Complex Thermoelectric Materials – G.J. Snyder & E.S. Toberer

Refresher: high TE figure of merit (zT) requires
1) high electrical conductivity
2) low thermal conductivity
3) large thermopower (large abs. Seebeck coef

$$zT = \frac{S\alpha^2}{(K_e + K_L)} T$$

3 strategies for optimizing zT
1) Scattering phonons w/in unit cell by creating rattling structures or point defects (interstitials, vacancies, alloying)
2) Use complex crystal structures to separate electron-crystal from phonon-glass
3) Scatter phonons at interfaces (nanoscale composites)

Focus on one approach to # 2 above: Zintl phases
⇒ common characteristic of nearly all good TE matr's is valence balance ⇒ which is why Zintl phases are good candidates!

Zintl phase characteristics:
- valence balance
- mixed bonding (ionic & covalent) (localized!)
- form small band gap semiconductors

- covalent bonding leads to higher mobility of charge carriers than found in purely ionic materials
- combination of bonding leads to complexity

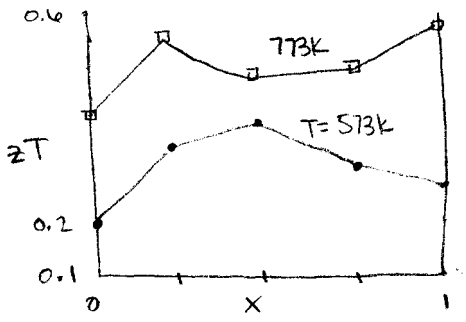
E.g. $Yb_{14}MnSb_{11}$ (structure pg 109)
- contains $[MnSb_4]^{9-}$ tetrahedra
- polyatomic $[Sb_3]^{7-}$ anions
- isolated Sb^{3-} anions & Yb^{2+} cations

→ structure shows zT of almost twice the p-type standard SiGe (@ 900°C (zT ≈ 1) (plot pg 108)

→ these structures may be ideal for another approach of substructuring

E.g. 2: Zintl Compound $Ca_xYb_{1-x}Zn_2Sb_2$ (layered)
(similar structure to Na_xCoO_2 as we discussed last week)
↳ similar concept to CuO layered high T_c - superconductors

→ can fine tune of carrier concentration due to Ca^{2+} doping on Yb^{2+} which is less electropositive
↳ doping also reduces thermal conductivity due to alloying effects but doesn't reduce carrier mobility or effect band gap b/c only on cation lattice
⇒ structure is too simple ; K_e is still too high



Gascoin, et al.