ELECTRONIC SUPPLEMENTARY INFORMATION

Estimating carrier relaxation times in thermoelectric clathrate materials by combining experimental results and first-principles calculations

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Non-analytical-term or polar correction (-nac)

Non-metallic crystals are polarized (long-range dipole–dipole interaction) by atomic displacements and the generated macroscopic field changes the force constants near the Γ point. This effect is reflected in the non-vanishing Born effective charge tensor Z*, taking the form of a non-analytical contribution $\widetilde{D}_{\alpha\beta}(q \to 0)$ to the dynamical matrix.[1-4]

$$\widetilde{D}_{\alpha\beta}(q \to 0) = \frac{1}{\sqrt{m_j m_j}} \frac{4\pi}{\Omega_0} \frac{\sum_\gamma q_j Z^*_{j,\gamma a} \sum_{\gamma'} q_{j'} Z^*_{j',\gamma'\beta}}{\sum_{\alpha,\beta} q_\alpha \epsilon^\infty_{\alpha\beta} q_\beta}, \tag{S1}$$

where: m_j – is the mass of the atom in the primitive cell, Ω_0 – is the volume of the primitive cell, q – is the phonon wave-vector, $\epsilon^\infty_{\alpha\beta}$ – is the high-frequency dielectric tensor, and Z^* – is the Born effective charge tensor, $\epsilon^\infty_{\alpha\beta}$ and Z^* may be calculated using density-functional perturbation theory[3] (DFPT). The calculated phonon dispersion curves including non-analytical contribution (-nac) are shown in figure S1. For comparison purposes, figure S1 also contains our results without including the non-analytical contribution (not including -nac). One can see from figure S1 that the effects on the phonon dispersion curves due to the inclusion of polar correction are negligible.
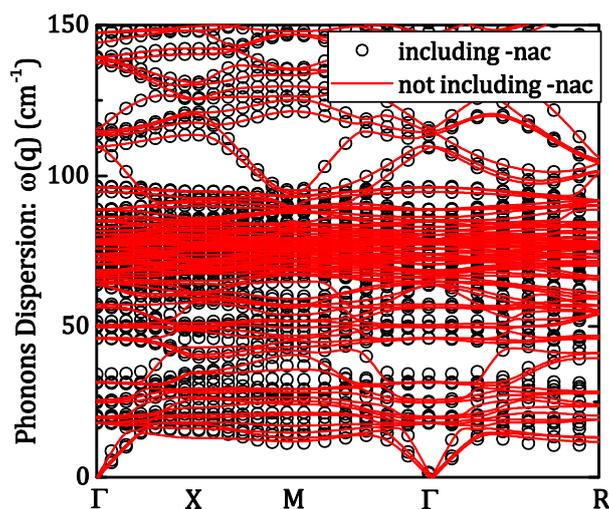
Figure S1: Phonon dispersion curves for $Ba_8Ga_{16}Ge_{30}$ clathrate. Empty symbols show the phonons dispersion curve including the polar correction (-nac).

Quasi-harmonic Approximation

We have employed the so-called quasi-harmonic approximation (QHA) to calculate the Grüneisen parameter (γ) at different temperatures. For solids, γ can be estimated using the equation [5, 6]:

$$\gamma = \frac{\alpha V}{\kappa_T C_V}, \tag{S2}$$

where α is the thermal expansion coefficient, V is the volume, κ_T is the isothermal compressibility, and C_V is the heat capacity at constant volume. Equation (S2) is derived for an isotropic system, i.e., the Helmholtz free energy depends only on the volume, temperature and number of atoms.

To study the thermal properties of solids it is necessary to take into account the effects of atomic thermal vibrations (phonons). The phonon contribution to the Helmholtz free energy is given by [7-9]:

$$F_{phonon} = \frac{1}{2}\sum_{\mathbf{q},\nu} \hbar\omega_{\mathbf{q},\nu}(V) + k_B T \sum_{\mathbf{q},\nu} ln\left[1 - exp\left(-\hbar\omega_{\mathbf{q},\nu}(V)/k_B T\right)\right], \tag{S3}$$

where $\mathbf{q}$ and ν are the wave vector and band index in the Brillouin zone, respectively, $\omega_{\mathbf{q},\nu}(V)$ is the phonon frequency at $\mathbf{q}$ and ν, T is the temperature, k_B, and $\hbar$ are the Boltzmann constant and the reduced Planck constant, respectively.

Within the QHA it is possible to obtain the Gibbs free energy $G(T, P)$ of the system as a function of temperature and pressure.

$$G(T,P) = \min_V\left[U(V) + F_{phonon}(T,V) + PV\right], \tag{S4}$$

where P is the pressure, and $U(V)$ is the total energy from the electronic structure calculations at constant volume. Eq. 4 means that, for each couple of T and P variables, the function inside the square brackets is to be minimized with respect to the volume.

The thermal expansion coefficient α and κ_T can be derived from:

$$\alpha = \frac{1}{V(P,T)}\left(\frac{\partial V(P,T)}{\partial T}\right)_P, \tag{S5}$$

$$\kappa_T = -\frac{1}{V(P,T)}\left(\frac{\partial V(P,T)}{\partial P}\right)_T, \tag{S6}$$

$V(P,T)$ is determined as a function of pressure and temperature by minimizing $G(T,P)$.

The total heat capacity at constant volume can be calculated as:

$$C_V = -T\left(\frac{\partial^2 F_{phonon}}{\partial T^2}\right)_V, \tag{S7}$$

The heat capacity at a constant pressure C_p can be calculated from the previous quantities through thermodynamic relationship and can be computed from,

$$C_p = C_v + T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V\bigg|_{V=V_0(T)}, \tag{S8}$$

Some quantities obtained in QHA are shown in figures S2 (volume at different temperature) and S3 (heat capacity at a constant pressure, C_p). It should be noted that the experimental[10] and calculated values of C_p are in very good agreement.
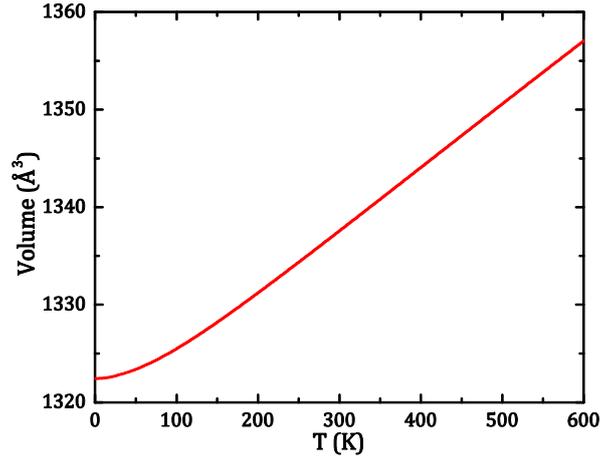
Figure S2: Equilibrium volume of $Ba_8Ga_{16}Ge_{30}$ clathrate as a function of temperature
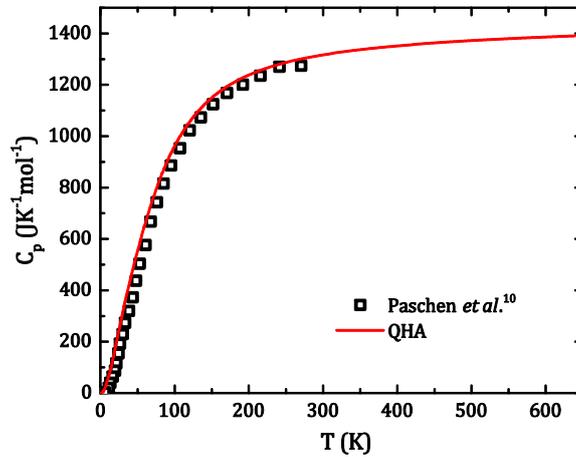
Figure S3: Heat capacities as a function of temperature. The solid curve denotes the calculated Cp of $Ba_8Ga_{16}Ge_{30}$ clathrate. The empty squares depict the experimental values reported in ref. 10

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