Investigations of Interfacial Structure in Thermoelectric Tellurides

Douglas L. Medlin

Sandia National Laboratories
Materials Physics Department
Org 8656 MS 9161
7011 East Avenue
Livermore, CA 94551

dlmedli@sandia.gov

Sandia National Laboratories

Collaborators for this work

Sandia:

Jessica Lensch-Falk
Josh Sugar
Peter Sharma
Nancy Yang
Catalin Spataru
Michelle Hekmaty
Mark Homer

Caltech:

Nick Heinz
Teruyuki Ikeda
G. Jeffrey Snyder

LBNL:

Quentin Ramasse
Currently: SuperSTEM, Daresbury, UK

Special thanks to:

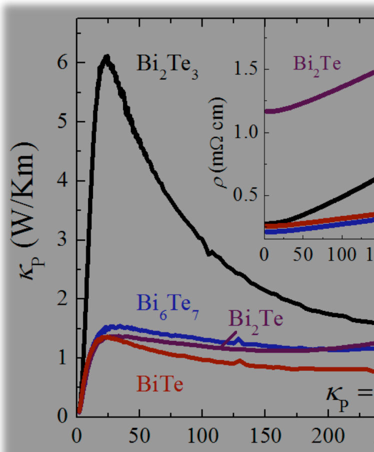
-LBNL: User program, National Center for Electron Microscopy
-LLNL: John Bradley, for use for LLNL's Titan 80/300 instrument
-UCD: Z. Zhang and E. Lavernia, for assistance with SPS processing

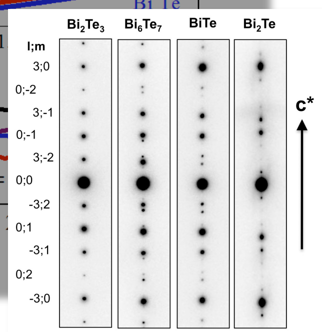
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy, National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Thermoelectric Materials Science at Sandia: Fundamental Science to Device Level Detail

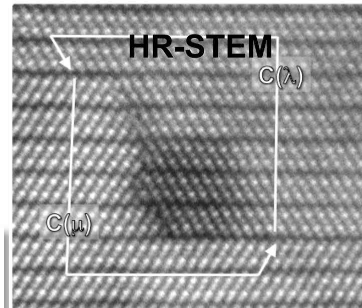
Transport Physics





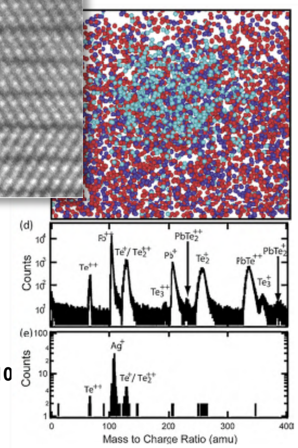
P. Sharma, et al. PRB (2011)

Advanced Microscopy



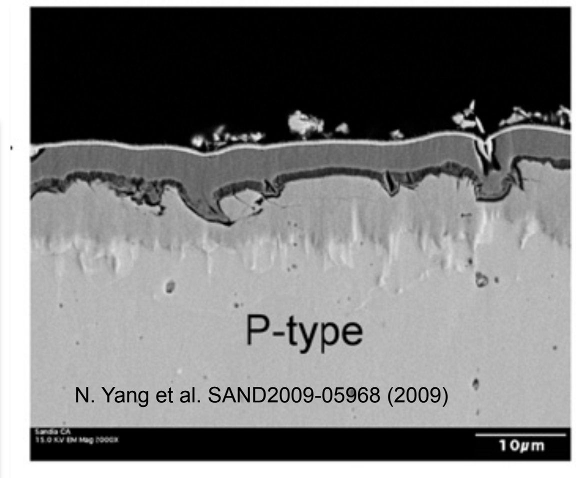
D. Medlin & N. Yang J. Elect. Mat (2012)

Atom Probe Tomography



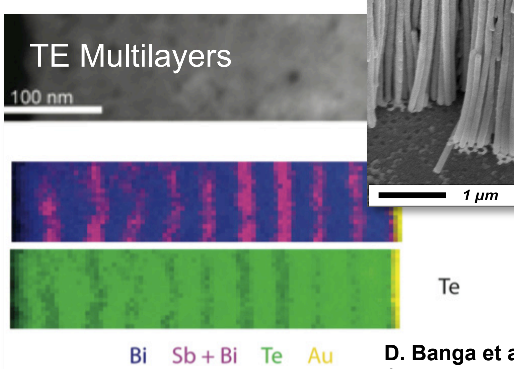
Lensch-Falk et al. J. Alloy Cmpds (2010

Aging & Compatibility

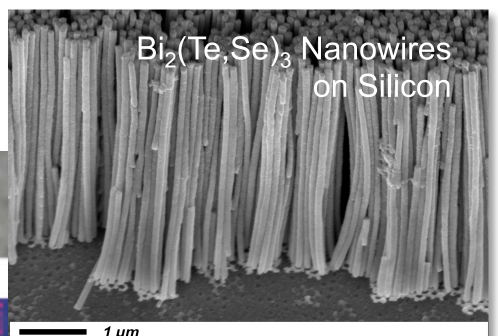


N. Yang et al. SAND2009-05968 (2009)

Materials Synthesis



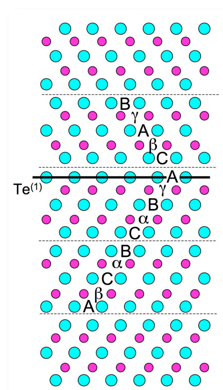
D. Banga et al. J. Cryst. Growth & Des. (2012).



S. J. Limmer, et al. J. Electrochem Society. (2012).

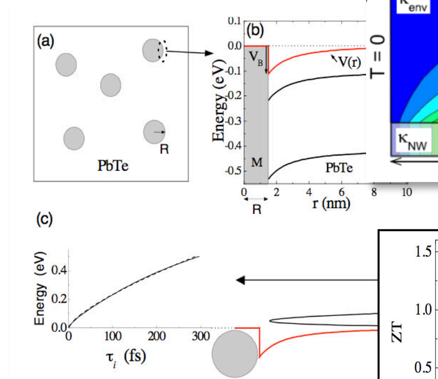
Theory and Modeling

Structure

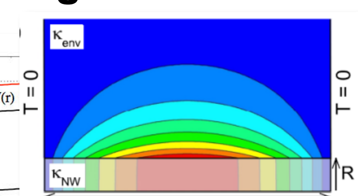


D.L. Medlin et al, J.Appl. Phys (2010)

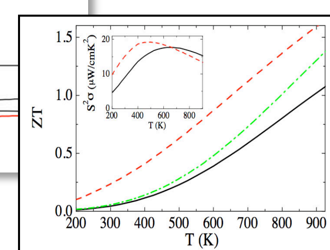
Transport



S. Faleev & F. Léonard, Physical Review B, 2008



F. Léonard, APL 2010



Important Roles for Interfaces in Thermoelectric Materials

Interfacial strategies to enhance ZT:

-phonon scattering: $\downarrow \kappa$

-energy filtering: $\uparrow S^2\sigma$

Bulk Thermoelectrics:

-grain size reduction

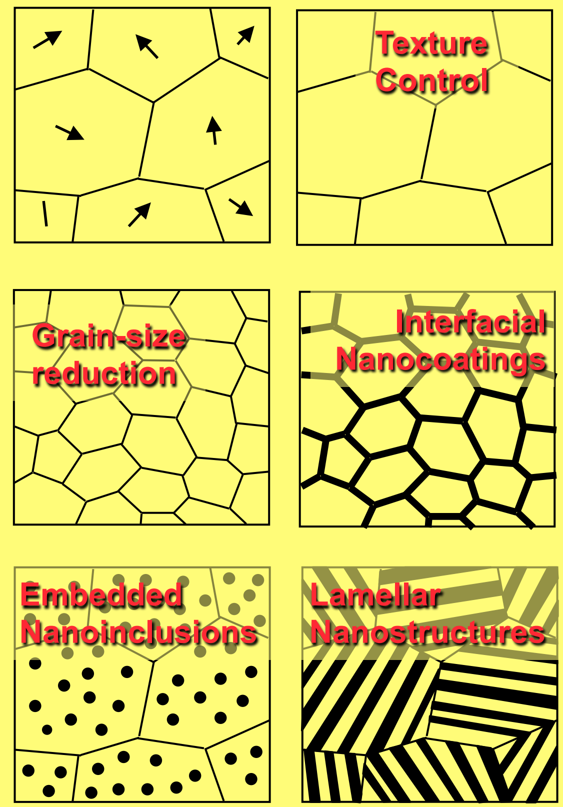
-solid state phase transformations

What are mechanisms of interface formation and stability?

How do interfaces control local transport properties?

Needed: foundational understanding of interfacial structure and composition in thermoelectric materials

Microstructural Strategies for Nanostructured Bulk Thermoelectrics

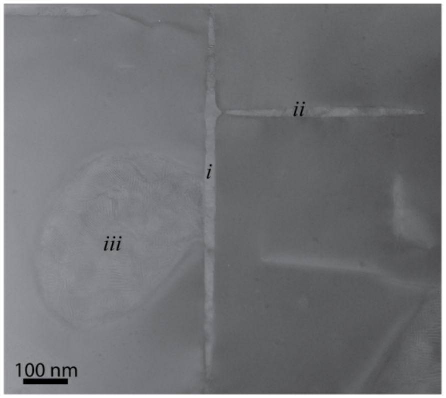


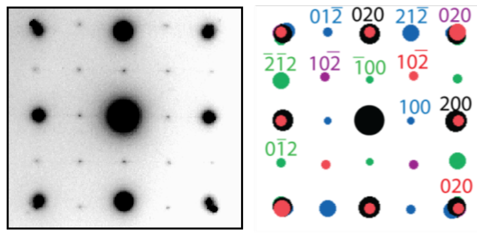
Medlin and Snyder, Current Opinion in Colloid and Interface Science, 2009

Sandia National Laboratories

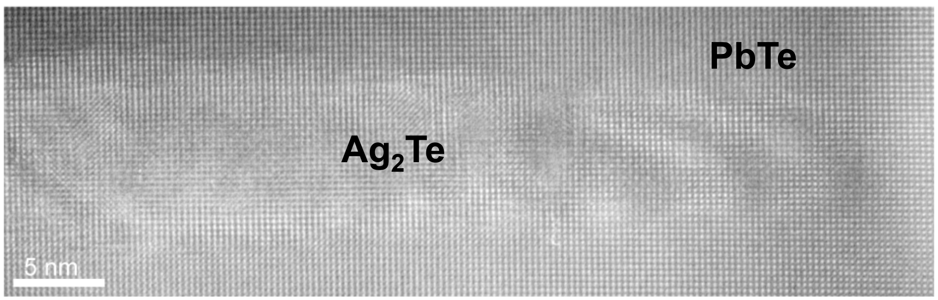
Example: Enhanced zT in Ag_2Te/PbTe system

Crystallographically aligned precipitates of Ag_2Te in thermoelectric PbTe matrix



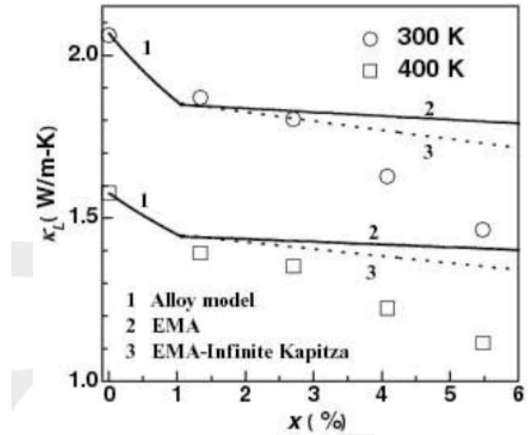


[201]monoclinic || [001]fcc
(-204)monoclinic || (2-20)fcc
+ symmetry-related variants



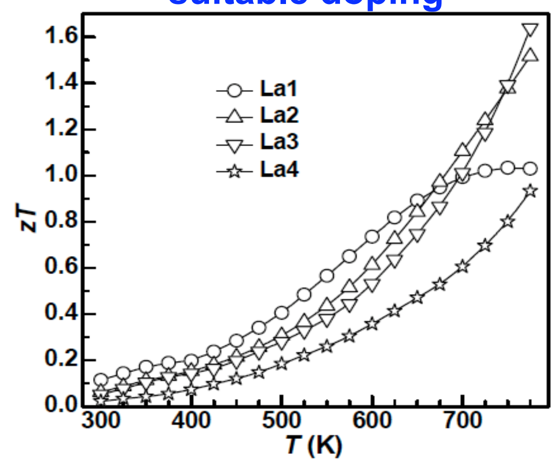
J. Lensch-Falk, J. Sugar, M. Hekmaty, D. Medlin, Journal of Alloys and Compounds (2010)

Ag_2Te precipitates reduce thermal conductivity by phonon scattering



Collaboration with Snyder Group, Caltech

zT as high as 1.6 with suitable doping



Y. Pei, J. Lensch-Falk, E.S. Toberer, D.L. Medlin, G.J. Snyder, *Advanced Functional Materials* (2011).

Initial precipitates form topotactically at high T in FCC phase

Transform to monoclinic on cooling to room temperature

Plate morphology relieves elastic strain.

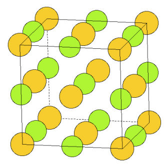
Same orientation relationship observed for Ag_2Te in $AgSbTe_2$.

J. Sugar & D. Medlin, Journal of Alloys and Compounds (2009)

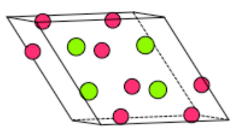
Sandia National Laboratories

Focus for this talk: Interfacial structure in Thermoelectric Tellurides

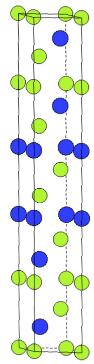
Rock-Salt
($PbTe$, $AgSbTe_2$)



Monoclinic
(Ag_2Te)



Tetradymite
(Bi_2Te_3,Sb_2Te_3)



Rich set of structures and phase relations

Can we begin to make sense of interfaces in these complex systems?

- **Structure of the basal twin in Bi_2Te_3**

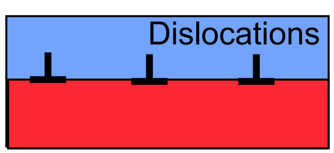
  -comparison with ab initio calculations
  -Analysis of a twin boundary defect
  -Analogies to twins in FCC materials

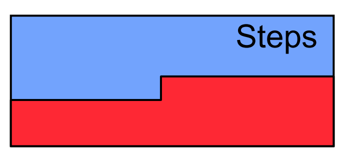
- **Rocksalt/Tetradymite Telluride Interfaces**

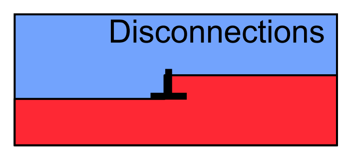
  -$AgSbTe_2$/Sb_2Te_3
  -$PbTe$/Sb_2Te_3

  -Tetradymite plate formation.
  - Interfacial strain accommodation.

Interfacial Line Defects: **Building blocks to general understanding of interface structure and behavior.**





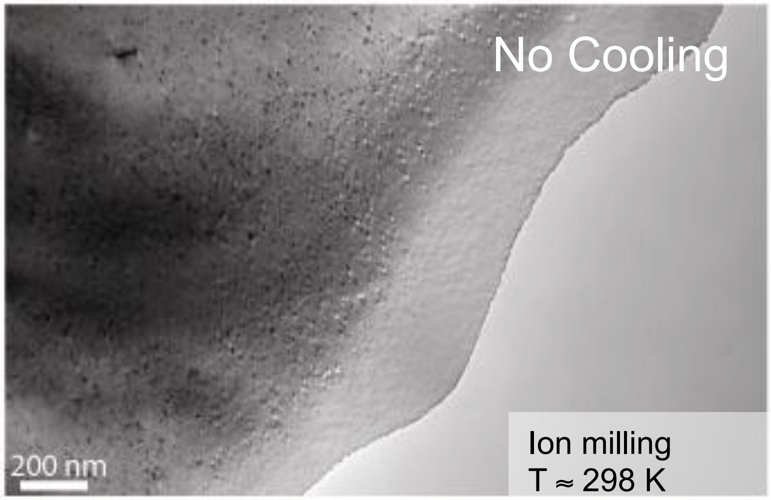


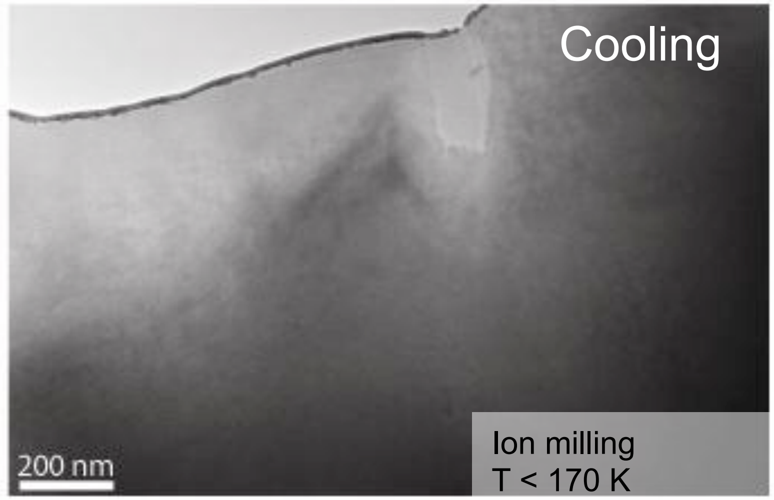
Sandia National Laboratories

An Experimental Challenge: TEM preparation of Tellurides

Example: **PbTe: Aggressive ion milling conditions produce nanoscale contrast features**

PbTe – 99.998% Sigma Aldrich





Artifacts can arise even with cooling if ion-milling power is too high

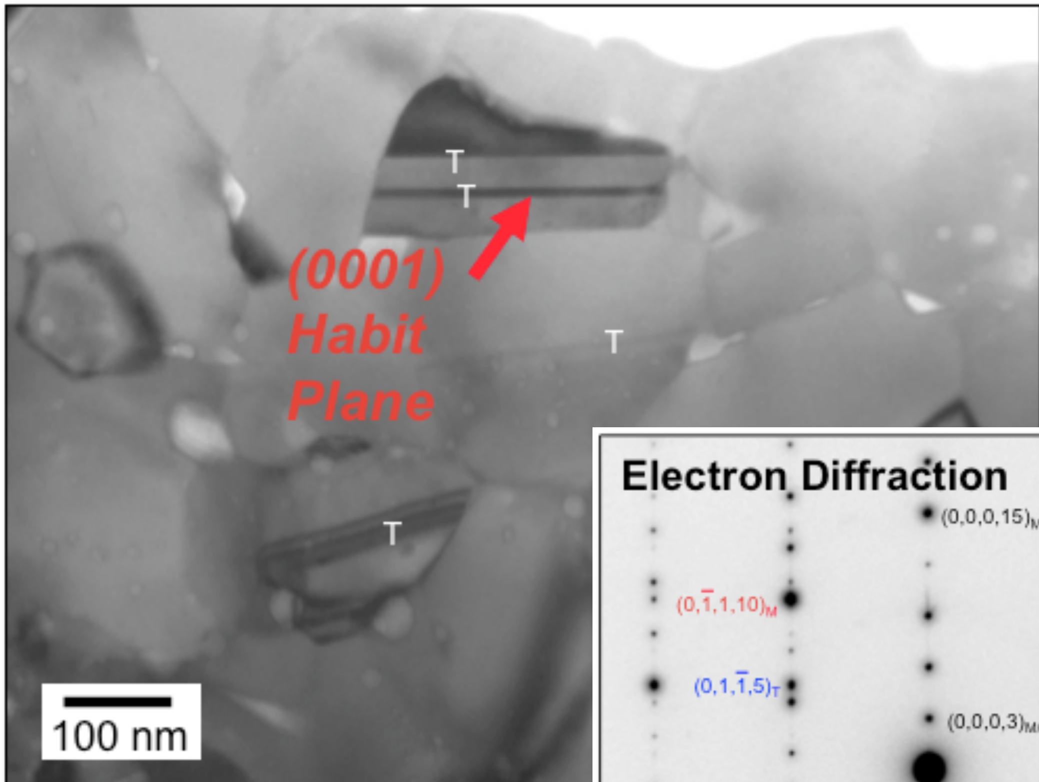
Best conditions are shallow angle (~6°) and low power (<1.5 kV, 3 mA).

Fischione 1010 ion mill

J.L. Lensch-Falk, J.D. Sugar, M.A. Hekmaty, D.L. Medlin,
Journal of Alloys and Compounds, 504 (2010) 37-44

Sandia National Laboratories

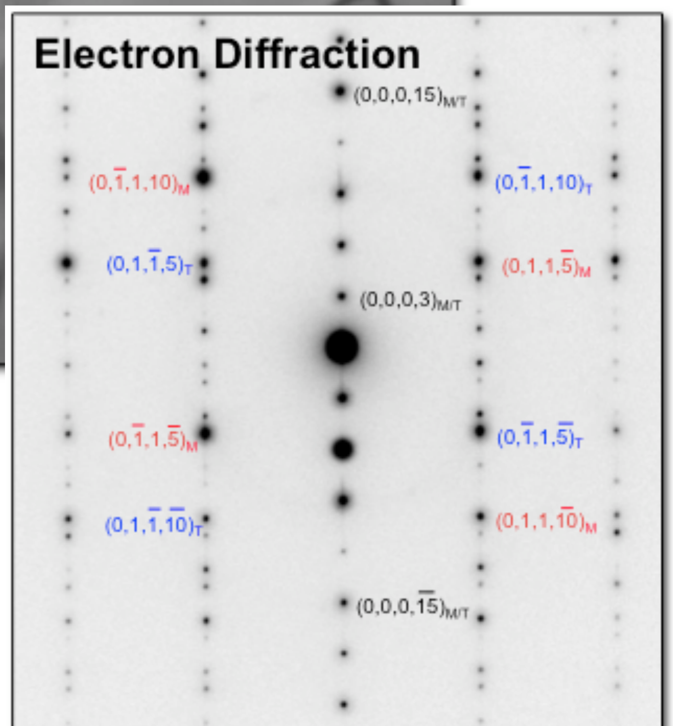
Basal Twin Boundaries in Bi_2Te_3



Good starting point for more complex grain boundaries

Potentially favorable TE electronic transport properties

-Coherent structure, near bulk-like coordination.



Bi_2Te_3: Powder consolidated by spark plasma sintering

TEM Specimen Preparation:
Low voltage ion milling (1kV)
Cryo-cooling: <-100°C

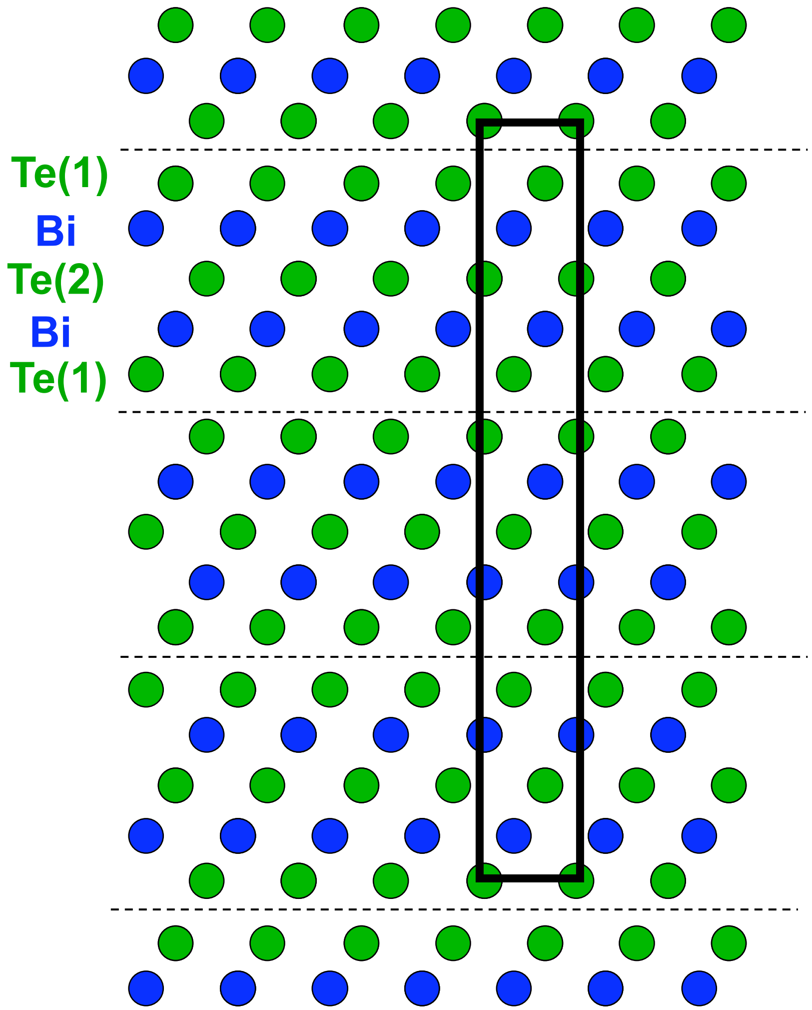
Orientation Relationship:
(0001)//(0001)
[2-1-10]//[-2110]

180° rotation about c-axis

Sandia National Laboratories

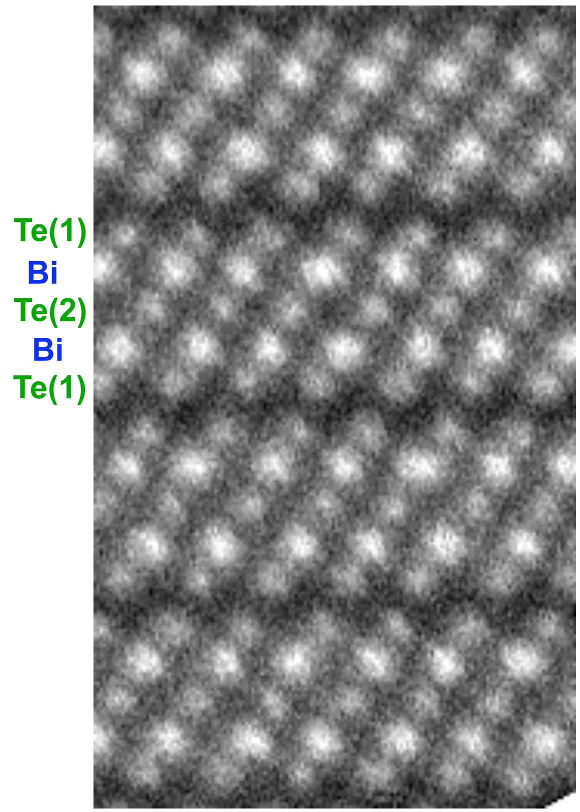
Bi_2Te_3: Three crystallographically distinct basal plane terminations

$\langle 2\bar{1}\bar{1}0 \rangle$ projection



- •Rhombohedral (R-3m) structure
- •Based on tetradymite (Bi_2STe_2) prototype

HAADF-STEM



Bi: Z=83
Te: Z=52

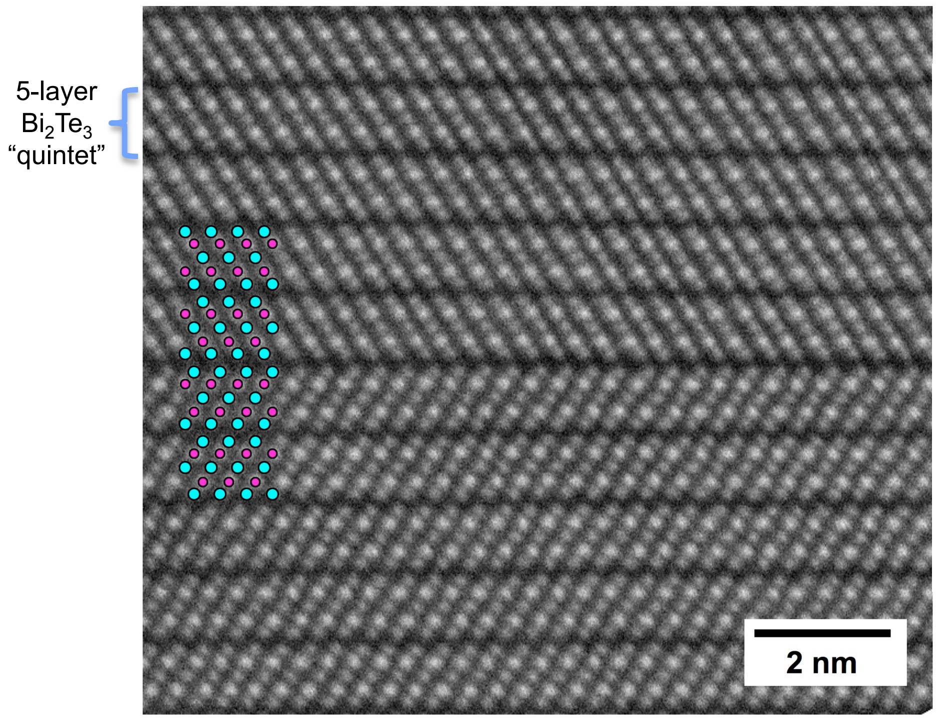
Atomic number difference enables Bi and Te to be distinguished in HAADF-STEM

Sandia National Laboratories

Basal (0001) Twin in Bismuth Telluride

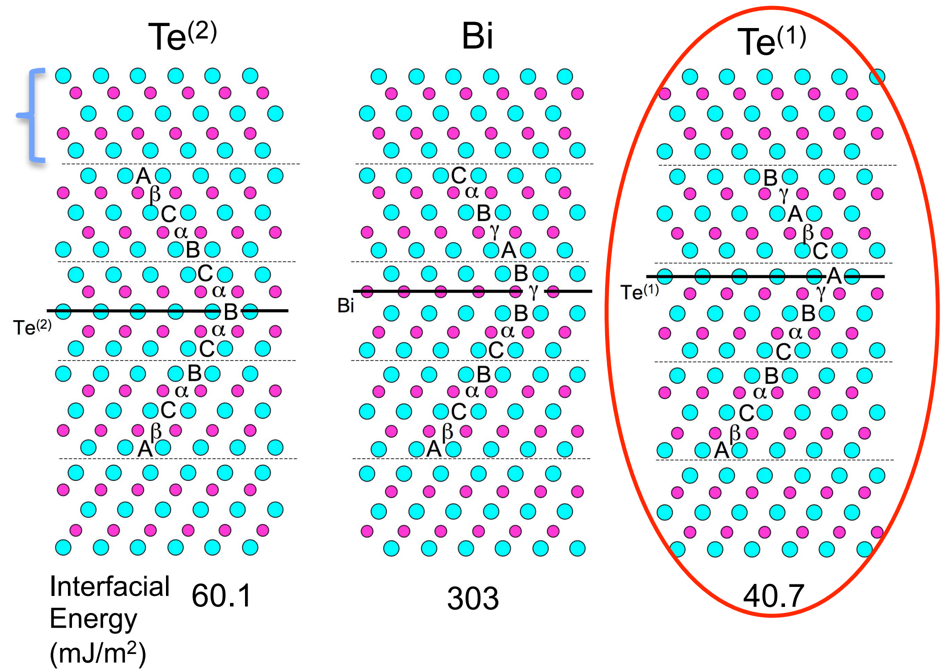
Twin boundary terminated at $Te^{(1)}$ layer

HAADF-STEM Imaging:



DFT Calculations:

Three Possible Compositional Terminations

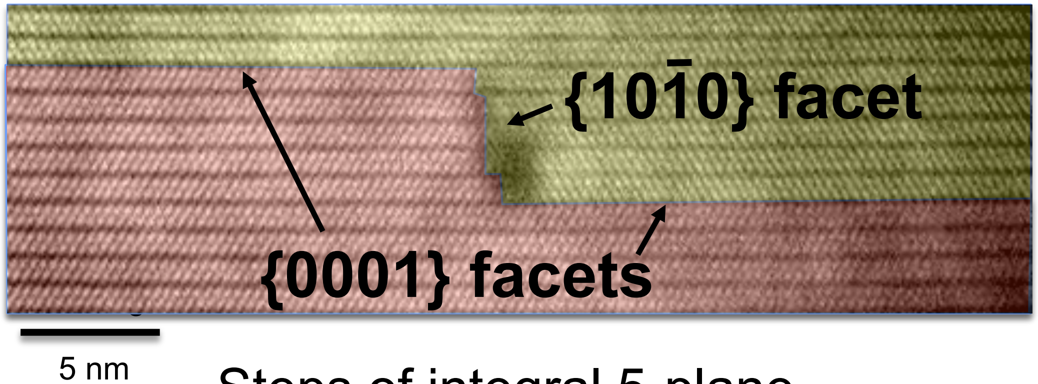


- -Strong energetic preference for twin termination at $Te^{(1)}$ layer.
- -High energy of Bi-terminated interface has implications for twinning mechanism.

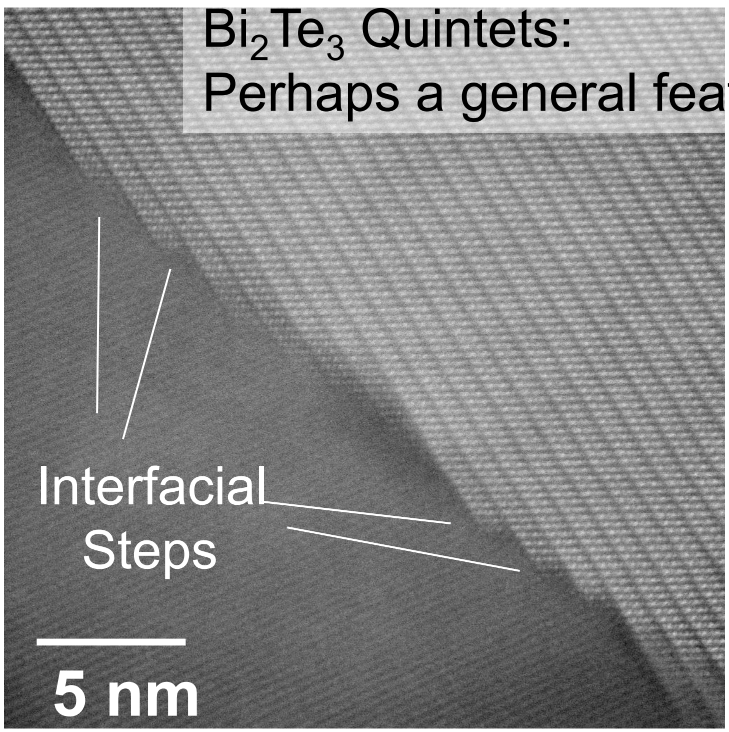
D.L. Medlin, Q.M. Ramasse, C. D. Spataru, N.C. Yang, J. Appl. Phys. (2010)

Sandia National Laboratories

Steps in the Bi_2Te_3 Twin Boundary

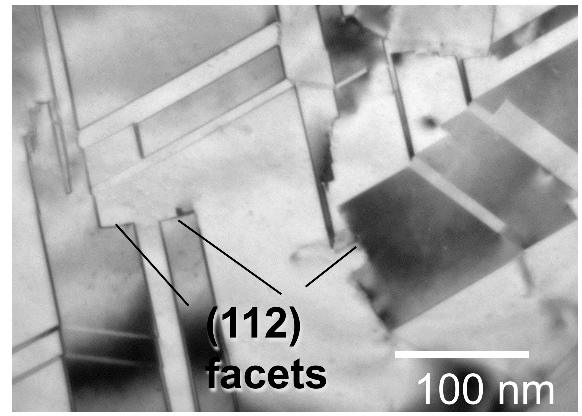


Steps of integral 5-plane Bi_2Te_3 Quintets:
Perhaps a general feature?

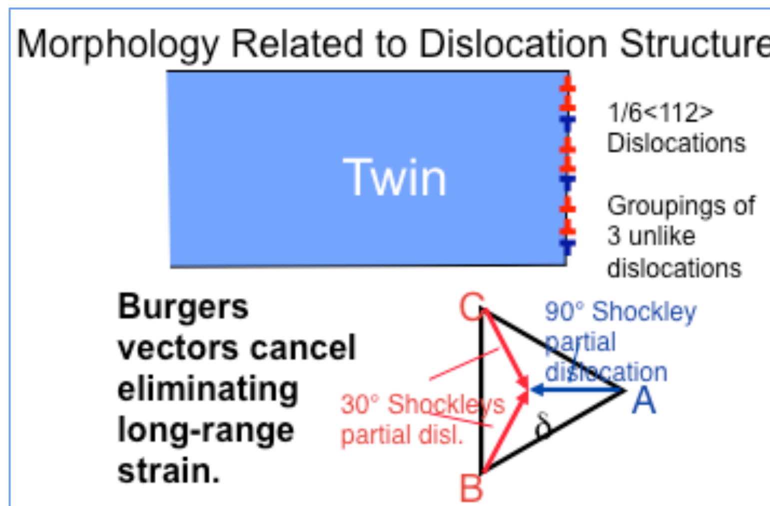


Morphology analogous to annealing and growth twins in FCC materials.

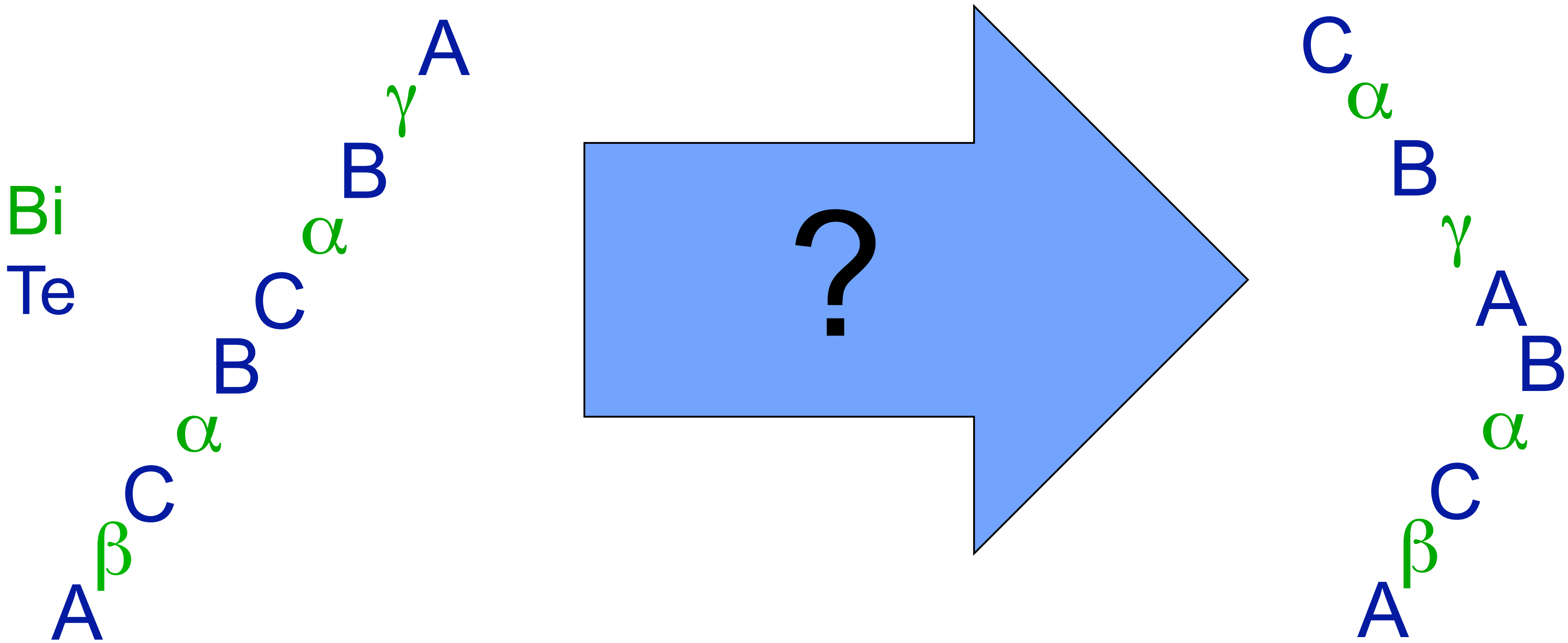
Example: Twins in Electrodeposited Ni



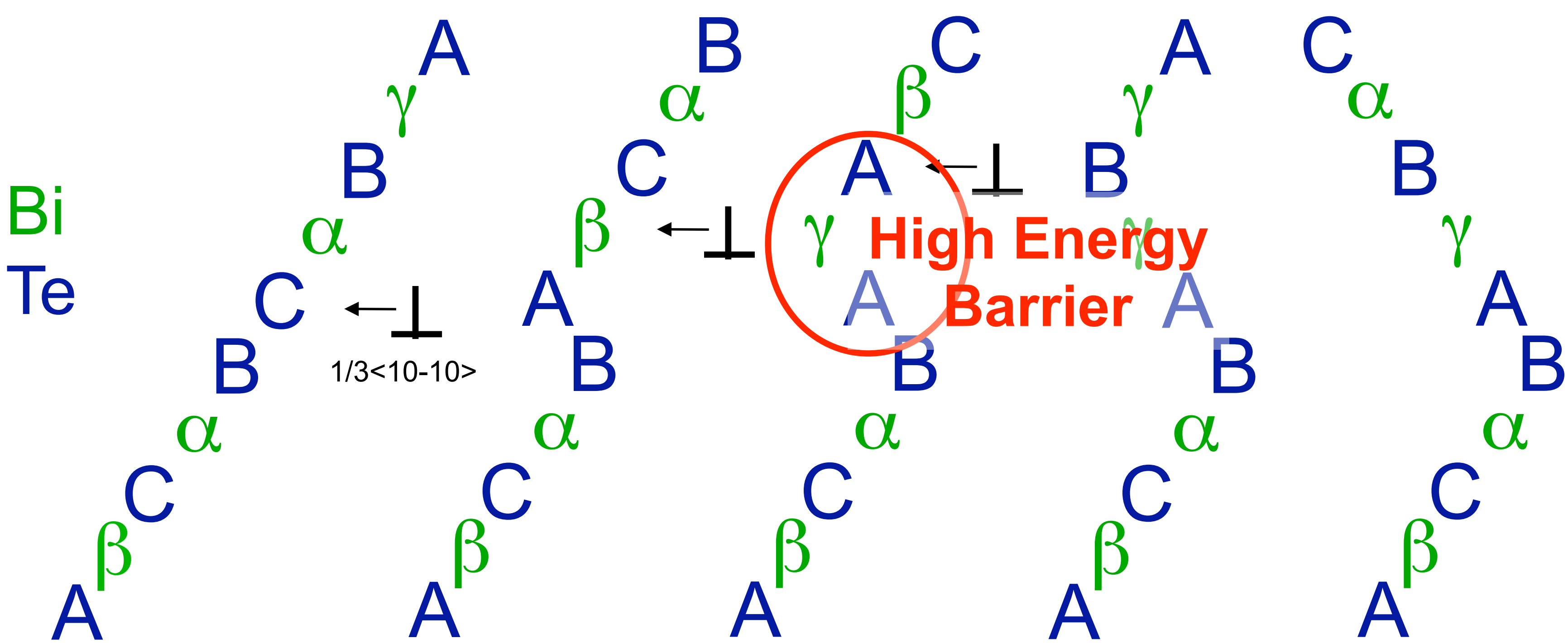
Lucadamo, Medlin, Talin, Yang, Kelly, Phil Mag 2005



Sequential motion of twinning dislocations?



Sequential motion of twinning dislocations?



-High energy barrier for Bi-terminated interface

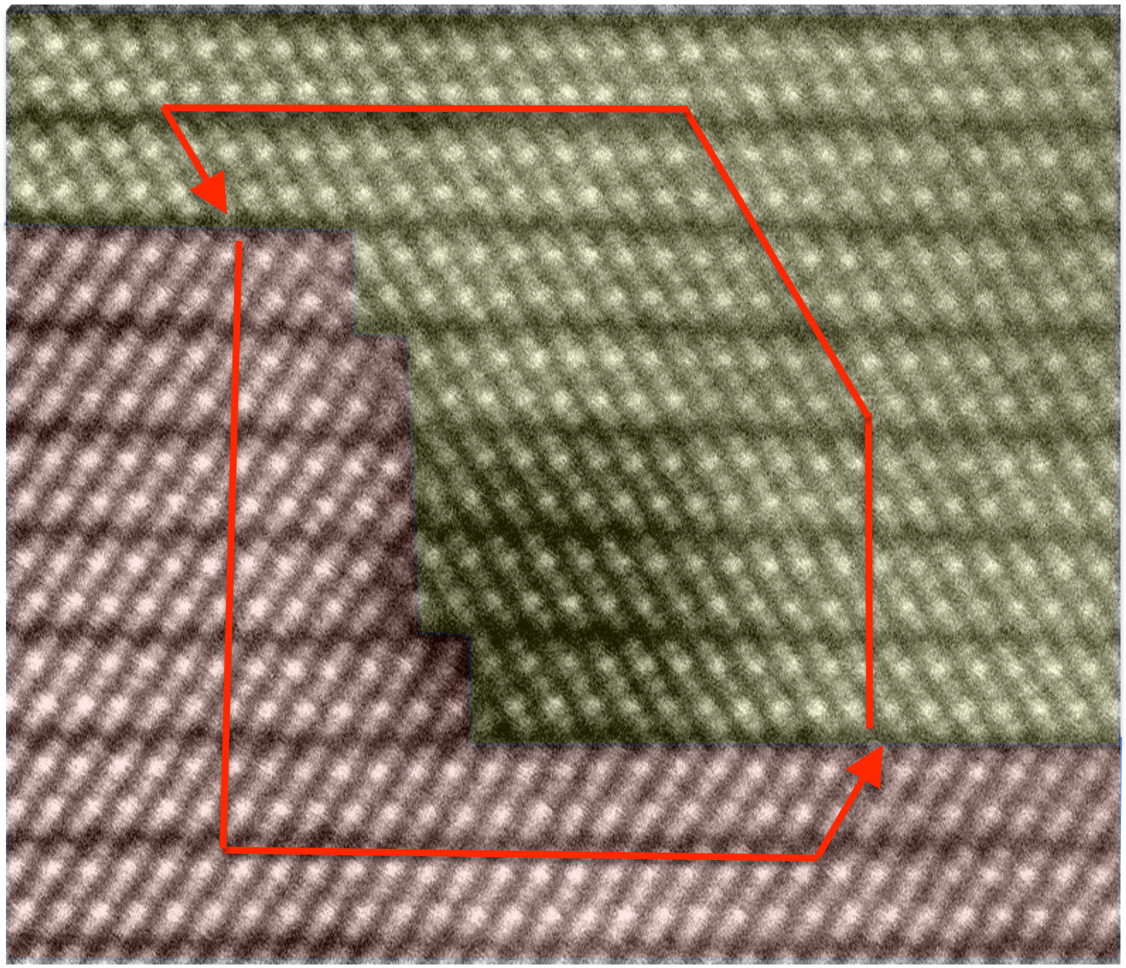
➔ *independent motion of elementary twinning dislocations unlikely.*

-Alternative: Coordinated defect motion.

Groupings of *unlike* twinning dislocations

Sandia National Laboratories

What is the dislocation content of the step?

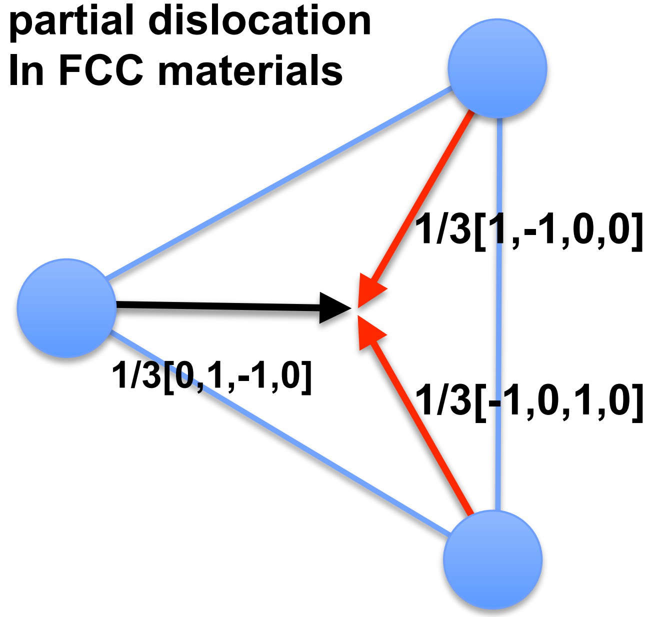


$$b=-(C_\lambda+PC_\mu)$$

Upper circuit — Coordinate transformation — lower circuit

b= 1/3[-1,0,1,0] or 1/3[1,-1,0,0]

Analogous to 30° Shockley partial dislocation In FCC materials

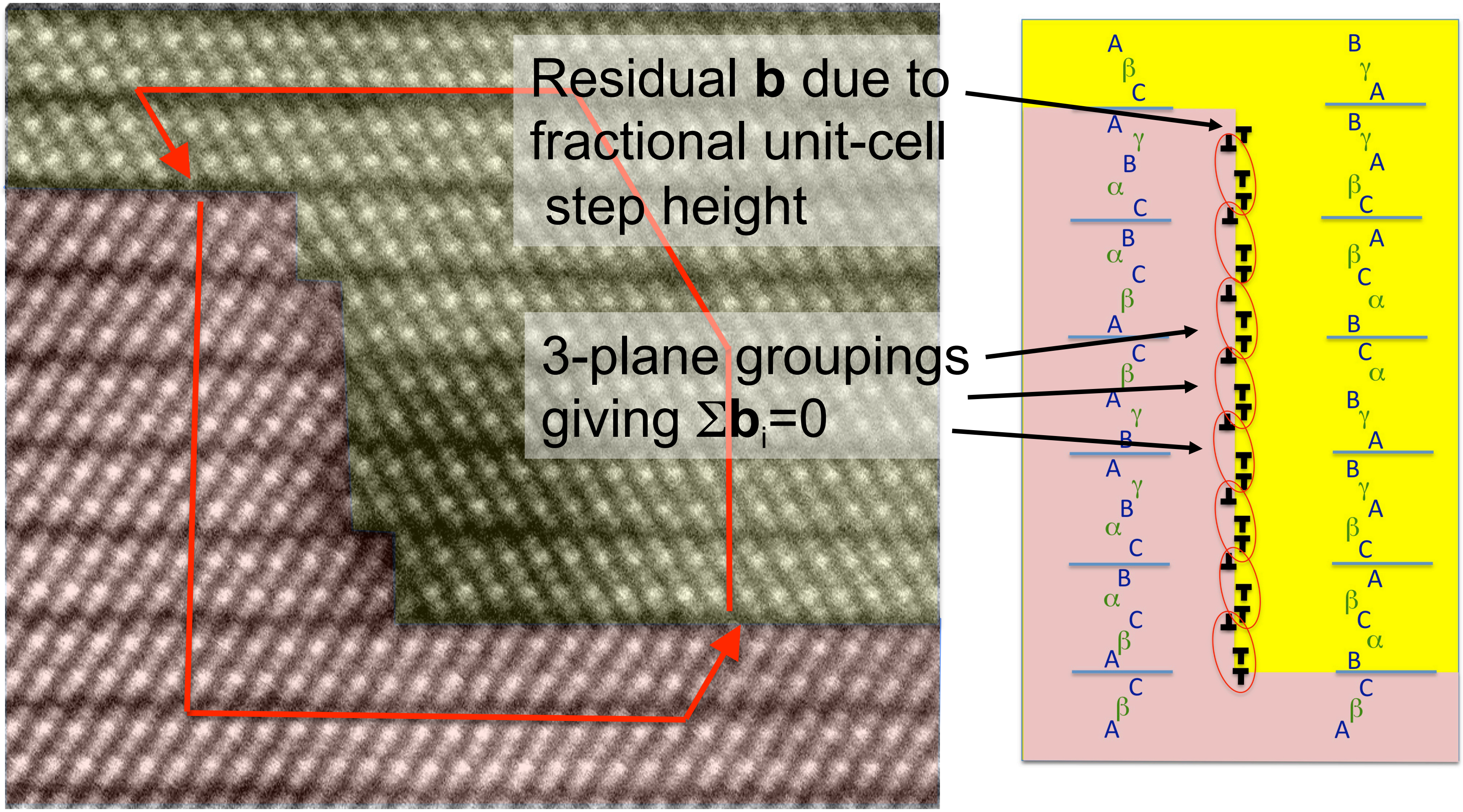


LLNL-Titan
HAADF-STEM
300 keV

Medlin and Yang, Journal of Electronic Materials (2012)

Sandia National Laboratories

What is the dislocation content of the step?



-Similar to {112} facets at annealing/growth twins in FCC materials

-Additional constraint: heterogeneity of chemical bonding.

-Dislocation models: route to generalizing to more complex boundaries

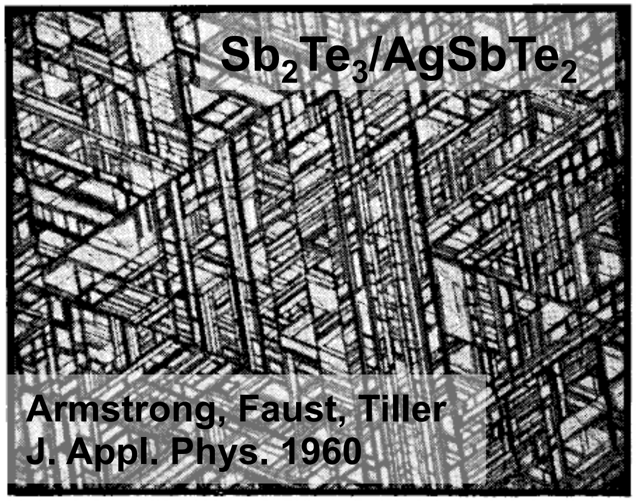
LLNL-Titan
HAADF-STEM
300 keV

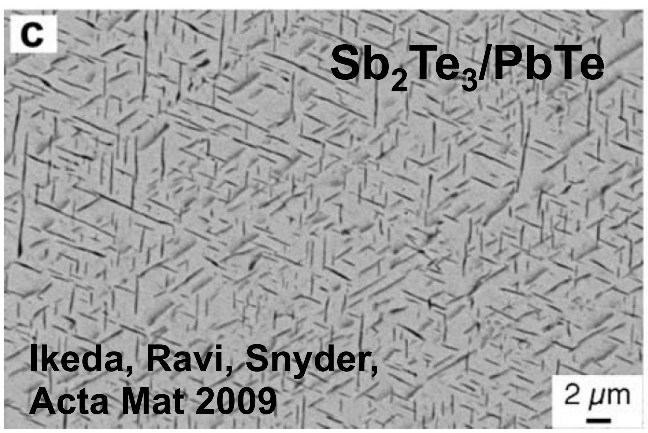
Medlin and Yang, Journal of Electronic Materials (2012)

Sandia National Laboratories

Heterophase Boundaries
Rocksalt/Tetradymite Telluride Interfaces

Widmanstätten plates





-Interest in forming thermoelectric nanocomposites of rock-salt and tetradymite tellurides:

-Possibility for well ordered interfaces.

-Transformations provide bulk route to synthesis.

Ikeda, et al., Chem Mater. 2007

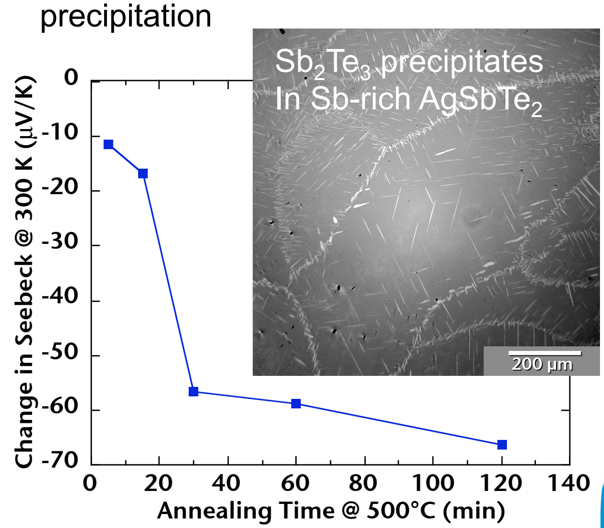
Snyder and Toberer, Nature Materials 2008

-$AgSbTe_2$:

-Constituent of TAGS $(GeTe)_x(AgSbTe_2)_{1-x}$ and LAST $(PbTe)_x(AgSbTe_2)_{1-x}$ zT ~ 1.8

-High performance TE material: zT > 1.2

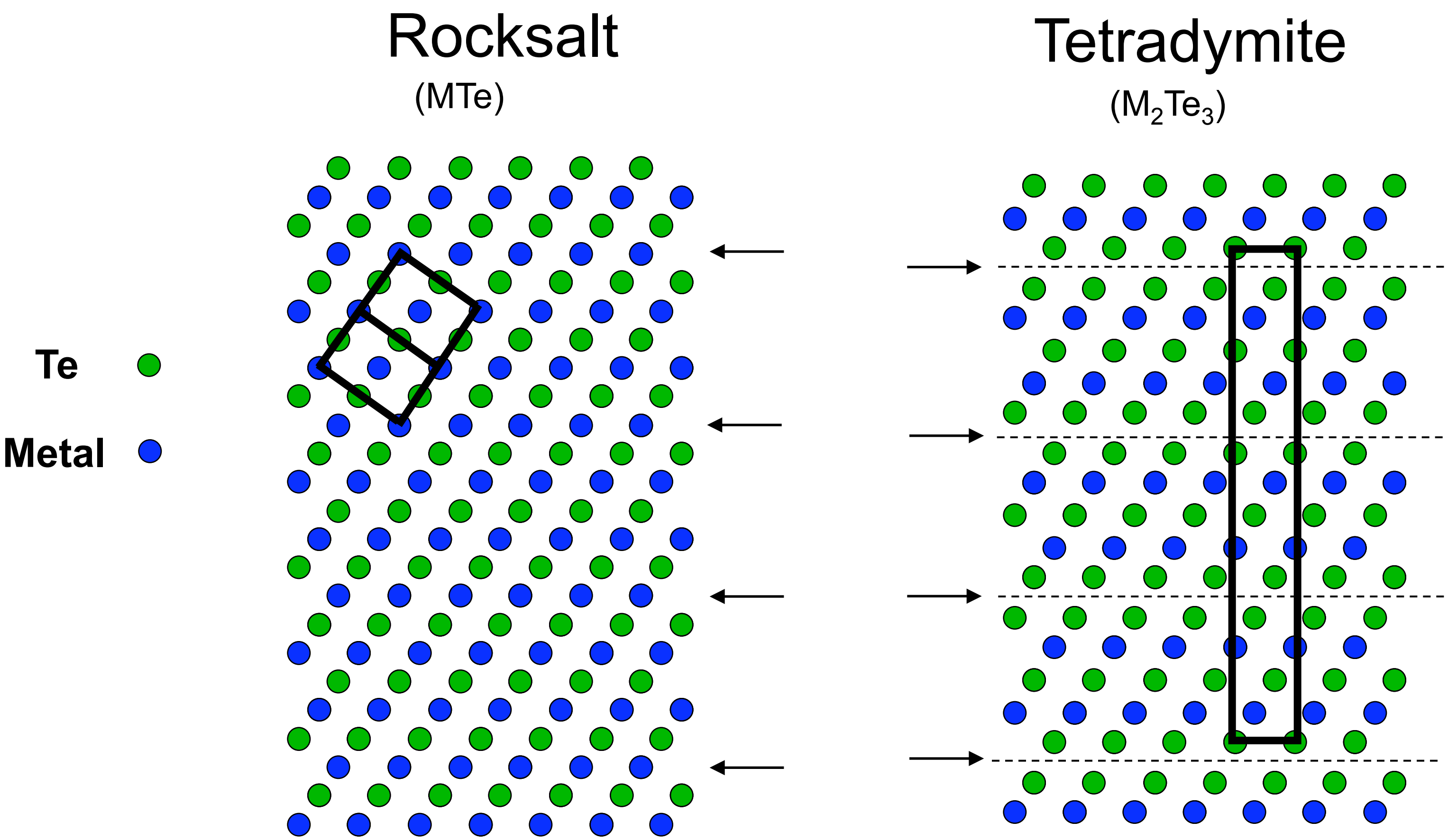
-Degradation of Seebeck coefficient with Sb_2Te_3 precipitation



Sharma, Sugar, Medlin J. Appl. Phys. 2010

Sandia National Laboratories

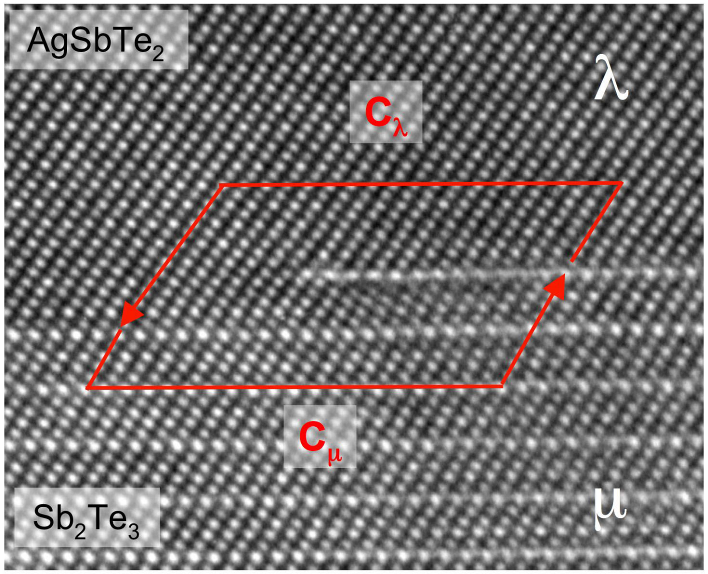
Rocksalt and Tetradymite-structured Tellurides are Closely Related



-Remove metal plane every 6 layers
-Shear blocks by 1/3<10-10>
(or 1/6<112> relative to cubic coordinates)

Transformation mechanism:
Motion of interfacial line defects

Example: +6/+5 disconnection



Resolve b into components normal and parallel to interface

$$\mathbf{b}_n = (a_{cub} - c_{hex}/3\sqrt{3})[111]$$

- *mismatch of step heights.*
- *$|b_n|$=0.37Å*

$$\mathbf{b}_{\|} = \frac{a_{cub}}{6}[\bar{1}2\bar{1}]$$

- *Analogous to Shockley partial Dislocation*
- *$|b_{\|}|$=2.48Å*

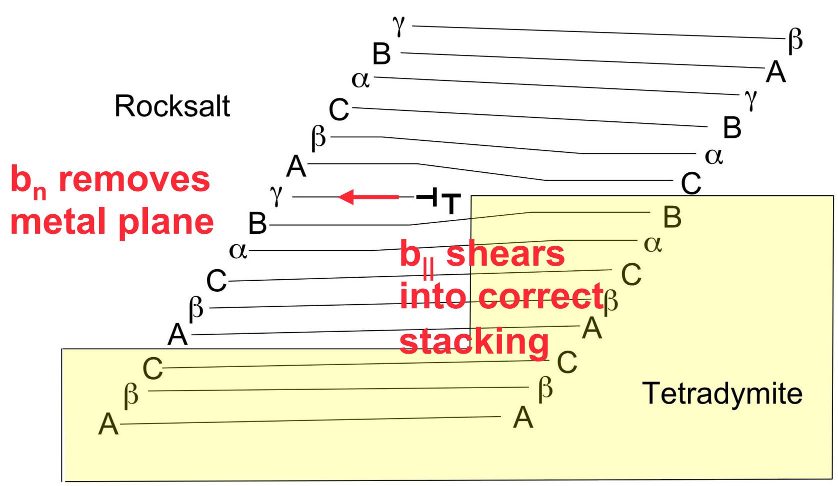
Circuit analysis to determine Burgers vector

$$\mathbf{b} = -(\mathbf{C}_\lambda + \mathbf{P}\mathbf{C}_\mu)$$

Upper crystal circuit

Lower crystal circuit

Coordinate Transformation From Tetradymite to Rock-salt reference frame (coherent frame)

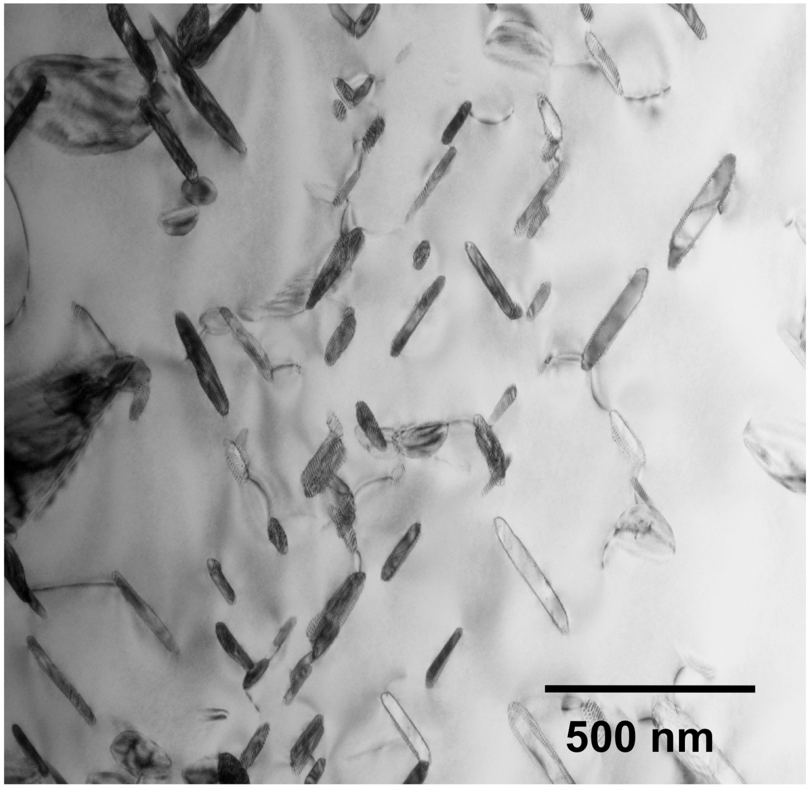


Medlin and Sugar, Scripta Materialia, 2010.

Sandia National Laboratories

A system with larger misfit: $PbTe/Sb_2Te_3$

Sb_2Te_3 Precipitates in PbTe



$AgSbTe_2(111)/Sb_2Te_3(0001)$
Misfit: +0.79%

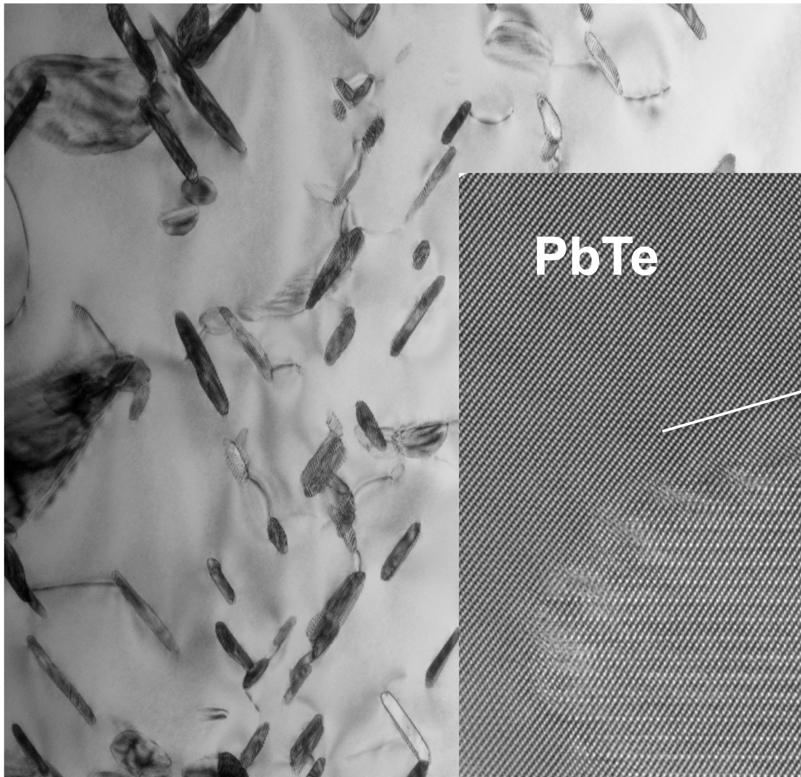
$PbTe(111)/Sb_2Te_3(0001)$
Misfit: +6.7%

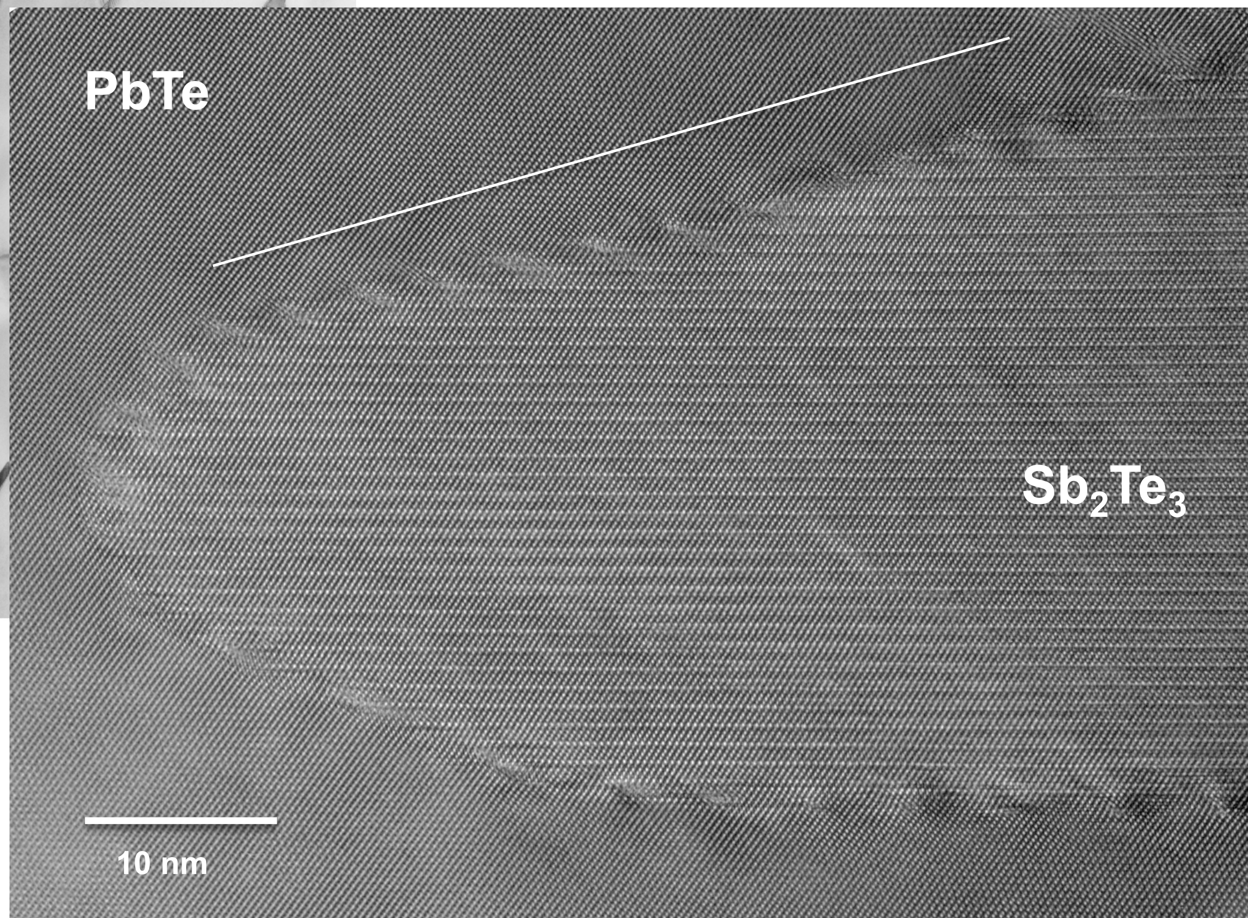
Heinz, Ikeda, Snyder, Medlin, Acta Materialia (2011)

Sandia National Laboratories

A system with larger misfit: $PbTe/Sb_2Te_3$

Sb_2Te_3 Precipitates in PbTe



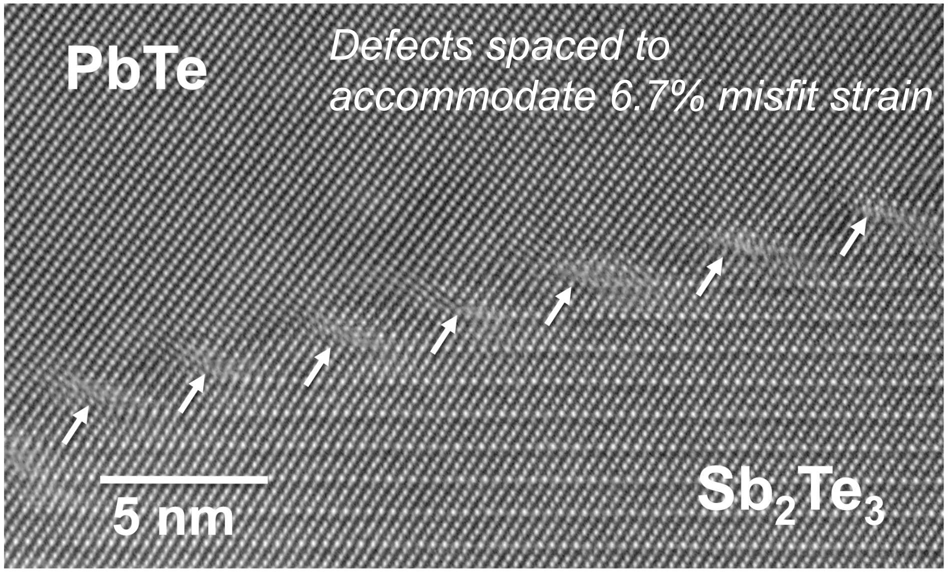


ndia
National
Laboratories

Heinz, Ikeda, Snyder, Medlin, Acta Materialia (2011)

Interfacial defects: dual roles in transformation and strain accommodation

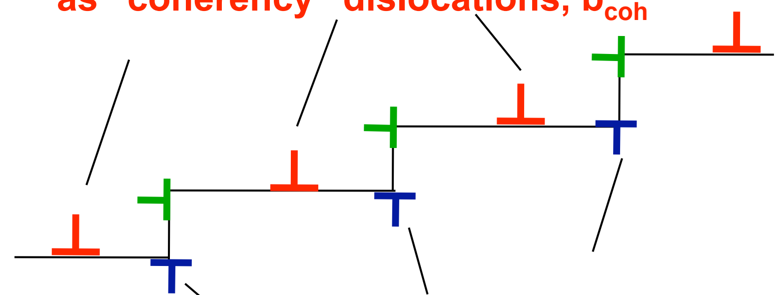
Array of +6/+5 disconnections at $PbTe/Sb_2Te_3$ Interfaces



Interface Geometry:

Inclination: θ =14.8°

Lattice rotation: ϕ = 1.2° ± 0.5°



Project components on inclined interface plane
Adjust spacing to cancel (ε'_{yy} = 0)

$$-\varepsilon = (b_y \tan\theta + b_z \tan^2\theta)h^{-1}$$ ➔ θ=16.2°

Pond, Celotto, Hirth, Acta Mater. 2003

Out of plane **b** components produce small rotation,

$$\phi = 2\sin^{-1}[(b_z\cos\theta - b_y\sin\theta - \varepsilon h\cos\theta)\sin\theta/2h]$$

➔ ϕ=1.7°

- **Local and long-range morphology of precipitates controlled by defect arrangements and connected to misfit strain relief.**

Sandia National Laboratories

Summary

•Line defects provide "building blocks" for larger-length scale models for interface structure, properties, and behavior.

• Essential to understanding interface formation and stability in nanostructured bulk thermoelectrics.

- **Bi_2Te_3 (0001) Twin boundary:**
  - **Termination at Te(1)-Te(1) layer**
    - -Lowest energy structure from *ab initio* calculations
    - -Structure confirmed with HAADF-STEM
  - **Step Structure:**
    - -Analogies to FCC twins and defects.
    - -chemical constraint due to energetics of interface termination
- **Mechanism for tetradymite plate growth by motion of interfacial defects:**
  - **-Defect plays two roles:**
    - -removes metal plane producing Te double-layer.
    - -Shears layers into correct stacking.
  - **-Defect spacing consistent with accommodation of misfit strain.**
    - -Systematic departure from (111)/(0001) habit plane
  - **-Motion of defects unlikely to be independent;**
    - *-instead must be coupled through strain interaction.*

Sandia National Laboratories

Related Publications

D.L. Medlin and N.Y.C. Yang, “Interfacial Step Structure at a (0001) Basal Twin in Bi_2Te_3,” *Journal of Electronic Materials* (in press) (2012). doi: 10.1007/s11664-011-1859-7

N.A. Heinz, T. Ikeda, G.J. Snyder, and D.L. Medlin, “Interfacial Disconnections at Sb_2Te_3 Precipitates in PbTe: Mechanisms of Strain Accommodation and Phase Transformation at a Tetradymite/Rocksalt Telluride Interface,” *Acta Materialia* 59 (20) (2011) 7724-7735. 10.1016/j.actamat.2011.08.043

J.D. Sugar and D.L. Medlin, "Solid-state Precipitation of Stable and Metastable Layered Compounds in Thermoelectric $AgSbTe_2$" *Journal of Materials Science* 46 (2011) 1668-1679. doi:10.1007/s10853-010-4984-4.

Y. Pei, J. Lensch-Falk, E.S. Toberer, D.L. Medlin, G.J. Snyder, "High Thermoelectric Performance in PbTe due to Large Nanoscale Ag_2Te Precipitates and La Doping" *Advanced Functional Materials* 2 (21) (2011) 241-249, doi: 10.1002/adfm. 201000878.

D.L. Medlin, Q.M. Ramasse, C.D. Spataru, N.Y.C. Yang, "Structure of the (0001) Basal Twin Boundary in Bi_2Te_3" *Journal of Applied Physics 108* (2010) 043517. doi:10.1063/1.3457902.

J. L. Lensch-Falk, J.D. Sugar, M.A. Hekmaty, D.L. Medlin, "Morphological Evolution of Ag_2Te Precipitates in Thermoelectric PbTe" *Journal of Alloys and Compounds 504* (2010) 37-44, doi:10.1016/j.jallcom.2010.05.054.

P.A. Sharma, J.D. Sugar, D.L. Medlin "Influence of Nanostructuring and Heterogeneous Nucleation on the Thermoelectric Figure of Merit in $AgSbTe_2$" *Journal of Applied Physics* 107 (2010) 113716. doi: 10.1063/1.3446094.

D.L. Medlin and J.D. Sugar, "Interfacial Defect Structure at Sb_2Te_3 Precipitates in the Thermoelectric Compound $AgSbTe_2$" *Scripta Materialia*. 62 (2010) 379-382 doi:10.1016/j.scriptamat.2009.11.028

J.D. Sugar and D.L. Medlin, “Precipitation of Ag_2Te in the Thermoelectric Material $AgSbTe_2$”, Journal of Alloys and Compounds 478 (2009) 75-82. doi:10.1016/j.jallcom.2008.11.054.

D.L. Medlin and G.J. Snyder, "Interfaces in Bulk Thermoelectric Materials", Current Opinion in Colloid and Interface Science 14 (2009) 226-235. doi: 10.1016/j.cocis.2009.05.001.

Collaborators for this work

Sandia:

Jessica Lensch-Falk
Josh Sugar
Peter Sharma
Nancy Yang
Catalin Spataru
Michelle Hekmaty
Mark Homer

Caltech:

Nick Heinz
Teruyuki Ikeda
G. Jeffrey Snyder

LBNL:

Quentin Ramasse
Currently: SuperSTEM, Daresbury, UK

Special thanks to:

-LBNL: User program, National Center for Electron Microscopy
-LLNL: John Bradley, for use for LLNL's Titan 80/300 instrument
-UCD: Z. Zhang and E. Lavernia, for assistance with SPS processing

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy, National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Sandia National Laboratories