Compositional Ordering and Stability in Nanostructured, Bulk Thermoelectric Alloys

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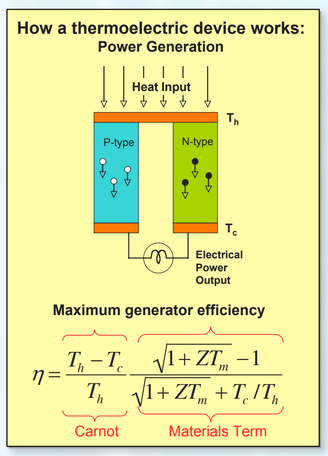
LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Problem

Materials Science Challenge for Thermoelectrics



A conflict of size-scales

- Improve conversion efficiency

thermoelectric materials figure-of-merit

$$ZT = \frac{S^2\sigma}{\kappa}T$$

Seebeck Coefficient; Electrical Conductivity; Thermal Conductivity

⇒ Nanostructuring

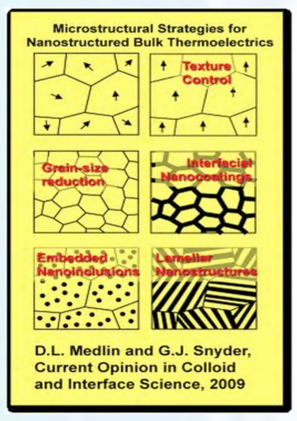
- Generate useful amounts of power or cooling capacity

⇒ Require materials on the mm to cm size-scale.

Nanostructured Bulk Thermoelectrics

- Emerging routes to improve bulk TE performance by embedding high densities of interfaces.
  - phonon scattering to reduce κ
  - energy filtering, quantum confinement to improve $S^2\sigma$
- Need for better understanding of formation mechanisms & stability of embedded nanostructures and quantitative link between structure and properties.

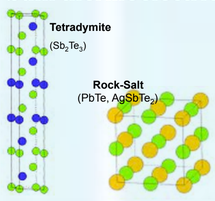
- Goals of our study:
  Establish the atomic mechanisms that govern formation and stability of embedded interfaces in nanostructured bulk thermoelectrics. Understand links between embedded nanostructure and thermoelectric performance..



Approach

Our approach: Connect nanostructure to properties through detailed microscopy and theory

Synthesize nanostructured, bulk thermoelectric alloys

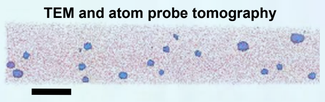


-Focus on tellurides.
-Nanostructuring by controlling solid-state precipitation.

Measure transport properties

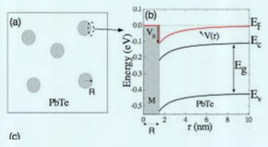
Measure nanostructure using advanced microscopies

TEM and atom probe tomography



50 nm — Ag_2Te nano-inclusions in PbTe

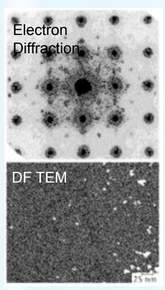
Develop theory to connect transport to nanostructure



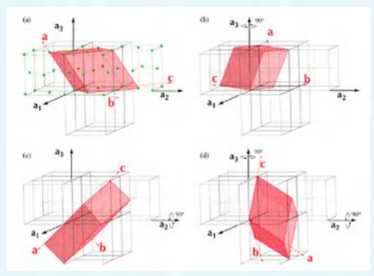
Results

We are investigating mechanisms of nanostructure formation in rock-salt tellurides

Example: Ag_2Te Nanoinclusions in $AgSbTe_2$



Monoclinic Ag_2Te Adopts multiple variants in rock-salt matrix



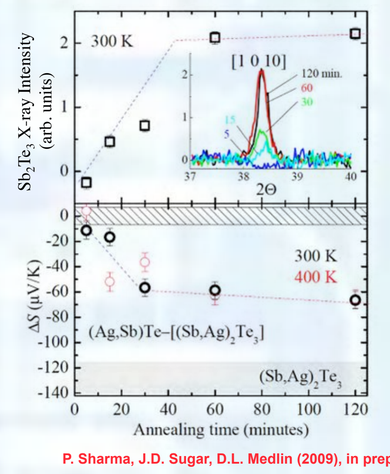
J.D. Sugar, D.L. Medlin, J. Alloys and Compounds 2009

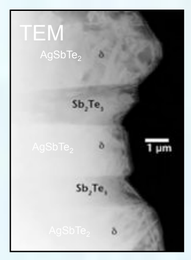
- High thermoelectric energy conversion efficiency in complex, rock-salt structured tellurides has been attributed to long-range compositional superlattice ordering.
- However, our investigation has shown that apparent "superlattice" reflections in diffraction from such tellurides can actually arise from topotactically aligned nanoprecipitates.

Results

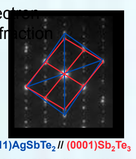
We are linking thermoelectric performance to evolution of internal interfacial structure

Sb_2Te_3 growth reduces Seebeck coefficient





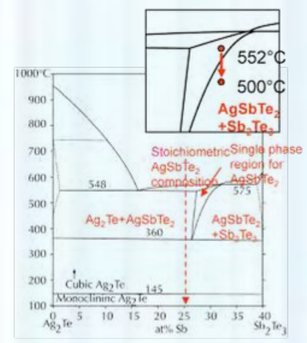
Electron Diffraction



(111)$AgSbTe_2$ // (0001)Sb_2Te_3
[-101]$AgSbTe_2$ // [2-1-10]Sb_2Te_3

P. Sharma, J.D. Sugar, D.L. Medlin (2009), in preparation.

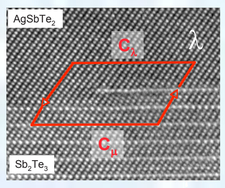
Sb_2Te_3 plates form during Annealing Of Sb-rich $AgSbTe_2$ ($Ag_{16.7}Sb_{30}Te_{53.3}$)

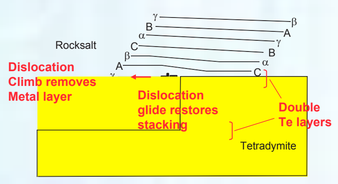


- Formation of interconnected network degrades properties.
- Heterogeneous nucleation (e.g., at grain boundaries) must be suppressed.

We are investigating atomic mechanisms governing nanoprecipitate growth and stability

Example: Atomic Step at $AgSbTe_2$/Sb_2Te_3 interface





Resolve Burgers vector (b) of step into components normal and parallel to interface

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

- *mismatch of step heights.*
- *$|b_n|$=0.3747Å*

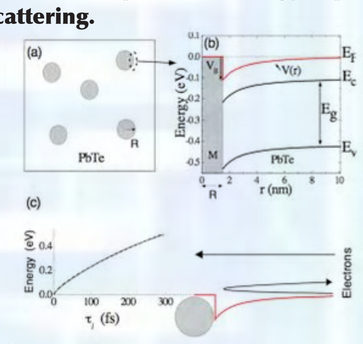
$$\mathbf{b}_{\parallel} = \frac{a_{cub}}{6}[\bar{1}2\bar{1}]$$

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

- Generic mechanism for transformation from rock-salt to tetradymite tellurides.
- Insight concerning misfit accommodation and morphological stability.

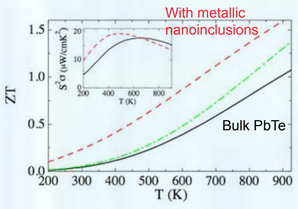
We have developed a theory of TE enhancement due to nanoinclusions

Charge Transfer at metal/semiconductor interface produces energy dependent scattering.



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

Predicted enhancement of ZT with metallic nanoinclusions



- Enhancement of Seebeck coefficient by filtering low energy charge carriers ($\tau i \sim E^{3/2}$).
- Suppression of both electronic and phononic contributions to thermal conductivity.
- Our current experiments on Ag_2Te nanoinclusions in PbTe will seek to test this theory

Significance

Impact

- Work is providing fundamental understanding of mechanisms underpinning interface formation and stability in nanostructured bulk thermoelectric materials.
- New insights from theory and experiment are establishing links between nanostructure and thermoelectric properties.
- Results from this project provide foundational knowledge for new microstructural strategies to tailor advanced thermoelectric materials.

Publications:

- S.V. Faleev and F. Léonard, "Theory of Enhancement of Thermoelectric Properties of Materials with Nanoinclusions", Physical Review B 77 (2008) 214304.
- J.D. Sugar, D.L. Medlin, "Precipitation of Ag2Te in the Thermoelectric Material AgSbTe2" Journal of Alloys and Compounds 478 (2009) 75-82
- D.L. Medlin and G.J. Snyder, "Interfaces in Bulk Thermoelectric Materials" Current Opinion in Colloid and Interface Science 14 (2009) 226-235 (Invited Review Article).
- P. A. Sharma, J.D. Sugar, D.L. Medlin "Link between Thermoelectric Figure of Merit and Microstructure in Nanostructured AgSbTe2" In preparation for submission to Physical Review B (2009).
- D.L. Medlin and J.D. Sugar, "Interfacial Defect Structure at Sb2Te3 Plates in the Thermoelectric Compound AgSbTe2" in preparation for submission to Scripta Materialia (2009).

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2009-4989P

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