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

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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 with 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, $\Lambda$, in narrow gap materials ($\Lambda$ 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 ($\hbar = \frac{\hbar}{2\pi}$)
- $m_e$ – 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 ($\frac{1}{R_H e}$)
- $\sigma$ – Electrical conductivity ($ne\mu$)
- $\rho$ – Electrical resistivity ($1 / \sigma$)
- $\mu$ – Carrier drift mobility
- $\mu_H$ – Hall Mobility ($\sigma R_H$)
- $\tau$ – Scattering time
- $\lambda$ – Scattering coefficient (exponent)
- $v$ – Drift velocity of electrons
- $S$ – Seebeck coefficient
- $|S|$ – Thermopower (magnitude of $S$)
- $L$ – Lorenz number
- $\kappa$ – Total thermal conductivity
- $\kappa_e$ – 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
- $\alpha_L$ – 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 ($v_l^2d$)
- $\tau_0$ – Scattering time prefactor
- $\mu_0$ – Mobility prefactor ($e\tau_0/m^*_c$)
- $n_0$ – Carrier concentration prefactor
- $\sigma_0$ – Conductivity prefactor ($n_0e\mu_0$)
- $m^*$ – 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)
- $m^*_{\|}$ – Effective mass along the longitudinal ellipsoid direction
- $m^*_{\perp}$ – Effective mass along the transverse ellipsoid direction
- $\mu_0m^*_S^{3/2}$ – Weighted mobility
- $B$ – Thermoelectric quality factor ($\frac{\mu_0m^*_S^{3/2}}{k_L}$)
- $A$ – Majority-to-minority carrier weighted mobility ratio
- $N_0$ – Valley degeneracy
- $N_0^*$ – Effective valley degeneracy
- $K$ – Ellipsoidal mass anisotropy parameter ($\frac{m^*_S}{m^*_L}$)
- $K^*$ – Effective anisotropy parameter
- $f$ – Fermi distribution function
- $F_j$ – Fermi integral of order $j$
- $\frac{n_P}{F_L^m}$ – Generalized Fermi integral
- $E_g$ – Band gap
- $E_{g,thermal}$ – Thermal band gap
- $\Delta E$ – Band offset
- $T_{cvg}$ – Band convergence temperature
- $\beta$ – Dimensionless Kane band parameter ($\approx k_BT/E_g$)
- $m^*_0$ – Band edge effective mass (Kane bands)
- $P$ – Kane band 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
• $\epsilon$ – Dimensionless energy ($E/k_BT$)
• $\xi$ – Chemical potential
• $E_F$ – Fermi level
• $\eta$ – Dimensionless chemical potential ($\xi/k_BT$)
• $A_F$ – Fermi surface area
• $V_F$ – Volume enclosed by the Fermi surface

Optical Properties

• $F(R)$ – Kubelka Munk Function, equivalently: $\frac{\alpha}{K}$
• $\alpha$ – Absorption coefficient
• $K$ – Scattering coefficient
• $\omega$ – Photon frequency
• $\hbar\omega$ – Photon energy
• $\epsilon_\infty$ – Complex dielectric constant ($\epsilon_1 + i\epsilon_2$)
• $\epsilon_1$ – Real dielectric constant
• $\epsilon_2$ – Imaginary dielectric constant
• $n_r$ – Real part of the refractive index
• $\kappa_r$ – Imaginary part of the refractive index
• $E$ – Electric field
• $\omega_p$ – Plasma frequency
• $\epsilon_\infty$ – Screening dielectric constant
• $E_{g,opt}$ – Optical band gap
• $\Delta_{RN}$ – Band gap renormalization