Band Engineering in Thermoelectric Materials Using Optical, Electronic, and Ab-Initio Computed Properties

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2015

(Defense Date: May 11, 2015)

Acknowledgements

I would like to acknowledge many people who helped me along the way during this PhD thesis. First, I would like to thank my lovely wife Gina for loving and supporting me during my time at Caltech. I would also like to thank my Australian cattle dog, Aspen, for understanding that I could not play fetch because I had to do more thermoelectrics research. I would like to thank my family for their support (even from afar) during my PhD.

Professionally, I have many colleagues to thank and acknowledge. Of course the entirety of the Snyder group has been wonderful over the years. I would like to especially thank Yanzhong Pei and Heng Wang (for mentoring me through the band engineering concepts); Nick Heinz, Tristan Day, Wolfgang Zeier, and Hyun Sik Kim (for providing endless entertainment at lunch time); and collaborators and coauthors Yinglu Tang, Hyun Sik Kim, Min Zhou, Wolfgang Zeier, and Jennifer Schmitt. I would like to acknowledge Jeff Snyder for always being willing to talk about a project and being an overall wonderful adviser. I would like to acknowledge the Molecular Materials Research Center (MMRC) in the Beckman Institute at Caltech for allowing use of their optical measurement systems free-of-charge. I would like to acknowledge several collaborators who performed DFT calculations in this thesis including Hyoungchul Kim, Massoud Kaviany (University of Michigan), and Luis Agapito (University of North Texas). I would also like to acknowledge funding and support from the Materials Project; I would like to especially acknowledge useful discussions with Geoffroy Hautier, Anubhav Jain, and Hong Zhu.

Abstract

Thermoelectric materials have demanded a significant amount of attention for their ability to convert waste heat directly to electricity with no moving parts. A resurgence in thermoelectrics research has led to significant enhancements in the thermoelectric figure of merit, zT, even for materials that were already well studied. This thesis approaches thermoelectric zT optimization by developing a detailed understanding of the electronic structure using a combination of electronic/thermoelectric properties, optical properties, and ab-initio computed electronic band structures. This is accomplished by applying these techniques to three important classes of thermoelectric materials: IV-VI materials (the lead chalcogenides), Half-Heusler's (XNiSn where X=Zr, Ti, Hf), and $CoSb_3$ skutterudites.

In the IV-VI materials (PbTe, PbSe, PbS) I present a shifting temperature-dependent optical absorption edge which correlates well to the computed *ab-initio* molecular dynamics result. Contrary to prior literature that suggests convergence of the primary and secondary bands at 400 K, I suggest a higher convergence temperature of 700, 900, and 1000 K for PbTe, PbSe, and PbS, respectively. This finding can help guide electronic properties modelling by providing a concrete value for the band gap and valence band offset as a function of temperature.

Another important thermoelectric material, ZrNiSn (half-Heusler), is analyzed for both its optical and electronic properties; transport properties indicate a largely different band gap depending on whether the material is doped n-type or p-type. By measuring and reporting the optical band gap value of 0.13 eV, I resolve the discrepancy in the gap calculated from electronic properties (maximum Seebeck and resistivity) by correlating these estimates to the electron-to-hole weighted mobility ratio, A, in narrow gap materials (A is found to be approximately 5.0 in ZrNiSn).

I also show that $CoSb_3$ contains multiple conduction bands that contribute to the thermoelectric properties. These bands are also observed to shift towards each other with temperature, eventually reaching effective convergence for T>500 K. This implies that the electronic structure in $CoSb_3$ is critically important (and possibly engineerable) with regards to its high thermoelectric figure of merit.

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List of Symbols and Notation

Fundamental Constants

- e – Fundamental electron charge
- $\hbar$ – Planck's constant (h) divided by 2π
- m_e – Electron rest mass
- k_B – Boltzmann constant
- c – Speed of light

Transport Properties

- V – Voltage
- R– Resistance
- I – Electric Current
- V_H – Hall voltage
- B – Magnetic Field
- n – Carrier concentration (electrons)
- p – Carrier concentration (holes)
- R_H – Hall coefficient
- r_H – Hall factor (n/n_H)
- n_H – Carrier concentration ($\frac{1}{R_H e}$)
- σ – Electrical conductivity ($ne\mu$)
- ρ – Electrical resistivity ($1/\sigma$)
- μ – Carrier drift mobility
- μ_H – Hall Mobility (σR_H)
- τ – Scattering time
- λ – Scattering coefficient (exponent)
- v – Drift velocity of electrons
- S – Seebeck coefficient
- $|S|$ – Thermopower (magnitude of S)
- L – Lorenz number
- κ – Total thermal conductivity
- κ_e – Electronic thermal conductivity ($L\sigma T + \kappa_{bipolar}$)
- $\kappa_{bipolar}$ – Bipolar thermal conductivity
- C_p – Heat capacity (constant pressure)
- d – Density
- D – Thermal diffusivity
- zT –Thermoelectric figure of merit
- $S^2\sigma$ –Thermoelectric power factor
- L^* – Sample dimension

- A^* – Sample cross sectional area
- t – Sample thickness
- α_L – Linear thermal expansion coefficient
- K_B – Bulk modulus

Band Engineering

- v_l – Longitudinal speed of sound
- E_{def} – Deformation potential
- C_l – Average longitudinal elastic moduli ($v_l^2 d$)
- τ_0 – Scattering time prefactor
- μ_0 – Mobility prefactor ($e\tau_0/m_c^*$)
- n_0 – Carrier concentration prefactor
- σ_0 – Conductivity prefactor ($n_0 e\mu_0$)
- m^* – Effective mass
- m_c^* – Conductivity effective mass
- m_d^* – Density of states effective mass
- m_b^* – Single valley effective mass
- m_P^* – Effective mass obtained from electronic momentum
- m_S^* – Effective mass obtained from Seebeck coefficient (single parabolic band)
- $m_\parallel^*$ – Effective mass along the longitudinal ellipsoid direction
- $m_\perp^*$ – Effective mass along the transverse ellipsoid direction
- $\mu_0 {m_S^*}^{3/2}$ – Weighted mobility
- B– Thermoelectric quality factor ($\frac{\mu_0 m_S^{*\frac{3}{2}}}{\kappa_L}$)
- A – Majority-to-minority carrier weighted mobility ratio
- N_v – Valley degeneracy
- N_v^* – Effective valley degeneracy
- K – Ellipsoidal mass anisotropy parameter ($\frac{m_\parallel^*}{m_\perp^*}$)
- K^* – Effective anisotropy parameter
- f – Fermi distribution function
- F_j – Fermi integral of order j
- ${}^nF_l^m$ – Generalized Fermi integral
- E_g – Band gap
- $E_{g,thermal}$ – Thermal band gap
- ΔE – Band offset
- $\mathrm{T_{cvg}}$ – Band convergence temperature
- β – Dimensionless Kane band parameter ($\approx k_B T/E_g$)
- m_0^* – Band edge effective mass (Kane bands)
- P– Kane band interaction matrix element

- $D(E)$ – Density of states
- N_A – Number of acceptors
- N_d – Number of donors
- s_i – Sign of the charge carriers in the i^{th} band
- E – Electron energy
- ϵ – Dimensionless energy (E/k_BT)
- ξ – Chemical potential
- E_F – Fermi level
- η – Dimensionless chemical potential (ξ/k_BT)
- A_k – Fermi surface area
- V_k – Volume enclosed by the Fermi surface

Optical Properties

- $F(R)$ – Kubelka Munk Function, equivalently: $\frac{\alpha}{\widetilde{K}}$
- α – Absorption coefficient
- $\widetilde{K}$ – Scattering coefficient
- ω – Photon frequency
- $\hbar\omega$ – Photon energy
- ϵ_c – Complex dielectric constant ($\epsilon_1 + i\epsilon_2$)
- ϵ_1 – Real dielectric constant
- ϵ_2 – Imaginary dielectric constant
- n_r – Real part of the refractive index
- κ_r – Imaginary part of the refractive index
- $\boldsymbol{E}$ – Electric field
- ω_p – Plasma frequency
- ϵ_∞ – Screening dielectric constant
- $E_{g,opt}$ – Optical band gap
- Δ_{RN} – Band gap renormalization