Enhancing the Performance of Zintl Phases via Defect Chemistry

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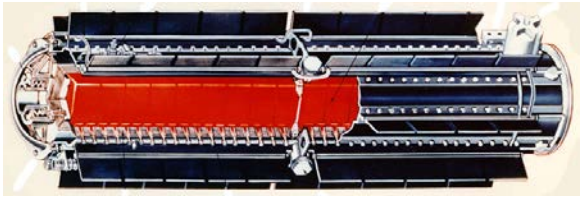
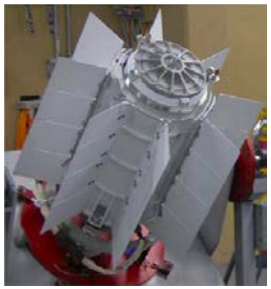
Albuquerque, NM

Current State of the Art (SOA) Materials

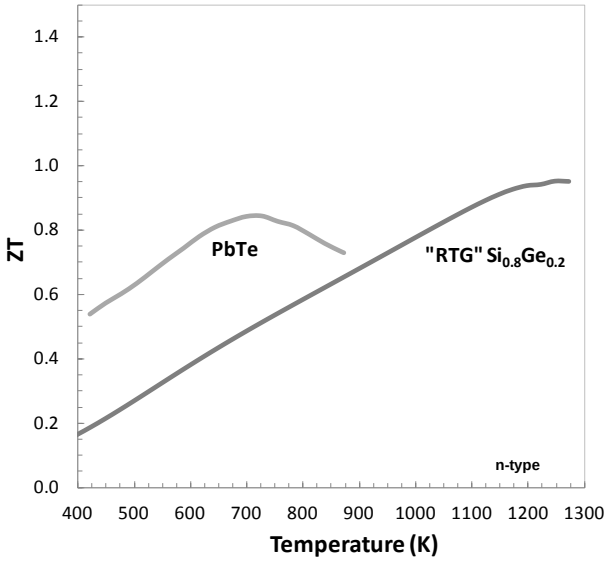


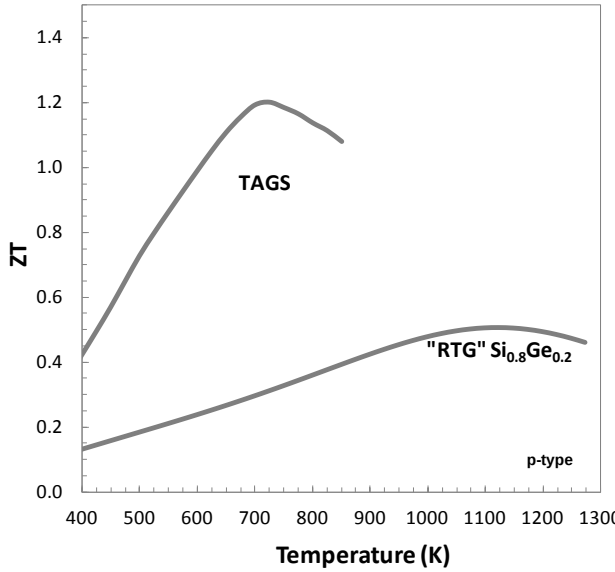
SiGe GPHS RTG (1980-2006)



PbTe/TAGS MMRTG

(2006-present)





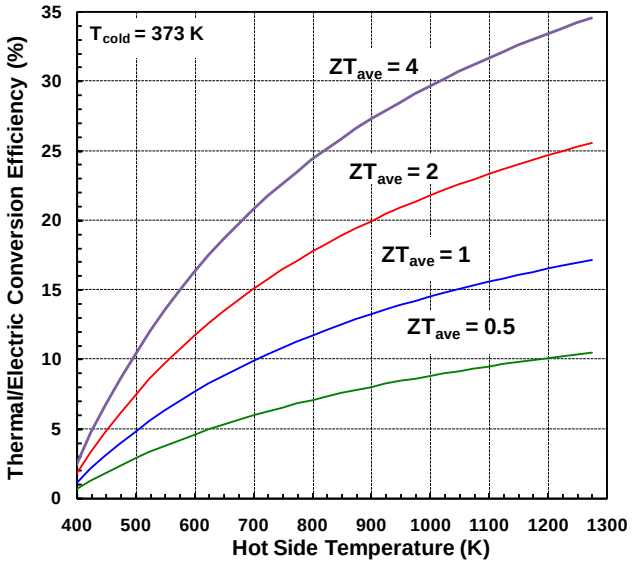
- **RTGs for the past 50 years have either been PbTe (ZTave 0.7) or SiGe (ZTave 0.6) based**
  - High level of reliability and redundancy and long life
  - ~6.5% efficiency at the system level
- **Increasing demand for higher scientific payload and higher specific power per kilogram**
  - Limited amount of expensive heat source….Need **Higher ZT materials!!**

Thermoelectrics: Power Generation

$$\text{Efficiency} = \frac{\Delta T}{T_h} f(zT)$$

Carnot efficiency

$$f = \frac{\sqrt{1+z\bar{T}}-1}{\sqrt{1+z\bar{T}}+\frac{T_c}{T_h}}$$



Conversion efficiency is a direct function of ZT and ΔT

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

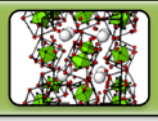
S, Seebeck coefficient
σ , electrical conductivity
λ, total thermal conductivity
T, temperature

$$\lambda = \lambda_{lattice} + \lambda_{electronic}$$

$$S = \Delta V/\Delta T$$

Radioisotope Power Systems Program: Advanced Thermoelectrics Technology Roadmap

Fundamental materials research (NASA, Academia)



Advanced Thermoelectric Materials (ATOM) (TRL 0-2)

2005 — 10% Efficient TE Materials

2010 — 15% Efficient TE Materials

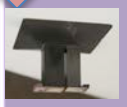
2020 — > 20% Efficient TE Materials

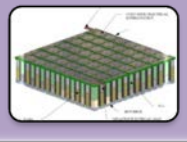
Advanced TE Couples (ATEC) (TRL 2-4)

2013 — 10% Efficient TE Couple Tech

Materials, Device production (Industry, NASA)

2019 — 15% Efficient TE Couple Tech





Technology Maturation (TRL 4-5)

2018 — eMMRTG

Converter and generator system engineering (Industry, DOE, NASA)

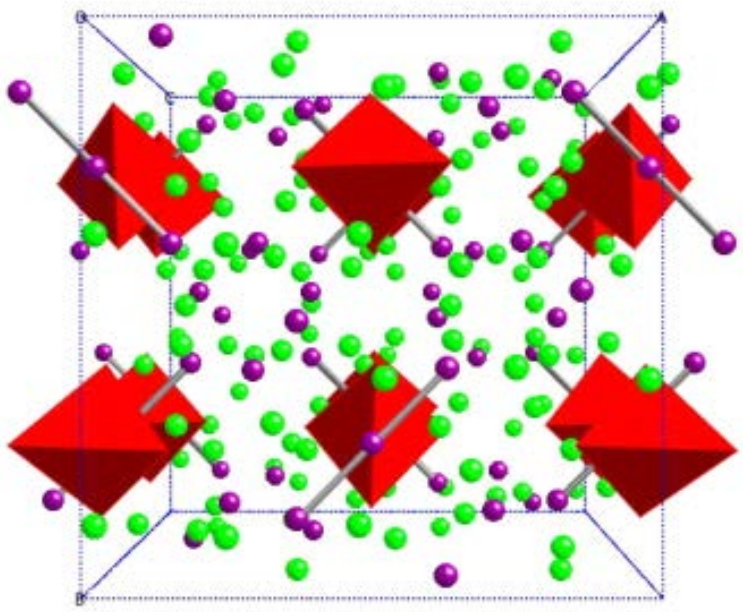
Flight system development and support (Industry, DOE, NASA)

Technical Approach to > 20% Efficiency

Key materials design strategies to achieve high ZT values across wide ΔT

- Complex crystal structures
  - Inherently low thermal conductivity due to structural complexity
  - Need to control and optimize electronic properties

- Main experimental challenge:
  - Develop synthesis methods that enable precise stoichiometric control and practical scaling up
  - Provide theoretical guidance using first principles simulations



$Yb_{14}MnSb_{11}$ Zintl Phase
104 atoms/unit cell

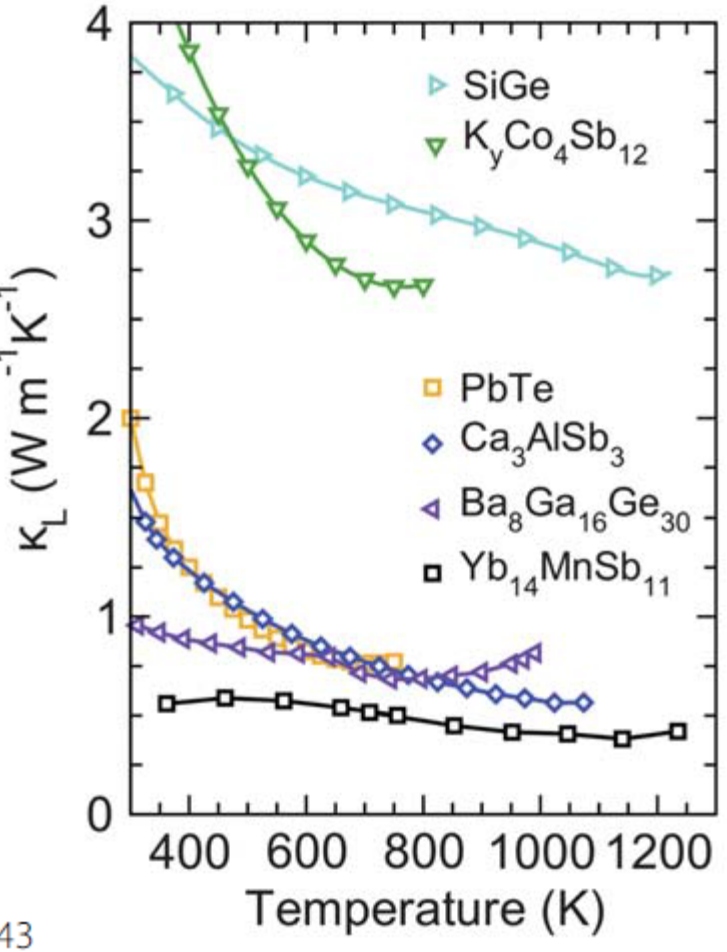
Structural Complexity and Thermal Transport

- **Low thermal conductivity in complex crystal structures**
  - Some of the lowest seen in Zintl structures

Table 1

Material	N	κ_L (300 K) W/mK
$LaPO_4$	24	2.5
$W_3Nb_{14}O_{44}$	61	1.8
$LaMgAl_{11}O_{19}$	64	1.2
$La_2Mo_2O_9$	624	0.7
α $Al_{14.7}Mn_{3.5}Si_{1.8}$	138	1.5
$Ca_5Al_2Sb_6$	26	1.5
Ca_3AlSb_3	28	1.6
$Yb_{11}Sb_{10}$	42	0.8
$Yb_{11}InSb_9$	42	0.8
$Ba_8Ga_{16}Ge_{30}$	54	1.1
$Yb_{14}AlSb_{11}$	104	0.6

J. Mater. Chem., 2011, **21**, 15843

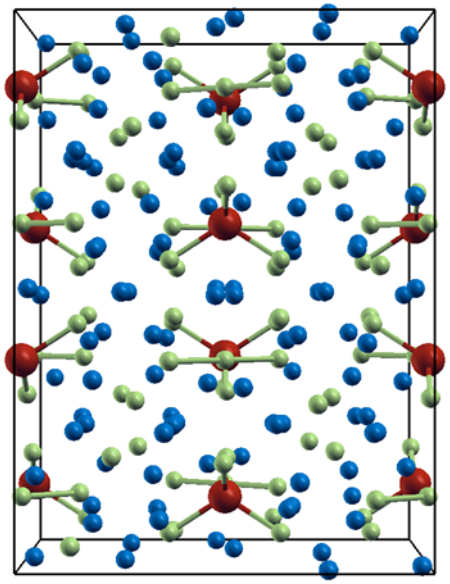


Toberer, E. et. al. *J. Mater. Chem*. 2011, 21, 15843; Star, K. et. al. *Manuscript in progress.*

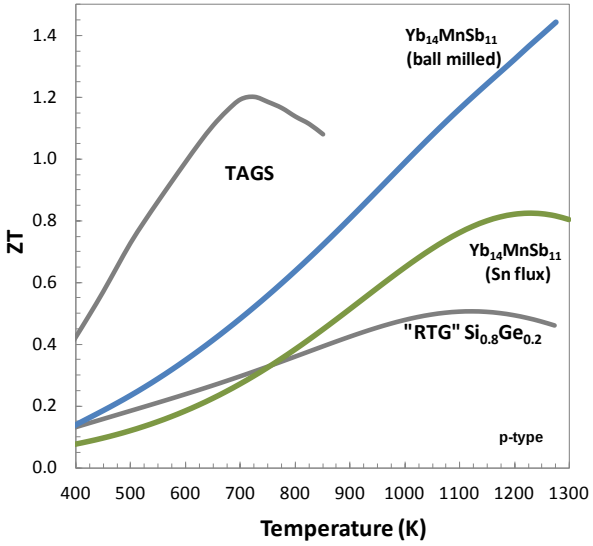
Introduction to Zintl Phases

- Zintl Structures
  - Covalent, anionic substructures
  - Zintl-Klemm valence count
- Thermal properties:
  - Complex structures leads to low thermal conductivity
- Electronic properties
  - Semiconducting-metallic
  - Carrier concentration optimized through doping

- $Yb_{14}MnSb_{11}$
  - 104 atoms per unit cell
  - TE properties reported in 2006
  - Peak ZT ~1.4 at 1275 K
    - Factor of 3x over SOA SiGe



Body centered tetragonal $I4_1/acd$ space group
Unit cell: total of 104 atoms
Block (4X): $[MPn_4]^{9-}$, $[Pn_3]^{7-}$, $4Pn^{3-}$, $14A^{2+}$

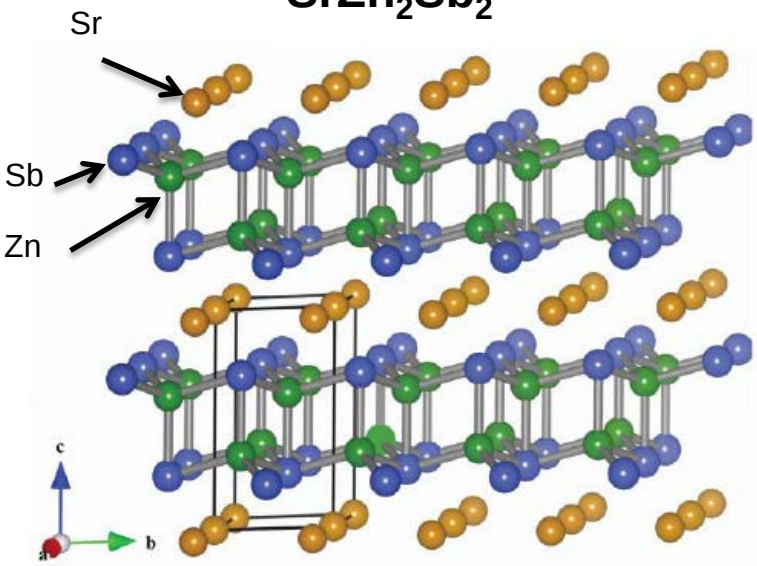


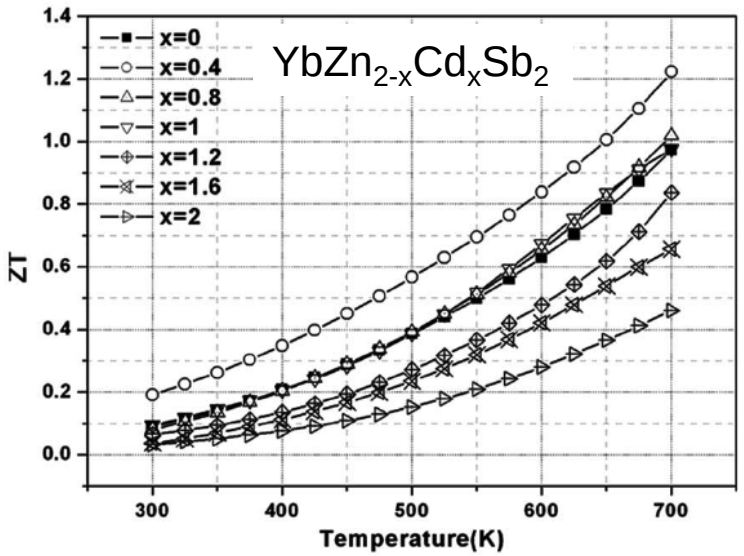
Toberer et. al. *Adv. Funct. Mater.* 2008, 18, 2795; Star, K. et. al. *Manuscript in progress.*

AM_2Sb_2 Zintl compounds

- **$CaAl_2Si_2$ structure type**
  - slabs of covalently bonded M_2Sb_2 are separated by rows of *A* atoms
  - *M* = Zn, Cd, Mn
  - *A* = Ca, Sr, Yb, Eu
  - only 5 atoms per unit cell

$SrZn_2Sb_2$





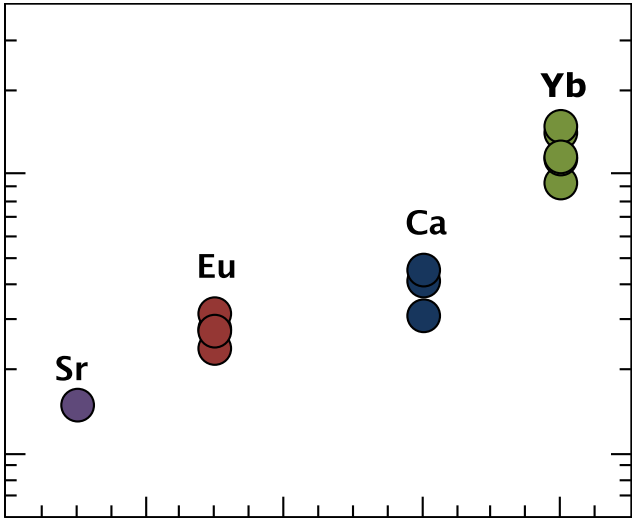
X.-J. Wang, M.-B. Tang, H.-H. Chen, X.-X. Yang, J.-T. Zhao, U. Burkhardt, Y. Grin, *Appl. Phys. Lett.* **2009**, *94*, 092106.

- **One of most studied Zintls, peak *zT* ~ 1.2 at 775 K**
- **Similar performance to skutterudites**

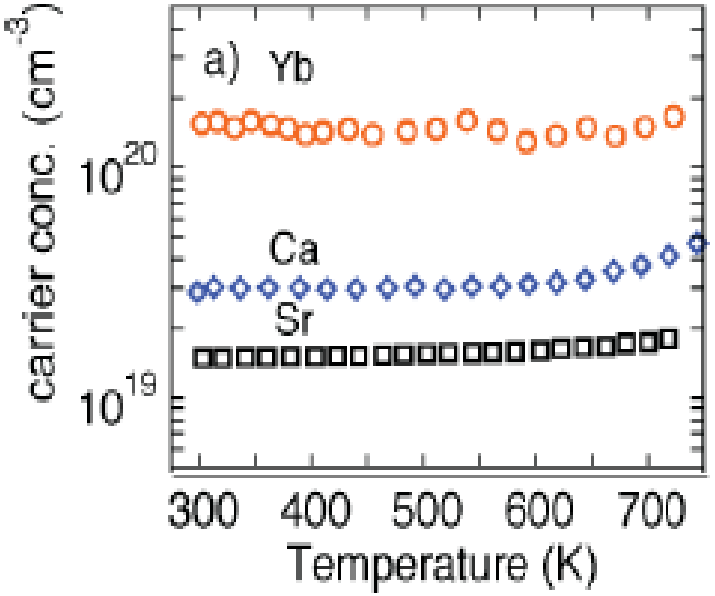
E.S. Toberer, A.F. May, et. al. Dalton Trans., 2010, **39**, 1046–1054

AZn_2Sb_2 Carrier Concentrations

- **Zintl phases: valence precise with expected semiconducting properties**
  - Classically thought as line compounds
- Orders of magnitude changes in carrier concentration observed in system despite isoelectronic substitution



Allred-Rochow electronegativity

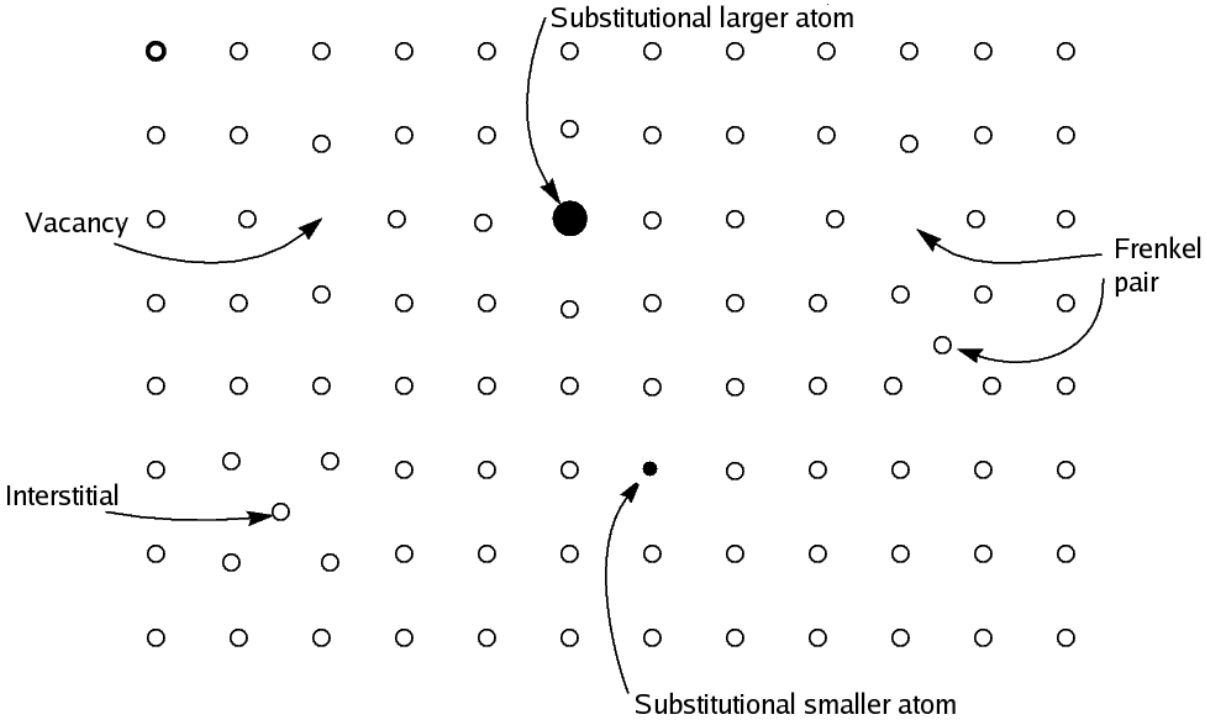


Sr –> forms most ionic bonds
Yb --> forms the most covalent bonds

E.S. Toberer, A.F. May, E. Flage-Larsen et. al. Dalton Trans., 2010, **39**, 1046–1054

Role of Defects

- **What causes crystallographic defects?**
  - Thermodynamic competition between entropy gain from defect formation vs energy needed to form the defect
  - Many types of defects

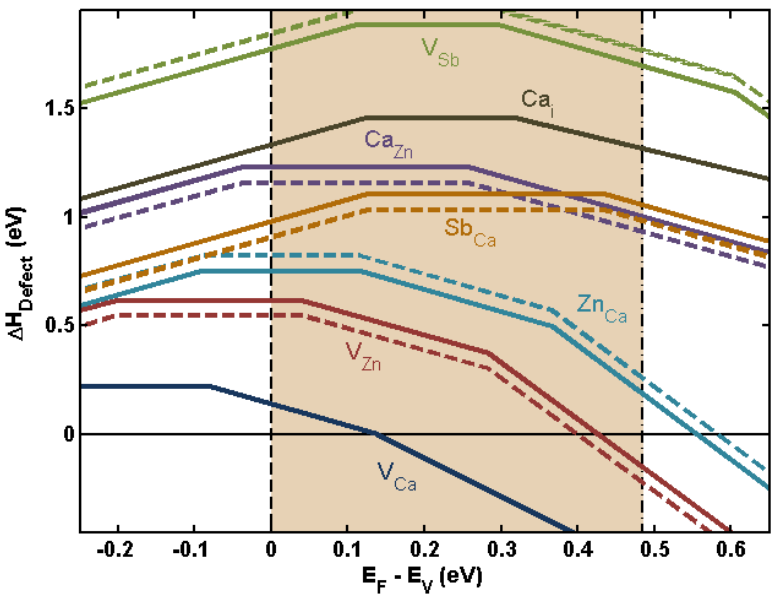


- **Impact of defects?**
  - Some defects can significantly impact TE properties
    - Previously demonstrated in other TE material systems such as oxides, clathrates, and chalcogenides
    - ***Effect of defects not studied in Zintl phases***

http://en.wikipedia.org/wiki/Crystallographic_defect

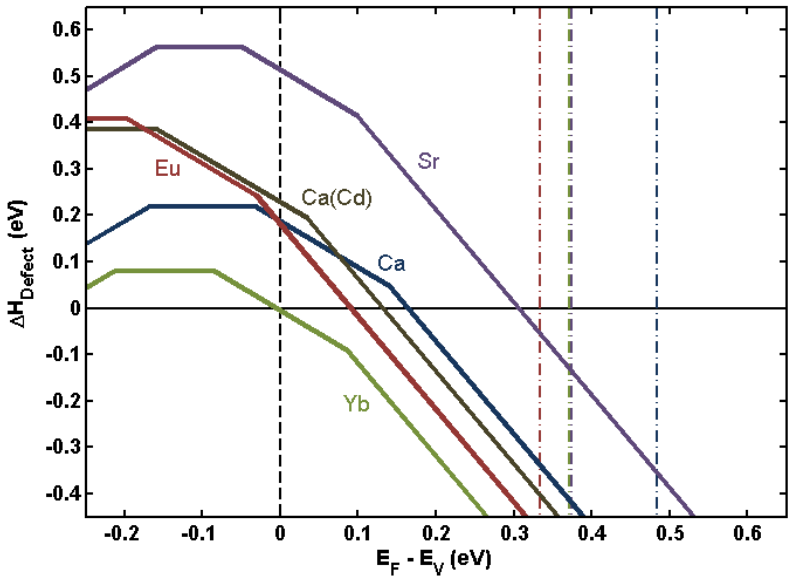
Thermodynamics of Defects in AM_2Sb_2

ΔH_{defect} at 0 K for selected defects in $CaZn_2Sb_2$



- Vacancies on the Ca and Zn sites have lowest energies
- In all AZn_2Sb_2 compounds, *A*-site vacancy is most favorable

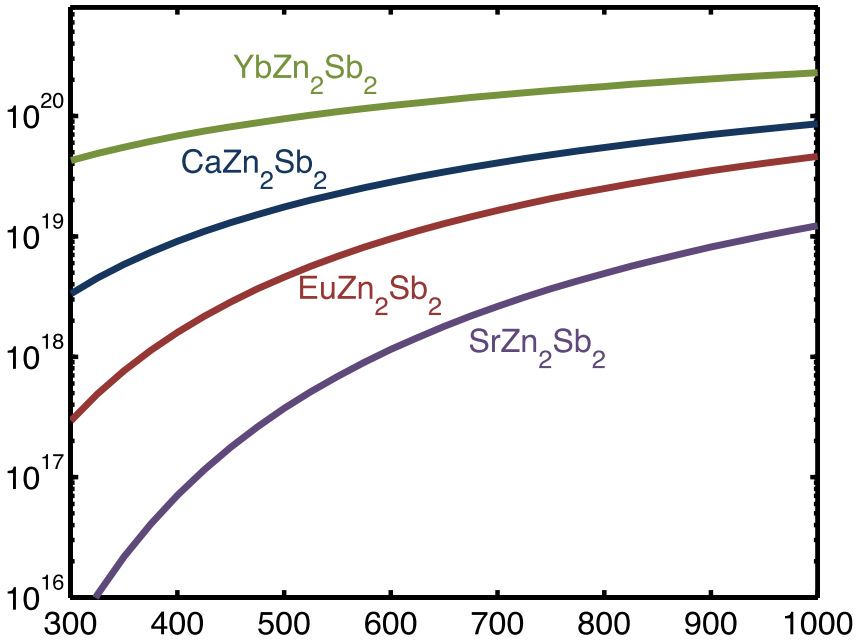
A site vacancies only – at 0 Kelvin

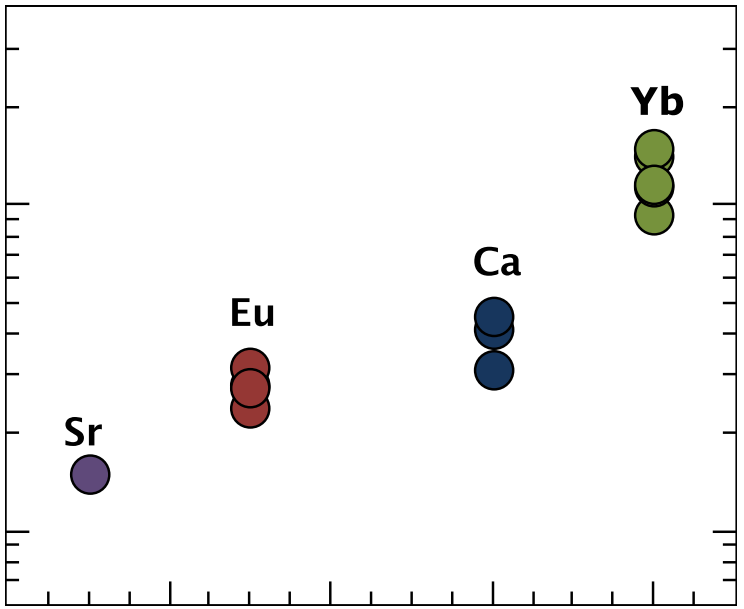


- Yb vacancies are more favorable than ionic Sr vacancies

Pomrehn, G.; Zevalkink, A.; Zeier, W. G.; van de Walle, A.; Snyder, G. J. *Angew. Chem., Int. Ed*. 2014, 53, 3422−3426.

Expected Carrier Concentration Accounting for Defects in AZn_2Sb_2



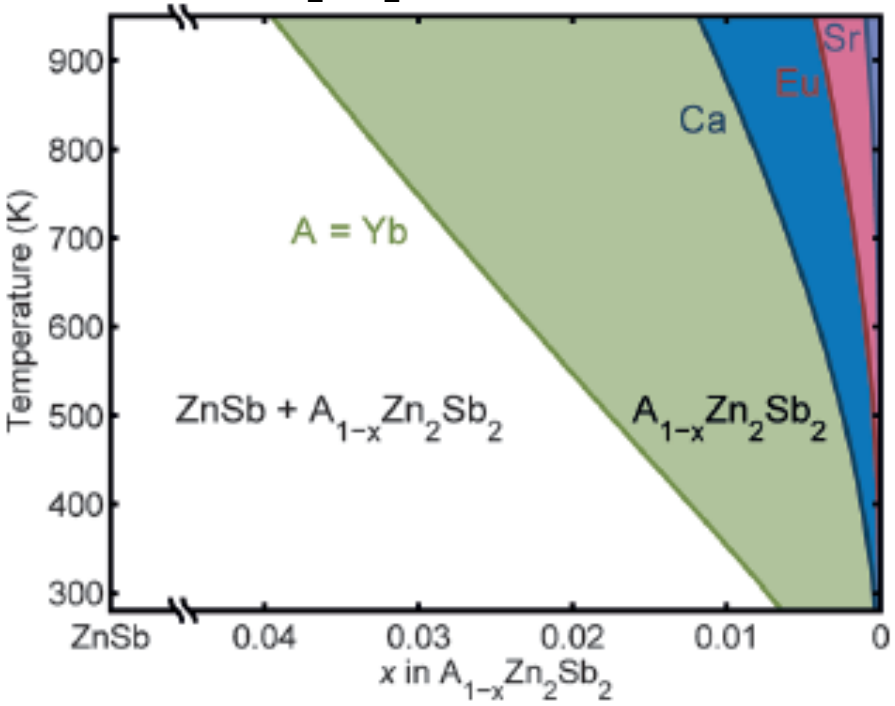


- Calculated trend in carrier concentrations matches trends in experimental results

Pomrehn, G.; Zevalkink, A.; Zeier, W. G.; van de Walle, A.; Snyder, G. J. *Angew. Chem., Int. Ed*. 2014, 53, 3422−3426.

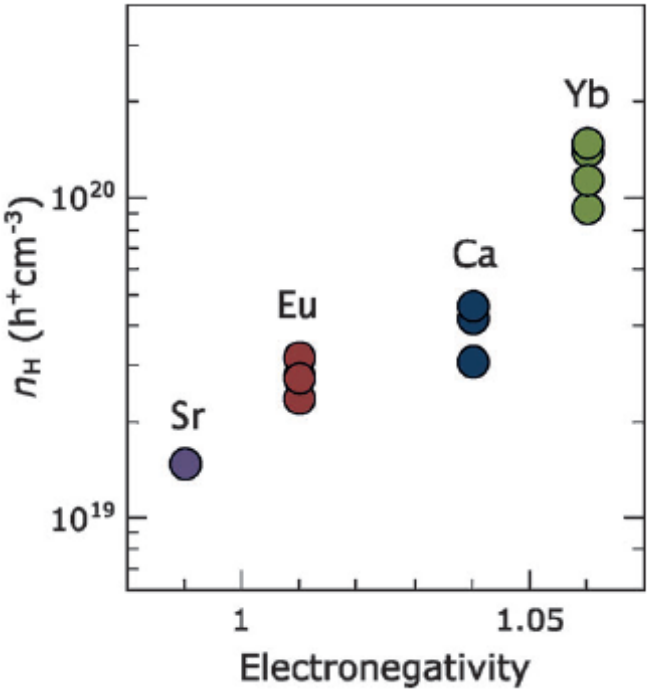
AZn_2Sb_2 phase diagram

AZn_2Sb_2 phase diagram



- *A* vacancies in lead to wide single-phase region
- Maximum vacancy concentration depends on electronegativity of *A*

Experimental n_H



- AZn_2Sb_2 samples have large experimental *n*
- Trend in *n* is consistent with calculated phase diagrams

Pomrehn, G.; Zevalkink, A.; Zeier, W. G.; van de Walle, A.; Snyder, G. J. *Angew. Chem., Int. Ed*. 2014, 53, 3422−3426.

Evaluating Impact of Defects in $Yb_{1-\delta}Zn_2Sb_2$

Objective:

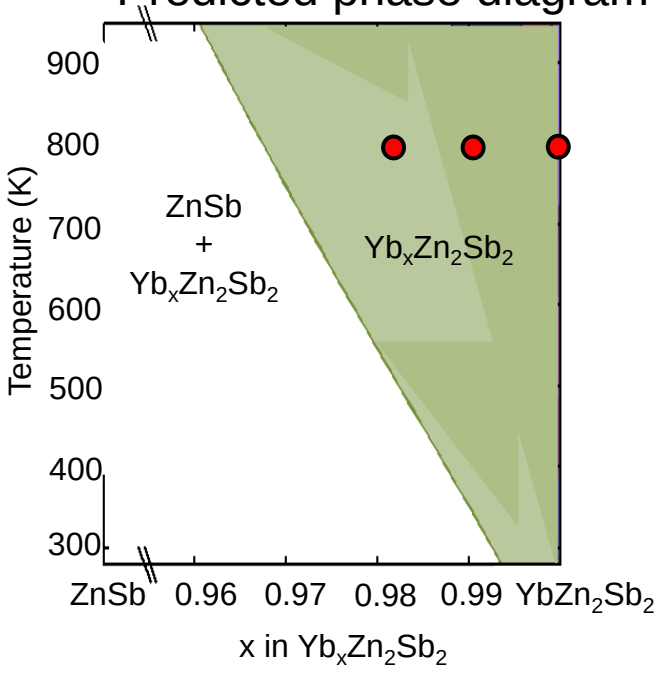
- Determine phase width of $YbZn_2Sb_2$
- Optimize the carrier concentration and ZT via Yb content

Nominal Yb content, x, in $Yb_xZn_2Sb_2$

0.98	0.99	1.00	1.025	1.05

← Yb deficient Excess Yb →

Predicted phase diagram



Predicted behavior:

Yb deficient samples

- Phase pure
- Linear change in lattice parameters and carrier concentration

Yb excess:

- Precipitation of secondary phase
- No change to majority phase
- Similar carrier concentration

Zevalkink, A.; Zeier, W. G.; Cheng, E.; Snyder, J.; Fleurial, J.-P.; Bux, S. *Chem. Mater.* **2014**, *26*, 5710–5717.[14]

Experimental Methods

Synthesis:

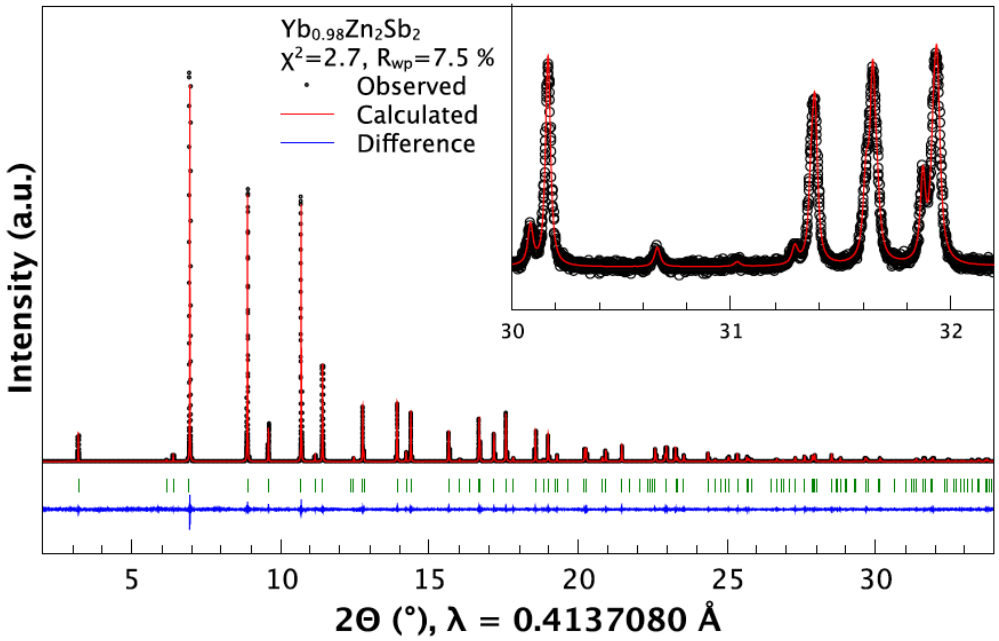
- **$Yb_xZn_2Sb_2$ (x = 0.98, 0.99, 1.00,1.025, and 1.05)**
  - Ball milling of elements in Ar glove box to homogenize powder
- **Hot pressed for 1.5 h at 823 K using 160 MPa of pressure.**
  - Pellets ~99% of theoretical density

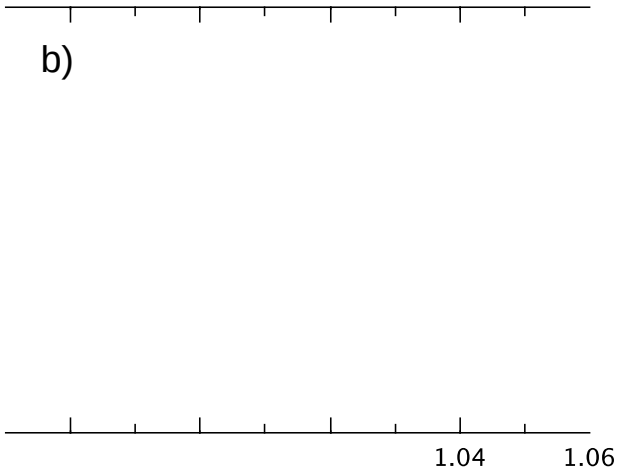
Special Characterization techniques:

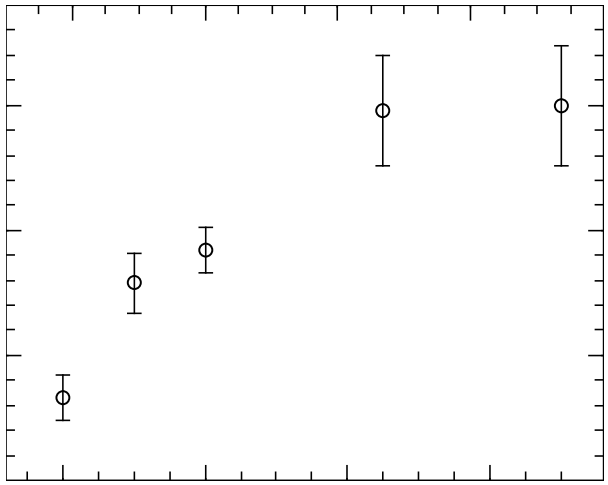
- **High resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory**

Results: Synchrotron XRD results

11-BM Synchrotron XRD







All samples highly phase pure

With decreasing nominal Yb content:

I. Lattice contracts in z-direction

II. Vegard's law obeyed in Yb-deficient samples ($x < 1.00$)

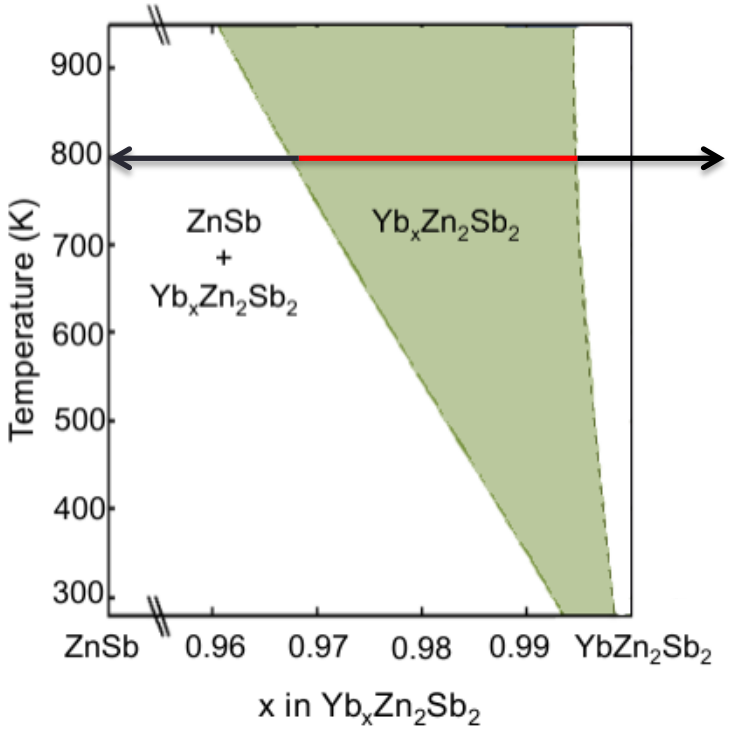
Results: Carrier Concentration

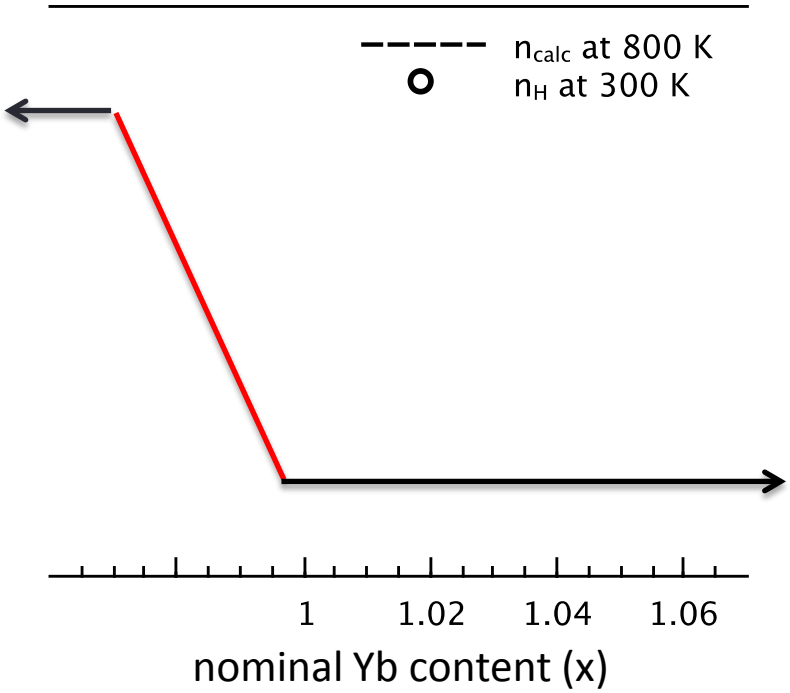
Assumptions:

1. composition is "frozen" at 800 K
2. *n* varies linearly in single phase region
3. *n* is constant outside single phase region

Conclusions:

1. n_H confirms calculated Yb-deficient stability line.
2. Max Yb content may be < 1.00





Results: Transport properties

b)

ρ (mΩcm)

more vacancies

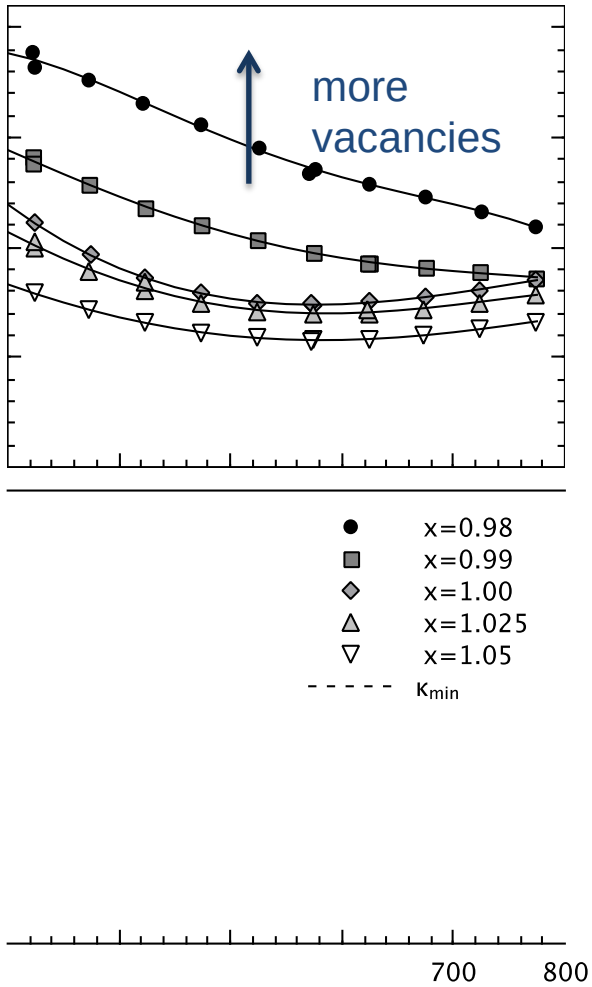
α (μV/K)

more vacancies

κ (W/mK)

more vacancies

κ$_L$ (W/mK)



Yb-deficient samples:

- Yb content determines n_H
- Yb vacancies lead to degenerate behavior

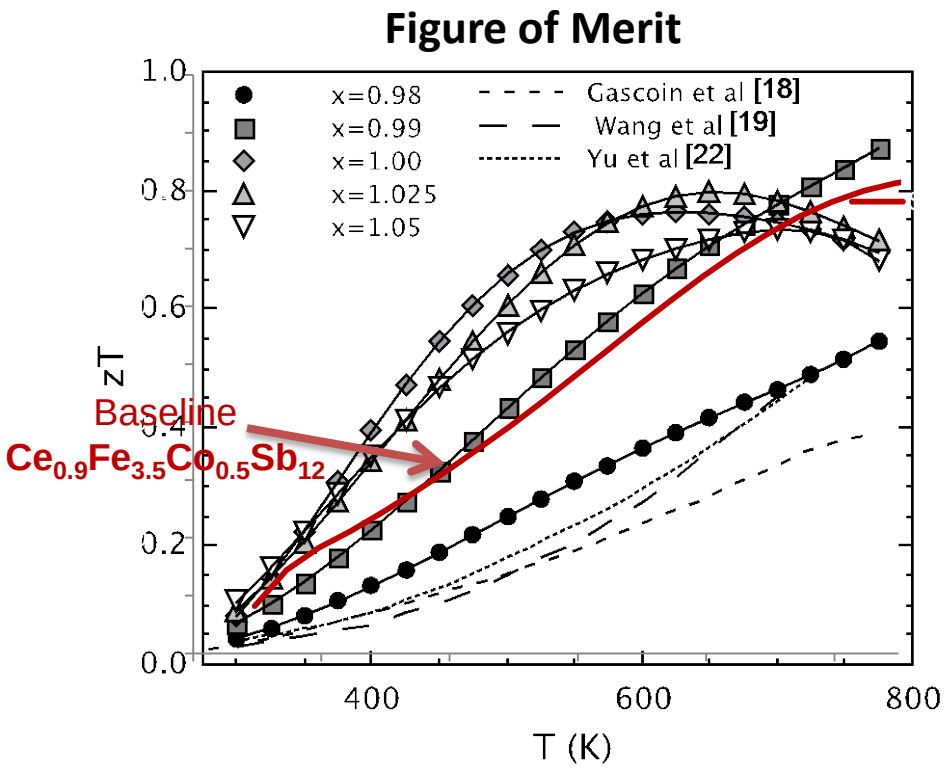
Yb-excess samples:

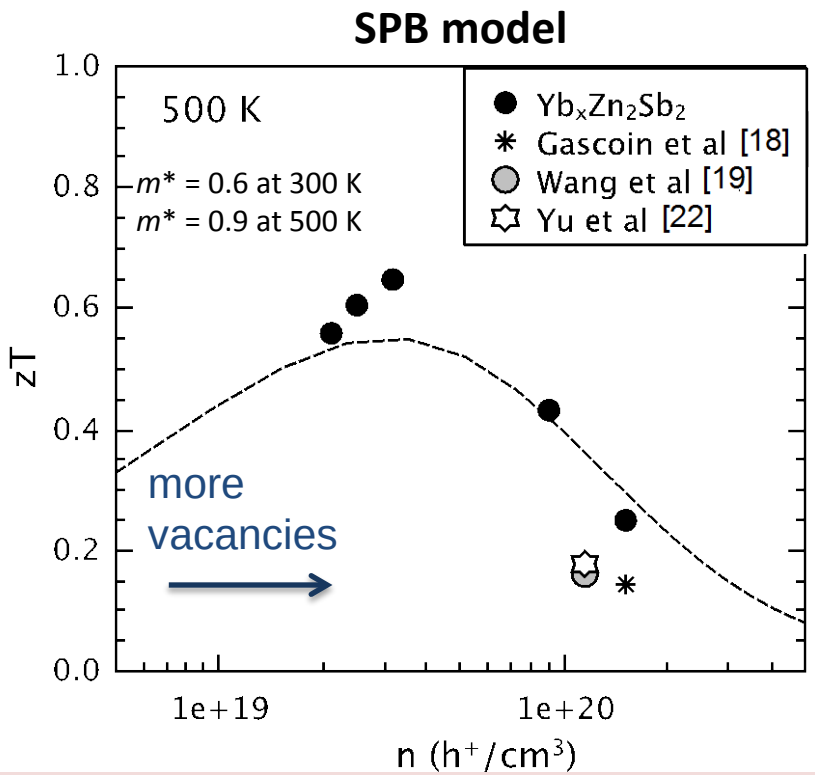
- Yb content has no effect on n_H

Peak Seebeck:

α_{max} yields E_g = 0.25 eV

ZT $Yb_{1-\delta}Zn_2Sb_2$





- Yb deficient samples (lower vacancy concentrations) have optimized carrier concentrations
- Peak *zT* = 0.85
  - 50% improvement in peak *zT,* 100% improvement in average *zT relative to previous literature reports*
- *New method of controlling carrier concentration in Zintl phases*

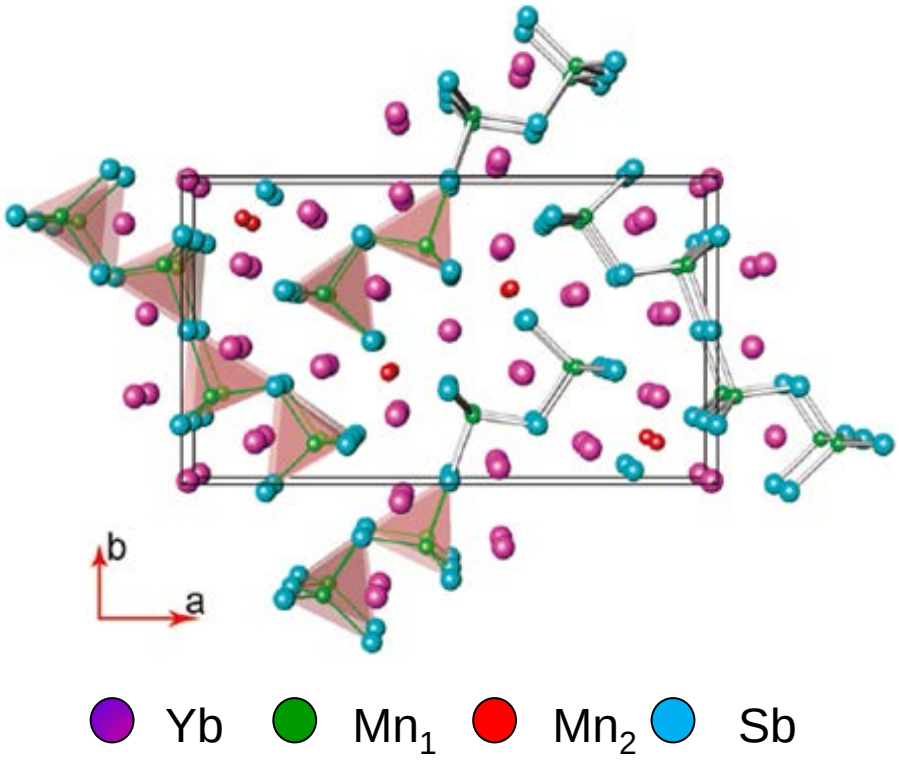
- 30% improved average ZT vs p-type skutterudites

Defect Chemistry and Thermal Transport

$Yb_9Mn_{4.2}Sb_9$

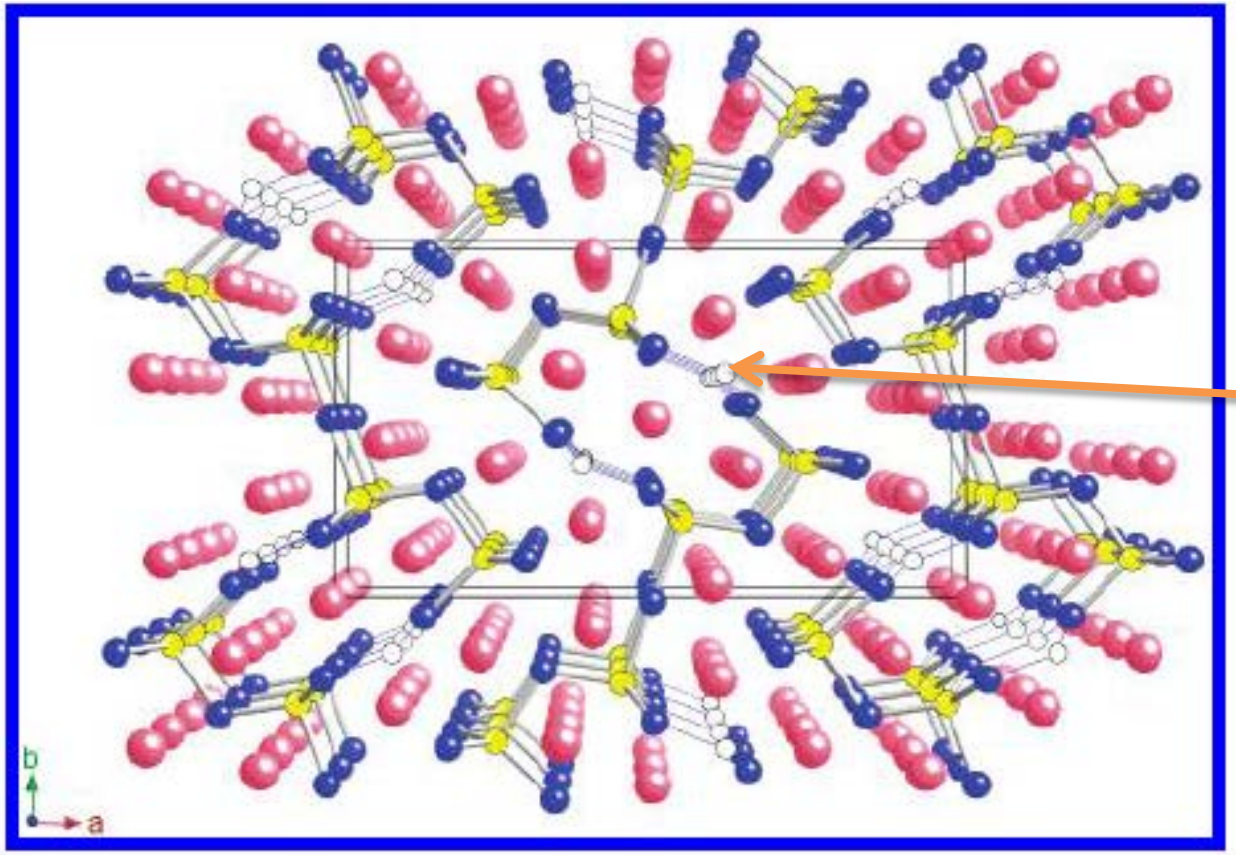
- **In some systems, vacancies effect thermal transport more than electronic**
  - Vacancies behave as point defect scattering sites

- Crystal structure reported by Bobev et al 2010
- Complex Zintl structure
  - 9 Yb^{2+} coordinated to chains of $[Mn_4Sb_9]^{19-}$ sublattice of corner shared $MnSb_4$ tetrahedra
  - Defect structure
    - Interstitial Mn connecting chains,
    - Nominal Zintl composition: $Yb_9Mn_{4.5}Sb_9$
      - Difficult to synthesize due to high entropy of defect formation
- 44 atoms/UC
- Orthorhombic structure



Bobev, S. et. al. *Chem. Mater.* 2010, 22, 840

Interstitial Mn in $Yb_9Mn_{4.2}Sb_9$



Yb
Mn_1
Mn_2
Sb

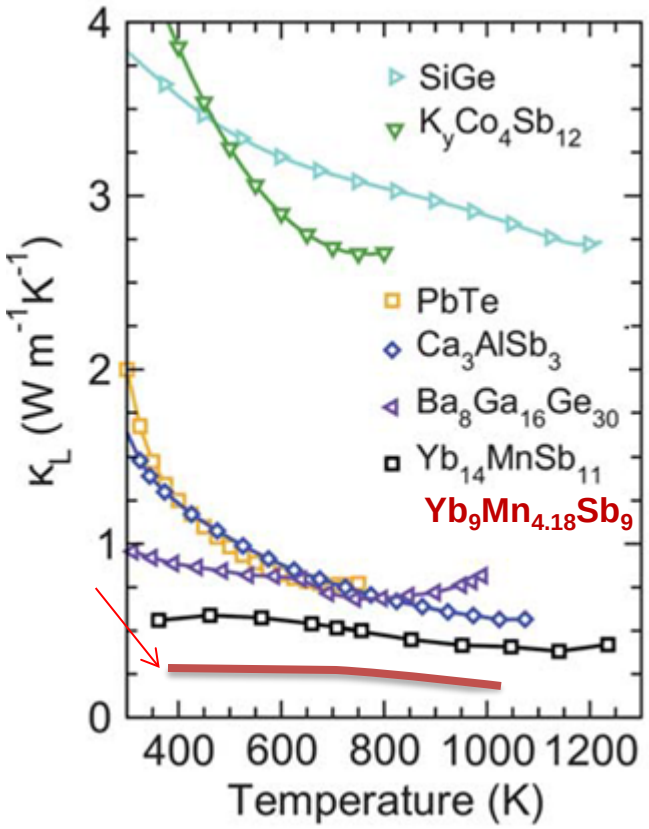
Interstitial Mn

- **Idealized: $Yb_9Mn_{4.5}Sb_9$ structure**
- **Partially filled interstitial Mn**
  - links Mn_4Sb_9 sublattice chains

Bobev et. al. *Inorg. Chem.* (2004) 43, 5044-5052

Structural Complexity and Thermal Properties

- **$Yb_9Mn_{4.18}Sb_9$ possesses one of the lowest thermal conductivities,**
  - Yet it has a relatively smaller unit cell of 44 atoms



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$Yb_{11}Sb_{10}$	42	0.8
$Yb_{11}InSb_9$	42	0.8
$Yb_9Mn_{4.18}Sb_9$	44	0.5
$Ba_8Ga_{16}Ge_{30}$	54	1.1
$Yb_{14}AlSb_{11}$	104	0.7

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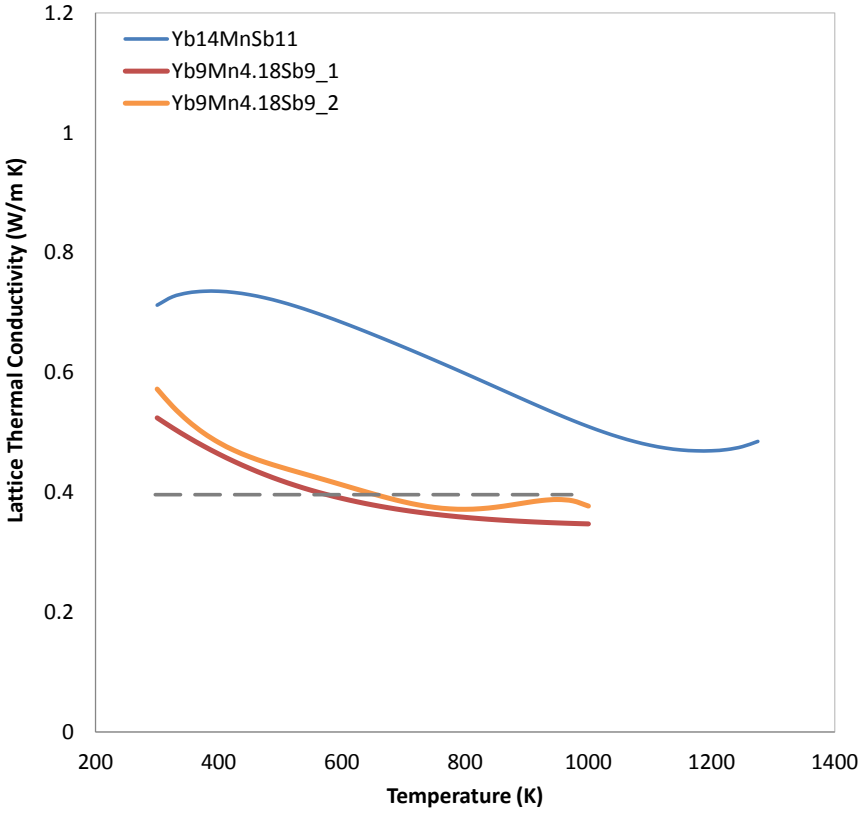
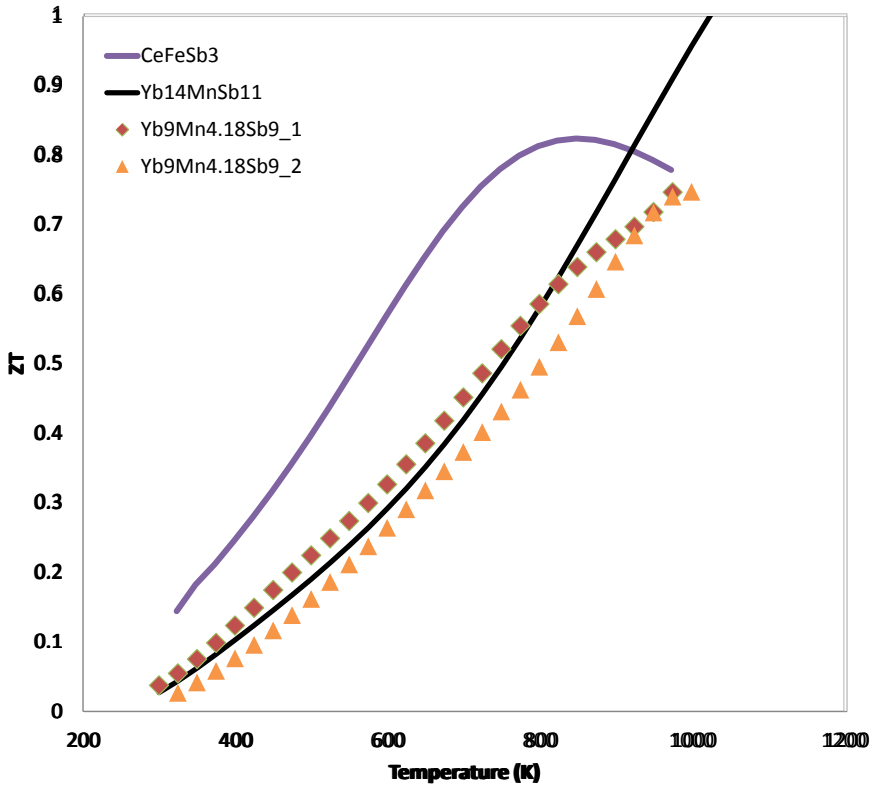
ZT $Yb_9Mn_{4.2}Sb_9$





Thermal conductivity approaches glassy limit at moderate temperatures

ZT of 0.7 at 1000K
Comparable to skutterudites and 14-1-11

Conclusions

- **Defects can play a significant role on the electronic and thermal properties of Zintl phases**
  - Electronic
    - DFT predicts large cation vacancy concentrations in $A_{1-\delta}Zn_2Sb_2$.
    - Controlling the vacancy concentration allows for control of electronic properties, improved zT.
  - Thermal:
    - Defects can lead to low glass like thermal conductivities in already low thermal conductivity complex Zintl phases
- **New mechanisms and insights to improve efficiency of thermoelectric materials**
- **New Zintl phases, could be potential alternates to p-type skutterudites for advanced RTG applications**

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