

Type VIII Si based Clathrates: Prospects for Giant Thermoelectric Power Factor

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Supporting Information

Dielectric Constant

The optical properties of a compound can be extracted from the frequency dependent complex dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega) \quad (1)$$

in which $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real and imaginary parts, respectively. The complex dielectric tensor is given by:¹

$$\varepsilon_{ij}(\omega) = \delta_{ij} + \frac{4\pi}{\Omega} \sum_{klm} f_{lm}(k) \frac{r_{lm}^i(k)r_{lm}^j(k)}{\omega_{lm}(k) - \omega} \quad (2)$$

where $\varepsilon_{ij}(\omega)$ is the ij^{th} component of the dielectric tensor, and the $r_{lm}(k)$ are the wave vector dependent position matrix elements, which can be derived from the derivative of the wave function with respect to the three dimensional wave vectors.² The dielectric permittivity describes the response of the electron gas to an electric field when the ions are at their equilibrium positions. It is related to the second derivative of the energy with respect to an electric field.

The real and imaginary parts of the complex dielectric function have been presented in Figure 1. The calculated values of the static and high frequency dielectric constants of Si₄₆-VIII, which were used in the Boltzmann transport equation, are 12.14 and 12.05, respectively.

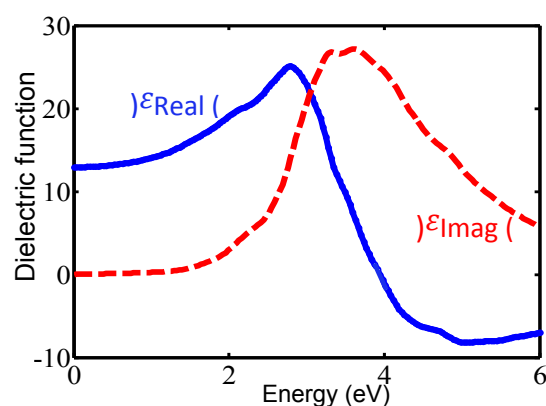


Figure 1: Real (blue curve) and imaginary (dashed red curve) parts of dielectric function for type-VIII clathrate Si₄₆ versus photon energy.

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I. Relaxation times

The scattering processes in a material are taken into account by relaxation times. Various approximations of the relaxation times can be found in the literature.^{3,4} The relaxation times used here incorporate nonparabolicity of the band. The relaxation time for the ionized impurity scattering is given by the standard Brooks-Herring formula:^{3,4}

$$\tau_{ii}^{-1} = \frac{z^2 e^4 n_I}{16\pi\epsilon^2 \sqrt{2m^*}} E^{-3/2} \left[\log \left(1 + \frac{8m^* \lambda_s^2 E}{\hbar^2} \right) - \frac{8m^* \lambda_s^2 E / \hbar^2}{1 + 8m^* \lambda_s^2 E / \hbar^2} \right] \quad (3)$$

where λ_s is the Debye screening length. We used the Thomas-Fermi approximation for the screening length as the following:⁵

$$\frac{1}{\lambda_s^2} = \frac{4\pi e^2 z}{\epsilon_\infty} \int_0^\infty \left(-\frac{\partial f_0}{\partial E} \right) D(E) dE \quad (4)$$

The acoustic phonon scattering rate was calculated based on the effective deformation potential approximation.⁶

The scattering rates for equivalent and non-equivalent valleys for electron transfer from i to j valley are given, respectively, by the following relations:⁴

$$\tau_{iv}^{-1} = \frac{(Z_e - 1)(m_j^*)^{\frac{3}{2}} D_{ij}^2}{\sqrt{2\pi\rho\omega_{ij}} \hbar^3} E_f^{\frac{1}{2}} \times \begin{cases} N & \text{absorption} \\ N + 1 & \text{emission} \end{cases} \quad \text{and} \quad (5)$$

$$E_f = \begin{cases} E + \hbar\omega_{ij} & \text{absorption} \\ E - \hbar\omega_{ij} & \text{emission} \end{cases}$$

and

$$\tau_{iv}^{-1} = \frac{Z_j (m_j^*)^{\frac{3}{2}} D_{ij}^2}{\sqrt{2\pi\rho\omega_{ij}} \hbar^3} [E_f (1 + \alpha_f E_f)]^{\frac{1}{2}} (1 + 2\alpha_f E_f) G_{ij}(E_i, E_f) \times \begin{cases} N \\ N + 1 \end{cases} \quad (6)$$

in which G_{ij} is defined as
$$G_{ij}(E_i, E_f) = \frac{(1 + \alpha_i E_i)(1 + \alpha_f E_f)}{(1 + 2\alpha_i E_i)(1 + 2\alpha_f E_f)}$$
 Z_e , D_{ij} , ω_{ij} , ρ and E_f are the number of equivalent valleys, deformation potential, the phonon frequency which allows the intervalley scattering, density, and Fermi energy, respectively. In case of non-equivalent intervalley scattering, $Z_e - 1$ is replaced by Z_j which is the number of available final valleys for scattering. We assumed similar deformation potential as in silicon for the intervalley scattering. Our calculations showed that the acoustic phonon scattering rate is stronger by orders of magnitude than the intervalley scattering rate. Therefore, even for stronger values of intervalley deformation potential, we expect that the acoustic phonon scattering remains dominant.

The relaxation time τ_{DP} for acoustic phonon scattering according to Ravich is:⁸

$$\tau_0^{-1} = \frac{\pi k_B T D_A^2}{\rho v_s^2 \hbar} D(E), \quad \tau_{ac}^{-1} = \tau_0^{-1} \left\{ \left[1 - \frac{\alpha E}{1 + 2\alpha E} \left(1 - \frac{D_v}{D_A} \right) \right]^2 - \frac{8\alpha E (1 + \alpha E) D_v}{3 (1 + \alpha E)^2 D_A} \right\} \quad (7)$$

where E is the energy relative to the band edge, α is the nonparabolicity parameter, $D(E)$ is the density of states, ρ is the density, v_s is the sound speed, D_A and D_v are the conduction-band and valence-band deformation potentials, respectively. The values of the charge carrier deformational potentials used are listed in Table I. To obtain the total relaxation time, we applied the Matthiessen's rule:³

$$\frac{1}{\tau} = \frac{1}{\tau_{ii}} + \frac{1}{\tau_{iv}} + \frac{1}{\tau_{ac}} \quad (8)$$

II. The main thermoelectric properties

In the following the formulas used in the paper to describe the electrical conductivity, Seebeck coefficient, and electronic thermal conductivity as applied in a multiband model of Boltzmann transport theory. The electrical conductivity and Seebeck coefficient are given by:

$$\sigma = \frac{e^2 (2m_{DOS}^* k_B T)^2}{m_{nx} \pi^2 \hbar^3} \int_{x_f}^{\infty} \left(\frac{-\partial f_0}{\partial x} \right) \tau(x) \frac{(x + \beta x^2)^{3/2}}{1 + 2\beta x} dx \quad (9)$$

and

$$S = -\frac{k_B}{e} \left(\frac{\int_{x_f}^{\infty} \left(\frac{-\partial f_0}{\partial x} \right) \tau(x) x (x + \beta x^2)^{\frac{3}{2}}}{1 + 2\beta x} dx}{\int_{x_f}^{\infty} \left(\frac{-\partial f_0}{\partial x} \right) \tau(x) (x + \beta x^2)^{\frac{3}{2}}}{1 + 2\beta x} dx} - x_{Fermi} \right) \quad (10)$$

$$\left(-\frac{\partial f_0}{\partial E} \right) = \frac{1/k_B T}{e^{\frac{(E - E_F)/k_B T}{2}} + 2 + e^{-\frac{(E - E_F)/k_B T}{2}}} = \frac{1/k_B T}{4 \cosh^2((E - E_F)/2k_B T)} \text{ in which}$$

is the derivative of Fermi-Dirac distribution function, $x = E/k_B T$ is the reduced energy, $\beta = \alpha k_B T$ is the reduced non-parabolicity, and τ is the total scattering time. m_{nx} is the conductivity effective mass.⁷ This procedure can be repeated for each temperature, doping concentration, and different bands allowing all of the thermoelectric properties to be determined over the desired temperature, doping concentration ranges, or for multibands. For the multiband transport model, the effective total electrical conductivity and Seebeck coefficient can be calculated as

$$\sigma_{tot} = \sum_i \sigma_i, \quad S_{tot} = \frac{\sum_i \sigma_i S_i}{\sigma_i} \quad (11)$$

where σ_i and S_i are the electrical conductivity and Seebeck coefficients, respectively, for each individual band. The contribution of the carriers of different bands to the thermal transport is calculated using the Wiedemann-Franz law⁸

$$\kappa_e = \sum_i L_i \sigma_i T \quad (12)$$

, are the Lorentz number, and the electrical $\sigma_i L_i$ is the absolute temperature, and T in which conductivity, for each band. The Lorentz number is known to vary with the carrier concentration especially at low carrier concentrations, where as function of carrier concentration L the free-electron value, so, we calculated

$$L_i = \left(\frac{k_B}{e} \right)^2 \left\{ \frac{2 \zeta^{-3/2}}{1 \zeta^{-1}} - \left[\frac{1 \zeta^{-3/2}}{0 \zeta^{-3/2}} \right]^2 \right\} \quad (13)$$

where we have

$$\zeta_r^n = \int_0^\infty \left(-\frac{\partial f}{\partial x}\right) x^n (x + \beta x^2)^m \tau(x)^k (1 + 2\beta x)^r dx \quad (14)$$

and the summation is achieved over all contributing bands. The bipolar thermal conductivity can be calculated as

$$\kappa_b = \frac{1}{2} T \sum_{i,j} \sigma_i \sigma_j (S_i - S_j)^2 \quad (15)$$

is the Seebeck coefficient. S are the valley indices, and i, j where

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