The Bottom-Up Approach for Thermoelectric Nanocomposites, plus…

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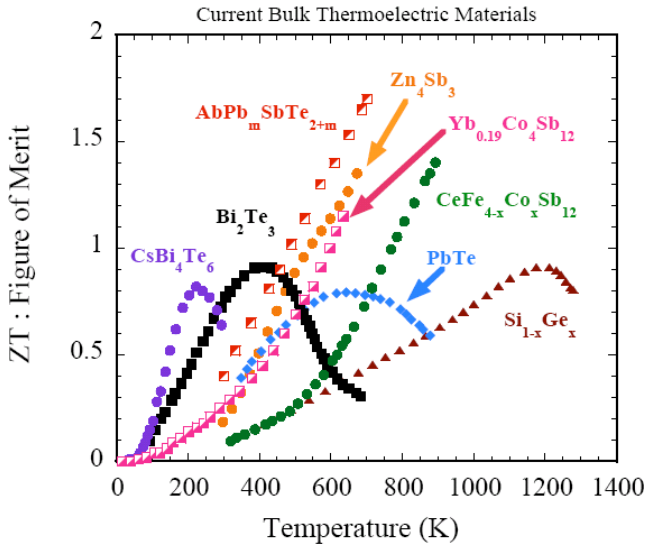
2011 DOE Thermoelectric Applications Workshop

31 26

NOVEL MATERIALS LABORATORY
UNIVERSITY OF SOUTH FLORIDA

New Directions in TE materials Research

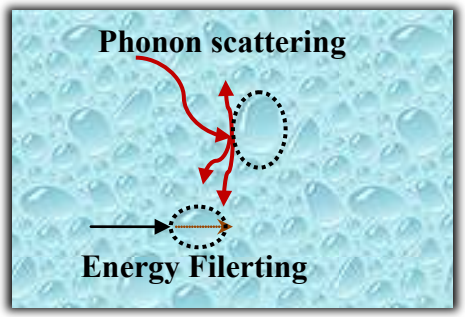


*T.M. Tritt and M.A. Subramanian, MRS Bulletin 2006, **31**,188*

More control of scattering parameters, Fermi level position, carrier density

Thermopower, Electrical Conductivity, Thermal Conductivity

Figure of Merit $ZT = \frac{S^2 \sigma T}{\kappa_L + \kappa_e}$



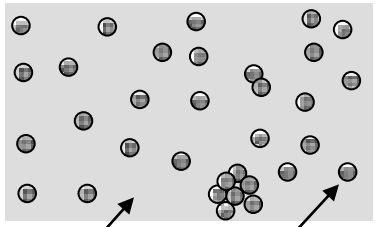
Increase number of grains

Increase grain boundaries

- Enhanced ***S*** due to charge carrier scattering
- Boundary scattering at the interfaces reduces κ_L

How to Increase grain boundaries?

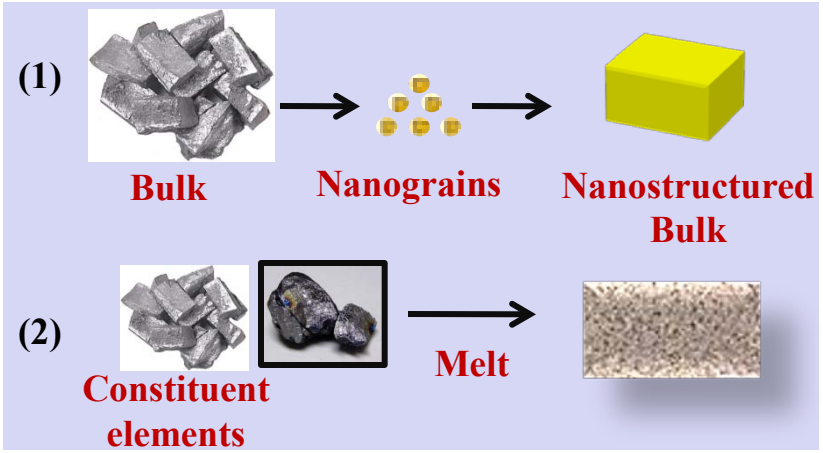
'Dimensional' Nanocomposites



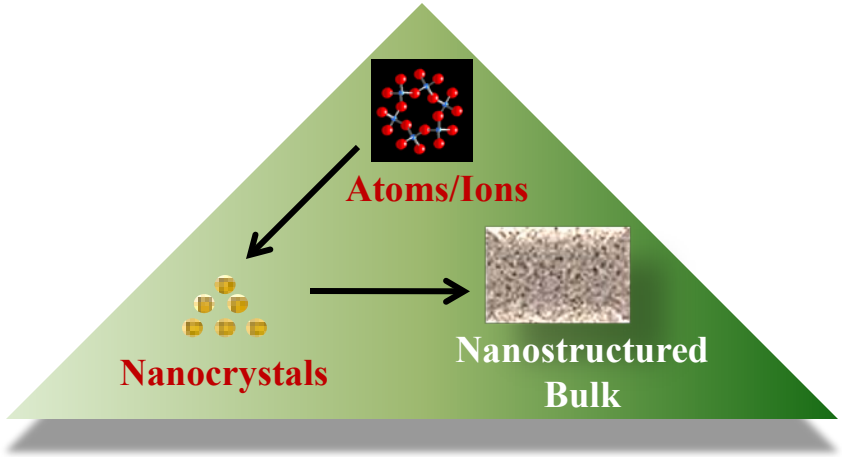
Incorporate nano-scale domains within a bulk matrix

Processing Techniques

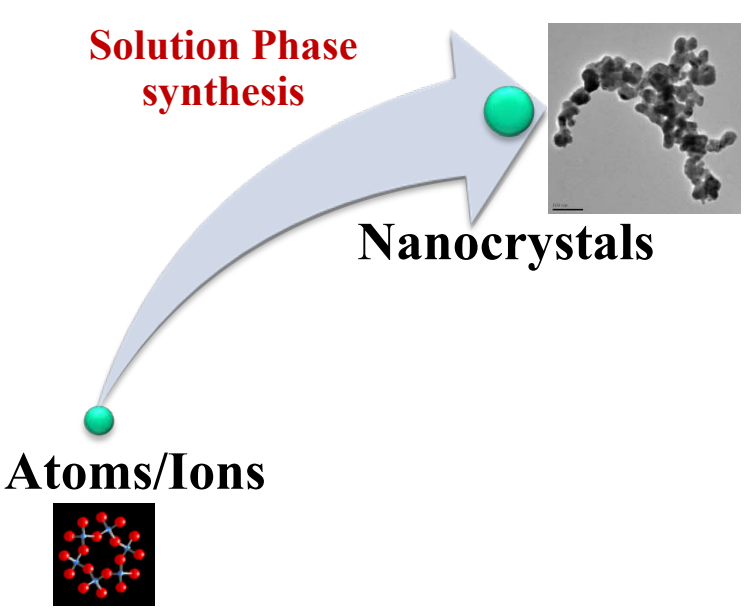
"TOP-DOWN"

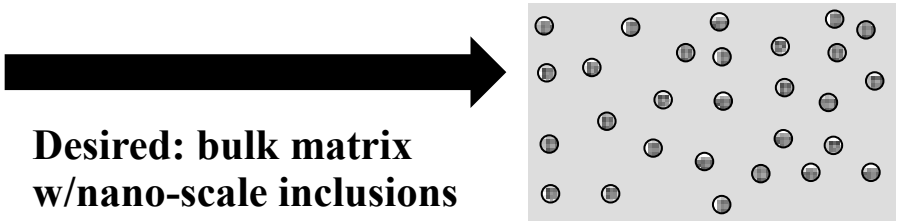


"BOTTOM-UP"



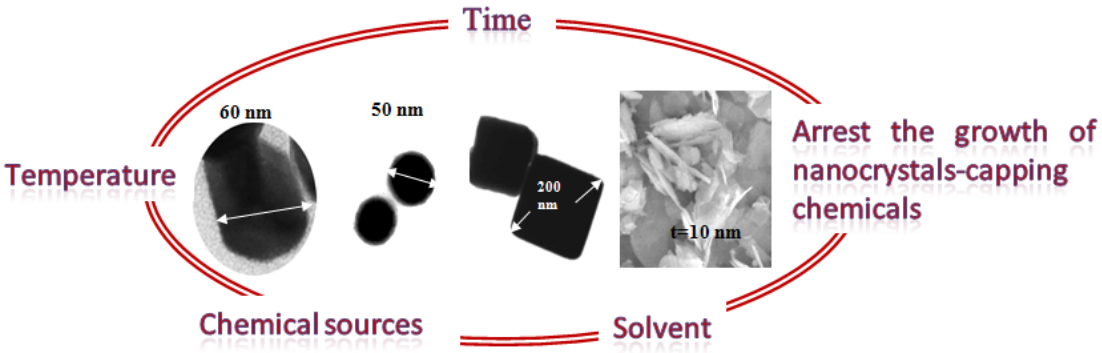
The "Bottom-Up" Strategy

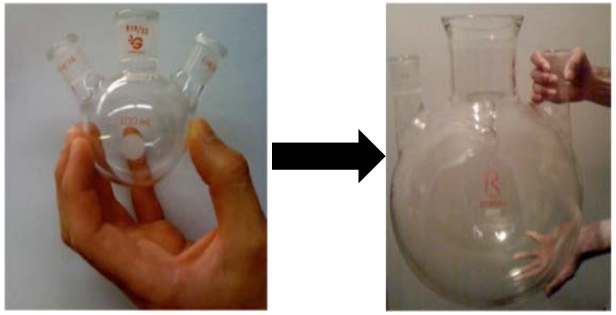




Desired: bulk matrix w/nano-scale inclusions

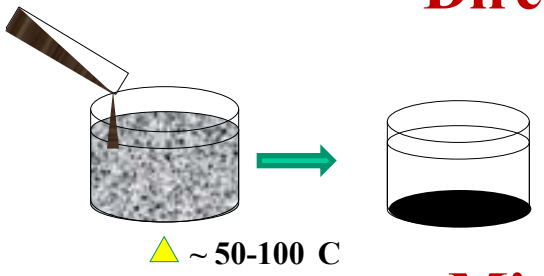
- **Controllability of compositions and doping**
- **Control of crystal size and size distribution**
- **Reproducible and Scalable**
- **Economical**



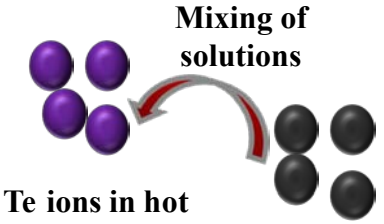


Synthesizing nanocrystals in solution

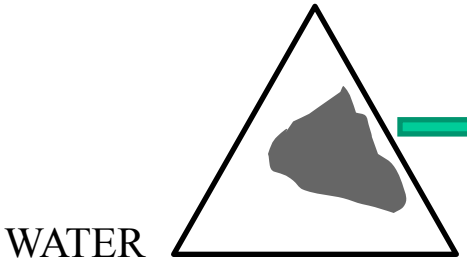
Direct Precipitation



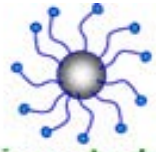
PbTe nanocrystals



Micro Emulsion



"Oil-in-water"



"Water-in-oil"

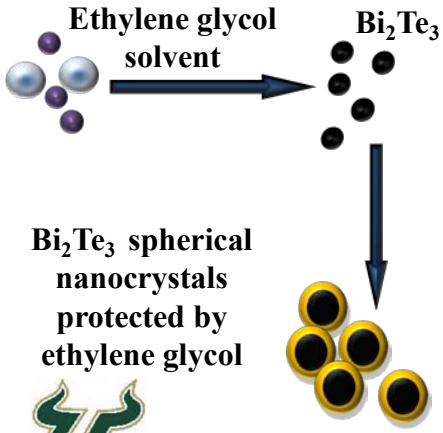
PbTe and Bi_2Te_3 nanocrystals

Solvothermal

Pressurized

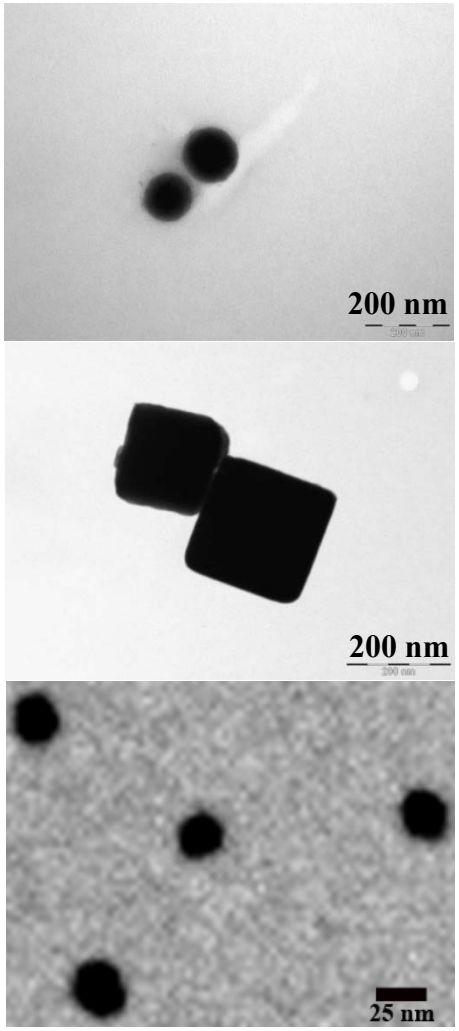
Boiling point of the solvent

Bi_2Te_3 & $Bi_{2-x}Sb_xTe_3$ nanocrystals



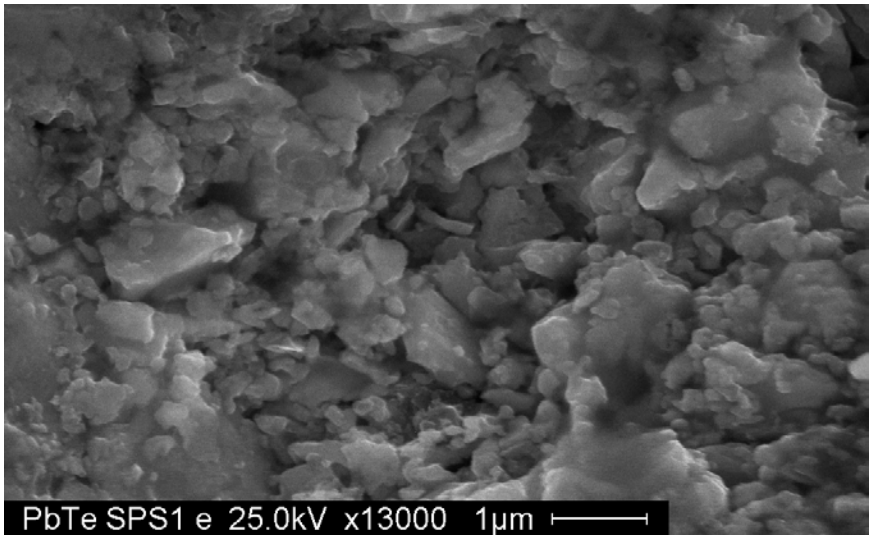
PbTe 'Nanocomposites'

Size & Shape Selectivity

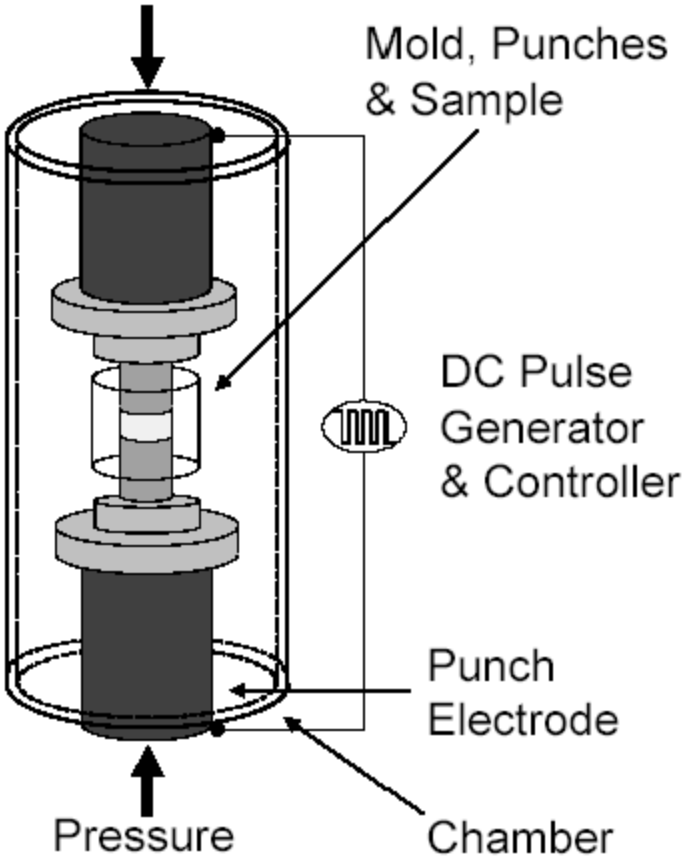


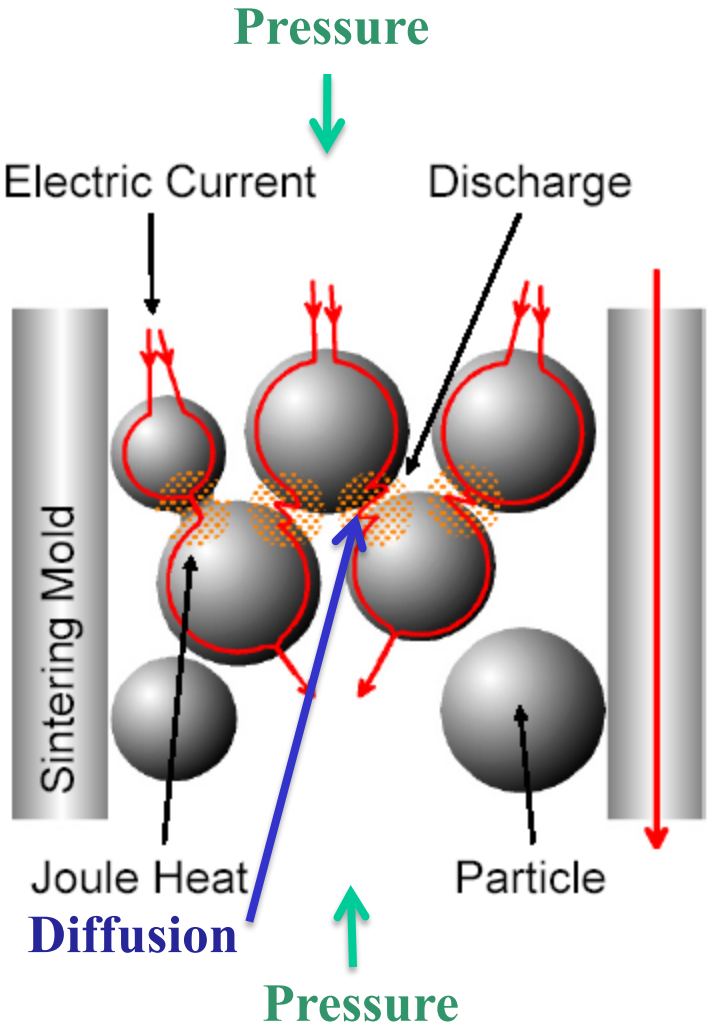
SPS

Consolidation



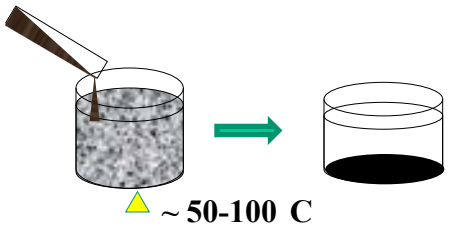
Spark Plasma Sintering



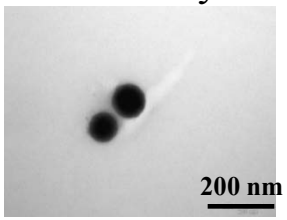


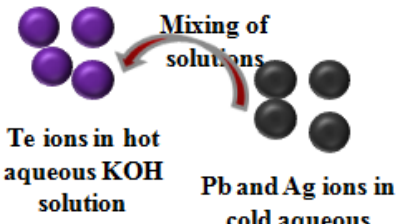
Chemical Synthesis for TE Materials Research

Direct Precipitation



PbTe nanocrystals

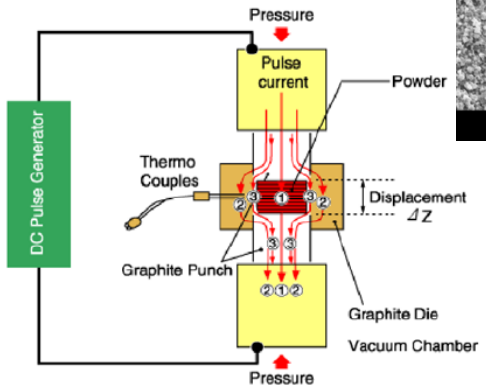




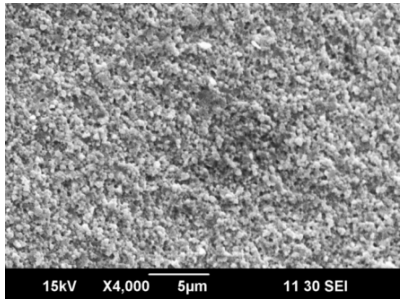
crystal size from 50 nm - 250 nm

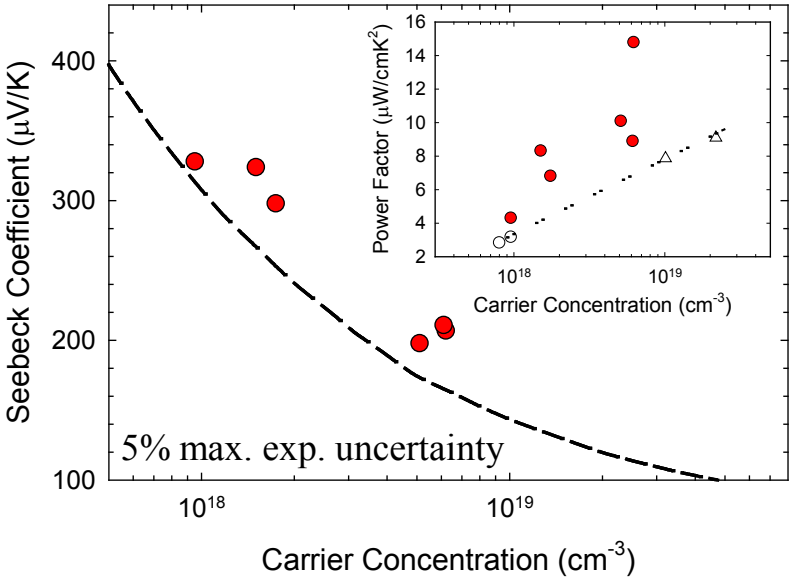
1-20% Ag doped P-type PbTe nanocrystals

SPS



P-type PbTe nanocomposite





red p-type PbTe Nanocomposites

△,○ Bulk p-type PbTe

---- A.J. Crocker *et al.*, Brit. J. Appl. Phys. **18**, 563 (1967)

J. Martin, G. S. Nolas, W. Zhang, and L. Chen, Appl. Phys. Lett. ***90****, 222112 (2007)*

J. Martin, L. Wang, L. Chen, and G.S. Nolas, Phys. Rev. B ***79****, 115311 (2009)*

A. Popescu, L.M. Woods, J. Martin, and G.S. Nolas, Phys. Rev. B ***79****, 305302 (2009)*

Chemical Synthesis for TE Materials Research

Solvothermal

Pressurized

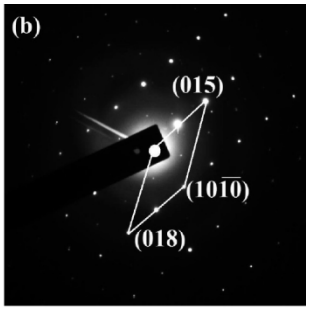
>Boiling point of the solvent

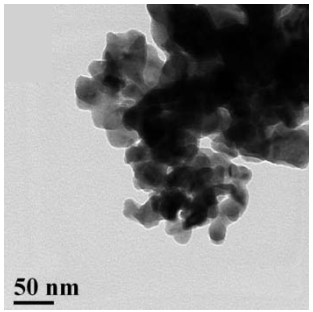
Ethylene glycol solvent

Bi_2Te_3 nuclei

Se doped Bi_2Te_3 or Sb_2Te_3 nanocrystals

selective crystal size from ~ 10 – 50 nm





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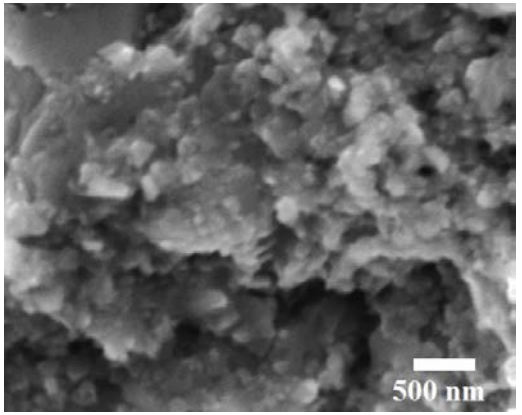
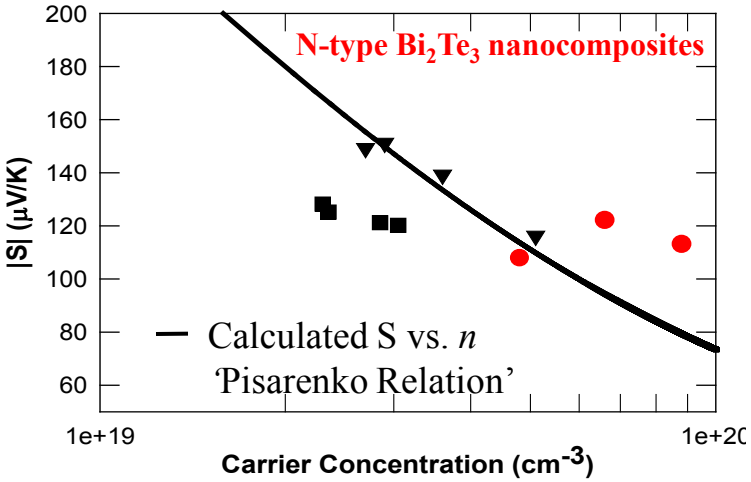




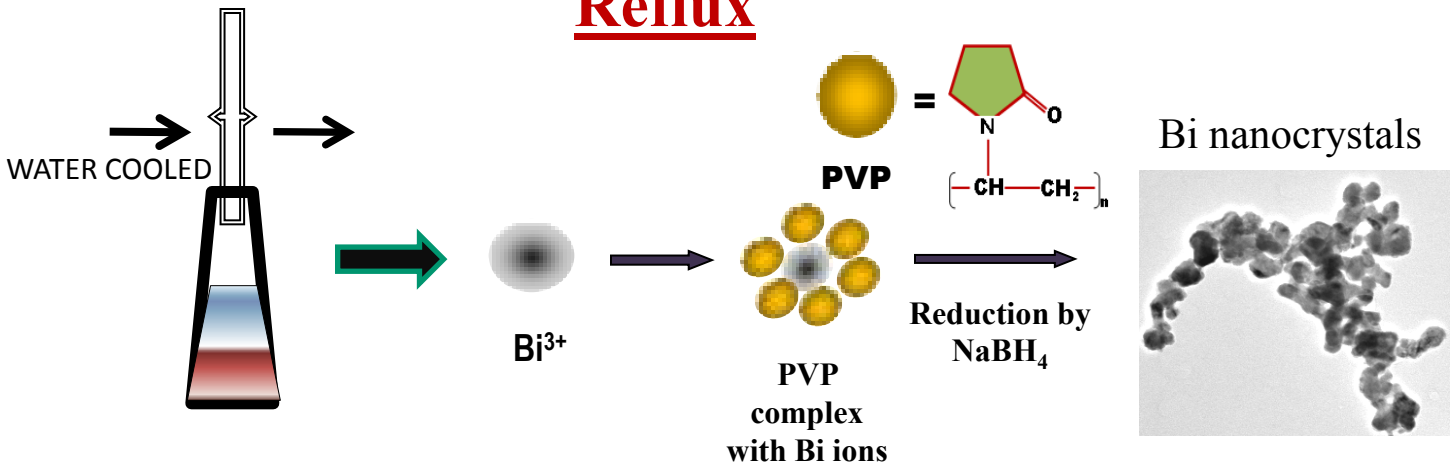
- n-type Bi_2Te_3 Nanocomposites
  - Kim, *et al,* J. Alloys Comp. **399**, 14 (2005)
  - Zhao, *et al*, J. Alloys Comp. **467**, 91 (2009)

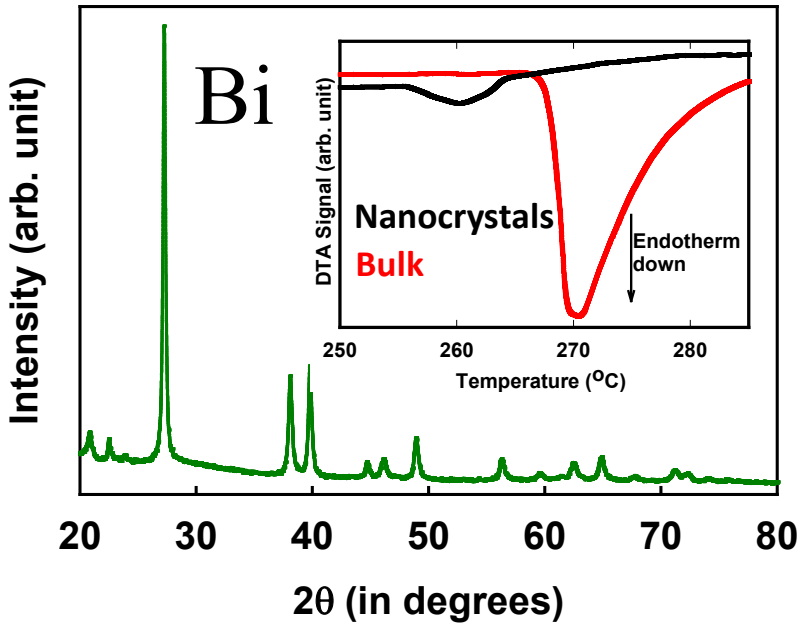
A. F. Ioffe, Semiconductor thermoelements and thermoelectric cooling, Infosearch Limited, 1957

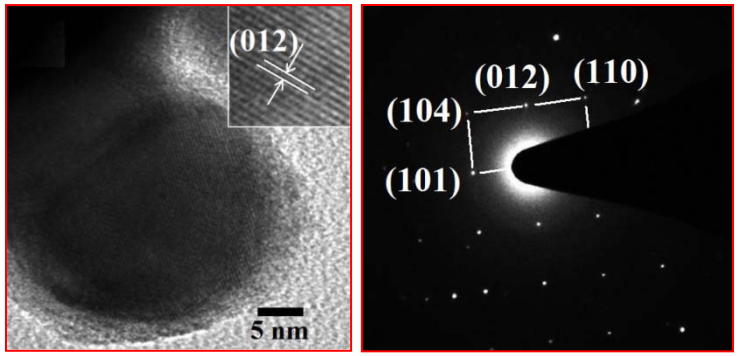
*A. Datta, J. Paul, A. Kar, A. Patra, Z. Sun, L. Chen, J. Martin, and G. S. Nolas, Cryst. Growth Design **10** , 3983 (2010)*

Chemical Synthesis for TE Materials Research

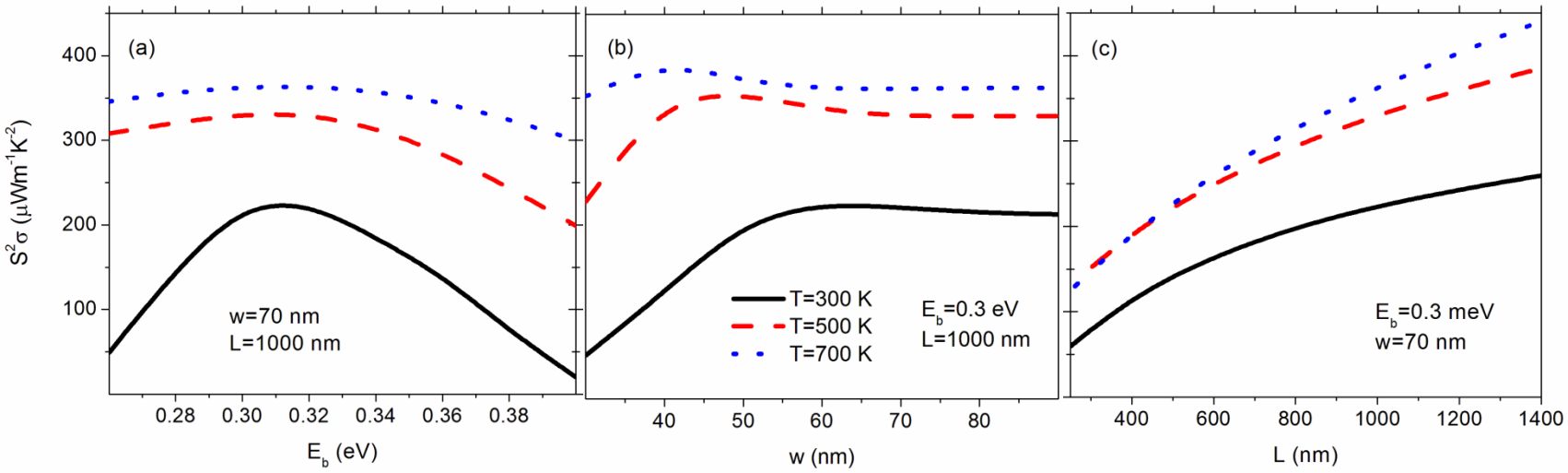
Reflux







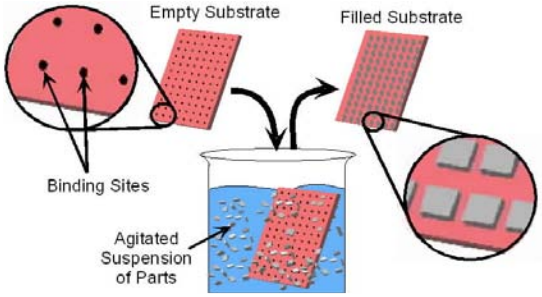
$S^2\sigma$ for $CoSb_3$ granular nanocomposites

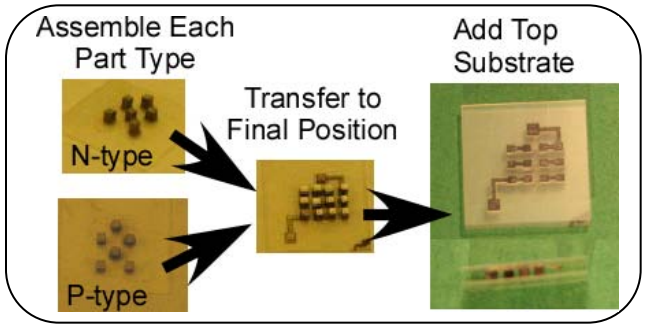


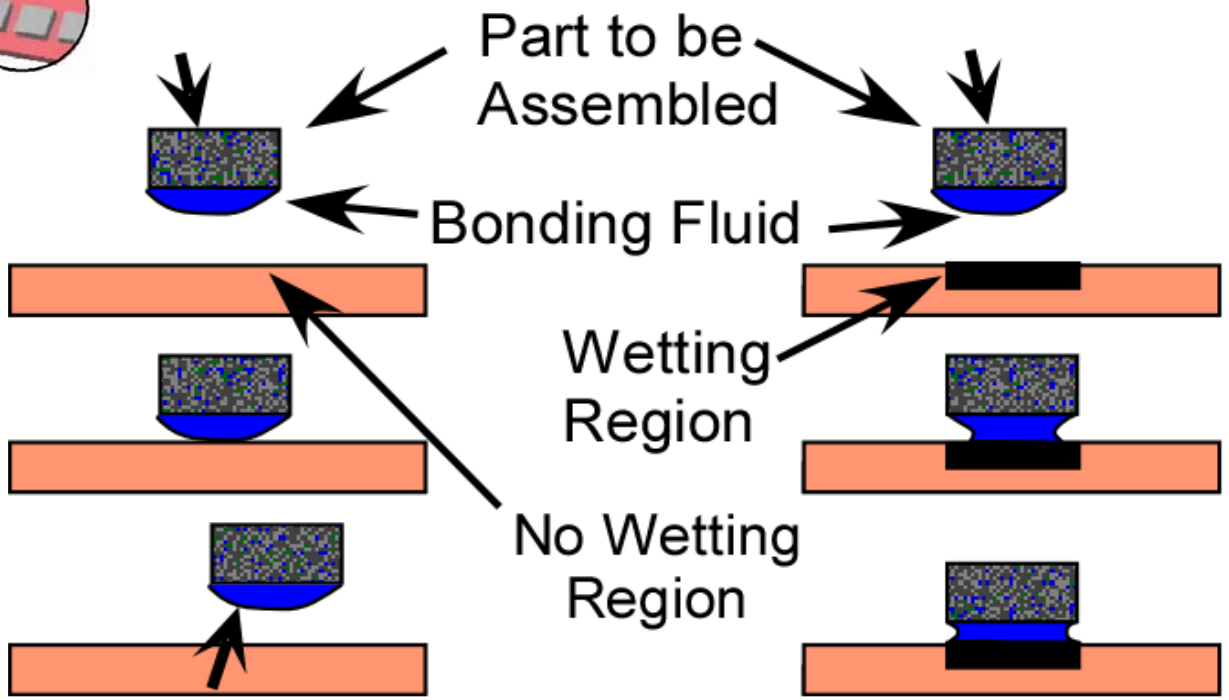
L.M. Woods, A. Popescu, J. Martin, and G.S. Nolas, Proc. Mater. Rec. Soc. ***1166*** *(2009)*

A. Popescu, L.M. Woods, J. Martin, and G.S. Nolas, Phys. Rev. B ***79****, 305302 (2009)*

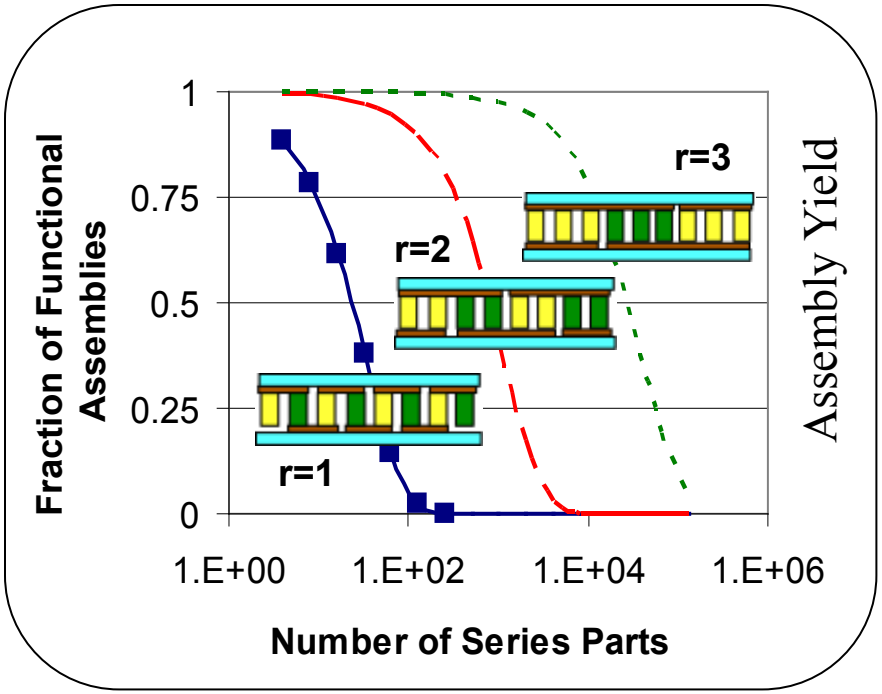
Device manufacturing: Self Assembly







Challenge of Self Assembly: Rate & Yield

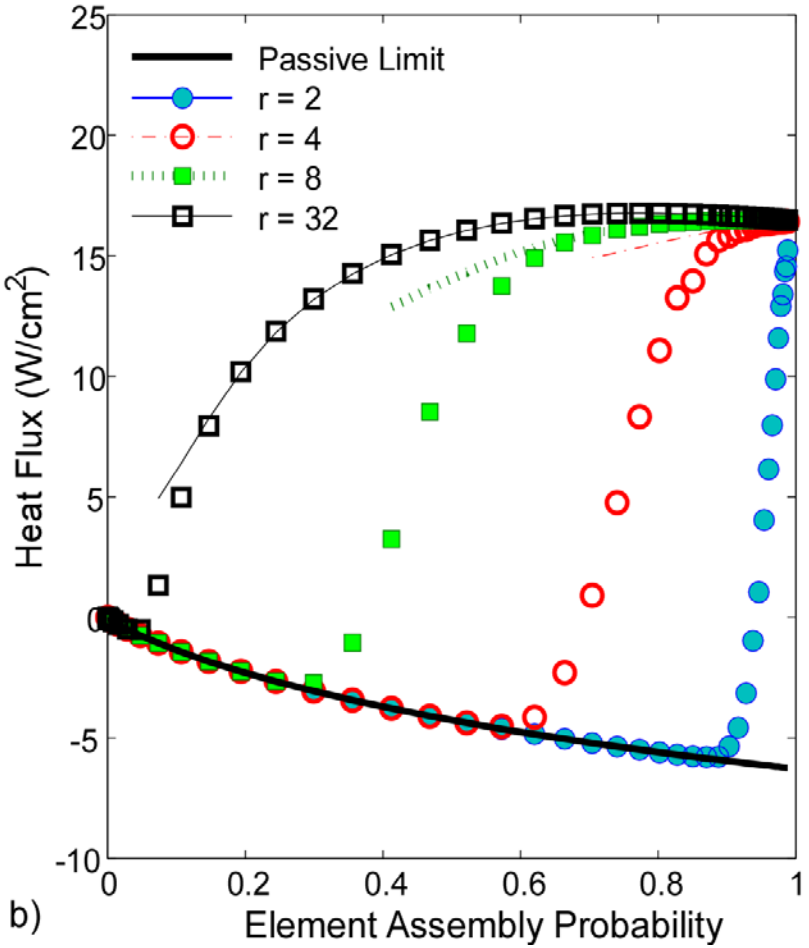


Assembly yields depend on process and design parameters.

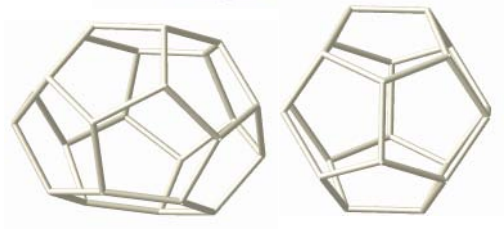
Goal: Develop predictive models of self assembly process rate and yield to facilitate design of high rate and yield processes at industrial scales.

N. Crane, P. Mishra, J. Murray and G.S. Nolas, J. Electronic Mater ***38****, 1252 (2009)*

Modelling Performance

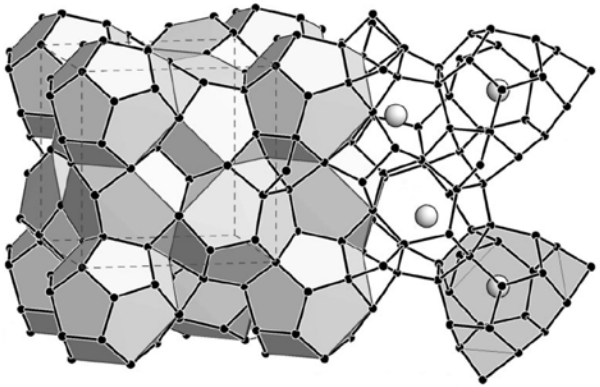


"Open-framework" Materials
Example: clathrates

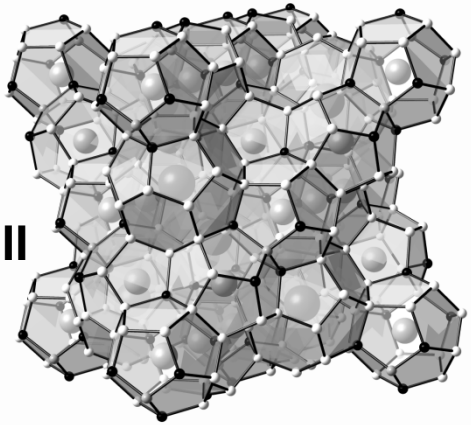


Polyhedral "Building Blocks"

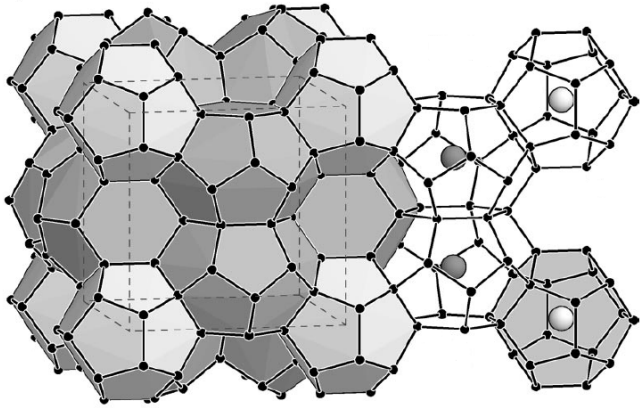
Type VIII

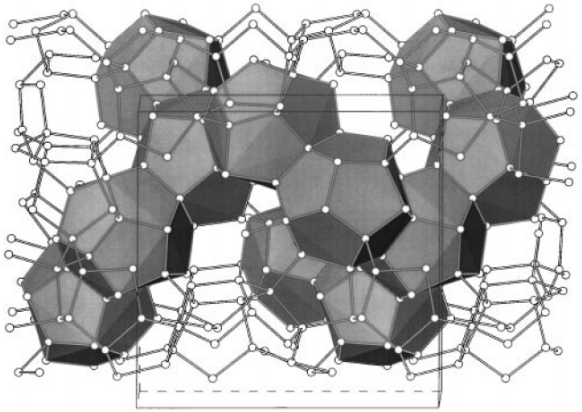


Type II



Type I

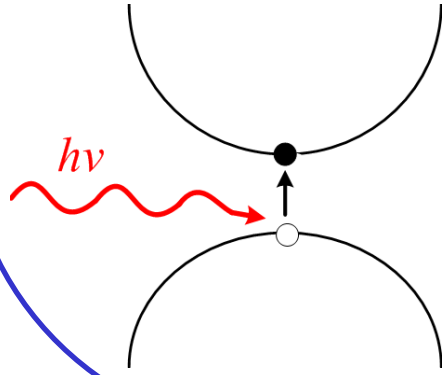




- *M. Beekman & G.S. Nolas, J. Mater. Chem.* ***18****, 842 (2008)*
- *G.S. Nolas et al in Semiconductors and Semimetals, Vol. 69, Academic Press, 2001*

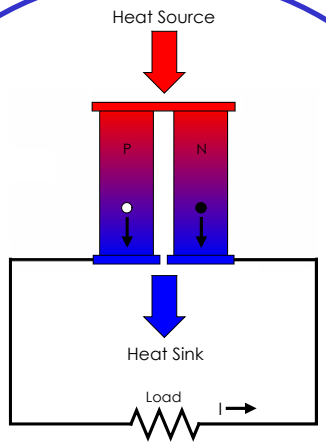
Applications

Photovoltaics & Optoelectronics

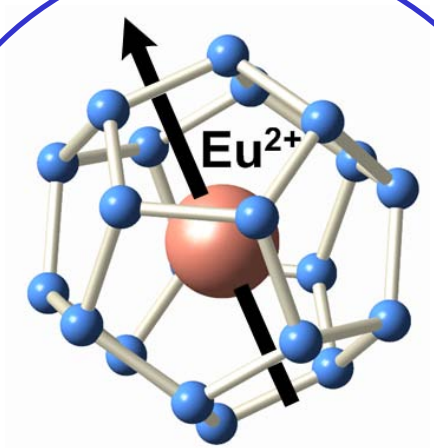


Li-ion Batteries

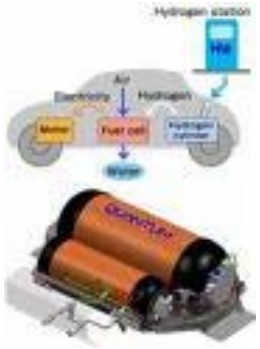
Thermoelectrics



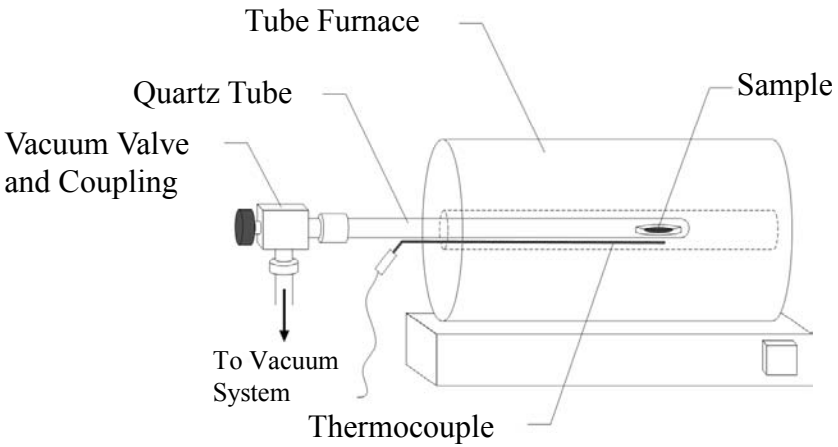
Magnetism



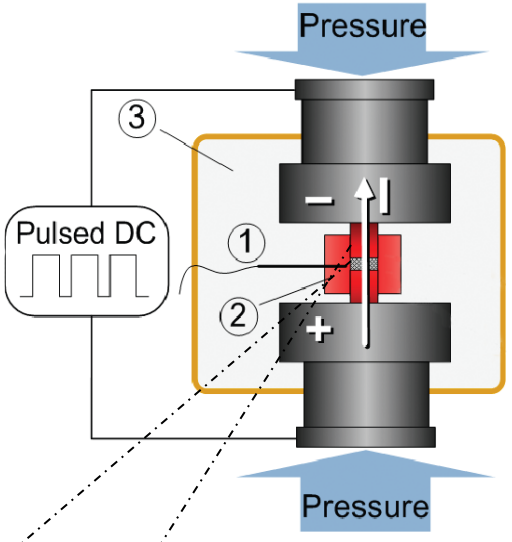
Hydrogen Storage

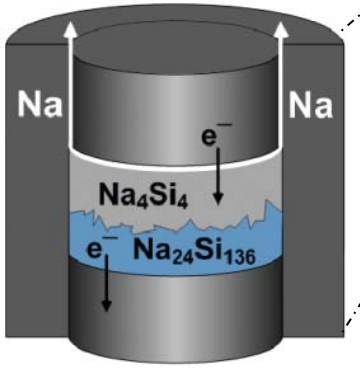


Synthetic Routes for Clathrate-II Intermetallics



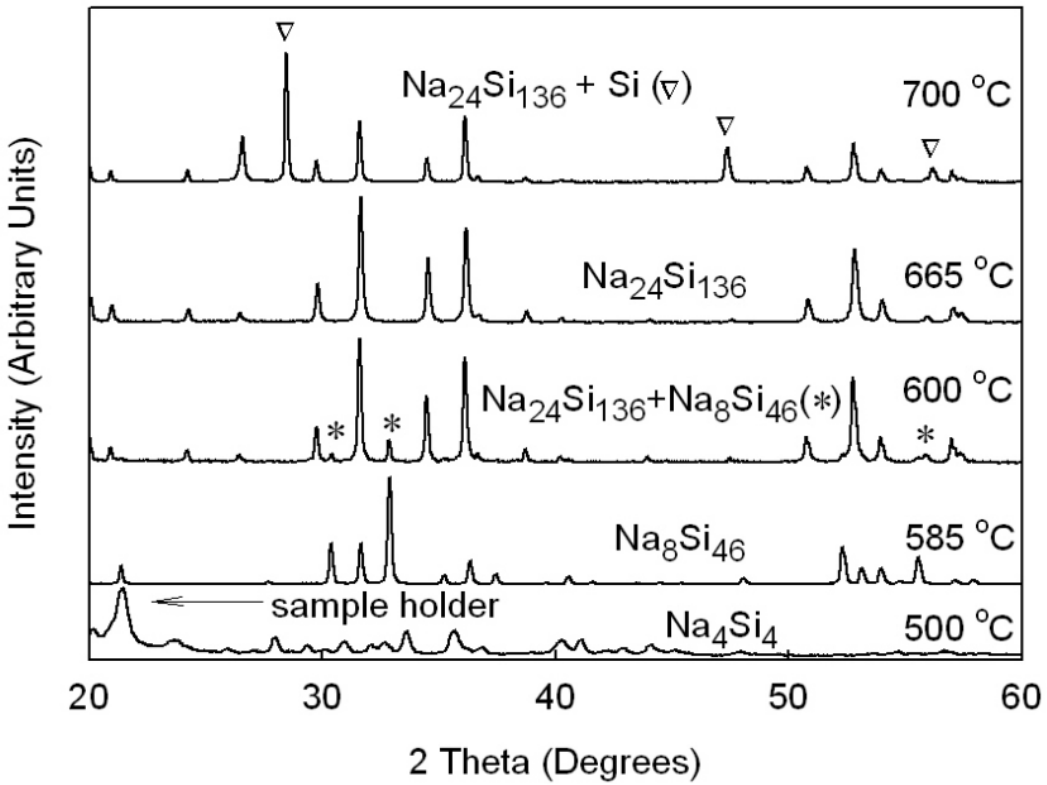
M. Beekman & G.S. Nolas, J. Mater. Chem. ***18****, 842 (2008)*

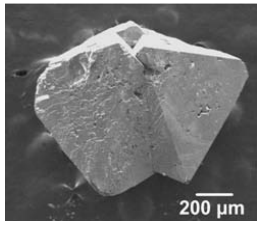




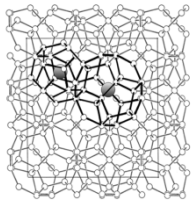
M. Beekman, M. Baitinger, H. Borrmann, W. Schnelle, K. Meier, G.S. Nolas, and Yu. Grin., J. Am. Chem. Soc.,131, 9642 (2009).

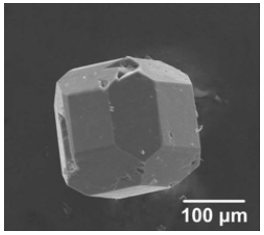
New Synthetic Techniques*



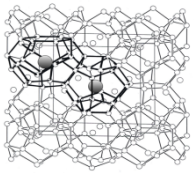


$Na_{24}Si_{136}$



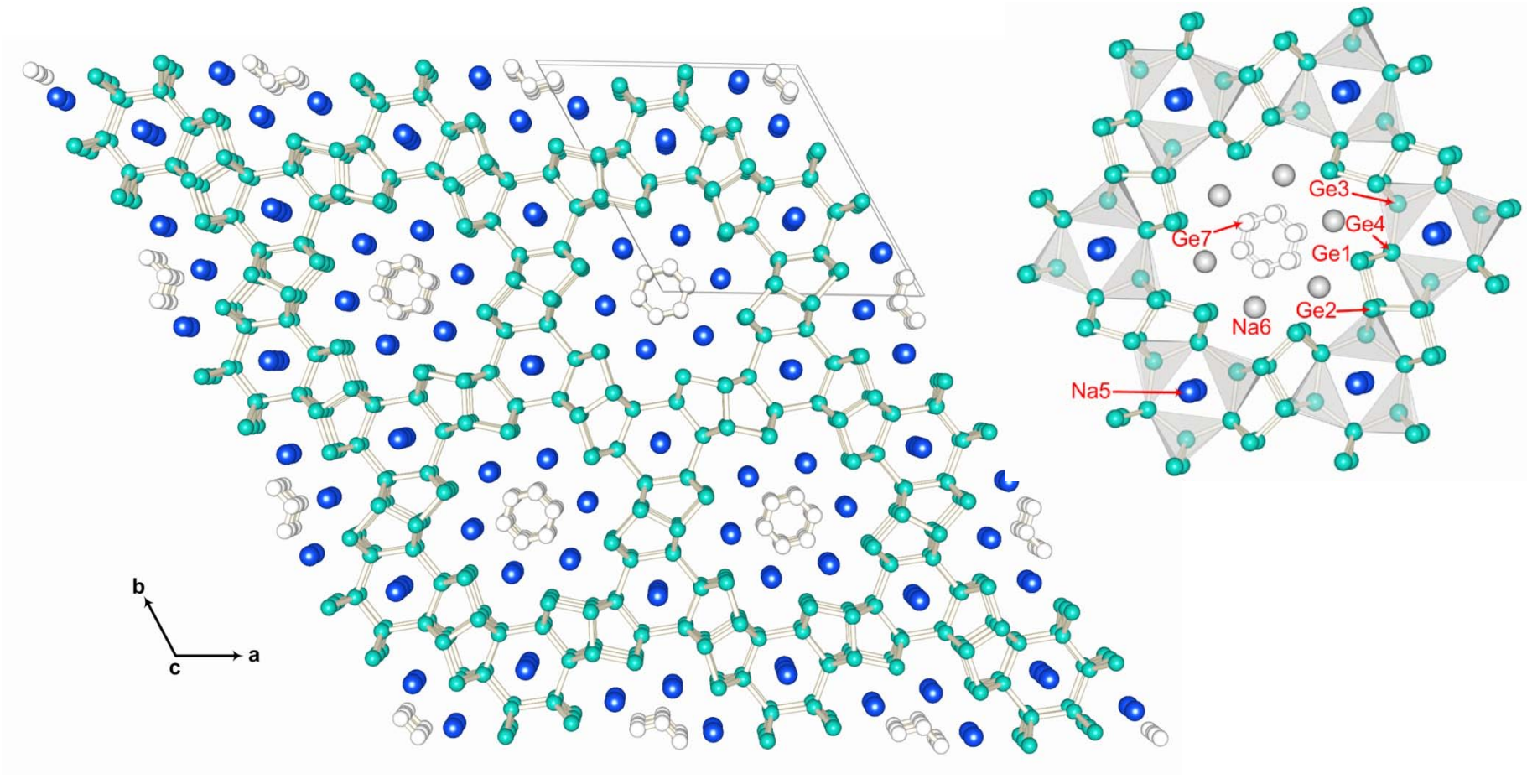


Na_8Si_{46}



*"Novel Methods for Solid State Crystal Growth", Patent Pending, Serial No. 12/859,534, submitted August 19, 2010

Discovery of the 'Novel' Phase $Na_{1-x}Ge_{3+z}$



M. Beekman et al, Chem. Commun. 837 (2007)
M. Beekman et al, J. Solid State Chem. ***183****, 1272 (2010)*

Conclusions

"Bottom-up" processing, a cost-effective approach towards enhanced TE performance

- Chemical processes for TE materials in the required quality and quantity.
- Doping of nanocrystals in tuning the carrier concentration in bulk nanocomposites.
- Theoretical calculations corroborate and focus experimental efforts.
- Studies on mechanical and thermal stability of nanocomposites at higher temperature are ongoing.

"Open-framework" (bulk) materials offer an opportunity to better understand the complex structure-property relationships that define the suitability of a material for:

- thermoelectric applications
- battery technology
- solid-state refrigeration
- opto-electronics
- hydrogen storage

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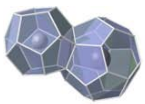

The USF Novel Materials Laboratory