

# 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 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  $2\pi$
- $m_e$  – 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 ( $v_l^2 d$ )
- $\tau_0$  – Scattering time prefactor
- $\mu_0$  – Mobility prefactor ( $e\tau_0/m_c^*$ )
- $n_0$  – Carrier concentration prefactor
- $\sigma_0$  – 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 ( $\frac{\mu_0 m_s^{*3}}{\kappa_L}$ )
- $A$  – 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
- ${}^n F_l^m$  – 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 ( $\approx k_B T / E_g$ )
- $m_0^*$  – 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  $i^{\text{th}}$  band
- $E$  – Electron energy
- $\epsilon$  – Dimensionless energy ( $E/k_B T$ )
- $\xi$  – Chemical potential
- $E_F$  – Fermi level
- $\eta$  – Dimensionless chemical potential ( $\xi/k_B T$ )
- $A_k$  – Fermi surface area
- $V_k$  – Volume enclosed by the Fermi surface

### Optical Properties

- $F(R)$  – Kubelka Munk Function, equivalently:  $\frac{\alpha}{\tilde{K}}$
- $\alpha$  – Absorption coefficient
- $\tilde{K}$  – Scattering coefficient
- $\omega$  – Photon frequency
- $\hbar\omega$  – Photon energy
- $\epsilon_c$  – 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
- $\mathbf{E}$  – Electric field
- $\omega_p$  – Plasma frequency
- $\epsilon_\infty$  – Screening dielectric constant
- $E_{g,opt}$  – Optical band gap
- $\Delta_{RN}$  – Band gap renormalization