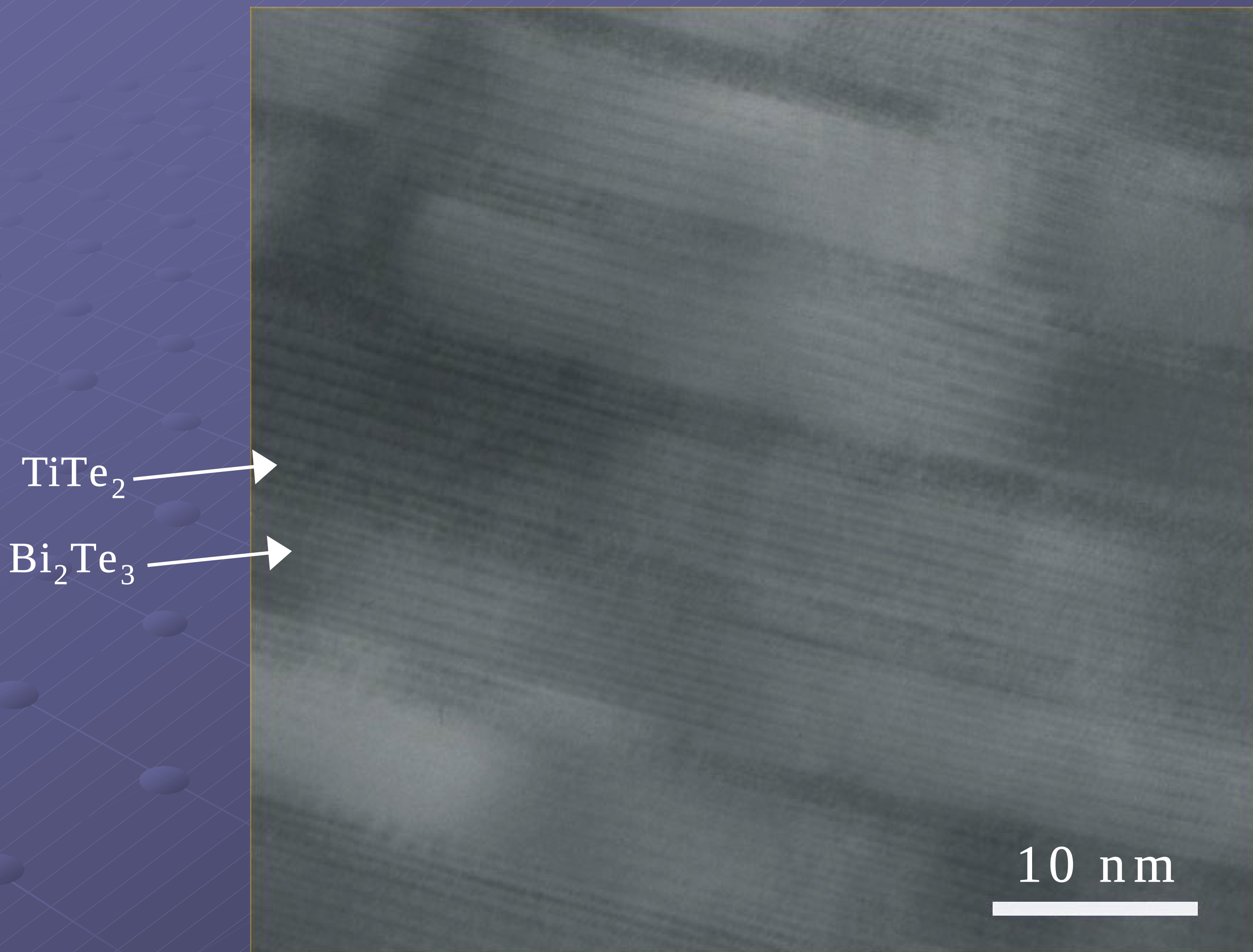
Calibrating Absolute Thickness



Calibrating Absolute Thickness



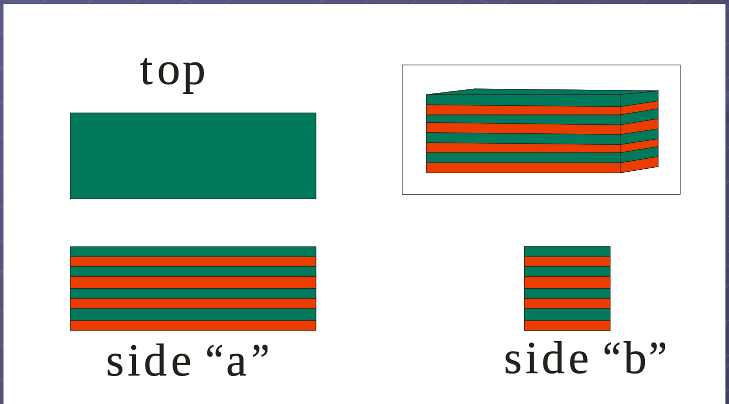
$[(Bi_2Te_3)_6(TiTe_2)_3]$

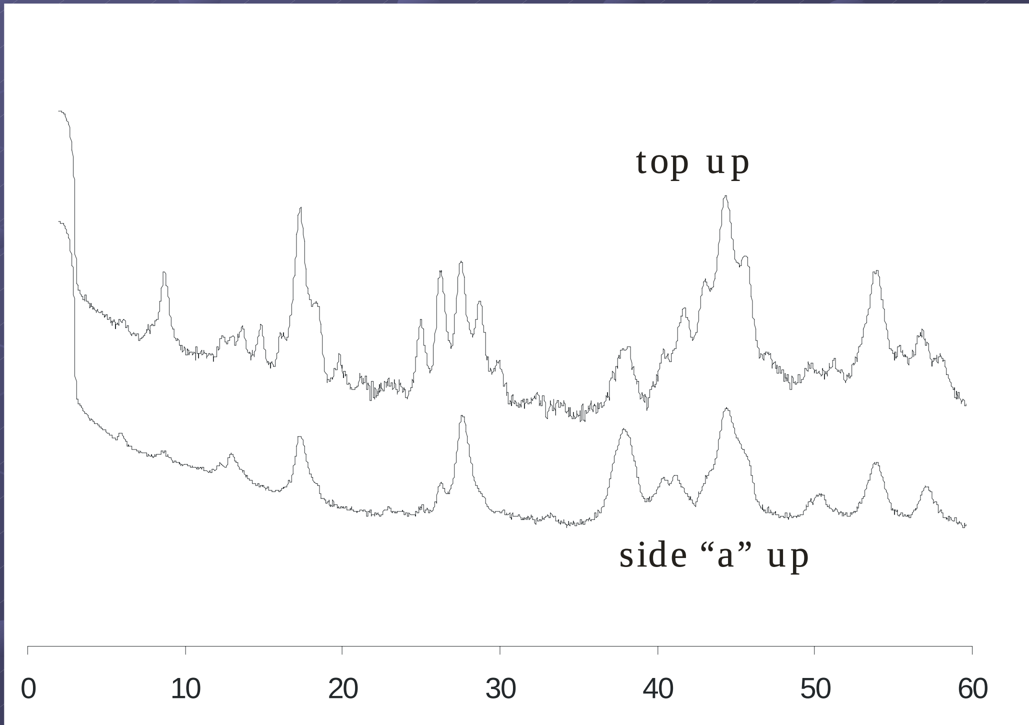


Bulk Samples

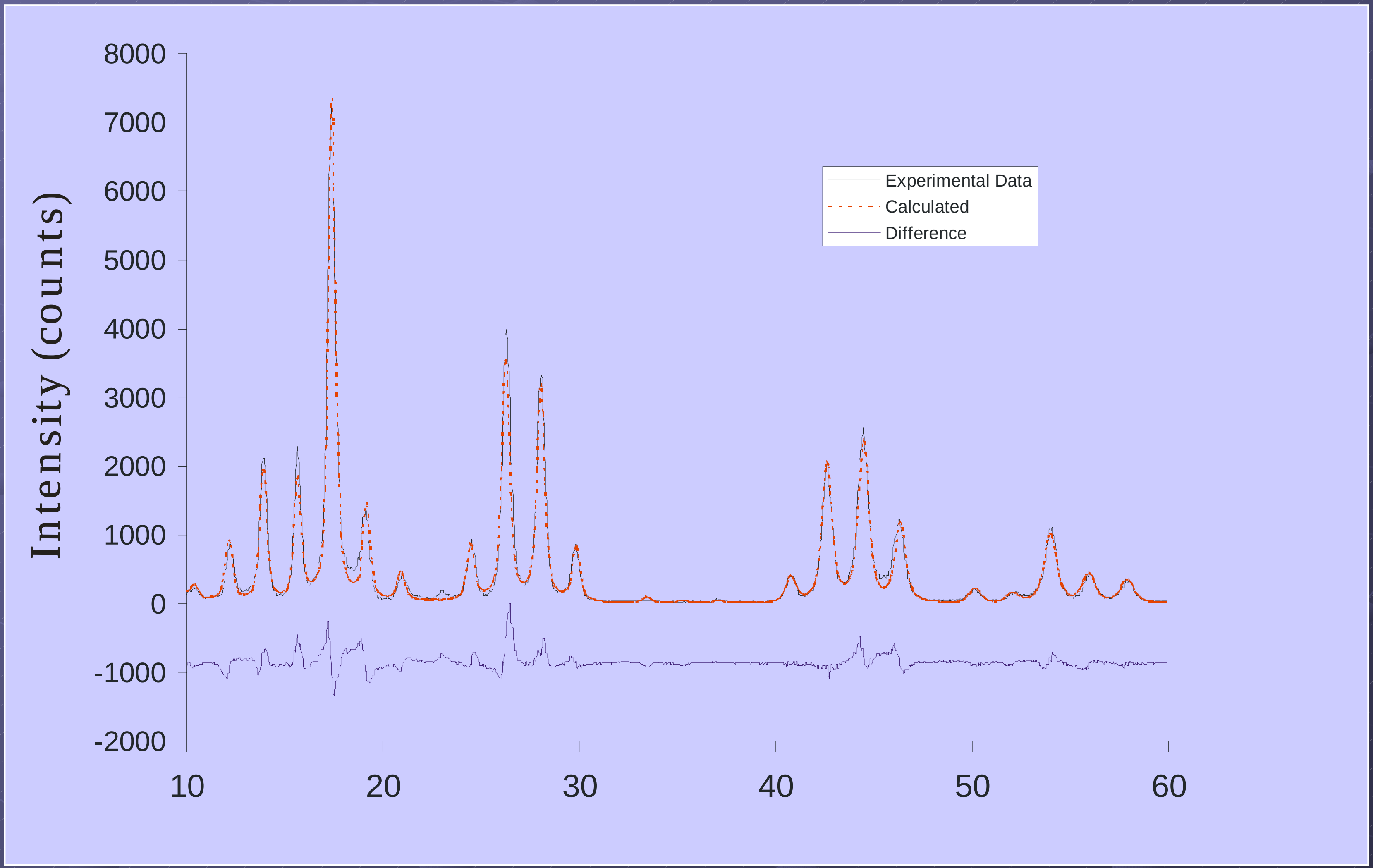
MER can make bulk amounts

2.01 ^{w} × 8.03 ^{l} × 2.06 ^{h} mm
Weight: 0.2248 g





Structure Analysis via Rietveld Refinement

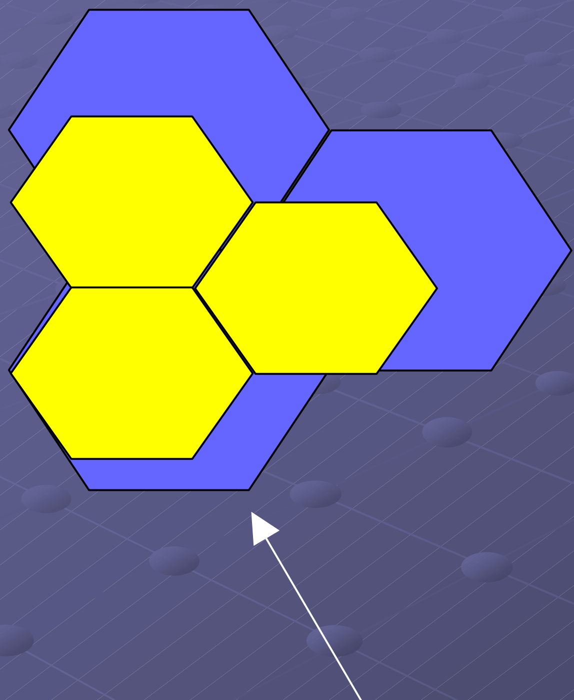


Summary of Rietveld Refinement Results

- Bi_2Te_3 layers spacings similar to the bulk
- $TiTe_2$ layer spacings similar to the bulk
- Van der Waals gap between Bi_2Te_3 and $TiTe_2$ resembles more closely the van der Waals gap in $TiTe_2$
- The relative density of the layers are close to bulk values ($TiTe_2$: Bi_2Te_3) = 1.36 : 1.00

An Interesting Question…

There is a wealth of data that suggests each component layer looks like its respective bulk material…



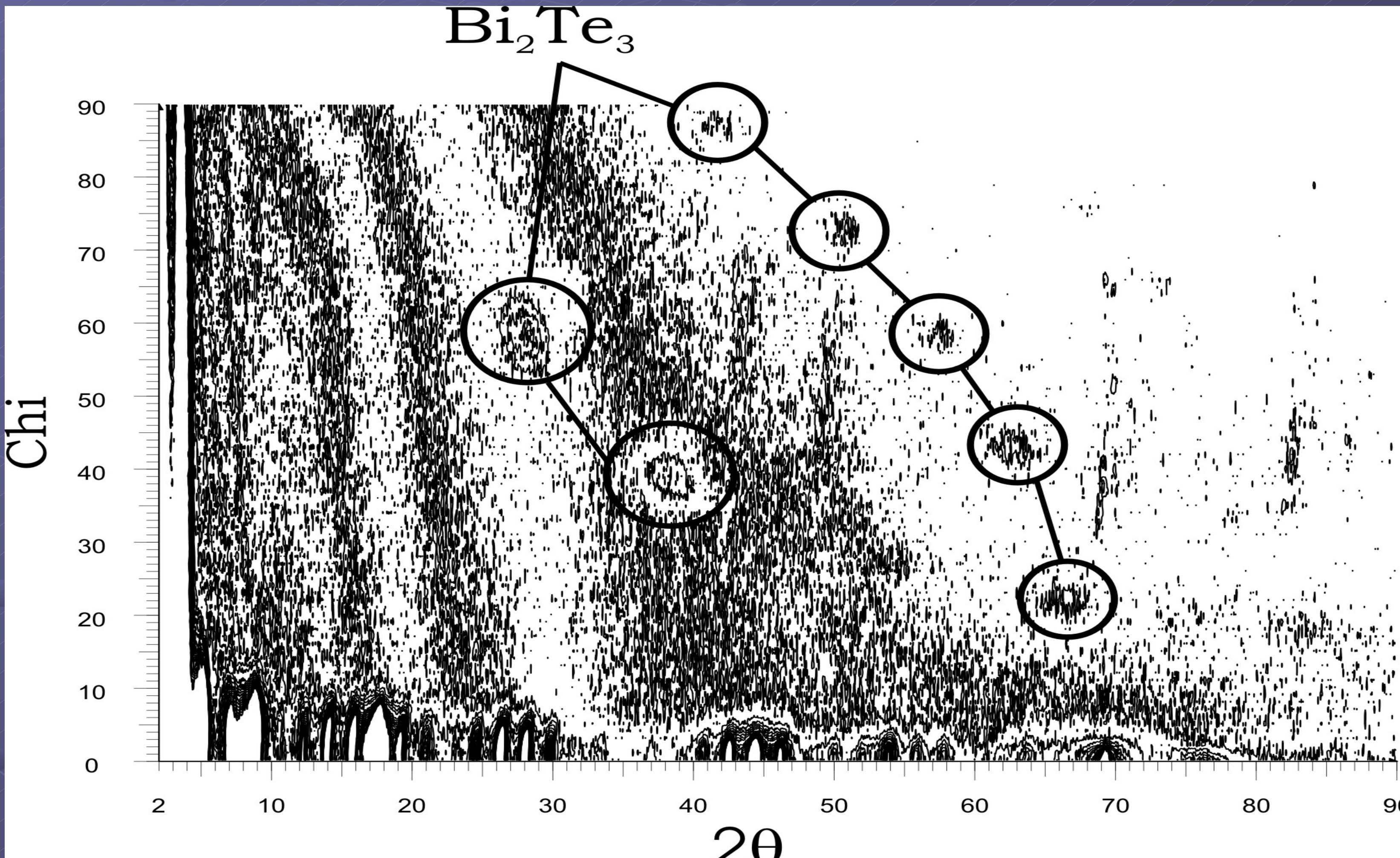
What is the crystallographic relationship between layers in the *a*-*b* direction?

19% Mismatch in the *a* lattice parameter between the end of a $TiTe_2$ layer and the start of a Bi_2Te_3 layer

a lattice parameters

Bi_2Te_3	= 4.4 Å
$TiTe_2$	= 3.7 Å

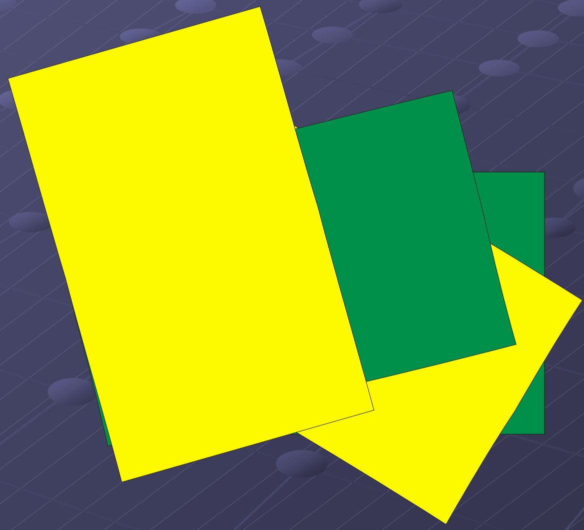
A K-space Map of $[(Bi_2Te_3)_3(TiTe_2)_3]$

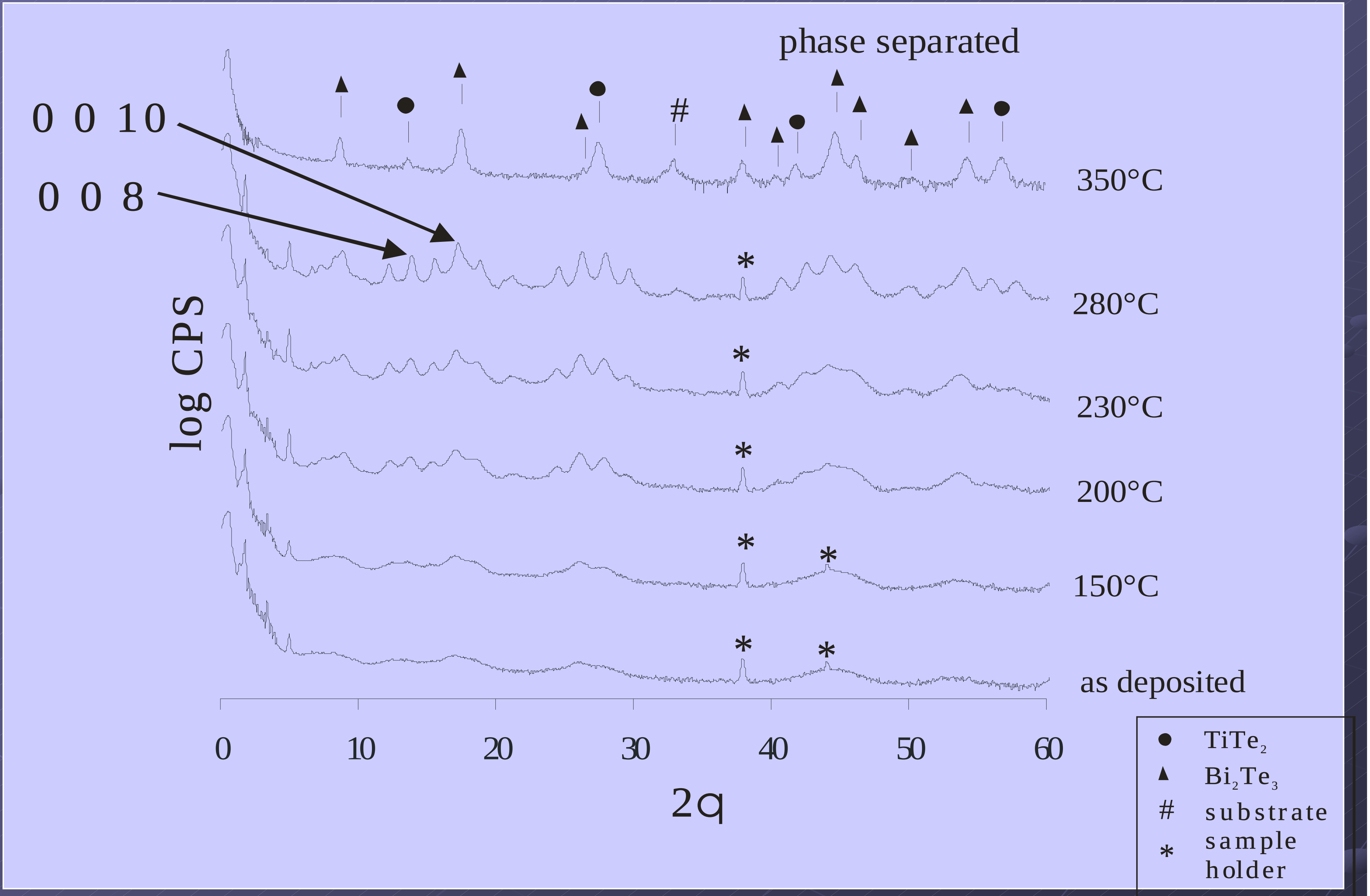


The Short Story

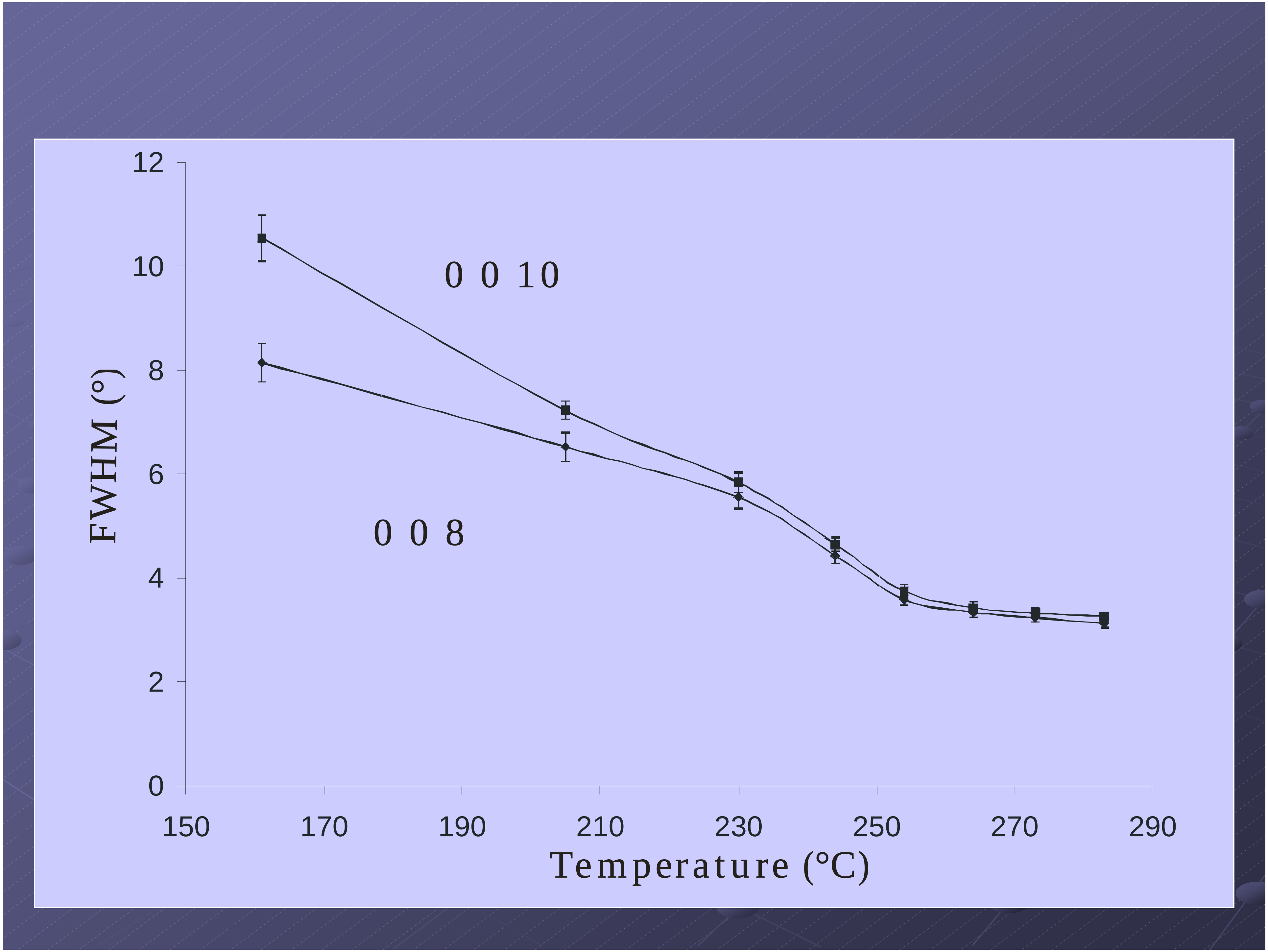
XRD data suggests that the layers are turbostratic

Much like a deck of cards carelessly thrown on a table, there is crystallographic alignment in the *c* direction, but random alignment between the layers in the *a*-*b* plane.





phase separated
0 0 10
0 0 8
350°C
280°C
230°C
200°C
150°C
as deposited
log CPS
0
10
20
30
40
50
60
2q
TiTe2
Bi2Te3
substrate
sample holder

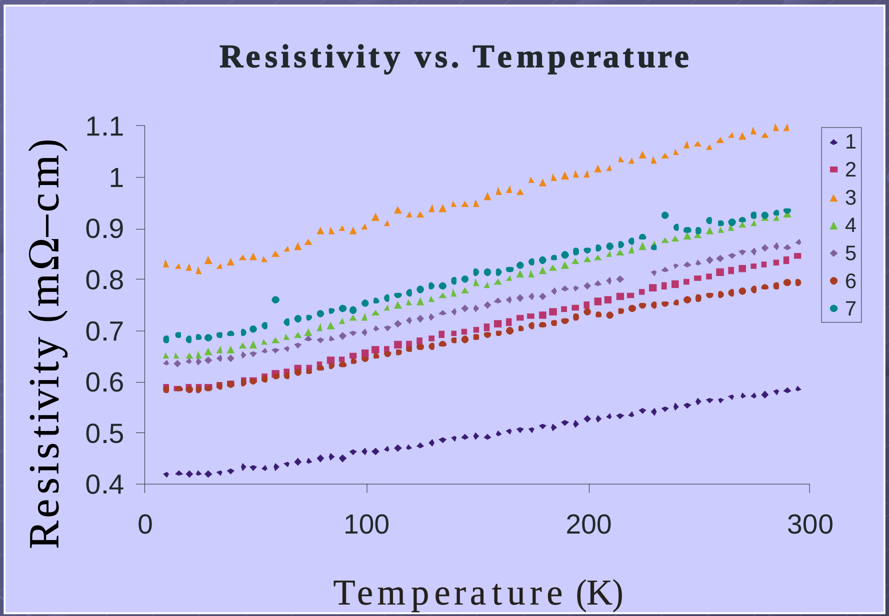


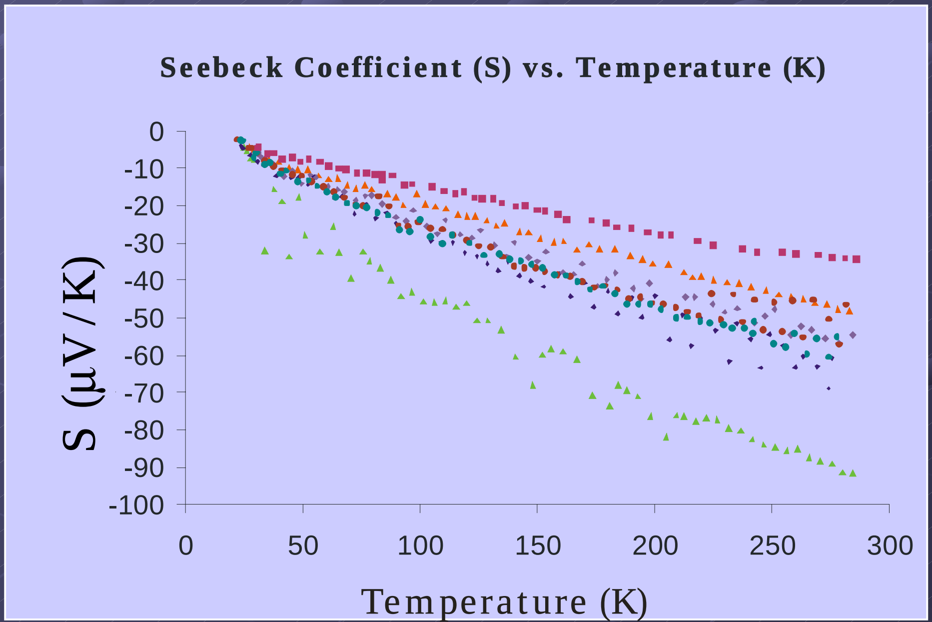
12
10
8
6
4
2
0
150
170
190
210
230
250
270
290
FWHM (°)
Temperature (°C)
0 0 10
0 0 8

Electrical Properties of $[(Bi_2Te_3)_x(TiTe_2)_y]$ Superlattices

Precision Experiment

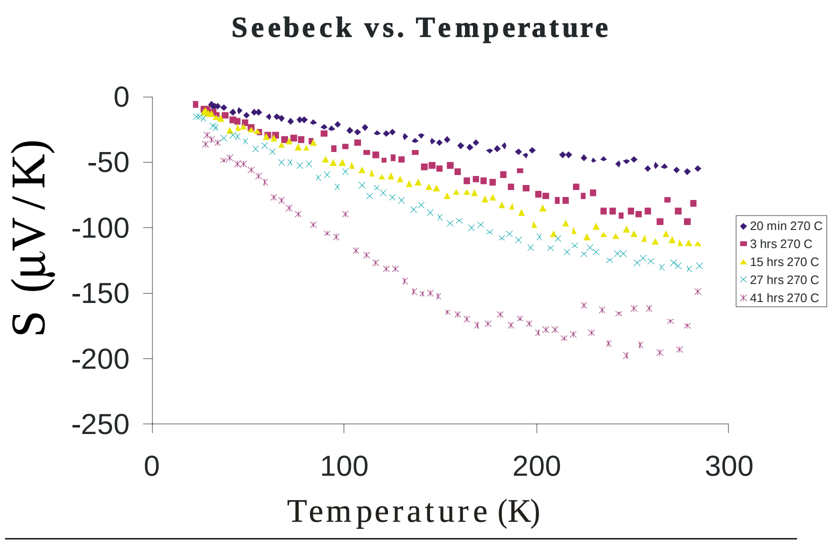
7 different samples of $[(Bi_2Te_3)_5(TiTe_2)_4]$ were made

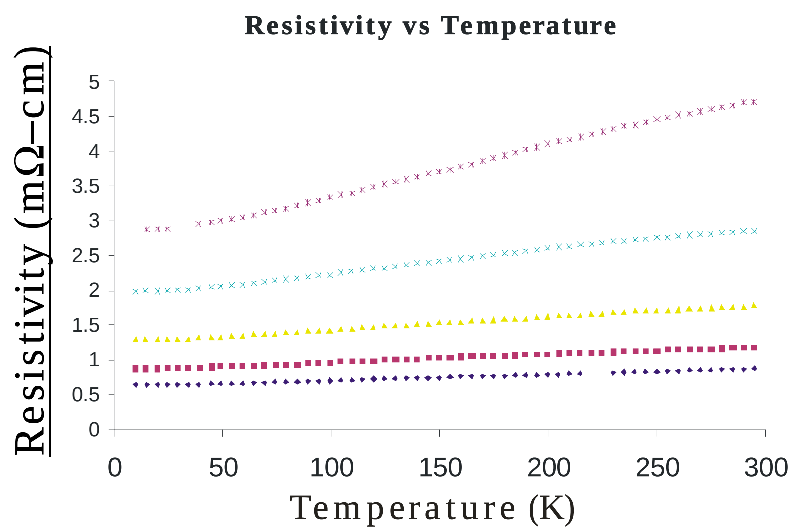




Annealing Study

Annealing makes electrical properties more desirable





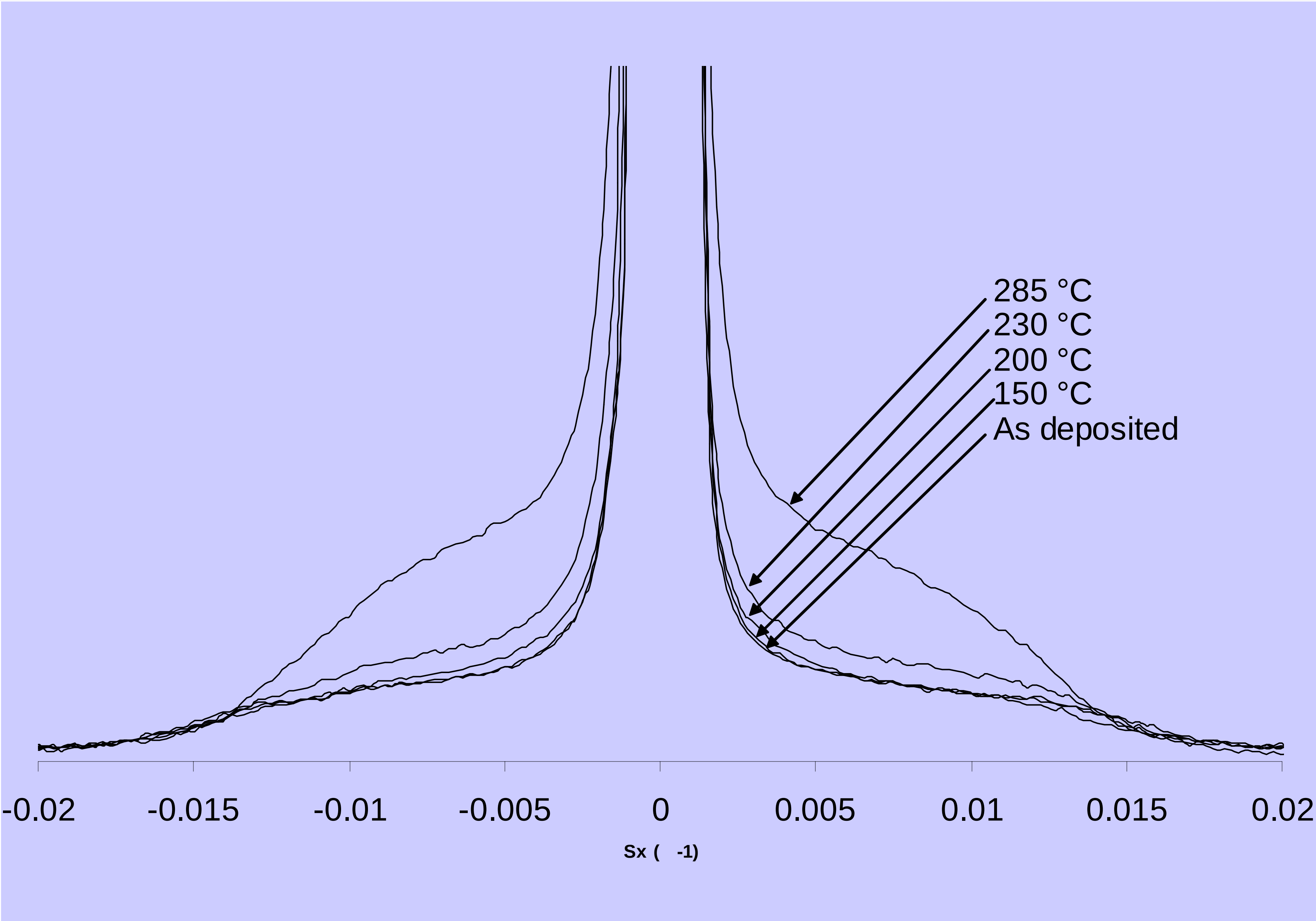
20 Minutes 270

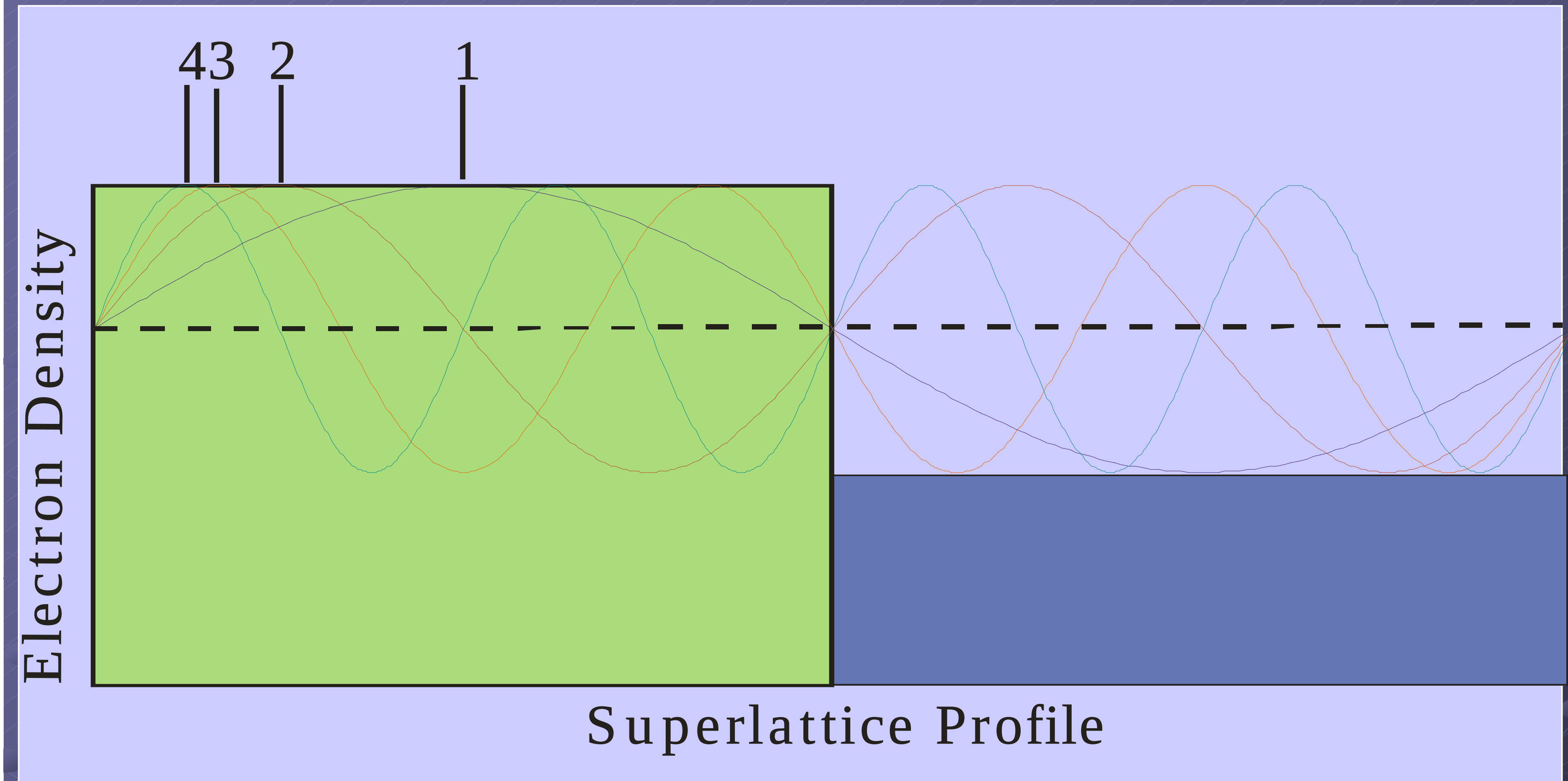
3 Hours 270

15 Hours 270

27 Hours 270

41 Hours 270


285 °C
230 °C
200 °C
150 °C
As deposited
-0.02
-0.015
-0.01
-0.005
0
0.005
0.01
0.015
0.02
Sx (-1)



X-ray diffraction is nothing more than a Fourier transform of the electron density normal to the scanning axis

Future Work

- Analyze Electrical properties of $[(Bi_2Te_3)_x(TiTe_2)_y$ as a function of x and y
- Analyze order between *a*-*b* planes as a function of x and y
- Analyze thermal conductivity as a function of x and y

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