Anomalously low thermal conductivity in superhard cubic-Si$_3$N$_4$

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ABSTRACT

Super hard bulk materials with large bulk modulus like diamond and cubic BN (c-BN) show high thermal conductivity ($\kappa$) reaching 2000-3000 Wm$^{-1}$K$^{-1}$. The large modulus means large group velocity, which contributes to high lattice thermal conductivity. However, whether the hardening of phonon bands would increase or decrease the phonon scattering rate through the phonon-phonon scattering phase space is not evident and should depend on the material kind. In this work, we target cubic silicon nitride (c-Si$_3$N$_4$), which was recently developed and found to be the third super hardest materials next to the diamond and c-BN. The $\kappa$ of polycrystalline c-Si$_3$N$_4$ was measured by time domain thermoreflectance method, and thermal conductivity of 23 Wm$^{-1}$K$^{-1}$ was obtained at room temperature. The first-principles

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thermal conductivity calculations identified that this translates to single-crystal value of about 88 Wm⁻¹K⁻¹, which is more than an order of magnitude smaller than those of diamond and c-BN. The calculation further identified that difference arises from that the large scattering phase space and anharmonic amplitude of c-Si₃N₄ which are 2-3 times larger than the values of diamond. It is found that the scattering phase space of c-Si₃N₄ optical phonons with small dispersion anomalously increases with the frequency.

I. INTRODUCTION

There is a common understanding that the thermal conductivity (κ) positively correlates with the hardness. The large modulus means large group velocity, which contributes to high lattice thermal conductivity. Representative examples are diamond and cubic boron nitride (c-BN) that are the top two hardest materials [1-3] and exhibit extremely high thermal conductivity [4]. The thermal conductivity of single crystalline diamond calculated from first-principles is as high as 3450 Wm⁻¹K⁻¹ at room temperature [4], while the κ of isotopically pure diamond obtained by experiment can reach 2270 Wm⁻¹K⁻¹ at room temperature [5,6]. c-BN has a high κ of ~ 2000 Wm⁻¹K⁻¹ from first-principles study and κ of 768 Wm⁻¹K⁻¹ from experiment [4,7,8].

Apart from the hardness, there are other factors that possibly plays role in determining the thermal conductivity according to Slack’s criteria: (1) low atomic mass, (2) strong interatomic bonding, (3) simple crystal structure and (4) low anharmonicity [8]. Criteria (1) and (3) usually imply high Debye temperature [6], which corresponds to high cut-off
frequency of phonons. Criterion (3) indicates fewer phonon bands compared with complex
crystal structure, which leads to smaller phonon scattering rates. Criteria (4) was put forward
due to the fact that the thermal resistance in nonmetallic crystal arises from the anharmonic
phonon-phonon scattering at room temperature. Therefore, some superhard materials may
have counterintuitively limited thermal conductivity when other factors become dominant.

It is important to note here that Slack’s criteria do not provide quantitative measures of
which criterion have how much absolute or relative impact to thermal conductivity. Recently,
the Slack’s criteria were challenged by reported high thermal conductivity materials of boron
arsenide (BAs). The thermal conductivity of BAs was theoretically predicted to be 2240 Wm⁻¹
K⁻¹ [4] and 1400 Wm⁻¹K⁻¹ after including four-phonon scattering [9], and then
experimentally confirmed to exceed 1000 Wm⁻¹K⁻¹ at room temperature despite that it has
relatively large average atomic mass and intermediate atomic bonding [10-12]. The high
thermal conductivity was attributed to the band gap between acoustic and optical phonons
[4], which suggests that one of the Slack’s criteria can overwhelm the others. Therefore,
quantitative case studies of specific superhard materials are need to gain understanding in
thermal conductivity and underlying mechanism.

In this work, we particularly targeted superhard crystals with strong interatomic bonds.
The lattices of super hard materials are more resistant to deformation due to the strong
interatomic bonds [13,14], which leads to low anharmonicity in materials [13,14]. Silicon
nitride (Si₃N₄) is a newly developed super hard material, which has three polymorphs: α, β
and γ phases. α-Si₃N₄ or β-Si₃N₄ are the thermo-dynamically stable phases with hexagonal
structures at ambient condition. The γ phase Si$_3$N$_4$ which is also called cubic-Si$_3$N$_4$ (c-Si$_3$N$_4$) shows a cubic spinel structure [15]. c-Si$_3$N$_4$ is recognized as the third hardest material next to diamond and c-BN [1,2], with the potential application including cutting tools, anti-friction bearings [15], and optic windows under extreme condition [2]. The bond strengths of C-C, B-N and Si-N were reported to be 610 [16], 389 [16], and 470 kJ/mol [17], and thus, the strength of interatomic bond of c-Si$_3$N$_4$ is in between those of diamond (C-C) and c-BN (B-N). Even though c-Si$_3$N$_4$ has large bulk modulus, the previous first-principles thermal conductivity calculation of c-Si$_3$N$_4$ has shown that $\kappa$ is not as high as those of diamond and c-BN, suggesting that bulk modulus may not be a good indicator of thermal conductivity [18].

Here, we report the $\kappa$ of polycrystalline c-Si$_3$N$_4$ measured by time-domain thermoreflectance (TDTR) method. First-principles single-crystal calculation is further performed to investigate the underlying mechanism governing the $\kappa$ of c-Si$_3$N$_4$, by comparing the phonon group velocity, the phonon relaxation time, phonon scattering phase space, and anharmonic amplitude with those of diamond and c-BN. The consistency between the experiment and calculation is finally confirmed by extending the calculation to polycrystalline c-Si$_3$N$_4$ using an empirical model.

II. EXPERIMENT

A. Sample fabrication and structure analysis

The starting material for fabrication of the polycrystalline c-Si$_3$N$_4$ is commercially available α-Si$_3$N$_4$ powder (SN-E10., Ube Industries, Ltd., Ube, Japan), which is not isotope-enriched. The as-received powder was first dried for 8 hours under 200 °C and then enclosed
into a sample capsule. After loading the capsule into a MgO sleeve with MgO lids, the assembled sample container was dried in the vacuum oven for 2 hours under 150 °C. A Kawai-type apparatus, installed at DESY, with a Walker-module (mavo press LPR 1000-400/50; Max Voggenreiter GmbH, Mainleus, Germany) was used to offer the high pressure (15.6 GPa) and high temperature ambient (1700-1800 °C) for the sample synthesis. More details of the fabrication process are described in the previous report [2]. The unit cell parameter of c-Si$_3$N$_4$ was determined by the XRD pattern: $a = 7.7373 \pm 0.0006\text{Å}$, which is consistent with former research [19]. Both the unit cell parameter and density of our sample indicate that the sample is in cubic phase [2]. From the TEM image, the sample was found to be polycrystalline with the average grain size of 143 ± 59 nm [2]. More details about structure analysis can be found also in the previous report [2].

**B. Thermal conductivity measurement**

Two-color TDTR method was employed to measure the $\kappa$ of polycrystalline c-Si$_3$N$_4$. TDTR is a well-developed method, which utilizes the pulsed pump beam centered at 400 nm and probe beam centered at 800 nm to characterize the thermal transport [20-22]. First, the smoothed side of the c-Si$_3$N$_4$ sample was coated with an Al transducer film by vacuum evaporation. During the measurement, a pulse train of pump beam was first irradiated to the sample from the Al-transducer side. The temperature evolution of the transducer was sensed by the probe beam with certain delay time. A lock-in amplifier was used to detect the intensity of the reflected probe beam, which was proportional to the temperature. The detected signal includes two parts: in phase signal ($V_{in}$) and out of phase signal ($V_{out}$). The ratio $R = -V_{in}/V_{out}$ was fitted to the solution of the physical model (heat conduction equation) to extract the
unknown parameters. The thickness of Al, heat capacity ($\rho C_p$) and $\kappa$ of Al film that were
either known or measured in advanced were input to the physical model. Then the remaining
two unknown parameters, $\kappa$ and interface thermal conductance between Al and c-Si$_3$N$_4$, were
extracted by the fitting. The fitting curve is shown in Fig. 1(a). The robustness of the fitting
was checked by analyzing the sensitivity $S_{R,x} = \frac{d\ln R}{d\ln x}$, where $x$ is the target parameter. As
shown in Fig. 1(b), $R$ is sensitive to the changes of sample thermal conductivity and interface
thermal conductance between polycrystalline c-Si$_3$N$_4$ and Al film, and thus, it is valid and
trustworthy to fit the two parameters simultaneously. As the result, the $\kappa$ of polycrystalline
c-Si$_3$N$_4$ and the interface thermal conductance between Al and polycrystalline c-Si$_3$N$_4$ were
obtained to be $23.0 \pm 1.6$ Wm$^{-1}$K$^{-1}$ and $62.0 \pm 4.5$ MWm$^{-2}$K$^{-1}$, respectively. The $\kappa$ of
polycrystalline c-Si$_3$N$_4$ is two order of magnitude smaller than the thermal conductivity of
superhard materials like diamond and c-BN.

III. THEORETICAL ANALYSIS

A. Lattice thermal conductivity calculations

We performed bulk thermal conductivity calculation of c-Si$_3$N$_4$ based on anharmonic
lattice dynamics using IFCs obtained from first principles [23-25]. To obtain both the
harmonic and anharmonic IFCs using the real-space displacement method, we adopted $2 \times 2$
$\times 2$ conventional supercell containing 448 atoms. The density-functional theory (DFT)
calculations were performed using Quantum ESPRESSO with revised Perdew-Burke-
Ernzerhof exchange-correlation functions based on generalized gradient approximation
(GGA) that improves equilibrium properties for solids (PBEsol) [26,27]. The kinetic energy
cutoff was 60 and 400 Ry, respectively, for wave functions and charge density with the \( k \)-
mesh of \( 2 \times 2 \times 2 \). Using the IFCs, phonon relaxation time were calculated by the anharmonic
lattice dynamics (ALD) method rigorously solving the Fermi’s Golden rule for phonon self-
energies. The Boltzmann transport equation (BTE) with relaxation time approximation
(RTA) was employed to calculate the \( \kappa \). The ALD and BTE calculations were performed
using the ALAMODE package [28]. The theoretical \( \kappa \) of single crystalline c-Si\(_3\)N\(_4\), diamond,
and c-BN as a function of temperature are plotted in Fig. 2. After accounting for the isotope
scattering due to the nature isotope distribution using Tamura’s model [29], the calculated
thermal conductivity of c-Si\(_3\)N\(_4\) at room temperature is 88 Wm\(^{-1}\)K\(^{-1}\). This result is consistent
with 81 Wm\(^{-1}\)K\(^{-1}\) of Tatsumi et al. obtained by similar ALD-BTE calculations using first-
principles IFCs including the same isotope scattering [14]. The values are different from 272
Wm\(^{-1}\)K\(^{-1}\) recently reported by Xiang et al. [30]. But that could be due to the approximation
in the modified Debye-Callaway’s model used in their work [31]. Recently, four-phonon
scattering has been reported to play an important role in reducing the thermal conductivity
of crystals [9,32]. Previous works have found that the four-phonon scattering process
becomes important under high temperature and materials with high thermal conductivity or
acoustic-optical phonon band gaps [9,33]. In this work, since we mainly focus on the thermal
conductivity of c-Si\(_3\)N\(_4\) at RT and c-Si\(_3\)N\(_4\) does not exhibit the band gap, only three-phonon
scattering process was considered. In Table 1, the mechanical properties and \( \kappa \) of c-Si\(_3\)N\(_4\) at
300 K are compared with those of diamond and c-BN. Despite that c-Si\(_3\)N\(_4\) is ranked as the
third hardest material, its \( \kappa \) is only about 2.6% of that of diamond, and 4.2% of that of c-BN
at room temperature [4].
B. Scattering phase space and anharmonic amplitude

It is well known that in nonmetallic materials, the thermal resistance at high temperature rises by the phonon-phonon scattering. Figure 3(a) shows the phonon dispersion relation of c-Si$_3$N$_4$. In a primitive cell, c-Si$_3$N$_4$ has 42 phonon modes while diamond and c-BN only have 6 phonon modes. More optical phonon bands in the c-Si$_3$N$_4$ is expected in general to offer more phonon scattering channels when compared with those of diamond and c-BN. For quantitative analysis, phonon group velocities of the c-Si$_3$N$_4$, diamond and c-BN in frequency domain are illustrated in Fig. 3(b). Here, the average group velocities are obtained from the acoustic phonons since they mainly contribute to thermal conductivity. The average phonon velocity in c-Si$_3$N$_4$ is 5001 m/s, while those in diamond and c-BN are 9241 m/s and 8240 m/s, respectively. Thus, the squared average group velocity of c-Si$_3$N$_4$ is 30% of that of diamond. The difference in phonon velocities partly contribute to the lower thermal conductivity in c-Si$_3$N$_4$ when compared with diamond. However, phonon velocity is not the decisive reason leading to low $\kappa$ in c-Si$_3$N$_4$ considering the fact that the $\kappa$ of c-Si$_3$N$_4$ is 3% of that of diamond. We thus hypothesize that there is a significant influence from the relaxation time difference.

To clarify the above hypothesis, the relaxation time of single crystal c-Si$_3$N$_4$ was calculated for the three-phonon scattering process as shown in Fig. 3(c). As frequency increases, the relaxation time decreases from 100 ps to 1 ps for single crystal c-Si$_3$N$_4$. As a comparison, the phonon lifetime in diamond decreases from 1000 ps to 10 ps as frequency increases from 1 THz to 30 THz [34]. It is easily concluded that the extremely short phonon relaxation time is the main cause for the low $\kappa$ in c-Si$_3$N$_4$. To further explore the fundamental
reason for the difference in the phonon relaxation time, we need to revisit what impacts the 
relaxation time. The relaxation time for each phonon mode is determined by the Bose-
Einstein distribution, scattering phase space \( (P_3(\omega)) \) and anharmonic amplitude \( (V_3(\omega)) \) [35].
Here, \( \omega \) is the phonon frequency. The scattering phase space describes the amount of the 
phonon scattering channels [36]. More phonon scattering channels lead to larger \( P_3 \) and 
shorter phonon relaxation time. Anharmonic amplitude indicates the strength of 
anharmonicity of each three-phonon scattering process. The anharmonic amplitude in 
frequency domain can be estimated by \( 1/(\tau(\omega)P_3(\omega)) \) [36]. The details of the calculation of 
anharmonic amplitude can be found in the Appendix. Here \( \tau \) is the phonon relaxation time.
In the following, we explore the impact of the scattering phase space (SPS) and anharmonic 
amplitude on determining the relaxation time.

Three-phonon scattering process, which was constrained by the momentum and energy 
conservation was considered when calculating the SPS [37]. Figure 4(a) shows the \( P_3 \) in 
frequency domain for c-Si$_3$N$_4$, diamond, and c-BN. It is seen that although the \( P_3 \) of c-Si$_3$N$_4$
is similar to those of diamond and c-BN in the low frequency regime, at the frequency 
exceeds about 15 THz, \( P_3 \) of c-Si$_3$N$_4$ anomalously increases and becomes considerably larger 
than those of diamond and c-BN. We expect this to be due to the flat phonon bands in phonon 
dispersion relations (Fig. 3(a)) arising from the complex unit cell of c-Si$_3$N$_4$ (39 optical 
phonon branches). Figure 2(b) shows the dependence of cumulative \( \kappa \) on frequency for c-
Si$_3$N$_4$. The phonons with frequency higher than 20 THz hardly contribute to the thermal 
conductivity. Instead, these phonons act as the scatters for lower frequency phonons to 
suppress the thermal conductivity. To confirm that such scattering processes are important in
determining the thermal conductivity of c-Si$_3$N$_4$, we have performed calculations by artificially turning off the specific group of three-phonon scattering processes [36], AAA, AAO, AOO, and OOO, where “A” and “O” denote acoustic and optical phonons. As shown in Fig. 5, it is found that the dominating process that limits the thermal conductivity in deed is AOO, where at least one of the optical phonons is expected to have high frequency. c-Si$_3$N$_4$. The anharmonic amplitude in frequency domain is shown in Fig. 4(b). The detailed description of anharmonic amplitude calculation can be found in the supplementary materials [38]. For c-Si$_3$N$_4$, $V_3$ increases with increasing frequency in the entire frequency domain, whereas in the case of diamond and c-BN, $V_3$ increases only minutely until the frequency reaches about 20 THz, and then it begins to increase with a gradient similar to c-Si$_3$N$_4$. The total $P_3$ and average $V_3$ for c-Si$_3$N$_4$, diamond and c-BN are summarized in Table 1. We can find that both the total $P_3$ and average $V_3$ of c-Si$_3$N$_4$ are 260% and 190% of diamond, respectively. Together with the above result that the average group velocity of c-Si$_3$N$_4$ is 30% of diamond, estimating the thermal conductivity as $\kappa \sim v^2/(P_3V_3)$, the ration of thermal conductivity becomes 6%, which reasonably agrees with the actual value 3%. Therefore, it is concluded that the phonon scattering space and anharmonic amplitude play equal roles in suppressing the thermal conductivity of c-Si$_3$N$_4$ with respect to diamond.

C. Theoretical thermal conductivity of polycrystalline c-Si$_3$N$_4$

In order to check the consistency between the experiment and calculation, we have extended the thermal conductivity calculation to incorporate also phonon impurity scattering by imperfection of the actual sample and boundary scattering at the polycrystalline grain
boundaries. According to the phonon kinetic gas theory, the thermal conductivity ($\kappa_{\text{poly}}$) can be expressed as:

$$\kappa_{\text{poly}} = \frac{1}{3V} \sum_{\mathbf{k}, s} C_{\mathbf{k}, s} v_{\mathbf{k}, s}^2 \tau_{\mathbf{k}, s}. \quad (1)$$

Here, $V$ is the volume of primitive cell. $C$, $v$ and $\tau$ are heat capacity, phonon velocity and phonon relaxation time, respectively. $\mathbf{k}$ and $s$ are phonon wave vector and phonon polarization, respectively. By adopting to the Mattheissen’s rule, the effective relaxation time of a polycrystalline can be written as:

$$\tau^{-1}(\mathbf{k}, s) = \tau^{-1}_{\text{ph-ph}}(\mathbf{k}, s) + \tau^{-1}_{\text{imp}}(\mathbf{k}, s) + \tau^{-1}_{B}(\mathbf{k}, s), \quad (2)$$

Here, $\tau_{\text{ph-ph}}$, $\tau_{\text{imp}}$ and $\tau_{B}$ are the relaxation time due to phonon-phonon scattering, phonon-impurity (including vacancy and oxygen contaminates) scattering and phonon-boundary scattering, respectively. Here, the phonon-impurity scattering were calculated using the Tamura model [29]. While the chemical composition of the sample measured by energy dispersive spectroscopy was Si: $60.1 \pm 0.3$ wt%; N: $37.1 \pm 0.4$ wt%; O: $2.5 \pm 0.2$ wt%, assuming that the lattice structure does not change, and nitrogen is substituted either by oxygen or atom with zero mass (vacancy), judging from the stoichiometry of c-Si$_3$N$_4$, we obtain effective composition of Si$_{3.71}$N$_{3.02}$O$_{0.07}$, with X indicating vacancy. When adopting the Tamura model, which was derived for isotope impurity and only accounts for mass difference, we ignore the modulation of force field due to the substitution [39]. As for the boundary scattering, we model with the Casimir-limit, where phonon-boundary scattering rate is given as: $\tau^{-1}_{B} = v/D$. Here $v$ and $D$ are the phonon velocity and the average gain size, respectively. The calculated $\tau_{\text{ph-ph}}$, $\tau_{\text{ph-ph+imp}}$, $\tau_{\text{ph-ph+imp+B}}$ are shown in Fig. 3(d). The impurities
and vacancies suppress the thermal conductivity by shortening the relaxation time of high-frequency phonons. On the contrary, the grain boundaries mostly shorten the relaxation time of low-frequency phonons. The temperature dependence of theoretical $\kappa$ considering all the phonon scattering processes is also shown in Fig. 2. At room temperature, the theoretical $\kappa$ is determined to be 31.0 Wm$^{-1}$K$^{-1}$, boundary which, considering the general boundary scattering model that ignores the detail features of the interface, is reasonably close to 23.0 Wm$^{-1}$K$^{-1}$ obtained by the experiment.

IV. CONCLUSION

In summary, the thermal conductivity of the third superhard c-Si$_3$N$_4$ was measured for the first time by the time-domain thermoreflectance method. The value is 23.0 Wm$^{-1}$K$^{-1}$ which is almost two orders of magnitude lower than that of super hardest diamond and c-BN. The first-principles anharmonic lattice dynamics calculation reveals that even for single crystal phase the thermal conductivity is 88 Wm$^{-1}$K$^{-1}$. By further analysis of phonon transport, the low thermal conductivity is attributed to large SPS and anharmonic amplitude in c-Si$_3$N$_4$ that are 200-300% of diamond, in addition to the fact that squared average group velocity of acoustic phonons is 30% of that of diamond. For polycrystalline c-Si$_3$N$_4$, the thermal conductivity obtained from the theoretical calculation is consistent with the value obtained by experiment. The theoretical analysis also indicates that the impurities and vacancies mostly shorten the phonon relaxation time of high-frequency phonons while the grain boundaries shorten the phonon relaxation time of low-frequency phonons.
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TABLE I. Summary of mechanical properties and thermal properties of super hard materials.

$B$: bulk modulus, $G$: shear modulus, $H_V$: Vickers hardness, $\kappa$: thermal conductivity obtained by experiment; $P_3$: total scattering phonon space value, $V_3$: anharmonic amplitude.

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<th>$B$</th>
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<th>$\kappa^a$</th>
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<td>GPa</td>
<td>GPa</td>
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<td>Wm$^{-1}$K$^{-1}$</td>
<td>$10^{-4}$ cm</td>
<td>$10^{19}$</td>
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<td>535$^d$</td>
<td>96$^g$</td>
<td>2270$^e$</td>
<td>3450$^e$</td>
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<tr>
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<td>409.0$^d$</td>
<td>66$^g$</td>
<td>768$^e$</td>
<td>2145$^e$</td>
<td>1.33</td>
<td>3.50</td>
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<td>247.5$^f$</td>
<td>34.9$^f$</td>
<td>23.0$^e$</td>
<td>88$^e$</td>
<td>2.72</td>
<td>5.51</td>
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$^a$ Measured values by experiments.
$^b$ Theroretical values for single-crystalline materials.
$^c$ This work.
$^d$ Reference [3].
$^f$ Reference [2].
$^g$ Reference [13].
FIG. 1 (a) $-V_{\text{in}}/V_{\text{out}}$ signal fitting for Al on c-Si$_3$N$_4$ with two-unknown parameters: thermal conductivity of c-Si$_3$N$_4$, and interface thermal conductance between Al and c-Si$_3$N$_4$. Here $V_{\text{in}}$ and $V_{\text{out}}$ are the in-phase and out-of-phase of the detected signal in the time-domain thermoreflectance (TDTR) measurement, respectively. (b) The sensitivities of $-V_{\text{in}}/V_{\text{out}}$ signal to the properties. The red line and the blue line represent the sensitivity of thermal conductivity of c-Si$_3$N$_4$ and the interface thermal conductance between Al and c-Si$_3$N$_4$. 
FIG. 2 (a) The squares are the temperature dependences of thermal conductivity of single crystalline c-Si$_3$N$_4$, diamond [34, 40] and c-BN [31] obtained by first-principles calculations. The circles are the thermal conductivity of polycrystalline c-Si$_3$N$_4$ calculated by adopting an empirical model. The triangle is the thermal conductivity of polycrystalline c-Si$_3$N$_4$ obtained by the time-domain thermoreflectance (TDTR) method. (b) Dependence of cumulative thermal conductivity on frequency for c-Si$_3$N$_4$. 
FIG. 3 (a) Dispersion relations of single crystal c-Si$_3$N$_4$. (b) Frequency-dependent phonon group velocity and (c) relaxation time for single crystal c-Si$_3$N$_4$, diamond, and c-BN. (d) Relaxation times of single crystalline c-Si$_3$N$_4$ and polycrystalline c-Si$_3$N$_4$, where subscripts ph-ph, imp, and B denote phonon-phonon scattering, phonon-impurity scattering, and phonon-boundary scattering, respectively.
FIG. 4. Comparison of (a): SPS ($P_3$) and (b): anharmonic amplitude ($V_3$) in frequency domain for single crystal c-Si$_3$N$_4$, diamond, and c-BN.
FIG. 5. Analysis of the impact of different groups of three-phonon scattering processes on thermal conductivity by evaluating the enhancement when turning off the processes. “A” and “O” denote acoustic and optical phonon, respectively.
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[38] See Supplemental Material at [URL will be inserted by publisher] for calculation of average anharmonic amplitude in frequency domain.
