

Strong Quartic Anharmonicity and Thermoelectric Performance in Antiperovskites Sr_3XN (X=P, As, Sb, and Bi)

1. method

1.1. Self-Consistent Phonon (SCPH) Theory in ALAMODE

1.1.1. DFT Total Energy

The ground-state total energy functional in DFT is:

$$E_{\text{DFT}}[\rho(\mathbf{r})] = T_s[\rho] + E_{\text{xc}}[\rho] + E_{\text{H}}[\rho] + E_{\text{ion-ion}} \quad (1)$$

1.1.2. Second-Order IFCs

$$\Phi_{\alpha\beta}^{(2)}(l, l') = \frac{\partial^2 E}{\partial u_{\alpha}(l) \partial u_{\beta}(l')} \quad (2)$$

1.1.3. Dynamical Matrix

$$D_{\alpha\beta}(\mathbf{q}) = \sum_{l'} \frac{\Phi_{\alpha\beta}^{(2)}(0, l')}{\sqrt{m_0 m_{l'}}} e^{i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_{l'})} \quad (3)$$

1.1.4. Self-Consistent Phonon (SCPH) Equation

$$\tilde{\omega}^2(q, s) = \omega^2(q, s) + 2\Pi(q, \omega) \quad (4)$$

1.1.5. One-Loop Self-Energy

$$\Pi^{(2)}(q, s) = \sum_{q', s'} \frac{|V_{qq'ss'}|^2}{\omega(q') + \omega(q'')} \quad (5)$$

1.2. SCP in ShengBTE

SCP calculations at finite temperatures were executed to acquire anharmonic phonon frequencies and their corresponding eigenvectors. These computations made use of Interatomic Force Constants (IFCs) derived under both harmonic and anharmonic conditions at 0 K. Temperature-dependent anharmonic frequencies, denoted as $\Omega_{qj}(T)$. $|Q_{q'}^* Q_{q'}\rangle = [\frac{\hbar}{2\Omega_{q'}}][1 + 2n(\Omega_{q'})]$

With the inclusion of four-phonon scattering, Δ_λ represents zeroth-order in iterations computed as:

$$\begin{aligned}
\Delta_\lambda = & \frac{1}{N} \sum_{\lambda'\lambda''}^{(+)} \Gamma_{\lambda\lambda'\lambda''}^{(+)} (\xi_{\lambda\lambda''} \mathbf{F}_{\lambda''} - \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'}) \\
& + \frac{1}{N} \sum_{\lambda'\lambda''}^{(-)} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''}^{(-)} (\xi_{\lambda\lambda''} \mathbf{F}_{\lambda''} + \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'}) \\
& + \frac{1}{N} \sum_{\lambda'\lambda''\lambda'''}^{(++)} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(++)} (\xi_{\lambda\lambda'''} \mathbf{F}_{\lambda'''} - \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'} - \xi_{\lambda\lambda''} \mathbf{F}_{\lambda''}) \\
& + \frac{1}{N} \sum_{\lambda'\lambda''\lambda'''}^{(+-)} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(+-)} (\xi_{\lambda\lambda'''} \mathbf{F}_{\lambda'''} - \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'} - \xi_{\lambda\lambda''} \mathbf{F}_{\lambda''}) \\
& + \frac{1}{N} \sum_{\lambda'\lambda''\lambda'''}^{(--)} \frac{1}{2} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(--)} (\xi_{\lambda\lambda'''} \mathbf{F}_{\lambda'''} - \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'} - \xi_{\lambda\lambda''} \mathbf{F}_{\lambda''}) \\
& + \frac{1}{N} \sum_{\lambda'}^{(iso)} \Gamma_{\lambda\lambda'}^{(iso)} \xi_{\lambda\lambda'} \mathbf{F}_{\lambda'}
\end{aligned} \tag{6}$$

$$\begin{aligned}
\frac{1}{\tau_\lambda^0} = & \frac{1}{N} \left(\sum_{\lambda'\lambda''}^{(+)} \Gamma_{\lambda\lambda'\lambda''}^{(+)} + \frac{1}{2} \sum_{\lambda'\lambda''}^{(-)} \Gamma_{\lambda\lambda'\lambda''}^{(-)} \right) + \frac{1}{N} \sum_{\lambda'}^{(iso)} \Gamma_{\lambda\lambda'}^{(iso)} \\
& + \frac{1}{N} \left(\frac{1}{2} \sum_{\lambda'\lambda''\lambda'''}^{(++)} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(++)} + \frac{1}{2} \sum_{\lambda'\lambda''\lambda'''}^{(+-)} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(+-)} + \frac{1}{6} \sum_{\lambda'\lambda''\lambda'''}^{(--)} \Gamma_{\lambda\lambda'\lambda''\lambda'''}^{(--)} \right)
\end{aligned} \tag{7}$$

The scattering rate of an electron, transitioning from its initial state $n\mathbf{k}$, where n represents the band index, and $\mathbf{k}$ denotes the wave vector, to its

final state $m\mathbf{k} + q$, is quantified by Fermi's golden rule, as follows:

$$\tau_{n\mathbf{k} \rightarrow m\mathbf{k}+q}^{-1} = \frac{2\pi}{\hbar} |g_{nm}(\mathbf{k}, q)|^2 \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+q}) \quad (8)$$

where $\hbar$ represents the reduced Planck's constant, ε signifies the electron energy, δ corresponds to the Dirac delta function, and g stands for the coupling matrix element. Generally, the influence of various scattering mechanisms is encapsulated by the coupling matrix element

$$g_{nm}^{ad}(\mathbf{k}, q) = \sqrt{\mathbf{k}_B T} \sum_{G \neq -q} \left[\frac{\tilde{D}_{n\mathbf{k}} : \tilde{\mathbf{S}}_l}{c_l \sqrt{\rho}} + \frac{\tilde{D}_{n\mathbf{k}} : \tilde{\mathbf{S}}_{t_1}}{c_{t_1} \sqrt{\rho}} + \frac{\tilde{D}_{n\mathbf{k}} : \tilde{\mathbf{S}}_{t_2}}{c_{t_2} \sqrt{\rho}} \right] \langle m\mathbf{k} + \mathbf{q} | e^{i(q+G) \cdot r} | n\sqrt{k} \rangle \quad (9)$$

$$g_{nm}^{pi}(\mathbf{k}, q) = \sqrt{\mathbf{k} T} \sum_{G \neq -q} \left[\frac{\tilde{n}h : \tilde{S}_l}{c_l \sqrt{\rho}} + \frac{\tilde{n}h : \tilde{S}_{t_1}}{c_{t_1} \sqrt{\rho}} + \frac{\tilde{n}h : \tilde{S}_{t_2}}{c_{t_2} \sqrt{\rho}} \right] \frac{\langle m\mathbf{k} + q \rangle | e^{i(\mathbf{q}+\mathbf{G}) \cdot r} | n\mathbf{k} \rangle}{|\mathbf{q} + \mathbf{G}|} \quad (10)$$

$$g_{nm}^{po}(\mathbf{k}, q) = \sqrt{\hbar \omega_{po}/2} \sum_{G \neq -q} \left(\frac{1}{\tilde{n} \cdot \epsilon_{\infty} \cdot \tilde{n}} - \frac{1}{\tilde{n} \cdot \epsilon_s \cdot \tilde{n}} \right)^{1/2} \times \frac{\langle m\mathbf{k} + q | e^{i(q+G) \cdot r} | n\mathbf{k} \rangle}{|\mathbf{q} + \mathbf{G}|} \quad (11)$$

$$g_{nm}^{ii}(\mathbf{k}, q) = \sum_{G \neq -q} \frac{n_{ii}^{1/2} Z e}{\tilde{n} \cdot \epsilon_s \cdot \tilde{n}} \frac{m\mathbf{k} + \mathbf{q} | e^{i(q+G) \cdot r} | n\mathbf{k}}{|\mathbf{q} + \mathbf{G}|^2 + \beta^2} \quad (12)$$

Several scattering mechanisms play pivotal roles in the electron scattering rate, including acoustic deformation potential scattering (g_{nm}^{ad}), scattering by acoustic phonons through the piezoelectric interaction (g_{nm}^{pi}), polar optical phonon scattering (g_{nm}^{po}), and scattering from fully ionized impurities (g_{nm}^{ii}). Here, $\tilde{D}_{n\mathbf{k}} = D_{n\mathbf{k}} + v_{n\mathbf{k}} \otimes v_{n\mathbf{k}}$. The symbols l , t_1 , and t_2 pertain to properties related to longitudinal and transverse modes. $\tilde{n}$ is a unit vector in the direction of scattering, calculated as $(\mathbf{q} + \mathbf{G})/|\mathbf{q} + \mathbf{G}|$; ϵ_s and ϵ_{∞} refer to the static and high-frequency dielectric tensors, respectively; Z denotes the charge state of the impurity center; e is the elementary electron charge; n_{ii} represents the concentration of ionized impurities, calculated as $(n_h - n_e)/Z$; and β is the reciprocal screening length. In 3ph and 4ph scattering processes, specific wave vector relationships, such as $q'' = q \pm q' + Q$ and $q''' = q \pm q' \pm q'' + Q$, where Q represents a reciprocal lattice vector, come into play. The scattering probability matrices

$$\Lambda_{\pm} = \frac{\pi \hbar}{4N} |V_{\pm}^{(3)}|^2 \Delta_{\pm} \frac{\delta(\omega_{\lambda} \pm \omega_{\lambda'} - \omega_{\lambda''})}{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''}} \quad (13)$$

$$\Lambda_{\pm\pm} = \frac{\pi\hbar}{4N} \frac{\hbar}{2N} |V_{\pm\pm}^{(4)}|^2 \Delta_{\pm\pm} \frac{\delta(\omega_\lambda \pm \omega_{\lambda'} \pm \omega_{\lambda''} - \omega_{\lambda'''}).}{\omega_\lambda \omega_{\lambda'} \omega_{\lambda''} \omega_{\lambda'''}} \quad (14)$$

$$\Lambda_{iso} = \frac{\pi}{2N} \omega_\lambda \omega_{\lambda'} \sum_b^n g_b |e_b^\lambda \cdot e_b^{\lambda'*}|^2 \delta(\omega_\lambda - \omega_{\lambda'}) \quad (15)$$

are given by the Fermi's golden rule. N is the total number of k points or primitive cells. the Kronecker deltas $\Delta_\pm$ and $\Delta_{\pm\pm}$ describe the momentum selection rule. The matrix elements V are given by the Fourier transformation of force constants, or transition probability matrices:

$$V_{\lambda\lambda'\lambda''}^{(\pm)} = \sum_{ijk} \sum_{\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} \frac{e_\alpha^\lambda(i) e_\beta^{\pm\lambda'}(j) e_\gamma^{-\lambda''}(k)}{\sqrt{M_i M_j M_k}} e^{\pm i q' \cdot r_j} e^{-i q'' \cdot r_k} \quad (16)$$

$$V_{\lambda\lambda'\lambda''\lambda'''}^{(\pm\pm)} = \sum_{ijkl} \sum_{\alpha\beta\gamma\theta} \Phi_{ijkl}^{\alpha\beta\gamma\theta} \frac{e_\alpha^\lambda(i) e_\beta^{\pm\lambda'}(j) e_\gamma^{\pm\lambda''}(k) e_\theta^{-\lambda'''}(l)}{\sqrt{M_i M_j M_k M_l}} e^{\pm i q' \cdot r_j} e^{-i q'' \cdot r_k} e^{-i q''' \cdot r_l} \quad (17)$$

2. mechanical stability

For cubic APVs, there are three independent elastic constants: C_{11} , C_{12} , and C_{44} , as follow:

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \quad (18)$$

3. results

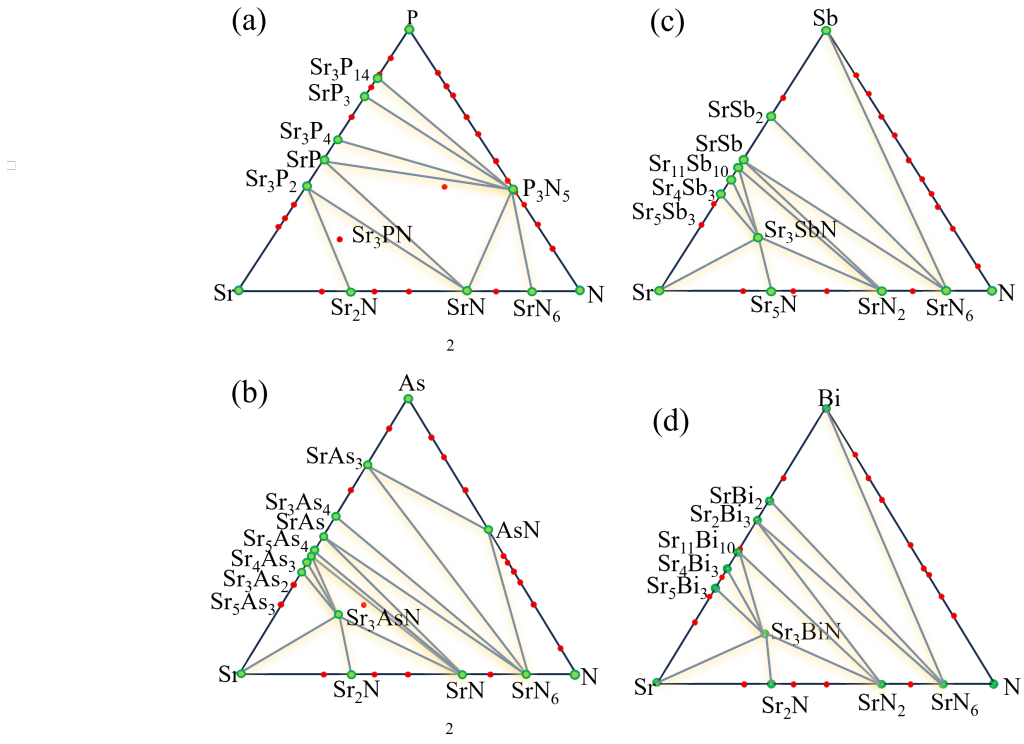


Figure S1: OQMD Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

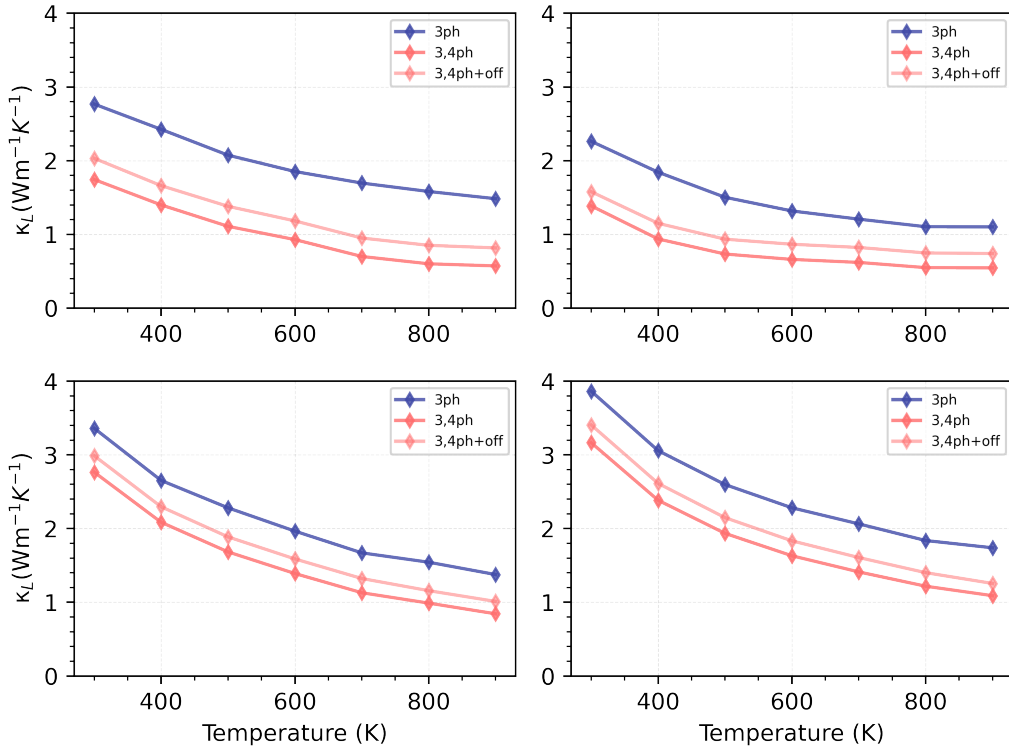


Figure S2: The temperature-dependent κ_L including off-diagonal terms for Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

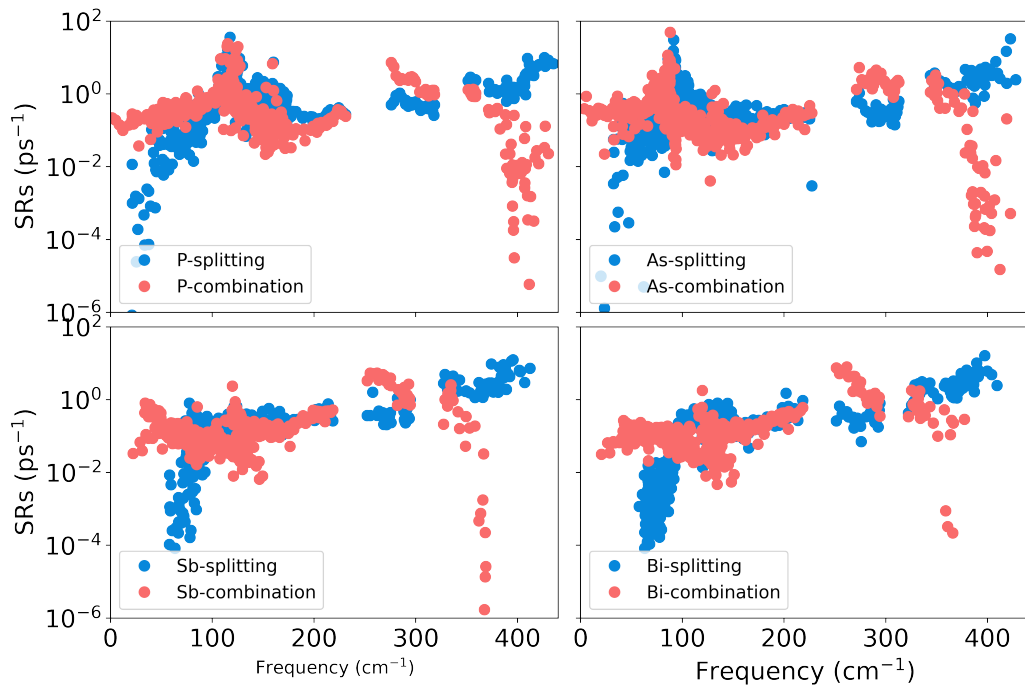


Figure S3: Decomposed 3ph SRs into slitting and combination process for Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

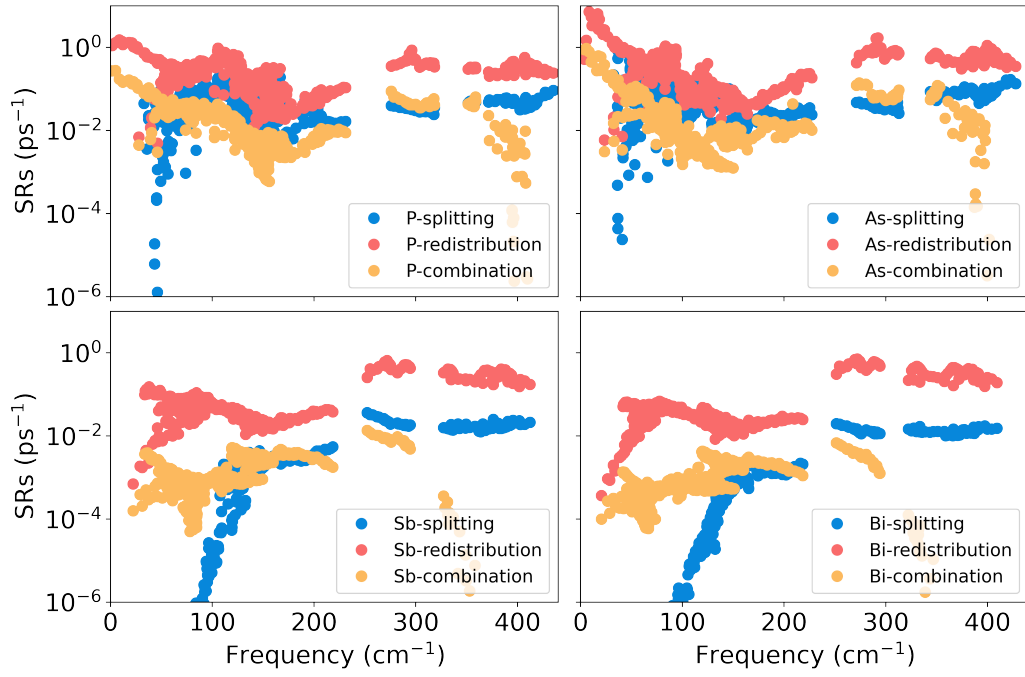


Figure S4: Decomposed 4ph SRs into splitting, redistribution and combination process for Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

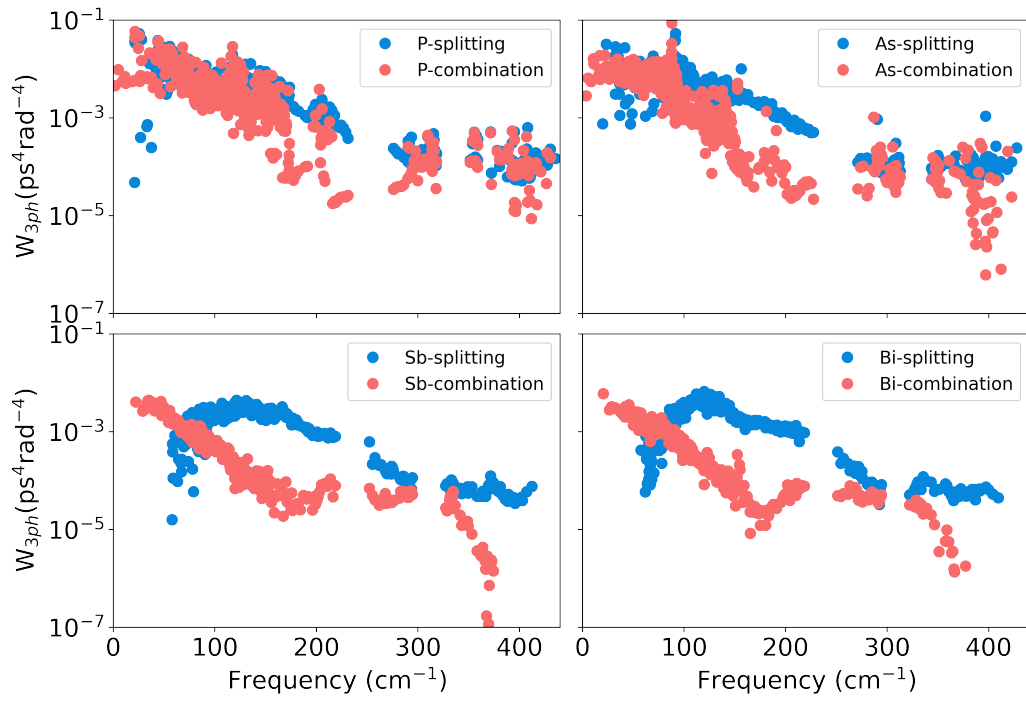


Figure S5: 3ph scattering phase spaces including splitting and combination process for Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

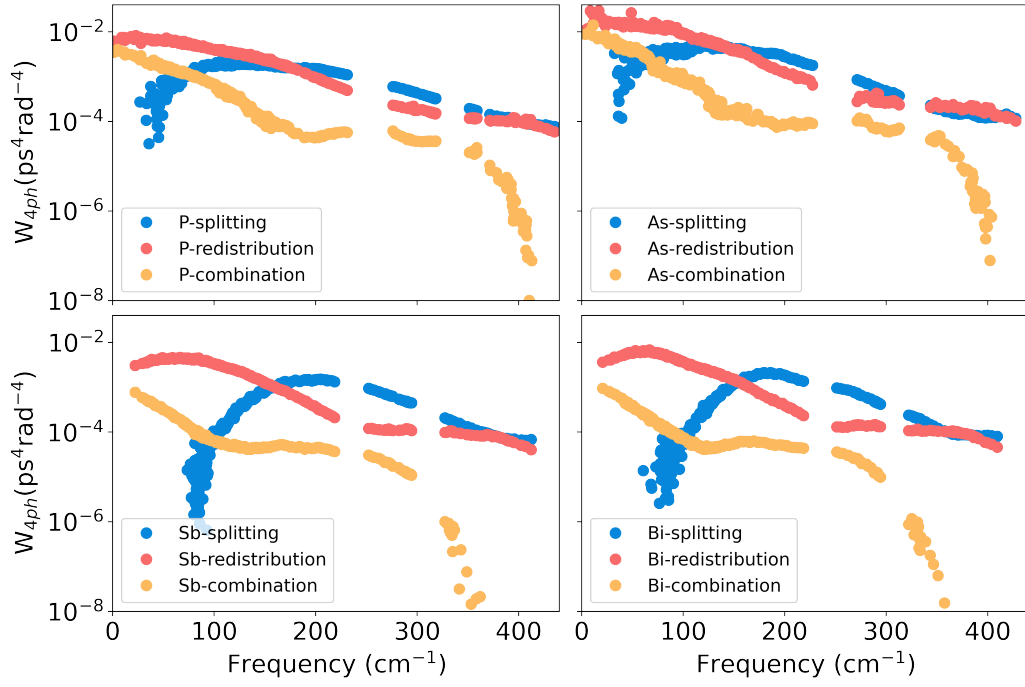


Figure S6: 4ph scattering phase spaces including splitting and combination process for Sr_3PN , Sr_3AsN , Sr_3SbN and Sr_3BiN .

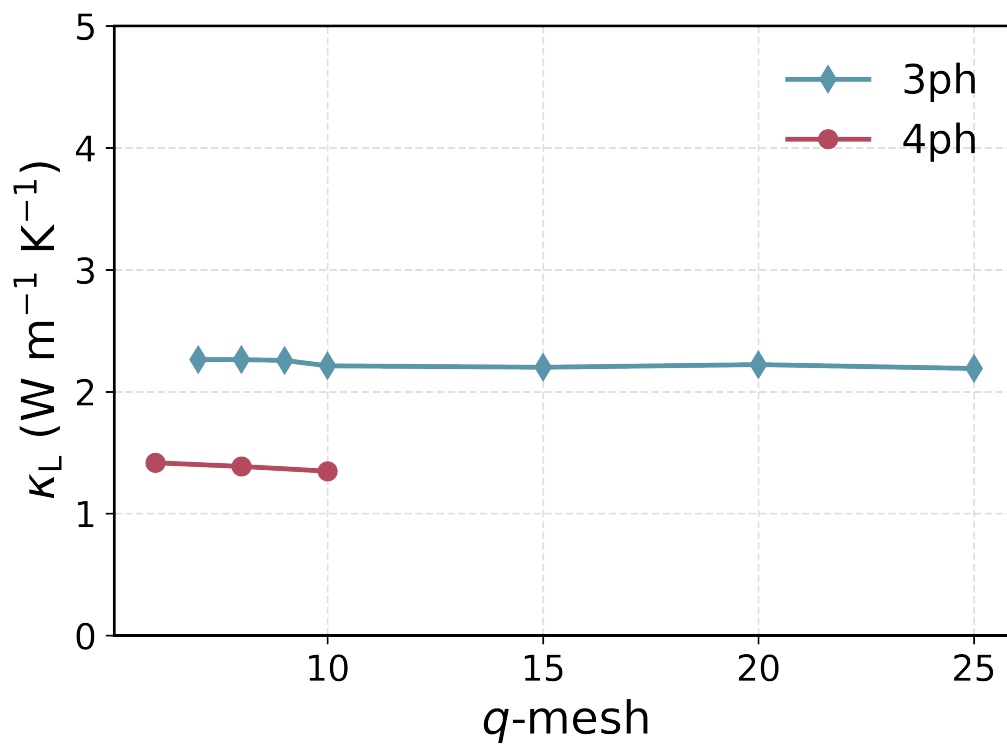


Figure S7: Convergence test of q mesh in BTE calculation.