

Higher-Order-Phonon Scattering Governs Targeted Control of Heat Conduction in Bulk Boron Arsenide

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Abstract

Here, using boron arsenide (BAs) as a physically motivated case study, we reveal the role of higher-order phonon scattering in thermal conductivity modulation through targeted phonon excitation. Using first-principles calculations and phonon Boltzmann transport analysis, it is found that targeted phonon excitation induces strongly frequency-dependent thermal-conductivity responses in bulk BAs. Within the three-phonon-only framework, the modulation effect at 300 K is weak, with only marginal enhancement tendencies observed when exciting phonons in a narrower frequency range of about 6.4~7.0 THz. However, in the combined three- and four-phonon scatterings, the response is changed toward suppressive modulation. The strongest suppression occurs at 20.5 THz, with κ/κ_0 dropping to 0.828 and 0.415 for occupation multipliers of 5 and 25, respectively. The scattering-rate analysis reveals that four-phonon scattering elevates the intrinsic scattering background and enhances population-modification-induced scattering of low-frequency heat-carrying phonons. Furthermore, comparing 300 K and 100 K shows that lowering temperature weakens the contribution of four-phonon scattering and partially restores three-phonon-like modulation features. These findings provide mechanistic insight into the role of higher-order phonon scattering in targeted phonon-population control of bulk BAs and advance the understanding of phonon-based thermal modulation in bulk anharmonic materials.

Keywords: thermal conductivity modulation, targeted phonon excitation, boron arsenide, higher-order phonon scattering, four-phonon scattering, phonon engineering

Introduction

Thermal conductivity, which quantifies the ability of a material to conduct heat, plays a vital role in numerous technological applications^[1-4]. Materials with high thermal conductivity, such as graphene and boron nitride, are ideal for heat dissipation in electronic devices^[5], whereas low thermal conductivity is crucial for achieving high thermoelectric figure of merit (zT) and energy conversion efficiency^[6-8]. The capability to precisely modulate thermal conductivity is therefore essential for addressing these contrasting demands.

Conventional strategies for tuning thermal conductivity^[9-14] including nanostructuring^[15-17], doping^[18-20], introducing disorder^[21-23], and applying strain^[24,25] primarily rely on manipulating phonon transport through structural modifications. For instance, Wan et al. minimized the thermal conductivity of graphene nanoribbons through resonance-hybridized nanopillar designs that optimize phonon transport^[26], while Chen et al. significantly enhanced polyethylene thermal conductivity via stretch-induced polymer chain alignment^[27]. Although effective, these methods typically induce irreversible structural changes, preventing dynamic and reversible thermal modulation. Consequently, there is a pressing need for thermal conductivity control mechanisms that preserve intrinsic material structure.

Recently, targeted phonon excitation has emerged as a promising strategy for modulating thermal transport by selectively perturbing phonon populations, scattering, and mode coupling without introducing permanent structural changes^[28-31]. In two-dimensional materials, this idea has already shown remarkable potential: graphene exhibits a 28% enhancement or 49% suppression in thermal conductivity^[30], while hexagonal boron nitride (hBN) shows tunability ranging from 30% enhancement to 60% suppression^[28]. In parallel, terahertz phonon engineering in van der Waals heterostructures has further highlighted the unusual ability of low-dimensional systems to generate, manipulate, and confine nonequilibrium phonon excitations^[29].

Experimental studies have also begun to demonstrate the feasibility of selective phonon control; for example, direct terahertz excitation of low-energy phonons was shown to prolong hot-carrier cooling in halide perovskites^[31], and intense terahertz pulses were found to excite a Raman-active A_{1g} phonon in bismuth^[32]. These advances collectively suggest that targeted phonon excitation provides a fundamentally new route for in situ control of heat transport beyond conventional structure-modification strategies. However, extending this strategy to three-dimensional bulk crystals requires the consideration of richer phonon scattering phase space and coupling pathways associated with the full three-dimensional Brillouin zone.

Boron arsenide (BAs), with an ultrahigh thermal conductivity^[33-36] and weak anharmonicity, provides a physically motivated case study for examining thermal conductivity modulation response to targeted phonon excitation in bulk materials. Unlike many conventional bulk crystals in which three-phonon (3ph.) scattering usually dominates thermal resistance and higher-order scattering is often a minor correction, BAs has a strongly restricted three-phonon scattering phase space associated with its large acoustic–optical phonon gap. As a result, four-phonon (4ph.) scattering contributes appreciably to phonon relaxation and can substantially modify its thermal conductivity. This unusual balance between weak three-phonon scattering and non-negligible four-phonon scattering makes BAs a suitable system for investigating how higher-order anharmonicity influences targeted phonon-population control within this material.

This work takes bulk boron arsenide (BAs) as a physically motivated case study to investigate how higher-order phonon scattering influences thermal conductivity modulation response to targeted phonon excitation in bulk materials. Based on first-principles calculations and phonon Boltzmann transport analysis, we first map out the frequency-dependent modulation behavior of thermal conductivity in BAs at room temperature within both the three-phonon-only and the combined three-phonon plus four-phonon scatterings. By comparing these two frameworks, we reveal how four-

phonon scattering alters the thermal-transport response from weak modulation with marginal enhancement tendencies to predominantly suppressive behavior. In addition, the temperature dependence modulation is examined by comparing the results at 300 K and 100 K. Finally, the microscopic origin of the modulation is analyzed from the perspective of intrinsic scattering background and population-modification-induced scattering enhancement of low-frequency heat-carrying phonons.

Methods

First-principles calculations were performed using density functional theory (DFT) with the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP)^[37,38]. The calculations used for the initial phonon-property benchmark employed the corresponding DFT settings to obtain the structural and harmonic properties of BAs. The lattice constants and internal atomic positions were fully relaxed until atomic forces were below 1×10^{-9} eV/Å. The optimized lattice constant of BAs is 4.742 Å, consistent with the experimental value of 4.777 Å^[35,39].

The crystal structure and a set of interatomic force constants (IFCs), including the second-, third-, and fourth-order terms, are obtained based on first-principles calculations using the PBEsol functional in a previous work^[40]. These were adopted for the phonon and thermal properties calculations. For the direct comparison between the three-phonon-only (3ph.-only) and combined three-phonon plus four-phonon (3ph.+4ph.), the same BAs crystal structure and consistent IFCs were used.

The three-phonon lattice thermal conductivity was calculated by iteratively solving the linearized phonon Boltzmann transport equation (BTE) using ShengBTE^[40,41]. A Γ -centered $30 \times 30 \times 30$ q-mesh was used. The q-mesh convergence was evaluated by comparing the intrinsic thermal conductivity obtained with increasingly dense q-point samplings, and a relative variation below 1% upon further refinement was adopted as the convergence criterion.

Because four-phonon scattering plays an important role in BAs^[42,43], the targeted-excitation calculations were further extended to the combined three-phonon plus four-phonon framework using the open-source FourPhonon package^[40], which is implemented as an extension of ShengBTE^[41]. In these calculations, the three-phonon contribution was treated through the iterative solution of the linearized BTE, whereas the four-phonon scattering contribution was incorporated through the diagonal term within the single-mode relaxation time approximation (SMRTA), following the implementation of the FourPhonon framework.

A customized script was developed based on the ShengBTE/FourPhonon package to implement targeted phonon excitation by modifying distributions of phonons in selected frequency windows, while the thermal conductivity calculations themselves were performed within the original semi-classic BTE framework implemented by ShengBTE/FourPhonon package^[40].

The lattice thermal conductivity was evaluated within the phonon BTE using ShengBTE package^[40,41]. The expression is given by

$$\kappa_l^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0(f_0 + 1) (\hbar \omega_{\lambda})^2 v_{\lambda}^{\alpha} v_{\lambda}^{\beta} \tau_{\lambda} \quad (1)$$

where k_B is the Boltzmann constant, Ω is the volume of the unit cell, T is the absolute temperature, N is the number of q-points sampling the Brillouin zone, f_0 is the Bose-Einstein distribution function $f_0(\omega_{\lambda}) = \frac{1}{\exp(\hbar \omega_{\lambda}/k_B T) - 1}$, $\hbar$ is the reduced Planck constant, ω_{λ} is the angular frequency of phonon mode λ , v_{λ}^{α} and v_{λ}^{β} are the group velocity components of phonon mode λ along the α and β directions, respectively, and τ_{λ} is the lifetime of phonon mode λ . For calculations including four-phonon scattering, the three-phonon contribution was retained in the iterative BTE solution, while the four-phonon scattering contribution was incorporated through the diagonal relaxation term within the single-mode relaxation time approximation (SMRTA), following the implementation of the FourPhonon framework. The total

scattering rate was determined according to Matthiessen's rule as

$$\tau_{\lambda}^{-1} = \tau_{\lambda,3ph}^{-1} + \tau_{\lambda,4ph}^{-1} + \tau_{\lambda,iso}^{-1} \quad (2)$$

where $\tau_{\lambda,3ph}^{-1}$, $\tau_{\lambda,4ph}^{-1}$ and $\tau_{\lambda,iso}^{-1}$ denote the scattering rates arising from three-phonon, four-phonon, and isotope scattering, respectively. The four-phonon contribution was further written as

$$\tau_{\lambda,4ph}^{-1} = \tau_{\lambda,(++)}^{-1} + \tau_{\lambda,(+-)}^{-1} + \tau_{\lambda,(--)}^{-1} \quad (3)$$

where $(++)$, $(+-)$, and $(--)$ represent the recombination, redistribution, and splitting channels of four-phonon scattering, respectively.

Targeted phonon population modification was modeled as a prescribed modification of the population of selected phonon modes rather than a direct simulation of a specific transient excitation process. For phonon modes within the targeted frequency window W , the reference nonequilibrium population was defined as

$$n_{\lambda}^* = \begin{cases} N n_{\lambda}^0, & \lambda \in W \\ n_{\lambda}^0, & \lambda \notin W \end{cases} \quad (4)$$

where n_{λ}^0 represents the equilibrium Bose–Einstein population at temperature T_0 , W denotes the selected frequency window with a width of 0.1 THz, and N is a dimensionless occupation multiplier used to parameterize the population enhancement of selected phonon modes.

Note that the occupation multiplier N is introduced as a controlled parameter to study how a prescribed mode-selective nonequilibrium population modifies phonon scattering and thermal transport. It does not represent an experimental pump fluence, electric-field strength, pulse energy, or lattice temperature.

Within the phonon transport calculation, the total phonon population was considered as

$$n_{\lambda} = n_{\lambda}^* + \delta n_{\lambda} \quad (5)$$

where n_{λ}^* represents the prescribed driven nonequilibrium reference population and δn_{λ} denotes the small deviation induced by the temperature gradient during thermal transport. In this formulation, n_{λ}^* is treated as a prescribed driven reference population assumed to be maintained by an external source, and the linearization is applied only to the temperature-gradient-induced perturbation δn_{λ} around this reference state. Therefore, the present approach does not describe the formation or transient relaxation of the modified phonon population. Instead, it evaluates the thermal-conductivity response in a steady-state simulation with prescribed modification of selected phonon populations.

The thermal conductivity was recalculated within the same transport framework using the modified phonon population. This treatment is intended to investigate how higher-order phonon scattering affects the thermal-conductivity response in steady-state simulations with prescribed targeted phonon excitation, rather than to describe the complete formation, relaxation, or pump–probe dynamics of nonequilibrium phonons. The applicability of this framework relies on the validity of the phonon quasiparticle picture and on the assumption that the external driving modifies the selected phonon populations without substantially altering the underlying atomic interactions.

Because direct 3ph.+4ph. calculations for every targeted-excitation case were computationally prohibitive, we further employed the sampling and maximum-likelihood-estimation (sampling-MLE)^[44] approach to accelerate the evaluation of phonon scattering rates and the resulting thermal conductivity. In this approach, a subset of three-phonon and four-phonon scattering processes was sampled for each phonon mode, and the corresponding modal scattering rates were directly estimated under RTA instead of exhaustively enumerating all allowed scattering processes. A Γ -centered $16 \times 16 \times 16$ q-mesh was used for the 3ph.+4ph. calculations, and its convergence was examined as described in the Supplementary Information.

Results and Discussion

The harmonic phonon properties of bulk BAs, including the phonon dispersion and density of states (DOS), were first examined to identify suitable frequency ranges for targeted phonon excitation. As shown in Fig. 1a, our calculated phonon dispersion shows good consistency with previously reported theoretical and experimental results^[34,43]. The phonon dispersion exhibited an obvious band gap spanning approximately 10 to 19 THz. Correspondingly, the phonon DOS showed a dominant distribution over low-frequency acoustic and high-frequency optical modes. This band gap not only reduced the phonon group velocity by compressing the phonon bands, but also reduced the coupling pathways between acoustic and optical branches by limiting the available phonon scattering phase space. These results suggested that 0–10 THz and 19–22 THz were candidate frequency domains for targeted phonon excitation.

To identify the phonon modes that dominate equilibrium thermal transport, the phonon scattering rates and the spectral thermal conductivity $\kappa(\omega)$ were further calculated at 300 K. As shown in Fig. 1b, the scattering rates of low-frequency acoustic phonons were significantly lower than those of high-frequency optical phonons, indicating weaker scattering and thus longer phonon lifetimes of acoustic phonons. Consequently, the spectral thermal conductivity shown in Fig. 1c was dominated by low-frequency acoustic phonons, with a pronounced peak in the range of 4–8 THz, whereas the direct contribution of optical phonons was negligible. These results indicate that low-frequency acoustic phonons dominate the equilibrium heat transport in bulk BAs. However, high-frequency optical phonons can still participate in anharmonic scattering processes and may influence thermal transport responses under targeted phonon excitation. The large acoustic–optical phonon gap also gives BAs an unusual scattering hierarchy compared with many conventional bulk crystals. The restricted three-phonon scattering phase space leaves higher-order four-phonon processes with a non-negligible contribution to phonon relaxation, making BAs a suitable system for examining how higher-order phonon scattering influences targeted

phonon-population control within this material.

In addition, the intrinsic thermal conductivity of bulk BAs at 300 K is calculated to be 2302 W/(m·K) in considering 3ph.-only, while it decreases to 1220 W/(m·K) when four-phonon scattering is further included. This significant reduction directly indicates the important role of four-phonon scattering in phonon transport in BAs and further justifies the separate analyses based on the 3ph.-only and 3ph.+4ph. scatterings in the following sections.

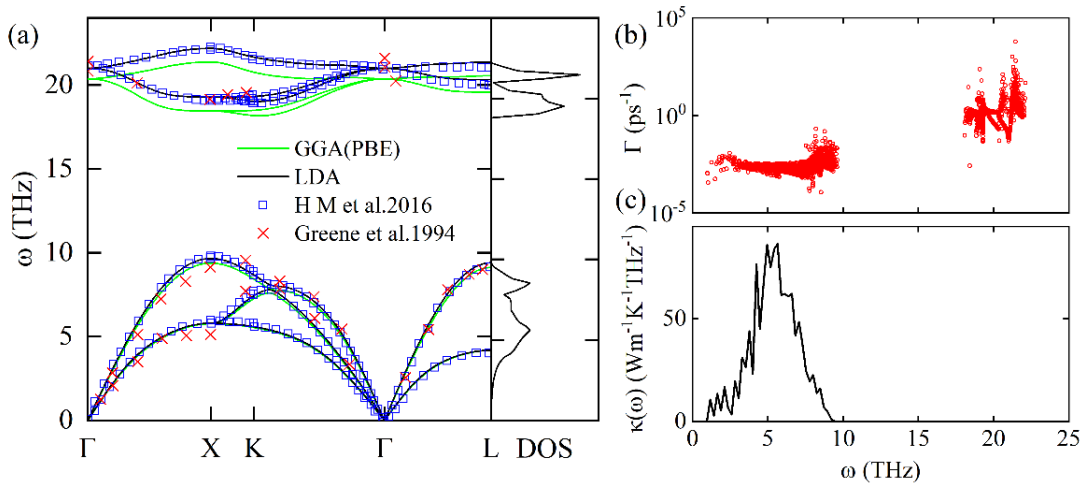


Figure 1 (a) Phonon dispersion relations and density of states of bulk BAs in the equilibrium state. (b) Phonon scattering rates. (c) Spectral thermal conductivity of BAs at 300K.

After obtaining the dominant phonon modes, they are successively excited for thermal conductivity modulation. Firstly, the thermal conductivity of bulk BAs at 300 K was examined under targeted phonon excitation with solely considering three-phonon scatterings across the accessible phonon frequency range. In each calculation, only phonons within a 0.1 THz-wide frequency window were excited, while all other phonon modes retained their intrinsic distribution. Two excitation intensities, namely 5 and 25, were considered, and the modulation effect was quantified by the relative thermal conductivity, κ/κ_0 .

As shown in Fig. 2a, targeted phonon excitation with considering 3ph.-only

produced weak frequency-dependent modulation with narrow enhancement and suppression regions. Over most of the scanned spectrum, the modulation remained limited in magnitude, but distinct enhancement and suppression windows could still be identified. In particular, the response near the upper edge of the acoustic branches, approximately in the 6–9 THz range, was especially sensitive to the occupation multiplier. At an occupation multiplier of 5, a slight enhancement appeared around 8.3–8.9 THz, where κ/κ_0 slightly exceeded 1. When the occupation multiplier was increased to 25, this enhancement was no longer retained in the same frequency range, and the modulation there became suppressive. Meanwhile, a weak enhancement survived only in a narrower frequency range of about 6.4~7.0 THz, where κ/κ_0 reached approximately 1.02. Considering the limited magnitude of this increase, it is interpreted as a marginal enhancement tendency rather than a robust thermal-conductivity enhancement.

These results show that, with considering three-phonon-only, targeted phonon excitation produces weak frequency-dependent modulation, where the response sign and magnitude depend on both the targeted frequency and the occupation multiplier.

Since the intrinsic thermal conductivity is substantially reduced from 2302 W/(m·K) with 3ph.-only to 1220 W/(m·K) with 3ph.+4ph., four-phonon scattering is expected to play an important role in the targeted phonon-population-modification response of bulk BAs^[36,42]. Therefore, the same frequency-dependent excitation calculations were further performed within the combined three-phonon plus four-phonon scatterings.

As shown in Fig. 2b, the modulation behavior changes qualitatively once four-phonon scattering is included. In contrast to the weak and frequency-dependent response with 3ph.-only in Fig. 2a, the considering of 3ph.+4ph. produces a predominantly suppressive modulation over the scanned frequency range. No robust enhancement window is retained after four-phonon scattering is taken into account.

For an occupation multiplier of 5, the relative thermal conductivity remains nearly

unchanged below 2 THz and within 9.6–17.6 THz, whereas clear suppression appears in the low-frequency region of 2.0–9.6 THz and the high-frequency region of 17.6–21.6 THz. The strongest suppression at this occupation multiplier occurs at 20.5 THz, where κ/κ_0 decreases to 0.828. In addition, a broad low-frequency suppression band is observed around 4–6 THz, with representative local minima near 4.4 and 4.8 THz.

When the occupation multiplier is increased to 25, the suppressive modulation is markedly amplified while the overall frequency dependence remains similar. The strongest suppression again appears at 20.5 THz, where κ/κ_0 drops to 0.415. Pronounced suppression is also observed throughout a wide low-frequency interval of approximately 2.2–9.2 THz and a high-frequency interval of approximately 18.0–21.3 THz. In particular, the low-frequency region around 4.1–5.8 THz and the high-frequency region around 18.4–20.5 THz show especially strong responses, indicating that these windows produce pronounced suppressive responses.

The comparison between Fig. 2a and Fig. 2b indicates that higher-order phonon scattering does not merely rescale the magnitude of thermal-conductivity modulation. Instead, represented here by four-phonon processes, it qualitatively changes the net response from weak frequency-dependent modulation. That is, it is changed from a marginal enhancement tendency with 3ph.-only to a predominantly suppressive modulation with 3ph.+4ph.. This contrast highlights the important role of higher-order phonon scattering in shaping the targeted thermal-transport response of bulk BAs and motivates the following scattering-rate analysis.

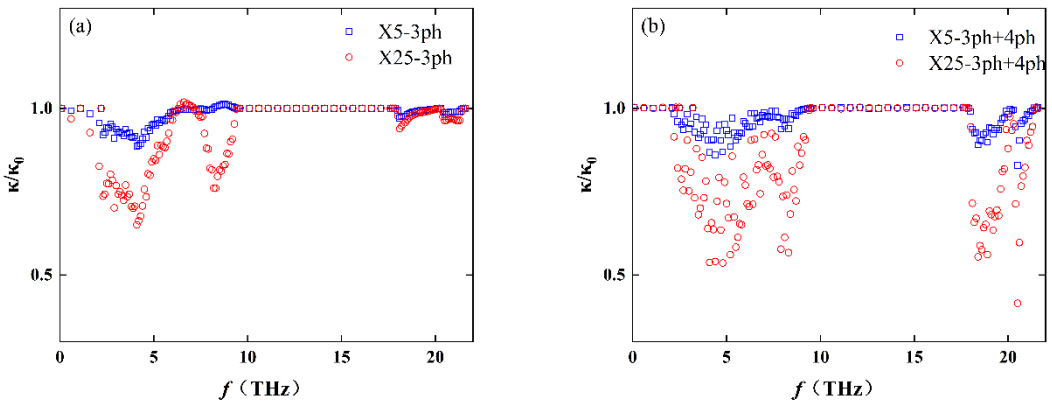


Figure 2 Relative thermal conductivity κ/κ_0 of bulk BAs as a function of the center frequency of the targeted phonon excitation window at 300 K for occupation multipliers of 5 and 25. (a) Results obtained with considering three-phonon-only. (b) Results obtained in the combined three-phonon and four-phonon. In each calculation, only phonons within a 0.1 THz-wide frequency window were excited, while all other phonon modes retained their intrinsic distribution. Coarse scans with a 0.5 THz step were used over the full frequency range, while finer scans with a 0.1 THz step were performed in the strongly modulated regions. κ_0 denotes the intrinsic thermal conductivity calculated as 2302 W/(m·K) with 3ph.-only and 1220 W/(m·K) with 3ph.+4ph..

To clarify why the inclusion of four-phonon scattering changes the targeted thermal-transport response of bulk BAs, it is further analyzed the frequency-dependent phonon-scattering characteristics with considering both 3ph.-only and 3ph.+4ph.. The different modulation behaviors do not originate from a simple rescaling of thermal conductivity, but rather from the combined effects of different intrinsic scattering backgrounds and population-modification-induced variations in the scattering of heat-carrying phonons.

The intrinsic phonon scattering-rate spectra at 300 K are compared in Fig. S5. After four-phonon scattering is included, the overall scattering rates increase over a broad frequency range, and this increase is especially relevant in the low-frequency acoustic region that dominates heat transport. Therefore, even before targeted phonon excitation is introduced, the considering of 3ph.+4ph. already establishes a stronger anharmonic scattering background than that of 3ph.-only. This stronger scattering background provides the basis for understanding why population-modification-induced scattering enhancement becomes more pronounced after four-phonon scattering is included.

On this basis, two representative excitation windows are selected to examine how the scattering rates respond to targeted phonon excitation. The first case is the 8.2–8.3 THz window at an occupation multiplier of 5, where the 3ph.-only calculation gives a

weak enhancement or nearly unchanged response, whereas the 3ph.+4ph. result becomes suppressive.

As shown in Fig. 3a and Fig. 3b, the population-modification-induced change in the scattering rates of low-frequency heat-carrying phonons remains relatively limited with 3ph.-only. In contrast, with 3ph.+4ph., the same population modification acts on an elevated intrinsic scattering background and produces a more systematic increase in the scattering rates of low-frequency heat-carrying phonons. Therefore, the marginal enhancement tendency observed with considering three-phonon only is no longer retained after four-phonon scattering is included.

The second representative case is the 4.1–4.2 THz frequency window at an occupation multiplier of 25, where both situations yield suppressive responses. As shown in Fig. 3c and Fig. 3d, targeted phonon excitation increases the scattering rates of low-frequency heat-carrying phonons in both situations. However, the scattering rates with 3ph.+4ph. remain systematically higher than those with 3ph.-only. Therefore, although the response sign is identical in both situations, the suppression becomes substantially stronger when four-phonon scattering is included.

To further identify the microscopic origin of the enhanced four-phonon scattering, the total four-phonon scattering rate was decomposed into three scattering channels: recombination (++), redistribution (+−), and splitting (−−). This process-resolved analysis can determine which anharmonic pathways are primarily responsible for the population-modification-induced increase in four-phonon scattering.

Figure 4a compares the intrinsic contributions of the three four-phonon channels in bulk BAs. The three channels exhibit distinct frequency-dependent behaviors, reflecting different anharmonic scattering pathways. Among them, the redistribution (+−) channel contributes significantly over the frequency range associated with heat-carrying acoustic phonons, suggesting that redistribution processes constitute an important component of the intrinsic four-phonon scattering background in BAs.

Figures 4b, 4c and 4d show the population-modification-induced variations of the three four-phonon channels after modifying the population of optical modes from 20.5 THz to 20.6 THz. Compared with the recombination ($++$), and the splitting ($--$) channels, the redistribution ($+-$) channel exhibits the most pronounced increase. Importantly, this enhancement is not restricted to the excited optical-frequency region but extends into the low-frequency acoustic range where the dominant heat-carrying phonons are located. This indicates that the increased population of high-frequency optical modes primarily strengthens redistribution pathways involving excited optical phonons and low-frequency acoustic phonons.

These results suggest that the enhanced four-phonon scattering responsible for the suppressive thermal-transport response is mainly associated with redistribution-type processes. Therefore, the role of optical phonon excitation to modify the anharmonic scattering network through redistribution pathways which increase the scattering of heat-carrying acoustic phonons, instead of directly contribute to heat conduction.

These results, together with the intrinsic scattering-rate comparison in Fig. S5, indicate that higher-order phonon scattering plays a key role in shaping the targeted thermal-transport response of bulk BAs within the present framework. The four-phonon contribution modifies the response through two coupled effects: it increases the intrinsic anharmonic scattering background and enhances population-modification-induced scattering of low-frequency heat-carrying phonons, with a dominant contribution from redistribution-type pathways. As a result, the marginal enhancement tendency observed in the 3ph.-only framework disappears after four-phonon scattering is included, leading to a predominantly suppressive response.

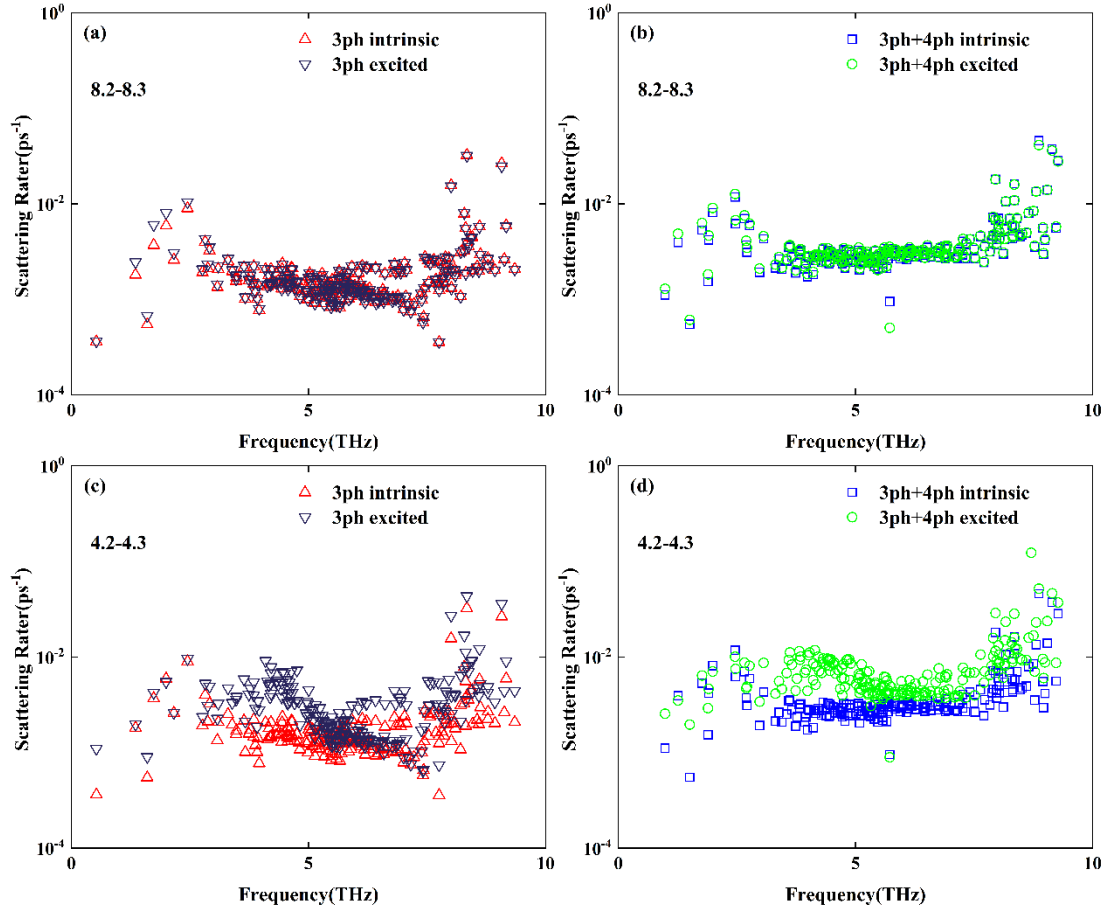


Figure 3 Phonon scattering-rate spectra of bulk BAs at 300 K in the 0–10 THz range for the intrinsic and excited states with considering 3ph.-only and 3ph.+4ph.. (a) 8.2–8.3 THz frequency range at an occupation multiplier of 5 with 3ph.-only. (b) 8.2–8.3 THz frequency range at an occupation multiplier of 5 with 3ph.+4ph.. (c) 4.1–4.2 THz frequency range at an occupation multiplier of 25 with 3ph.-only. (d) 4.1–4.2 THz frequency range at an occupation multiplier of 25 with 3ph.+4ph..

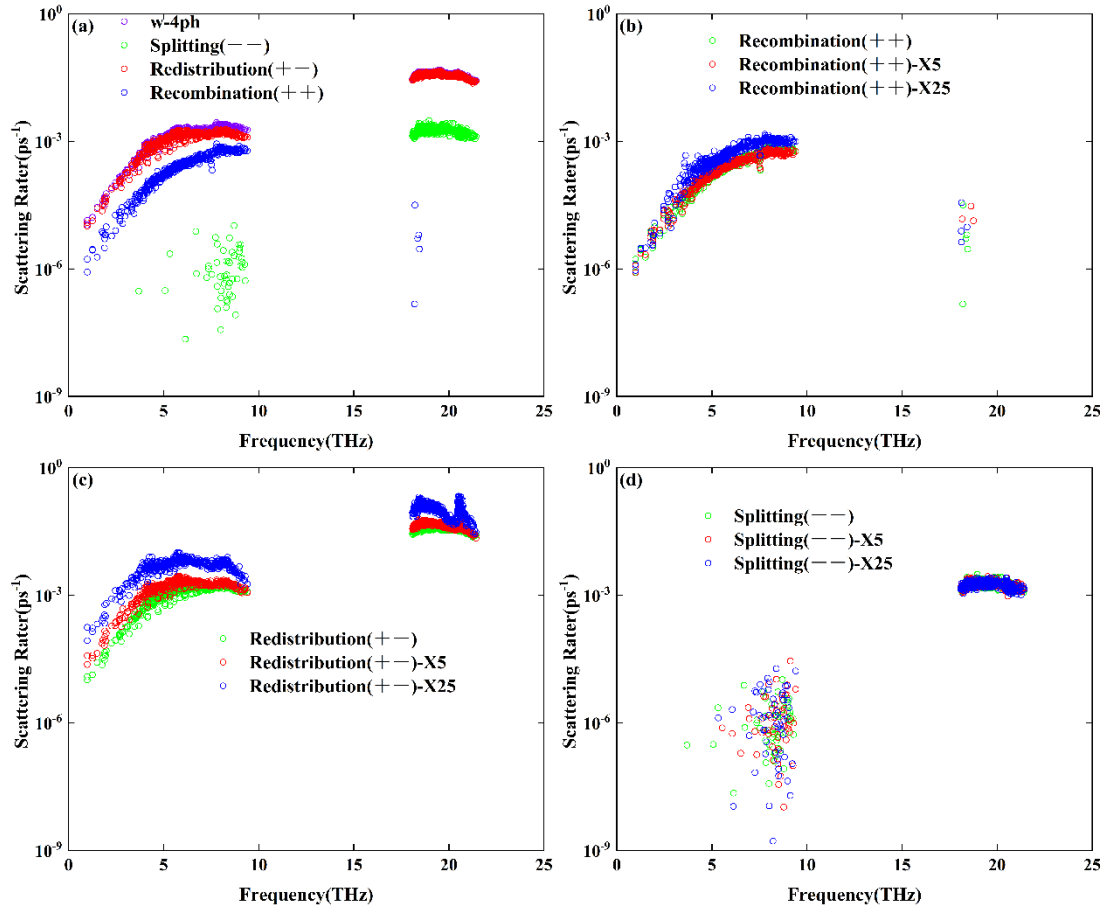


Figure 4 Process-resolved analysis of four-phonon scattering channels in bulk BAs at 300 K. (a) Intrinsic four-phonon scattering rates resolved into recombination (++), redistribution (+-), and splitting (--) channels. (b–d) Population-modification-induced changes of recombination (++), redistribution (+-), and splitting (--) contributions after targeted population modification of the 20.5–20.6 THz optical modes. The results show that redistribution (+-) processes exhibit the strongest population-modification-induced variation among the three channels.

To further examine the temperature dependence of targeted phonon excitation and the role of four-phonon scattering, we compared the 3ph.+4ph. results at 300 K and 100 K. The relative thermal conductivity under occupation multipliers of 5 and 25 is shown separately in Figs. 5a and 5b, respectively. In addition, the ratio between the intrinsic four-phonon and three-phonon scattering rates, $\Gamma_{4\text{ph.}}/\Gamma_{3\text{ph.}}$, was analyzed in Fig. 5c to quantify the relative contribution of four-phonon scattering at different temperatures.

As shown in Fig. 5a, at an occupation multiplier of 5, lowering the temperature

generally weakens the modulation effect with 3ph.+4ph..The 100 K curve remains closer to unity than the 300 K curve over most of the scanned frequency range. In the low-frequency region, the strongest suppression at 100 K occurs around 4.1 THz, where κ/κ_0 decreases to 0.905, whereas the corresponding value at 300 K is 0.864. Meanwhile, near the upper edge of the acoustic branches, a weak enhancement tendency reappears at 100 K. Around 8.1 THz, κ/κ_0 slightly exceeds unity at an occupation multiplier of 5, while the corresponding 300 K result remains suppressive. These features indicate that the predominantly suppressive modulation observed at 300 K is weakened at lower temperature, and 3ph.-like modulation features can partially reappear.

When the occupation multiplier is increased to 25, as shown in Fig. 5b, the suppressive response is amplified at both temperatures. However, the 300 K result still shows a much stronger suppression than the 100 K result. In the low-frequency region, excitation around 4.1 THz gives $\kappa/\kappa_0 = 0.643$ at 100 K and 0.540 at 300 K. The temperature dependence is even more evident in the high-frequency region. At 300 K, targeted population modification above 18 THz produces pronounced suppression, whereas at 100 K the relative thermal conductivity in the same frequency range remains much closer to unity. For example, under an occupation multiplier of 25, modification around 18.6 THz gives $\kappa/\kappa_0 = 0.578$ at 300 K, but only weakly reduces it to 0.971 at 100 K. These results show that lowering the temperature does not simply reduce the modulation amplitude uniformly; instead, it strongly weakens the high-frequency suppressive response and shifts the behavior closer to the situation of 3ph.-only.

The microscopic origin of this temperature dependence is further clarified by the scattering-rate ratio shown in Fig. 5c. Compared with 100 K, the ratio $\Gamma_{4ph.}/\Gamma_{3ph.}$ at 300 K is significantly larger over the relevant frequency range, indicating that four-phonon scattering contributes much more strongly to the total anharmonic scattering at room temperature. This enhanced four-phonon contribution is especially important for the low-frequency acoustic phonons that dominate heat transport and for the high-frequency excitation windows that can affect low-frequency heat-carrying modes

through phonon-phonon coupling. Therefore, at 300 K, targeted phonon excitation occurs on a stronger four-phonon scattering background, leading to a more pronounced suppressive response. Additional low-temperature calculations down to 10 K are provided in Fig. S6, showing that the weak enhancement near the 8.1–8.2 THz window appears only within an intermediate-temperature range and becomes nearly negligible at 10 K.

In contrast, at 100 K, the relative contribution of four-phonon scattering is substantially reduced, as reflected by the smaller $\Gamma_{4\text{ph.}}/\Gamma_{3\text{ph.}}$ ratio. Under this weaker four-phonon scattering background, the population-modification-induced increase in scattering becomes less pronounced. As a result, the high-frequency suppressive response is strongly weakened, and 3ph.-like modulation characteristics can reappear near the upper edge of the acoustic branches. These temperature-dependent results further support the mechanism discussed above: four-phonon scattering plays an important role in determining the targeted thermal-conductivity response of bulk BAs at room temperature, whereas lowering temperature weakens this higher-order scattering contribution and shifts the modulation behavior closer to the 3ph.-only picture.

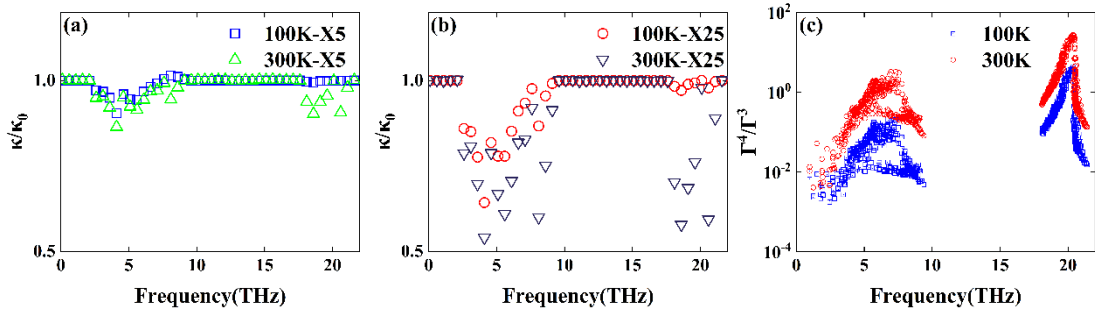


Figure 5 Temperature-dependent modulation of thermal conductivity and relative four-phonon scattering strength in bulk BAs. (a, b) Relative thermal conductivity κ/κ_0 as a function of the center frequency of the targeted phonon-population modification window in the 3ph.+4ph. framework at 300 K and 100 K for occupation multipliers of (a) 5 and (b) 25. In each calculation, only phonons within a 0.1 THz-wide frequency

window were excited, while all other phonon modes retained their intrinsic distribution. (c) Intrinsic scattering-rate ratio $\Gamma_{4\text{ph.}}/\Gamma_{3\text{ph.}}$ as a function of phonon frequency at 300 K and 100 K. Only phonon modes with nonzero three-phonon scattering rates are included in the ratio plot.

Conclusion

In this work, we reveal the role of higher-order phonon scattering in thermal conductivity modulation via targeted phonon excitation of bulk boron arsenide (BAs). Based on first-principles calculations and phonon Boltzmann transport analysis, it is found that targeted phonon excitation modulates the thermal conductivity of bulk BAs in a strongly frequency-dependent manner. With considering three-phonon scatterings only, targeted phonon excitation at 300 K produces a weak but clearly bidirectional modulation of thermal conductivity. However, once higher-order four-phonon scattering is included, the modulation changes qualitatively to a predominantly suppressive behavior. In the combined three-phonon and four-phonon scatterings, the strongest suppression occurs at 20.5 THz, where κ/κ_0 decreases to 0.828 and 0.415 for excitation intensities for occupation multipliers of 5 and 25, respectively. The present study focuses on the relative modulation of thermal conductivity within a consistent structural and force-constant framework, rather than establishing an absolute thermal-conductivity benchmark for bulk BAs.

Mechanistically, higher-order four-phonon scattering plays a dual role in targeted thermal-conductivity modulation of bulk BAs. It raises the intrinsic scattering background and promotes a more systematic population-modification-induced increase in the scattering of low-frequency heat-carrying phonons. As a result, the weak enhancement windows retained in the three-phonon-only scatterings are removed, and the net modulation becomes predominantly suppressive. Moreover, the comparison between 300 K and 100 K shows that lowering temperature weakens the predominance of four-phonon scattering and partially restores 3ph.-like modulation features. These

results provide mechanistic insight into how higher-order phonon scattering modifies targeted phonon-population control in bulk BAs. Accordingly, the present work should be understood as a computational mechanistic study of the thermal-conductivity response in bulk BAs under steady-state simulations with prescribed mode-selective targeted phonon excitation, rather than as a complete prediction of transient nonequilibrium or dynamic thermal-control experiments.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] A. Anitha, A. Hemalatha, P. Udhayakumar. Heat resistant coatings—an overview, in: *Coatings for High-temperature Environments: Anti-corrosion and Anti-wear Applications*, Cham: Springer Nature Switzerland, 2024: 403-430
- [2] Q. Zheng, M. Hao, R. Miao, J. Schaadt, Chris Dames. Advances in thermal conductivity for energy applications: a review. *Progress in Energy*, 2021, 3(1): 12002
- [3] A. Henry, R. Prasher, Arun Majumdar. Five thermal energy grand challenges for decarbonization. *Nature Energy*, 2020, 5(9): 635-637
- [4] S. Wu, T. Yan, Z. Kuai, Weiguo Pan. Thermal conductivity enhancement on phase change materials for thermal energy storage: a review. *Energy Storage Materials*, 2020, 25: 251-295
- [5] Z. He, Y. Yan, Zhien Zhang. Thermal management and temperature uniformity enhancement of electronic devices by micro heat sinks: a review. *Energy*, 2021, 216: 119223
- [6] X. L. Shi, J. Zou, Zhi-Gang Chen. Advanced thermoelectric design: from materials and structures to devices. *Chemical Reviews*, 2020, 120(15): 7399-7515

- [7] J. Mao, G. Chen, Z. Ren. Thermoelectric cooling materials. *Nature Materials*, 2021, 20(4): 454-461
- [8] J. Pei, B. Cai, H. L. Zhuang, Jing-Feng Li. Bi₂Te₃-based applied thermoelectric materials: research advances and new challenges. *National Science Review*, 2020, 7(12): 1856-1858
- [9] Z. Zong, S. Deng, Y. Qin, X. Wan, J. Zhan, D. Ma, et al. Enhancing the interfacial thermal conductance of Si/PVDF by strengthening atomic couplings. *Nanoscale*, 2023, 15(40): 16472-16479
- [10] L. Dong, B. Liu, Y. Wang, X. Xu. Tunable thermal conductivity of ferroelectric P(VDF-TrFE) nanofibers via molecular bond modulation. *Chinese Physics Letters*, 2022, 39(12): 127201
- [11] J. Chen, J. He, D. Pan, X. Wang, N. Yang, J. Zhu, et al. Emerging theory and phenomena in thermal conduction: a selective review. *Science China Physics, Mechanics & Astronomy*, 2022, 65(11): 117002
- [12] S. Deng, J. Yuan, Y. Lin, X. Yu, D. Ma, Y. Huang, et al. Electric-field-induced modulation of thermal conductivity in poly(vinylidene fluoride). *Nano Energy*, 2021, 82: 105749
- [13] S. Deng, D. Ma, G. Zhang, N. Yang. Modulating the thermal conductivity of crystalline nylon by tuning hydrogen bonds through structure poling. *Journal of Materials Chemistry A*, 2021, 9(43): 24472-24479
- [14] Bruce L. Davis, M. I. Hussein. Nanophononic metamaterial: thermal conductivity reduction by local resonance. *Physical Review Letters*, 2014, 112(5): 55505
- [15] Jin-Wu Jiang, J. S. Wang, B. Li. Topological effect on thermal conductivity in graphene. *Journal of Applied Physics*, 2010, 108(6): 64307
- [16] Jen-Kan Yu, S. Mitrovic, D. Tham, J. Varghese, J. R. Heath. Reduction of thermal conductivity in phononic nanomesh structures. *Nature Nanotechnology*, 2010, 5(10): 718-721
- [17] N. Yang, X. Ni, J. W. Jiang, B. Li. How does folding modulate thermal conductivity of graphene. *Applied Physics Letters*, 2012, 100(9): 93107
- [18] S. Hu, J. Chen, N. Yang, B. Li. Thermal transport in graphene with defect and

- doping: phonon modes analysis. *Carbon*, 2017, 116: 139-144
- [19] J. Y. Cho, X. Shi, J. R. Salvador, G. P. Meisner, J. Yang, H. Wang, et al. Thermoelectric properties and investigations of low thermal conductivity in Ga-doped Cu_2GeSe_3 . *Physical Review B*, 2011, 84(8): 85207
- [20] Shanshan Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, et al. Thermal conductivity of isotopically modified graphene. *Nature Materials*, 2012, 11(3): 203-207
- [21] Y. Yang, D. Ma, L. Zhang. Introduction of asymmetry to enhance thermal transport in porous metamaterials at low temperature. *Chinese Physics Letters*, 2023, 40(12)
- [22] C. Bera, Natalio Mingo, S. Volz. Marked effects of alloying on the thermal conductivity of nanoporous materials. *Physical Review Letters*, 2010, 104(11): 115502
- [23] Chunlei Wan, Z. Qu, A. Du, W. Pan. Order–disorder transition and unconventional thermal conductivities of the $(\text{Sm}_{1-x}\text{Yb}_x)_2\text{Zr}_2\text{O}_7$ series. *Journal of the American Ceramic Society*, 2011, 94(2): 592-596
- [24] M. An, H. Wang, Y. Yuan, D. Chen, W. Ma, S. W. Sharshir, et al. Strong phonon coupling induces low thermal conductivity of one-dimensional carbon boron nanotube. *Surfaces and Interfaces*, 2022, 28: 101690
- [25] Yangjun Qin, L. Mu, X. Wan, Z. Zong, T. Li, H. Fang, et al. Deep potential for interaction between hydrated Cs^+ and graphene. *Langmuir*, 2025, 41(18): 11506-11514
- [26] X. Wan, D. Ma, D. Pan, L. Yang, N. Yang. Optimizing thermal transport in graphene nanoribbon based on phonon resonance hybridization. *Materials Today Physics*, 2021, 20: 100445
- [27] S. Shen, A. Henry, J. Tong, R. Zheng, Gang Chen. Polyethylene nanofibres with very high thermal conductivities. *Nature Nanotechnology*, 2010, 5(4): 251-255
- [28] D. Pan, T. Li, X. Wan, Z. Zong, Y. Qin, N. Yang. Using targeted phonon excitation to modulate thermal conductivity of boron nitride. *Chin. Phys. Lett.*, 2025, 42(7): 070801.

- [29] Y. Yoon, Z. Lu, C. Uzundal, R. Qi, W. Zhao, S. Chen, et al. Terahertz phonon engineering with van der waals heterostructures. *Nature*, 2024, 631(8022): 771-776
- [30] X. Wan, Z. Zong, Y. Qin, J. T. Lü, S. Volz, L. Zhang, et al. Modulating thermal conductivity via targeted phonon excitation. *Nano Letters*, 2024, 24(23): 6889-6896
- [31] F. Sekiguchi, H. Hirori, G. Yumoto, A. Shimazaki, T. Nakamura, A. Wakamiya, et al. Enhancing the hot-phonon bottleneck effect in a metal halide perovskite by terahertz phonon excitation. *Physical Review Letters*, 2021, 126(7): 77401
- [32] B. Cheng, P. L. Kramer, M. Trigo, M. Liu, C. Uher, D. A. Reis, et al. Terahertz-induced tunnel ionization drives coherent raman-active phonon in bismuth. *Physical Review Letters*, 2025, 135(14): 146901
- [33] L. Lindsay, D. A. Broido, T. L. Reinecke. First-principles determination of ultrahigh thermal conductivity of boron arsenide: a competitor for diamond? *Physical Review Letters*, 2013, 111(2): 25901
- [34] H. Ma, C. Li, S. Tang, J. Yan, A. Alatas, L. Lindsay, et al. Boron arsenide phonon dispersion from inelastic x-ray scattering: potential for ultrahigh thermal conductivity. *Physical Review B*, 2016, 94(22): 220303
- [35] Sang Kang Joon, M. Li, H. Wu, H. Nguyen, Y. Hu. Experimental observation of high thermal conductivity in boron arsenide. *Science*, 2018, 361(6402): 575-578
- [36] Sheng Li, Q. Zheng, Y. Lv, X. Liu, X. Wang, Y. Huang Pinshane, et al. High thermal conductivity in cubic boron arsenide crystals. *Science*, 2018, 361(6402): 579-581
- [37] G. Kresse, J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 1996, 6(1): 15-50
- [38] G. Kresse, J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 1996, 54(16): 11169
- [39] J. A. Perri, S. La Placa, B. Post. New group III-group V compounds: BP and BAs. *Acta Crystallographica*, 1958, 11(4): 310-310

- [40] Z. Han, X. Yang, W. Li, T. Feng, X. Ruan. FourPhonon: an extension module to ShengBTE for computing four-phonon scattering rates and thermal conductivity. *Computer Physics Communications*, 2022, 270: 108179
- [41] W. Li, J. Carrete, N. A. Katcho, N. Mingo. ShengBTE: a solver of the boltzmann transport equation for phonons. *Computer Physics Communications*, 2014, 185(6): 1747-1758
- [42] T. Feng, X. Ruan. Four-phonon scattering reduces intrinsic thermal conductivity of graphene and the contributions from flexural phonons. *Physical Review B*, 2018, 97(4) : 045202.
- [43] R. G. Greene. Pressure induced metastable amorphization of BAs: evidence for a kinetically frustrated phase transformation. *Physical Review Letters*, 1994, 73(18): 2476-2479
- [44] Z. Guo, Z. Han, D. Feng, G. Lin, X. Ruan. Sampling-accelerated prediction of phonon scattering rates for converged thermal conductivity and radiative properties. *npj Computational Materials*, 2024, 10(1): 31

Higher-Order-Phonon Scattering Governs Targeted Control of Heat Conduction in Bulk Boron Arsenide

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S1. Benchmark of harmonic phonon properties

To assess the sensitivity of the harmonic phonon properties to the choice of exchange-correlation functional, the phonon dispersion relations of bulk BAs were calculated using both the PBE and LDA functionals. As shown in Fig. S1, the acoustic branches obtained from the two functionals are similar, whereas the optical phonon frequencies calculated using PBE are systematically lower than those obtained from LDA. This comparison was performed only as a benchmark of the harmonic phonon properties, it was not used to determine the force constants employed in the final thermal conductivity calculations.

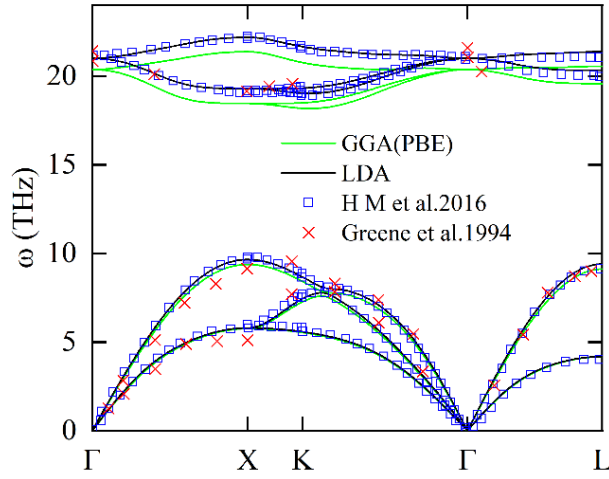


Figure S1 Comparison of the phonon dispersion relations of bulk BAs calculated using the PBE and LDA functionals.

The targeted-excitation calculations discussed in the main text were performed using the publicly available BAs force-constant dataset provided in the FourPhonon framework, as described in the Methods section.

S2. Additional details of three-phonon scattering formalism

The three-phonon scattering formalism used in the phonon transport calculations is briefly summarized below. These expressions describe the general three-phonon scattering processes, whereas the final targeted-excitation comparisons between the 3ph-only and 3ph+4ph frameworks were performed using the unified BAs force-constant dataset within the FourPhonon framework, as described in the Methods section.

The anharmonic phonon linewidth Γ^{anh} can be expressed in terms of the three-phonon scattering rates $\Gamma_{\lambda\lambda'\lambda''}^{\pm}$ as

$$\Gamma_{\lambda\lambda'\lambda''}^{+} = \frac{\hbar\pi}{4} \frac{f_0' - f_0''}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^{+}|^2 \delta(\omega_{\lambda} + \omega_{\lambda'} - \omega_{\lambda''}) \quad (S1)$$

and

$$\Gamma_{\lambda\lambda'\lambda''}^{-} = \frac{\hbar\pi}{4} \frac{f_0' + f_0'' + 1}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} |V_{\lambda\lambda'\lambda''}^{-}|^2 \delta(\omega_{\lambda} - \omega_{\lambda'} - \omega_{\lambda''}) \quad (S2)$$

where f_0' denotes $f_0(\omega_{\lambda'}) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$ for the simplicity, $\Gamma_{\lambda\lambda'\lambda''}^{+}$ is the scattering rate of phonon absorption process, in which two incident phonons (λ , λ') combine into one phonon (λ''), satisfying $\omega_{\lambda} + \omega_{\lambda'} = \omega_{\lambda''}$. Conversely, $\Gamma_{\lambda\lambda'\lambda''}^{-}$ is the scattering rate of phonon emission process where one incident phonon (λ) decays into two phonons (λ' , λ''), satisfying $\omega_{\lambda} = \omega_{\lambda'} + \omega_{\lambda''}$. Energy conservation in both absorption and emission processes is enforced by the δ -distribution in the Eqs. (S1) and (S2).

The corresponding three-phonon scattering matrix elements $V_{\lambda\lambda'\lambda''}^{\pm}$ were obtained from the third-order interatomic force constants (IFCs) as

$$V_{\lambda\lambda'\lambda''}^{\pm} = \sum_{i \in \text{UC}} \sum_{j,k} \sum_{\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} \frac{e_{\lambda}^{\alpha}(i) e_{\lambda'}^{\beta}(j) e_{\lambda''}^{\gamma}(k)}{\sqrt{M_i M_j M_k}} \quad (S3)$$

where $\Phi_{ijk}^{\alpha\beta\gamma} = \frac{\partial^3 E}{\partial \partial r_i^{\alpha} r_j^{\beta} r_k^{\gamma}}$ represents the third-order IFCs (where E is the system potential energy) for atoms i, j, k along Cartesian directions α, β, γ , $e_{\lambda}^{\alpha}(i)$ denotes the α -component of the polarization vector of phonon mode λ for atom i , and M_i is the mass of atom i .

S3. Occupation-multiplier dependence in representative suppression windows at 300 K

To further examine the dependence of the suppressive modulation on the prescribed phonon population modification in the 3ph+4ph framework, we selected four representative frequency windows corresponding to pronounced local minima in the room-temperature modulation profile, namely 4.1–4.2, 8.3–8.4, 18.4–18.5, and

20.5–20.6 THz, and calculated the thermal conductivity as a function of the occupation multiplier. As shown in Fig. S2, all four frequency windows exhibited an overall suppressive response that became stronger as the occupation multiplier increased, indicating that the suppression response shows a clear dependence on the prescribed phonon population level within these representative windows.

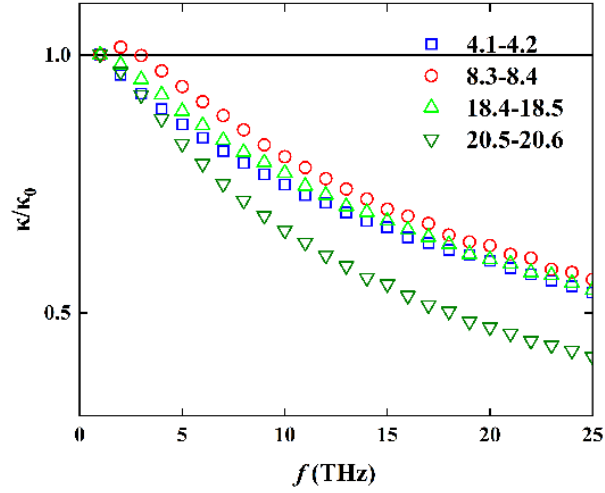


Figure S2 Relative thermal conductivity κ/κ_0 of bulk BAs under targeted phonon excitation of phonons in the 4.1–4.2, 8.3–8.4, 18.4–18.5, and 20.5–20.6 THz windows at 300 K as a function of the occupation multiplier N in the 3ph+4ph framework. The horizontal dashed line indicates the intrinsic value $\kappa/\kappa_0=1$.

Among the four cases, the 20.5–20.6 THz window showed the strongest dependence on the occupation multiplier. As the occupation multiplier increased from 1 to 25, the relative thermal conductivity κ/κ_0 decreased monotonically from 1.00 to 0.415, showing the strongest suppression response among the investigated windows. The 4.1–4.2 and 18.4–18.5 THz windows also exhibited strong and nearly parallel suppression trends, with κ/κ_0 decreasing to 0.539 and 0.544 at the highest occupation multiplier, respectively. By comparison, the 8.3–8.4 THz window showed a weaker overall response, reaching $\kappa/\kappa_0 = 0.565$ at an occupation multiplier of 25. It should be noted that this frequency window displayed a slight increase in thermal conductivity at the very low occupation multiplier of 2, but the thermal conductivity decreased continuously with further increasing occupation multiplier. Therefore, despite the small deviation in the initial low-population-modification regime, the overall trend in this

window remained suppressive.

These results indicate that, once four-phonon scattering is included, the thermal-conductivity suppression in bulk BAs depends not only on the targeted frequency but also on the occupation multiplier within the prescribed population-modification framework.

S4. Extended spectral thermal conductivity analysis for representative excitation windows

To further examine the microscopic origin of the suppressive modulation in the 3ph+4ph framework, we analyzed the spectral thermal conductivity for two representative targeted phonon excitation windows, namely 4.1–4.2 and 20.5–20.6 THz, under occupation multipliers of 5 and 25. As shown in Fig. S3, although the targeted phonon excitation were introduced in different frequency windows, the most pronounced reduction in spectral thermal conductivity occurred mainly in the low-frequency range of approximately 3–9 THz, which is also the dominant frequency range for heat transport in intrinsic BAs.

For the 4.1–4.2 THz targeted phonon excitation case, the spectral thermal conductivity in the 4–6 THz range decreased substantially from the intrinsic state to occupation multipliers of 5 and 25. A similar trend was also observed for the 20.5–20.6 THz targeted phonon excitation case, even though the modified modes themselves are located in a high-frequency region with only a minor direct contribution to the total thermal conductivity. These results indicate that the suppressive response induced by targeted phonon excitation is not limited to the directly modified modes, but instead arises from the altered scattering response of heat-carrying phonons over a broader frequency range. The detailed microscopic origin of this scattering enhancement is further analyzed through process-resolved four-phonon channel decomposition in the main text.

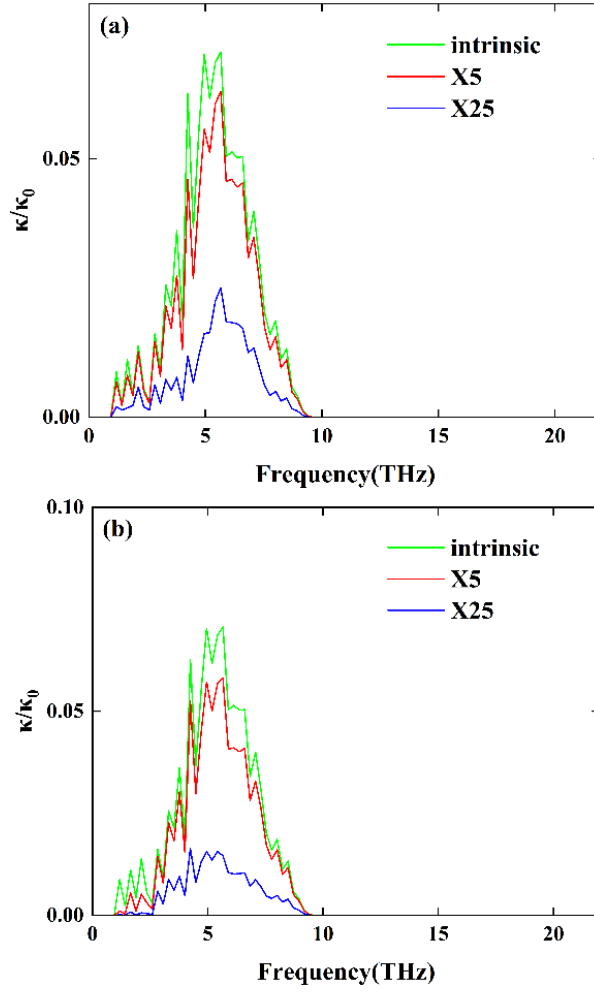


Figure S3 Spectral thermal conductivity of bulk BAs at 300 K for the intrinsic state and under targeted phonon excitation with occupation multipliers of 5 and 25 in the 3ph+4ph framework. Panels (a) and (b) correspond to targeted phonon excitation in the 4.1–4.2 and 20.5–20.6 THz windows, respectively.

S5. Extended phonon scattering-rate analysis for representative excitation windows

The corresponding scattering-rate spectra, shown in Fig. S4, provide a consistent explanation for the suppressive modulation behavior. For both representative targeted phonon excitation windows, the phonon scattering rates in the low-frequency region of approximately 3–9 THz increase systematically from the intrinsic state to occupation multipliers of 5 and 25. Therefore, the reduction in low-frequency spectral thermal conductivity can be directly associated with the population-modification-induced enhancement of phonon scattering. Since the low-frequency acoustic phonons dominate

thermal transport in bulk BAs, the increase in their scattering rates leads to a marked suppression of the overall thermal conductivity.

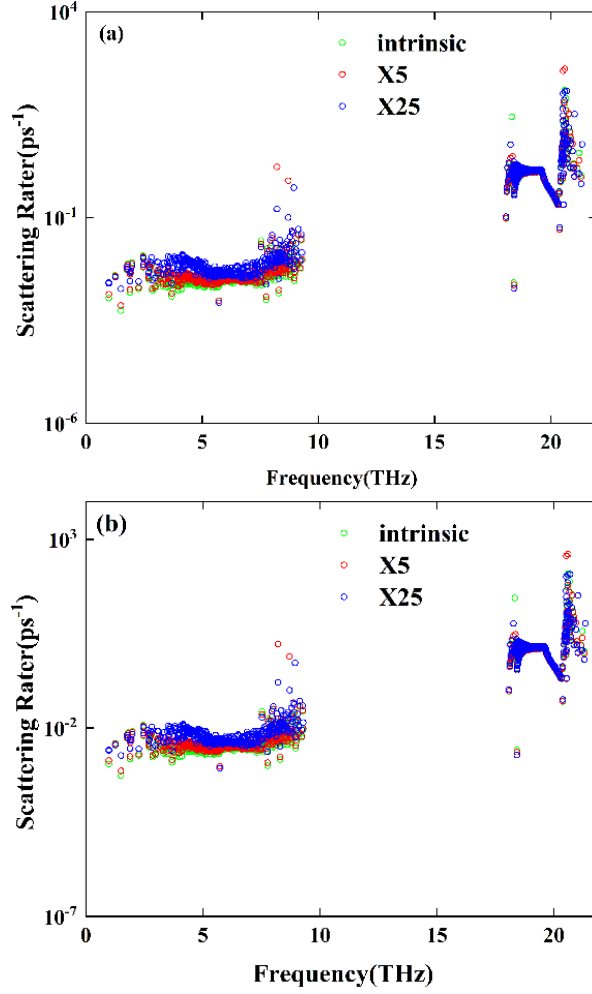


Figure S4 Phonon scattering rates of bulk BAs at 300 K for the intrinsic state and under targeted phonon excitation with occupation multipliers of 5 and 25 in the 3ph+4ph framework. Panels (a) and (b) correspond to targeted phonon excitation in the 4.1–4.2 and 20.5–20.6 THz windows, respectively.

A notable difference nevertheless exists between the two representative targeted phonon excitation windows. For the 4.1–4.2 THz case, the modified phonon modes are already located within the main heat-carrying acoustic range, so the suppressive effect on low-frequency spectral thermal conductivity is more direct. In contrast, for the 20.5–20.6 THz case, the modified modes belong to a high-frequency optical region with only a minor direct contribution to thermal transport. Nevertheless, the population modification of these optical modes significantly enhances the scattering of low-

frequency heat-carrying phonons through anharmonic scattering pathways, resulting in a stronger suppression of thermal conductivity. This behavior indicates that high-frequency targeted phonon excitation can influence thermal transport indirectly through phonon–phonon scattering processes rather than through its direct contribution to heat conduction.

Overall, the extended scattering-rate analyses show that the dominant mechanism of targeted phonon excitation in bulk BAs is the enhancement of phonon scattering, especially in the low-frequency heat-carrying region. This scattering enhancement suppresses the spectral thermal conductivity of acoustic phonons and ultimately reduces the total thermal conductivity.

S6. Intrinsic scattering-rate comparison between the 3ph-only and 3ph+4ph frameworks

To support the discussion of the different modulation behaviors in the 3ph-only and 3ph+4ph frameworks, we compared the intrinsic phonon scattering-rate spectra of bulk BAs at 300 K before targeted phonon excitation. As shown in Fig. S5, the inclusion of four-phonon scattering increases the overall phonon scattering rates over a broad frequency range compared with the 3ph-only framework. This increase is particularly important for the low-frequency acoustic phonons, which dominate heat transport in intrinsic BAs.

The elevated intrinsic scattering background provides the baseline for understanding the predominantly suppressive modulation observed in the 3ph+4ph framework. When targeted phonon excitation is introduced, the additional scattering enhancement occurs on top of this stronger anharmonic scattering background. As a result, the enhanced scattering of low-frequency heat-carrying phonons becomes a dominant factor determining the net thermal-transport response within the present framework. Therefore, the intrinsic scattering-rate comparison in Fig. S5 supports the mechanism discussed in the main text and explains why the modulation behavior changes from weak frequency-dependent modulation with marginal enhancement tendencies in the 3ph-only framework to predominantly suppressive modulation after

four-phonon scattering is included.

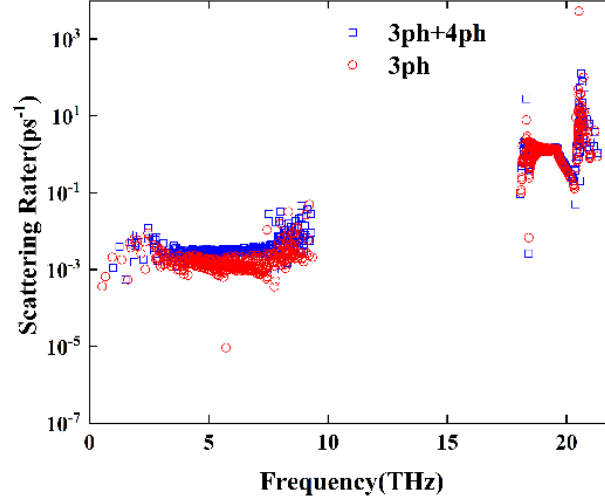


Figure S5 Comparison of the intrinsic phonon scattering rates of bulk BAs at 300 K in the 3ph-only and 3ph+4ph frameworks. The 3ph+4ph framework shows higher scattering rates over a broad frequency range, providing a stronger intrinsic scattering background for the targeted phonon excitation calculations discussed in the main text.

S7. Additional low-temperature modulation results

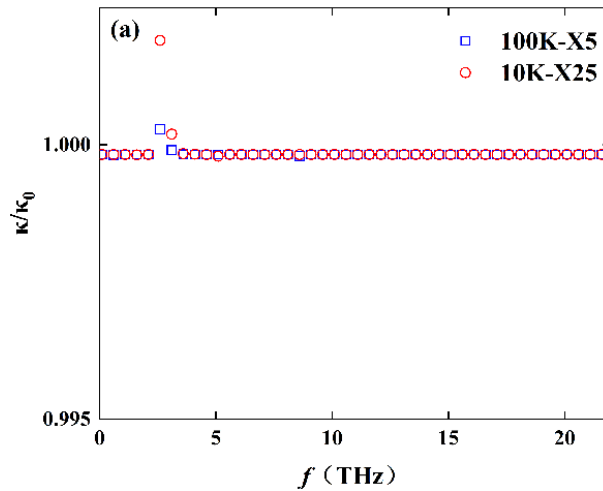
To further support the temperature-dependent discussion in the main text, we performed additional 3ph+4ph calculations at lower temperatures. Figure S6a shows the frequency-dependent modulation of the relative thermal conductivity at 10 K under occupation multipliers of 5 and 25. In contrast to the pronounced suppression observed at 300 K and the weakened but still visible response at 100 K, the 10 K results remain extremely close to unity over nearly the entire scanned frequency range. The largest deviation appears near the 2.6 THz window under an occupation multiplier of 25, where κ/κ_0 reaches only about 1.0019. Therefore, the targeted phonon excitation response becomes nearly negligible at 10 K.

This behavior indicates that lowering temperature does not continuously enhance the weak modulation response. At very low temperature, both the available phonon population and the effective anharmonic scattering channels are strongly reduced, so the population-modification-induced changes in phonon scattering become negligible. As a result, the relative thermal conductivity remains nearly unchanged even when

selected phonon modes are modified.

We further examined the temperature dependence of a representative marginal enhancement tendency, namely the 8.1–8.2 THz window under an occupation multiplier of 5. As shown in Fig. S6b, the relative thermal conductivity is nearly unchanged at very low temperatures, then increases gradually with temperature and reaches a maximum of about 1.0177 around 80 K. With further increasing temperature, this enhancement tendency decreases and becomes much weaker by 150 K. This nonmonotonic behavior suggests that the marginal enhancement tendency appears only within an intermediate-temperature regime. In this regime, four-phonon scattering is weakened compared with room temperature, allowing the weak enhancement tendency observed in the 3ph-only-like regime to emerge. At higher temperatures, stronger four-phonon scattering suppresses this tendency, whereas at very low temperatures the overall modulation response becomes nearly inactive.

These additional low-temperature results further support the temperature-dependent mechanism discussed in the main text. The predominantly suppressive modulation at room temperature is associated with the strong contribution of four-phonon scattering, while lowering temperature weakens this suppression and allows marginal 3ph-like enhancement tendencies to appear in selected frequency windows. However, at extremely low temperatures, such as 10 K, the overall targeted phonon excitation response becomes nearly negligible.



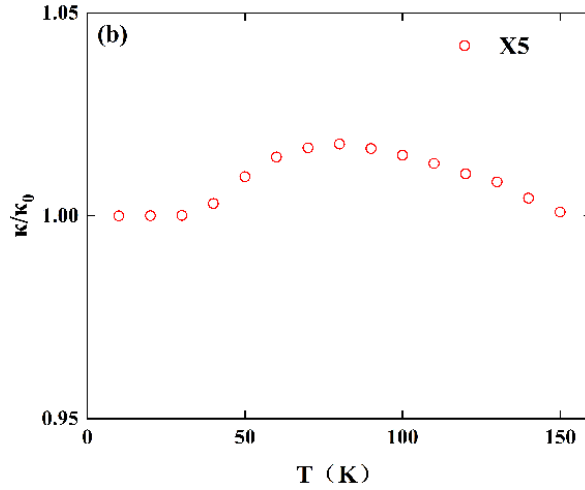


Figure S6 Additional low-temperature modulation results of bulk BAs in the 3ph+4ph framework. (a) Relative thermal conductivity κ/κ_0 as a function of the targeted phonon excitation window at 10 K for occupation multipliers of 5 and 25. (b) Temperature dependence of κ/κ_0 under targeted phonon excitation in the 8.1–8.2 THz window with an occupation multiplier of 5. In each calculation, only phonon populations within a 0.1 THz-wide frequency window were modified, while all other phonon modes retained their equilibrium distributions.

S8. The convergence tests for thermal conductivity calculation

To evaluate the numerical reliability of the thermal conductivity calculations, we examined the convergence with respect to the q-mesh size and the sampling size used in the sampling-MLE approach. The convergence tests were performed for intrinsic thermal conductivity within 3-ph only and 4-ph frameworks, and for modulated thermal conductivity by targeted phonon excitation within 4-ph framework.

A. q-mesh convergence of intrinsic TC within 3-ph framework

The convergence of thermal conductivity with respect to q-mesh size was examined using Γ -centered q-meshes ranging from $10 \times 10 \times 10$ to $35 \times 35 \times 35$ within the three-phonon framework. As shown in Fig. S7a, the intrinsic thermal conductivity gradually converges with the increasing q-mesh size. When the q-mesh is increased from $25 \times 25 \times 25$ to $30 \times 30 \times 30$, the calculated thermal conductivity changes from 2288.63 to 2302.61 $\text{W m}^{-1} \text{K}^{-1}$, corresponding to a relative variation of 0.61%. Further increasing the q-mesh to $35 \times 35 \times 35$ results in a thermal conductivity of 2312.42 W m^{-1}

K^{-1} , with a relative difference of 0.43% compared with the result obtained from $30 \times 30 \times 30$. Therefore, the $30 \times 30 \times 30$ q-mesh satisfies the convergence criterion adopted in this work, where further refinement leads to changes below 1%.

B. q-mesh convergence of intrinsic TC within 3-ph+4-ph framework

The convergence of intrinsic thermal conductivity with respect to q-mesh size was examined using Γ -centered q-meshes ranging from $6 \times 6 \times 6$ to $18 \times 18 \times 18$ and a constant sampling size of 100000 within the 3ph.+4ph. framework. As shown in Fig. S7b, the calculated thermal conductivity gradually converges with the increasing q-mesh size. When the q-mesh is increased beyond $16 \times 16 \times 16$, the variation in thermal conductivity becomes negligible, with the difference between the results obtained from $16 \times 16 \times 16$ and $18 \times 18 \times 18$ being approximately 0.2%, which meets the convergence criterion of 1%. Therefore, the $16 \times 16 \times 16$ q-mesh was adopted for subsequent thermal conductivity calculations involving targeted phonon excitation.

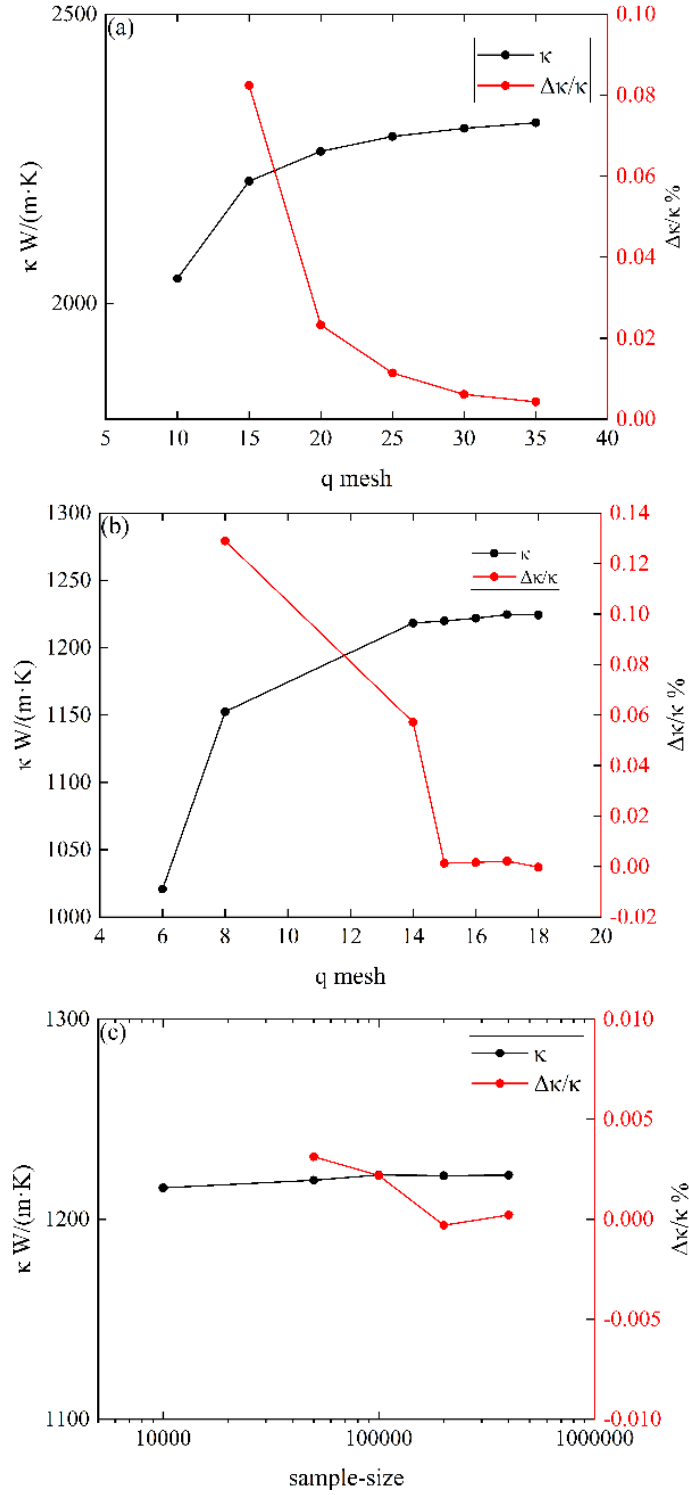
C. Sampling size convergence of intrinsic TC within 3-ph+4-ph framework

The convergence of the intrinsic thermal conductivity with respect to the sampling size was examined using different sampling numbers while a constant q-mesh size of $16 \times 16 \times 16$ within the 3-ph+4-ph framework. As shown in Fig. S7c, increasing the sampling number from 100,000 to 400,000 leads to only minor variations in the intrinsic thermal conductivity. The calculated value changes from $1215.73 \text{ W m}^{-1} \text{ K}^{-1}$ at sampling number of 100,000 to $1222.11 \text{ W m}^{-1} \text{ K}^{-1}$ at 400,000, while the variation between the results obtained from 200,000 and 400,000 remains below 0.03%. These results indicate that the adopted sampling size of 100,000 for sampling-MLE approach provides a numerically stable evaluation of four-phonon scattering contributions.

D. Sampling size convergence of modulated TC within 3-ph+4-ph framework

To further verify that the main modulation results are not sensitive to the sampling uncertainty, we examined the relative thermal conductivity κ/κ_0 for several representative targeted phonon excitation windows under an occupation multiplier of 25. As shown in Fig. S7d, the calculated κ/κ_0 values for the 20.5–20.6 THz, 4.2–4.3 THz, and 20.1–20.2 THz windows remain nearly unchanged when the sampling number increases from 50,000 to 150,000. Specifically, κ/κ_0 remains within 0.413–

0.416 for the strongest suppression window at 20.5–20.6 THz, while the other representative windows also exhibit only minor variations. These results demonstrate that the sampling-MLE approach adopted in this work is sufficient to capture the qualitative and quantitative trends of targeted phonon excitation responses.



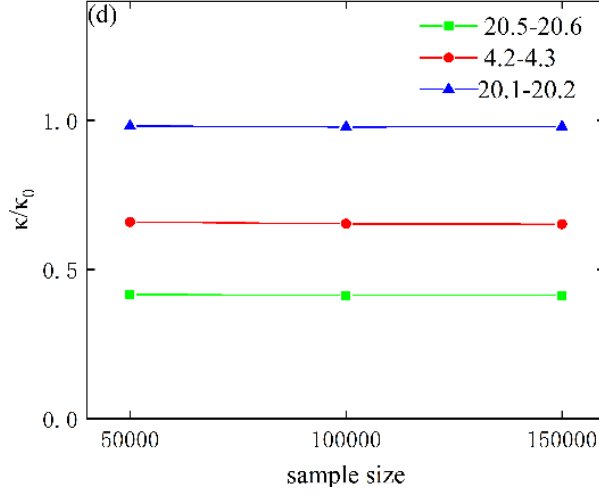


Figure S7 Numerical convergence tests for thermal conductivity calculations of bulk BAs. (a) The q-mesh size convergence of intrinsic thermal conductivity within the 3ph. framework; (b) The q-mesh size convergence of intrinsic thermal conductivity within the 3ph.+4ph. framework; (c) The sampling size convergence of intrinsic thermal conductivity within the 3ph.+4ph. framework; (d) The sampling size convergence of relative thermal conductivity κ/κ_0 for representative frequency windows under an occupation multiplier of 25 within the 3ph.+4ph. framework.

S9. Physical scale of occupation multiplier N

To clarify the physical scale of the occupation multiplier N used in the targeted phonon excitation model, we estimated the excess phonon energy density and the corresponding mode-equivalent temperature for representative occupation multipliers.

In the present model, the population of phonon modes within the targeted frequency window is modified according to

$$n_{\lambda}^* = \begin{cases} Nn_{\lambda}^0, & \lambda \in W \\ n_{\lambda}^0, & \lambda \notin W \end{cases} \quad (\text{S4})$$

where n_{λ}^0 denotes the equilibrium Bose–Einstein population at 300 K, W represents the selected 0.1 THz frequency window, and N is a dimensionless occupation multiplier used to parameterize the population enhancement of selected phonon modes.

The excess phonon energy density introduced by the population modification was calculated as

$$E_N = \frac{1}{V} \sum_{\lambda \in W} \hbar \omega_{\lambda} (n_{\lambda}^* - n_{\lambda}^0) \quad (\text{S5})$$

where V is the crystal volume, ω_{λ} is the phonon angular frequency, and the summation is performed over phonon modes within the targeted frequency window W . For the representative optical phonon window from 20.5 THz to 20.6 THz, the occupation multipliers N are set as 5 and 25 corresponding to excess phonon energy densities as 36.3 J cm^{-3} and 217.9 J cm^{-3} at 300 K, respectively.

To characterize the magnitude of the modified phonon populations, a mode-equivalent temperature T_{eff} was estimated according to

$$n_{\text{BE}}(\omega, T_{\text{eff}}) = N n_{\text{BE}}(\omega, T_0) \quad (\text{S6})$$

where $T_0 = 300 \text{ K}$. For the selected optical phonon modes, the values of N are set as 5 and 25 corresponding to mode-equivalent temperatures of approximately 543 K and 1392 K, respectively.

It should be emphasized that these values only characterize the population level of the selected phonon modes and do not represent the lattice temperature of the entire BAs crystal. The occupation multiplier N is therefore not equivalent to an experimental pump fluence, electric-field amplitude, pulse energy, or lattice temperature. Instead, it serves as a dimensionless parameter describing a prescribed driven nonequilibrium phonon population.

In this model, the prescribed population represents a driven reference state maintained by an external source rather than the freely relaxing state after removal of excitation. The present work does not determine the experimental driving conditions required to establish this population, nor does it solve the complete formation and relaxation dynamics of the nonequilibrium phonon distribution.

S10. Experimental background of mode-selective phonon excitation

Although the occupation multiplier N introduced in this work is not directly mapped to a specific experimental pump parameter, selective manipulation of phonon populations has been experimentally demonstrated in several material systems. These studies provide physical motivation for considering mode-selective nonequilibrium

phonon populations.

Sekiguchi^[1] demonstrated selective excitation of specific transverse optical phonon modes in methylammonium lead iodide MAPbI₃ using resonant terahertz pulses. By tuning the terahertz excitation frequency to phonon resonances near 0.9 and 1.9 THz, the authors selectively excited the phonon modes and observed corresponding changes in carrier cooling dynamics.

More recently, Gareev^[2] demonstrated mode-selective coherent phonon excitation in DyFeO₃ through resonant optical pumping of electronic transitions. The amplitude of the B_{2g} phonon mode exhibited pronounced resonance enhancement near the corresponding excitation energy, further illustrating the possibility of selective phonon-mode manipulation.

These experimental studies demonstrate the feasibility of selectively modifying phonon populations or amplitudes through resonant driving. However, the present work does not attempt to reproduce a specific experimental excitation pathway or determine the required pump conditions. Instead, the occupation multiplier N is introduced as a controlled parameter to investigate how prescribed targeted phonon excitation affects thermal transport and higher-order phonon scattering in bulk BAs.

References

- [1] F. Sekiguchi, H. Hirori, G. Yumoto, A. Shimazaki, T. Nakamura, A. Wakamiya, et al. Enhancing the hot-phonon bottleneck effect in a metal halide perovskite by terahertz phonon excitation. *Physical Review Letters*, 2021, 126(7): 77401
- [2] T. T. Gareev, A. Sasani, D. I. Khusyainov, E. Bousquet, Z. V. Gareeva, A. V. Kimel, et al. Optical excitation of coherent THz dynamics of the rare-earth lattice through resonant pumping of f - f electronic transition in a complex perovskite DyFeO₃. *Physical Review Letters*, 2024, 133(24): 246901